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1 **Using stable Mg isotope signatures to assess the**
2 **fate of magnesium during the *in situ***
3 **mineralisation of CO₂ and H₂S at the CarbFix site**
4 **in SW-Iceland**

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23 **Abstract** - The *in-situ* carbonation of basaltic rocks could provide a long-term carbon
24 storage solution. To investigate the viability of this carbon storage solution, 175 tonnes of
25 pure CO₂ and 73 tonnes of a 75% CO₂-24% H₂S-1% H₂-gas mixture were sequentially
26 injected into basaltic rocks as a dissolved aqueous fluid at the CarbFix site at Hellisheidi,
27 SW-Iceland. This paper reports the Mg stable isotope compositions of sub-surface fluids
28 sampled prior to, during, and after the CO₂ injections. These Mg isotopic compositions
29 are used to trace the fate of this element during the subsurface carbonation of basalts. The
30 measured Mg isotopic compositions of the monitoring well fluids are isotopically lighter
31 than the dissolving basalts and continue to become increasingly lighter for at least two
32 years after the gas-charged water injection was stopped. The results indicate that the
33 formation of isotopically heavy Mg-clays rather than Mg-carbonates are the predominant
34 Mg secondary phases precipitating from the sampled fluids. Isotope mass balance
35 calculations suggest that more than 70% of the Mg liberated from the basalt by the
36 injected gas charged water was precipitated as Mg-clays, with this percentage increasing
37 with time after the injection, consistent with the continued precipitation of Mg clays over

38 the whole of the study period. The formation of Mg clays in response to the injection of
39 CO₂ into basalts, as indicated in this study, could be detrimental to carbon storage efforts
40 because the formation of these minerals consume divalent Mg that could otherwise be
41 used for the formation of carbonate minerals and because such clays could decrease host
42 rock permeability.

43

44 **1. Introduction**

45 The CarbFix project was created to develop the technology to store carbon dioxide as
46 stable carbonate minerals directly in the subsurface by reacting gas charged injection
47 waters with basaltic rocks (Gislason et al., 2010, 2018; Aradóttir et al., 2011, 2018).
48 Carbon storage in basaltic rocks offers numerous advantages including their ability to
49 promote mineral carbonation and their large potential storage volume (McGrail et al.,
50 2006; Goldberg and Slagle, 2009; Goldberg et al., 2010; Gislason and Oelkers, 2014;
51 Snæbjörnsdóttir et al., 2014). As such, numerous studies have focused on developing the
52 technology to safely store CO₂ in basaltic rocks including laboratory (Assayag et al.,
53 2009; Flaathen et al., 2009; Gudbrandsson et al., 2011; Stockmann et al., 2011; Gysi and
54 Stefánsson, 2012; Rosenbauer et al., 2012; Galeczka et al., 2014; Marenzi et al., 2018),
55 modelling (McGrail et al., 2006; Van Pham et al., 2012; Goldberg et al., 2009, 2013;
56 Rosenbauer et al., 2012; Bacon et al., 2014) and field efforts (Rogers et al., 2006; Matter
57 et al., 2007; McGrail et al., 2011, 2012; Siggfusson et al., 2015). Basaltic rocks are rich in
58 divalent cations such as Ca²⁺, Mg²⁺, and Fe²⁺. The injection of acidic CO₂-charged water
59 promotes the release of these metals, potentially leading to the formation of carbonate
60 minerals such as calcite, magnesite, and siderite as the continued dissolution of basalt
61 increases the pH of the aqueous fluid (Oelkers et al., 2008; Gislason et al., 2010, 2014;
62 Stefánsson et al., 2011; Gislason and Oelkers, 2014; Olsson et al., 2014). About 5% of
63 the continents and most of the oceanic floor are comprised of basaltic rocks, including the
64 mid-oceanic ridges. As such the largest basaltic storage potential lies offshore;
65 theoretically all CO₂ from the burning of fossil fuel carbon (estimated to be ~5000 Gt;
66 Archer, 2005) could be stored by mineral carbonation along the mid-ocean ridges
67 (Snæbjörnsdóttir et al., 2014). The flanks of these ridges contain highly fractured and
68 permeable basaltic layers (Fisher, 1998) with a pervasive circulation of about 1,000 Gt

69 seawater/yr (Harris and Chapman, 2004). The potential for using these marine systems
70 for carbon storage is confirmed by the results of Wolff-Boenisch et al. (2011), who
71 demonstrated the rapid dissolution of basaltic rocks in CO₂ charged seawater.

72

73 The efficiency of mineral carbonation, however, can be limited if Mg clay minerals
74 rather than Mg carbonate minerals form in response to the injection of CO₂ into basalts.
75 Magnesium clay formation is detrimental to carbon storage efforts because these minerals
76 consume divalent Mg that could otherwise be used for the carbonate mineral formation,
77 and because Mg-bearing clays could decrease host rock permeability. The fate of Mg
78 during mineral carbonation efforts in basalts will be assessed in this study through the
79 application of Mg isotopes. The stable isotopes of magnesium (²⁴Mg, ²⁵Mg and ²⁶Mg)
80 are increasingly being used as tracers of geochemical processes, including their use to
81 assess mineral reactions during weathering (Brenot et al., 2008; Huang et al., 2012; Liu et
82 al., 2014; Pogge von Strandmann et al., 2012; Tipper et al., 2006, 2008, 2012a, 2012b;
83 Wimpenny et al., 2011). Like all major elements, magnesium and its isotopes are affected
84 by a number of processes. For example, the magnitude and sign of Mg isotope
85 fractionation during precipitation appears to be dependent on the type of mineral forming
86 (Geske et al., 2012; 2015; Immenhauser et al., 2010; Li et al., 2012, 2015; Saulnier et al.,
87 2012; Wombacher et al., 2011), organic vs. inorganic precipitation (Chang et al., 2004;
88 Pogge von Strandmann, 2008; Saenger and Wang, 2014), precipitation rate (Mavromatis
89 et al., 2013), fractionation mechanism (Buhl et al., 2007), and aqueous speciation (Li et
90 al., 2014; Schott et al., 2016). In addition, isotopic fractionation can also occur due to
91 both the preferential incorporation and preferential adsorption of specific Mg isotopes
92 (Huang et al., 2012; Liu et al., 2014; Opfergelt et al., 2011; Pogge von Strandmann et al.,
93 2008, 2012; Tipper et al., 2012a; Wimpenny et al., 2010, 2014). Finally, the uptake of
94 Mg by plants and microbes causes variable isotope fractionation (Black et al., 2006;
95 Bolou-Bi et al., 2010, 2012; Oelkers et al., 2015; Pokharel et al., 2017; Uhlig et al.,
96 2017).

97

98 In this study the Mg isotope systematics of subsurface fluids sampled prior to, during,
99 and after the injection of CO₂-charged waters into subsurface basalts was measured to

100 provide insight into the mineralisation reactions that occurred in response to this
101 injection. This approach takes advantage of the distinct Mg isotope fractionation
102 signatures of primary and secondary phases. The Mg isotope ratio of primary igneous
103 silicate rocks is virtually uniform (Teng et al., 2010a; Pogge von Strandmann et al., 2011)
104 and it differs markedly from that in carbonates (Chang et al., 2004; Pogge von
105 Strandmann, 2008; Wombacher et al., 2011; Li et al., 2012, 2014; Saenger and Wang,
106 2014, Teng 2017). As such, the Mg isotope composition of surface waters is often
107 controlled by the balance of dissolution of silicate to carbonate rocks in the host
108 catchment and/or the relative precipitation rates of Mg-clays compared to Mg-bearing
109 carbonates (Tipper et al., 2006a, 2006b, 2008; Pogge von Strandmann et al., 2008, 2014).
110 It is thus anticipated that a similar approach will provide insight into the identity of Mg
111 minerals formed during subsurface processes occurring at the CarbFix site.

112

113

114 **2. Background of the CarbFix Project**

115 This study focuses on the fate of Mg liberated from dissolving basalts in response to
116 the injection of CO₂-charged water at the CarbFix injection site. A number of past
117 publications have reported the details of this injection, including the temporal evolution
118 of dissolved element compositions and chemical tracers following these injections. A
119 description of the injection method was presented by Sigfússon et al. (2015). The
120 temporal evolution of chemical tracers, dissolved carbon and pH in the first monitoring
121 well downstream from the injection well was reported by Matter et al. (2016), as well as
122 an estimate of the fraction of injected carbon fixed by carbonation reactions. This study
123 concluded that more than 95% of the dissolved carbon injected into the subsurface was
124 fixed as stable carbonate minerals within 2 years. The concentrations of dissolved major
125 elements during and after injection in the first monitoring well, as well as the saturation
126 indices of potential secondary minerals were described by Snæbjörnsdóttir et al. (2017).
127 Reaction path modelling of the carbon dioxide charged injection fluids, as they reacted
128 with the subsurface basalts were reported by Snæbjörnsdóttir et al. (2018).

129

130 The CarbFix injection site is equipped with a 2000 m deep injection well and 8

131 monitoring wells ranging in depth from 50 to 1300 m in depth. The subsurface rocks at
132 the injection site are primarily olivine tholeiite basalts consisting of lava flows and
133 hyaloclastite formations (see Fig. 1). The hyaloclastites are relatively low permeability
134 glassy rocks formed under ice and melt water during glaciations; the boundaries between
135 hyaloclastites and lava flows, and those between individual lava flows boundaries are
136 preferential fluid flow pathways (Alfredsson et al., 2013). Some alteration is observed in
137 the hyaloclastite rocks starting at 120 to 300 m depth. The common alteration minerals at
138 this depth are smectite, calcite, Ca-rich zeolites, and poorly crystalline iron-hydroxides
139 (Alfredsson et al., 2013). Fluid injection was targeted at a lava flow sequence located
140 400–800 m below the surface with the main aquifer located at ~530 m depth. Loss on
141 ignition measurements on rock samples suggest that over 80% of the primary rocks in the
142 target zone are currently unaltered. Tracer tests were conducted both under natural and
143 forced flow conditions from 2008 to 2011 to define the system hydrology (Aradóttir et
144 al., 2012; Gislason et al., 2010; Khalilabad et al., 2008). These tests indicated that the
145 flow from the HN-02 injection well to the first monitoring well (HN-04) consists of
146 relatively homogenous porous media intersected by a low volume and fast flow path that
147 channels about 3% of the tracer flow (Khalilabad et al., 2008).

148

149 The water in the target zone prior to the injection ranged in temperature from 15 to 35
150 °C and had *in situ* pH ranging from 8.4 to 9.8. The concentrations of dissolved CO₂ and
151 O₂ collected from the injection well from the target reservoir were 1.27 x10⁻³ and 1.1x10⁻⁵
152 mol/kg, respectively, prior to the injection (Alfredsson et al., 2013). These values are
153 substantially undersaturated with respect to the composition of these gases in the
154 atmosphere, suggesting that the target injection reservoir was isolated from the surface.
155 The concentration of Ca and Mg in these waters prior to the injection was limited by
156 secondary mineral precipitation (Alfredsson et al., 2013). All the water samples collected
157 from the target reservoir prior to the injection of CO₂ charged water were supersaturated
158 with respect to Ca-zeolite, analcime, Ca–Mg–Fe smectite, calcite, and aragonite, and
159 some are supersaturated with respect to dolomite and Fe–Mg carbonates (Snæbjörnsdóttir
160 et al., 2017).

161

162 Approximately 175 tons of pure commercial CO₂ and 73 tons of a 75%–24%–0.8%
163 mixture of CO₂–H₂S–H₂ gases were dissolved into water during their injection from
164 January until August 2012. This latter gas mixture was captured directly from the
165 adjoining Hellisheidi power plant by its dissolution into water at elevated pressure
166 (Gislason et al., 2018; Sigfusson et al., 2018). The injected water had a temperature of
167 ~25 °C and was equilibrated with 26 to 28 bars pressure of the CO₂ gas or ~14 bars
168 pressure of the CO₂–H₂S–H₂ mixture. The injected fluid equilibrated with pure carbon
169 dioxide had dissolved CO₂ concentrations of ~0.8 mol/kg H₂O and a pH of 3.85, whereas
170 the fluid equilibrated with the gas mixture had a dissolved CO₂ concentration of ~0.43
171 mol/kg H₂O and a pH of 4.0 (Snæbjörnsdóttir et al., 2017). All host rock minerals and
172 glass were strongly undersaturated with respect to the gas charged injection waters
173 (Snæbjörnsdóttir et al., 2018). The interaction of these acidic fluids with the host basalts
174 creates porosity near the injection well by dissolving primary and secondary minerals. As
175 gas-charged water continues to dissolve the basaltic host rock, this fluid becomes
176 increasingly basic and secondary minerals will precipitate, potentially clogging the
177 system. Reaction path calculations reported by Snæbjörnsdóttir et al. (2018) suggested
178 that Mg–Fe–carbonates and siderite became supersaturated in the subsurface fluids at pH
179 <5, whereas Ca–Mg–Fe–carbonates and calcite were saturated or supersaturated at higher
180 pH. Mg bearing clays and Ca, Na-rich zeolites also became saturated in the subsurface
181 fluids at pH >7.

182

183 **3. Sampling and Analytical Methods**

184 A detailed overview of fluid injection and sampling before, during and after the
185 CarbFix injections have been reported by Snæbjörnsdóttir et al. (2017). Sampling of the
186 fluids from the HN-04 monitoring well and other wells surrounding the injection well
187 began in 2008. Water samples for chemical analysis were collected several times prior to
188 the injections, which began during January 2012 (Alfredsson et al., 2013). During the
189 injections and until mid-September 2012 the HN-04 injection well was sampled twice
190 weekly. Weekly sampling continued until mid-July 2013 with few exceptions. Water was

191 pumped from this monitoring well at the rate of 3.5 m³/h throughout this study
192 maintaining a constant head from the injection to the monitoring well.

193

194 Fluid samples were collected via a 10 m long, 10 mm diameter stainless steel pipe
195 connected to the 53 mm diameter monitoring well lining pipe extending down to the
196 pump (Alfredsson et al., 2016). The sample pipe was connected directly to a sampling
197 valve inside an on-site field laboratory. After flushing the sampling pipe, the sampled
198 waters were immediately filtered through 0.2 µm Millipore cellulose acetate membranes
199 using silicon tubing and a 140 mm Sartorius® filter holder. All air in the filtration system
200 was expelled through a valve prior to sampling and at least 3 L of water was pumped
201 through the system before the samples were collected in acid washed high density
202 polyethylene bottles for cation and isotopic analysis. The sampling bottles were also
203 washed with the monitoring well fluids three times before the final sampling. These
204 samples were acidified using Suprapur® HNO₃, 1% (v/v) then stored prior to analysis.
205 The fluid sample Si, Ca, Mg concentrations, alkalinity and pH data used in this study
206 were previously reported by Snæbjörnsdóttir et al. (2017) and Alfredsson et al. (2013).
207 Four pre-CO₂-injection fluid samples from different shallow wells and 19 post-injection
208 monitoring well (HN-04) samples were selected for Mg isotope measurements (Table 1).
209 Samples collected prior to the acid gas injections from the deep wells (> 400 m),
210 including the HN-04 monitoring well, could not be analysed for their Mg isotopic ratios
211 due to their low Mg concentrations (see Fig. 2). These concentrations did not exceed 6
212 µmol kg⁻¹ (Alfredsson et al., 2013; Snæbjörnsdóttir, et al., 2017).

213

214 ***Mg isotope analyses*** - Prior to stable Mg isotope analyses, the fluid samples were
215 chemically purified by cation exchange chromatography in a clean laboratory equipped
216 with filtered air laminar flow workstations at GET Toulouse following a protocol similar
217 to that reported by Mavromatis et al. (2012, 2013), Pearce et al. (2012), and Shirokova et
218 al. (2013). Briefly, fluid samples were evaporated to dryness and re-dissolved in 1M
219 HNO₃ prior to loading onto 10 ml Bio-Rad poly-prop columns containing AG-50W-X12
220 resin (200–400 mesh) for separation of Mg from other elements. A total of 23 samples
221 were processed in two batches of Mg column chemistry. With each batch of samples, the

222 IAPSO seawater reference material and a procedure blank was processed for quality
223 control. Mg recovery after chromatographic separation was >99.5%. After column
224 chemistry, samples were evaporated, treated with H₂O₂/HNO₃ at 150°C to remove any
225 remaining organics, and finally re-dissolved in 0.3M HNO₃.

226

227 Mg isotope measurements were performed at the HELGES lab, GFZ Potsdam,
228 following protocols described by Uhlig et al. (2017) and Pokharel et al. (2017). Before
229 Mg isotope ratio analysis, the purity of the Mg sample solutions and the Mg content in
230 procedure blanks were checked by ICP-OES (Varian 720ES) and quadrupole ICP-MS
231 (Thermo iCAP-Qc), respectively. Most of the samples showed a purity of higher than
232 99% Mg; for some samples that did not, we tested that the remaining impurities of Na
233 and K would cause no analytical bias. Doping DSM-3 with Na and K and measuring the
234 Mg isotopic composition showed that the impurities did not bias the Mg isotope
235 measurements, i.e., the Na-K-doped DSM-3 ($\delta^{26}\text{Mg} = -0.05 \pm 0.10 \text{ ‰}$, 2SD) was identical
236 to pure DSM-3 within analytical uncertainty, consistent with previous findings (Pokharel
237 et al., 2017). Procedural blanks contributed less than 0.9% to the Mg processed through
238 column chemistry (15 μg) and are therefore considered insignificant (potential bias in
239 $\delta^{26}\text{Mg}$ is less than 0.04 ‰). All Mg isotope ratio measurements were performed in
240 medium resolution mode on a Thermo Neptune multi-collector inductively coupled
241 plasma mass spectrometer (MC-ICP-MS). Samples and the DSM3 bracketing standard
242 were diluted in 0.3 M HNO₃ to 500 ppb. The solutions were introduced to the MC-ICP-
243 MS via a quartz-glass spray chamber (double pass cyclon-scott type, Thermo SIS)
244 equipped with a self-aspirating ca. 100 $\mu\text{L}/\text{min}$. The Mg isotope signals ($^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$,
245 $^{26}\text{Mg}^+$) were measured simultaneously on Faraday detectors. ^{26}Mg was measured on the
246 interference-free low mass side of the flat-top peak to avoid interference from $^{12}\text{C}^{14}\text{N}^+$.
247 Sample signal intensities of ca. 12 V for $^{24}\text{Mg}^+$ were obtained. Background intensities (<
248 8 mV $^{24}\text{Mg}^+$) were measured on-peak in 0.3 M HNO₃ before and after each sample
249 measurement block and were subtracted from sample signal intensities. Instrumental
250 mass bias on measured Mg isotope ratios was corrected by the sample-standard
251 bracketing method using concentration-matched DSM3 as a standard.

252

253 We report isotope ratios of samples as per mil deviation of the $^{26}\text{Mg}/^{24}\text{Mg}$ and
254 $^{25}\text{Mg}/^{24}\text{Mg}$ ratios from the DSM3 international reference material using the delta
255 notation, as $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively. All results are consistent with mass
256 dependent isotope fractionation. Average δ -values obtained from 2 to 6 replicate
257 measurements of the same fluid are reported in Table 1 together with twice the standard
258 deviation (2SD), which indicates the instrument repeatability. To assess total analysis
259 uncertainty, IAPSO Atlantic seawater was also analysed with our samples and gave a
260 mean $\delta^{26}\text{Mg}$ of -0.90 ± 0.08 (n = 12), which is in agreement with literature reference values
261 (-0.83 ± 0.09 ‰, 2SD, Foster et al. 2010, Ling et al. 2011 and references therein). The
262 pure Mg solution Cambridge-1 was measured 21 times during this study and gave a $\delta^{26}\text{Mg}$
263 of -2.62 ± 0.10 ‰ (2SD), which is also in close agreement with literature values (-2.59 to
264 2.78 ‰ – see compilations by Pogge von Strandmann et al., 2011; An and Huang, 2014).
265 These observations are consistent with previously established long-term uncertainty
266 estimates of the MC-ICP-MS method at GFZ HELGES of ± 0.06 ‰ (2SD) for $\delta^{26}\text{Mg}$ and
267 ± 0.10 ‰ (2SD) for $\delta^{25}\text{Mg}$ (Uhlig et al., 2017; Pokharel et al., 2017).

268

269 **4. Results**

270 The Mg isotope compositions of four pre-injection shallow well samples,
271 collected during 2008 and 2010 from wells HK-12, HK-13, and HK-25, which are drilled
272 to depths of 130, 210 and 310 m, respectively, are shown in Fig. 3, and listed in Table 1;
273 the composition of selected elements in these fluids are provided in Table 2. The
274 measured $\delta^{26}\text{Mg}$ of these samples ranged from -0.57 to -0.69 ‰, which is ~ 0.3 ‰ lower
275 than basaltic rocks from this area and previously measured groundwaters in Iceland
276 (Pogge von Strandmann et al., 2008), but within the range of precipitation-uncorrected
277 Icelandic soil pore waters (Pogge von Strandmann et al., 2012). Note that the formation
278 of Mg-bearing clays in these systems occurs only at depths greater than 120 to 300 m
279 (Alfredsson et al., 2013), such that these shallow water samples are likely relatively
280 unaffected by Mg clay precipitation compared to deeper wells, which is also consistent
281 with the relatively high Mg concentrations of these fluids.

282

283 The fluid compositions of the HN-04 monitoring well fluids are provided in Tables
284 1 and 2. The first of these samples analysed for $\delta^{26}\text{Mg}$ was collected on 9 February 2012,
285 17 days after the start of the initial CO_2 -charged water injection. This sample had a Mg
286 concentration of $36 \mu\text{mol kg}^{-1}$ and a $\delta^{26}\text{Mg}$ of -0.84‰ , which is approximately 0.25‰
287 lower than that of the pre-injection shallow well samples. As the aqueous Mg
288 concentrations of the monitoring well fluids increased with time up to $101 \mu\text{mol kg}^{-1}$ on
289 26 March 2012 (Fig. 2b) the $\delta^{26}\text{Mg}$ values of these fluids decreased to -0.94‰ . These
290 $\delta^{26}\text{Mg}$ values continued to decrease with time to about -1.3‰ through June 2013 as the
291 dissolved Mg concentration decreased, increased, and decreased again in response to the
292 arrival to the monitoring well of fluids influenced by the injection of the acid gases (see
293 Fig. 2, 3). The isotopically lightest $\delta^{26}\text{Mg}$ value of -1.34‰ was measured in the final
294 sample collected on 8 June 2014.

295

296 **5. Discussion**

297 The basaltic glass in the region of CarbFix injection site has a $\delta^{26}\text{Mg}$ value
298 of -0.28‰ (Pogge von Strandmann et al., 2008; Wimpenny et al., 2010), which is
299 identical to State University of New York (SUNY) Mid-Ocean Ridge Basalt (MORB;
300 Teng et al., 2007), as well as the bulk silicate Earth (Hin et al., 2017). This glass is
301 susceptible to dissolution in response to the injection of acidic fluids (Gislason et al,
302 1996; Oelkers, 2001; Oelkers and Gislason, 2001; Gislason and Oelkers, 2003) and has
303 been identified as the major phase dissolving in response to the CarbFix gas charged
304 water injections (Snæbjörnsdóttir et al., 2018). The rapid fluid-flow pathway, channeling
305 $\sim 3\%$ of the injected gas charged fluid was attributed to a fracture network located in
306 crystalline basalts containing mainly plagioclase, olivine, and pyroxene. Nevertheless
307 olivines and crystalline basalts near the CarbFix site have an identical $\delta^{26}\text{Mg}$ composition
308 to each other and the basaltic glass (Pogge von Strandmann et al., 2008, 2012). This is
309 consistent with other studies suggesting basaltic olivines have a narrow isotopic range,
310 with a similar Mg isotope composition to that of its coexisting basalt glass (Norman et
311 al., 2006; Teng et al., 2007; Wimpenny et al., 2010; Liu et al., 2017). Although such
312 results indicate that the preferential dissolution of distinct primary phases will not cause
313 significant Mg isotope fractionation, it should be noted that both Wimpenny et al. (2010)

314 and Maher et al. (2016) reported an initial preferential loss of light Mg during the
315 dissolution of basaltic glass and olivine. Longer-term experiments reported by Oelkers et
316 al. (2015) however, suggest that for the case of olivine, this preferential release of light
317 Mg is limited to the initial stages of dissolution.

318

319 The low Mg concentrations in the target reservoir fluids prior to the gas injection
320 indicate that essentially all the Mg dissolved in the HN-04 monitoring well samples
321 collected in this study after January 2012 originates from the injected fluids or the
322 dissolution of the host minerals in response to fluid-rock interaction. The low Mg
323 concentrations of the target reservoir prior to injection have been attributed to the
324 formation of Mg-bearing secondary minerals in the subsurface reservoirs, and in
325 particular to Mg-bearing clay precipitation. Indeed, the smectite, Mg-saponite, is
326 calculated to be strongly supersaturated in these fluids prior to injection, whereas
327 dolomite and magnesite are undersaturated (Snæbjörnsdóttir, et al., 2017). These
328 calculated results are consistent with the observed secondary minerals in the target basalt
329 formations (Alfredsson et al., 2013). They also explain the low $\delta^{26}\text{Mg}$ of the pre-injection
330 shallow reservoir fluids compared to that of the host basalt, as Mg-bearing silicate
331 minerals preferentially incorporate heavy Mg isotopes upon their formation (c.f. Young
332 and Galy, 2004; Tipper et al., 2006; Teng et al., 2007, 2010; Pogge von Strandmann et
333 al., 2008).

334

335 It seems likely, therefore, that the increasingly isotopically light composition of
336 the post-injection well samples must either be caused by continued dissolution of an
337 isotopically light and previously formed secondary phase, or the precipitation of an
338 isotopically heavy secondary phase. Evidence suggests the calcite present in the host
339 basalts dissolve as the acidic gas charged injection waters first interact with the
340 subsurface basalts (Snæbjörnsdóttir et al., 2017). This calcite likely has a $\delta^{26}\text{Mg}$ of no
341 more than -1.4‰ (Saenger and Wang 2014; Wombacher et al., 2011) such that the initial
342 dissolution of calcite would tend to make the fluids lighter. Nevertheless, after a short
343 initial time, saturation state and reactive path calculations indicate that calcite, as well as
344 dolomite and mixed Mg-Ca-Fe carbonates, become supersaturated in the monitoring

345 fluids collected from the HN-4 monitoring well (Snæbjörnsdóttir et al., 2017, 2018). The
346 initially dissolved calcite tends to precipitate from this fluid as its pH increases in
347 response to basalt dissolution. Due to the injection of carbon dioxide, more calcite
348 precipitates in this system than it initially dissolved (Matter et al., 2016; Snæbjörnsdóttir
349 et al., 2018). Such carbonate minerals likely tend to preferentially incorporate light Mg
350 into their structure. For example, Mavromatis et al. (2014) found that apparent dolomite-
351 pore fluid $\delta^{26}\text{Mg}$ fractionation factors were -2.6 ‰, a value similar to that reported by
352 Higgins and Schrag (2010). Numerous other studies have observed the preferential
353 incorporation of light Mg in Mg-bearing carbonates (Galy et al., 2002; Buhl et al., 2007;
354 Hippler et al., 2009; Immenhauser et al., 2010; Wombacher et al., 2011; Li et al., 2012,
355 2015; Pearce et al., 2012; Mavromatis et al., 2012, 2013; Shirokova et al., 2013; Beinlich
356 et al., 2014; Prikryl et al., 2018). Such observations suggests that carbonate precipitation
357 as observed at the CarbFix site would drive the sampled monitoring well to heavier rather
358 than lighter compositions. It seems therefore that carbonate precipitation is not the
359 dominant process controlling the Mg isotope composition of these monitoring well fluids.
360

361 The measured formation water composition requires, therefore, the incorporation
362 of heavy Mg into secondary phases. The calculations reported by Snæbjörnsdóttir et al.
363 (2017, 2018) suggest that Mg-smectites are supersaturated in most of the monitoring
364 fluids collected from the HN-4 monitoring well; the saturation state of the monitoring
365 fluids analyzed in this study with respect to Mg-clay are provided in Table 2. The Mg
366 isotopic compositions of clay minerals tend to be heavier than their co-existing fluid
367 phases (Young and Galy, 2004; Tipper et al., 2006; Teng et al., 2007, 2010; Pogge von
368 Strandmann et al., 2008). Similarly, Wimpenny et al. (2010) concluded that the formation
369 of secondary chrysotile, an Mg clay, lead to light Mg release from dissolving basaltic
370 glass and olivine. Ryu et al. (2016) estimated a clay-fluid Mg isotope fractionation factor
371 of 0.54 ‰, for T-O-T clays formed at temperatures from 90 to 250 °C. Moreover,
372 Wimpenny et al. (2014) measured the brucite-fluid $\delta^{26}\text{Mg}$ fractionation factor to be
373 0.50‰ at 80 °C and near to neutral pH. This study argued that this system provided a
374 good analogue to the incorporation of Mg into the octahedral sheets of Mg-rich clay
375 minerals. Note also that ^{26}Mg preferentially adsorbs on the surfaces of kaolinite type

376 minerals, including allophane (Huang et al., 2012; Pogge von Strandmann, 2012;
 377 Opfergelt et al., 2014). Thus, both precipitation and adsorption of exchangeable Mg onto
 378 clay minerals could lead to the observed pore fluid $\delta^{26}\text{Mg}$ decrease with time.

379

380 If, to a first approximation, it can be assumed that the Mg isotopic composition of
 381 the HN-04 monitoring fluids stem exclusively from the conservative dissolution of
 382 basalt¹ having an isotopic composition of $\delta^{26}\text{Mg}_{\text{basalt}} = -0.28\text{‰}$ (Pogge von Strandmann et
 383 al., 2008), coupled to the precipitation of a Mg-clay having a $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ fractionation
 384 factor of 0.50‰ (Wimpenny et al., 2014), the fraction of Mg released to the fluid by the
 385 basalt and originally injected into the well with the gas charged fluid that was
 386 incorporated into clays can be estimated from mass balance constraints. The Mg
 387 concentration of the sampled monitoring well fluids is equal to the sum of contributions
 388 from the Mg concentration of the injected gas charged water ($c_{\text{Mg},\text{inject}}$), the Mg
 389 concentration of the original formation water ($c_{\text{Mg},\text{fw}}$), and the change in Mg
 390 concentrations due to basalt dissolution ($\Delta c_{\text{Mg},\text{basalt}}$) and Mg-clay precipitation ($\Delta c_{\text{Mg},\text{clay}}$)
 391 such that

392

$$393 \quad c_{\text{Mg,measured}} = X_{\text{fw}} c_{\text{Mg},\text{fw}} + X_{\text{inject}} c_{\text{Mg},\text{inject}} + \Delta c_{\text{Mg},\text{basalt}} - \Delta c_{\text{Mg},\text{clay}} \quad (1)$$

394

395 where X_{fw} and X_{inject} are the fraction of formation water and injected water in the
 396 collected monitoring well sample, determined by the concentrations of SF_6 and SF_5CF_3
 397 tracers in these fluids (Matter et al., 2016) such that $X_{\text{fw}} + X_{\text{inject}} = 1$. If it can be assumed
 398 that the fluids mix and basalt dissolved prior to the precipitation of the Mg-bearing clay,
 399 the isotopic composition of the fluid before clay precipitation ($\delta^{26}\text{Mg}_1$) is given by

400

$$401 \quad \delta^{26}\text{Mg}_1 = \frac{(\delta^{26}\text{Mg}_{\text{fw}} X_{\text{fw}} c_{\text{Mg},\text{fw}} + \delta^{26}\text{Mg}_{\text{inject}} X_{\text{inject}} c_{\text{Mg},\text{inject}} + \delta^{26}\text{Mg}_{\text{basalt}} \Delta c_{\text{Mg},\text{basalt}})}{(X_{\text{fw}} c_{\text{Mg},\text{fw}} + X_{\text{inject}} c_{\text{Mg},\text{inject}} + \Delta c_{\text{Mg},\text{basalt}})} \quad (2)$$

402

¹ The term conservative dissolution in this regard refers to a process where the dissolution releases to the fluid Mg having the same isotopic composition as the dissolving rock.

403 where $\delta^{26}\text{Mg}_i$ designates the isotopic composition of the indicated source. The Mg
404 isotope compositions of the monitoring well samples can then be determined from an
405 expression of the Rayleigh equation of the form:

$$406 \quad \delta^{26}\text{Mg}_{\text{sampled fluid}} = \delta^{26}\text{Mg}_1 - f^{\Delta^{26}\text{Mg}_{\text{clay-fluid}}} \quad (3)$$

407

408 where $\delta^{26}\text{Mg}_{\text{sampled fluid}}$ designates the isotopic composition in the sampled monitoring
409 well fluid, $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ stands for the indicated isotope fractionation factor, and f ,
410 the fraction of the Mg remaining in the fluid following clay mineral precipitation in each
411 sample. Equations (1) to (3) were solved simultaneously to generate the values of f shown
412 in Fig. 4. The values of X_{fw} and X_{inject} in Eqn. (2) required for this calculations were
413 taken from Matter et al. (2016), and values of $\delta^{26}\text{Mg}_{\text{inject}}$ and $c_{\text{Mg,inject}}$ are provided in
414 Tables 1 and 2. Note the $\delta^{26}\text{Mg}_{fw} X_{fw} c_{\text{Mg, fw}}$ term is negligible compare to the other
415 terms in Eqn. (2) due to the low Mg concentration of the pre-injection formation waters
416 (compare the composition of sample 12KMG01 with the others in Table 2). The
417 calculated fraction of the Mg remaining in solution into clay minerals, as shown in Fig. 4,
418 tends to decrease with time. Calculations suggest that this fraction decreases
419 continuously from 33 to 12 percent with time from February 8, 2012 to June 8, 2014.
420 This behavior contrasts somewhat with the saturation index of Mg clays, which becomes
421 undersaturated in the sampled monitoring fluids when the injected acid fluid first arrive at
422 the monitoring well – see Table 2. It can be seen in Fig. 4 that the distribution of
423 calculated Mg precipitation fractions exhibit a concave distribution consistent with the
424 slowing of clay formation rates with time. Consistent with the very dilute Mg
425 concentrations of the deep well fluid prior to the injection, it seems likely that this
426 fraction would approach zero over the long-term.

427

428 This estimate, however, is likely a minimum estimate as evidence indicates that
429 calcite dissolved into the gas charged injection waters shortly after they arrive in the
430 subsurface (Matter et al., 2016; Snæbjörnsdóttir et al., 2017, 2018). The dissolution of
431 these calcites would likely release some light Mg to the fluid phase. In addition, the
432 dissolution of basaltic glass and olivine has been reported to initially release light Mg to

433 the fluid (Wimpenny et al., 2010). Indeed, mass balance and reactive path calculations
434 reported by Snæbjörnsdóttir et al. (2017, 2018) suggest that more than 95% of the Mg
435 release by dissolving basaltic glass needed to be incorporated into secondary phases to be
436 consistent with the measured dissolved Mg concentration of the HN-04 monitoring well
437 fluids in March 2013. The stable Mg isotope measurements reported here suggest that the
438 bulk of these secondary Mg phases formed following the CarbFix injections were Mg
439 bearing clays (e.g. smectite).

440

441 It should be emphasized, however, that the calculated results shown in Fig. 4 are
442 highly uncertain due to poor understanding of the Mg isotope fractionation factor
443 between Mg clay minerals and the aqueous fluid. For example, Teng et al. (2010)
444 suggested that the $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ deduced from the compositions of South Carolina
445 saprolites range from 0.05‰ to -0.4‰. In contrast, Huang et al. (2012) reported that
446 $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ based on the compositions of southern Chinese saprolites ranged from -
447 0.94‰ to -1.94‰. Wimpenny et al. (2014), however, concluded that the Huang et al.
448 (2012) observations were more consistent with a $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ of -0.57‰. The
449 computed value of f , the fraction of the Mg remaining in the fluid following clay mineral
450 precipitation in each sample determined in this study depends strongly on the value
451 chosen for $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$. A value of $\Delta^{26}\text{Mg}_{\text{clay-fluid}} = -0.40‰$ would yield a final f
452 value for the June 8, 2014 sample of 0.07, whereas a $\Delta^{26}\text{Mg}_{\text{clay-fluid}} = -1.00‰$ would
453 yield a final f value for the June 8, 2014 sample of 0.34. Moreover, it should also be
454 noted that at the pH and fluid composition changed (Schott et al., 2016), so too would
455 $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$. Such changes also would alter the calculated values of f . It follows
456 that precise and accurate values of $\Delta^{26}\text{Mg}_{\text{clay-fluid}}$ are an essential prerequisite to using
457 the compositions the Mg isotopic compositions of minerals and fluids to quantify natural
458 geochemical processes.

459

460 The formation of Mg clays in response to the injection of CO₂ into basalts, as
461 indicated in this study, is detrimental to carbon storage efforts for two main reasons.
462 First, the formation of these Mg-bearing silicates consume divalent Mg that could

463 otherwise be used for the formation of carbonate minerals. Second, Mg-bearing clays are
464 voluminous, such that they consume valuable porosity and could decrease host rock
465 permeability. The formation of these clays, however, will occur at a distance from the
466 injection well, as their precipitation requires sufficient basalt dissolution to increase the
467 fluid pH to at least 7 (Snæbjörnsdóttir et al., 2017). As such their formation will not
468 likely clog flow pathways near the injection well. Nevertheless, their formation at a
469 distance from these wells will limit somewhat the efficiency of carbon storage efforts in
470 basalts. This potential challenge might be overcome by injecting at higher temperatures,
471 where the formation of magnesite rather than Mg-bearing clays might be favored,
472 however, Mg-silicate alteration phases including mixed-layered clays, chlorite, and
473 epidote are common alteration phases in basalts to at least 280 °C (Snæbjörnsdóttir et al.,
474 2018). Nevertheless, the continuous injection of acidic CO₂-charged fluids may lead to a
475 propagating reaction front that would progressively move these clay minerals further
476 away from the injection well.

477

478 **6. Conclusions**

479 The Mg isotope compositions of monitoring well samples collected in this study
480 are lighter than the host basalts that dissolved in response to the injection of gas charged
481 waters into the CarbFix site. This observation is consistent with the consumption of the
482 divalent Mg cations released by basalt dissolution by isotopically heavier Mg clay
483 minerals, rather than carbonate minerals, which tend to favor the incorporation of
484 isotopically light Mg. This conclusion is supported by the fact that Mg-smectites rather
485 than Mg carbonate phases are commonly observed as secondary phases in basalts altered
486 at low temperatures. Such results demonstrate that the Mg isotopic compositions of
487 monitoring well fluids can be used to provide insight into the fate of Mg during
488 subsurface carbon storage efforts.

489

490 The rates at which Mg precipitates as clay minerals appear to be relatively slow;
491 mass balance calculations suggest that smectite is still continuing to precipitate 2 years
492 after the termination of the acid gas injection – calculations suggest that ~12 percent of
493 the Mg released to the fluid by basalt dissolution remains to be precipitated after two

494 years. This contrasts with calcite, which has demonstrated to precipitate more than 95%
495 of the injected CO₂ in less than 2 years (Matter et al., 2016). Although Mg clay mineral
496 precipitation is relatively slow, its precipitation may limit significantly the efficiency of
497 carbon storage efforts based on the enhanced weathering of mafic or ultramafic rocks
498 over the long term (Rigopoulos et al., 2018).

499

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516

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829 **Figure Captions**

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831 Fig. 1. Maps showing location of the study area (a) Map showing active volcanic zones in
832 Iceland: RP = Reykjanes Peninsula, WVZ = Western Volcanic Zone, SISZ = South
833 Iceland Seismic Zone, MVZ = Mid-Iceland Volcanic Zone, EVZ = Eastern Volcanic
834 Zone and NVZ = Northern Volcanic Zone. (b) Map showing location of central
835 volcanoes (dark gray) on Reykjanes Peninsula and associated fissure swarms (gray).
836 (c) Map of the CO₂ injection site in, Hellisheidi, SW-Iceland. The CarbFix wells are
837 shown as labeled gray dots. Mapped bedrock faults are located toward east and are
838 part of the Hengill fissure swarm - after Alfredsson et al. (2013).

839 Fig 2. The temporal evolution of a) pH and b) Mg concentration of fluids collected from
840 the HN-04 monitoring well, located 500 m away from the HN-02 injection well
841 before during and after the injection of gas charged waters at the CarbFix site. The
842 timing of the two injections is indicated by the two blue bars. Data from
843 Snæbjörnsdóttir et al. (2017) and Alfredsson et al. (2013). The reported
844 uncertainties on these analyses were reported to be ± 0.02 units on pH and $\pm 3\%$ on
845 the Mg concentration analyses.

846 Fig 3. The temporal evolution of $\delta^{26}\text{Mg}$ of fluids collected from the CarbFix site. Open
847 diamonds illustrate the compositions of shallow wells prior to the injection, whereas
848 the filled circles represent the composition of monitoring well samples. The dashed
849 horizontal line shows the compositions of the basalts at the CarbFix site whereas the
850 timing of the two injections is indicated by the two blue bars – see text.

851 Fig 4. The temporal evolution of the fraction of Mg released by basalt dissolution that has
852 been incorporated into clay minerals ($f_{\text{Mg, clay}}$). Fractions were calculated assuming a
853 closed-system Rayleigh model (see text).

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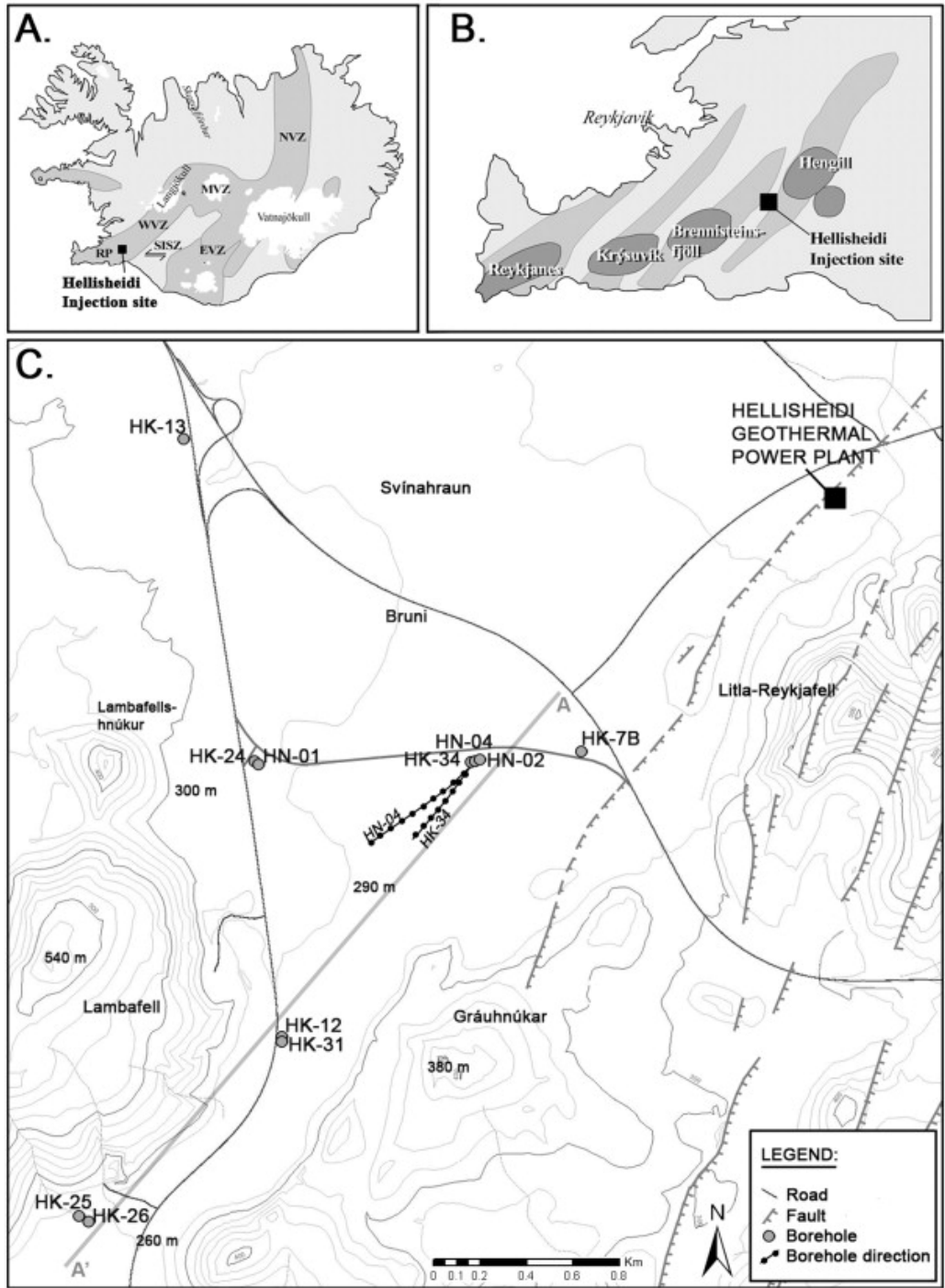
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Table 1. Summary of measured Mg isotopic compositions of pre-injection shallow well fluids, and post-injection monitoring well fluids collected from HN-04. All isotopic compositions were measured at the HELGES lab, GFZ Potsdam. 2SD refers to twice the standard deviation of n MC-ICP-MS measurements of the same solution. The uncertainty of the presented data (relevant for geological interpretation) is estimated to be 0.10 ‰ (2SD) for $\delta^{26}\text{Mg}$ and 0.06 ‰ (2SD) for $\delta^{25}\text{Mg}$ based on long-term repeated analyses of samples and references materials – see text.

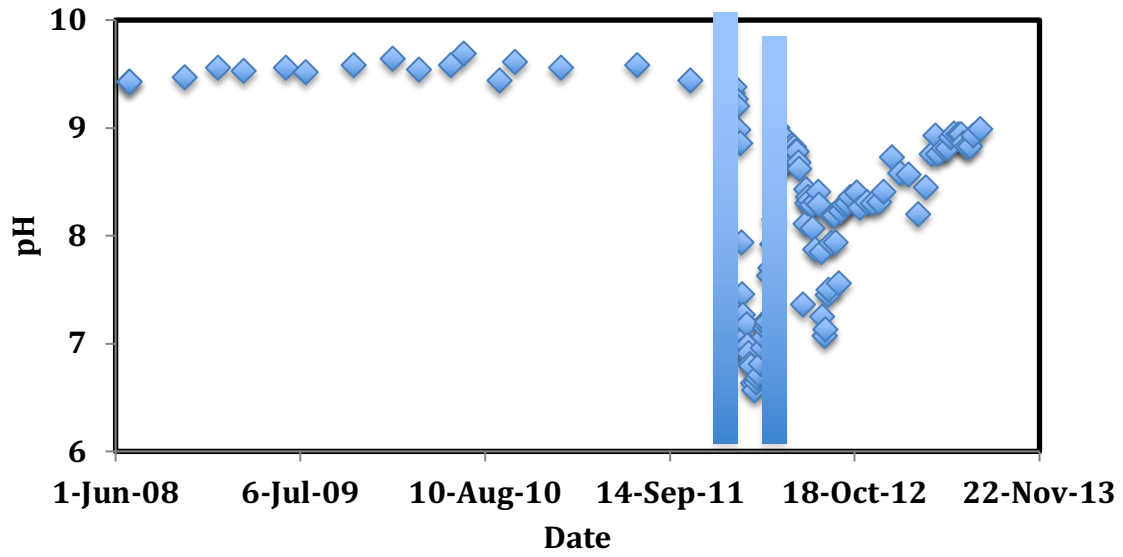
sample	date (day/month/year)	c_{Mg} (mol kg ⁻¹) x 10 ⁻⁶	$\delta^{25}\text{Mg}_{\text{DSMB}}$ (‰)	2SD	$\delta^{26}\text{Mg}_{\text{DSMB}}$ (‰)	2SD	n	Well
<i>Post-injection monitoring well samples collected from HN-04</i>								
12KGM08	09/02/2012	36	-0.43	0.05	-0.84	0.09	6	HN-04
12KGM11	16/02/2012	51	-0.45	0.06	-0.88	0.10	4	HN-04
12KGM19	27/02/2012	58	-0.49	0.05	-0.94	0.09	4	HN-04
12KGM25	08/03/2012	86	-0.49	0.05	-0.93	0.02	4	HN-04
12KGM33	26/03/2012	101	-0.48	0.04	-0.94	0.01	4	HN-04
12KGM44	18/04/2012	74	-0.54	0.05	-1.05	0.07	4	HN-04
12KGM49	04/05/2012	36	-0.48	0.06	-0.93	0.12	4	HN-04
12KGM60	30/05/2012	54	-0.52	0.06	-1.01	0.12	4	HN-04
12SOS01	08/06/2012	73	-0.53	0.07	-1.02	0.08	4	HN-04
12SOS09	17/07/2012	64	-0.52	0.07	-0.98	0.10	3	HN-04
12SOS15	31/07/2012	66	-0.57	0.04	-1.1	0.08	4	HN-04
12SOS21	14/08/2012	86	-0.51	0.03	-0.99	0.09	4	HN-04
12SOS28	28/08/2012	79	-0.67	0.06	-1.26	0.07	3	HN-04
12SOS34	24/09/2012	69	-0.57	0.04	-1.11	0.05	3	HN-04
12SOS39	29/10/2012	62	-0.59	0.04	-1.14	0.07	4	HN-04
13SOS01	07/01/2013	42	-0.64	0.07	-1.23	0.06	4	HN-04
13SOS10	16/04/2013	39	-0.69	0.07	-1.31	0.04	3	HN-04
13SOS17	10/06/2013	40	-0.62	0.01	-1.22	0.03	4	HN-04
14SOS11	08/06/2014		-0.69	0.06	-1.34	0.10	4	HN-04
<i>Pre-injection samples taken from indicated shallow well.</i>								
08HAA09	07/08/2008	180	-0.33	0.08	-0.64	0.11	5	HK-25
09HAA18	29/05/2010	175	-0.31	0.03	-0.57	0.06	3	HK-12
10HAA25	02/06/2010	226	-0.35	0.08	-0.69	0.13	3	HK-25
10HAA32	25/06/2010	169	-0.29	0.02	-0.59	0.02	2	HK-13
<i>reference materials</i>								
IAPSO seawater (batch a)			-0.47	0.04	-0.90	0.08	8	
IAPSO seawater (batch b)			-0.45	0.05	-0.88	0.08	4	
IAPSO seawater mean (batch a & b)			-0.46	0.04	-0.90	0.08	12	
seawater (reference value)			-0.43	0.06	-0.83	0.09		
Cambridge-1			-1.35	0.06	-2.62	0.10	21	
Cambridge-1 (reference value)			-1.34	0.03	-2.61	0.05		

865 ^a Published reference values are from compilations by Pogge von Strandmann et al. (2011), An
 866 and Huang (2014), Foster et al. (2010), Ling et al. (2011) and references therein.
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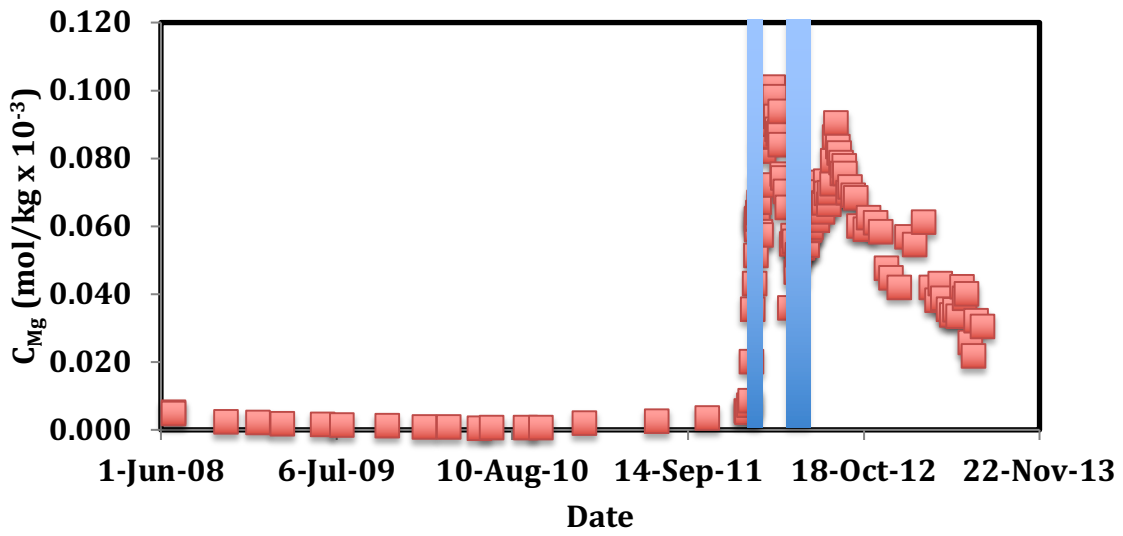


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Figure 1.



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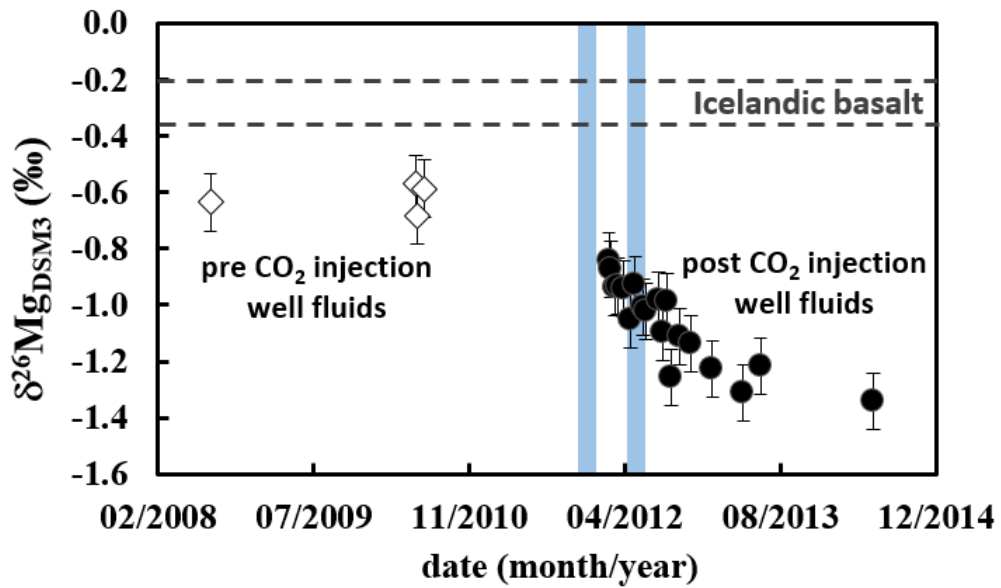


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873 **Figure 2.**

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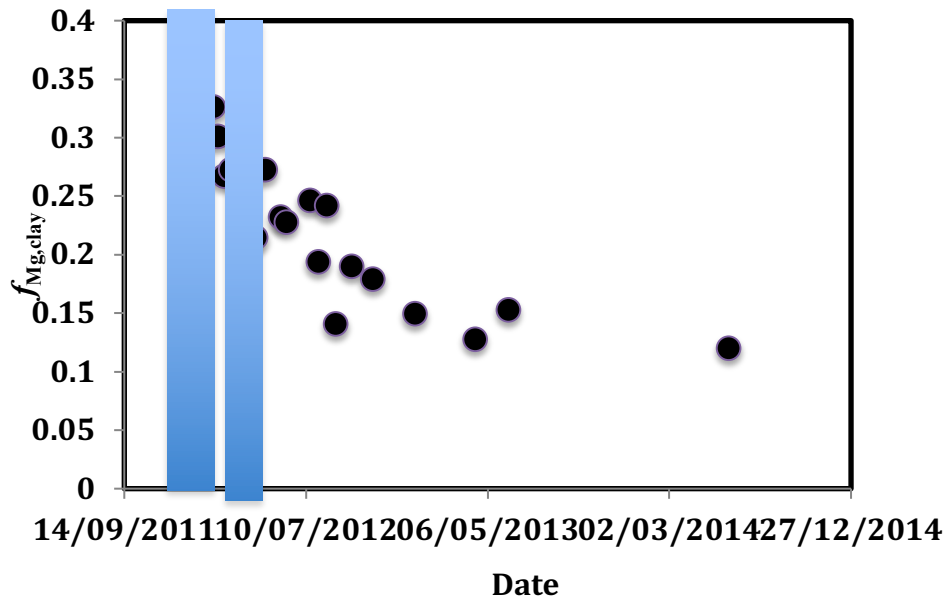
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877 **Figure 3.**

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880 **Figure 4.**

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