



This is not the published version of the article / Þetta er ekki útgefna útgáfa greinarinnar

Author(s)/Höf.: Kleine, B. I., Stefánsson, A., Halldórsson, S. A., & Barnes, J. D.
Title/Titill: Impact of fluid-rock interaction on water uptake of the Icelandic crust: Implications for the hydration of the oceanic crust and the subducted water flux.
Year/Útgáfuár: 2020
Version/Útgáfa: Pre-print (óritrýnt handrit)

Please cite the original version:

Vinsamlega vísið til útgefnu greinarinnar:

Kleine, B. I., Stefánsson, A., Halldórsson, S. A., & Barnes, J. D. (2020). Impact of fluid-rock interaction on water uptake of the Icelandic crust: Implications for the hydration of the oceanic crust and the subducted water flux. *Earth and Planetary Science Letters*, 538, 116210. doi:<https://doi.org/10.1016/j.epsl.2020.116210>

Rights/Réttur: © 2020 Elsevier Ltd. All rights reserved

1 **Impact of fluid-rock interaction on water uptake of the Icelandic crust: Implications for**
2 **the hydration of the oceanic crust and the subducted water flux**

3 Kleine, B.I.^{1*}, Stefánsson, A.¹, Halldórsson, S.A.¹, Barnes, J.D.²

4 ¹Nordic Volcanological Center, Institute of Earth Science, University of Iceland, Reykjavik,
5 Iceland

6 ²Department of Geological Sciences, University of Texas at Austin, USA

7 *corresponding author: barbarak@hi.is

8
9 **Abstract**

10 Oceanic crust is a major transport medium of water into the mantle wedge and the convecting
11 mantle. Yet, the water content of the oceanic crust remains uncertain. Active geothermal
12 systems situated at on-land spreading centers provide a unique opportunity to study the
13 hydration of the oceanic crust, with well constrained systems and boreholes reaching depths of
14 >4 km. Here, we present hydrogen isotope data of geothermal fluids and altered basalt for three
15 Icelandic geothermal systems: the meteoric water fed system at Krafla and the seawater fed
16 systems at Reykjanes and Surtsey. The bulk rock δD values of altered and hydrated basalts
17 from these localities, which exhibit significantly higher water contents (up to 8.9 wt.%) than
18 magmatic (non-hydrated) basalts, vary greatly from -125 to -96‰ at Krafla, from -80 to -46‰
19 at Reykjanes and from -78 to -46‰ at Surtsey. The corresponding fluids have δD values of -
20 84.1 to -81.1‰ at Krafla, -23.1 to -14.9‰ at Reykjanes and +2.1 to +4.3‰ at Surtsey.
21 Comparison of isotope modeling results to the natural data reveals that hydration of the
22 Icelandic crust and corresponding hydrogen isotopic characteristics are controlled by (1) the
23 isotope composition of the source fluid, (2) isotope fractionation between the aqueous
24 geothermal fluids and the alteration minerals formed, and (3) the type and quantity of alteration

25 minerals formed. These factors in turn depend on the extent of fluid-rock interaction and
26 temperature. Using the same modeling approach and expanding it to datasets available for the
27 oceanic crust, we assessed the hydration state and δD values of the oceanic crust as a function
28 of depth. We show that 1400 to 1650 Tg H_2O/yr is added to the igneous oceanic crust upon
29 alteration by seawater and that the upper part (<2 km) of oceanic crust hosts almost 50% of the
30 added water. The corresponding hydrogen isotope composition of the hydrated crust was
31 calculated to an average of $-55 \pm 6\text{‰}$. Upon subduction and subsequent dehydration, 80-90% of
32 water with δD values of -35 to -10‰ will be released to the crustal forearc and mantle wedge.
33 The remaining dehydrated slab with δD values of ~ -160 to -85‰ is expected to be transported
34 to deeper levels modifying the mantle's water budget and isotopic composition.

35 **Keywords**

36 hydrogen isotopes, water cycling, oceanic crust, fluid-rock interaction

37

38 **1. Introduction**

39 Hydration and subduction of oceanic crust plays a critical role in the Earth's water cycle.
40 Hydration of newly formed oceanic crust begins at mid-ocean ridges via production of
41 secondary (i.e., alteration) minerals and continues as the seafloor ages. In addition, sediments
42 are continuously deposited onto the seafloor adding material containing both pore and
43 structurally bound water. Water budget estimates for the oceanic lithosphere, including the
44 uppermost part of the serpentinized mantle and overlying marine sediments, suggest that a total
45 of 1800-2400 Tg H_2O/yr enters subduction zone trenches of which $\sim 80\%$ derives from the
46 hydrated oceanic crust and marine sediments and $\sim 20\%$ from the serpentinized upper mantle
47 (e.g., Hacker, 2008; Jarrard, 2003; Rüpke et al., 2004; van Keken et al., 2011). Although almost
48 85% of water stored in the pore space and hydrous minerals of the sediments is either recycled
49 back into the oceans or lost to the forearc, over $>60\%$ of water in the hydrated oceanic crust is

50 considered to be transported to deeper levels in subduction zones triggering the generation of
51 magma in the mantle wedge (Hacker, 2008; Jarrard, 2003). Outgassing of water deriving from
52 the descending oceanic crust at arc volcanoes is supported by chemical and isotopic data of
53 volcanic gas emissions (e.g., Giggenbach, 1992; Taran and Zelenski, 2015). Thus, the
54 hydration state of the oceanic crust is a significant input parameter needed for estimations of
55 water fluxes associated with descending slabs and for estimates of the amount of water reaching
56 beyond the zone of arc volcanism into deeper parts of the mantle.

57 The hydration of the oceanic crust is difficult to constrain and quantify. Marine
58 sediments covering the seafloor often limit the access to the underlying igneous oceanic crust.
59 Furthermore, low core recoveries with depth are common, thus limiting samples to be obtained
60 from the entire lithological sequence of the oceanic crust (Alt et al., 1996). Sonic-velocity and
61 direct measurements of the water content from DSDP/ODP boreholes are rare and mostly
62 restricted to shallow depths of the first 1-2 km and exposed ophiolite sequences. According to
63 available data, the bulk water content of the oceanic crust varies from 1 to 8 wt.% H₂O in the
64 upper oceanic crust (volcanics and sheeted dikes) and from 0.1 to 0.5 wt.% H₂O in the lower
65 gabbroic oceanic crust (Agrinier et al., 1995a; Agrinier et al., 1995b; Alt et al., 1996; Godard
66 et al., 2009; Kawahata et al., 1987; Kusakabe et al., 1989; Shilobreeva et al., 2011; Staudigel
67 et al., 1996). Although gabbro makes up ~ 6 km of the oceanic lithological stratigraphy, the
68 upper 1-2 km of the oceanic crust accounts for 70-85% of its total water budget assuming a
69 total crustal thickness of ~ 8 km (Bown and White, 1994). This significant contribution of the
70 upper oceanic crust to the total water budget of the oceanic crust highlights the need to carefully
71 evaluate and quantify the processes controlling the water uptake alteration at low (<50°C) to
72 geothermal temperatures (>400°C).

73 The alteration of the oceanic crust has been previously constrained by chemical and
74 isotope data coupled with geochemical modeling. Particularly, hydrogen isotopes have been

75 extensively applied to trace geothermal fluid origins and the degree of rock alteration and
76 hydration (e.g., Agrinier et al., 1995a; Agrinier et al., 1995b; Kawahata et al., 1987; Kusakabe
77 et al., 1989; Shilobreeva et al., 2011). The formation and abundance of hydrous secondary
78 minerals controlling the water content of the oceanic crust may be affected by several processes
79 such as extent of fluid-rock interaction, temperature and fluid composition. Hence, the extent
80 of alteration and hydration, i.e., the formation and abundance of hydrous minerals upon
81 alteration of the oceanic crust, is controlled by the crustal thermal gradients for on-rift and off-
82 rift regions to 8 km depths that in turn depend on the thickness and type of lithological units as
83 well as the age of the oceanic crust (Alt et al., 1996; Grose and Afonso, 2013; Heft et al., 2008).
84 Yet, only a few studies have considered the impact of temperature and extent of fluid-rock
85 reactions on the formation and abundance of alteration minerals in their model approaches
86 (e.g., Bowers and Taylor, 1985; Kyser and O'Neil, 1984).

87 Here, we quantify alteration and hydration processes occurring in the upper part of the
88 Icelandic crust using three geothermal systems hosted in dominantly basaltic rocks and fed by
89 both meteoric water and seawater. In addition, temperature in these systems is variable and
90 ranges from $<50^{\circ}\text{C}$ to $>400^{\circ}\text{C}$. The sample set comprises subsurface rocks, altered and
91 hydrated to variable extent, and fluid discharges from boreholes drilled to >2500 m at Krafla
92 (N Iceland), Reykjanes (SW Iceland) and Surtsey (S Iceland). The hydrogen isotope (δD)
93 composition of both fluids and rocks along with bulk rock water contents were combined with
94 geochemical and isotope modeling approaches to unravel the various processes controlling
95 crustal hydration and its hydrogen isotope composition. As the Icelandic crust has several
96 characteristics common to oceanic crust including primary lithologies and secondary
97 mineralogy, our results were further expanded to constrain the hydration state of the oceanic
98 crust and its respective δD composition. Therefore, our findings form an important basis for

99 estimates of the subducted water flux and corresponding δD values as the descending oceanic
100 crust enters subduction zones.

101

102 **2. Geological setting**

103 Iceland exhibits the only mid-oceanic ridge on Earth that exposes a largely submarine rift on
104 land. Even though the Icelandic crust exhibits unusually thick extrusive sections (>2000 m)
105 and differs chemically from defined MORB (Óskarsson et al., 1982), it has been repeatedly
106 used as an analogue to the oceanic crust for example for primary lithologies and geothermal
107 activity to study hydrothermal circulation, alteration processes, crustal construction and magma
108 evolution taking place elsewhere along submarine sections of the ridge (e.g., Lonker et al.,
109 1993; Marks et al., 2011; Óskarsson et al., 1982). Iceland's lithology is dominated by basalts
110 with some silicic volcanics and volcanoclastic sediments also being present (Sæmundsson,
111 1979). Geothermal activity occurs over a wide temperature range (<10 to >400 °C) (Stefánsson
112 et al., 2017), resulting in low-grade metamorphism within the crust (Kristmannsdóttir, 1979).

113 The present study investigates the hydrogen isotope composition of fluids and altered
114 basalts in three active geothermal systems at Krafla, Reykjanes and Surtsey (Fig. A.1) fed by
115 meteoric water and seawater, respectively. Boreholes reach depths of >4 km, temperatures
116 range from <50 to >400 °C and secondary mineral assemblages are well-constrained (Franzson
117 et al., 2002; Sæmundsson, 1991; Stefánsson et al., 2017). Additionally, samples can be
118 obtained as a function of both temperature and depth.

119 The Krafla high-temperature (100-350 °C) geothermal field is located within the ~ 8
120 km² collapsed Krafla caldera of the North Iceland Rift Zone that formed approximately 110 ka
121 ago (Sæmundsson, 1991). The caldera is mainly filled by basaltic lavas and hyaloclastites as
122 well as by periodically occurring rhyolites. Since 1974, 45 boreholes have been drilled into the
123 geothermal system to depths of 985 m to 2894 m with reservoir temperatures ranging from

124 50°C to 440°C. A prograde hydrothermal alteration assemblage has developed with depth with
125 the maximum grade at the epidote-actinolite zone (e.g., Sæmundsson, 1991). The alteration
126 mineralogy of the first 200 m comprises dominantly mixed layer clays and chlorite (Table A.1).
127 With increasing depth, chlorite, quartz, epidote, albite and calcite are among the most abundant
128 alteration minerals. At depths >800 m actinolite becomes part of the alteration mineralogy.
129 Geothermal fluids in Krafla originate from meteoric water and display low chloride
130 concentrations (~50 ppm) and close to neutral pH (7.46-9.75) (e.g., Gudmundsson and
131 Arnórsson, 2005).

132 The Reykjanes high-temperature geothermal field is located on the southwestern tip of
133 the Reykjanes Peninsula. It consists of highly fractured basalt lavas and hyaloclastites that have
134 been intruded by shallow dikes and sills (Franzson et al., 2002). Since 1956, 39 boreholes have
135 been drilled into the geothermal system reaching depths of 1036 m to 4500 m. The reservoir
136 temperatures range from 100°C to 420°C. Host rocks of the Reykjanes geothermal system are
137 extensively altered by the circulating geothermal fluids. As in Krafla, a prograde hydrothermal
138 alteration assemblage is developed with depth consisting of mixed layered clays and chlorite
139 in the top 700 m followed by an alteration zone composed of mainly chlorite, quartz, epidote
140 and anhydrite (Table A.1) (Franzson et al., 2002). At depths >1200 m, actinolite appears within
141 the alteration mineral assemblage. The geothermal fluids are characterized by elevated chloride
142 concentrations (~15900 ppm) and mildly acid pH values (~5.86) (Arnórsson, 1978) and
143 considered to be predominantly of seawater origin with addition of some meteoric water.

144 The oceanic island of Surtsey forms part of the Vestmannaeyjar volcanic system off the
145 south coast of Iceland. The volcano grew from the seafloor during explosive and effusive
146 eruptions from 1963 to 1967 (Thorarinsson et al., 1964). Four boreholes have been drilled into
147 the geothermal system to depths of 152 m to 354 m. Borehole water temperatures range from
148 ~50 to 141°C (Jackson et al., 2019). The hydrothermal system at Surtsey is hosted in the tephra

149 and tuff deposits (Jakobsson and Moore, 1986). Rapid alteration and consolidation of the basalt
150 tephra produced palagonitic tuff and the formation of secondary minerals such as sulfates,
151 carbonates, clays and zeolites (Jakobsson and Moore, 1986). Geothermal fluids in the Surtsey
152 submarine deposits originate exclusively from seawater that has been modified by reaction with
153 the surrounding basalt (Ólafsson and Jakobsson, 2009). The fluids are mildly acidic (pH = 6.22-
154 8.01) and Cl concentrations (~19500 ppm) are similar to those measured in seawater.

155

156 **3. Materials and methods**

157 *3.1. Hydrogen isotope analyses and water contents of bulk rock samples*

158 Bulk rock samples were collected from drill cuttings from the geothermal systems at Krafla
159 and Reykjanes and a continuous drill core from Surtsey. Samples from well number KG-25 at
160 Krafla, RN-10 at Reykjanes and SE-2B and SE-3 at Surtsey were taken at approximately 50 m
161 depth intervals from the top to the bottom and from each of the different alteration zones
162 encountered in the boreholes. The total depths and reservoir temperatures in the boreholes are
163 2105 m and 100-350°C in KG-25 at Krafla, 2054 m and 100-320°C in RN-10 at Reykjanes,
164 and 192 m to 354 m and 25-130°C in SE-2B and SE-3 at Surtsey, respectively.

165 The hydrogen isotope ratios of bulk rock samples were analyzed at University of Texas
166 at Austin by continuous-flow mass spectrometry using a ThermoElectron TC/EA (high
167 temperature conversion elemental analyzer) equipped with a Costech zero-blank autosampler
168 coupled to a ThermoElectron MAT 253 isotope ratio mass spectrometer (IRMS) following the
169 procedure described by Sharp et al. (2001). The bulk rock samples were milled to fine powder
170 (<70 µm) in an agate mill. Approximately 2 mg of sample were enclosed into silver foil
171 capsules, dried under vacuum at 70 °C for 24 h and then immediately transferred to the
172 autosampler and flushed with He gas. Five internationally referenced and certified standard
173 materials (IAEA-CH7, NBS-22, NBS-30, USGS-57, USGS-58) and one in-house working

174 glass standard were analyzed along with the samples. The raw δD values were corrected for
175 instrumental drift and then the unknowns were normalized to the SMOW scale using the
176 standards IAEA-CH7, NBS-22, USGS-57, and USGS-58. Measured δD values of standards
177 did not vary with sample size and the total peak areas of all unknowns were within the linear
178 range of this IRMS. Error based on reproducibility of standards in the analytical runs was $\pm 3\%$.
179 Water contents (wt.% H_2O) were calculated based on the sample peak area and the weight for
180 each replicate compared to the standard NBS-30, USGS-57, and USGS-58. A total of 112
181 individual unknown aliquots, i.e., 56 samples, were analyzed for this study. Hydrogen isotope
182 (δD) values reported in the main text are the mean of two individual replicate analyses. We
183 note that drill cutting samples might be potentially biased towards more resistant alteration
184 minerals with preferential loss of less resistant minerals such as clays (Fowler and Zierenberg,
185 2016). Thus, measured water contents in drill cuttings from Krafla and Reykjanes most likely
186 represent minimum values for bulk rock water contents for the Icelandic crust.

187

188 *3.2. Fluid sampling and analyses*

189 Fluid samples were collected from well discharges at the surface at Krafla and Reykjanes.
190 These consisted of liquid and vapor that were separated using a Webre separator followed by
191 sampling of the different phases (Arnórsson et al., 2006). The geothermal boreholes are cased
192 to few hundred meters depth to prevent shallow non-thermal groundwater inflow and the fluid
193 flow rate is very high, corresponding to a few minutes from the reservoir to the surface.
194 Consequently, it is generally considered that such high-temperature surface well discharges
195 like at Krafla and Reykjanes represent the reservoir fluid compositions at depth. Also, as the
196 total fluid discharge relative to the geothermal reservoir volume is very low, the chemical
197 composition of high-temperature geothermal well discharges typically stays unchanged for
198 decades (e.g., Arnórsson et al., 2007).

199 Fluid sampling at Surtsey was carried out using a bailer sampler that was lowered to
200 the desired sampling depths in borehole SE-3. An experimental and measuring device occupies
201 borehole SE-2B making it unavailable for water sampling.

202 Liquid and vapor samples were collected into 25 mL amber glass bottles with air-tight
203 caps. High-temperature liquid and vapor samples were cooled and condensed using an in-line
204 cooling coil prior sampling. To the samples, 1% Zn-acetate solution was added to remove any
205 dissolved sulfide that may potentially interfere with the analysis. The precipitates formed were
206 subsequently filtered off using 0.2 μm filter (cellulose acetate). Hydrogen (δD) and oxygen
207 ($\delta^{18}\text{O}$) isotope analyses of water samples were carried out using a Thermo Delta V Advantage
208 IRMS at University of Iceland after equilibration with the appropriated gas mixture and a Ti
209 catalysis in the case of hydrogen isotopes. Following the reactions, the gas mixture was cleaned
210 in line using water traps and a gas chromatography (GC) column followed by analysis on the
211 IRMS. Each sample was measured ten times and the average of eight was used to calculate the
212 respective isotope value. Oxygen and hydrogen isotope ratios are reported in standard delta
213 notation (‰) relative to VSMOW. The final values were corrected for the presence of Zn-
214 acetate added to the samples prior to analysis. The analytical precision was based on long term
215 analyses of the standard and was within $<1.0\text{‰}$ for δD and $<0.1\text{‰}$ for $\delta^{18}\text{O}$.

216

217 *3.3. Chemical and isotope modeling*

218 The extent of hydration and the δD and $\delta^{18}\text{O}$ values of altered basalt and secondary minerals
219 are controlled by a combination of fluid sources (e.g., meteoric water, seawater, or a mixture
220 thereof) and geothermal processes (e.g., fluid-rock interaction, fluid phase separation). To
221 quantify the effects of these various sources and processes associated with alteration and
222 hydration of the Icelandic crust on δD and $\delta^{18}\text{O}$ ratios, geochemical and isotope modeling was
223 conducted using PHREEQC (Parkhurst and Appelo, 1999), WATCH (Bjarnason, 2010) and

224 IsoGem programs (Stefánsson et al., 2017). The modeling scenarios conducted included: (1)
225 fluid-rock interaction as a function of extent of reaction, fluid source and temperature and (2)
226 fluid phase relations, including mixing and fluid phase separation. Calculation details, input
227 data and isotope fractionation factors are given in Appendix A.

228 Briefly, the fluid-rock interaction modelling included conventional titration reaction
229 path simulations in which basaltic rock was allowed to react in steps with water of meteoric,
230 seawater origin or mixture thereof. Saturated secondary minerals in each step were allowed to
231 precipitate. The secondary minerals included in the calculations were those commonly
232 observed in geothermal systems in Iceland at variable temperatures (Kristmannsdóttir, 1979).
233 Bulk rock water contents were calculated from the predicted modal abundance of hydrous
234 minerals and the initial water content of the residual fresh basalt that remained in each reaction
235 step. Chemical and isotope equilibrium were assumed for all calculations. The effects of fluid
236 phase separation (boiling) and cooling was further modeled. Geothermal fluids of meteoric and
237 seawater origin were allowed to boil upon pressure decrease from the reservoir temperature to
238 100 °C and cool at temperatures <100 °C. For these calculations, secondary minerals were
239 allowed to form when saturated.

240

241 **4. Results**

242 *4.1. Hydrogen isotope ratios and water contents of altered basalts*

243 The water content and δD values of altered bulk rocks collected from drill cores and cuttings
244 as a function of depth from Krafla (well KG-25), Reykjanes (well RN-10) and Surtsey
245 (borehole SE-2B and SE-3) are reported in Table A.1 and shown in Figure 1. The water content
246 of the samples ranged from 0.5 to 4.2 wt.% H₂O and 2.2 to 4.1 wt.% H₂O at Krafla and
247 Reykjanes, respectively. Water contents of samples from Surtsey ranged from 6.4 to 9.1 wt.%
248 H₂O with lowest water contents measured toward the bottom of the boreholes. δD values of

249 altered basalts from Krafla which is fed by meteoric water (e.g., Stefánsson *et al.*, 2017) ranged
250 from -125 to -96‰ (Fig. 1). In contrast, at Reykjanes where the geothermal system is fed by
251 seawater (e.g., Pope *et al.*, 2014), the corresponding δD values ranged from -80 to -59‰. At
252 Surtsey, a geothermal system also fed by seawater, δD values of altered basalts were similar to
253 those obtained from Reykjanes and ranged from -78 to -46‰. For both the Krafla and
254 Reykjanes geothermal systems, the water content was found to decrease and δD values became
255 progressively less negative with increasing depth (Fig. A.2) which is accompanied with a
256 decrease in degree of alteration and abundance of secondary hydrous minerals in the rock
257 (Table A.1).

258

259 4.2. Hydrogen and oxygen isotope ratios of geothermal fluids

260 The measured δD and $\delta^{18}O$ values in fluids at Krafla, Reykjanes and Surtsey are reported in
261 Table A.2 and shown in Figures 1 and A.3. At Krafla, δD values of the well discharge ranged
262 from -80.9 to -83.3‰ and -82.5 to -89.9‰ and $\delta^{18}O$ values ranged from -8.2 to -11.2‰ and -
263 10.5 to -13.1‰ for the liquid and vapor phases, respectively. At Reykjanes, δD values of the
264 well discharge ranged from -12.2 to -22.5‰ and -23.8 to -27.8‰ and $\delta^{18}O$ values ranged from
265 -0.3 to -3.0‰ and -3.2 to -4.0‰ for the liquid and vapor phases, respectively. Based on these
266 data, the total reservoir fluid discharge δD and $\delta^{18}O$ values were calculated from the expression,
267 $\delta_i^{total} = X^v \delta_i^v + (1 - X^v) \delta_i^{lq}$ where v and lq stands for vapor and liquid phases and X^v is the vapor
268 fraction at sampling. The vapor fraction was calculated with the WATCH program assuming
269 liquid only reservoir and adiabatic boiling to the sampling conditions. The total discharge
270 values were taken to represent the reservoir values. The δD values ranged from -88.9 to -82.3‰
271 and -23.1 to -14.9‰ and the $\delta^{18}O$ values ranged from -11.5 to -8.6‰ and -3.2 to -1.0‰ for the
272 total discharge at Krafla and Reykjanes, respectively. At Surtsey, fluids in borehole SE-3 occur

273 only in the liquid phase. δD and $\delta^{18}O$ values ranged from +2.1 to +4.3‰ and +0.3 to +0.6‰,
274 respectively.

275

276 *4.3. Modeling*

277 Geochemical and isotope modelling was applied to quantify the alteration process of basalts
278 by geothermal fluids (see Appendix A for details). The water content of fresh Icelandic basalts
279 is ~0.1 to 0.5 wt.% (Nichols et al., 2002). Upon alteration by geothermal fluids the water
280 content of the bulk rock increased due to formation of hydrous secondary minerals, and
281 according to our model results, reached a maximum of ~9.1 wt.% H₂O at low temperatures
282 (<150 °C) and ~4.2 wt.% H₂O at elevated temperatures (>200 °C) after complete (100%)
283 alteration of the basalt. The predominant source of hydrogen of the hydrated basalts was found
284 to be the aqueous fluid with insignificant juvenile water composition except at very low degree
285 of alteration (Figs. 2 and A.4).

286 Our model demonstrates that the origin of hydrogen in fresh basalt will shift instantly
287 from a juvenile to a meteoric or seawater fluid source upon water-rock interaction (Fig. 2).
288 Thus, the δD value of the basalt changed almost immediately from the value of the unaltered
289 rock of -80 ± 10 ‰ (typical Icelandic basalt) (Martin et al., 2017) to that of the hydrous
290 secondary minerals in isotopic equilibrium with the hydrothermal fluids (Fig. 3). With
291 progressive alteration, the δD value of the geothermal fluid became slightly less negative as
292 the light hydrogen isotope preferably fractionates into the newly formed secondary minerals.

293 Fluid phase separation (boiling) and formation of vapor and liquid water is common in
294 geothermal systems (e.g., Hayba and Ingebritsen, 1997). Modeling of phase separation of
295 geothermal fluids of meteoric water and seawater origin using WATCH and PHREEQC
296 revealed that minor quantities of hydrous minerals were predicted to form upon boiling of such
297 fluids. Consequently, the water content and δD values of the bulk altered rock remained

298 unchanged (Fig. A.6). However, the δD values of the vapor and liquid phases formed may
299 significantly differ from the bulk fluid composition, with the vapor phase becoming
300 isotopically more negative and the boiled liquid phase isotopically less negative relative to the
301 geothermal reservoir fluid.

302

303 **5. Discussion**

304 *5.1. The Krafla, Reykjanes and Surtsey analogues and comparison with the model results*

305 The studied sample set derives from boreholes where temperatures span a wide range of 180
306 to 340°C in the meteoric water-fed geothermal system at Krafla, 250 to 310°C in the seawater-
307 dominated geothermal system at Reykjanes and 50 to 130°C in the seawater-fed geothermal
308 system at Surtsey (Table A.1). The boreholes penetrate the Icelandic crust from shallow depths
309 (<260 m) at Surtsey to depths of >2000 m in Krafla and Reykjanes. This range in temperatures
310 and depths makes these localities ideal to investigate the effects of source fluid and the extent
311 of alteration of basalts on its water content and hydrogen isotope composition. The data
312 obtained from hydrated crustal rocks at Krafla, Reykjanes and Surtsey were compared to
313 chemical and isotope modeling results. The modeling was based on the approach from
314 Stefánsson et al. (2017) and is described in Appendix A. The model reproduced the values
315 observed in drill cuttings and core from the studied geothermal fields (Fig. 4). Hence, the
316 comparison between modelled and natural values revealed that the water content and δD
317 variations of the altered basalts are controlled by (1) the isotope composition of the source
318 fluid; (2) the equilibrium isotope fractionation between the aqueous fluids and the alteration
319 minerals formed; and (3) the type and quantity (mass) of secondary minerals formed. These
320 factors in turn depend on temperature and extent or progress of fluid-rock interaction.

321 The influence of the isotope composition of the source fluid on the δD value of altered
322 basalt is demonstrated by the interaction of meteoric water with basalt at Krafla which resulted

323 in δD values significantly more negative (-125 to -120‰) than at Reykjanes (-60 to -75‰) and
324 Surtsey (-78 to -45‰) where the source fluid primarily derives from a seawater-meteoric water
325 mixture or solely from seawater, respectively (e.g., Arnórsson, 1978; Ólafsson and Jakobsson,
326 2009). The δD values measured in altered basalt from Reykjanes and Surtsey do not differ
327 much despite substantially different temperatures and alteration mineralogy in the geothermal
328 systems (Fig. A.5, Table A.1). This is likely due to the large abundance of zeolites and Fe-rich
329 clays in drill cores from Surtsey. Isotope fractionation between these minerals and aqueous
330 fluids are reported to be large (see Table A.4). Thus, the presence of zeolites and Fe-rich clays
331 results in more negative δD values in the altered bulk rock than the values predicted for altered
332 basalt containing Mg-rich clays and limited amounts of zeolite (Fig. 4). Water contents of
333 altered basalt also depend on the type and quantity of hydrous secondary minerals. For
334 example, the water contents measured in altered basalts at both Krafla and Reykjanes are of
335 similar range (Fig. 1). According to both modeling results (Fig. A.5) and natural observations
336 (Table A.1) (Franzson et al., 2002; Sæmundsson, 1991), this is likely due to the occurrence of
337 the same types of hydrous minerals in these settings. At Surtsey, water contents of altered basalt
338 are significantly higher (up to 9.1 wt.%). The modeling results (Figs. 4 and A.4) and natural
339 observations (Table A.1) show that hydrous minerals such as clays and zeolites are the most
340 abundant secondary mineral phases forming upon low-temperature alteration. These minerals
341 carry significant amounts of water in their crystal lattice and are thus responsible for increased
342 water contents in basalts altered at low temperatures. Note, that Surtsey basalt contains a large
343 proportion of glassy components at the initiation of alteration (Jakobsson and Moore, 1986).
344 The reaction rates and ultimate hydration of basaltic glasses are faster than those of crystalline
345 basalt (e.g., Oelkers and Gislason, 2001; Gislason and Oelkers, 2003; Gudbrandsson et al.,
346 2011) resulting in higher water contents in Surtsey samples relative to crystalline basalt of
347 similar age and composition containing only minor amounts of glassy components.

348 In summary, comparison of the modelling results with natural datasets from Krafla,
349 Reykjanes and Surtsey (Fig. 4) shows that our model simulations can predict and reproduce
350 the secondary minerals forming upon alteration and hydration of a representative Icelandic
351 basalt over a range of temperatures and fluid source (i.e., meteoric versus seawater). The
352 predicted secondary mineral assemblage agrees well with observed secondary mineralogy from
353 the studied localities (Table A.1). Therefore, based on the abundance and type of secondary
354 minerals, the degree of alteration, the water content as well as the isotopic signature of the
355 altering and hydrating basalt can be assessed. The comparison of our modelling results with
356 our data measured in Krafla, Reykjanes and Surtsey demonstrate that the key parameters that
357 likely control hydrogen isotope systematics in altered crust comprise the isotopic composition
358 of the fluid source and host rock, equilibrium isotope fractionation between minerals and fluids,
359 temperature and extent of fluid-rock reaction. In the following, we will apply our modelling
360 approach to a pure seawater-basalt system and aim to constrain hydration processes taking
361 place in the oceanic crust.

362

363 *5.2. Implications for hydration of the oceanic crust*

364 The hydration and alteration of the oceanic crust is generally difficult to constrain as available
365 sonic-velocity and direct measurements of the water content from DSDP/ODP boreholes are
366 rare. Here, we apply our model to constrain the water uptake and hydrogen isotope
367 compositions of the basaltic oceanic crust upon alteration by seawater. Published δD values of
368 altered basalt retrieved from the upper part of the oceanic crust (~1-2 km) show overlapping
369 values of $-41 \pm 12.3\text{‰}$ (n=34) in the volcanics (Kawahata et al., 1987; Shilobreeva et al., 2011),
370 $-41 \pm 7.8\text{‰}$ (n=46) in the sheeted dikes (Agrinier et al., 1995a; Agrinier et al., 1995b; Kusakabe
371 et al., 1989; Shilobreeva et al., 2011) and $-44 \pm 6.8\text{‰}$ (n=7) in the gabbros (Shilobreeva et al.,
372 2011). The corresponding water content of altered basalt from the oceanic crust is reported to

373 be 1.6 ± 1.3 wt.% H_2O (n=34) in the volcanics (Kawahata et al., 1987; Shilobreeva et al., 2011),
374 1.6 ± 0.6 wt.% H_2O (n=46) in the sheeted dikes (Agrinier et al., 1995a; Agrinier et al., 1995b;
375 Kusakabe et al., 1989; Shilobreeva et al., 2011) and 0.8 ± 0.1 wt.% H_2O (n=7) in the gabbros
376 (Shilobreeva et al., 2011). Comparison of model results with the natural data shows that such
377 range of values is explained by alteration and hydration of basalts by seawater at low (<50 °C)
378 to geothermal temperatures (>300 °C) (Fig. 5). With increasing temperature and extent of
379 alteration, water contents in basalt may increase to >5.0 wt.%, whereas, δD values increase to
380 values of >-30 ‰. Even in relatively unaltered basalt, δD values deviate considerably from fresh
381 MORB and the δD values in altered basalt are expected to almost immediately shift toward
382 more positive values regardless of the low degree of alteration in the rock. This is due to initial
383 low water contents of basalt compared to the amount of hydrogen in seawater.

384 To investigate the water uptake of the oceanic crust upon alteration, the water content
385 and isotopic composition of an entire crustal sequence was constrained along typical thermal
386 gradients through young (<10 Ma) and old (>100 Ma) oceanic crust (Fig. 6). Details on the
387 thermal gradients and information on porosities, type of secondary minerals, water content and
388 hydrogen isotope composition of unaltered basalt and gabbro used in the calculations are given
389 in Appendix A. The calculations were carried out for various alteration degrees of the crust
390 (10-100%) (Fig. 6, Tables A.5 and A.6). The Monte Carlo method for error propagation
391 (Anderson, 1976) was applied to calculate the uncertainties of wt.% H_2O and δD values. The
392 uncertainty on the water content is ± 0.3 wt.% and the uncertainty on the δD values is ± 6 ‰ with
393 the potential main sources of error deriving from reported variations in water content and δD
394 values of MORB (Kyser and O'Neil, 1984; Michael, 1995) and limits in the availability of
395 hydrogen isotope fractionation factors between water and hydrous minerals.

396 In young (<10 Ma) oceanic crust, at shallow depths (<1 km) and low temperatures
397 (<150 °C), hydration is expected to be highest due to easy accessibility of seawater through

398 highly porous rocks (Johnson and Pruis, 2003) and presence of hydrous minerals such as
399 zeolites, clays, and chlorite. Under these conditions, water contents may reach 1.0 to 8.3 wt.%
400 H₂O and δ D values range from -60 ± 6 to -25 ± 6 ‰ depending on temperature and extent of
401 alteration of the rock (Fig. 6). At elevated temperatures >200 °C and depths of >1 -2 km, the
402 most common hydrous minerals include chlorite, epidote and amphibole. Basalt alteration
403 under these conditions would result in hydration corresponding to 0.7 to 4.2 wt.% H₂O and δ D
404 values ranging from -60 to -34‰. With increasing depth (>2 km), water contents and δ D values
405 are expected to range from 0.4 to 2.2 wt.% and -60 to -41‰, respectively, depending on the
406 extent of alteration of the gabbroic layer. As seawater infiltration becomes limited with depth
407 due to compaction and closure of pore space, it is likely that water contents and δ D values will
408 eventually reflect the values of the unaltered gabbro with increasing depth. Comparison of
409 modeling results with published values on the water content and δ D values from the lithological
410 layers of the oceanic crust revealed that alteration is typically least extensive <5 -15% in the
411 volcanic section but becomes progressively more extensive with increasing temperature and
412 depth with 25-75% in the sheeted dikes and <40 % in the uppermost part of the gabbroic layer
413 (Fig. 6).

414 Water content and δ D values in old (>100 Ma) oceanic crust remain difficult to
415 constrain due to the lack of natural data. The only reported δ D values derive from composites
416 (Alt, 2003) where samples are combined for specific depth intervals at a scale of tens to
417 hundreds of meters. Such samples are unfortunately not eligible for comparison with our
418 model. Coogan et al. (2019) reported that $\delta^{18}\text{O}$ values of altered basalts from the volcanic
419 section become progressively more positive with crustal age. A similar shift toward more
420 positive δ D values would be expected for all lithological sequences as the breakdown of high-
421 temperature hydrous minerals (amphibole, epidote) results in the enrichment of deuterium in
422 the forming hydrous low-temperature minerals (chlorite, clays) based on reported equilibrium

423 isotope fractionation factors (Table A.4). Water contents are expected to increase in the
424 previously least altered sections of the crust due to progressive alteration upon aging. For
425 example, water contents measured in the volcanic sequence (<600 m) of old igneous oceanic
426 crust cluster at 2.1 ± 1.6 wt.% H₂O (n = 129) (Floyd and Castillo, 1992; Staudigel et al., 1996)
427 which is significantly higher than water contents measured in young oceanic crust at similar
428 depths (Fig. 6). Such values would correspond to a crust altered by 10 to 50% according to our
429 model when adjusted to a colder geotherm (Table A.6). More extreme alteration is probably
430 limited due to the closure of pore space upon continuous secondary mineral formation and
431 extensive sedimentation onto the igneous basement. We highlight that simulating late stage
432 alteration of old oceanic crust remains a challenge due to the lack of data that could be used for
433 verification of our model. Later overprints are likely to change the petrological and chemical
434 composition of the oceanic crust, in particular with respect to its hydration.

435 Using the constraints on isotope and water content outlined above, the water flux to
436 young (<10 Ma) and old (>100 Ma) oceanic crust can be calculated (Fig. 7). The water flux to
437 young oceanic crust can be estimated knowing its uptake by seawater-rock interaction, amount
438 of porewater and the production rate of the oceanic crust (for details see Appendix A). The
439 annual water uptake of the young oceanic igneous crust upon alteration was calculated to be
440 1400-1650 Tg H₂O/yr with a δD value clustering at -55 ± 6 ‰ (Tables 1 and A.7). These
441 estimates on water fluxes and isotope composition for young oceanic crust differ significantly
442 from previously reported water fluxes (575 to 1150 Tg H₂O/yr) (Ito et al., 1983; Staudigel et
443 al., 1996) and δD values (-60‰) (Giggenbach, 1992). These discrepancies arise because
444 porewater has not been considered in the previously reported estimates. Excluding the
445 porewater component from our calculations would drive the water flux (560 to 790 Tg H₂O/yr)
446 and δD (-57 ± 1 ‰) estimates of the oceanic crust to values similar to those reported by Ito et al.
447 (1983), Staudigel et al. (1996) and Giggenbach (1992), respectively.

448 Based on the water uptake by seawater-rock interaction and amount of porewater in old
449 (>100 Ma) oceanic crust (Tables 1 and A.7), the water flux for igneous oceanic crust that enters
450 subduction trenches was calculated to be 610-1240 Tg H₂O/yr (Fig. 8, Table 1). Our calculated
451 values fall into a similar range – although wider – as most recent estimates of 920-930 Tg
452 H₂O/yr (Hacker, 2008; Jarrard, 2003). Departures from our estimates may derive from
453 differences in the assumption of crustal thickness, void volume and/or the initial water contents.
454 Importantly, the seawater uptake within the upper 2 km of the oceanic crust accounts for almost
455 50% of the total water budget of the oceanic crust. This implies that the water uptake is most
456 effective at relatively low temperatures (<200 °C) and shallow depths. Hence, low-temperature
457 alteration and hydration of the oceanic crust might play a significant role in increasing the water
458 budget of the aging and cooling oceanic crust.

459

460 *5.3. Implications for the deep water cycle*

461 As the descending slab reaches greater depths, almost all porewater is assumed to be released
462 to the accretionary prism and/or the forearc upon compaction and pore space reduction (Fig. 7)
463 (Jarrard, 2003). Thus, by taking the water fluxes from sediments and igneous crust expelled to
464 the forearc from Jarrard (2003), the amount of water carried by the igneous crust beyond the
465 forearc region is calculated to range from 270 to 910 Tg H₂O/yr (Fig. 7). This water flux agrees
466 with the most recent estimates of 460 to 630 Tg H₂O/yr at a similar depth (Hacker, 2008;
467 Jarrard, 2003; Rüpke et al., 2004; van Keken et al., 2011). Furthermore, this is a higher flux of
468 water than estimates for sediments of 70-160 Tg H₂O/yr (Bebout, 1995; Hacker, 2008; Jarrard,
469 2003; Peacock, 1990; van Keken et al., 2011) and mantle of 120-570 Tg H₂O/yr (Hacker, 2008;
470 Rüpke et al., 2004; van Keken et al., 2011). The bulk δD value of the subducted igneous crust
471 at this depth (~100 km) is calculated to range from ~ -60 to -50‰.

472 Hacker (2008) and van Keken et al. (2011) showed that 60-80 % of water would be
473 released by dehydration reactions from the oceanic crust and overlying sediments to the mantle
474 wedge triggering the formation of magmas. Based on the isotope fractionation factors between
475 mineral-water pairs (e.g., amphibole-water, chlorite-water) at temperatures >500 °C (Table
476 A.4) the isotopic signature of such water released from the subducted oceanic crust would result
477 in δD values of ~ -35 to -10 ‰. This agrees remarkably well with measured δD values of high-
478 temperature and fumarolic gases released from arc volcanoes that indicate an isotope value for
479 primary magmatic water of -33 to -10 ‰ (e.g., Giggenbach, 1992; Taran and Zelenski, 2015).

480 Assuming 60-80% dehydration of the oceanic igneous crust upon subduction, 55-360
481 Tg H₂O/yr would be further transported to deeper depths within the mantle. According to the
482 available dehydration models for subducting slabs (Shaw et al., 2008), the isotopic composition
483 of such dehydrated crust would become significantly more negative with values ranging from
484 -160 to -85 ‰. Considering the water flux at mid-ocean ridges of ~ 20 H₂O Tg/yr (Hirschmann
485 and Kohlstedt, 2012), our results are therefore consistent with water enrichment in the Earth's
486 mantle over a geological timescale (e.g., Parai and Mukhopadhyay, 2012). Moreover, our
487 results demonstrate that the water accumulating in the deep mantle is likely to display more
488 negative hydrogen isotope values relative to the upper mantle. This is supported by unusually
489 negative δD values (down to -120 ‰) measured in melt inclusions from Hawaii suggesting
490 recycling of subduction slabs in the mantle (e.g., Hauri, 2002). However, this subject remains
491 somewhat speculative as the water storage capacity in the mantle is limited and evaluating the
492 amount of water needed to change the isotope composition of the mantle is beyond the scope
493 of this paper.

494

495 **6. Conclusion**

496 The hydration state of the Icelandic crust and corresponding hydrogen isotope systematics were
497 constrained using quantitative geochemical and isotope modeling, hydrogen and oxygen
498 isotope compositions and water contents, of well constrained altered basalt from the
499 hydrothermal systems Krafla, Reykjanes and Surtsey, Iceland. The comparison of the natural
500 datasets from Krafla, Reykjanes and Surtsey with results from the modelling revealed that
501 hydration and hydrogen isotopic variations of basalt are controlled by (1) the isotope
502 composition of the source fluid, (2) isotope fractionation between the aqueous fluids and the
503 alteration minerals formed, and (3) the type and quantity of alteration minerals formed. These
504 factors in turn depend on the extent of fluid-rock reaction and temperature. Subsequently, the
505 same modelling approach was applied to a pure seawater-basalt system and verified with
506 available data on δD isotope values measured in the oceanic crust. The comparison confirmed
507 that our simulations could be further applied to a hydration model of the oceanic crust.
508 Quantification of the water uptake of the oceanic crust was based on the natural dataset from
509 Reykjanes (a seawater-dominated hydrothermal system) as well as on literature data on
510 hydrogen isotope systematics and water content in the upper part of the oceanic crust (~1-2
511 km), thermal gradients of the oceanic crust and rate of crustal generation at mid-ocean ridge
512 settings. Upon seawater-induced alteration 1400 to 1650 Tg H_2O/yr is added to the igneous
513 oceanic crust. Most porewater and structurally bound water is hosted by the upper part of the
514 oceanic crust (<2 km). Such hydrated crust would have a δD values of $\sim -55 \pm 6\%$. Upon
515 subduction and dehydration of the oceanic crust 80-90% will be released to the arc crust and
516 mantle wedge. The water flux from this almost completely dehydrated descending oceanic
517 crust to deeper levels in the mantle would comprise 55-360 Tg H_2O/yr . Such dehydrated crust
518 would have a δD value of ~ -160 to -85% . Since the water flux is comparatively low at mid-
519 ocean ridges (Hirschmann and Kohlstedt, 2012), subduction of hydrated oceanic crust might

520 ultimately enrich the water content in the mantle and consequently decrease its hydrogen
521 isotopic composition.

522

523 **Acknowledgements**

524 This project was financially supported by NordVulk, the International Continental Scientific
525 Drilling Program (ICDP) through a grant to the SUSTAIN project, and the Icelandic Research
526 Fund (project number: 163083-051). SAH acknowledges support from the Icelandic Research
527 Fund (project number: 196139-051). HS Orka and Landsvirkjun kindly provided access to the
528 drill cuttings. J. Cullen, T. Larson, R. Ólafsdóttir and Á.E. Sveinbjörnsdóttir are thanked for
529 assistance during sample preparation and data acquisition. We thank four anonymous reviewers
530 for their constructive comments and suggestions to an earlier version of this manuscript. Louis
531 Derry is thanked for careful editorial handling of this study.

532

533 **References**

534 Agrinier, P., Hékinian, R., Bideau, D., Javoy, M. (1995a) O and H stable isotope compositions
535 of oceanic crust and upper mantle rocks exposed in the Hess Deep near the Galapagos Triple
536 Junction. Earth and Planetary Science Letters 136, 183-196. [https://doi.org/10.1012-](https://doi.org/10.1016/0012-821X(95)00159-A)
537 [821X\(95\)00159-A](https://doi.org/10.1016/0012-821X(95)00159-A)

538 Agrinier, P., Laverne, C., Tartarotti, P. (1995b) Stable isotope ratios (oxygen, hydrogen) and
539 petrology of hydrothermally altered dolerites at the bottom of the sheeted dike complex of Hole
540 504B, Proceedings of the Ocean Drilling Program, Scientific Results, pp. 99-106.

541 Alt, J.C. (2003) Stable isotopic composition of upper oceanic crust formed at a fast spreading
542 ridge, ODP Site 801. Geochemistry, Geophysics, Geosystems 4, 1-11.
543 <https://doi.org/10.1029/2002GC000400>

544 Alt, J.C., Laverne, C., Vanko, D.A., Tartarotti, P., Teagle, D.A.H., Bach, W., Zuleger, E.,
545 Erzinger, J., Honnorez, J., Pezard, P.A. (1996) Hydrothermal alteration of a section of upper
546 oceanic crust in the Eastern Equatorial Pacific: a synthesis of results from site 504 (DSDP
547 LEGS 69, 70, and 83, and ODP LEGS 111, 137,140, and 148), Proceedings of the Ocean
548 Drilling Program, scientific results, pp. 417-434.

549 Anderson, G.M. (1978) Error propagation by the Monte Carlo method in geochemical
550 calculations. *Geochemica et Cosmochimica Acta* 40, 1533-1538. [https://doi.org/10.1016-](https://doi.org/10.1016/0016-7037(76)90092-2)
551 [7037\(76\)90092-2](https://doi.org/10.1016/0016-7037(76)90092-2)

552 Arnórsson, S. (1978) Major element chemistry of the geothermal sea-water at Reykjanes and
553 Svartsengi, Iceland. *Mineralogical Magazine* 42, 209-220.
554 <https://doi.org/10.1180/minmag.1978.042.322.07>

555 Arnórsson, S., Bjarnason, J.Ö., Giroud, N., Gunnarsson, I., Stefánsson, A. (2006) Sampling
556 and analysis of geothermal fluids. *Geofluids* 6, 203-216. [https://doi.org/10.1111/j.1468-](https://doi.org/10.1111/j.1468-8123.2006.00147.x)
557 [8123.2006.00147.x](https://doi.org/10.1111/j.1468-8123.2006.00147.x)

558 Arnórsson, S., Stefánsson, A., Bjarnason, J.O. (2007) Fluid-fluid interactions in geothermal
559 systems. *Reviews in Mineralogy and Geochemistry* 65, 259-312.
560 <https://doi.org/10.2138/rmg.2007.65.9>

561 Bebout, G.E. (1995) The impact of subduction-zone metamorphism on mantle-ocean chemical
562 cycling. *Chemical Geology* 126, 191-218. [https://doi.org/10.1016/0009-2541\(95\)00118-5](https://doi.org/10.1016/0009-2541(95)00118-5)

563 Bjarnason, J.Ö. (2010) The Chemical Speciation Program WATCH. Version 2.4 Iceland
564 GeoSurvey. Accessible at <http://www.hydrothermal.is/software> (2010).

565 Bowers, T.S., Taylor, H.P. (1985) An integrated chemical and stable-isotope model of the
566 origin of midocean ridge hot spring systems. *Journal of Geophysical Research: Solid Earth* 90,
567 12583-12606. <https://doi.org/10.1029/JB090iB14p12583>

568 Bown, J.W., White, R.S. (1994) Variation with spreading rate of oceanic crustal thickness and
569 geochemistry. *Earth and Planetary Science Letters* 121, 435-449. [https://doi.org/10.1016/0012-](https://doi.org/10.1016/0012-821X(94)90082-5)
570 [821X\(94\)90082-5](https://doi.org/10.1016/0012-821X(94)90082-5)

571 Coogan, L.A., Daëron, M., Gillis, K.M. (2019) Seafloor weathering and the oxygen isotope
572 ratio in seawater: insight from whole-rock $\delta^{18}\text{O}$ and carbonate $\delta^{18}\text{O}$ and $\Delta 47$ from the Troodos
573 ophiolite. *Earth and Planetary Science Letters* 508, 41-50.
574 <https://doi.org/10.1016/j.epsl.2018.12.014>

575 Fischer, T.P. (2008) Fluxes of volatiles (H_2O , CO_2 , N_2 , Cl , F) from arc volcanoes. *Geochemical*
576 *Journal* 42, 21-38. <https://doi.org/10.2343/geochemj.42.21>

577 Floyd, P.A., Castillo, P.R. (1992) Geochemistry and petrogenesis of Jurassic ocean crust
578 basalts, site 801, Proceedings of the Ocean Drilling Program, Scientific Results, pp. 361-388.

579 Franzson, H., Thordarson, S., Björnsson, G., Gudlaugsson, S.T., Richter, B., Fridleifsson,
580 G.O., Thorhallsson, S. (2002) Reykjanes high-temperature field, SW-Iceland: Geology and
581 hydrothermal alteration of well RN-10, Workshop on Geothermal Reservoir Engineering, pp.
582 233-240.

583 Fowler, A.P.G., Zierenberg, R.A. (2016) Geochemical bias in drill cutting samples versus drill
584 core samples returned from the Reykjanes Geothermal System, Iceland. *Geothermics* 62, 48-
585 60. <https://doi.org/10.1016/j.geothermics.2016.02.007>

586 Giggenbach, W.F. (1992) Isotopic shifts in waters from geothermal and volcanic systems along
587 convergent plate boundaries and their origin. *Earth and Planetary science letters* 113, 495-510.
588 [https://doi.org/10.1016/0012-821X\(92\)90127-H](https://doi.org/10.1016/0012-821X(92)90127-H)

589 Gislason, S.R., Oelkers, E.H. (2003) Mechanism, rates, and consequences of basaltic glass
590 dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of
591 pH and temperature. *Geochimica et Cosmochimica Acta* 67, 3817-3832.
592 [https://doi.org/10.1016/S0016-7037\(03\)00176-5](https://doi.org/10.1016/S0016-7037(03)00176-5)

593 Godard, M., Awaji, S., Hansen, H., Hellebrand, E., Brunelli, D., Johnson, K., Yamasaki, T.,
594 Maeda, J., Abratis, M., Christie, D. (2009) Geochemistry of a long in-situ section of intrusive
595 slow-spread oceanic lithosphere: Results from IODP Site U1309 (Atlantis Massif, 30 N Mid-
596 Atlantic-Ridge). *Earth and Planetary Science Letters* 279, 110-122.
597 <https://doi.org/10.1016/j.epsl.2008.12.034>

598 Grose, C.J., Afonso, J.C. (2013) Comprehensive plate models for the thermal evolution of
599 oceanic lithosphere. *Geochemistry, Geophysics, Geosystems* 14, 3751-3778.
600 <https://doi.org/10.1002/ggge.20232>

601 Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H. (2011) An experimental
602 study of crystalline basalt dissolution from $2 \leq \text{pH} \leq 11$ and temperatures from 5 to 75 °C.
603 *Geochimica et Cosmochimica Acta* 75, 5496-5509. <https://doi.org/10.1016/j.gca.2011.06.035>

604 Gudmundsson, B.T., Arnórsson, S. (2005) Secondary mineral–fluid equilibria in the Krafla and
605 Námafjall geothermal systems, Iceland. *Applied Geochemistry* 20, 1607-1625.
606 <https://doi.org/10.1016/j.apgeochem.2005.04.020>

607 Hacker, B.R. (2008) H₂O subduction beyond arcs. *Geochemistry, Geophysics, Geosystems* 9,
608 1-24. <https://doi.org/10.1029/2007GC001707>

609 Hauri, E. (2002) SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in
610 Hawaiian melt inclusions. *Chemical Geology* 183, 115-141. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2541(01)00374-6)
611 [2541\(01\)00374-6](https://doi.org/10.1016/S0009-2541(01)00374-6)

612 Hayba, D.O., Ingebritsen, S.E. (1997) Multiphase groundwater flow near cooling plutons.
613 *Journal of Geophysical Research: Solid Earth* (1978–2012) 102, 12235-12252.
614 <https://doi.org/10.1029/97JB00552>

615 Heft, K.L., Gillis, K.M., Pollock, M.A., Karson, J.A., Klein, E.M. (2008) Role of upwelling
616 hydrothermal fluids in the development of alteration patterns at fast spreading ridges: Evidence
617 from the sheeted dike complex at Pito Deep. *Geochemistry, Geophysics, Geosystems* 9, 1-21.
618 <https://doi.org/10.1029/2007GC001926>

619 Hirschmann, M., Kohlstedt, D. (2012) Water in Earth's mantle. *Physics Today* 65, 40-45.
620 <http://dx.doi.org/10.1063/PT.3.1476>

621 Ito, E., Harris, D.M., Anderson Jr, A.T. (1983) Alteration of oceanic crust and geologic cycling
622 of chlorine and water. *Geochimica et Cosmochimica Acta* 47, 1613-1624.
623 [https://doi.org/10.1016/0016-7037\(83\)90188-6](https://doi.org/10.1016/0016-7037(83)90188-6)

624 Jackson, M.D., Guðmundsson, M.T., Weisenberger, T.B., Rhodes, J.M., Stefánsson, A.,
625 Kleine, B.I., Lippert, P., Marquardt, J.M., Reynolds, H.I., Kück, J., Marteinson, V.T., Vannier,
626 P., Bach, W., Barich, A., Bergsten, P., Bryce, J.G., Cappelletti, P., Couper, S., Fahnestock,
627 M.F., Gorny, C.F., Grimaldi, C., Groh, M., Guðmundsson, Á., Gunnlaugsson, Á.T., Hamlin,
628 C., Högnadóttir, T., Jónasson, K., Jónsson, S.S., Jørgensen, S.L., Klonowski, A.M., Marshall,
629 B., Massey, E., McPhie, J., Moore, J.G., Ólafsson, E.S., Onstad, S.L., Perez, V., Prause, S.,
630 Snorrason, S.P., Türke, A., White, J.D.L., Zimanowski, B. (2019) SUSTAIN drilling at Surtsey
631 volcano, Iceland, tracks hydrothermal and microbiological interactions in basalt 50 years after
632 eruption. *Scientific Drilling* 25, 35-46. <https://doi.org/10.5194/sd-25-35-2019>

633 Jakobsson, S.P., Moore, J.G. (1986) Hydrothermal minerals and alteration rates at Surtsey
634 volcano, Iceland. Geological Society of America Bulletin 97, 648-659.
635 [https://doi.org/10.1130/0016-7606\(1986\)97<648:HMAARA>2.0.CO;2](https://doi.org/10.1130/0016-7606(1986)97<648:HMAARA>2.0.CO;2)

636 Jarrard, R.D. (2003) Subduction fluxes of water, carbon dioxide, chlorine, and potassium.
637 Geochemistry, Geophysics, Geosystems 4, 1-50. <https://doi.org/10.1029/2002GC000392>

638 Johnson, H.P., Pruis, M.J. (2003) Fluxes of fluid and heat from the oceanic crustal reservoir.
639 Earth and Planetary Science Letters 216, 565-574. [https://doi.org/10.1016/S0012-](https://doi.org/10.1016/S0012-821X(03)00545-4)
640 [821X\(03\)00545-4](https://doi.org/10.1016/S0012-821X(03)00545-4)

641 Kawahata, H., Kusakabe, M., Kikuchi, Y. (1987) Strontium, oxygen, and hydrogen isotope
642 geochemistry of hydrothermally altered and weathered rocks in DSDP Hole 504B, Costa Rica
643 Rift. Earth and Planetary Science Letters 85, 343-355. [https://doi.org/10.1016/0012-](https://doi.org/10.1016/0012-821X(87)90132-4)
644 [821X\(87\)90132-4](https://doi.org/10.1016/0012-821X(87)90132-4)

645 Kristmannsdóttir, H. (1979) Alteration of Basaltic Rocks by Hydrothermal-Activity at 100-
646 300° C. Developments in sedimentology 27, 359-367. [https://doi.org/10.1016/S0070-](https://doi.org/10.1016/S0070-4571(08)70732-5)
647 [4571\(08\)70732-5](https://doi.org/10.1016/S0070-4571(08)70732-5)

648 Kusakabe, M., Shibata, T., Yamamoto, M., Mayeda, S., Kagami, H., Honma, H., Masuda, H.,
649 Sakai, H. (1989) Petrology and isotope characteristics (H, O, S, Sr, and Nd) of basalts from
650 Ocean Drilling Program hole 504B, leg 111, Costa Rica Rift, Becker, K., Sakai, H., et al., Proc.
651 ODP, Sci. Results. Citeseer, pp. 47-60.

652 Kyser, T.K., O'Neil, J.R. (1984) Hydrogen isotope systematics of submarine basalts.
653 Geochimica et Cosmochimica Acta 48, 2123-2133. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(84)90392-2)
654 [7037\(84\)90392-2](https://doi.org/10.1016/0016-7037(84)90392-2)

655 Lonker, S.W., Franzson, H., Kristmannsdottir, H. (1993) Mineral-fluid interaction in the
656 Reykjanes and Svartsengi geothermal systems, Iceland. *American Journal of Science* 293, 605-
657 670. <https://doi.org/10.2475/ajs.293.7.605>

658 Marks, N., Schiffman, P., Zierenberg, R.A. (2011) High-grade contact metamorphism in the
659 Reykjanes geothermal system: Implications for fluid-rock interactions at mid-oceanic ridge
660 spreading centers. *Geochemistry, Geophysics, Geosystems* 12, 1-25.
661 <https://doi.org/10.1029/2011GC003569>

662 Martin, E., Bindeman, I., Balan, E., Palandri, J., Seligman, A., Villemant, B. (2017) Hydrogen
663 isotope determination by TC/EA technique in application to volcanic glass as a window into
664 secondary hydration. *Journal of Volcanology and Geothermal Research* 348, 49-61.
665 <https://doi.org/10.1016/j.jvolgeores.2017.10.013>

666 Michael, P. (1995) Regionally distinctive sources of depleted MORB: Evidence from trace
667 elements and H₂O. *Earth and Planetary Science Letters* 131, 301-320.
668 [https://doi.org/10.1016/0012-821X\(95\)00023-6](https://doi.org/10.1016/0012-821X(95)00023-6)

669 Nichols, A.R.L., Carroll, M.R., Höskuldsson, A. (2002) Is the Iceland hot spot also wet?
670 Evidence from the water contents of undegassed submarine and subglacial pillow basalts. *Earth
671 and Planetary Science Letters* 202, 77-87. [https://doi.org/10.1016/S0012-821X\(02\)00758-6](https://doi.org/10.1016/S0012-821X(02)00758-6)

672 Oelkers, E.H., Gislason, S.R. (2001) The mechanism, rates and consequences of basaltic glass
673 dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of
674 aqueous Al, Si and oxalic acid concentration at 25 °C and pH = 3 and 11. *Geochimica et
675 Cosmochimica Acta* 65, 3671-3681. [https://doi.org/10.1016/S0016-7037\(01\)00664-0](https://doi.org/10.1016/S0016-7037(01)00664-0)

676 Ólafsson, M., Jakobsson, S.P. (2009) Chemical composition of hydrothermal water and water-
677 rock interactions on Surtsey volcanic island. A preliminary report. *Surtsey Research* 12, 29-38.

678 Oskarsson, N., Sigvaldason, G.E., Steinthorsson, S. (1982) A dynamic model of rift zone
679 petrogenesis and the regional petrology of Iceland. *Journal of Petrology* 23, 28-74.
680 <https://doi.org/10.1093/petrology/23.1.28>

681 Parai, R., Mukhopadhyay, S. (2012) How large is the subducted water flux? New constraints
682 on mantle regassing rates. *Earth and Planetary Science Letters* 317, 396-406.
683 <https://doi.org/10.1016/j.epsl.2011.11.024>

684 Parkhurst, D.L., Appelo, C.A.J. (1999) User's guide to PHREEQC (Version 2): A computer
685 program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical
686 calculations, Water-Resources Investigations Report 99-4259. USGS, Denver, USA, pp. 1-312.

687 Peacock, S.A. (1990) Fluid processes in subduction zones. *Science* 248, 329-337.
688 <https://doi.org/10.1126/science.248.4953.329>

689 Rüpke, L.H., Morgan, J.P., Hort, M., Connolly, J.A.D. (2004) Serpentine and the subduction
690 zone water cycle. *Earth and Planetary Science Letters* 223, 17-34.
691 <https://doi.org/10.1016/j.epsl.2004.04.018>

692 Sæmundsson, K. (1979) Outline of the geology of Iceland. *Jökull* 29, 7-28.

693 Sæmundsson, K. (1991) Geology of the Krafla system. Íslenska náttúrufræðifélag, Reykjavík,
694 Iceland.

695 Sharp, Z.D., Atudorei, V., Durakiewicz, T. (2001) A rapid method for determination of
696 hydrogen and oxygen isotope ratios from water and hydrous minerals. *Chemical Geology* 178,
697 197-210. [https://doi.org/10.1016/S0009-2541\(01\)00262-5](https://doi.org/10.1016/S0009-2541(01)00262-5)

698 Shaw, A.M., Hauri, E.H., Fischer, T.P., Hilton, D.R., Kelley, K.A. (2008) Hydrogen isotopes
699 in Mariana arc melt inclusions: Implications for subduction dehydration and the deep-Earth

700 water cycle. Earth and Planetary Science Letters 275, 138-145.
701 <https://doi.org/10.1016/j.epsl.2008.08.015>

702 Shilobreeva, S., Martinez, I., Busigny, V., Agrinier, P., Laverne, C. (2011) Insights into C and
703 H storage in the altered oceanic crust: Results from ODP/IODP Hole 1256D. *Geochimica et*
704 *Cosmochimica Acta* 75, 2237-2255. <https://doi.org/10.1016/j.gca.2010.11.027>

705 Shinohara, H. (2013) Volatile flux from subduction zone volcanoes: Insights from a detailed
706 evaluation of the fluxes from volcanoes in Japan. *Journal of Volcanology and Geothermal*
707 *Research* 268, 46-63. <https://doi.org/10.1016/j.jvolgeores.2013.10.007>

708 Staudigel, H., Plank, T., White, B., Schmincke, H.U. (1996) Geochemical fluxes during
709 seafloor alteration of the basaltic upper oceanic crust: DSDP Sites 417 and 418. In G.E. Bebout,
710 D.W. Scholl, S.H. Kirby, J.P. Platt (eds.): *Subduction: top to bottom*. Geophysical Monograph
711 Series.96, 19-38. <https://doi.org/10.1029/GM096p0019>

712 Stefánsson, A., Hilton, D.R., Sveinbjörnsdóttir, Á.E., Torssander, P., Heinemeier, J., Barnes,
713 J.D., Ono, S., Halldórsson, S.A., Fiebig, J., Arnórsson, S. (2017) Isotope systematics of
714 Icelandic thermal fluids. *Journal of Volcanology and Geothermal Research* 337, 146-164.
715 <https://doi.org/10.1016/j.jvolgeores.2017.02.006>

716 Taran, Y., Zelenski, M. (2015) Systematics of water isotopic composition and chlorine content
717 in arc-volcanic gases. Geological Society, London, *Special Publications* 410, 237-262.
718 <https://doi.org/10.1144/SP410.5>

719 Thorarinsson, S., Einarsson, T., Sigvaldason, G., Elisson, G. (1964) The submarine eruption
720 off the Vestmann Islands 1963-64. *Bulletin Volcanologique* 27, 435-445.
721 <https://doi.org/10.1007/BF02597544>

722 van Keken, P.E., Hacker, B.R., Syracuse, E.M., Abers, G.A. (2011) Subduction factory: 4.
723 Depth-dependent flux of H₂O from subducting slabs worldwide. Journal of Geophysical
724 Research: Solid Earth 116, 1-15. <https://doi.org/10.1029/2010JB007922>

725

726 **Figure and table captions**

727 **Figure 1.** (A) Water content (in wt.% H₂O) of altered basalts from the geothermal systems at
728 Krafla, Reykjanes and Surtsey. Water contents for Icelandic fresh basalt are taken from Nichols
729 et al. (2002). (B) δ D values of altered basalts from the geothermal systems at Krafla, Reykjanes
730 and Surtsey. Values of fresh Icelandic basalt are taken from Martin et al. (2017). (C) δ D values
731 of liquid and vapor phases of geothermal fluids discharged from the geothermal systems at
732 Krafla, Reykjanes and Surtsey. Values for meteoric water and seawater are taken from
733 Stefánsson et al. (2017). MW = meteoric water, SW = seawater.

734

735 **Figure 2.** Modelled progress of alteration and source fraction of hydrogen as a function of bulk
736 water content (wt.% H₂O) of hydrated and residual fresh basalt. (A) and (B) Fluid-induced
737 alteration is accompanied by the formation of hydrous secondary minerals resulting in a linear
738 relationship between degree of alteration and water content as soon hydrous minerals start to
739 form. This relationship is rather insensitive to changes in temperature and type of reacting fluid
740 (meteoric water or seawater). However, differences in the modal abundance of chlorite and
741 zeolites at low temperatures (<150°C) may strongly affect the water content of the basalt with
742 progressive alteration. (C) and (D) The source fraction of hydrogen in the altered basalt. With
743 progressing hydration and alteration of the basalt, the hydrothermal fluid (either of meteoric or
744 seawater origin) would become the dominant source of hydrogen to the system. All presented
745 calculations were carried out using an initial water content of 0.2 wt.% H₂O for the reacting
746 basalt. Changing the initial water content of basalt to higher values would shift the curves to

747 the right, however there will not be any effects on their topology. Water contents for Icelandic
748 basalt are taken from Nichols et al. (2002). MW-BAS = meteoric water-rock interaction, SW-
749 BAS = seawater-rock interaction.

750

751 **Figure 3.** Simulated δD values of fluids, hydrous minerals and bulk rock upon progressive
752 fluid-rock interaction in both seawater (A-D) and meteoric water (E and F) hydrothermal
753 systems at various temperatures. Changes in the δD value of the bulk rock will occur rapidly
754 upon hydration. This is due to the relatively high abundance of hydrogen in the fluid phase
755 compared to the water content of Icelandic basalt. Water contents and δD values for Icelandic
756 basalt are taken from Nichols et al. (2002) and Martin et al. (2017), respectively. MW-BAS =
757 meteoric water-rock interaction, SW-BAS = seawater-rock interaction.

758

759 **Figure 4.** Comparison of simulated reaction pathways with δD values and water contents of
760 altered basalt from the geothermal fields at Krafla, Reykjanes (A) and Surtsey (B). Reaction
761 pathways have been calculated using equations A-1 and A-10. Isotopic values of the bulk rock
762 at Reykjanes can be simulated by envisioning mixing of modern local meteoric water and
763 seawater and subsequent interaction with basalt with a mixing ratio of seawater to meteoric
764 water of 80:20. Samples from the uppermost part of the drill hole deviate from our modelled
765 reaction pathways. It is likely that at shallow depths the seawater-meteoric water ratio is
766 slightly lower due to a more significant meteoric water source. Decreasing the mixing ratio
767 results in a shift of the reaction curves towards more negative isotope values of the bulk rock.
768 Water contents and δD values for Icelandic basalt are taken from Nichols et al. (2002) and
769 Martin et al. (2017), respectively. MW = meteoric water, SW = seawater.

770

771 **Figure 5.** Comparison of modelled reaction pathways for seawater-basalt interaction with
772 reported water content and δD values of the upper part of the oceanic crust (~1-2 km) including
773 volcanics, sheeted dikes and gabbros (Agrinier et al., 1995a; Agrinier et al., 1995b; Kawahata
774 et al., 1987; Kusakabe et al., 1989; Shilobreeva et al., 2011). The reaction pathways were
775 calculated based on reported mineral abundances of young altered oceanic crust (e.g., Alt et
776 al., 1996) using equations A-1 and A-10. Values of water content and δD for MOR basalts
777 were taken from Michael (1995) and Kyser and O'Neil (1984), respectively.

778

779 **Figure 6.** Simulated secondary mineral assemblage, water contents and δD values throughout
780 an entire section of the oceanic crust assuming alteration of 10%, 25%, 50%, 75% and 100%
781 (see from Table A.5). Water contents and bulk rock δD were calculated along a geotherm
782 typical for young (<10 Ma) oceanic crust using the presented modelling approach (Appendix
783 A). Highest water contents and least negative δD values are found within the first 1 km of the
784 oceanic crust. In this part of the crust, modal abundances of clays and chlorites are highest.
785 Most measurements of the water content and hydrogen isotope signature of the oceanic crust
786 from ODP/DSDP correspond to a degree of alteration of <5-10% in the volcanic sequence, up
787 to 75% in the sheeted dike sequence and 10-25% in the uppermost gabbroic section (Agrinier
788 et al., 1995b; Kawahata et al., 1987; Kusakabe et al., 1989; Shilobreeva et al., 2011). Upon
789 aging, water contents and δD values are expected to increase (indicated by grey arrows) due to
790 the breakdown of high temperature hydrous minerals and continuous alterations. Closure of
791 voids due to continuous secondary mineral formation as well as sedimentation onto the igneous
792 basement might, however, limit the access of fresh seawater.

793

794 **Figure 7.** Estimated H₂O fluxes from sediments and igneous crust into subduction zones and
795 the mantle. Corresponding hydrogen isotope values of fluids (δD_f), sediments (δD_{sed}), igneous

796 crust (δD_{ign}) and mantle (δD_{man}) (see also Tables 1 and A.7). The water fluxes in the igneous
797 crust were calculated using water contents obtained by our modelling approach (Tables A.5
798 and A.6) and pore water calculated using void volumes that are representative for the oceanic
799 crust (see Appendix A for details). Water fluxes in sediments, to the mantle, from arc volcanoes
800 and mid-ocean ridges are taken from previous published estimates (Bebout, 1995; Fischer,
801 2008; Hacker, 2008; Hirschmann and Kohlstedt, 2012; Jarrard, 2003; Peacock, 1990; Rüpke et
802 al., 2004; Shinohara, 2013; van Keken et al., 2011). δD values for sediments and igneous crust
803 are based on the distribution of porewater ($\delta D \sim 0\text{‰}$) and structurally bound water in both
804 sediments (Giggenbach, 1992) and igneous crust (Table A.5). Isotope values of degassing
805 fluids upon dehydration were based on isotope fractionation of hydrous mineral-water pairs
806 (Table A.4) at elevated temperature ($>500\text{ °C}$). The evolution of the δD value of the bulk rock
807 descending beyond the back arc are based on the dehydration model of (Shaw et al., 2008).
808 Note, that figure is not in scale.

809

810 **Table 1.** Estimates of water fluxes to the oceanic crust upon seawater alteration and the
811 subducted water flux.