

Magnesium isotope fractionation during hydrothermal seawater-basalt interaction

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Abstract

Fluid-rock interactions in hydrothermal systems at or near mid-oceanic ridges (MOR) play a major role in determining the composition of the oceanic crust and seawater. To quantify the processes that govern cation exchange in these environments we have experimentally studied the isotopic evolution of $\delta^{26/24}\text{Mg}$ in the fluid phase during seawater-basalt interaction at 250 and 290 °C. Mass balance constraints indicate that isotopically heavy Mg was preferentially incorporated into non-exchangeable (octahedral) sites in secondary clay minerals such as saponite (Mg-rich smectite), leaving residual fluids enriched in light Mg isotopes. The magnitude of fractionation observed during smectite precipitation in our experiments ($\epsilon_{\text{Smectite-Liquid}}^{26/24}$) ranged from 0.35 ‰ to 0.42 ‰. This observation, which contrasts with the preferential uptake of light Mg isotopes into biogenic and inorganic marine carbonates,

26 highlights the potential utility of Mg isotopes as tracers of the precipitation dynamics of
27 authigenic Mg-silicate and Mg-carbonate phases. Furthermore, although Mg isotopic
28 fractionation is often masked by the almost complete removal of Mg in high temperature
29 marine hydrothermal systems, our experiments demonstrate that it does become significant at
30 lower temperatures where Mg removal by clay formation is incomplete. Under such
31 conditions, this fractionation will create isotopically light fluids due to smectite precipitation,
32 thus potentially represents an important component of the marine Mg isotope inventory.

33 **1 Introduction**

34 The Mg isotopic composition of seawater is controlled by a combination of inputs and
35 outputs from reservoirs with distinct isotopic compositions, and exchange processes that
36 fractionate its three stable isotopes (^{24}Mg , ^{25}Mg and ^{26}Mg). Rivers, which transport Mg
37 derived from the weathering of continental carbonate and silicate rocks, are thought to be the
38 major source of Mg to the oceans, while seafloor hydrothermal systems and carbonate mineral
39 precipitation are the dominant sinks (Tipper et al., 2006b; Higgins and Schrag, 2015; Huang
40 et al., 2018). The study of marine evaporite minerals and carbonate-hosting sedimentary
41 successions suggest that the Mg concentration of seawater varied considerably over the
42 Phanerozoic and is currently increasing (Horita et al., 2002; Fantle and DePaolo, 2006;
43 Higgins and Schrag, 2012). The current and past state of the marine Mg isotopic system
44 nevertheless remains unclear, as Mg isotope records derived from foraminifera from the past
45 40 Ma indicate a rapid decrease in seawater $\delta^{26/24}\text{Mg}$ over the past ~ 15 Ma (Pogge von
46 Strandmann et al., 2014), whereas pelagic marine carbonates from the past 80 Ma suggest
47 only small changes in seawater $\delta^{26/24}\text{Mg}$ over this period (Higgins and Schrag, 2015). The
48 interpretation of such changes (or lack thereof) is challenging as the influence of the different
49 fluxes on the Mg isotope budget remains uncertain. In particular the extent of isotopic
50 fractionation occurring in marine hydrothermal systems is poorly constrained at present

51 (Pogge von Strandmann et al., 2014; Higgins and Schrag, 2015). Although basaltic rock
52 dissolution in hydrothermal systems temporarily releases Mg to the fluid phase, this release is
53 often counterbalanced by Mg-rich clay mineral precipitation. The net result of this coupled
54 process is the almost complete removal of Mg from the seawater in high-temperature
55 hydrothermal systems with temperatures exceeding 400 °C, as well as significant Mg removal
56 at lower temperature conditions (Mottl and Wheat, 1994; Elderfield and Schultz, 1996).
57 Consequently, there is a net transfer of Mg from seawater to the oceanic crust in such settings
58 (e.g., Elderfield and Schultz, 1996; Coogan and Dosso, 2012; German and Seyfried, 2014),
59 and in the case of non-complete Mg removal (especially at lower temperatures) this process
60 potentially affects the oceanic Mg isotope budget (Pogge von Strandmann et al., 2014;
61 Higgins and Schrag, 2015).

62 Although the number of studies of Mg isotopes in altered oceanic basalts to date are
63 limited (Teng, 2017; Huang et al., 2018; Guo et al., 2019), current data suggests a wide range
64 of Mg isotopic compositions can result from carbonate and clay mineral precipitation during
65 low-temperature seawater alteration. A relatively strong preferential uptake of light Mg
66 isotopes is commonly observed by Mg-containing carbonate mineral precipitation in shelf
67 regions, such as during the dolomitization of ancient platform carbonates (Galy et al., 2002;
68 Tipper et al., 2006b; Higgins and Schrag, 2010; Teng et al., 2010; Pearce et al., 2012;
69 Mavromatis et al., 2013); this process has been suggested to be the main driver of past
70 changes in seawater $\delta^{26/24}\text{Mg}$ (Pogge von Strandmann et al., 2014). On the other hand, Mg-
71 bearing silicate alteration minerals such as clays show a smaller degree of Mg isotopic
72 fractionation, with most studies suggesting the preferential incorporation of heavy Mg
73 isotopes into the non-exchangeable sites (i.e. octahedral sheets) of secondary clay minerals
74 (Tipper et al., 2006a; Higgins and Schrag, 2010; Teng et al., 2010; Wimpenny et al., 2014;
75 Ryu et al., 2016). There is also evidence for Mg isotope fractionation in the opposite sense -
76 the preferential incorporation of lighter Mg isotopes into the exchangeable interlayer sites of

77 Mg-bearing clay minerals (Pogge von Strandmann et al., 2008; Wimpenny et al., 2010). This
78 suggests that the metal ion (Mg) uptake by secondary clay minerals and the related isotope
79 fractionation mechanism are highly dependent on the starting fluid composition (including the
80 pH, concentration of elements required for mineral formation, and the presence or absence of
81 seed crystals and precipitation inhibitors). Furthermore, fractionation also depends on the
82 physicochemical and surface characteristics of the alteration mineral (such as crystal structure
83 and bond lengths, specific surface area, surface charge, etc., Li et al., 2014; Baldermann et al.,
84 2018). Such factors can be further complicated by aqueous solution speciation, as Mg isotope
85 fractionation can occur between individual species (e.g., Schott et al., 2016).

86 To better constrain the behaviour of Mg isotopes in marine hydrothermal systems, we
87 performed a series of experiments reacting glassy and crystalline basalt with seawater at
88 temperatures of 250 °C and 290 °C. These temperatures are intermediate between the low-
89 temperature marine hydrothermal systems at <100 °C and the high-temperature axial
90 hydrothermal systems that produce fluids of >400 °C, where necessary to 1) achieve
91 sufficiently fast reaction progress to study this isotopic exchange in the laboratory, and 2) to
92 avoid extremely rapid removal of Mg from the seawater into secondary phases at even higher
93 temperatures. The two rock types were chosen to explore the potential impact that the
94 presence of distinct mineral phases had on the chemical and isotopic evolution of the marine
95 basaltic crust relative to the more reactive glassy components. Unlike previous experimental
96 studies of such systems (e.g., Bischoff and Dickson, 1975; Seyfried and Bischoff, 1977; Mottl
97 and Holland, 1978; Seyfried and Bischoff, 1979; Mottl et al., 1979; Seyfried and Bischoff,
98 1981; Seyfried and Mottl, 1982; Seewald and Seyfried, 1990), the temporal evolution of the
99 aqueous Mg isotopic composition was followed during the experiments via regular sampling,
100 enabling the behaviour of Mg isotopes during the dissolution of basalt and the formation of
101 secondary alteration minerals to be constrained.

102 **2 Methods**

103 **2.1 Experimental design**

104 The experiments conducted in this study were designed to investigate chemical
105 exchange during seawater-basalt interaction by reacting two types of basalt with different
106 crystallinity with seawater in rocked closed-system Ti-reactors at 250 and 290 °C for 53 and
107 92 days, respectively (Fig. 1, Table 1). The basalt used consisted of either basaltic glass or
108 crystalline powders derived from Stapafell in SW Iceland (40-80 µm size fraction, obtained
109 by milling, sieving and subsequent cleaning from ultra-fine grains by repeated ultrasonic
110 cleaning in ultrapure water). The specific surface areas of the glass and crystalline powders
111 were 0.1 and 0.4 m²/g, respectively, as determined by the BET technique (Brunauer et al.,
112 1938) on a Quantachrome Autosorb 1-MP analyser using Kr gas. The chemical composition
113 of the samples, previously reported by Oelkers and Gislason (2001) and Gudbrandsson et al.
114 (2011), is provided in Table 2 and is nearly identical to that of mid-ocean ridge basalt
115 (MORB, which, on average, contains slightly less Mg and Fe but more Si and Al compared to
116 the basalt used in this study; White and Klein, 2014). Both powders were reacted with natural
117 seawater collected from the equatorial Pacific at a depth of 350 m (EqPac cruise November
118 1992; Murray et al., 1997). The seawater was acidified upon collection using distilled
119 concentrated HNO₃ to prevent the precipitation of solids and growth of organic material. The
120 pH of the seawater required for the experiments was re-adjusted to its natural value of ~8.14
121 by the gradual addition of a 25 % ammonia solution (EMD Millipore Suprapur) prior to use in
122 the experiments. The mass ratio of seawater to basaltic powder was ~10 in all experiments, in
123 line with previous experiments and estimates for submarine hydrothermal systems (Seyfried
124 and Bischoff, 1979; Seyfried and Bischoff, 1981). Fluid samples (~ 22 mL) were regularly
125 retrieved from the reactor during the experiments using a sampling valve with an attached
126 cooling apparatus that included a 0.45 µm cellulose acetate membrane filter. This sampling,

127 which was conducted more frequently at the beginning of the experiments due to the faster
128 rate of change expected in the measured parameters, decreased the water:rock ratio to
129 approximately 5 by the end of the experiments. The pressure in the reactors, which was
130 constrained by equilibrium between liquid and gas, was approximately 39 bar and 73 bar at
131 250 °C and 290 °C, respectively, as calculated using thermodynamic data for the H₂O-NaCl
132 system of Driesner and Heinrich (2007) and Driesner (2007). Further details on the fluid
133 sampling and experimental design used in this study are provided in Voigt et al. (2018b).

134 **2.2 Analytical methods**

135 **2.2.1 Aqueous concentrations**

136 The pH of all of the sampled fluids was measured at 22±1 °C using a Metrohm
137 microelectrode, calibrated against pH buffers of pH 4.0, 6.9, and 9.2. The uncertainty on these
138 pH measurements is ±0.07 pH units, based on replicate analyses. For the 250 °C experiments,
139 aqueous Na, Mg, Si, K, Ca, Sr, Li and Fe concentrations were determined by inductively
140 coupled plasma atomic emission spectrometer (ICP-AES, iCAP6000 Series, ThermoFisher),
141 and by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce) for the
142 290 °C experiments. The analytical uncertainties and detection limits of these analyses are
143 reported in Electronic Supplementary Table 1. For the 290 °C experiments, Na concentrations
144 were also determined by flame atomic absorption spectrometry (AAS, AAnalyst 600, Perkin
145 Elmer). The concentrations determined for the experimental samples using the different
146 techniques are consistent within the analytical uncertainties. Additionally, aqueous Al
147 concentrations were determined by furnace AAS, while aqueous SO₄²⁻ and Cl⁻ concentrations
148 were measured using ion chromatography (IC, Dionex ICS 2000). Additional details of these
149 analytical methods can be found in Voigt et al. (2018b).

150 **2.2.2 Characterisation of solids**

151 The mineralogical composition of the unreacted basalt powders and of the solids
152 recovered from the reactors were analysed by powder X-ray diffraction (PXRD, PANalytical
153 X'Pert PRO, Co-Ka radiation at 40 kV and 40 mA). Briefly, the solid materials were mixed
154 with 20 wt-% of ZnO as the internal standard, then randomly oriented preparations were
155 created using the top loading technique and subsequently examined in the range 4-85° 2 Θ
156 using a step size of 0.02° 2 Θ /s with a count time of 1 s/step. Rietveld-based phase
157 quantification was performed applying the PANalytical X'Pert HighScore Plus software and
158 the pdf-4 database. For further analysis of the neo-formed clay minerals, the < 2 μ m size
159 fraction was separated by centrifugation. Subsequently, oriented mounts were created as
160 described in Baldermann et al. (2014), and analysed in the range 3-30° 2 Θ using a step size of
161 0.02° 2 Θ /s and a count time of 2 s/step on a Philips PW 1830 diffractometer (Cu-Ka radiation,
162 40 kV and 30 mA), each under air dried conditions, after solvation with ethylene glycol (EG)
163 and after heating of the specimens to 550°C for 1 h. The chemical composition and hydration
164 state of the saponite-type precipitates were estimated from EG-solvated preparations using the
165 program Sybilla© developed at ChevronTexaco (Baldermann et al., 2013). In addition, the
166 basalt powders and reaction products were analysed by scanning electron microscopy (SEM)
167 using a Jeol JSM 6360LV equipped with an electron dispersive spectroscope (EDS).

168 **2.2.3 Isotopic composition measurements**

169 The Mg isotopic compositions of basalt and liquid samples were determined by
170 multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using a
171 ThermoFisher Neptune at the National Oceanography Centre, Southampton. The solid
172 samples were first dissolved in a mixture of bi-distilled HNO₃ and HF at 130 °C, evaporated
173 to dryness, and re-dissolved in double-distilled HCl. Prior to analysis, Mg was purified using
174 ion-exchange chromatography with a protocol adapted from Pogge von Strandmann et al.
175 (2008; 2012). For this, a sample aliquot containing 2000 ng Mg was evaporated to dryness

176 and re-dissolved in 200 μL of 0.8 mol/kg aqueous HNO_3 before loading onto pre-cleaned Bio-
177 Rad AG50W-X12 (200-400 mesh) resin equilibrated with 0.8 mol/kg HNO_3 in a Savillex
178 30 mL column to a height of 8.5 cm. Cations other than Mg were eluted using a total volume
179 of 51 mL of 0.8 mol/kg aqueous HNO_3 , followed by the elution of Mg in 20 mL of 2 mol/kg
180 aqueous HNO_3 . To ensure a 100 % yield, this elution protocol was tested using the IAPSO
181 seawater standard, the DSM3 Mg standard (Galy et al., 2003) as well as the BCR-2 basaltic
182 rock standard and SCo-1 shale standard from the USGS; each showed Mg isotopic
183 compositions in close agreement with previously reported values (Table 3). The column
184 procedure was repeated 2-3 times to achieve a sufficient purity for Mg analyses, which was
185 confirmed by measurement of Li, Na, Mg, Al, K, Ca, Ti, V, Mg, Fe, Ni, Sr, Sn and Pb
186 concentrations using a ThermoFisher X-Series ICP-MS. Despite the efficiency of this
187 procedure, complete removal of Ca was not achieved for four samples (BSW04-03,
188 BSW05-07, BSW07-03, and BSW07-04), resulting in isobaric interferences during the MC-
189 ICP-MS measurements; these analyses were corrected as described below.

190 Purified samples were introduced to the MC-ICP-MS in 3 % aqueous HNO_3 via a
191 standard injection system (SIS). Thirty measurements with a combined integration time of
192 252 s were made per sample. The samples, containing ~ 600 ppb Mg typically yielded ^{24}Mg
193 beam intensities of ~ 13.5 V. Mass fractionation occurring during the measurements was
194 corrected using the sample-standard bracketing technique, and values are reported as

195 $\delta^{26/24}\text{Mg} \equiv \frac{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{Sample}}}{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{DSM3}}} - 1$ relative to the DSM3 standard (Galy et al., 2003). Similar to

196 the method outlined by Paton et al. (2010), the drift of standard measurements was modelled
197 using smoothed cubic splines instead of simple linear interpolations for a more accurate
198 representation of changes in standard measurements based on statistical methods.
199 Uncertainties in this drift model and overdispersion correction were estimated using Monte
200 Carlo simulations, so that the given uncertainties were propagated from uncertainties in the

201 sample and standard measurements. All samples were run in duplicate, and their weighted
202 means and propagated uncertainties are given in Table 4. The long-term 2 standard deviations
203 in $\delta^{26/24}\text{Mg}$ determinations at the National Oceanography Centre, Southampton is 0.07 ‰,
204 similar to other studies (Pogge von Strandmann et al., 2011; Pogge von Strandmann et al.,
205 2012; Pearce et al., 2012; Teng, 2017). The magnitude of 2 standard deviations of the
206 measurements made during this study varied from 0.07 ‰ to 0.24 ‰. The higher variability is
207 reflected in the uncertainties propagated using the method described above.

208 Isobaric interference effects incurred during analysis from the residual Ca in four
209 samples (BSW04-03, BSW05-07, BSW07-03, and BSW07-04) were corrected by assuming
210 that observed deviations of the measured $\delta^{26/24}\text{Mg}$ and $\delta^{25/24}\text{Mg}$ values from the mass
211 dependent fractionation line (Young et al., 2002) were caused by ^{48}Ca interference with the
212 ^{24}Mg signal. This enabled the measured δ values to be corrected by back-tracking to the ‘true’
213 values that were consistent with mass dependent fractionation (see Supplementary Fig. 1).
214 Two of the affected samples were analysed by MC-ICP-MS after two and three repeats of the
215 ion-exchange separation, which lead to an increasingly better, but not complete, Ca removal.
216 For both samples, these two individual analyses are consistent with the same corrected
217 $\delta^{26/24}\text{Mg}$ and $\delta^{25/24}\text{Mg}$. Furthermore, the analysis after three separation runs indicates a smaller
218 amount of ^{48}Ca (Supplementary Fig. 1), consistent with the assumption that the deviations are
219 caused by Ca interference. Propagation of uncertainties in this inversion was performed using
220 Monte Carlo simulations, so that the uncertainties given for $\delta^{26/24}\text{Mg}$ and $\delta^{25/24}\text{Mg}$ of the
221 corrected samples include uncertainties of the interference correction.

222 **3 Results**

223 **3.1 Evolution of the liquid phase composition**

224 **3.1.1 General chemical trends**

225 The elemental composition of the experimental seawater changed significantly during
226 its reaction with basalt (Table 4). The rate of change was higher at 290 °C than at 250 °C, and
227 faster reaction progress, as monitored by the temporal evolution of reaction fluid
228 compositions, was also observed for the experiments performed using basaltic glass compared
229 to those using crystalline basalt as the reactant, even though the initial surface area of the
230 crystalline material (determined using the BET technique) was approximately 4 times higher.
231 Magnesium was constantly removed from the liquid through basalt-seawater interaction and
232 reached levels below the detection limit after 7 days in the basaltic glass experiment at
233 250 °C, while the final aqueous Ca concentrations were higher than the initial seawater in
234 both experiments (Fig. 2). Similar to Mg, the SO_4^{2-} initially present in the seawater was
235 removed from the liquid over time. A pH of 3.7 and 4.9 was attained in the crystalline basalt
236 experiments at 250 °C and 290 °C, respectively, before increasing to approximately pH 9.5. In
237 contrast, the pH values did not decrease significantly in the basaltic glass experiments before
238 they increased to similar values as in the crystalline basalt experiments (Fig. 2). Significant
239 concentrations of aqueous Fe (2.4 mmol/kg and 4.7 mmol/kg at 250 °C and 290 °C,
240 respectively, Supplementary Fig. 2) were reached and sustained in the experiments with
241 crystalline basalts, while the liquids had an acidic pH. Measurable quantities of aqueous silica
242 were present in all experiments from the first sample (which was taken after ~24 h),
243 stabilizing at 10-15 mmol/kg after decreasing from slightly higher values (20 and 25 mmol/kg
244 at 250 °C and 290 °C, respectively). Aluminium concentrations in the liquid remained low
245 (8 $\mu\text{mol/kg}$ with a standard deviation of 5 $\mu\text{mol/kg}$), but were higher compared to the initial
246 seawater.

247 Aqueous Na and Cl concentrations increased significantly at the end of most
248 experiments: The last two fluid samples collected from the experiments performed with
249 basaltic glass at 250 °C had $\approx 17\%$ higher Cl concentrations compared to seawater, and both
250 experiments at 290 °C showed a similar trend (with an up to 33 % increase). This can be
251 explained by the formation of low-NaCl vapour due to the removal of liquid by sampling
252 from the autoclaves, leading to an enrichment of solutes in the liquid phase (cf. Voigt et al.,
253 2018b for a detailed discussion). The reduced liquid volume due to this effect is taken into
254 account in the mass balance calculations presented below, where estimates of the amount of
255 low-NaCl vapour were determined using thermodynamic relationships for the H₂O-NaCl
256 system reported by Drieser (2007) and Drieser and Heinrich (2007). To a lesser extent,
257 uptake of H₂O due to the formation of hydrated minerals leads to the same effect.

258 **3.1.2 Magnesium isotopic compositions**

259 The basaltic glass used in this study had a $\delta^{26/24}\text{Mg}$ composition of $-0.28 \pm 0.18\%$,
260 while the crystalline basalt had a slightly lower value of $-0.38 \pm 0.18\%$ (uncertainties listed
261 here reflect the 95% confidence interval, corresponding to ~ 2 standard errors). These values
262 are thus identical within uncertainty, and are in agreement with the value of $-0.30 \pm 0.03\%$
263 obtained by Wimpenny et al. (2010) for the Stapafell basaltic glass. The seawater used as
264 reactant had a starting $\delta^{26/24}\text{Mg}$ composition of $-0.86 \pm 0.07\%$, which is identical within
265 uncertainty to the $\delta^{26/24}\text{Mg}$ value of $-0.83 \pm 0.09\%$ for seawater recommended by Teng et al.
266 (2015). Starting from the initial seawater composition, the liquid evolved towards isotopically
267 lighter compositions (Fig. 2, Table 4): In the 250 °C basaltic glass experiment $\delta^{26/24}\text{Mg}$
268 initially decreased to $-1.02 \pm 0.19\%$ during the first 24 h, then decreased to $-3.27 \pm 0.87\%$
269 between days 4 and 7 before the aqueous Mg concentrations became too low for isotopic
270 analysis. In the corresponding crystalline basalt experiment, a fluid $\delta^{26/24}\text{Mg}$ value of
271 $-1.11 \pm 0.13\%$ was reached within the first 14 days. The next sample, taken after 21 days of

272 total elapsed time, had a $\delta^{26/24}\text{Mg}$ composition of $-0.79\pm 0.14\text{‰}$, then decreased again to
273 $-1.26\pm 0.41\text{‰}$ at the end of the experiment (Fig. 2). At 290 °C, the fluid that was reacted with
274 basaltic glass decreased to a $\delta^{26/24}\text{Mg}$ value of $-1.07\pm 0.07\text{‰}$ within the first day, while later
275 samples did not contain sufficient Mg for isotopic analysis. At the same temperature, seawater
276 reacted with crystalline basalt showed a slight decrease in $\delta^{26/24}\text{Mg}$ values to $-1.01\pm 0.07\text{‰}$
277 within 4 days, followed by a drop to $-1.63\pm 0.29\text{‰}$ and another slow decrease to -
278 $1.75\pm 0.08\text{‰}$ after 35 days.

279 **3.2 Solid alteration products**

280 The basalt powders used as reactants were significantly altered during the
281 experiments. SEM images of the solids recovered from the reactors after the experiments
282 were terminated (Fig. 3) show that the basalt grains were completely covered by alteration
283 minerals with honeycomb-like structures, which is typical for smectite clays (e.g., Fiore et al.,
284 2001). Furthermore, anhydrite was formed during all experiments (Voigt et al., 2018b). The
285 massive formation of smectite minerals was confirmed by quantitative PXRD analyses (Table
286 5, Fig. 4). Modelling of XRD patterns obtained from EG-solvated, oriented clay films enabled
287 the smectite clays to be identified as trioctahedral ferrous saponite with Na ions occupying
288 mainly the exchangeable interlayer sites (Fig. 4). The ferrous saponite precipitated in this
289 study contains approximately 0.46 to 0.67 atoms per formula unit (a.p.f.u.) octahedral Fe in
290 the experiments with crystalline basalt, and from 0.71 to 0.98 a.p.f.u. octahedral Fe in the
291 basaltic glass experiments (Table 5; Supplementary Fig. 3). Furthermore, PXRD data suggest
292 that minor analcime/heulandite type zeolite formed during the two basaltic glass experiments.
293 At 290 °C, plagioclase (close to albitic composition) and minor proportions of mixed-layer
294 chlorite-smectite minerals were formed in the experiment with basaltic glass according to the
295 PXRD analyses (Table 5, Fig. 4).

296 **4 Discussion**

297 **4.1 Evolution of liquid chemistry and alteration reactions**

298 The reaction of basalt with seawater under hydrothermal conditions in our experiments
299 caused the rapid and abundant precipitation of ferrous saponite and minor anhydrite, which
300 removed Mg as well as Na, OH, Al, Si, Fe, SO_4^{2-} and Sr from the fluid (Voigt et al., 2018b).
301 A number of studies have previously concluded that the evolution of fluid pH in such systems
302 is controlled by the relative importance of two competing processes: (1) The uptake of
303 alkalinity (i.e. OH⁻ groups) along with Mg, Si and Fe by secondary hydrous minerals, which
304 drives a drop in pH as seen in the beginning of the experiments with crystalline basalt; and (2)
305 leaching of Ca and other cations from the basalt causing pH and aqueous Ca concentrations to
306 increase after Mg removal was near complete (Bischoff and Dickson, 1975; Seyfried and
307 Bischoff, 1977; Seyfried and Bischoff, 1979; Seyfried and Bischoff, 1981; Seyfried and
308 Mottl, 1982). The stronger increase in pH observed in this study compared to previous
309 experiments and marine high-temperature hydrothermal fluids (Fig. 2; Seyfried and Bischoff,
310 1979; Seyfried and Bischoff, 1981; German and Seyfried, 2014) is possibly related to the
311 uptake of HCl by the gas phase enabled by the high salinity, and/or the presence of small
312 amounts of NH₃ introduced during the pH adjustment of the seawater used in the experiments
313 (see Voigt et al., 2018b). The low initial pH in the crystalline basalt experiments also explains
314 the prolonged period of Fe enrichment in the liquid (released from basalt), after which it was
315 incorporated into the saponite clays as indicated by their high octahedral Fe contents (cf.
316 section 3.2) and the absence of secondary Fe-hydroxide minerals. Fluid enrichment in Fe is
317 also consistent with trends observed in natural marine hydrothermal fluids (e.g., German and
318 Seyfried, 2014). Furthermore, the correlation between the total mass of precipitated smectite
319 and the estimated structural Fe content of saponite formed in experiments with basaltic glass

320 and crystalline basalt (Table 5) suggests that a Fe-poor saponite was initially precipitated,
321 followed by an increasing more Fe-rich saponite during subsequent mineral growth.

322 **4.2 Magnesium isotope fractionation**

323 The changes in aqueous $\delta^{26/24}\text{Mg}$ during the experiments likely reflect the combined
324 effects of isotopic fractionation during saponite precipitation and the Mg release from basalt
325 dissolution. Consequently, an assessment of the extent of isotope fractionation into the
326 alteration products requires an estimate of the amount of Mg released from basalt dissolution,
327 which is later scavenged by clay mineral formation. Here, we estimate these values from mass
328 balance relationships between aqueous and solid phase Mg, assuming that all Mg released
329 from basalt dissolution is precipitated into a single alteration phase (i.e. saponite). It is also
330 assumed that no significant Mg is taken up by the low-NaCl vapour phase that is present at
331 the end of the experiments, as the vapour pressure of Mg is significantly lower than that of Na
332 (Lide, 2003); thus Mg is only expected to be present in trace quantities in the vapour phase
333 under the experimental conditions used in this study (Driesner, 2007; Driesner and Heinrich,
334 2007). The amount of Mg released from basalt dissolution was estimated from mass balancing
335 the components Mg, Ca and SO_4 . We assume that Ca and SO_4 are only removed from the
336 liquid by precipitation into anhydrite. The latter assumption is likely not entirely satisfied,
337 especially during the later stages of the experiments, when Ca could be incorporated into one
338 or more of the other observed alteration phases (saponite, zeolites, and albitic plagioclase).
339 Therefore, the calculated amounts of Mg released from basalt dissolution (symbols in Fig.
340 5a,b) and Mg incorporation into smectite are likely minimum estimates.

341 Based on the mass balance constraints described above, the evolution of $\delta^{26/24}\text{Mg}$
342 during the experiments was modelled using an incremental isotope mass balance model,
343 allowing for isotopic fractionation during the precipitation of a single Mg-incorporating
344 mineral (saponite). A constant isotopic fractionation factor describing irreversible isotopic

345 fractionation during smectite precipitation (i.e. the smectite does not react with the liquid after
346 precipitation) is assumed in this model, and is defined as

$$\alpha_{\text{Smectite-Liquid}}^{26/24} \equiv \frac{d^{26}\text{Mg}_{\text{Smectite}}/d^{24}\text{Mg}_{\text{Smectite}}}{d^{26}\text{Mg}_{\text{Liquid}}/d^{24}\text{Mg}_{\text{Liquid}}} \quad (4.1)$$

347 (see Appendix A for model details). The resulting model can be interpreted as a Rayleigh
348 type fractionation process, whereby the changes in $\delta^{26/24}\text{Mg}$ are primarily driven by smectite
349 precipitation from a limited volume of liquid. The possibility of coincident Mg isotopic
350 fractionation occurring during basaltic glass dissolution was suggested by experiments of
351 Wimpenny et al. (2010) and for Si isotopes by data of Ziegler et al. (2005). However, it was
352 possible to reproduce the Mg isotope trends observed in our experiments without including
353 isotope fractionation during basalt dissolution, and preliminary model runs that did include
354 constant isotopic fractionation during the release of Mg from basalt dissolution did not
355 significantly improve the model fit (resulting in $\alpha_{\text{Smectite-Liquid}}^{26/24}$ values similar to those
356 presented below). In contrast, it was found that different fractionation factors for the two
357 experimental temperatures applied in this study were necessary to explain the isotopic trends
358 with this mass balance model.

359 The results, shown in Fig. 5c-d, reproduce the major trends seen in the experimental
360 $\delta^{26/24}\text{Mg}$ data: The $\delta^{26/24}\text{Mg}$ composition of the fluid decreased slowly during the early stages
361 of the experiments following the preferential incorporation of heavy Mg into smectite
362 ($\epsilon_{\text{Smectite-Liquid}}^{26/24} > 0$). The short-lived increase in liquid $\delta^{26/24}\text{Mg}$ values observed in the 250 °C
363 crystalline basalt experiment may be attributed to the release of isotopically heavy Mg from
364 basalt dissolution (as can be seen from the mass balance and strongly increasing fluid Ca
365 concentrations, Figs. 1 and 3), which likely results from an increase in Al removal from the
366 fluid into secondary minerals when pH increases. Conversely, the strong decrease of $\delta^{26/24}\text{Mg}$

367 in the liquid towards the end of the experiments is caused by the irreversible (Rayleigh-type)
368 nature of the Mg fractionation into smectite.

369 The best estimate and uncertainty (i.e. analytical uncertainties propagated through the
370 model, 95 % confidence intervals) for $\epsilon_{\text{Smectite-Liquid}}^{26/24}$ (defined as $\epsilon^{26/24} = (\alpha^{26/24} - 1)$) is
371 0.422 ± 0.065 ‰ at 250 °C and 0.346 ± 0.016 ‰ at 290 °C. These values are similar to the
372 $\epsilon_{\text{Brucite-Liquid}}^{26/24} = 0.5$ value obtained experimentally by Wimpenny et al. (2014) for brucite at
373 80 °C, which is used as an analogue to describe Mg incorporation into clay minerals, and are
374 qualitatively in agreement with a decrease in the magnitude of isotopic fractionation with
375 increasing temperature. They are also consistent with the fractionation factor of
376 $\epsilon_{\text{Clay-Liquid}}^{26/24} = 0.59 \pm 0.14$ ‰ determined during synthetic lizardite and kerolite formation at
377 250 °C by Ryu et al. (2016), as well as with the behaviour of Mg during saprolite formation in
378 the context of diabase weathering, as Teng et al. (2010) suggested fractionation factors of
379 around $\epsilon_{\text{Saprolite-Fluid}}^{26/24} \approx 0.4$ ‰ for smectite-rich saprolite at Earth surface temperatures. The
380 preferential enrichment of smectite in heavier Mg isotopes is also in agreement with the deep-
381 sea pore-fluid data of Higgins and Schrag (2010), who observed a decrease in pore-fluid
382 $\delta^{26/24}\text{Mg}$ with depth at some sites, indicative of the presence of an isotopically enriched Mg
383 sink (likely clay minerals) relative to the pore-fluid. Our results also support the conclusions
384 drawn by Huang et al. (2018), who studied the Mg isotope compositions of oceanic crustal
385 rocks that have been subjected to low-temperature alteration, and inferred a preferential
386 incorporation of heavy Mg isotopes in sections where saponite formation occurred.
387 Furthermore, silicate soil samples from the Southern Tibetan Plateau show higher $\delta^{26/24}\text{Mg}$
388 values compared to associated silicate host rocks, a difference that can be attributed to silicate
389 rock weathering (Tipper et al., 2006a). Conversely, the direction of Mg isotope fractionation
390 observed in this study is opposite to the results of Pogge von Strandmann et al. (2008), who

391 suggested that secondary minerals such as talc and chlorite preferentially uptake isotopically
392 light Mg from high pH fluids.

393 Variations in Mg isotope fractionation factors during clay mineral formation can be
394 explained by a number of parameters, including temperature, the mineral composition,
395 reaction kinetics, and fluid speciation. For example, Schott et al. (2016) showed that the
396 presence of organic complexes in seawater can have significant effects on Mg aqueous
397 speciation in seawater and thus Mg isotopic fractionation during mineral precipitation. The
398 speciation of aqueous Mg in our experiments, as calculated with PHREEQC (Parkhurst and
399 Appelo, 2013) together with the CarbFix database (Voigt et al., 2018a) at the experimental
400 temperatures (Fig. 5g-h), is dominated by the MgCl^+ complex, representing between 66 and
401 90 mol% of the total aqueous Mg in the initial seawater, while the Mg^{2+} complex is estimated
402 to have an abundance of 10 to 20 mol%, and the initially present aqueous MgSO_4 (up to 16
403 mol%) decreased with the rapid SO_4 removal from seawater. The degree to which the
404 fractionation factors determined in this study might be affected by aqueous Mg speciation
405 remains unresolved at present.

406 **4.3 Consequences for the marine Mg isotopic budget**

407 Recent studies of the marine Mg isotopic budget suggest that variations in carbonate
408 mineral formation (such as dolomitization) and riverine inputs have exerted a major influence
409 on the composition of seawater through time (Pogge von Strandmann et al., 2014; Higgins
410 and Schrag, 2015), and that a decrease in seawater $\delta^{26/24}\text{Mg}$ over the past ~15 Ma may have
411 been driven by a decrease in the extent of dolomite precipitation (Pogge von Strandmann et
412 al., 2014). Although the influence of Mg-clay formation in marine hydrothermal
413 environments and in marine sediments on the global marine budget has been proposed by
414 Higgins and Schrag (2015) and Dunlea et al. (2017), the magnitudes of these effects are
415 poorly constrained at present, and are expected to vary as a function of the degree of Mg

416 removal in these settings. Our experimental results provide the first evidence for Mg isotope
 417 fractionation during clay formation in intermediate temperature hydrothermal settings, and
 418 imply that the return of isotopically light fluids that have undergone partial Mg removal into
 419 clay minerals to seawater might significantly impact $\delta^{26/24}\text{Mg}$ mass balance.

420 The potential effect of Mg isotope fractionation in these systems on the marine Mg
 421 budget (here called E_{Clays}) is a combination of: (i) the isotopic composition (i.e. the $\delta^{26/24}\text{Mg}$
 422 value) of the precipitated clay minerals relative to seawater; and (ii) the flux of Mg between
 423 these systems $F_{\text{Mg}}^{\text{Clays}}$, since

$$\begin{aligned} \frac{d(\delta^{26/24}\text{Mg})_{\text{SW}}}{dt} \cdot c_{\text{Mg}}^{\text{SW}} &= \left((\delta^{26/24}\text{Mg})_{\text{Clays}} - (\delta^{26/24}\text{Mg})_{\text{SW}} \right) \cdot F_{\text{Mg}}^{\text{Clays}} + \dots \\ &\equiv \underbrace{(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}} \cdot F_{\text{Mg}}^{\text{Clays}}}_{E_{\text{Clays}}} + \dots \end{aligned} \quad (4.2)$$

424 where ... reflects the contributions of other fluxes on the marine Mg budget (e.g. Tipper et al.,
 425 2006b; Pogge von Strandmann et al., 2014; Higgins and Schrag, 2015). Assuming that
 426 irreversible isotopic fractionation occurs in a closed system, it can be shown (Appendix B)
 427 that for a given fraction f of Mg removal from the seawater, the isotopic evolution can be
 428 described by

$$(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}} \approx \frac{((1-f)^\varepsilon - 1)(f-1)}{f} \quad (4.3)$$

429 This function has its maximum of ε at $f=0$ and is shown in Fig. 6a for $\varepsilon_{\text{Smectite-Liquid}}^{26/24} =$
 430 0.35 ‰, which is the mean of our experimental best fit weighted by the inverse of their
 431 variance. Since $F_{\text{Mg}} \propto f$, the effect of Mg isotope fraction in these clays is proportional to

$$E_{\text{Clays}} \propto ((1-f)^\varepsilon - 1)(f-1) \quad (4.4)$$

432 illustrating that the effect of clay precipitation on the marine budget is largest at $f \approx 1 -$
 433 $1/e \approx 0.63$ for a constant ε , and is zero at both no clay mineral precipitation and complete
 434 Mg removal (Fig. 6b).

435 This result shows that the impact of Mg isotopic fractionation during smectite
436 formation in high-temperature marine hydrothermal systems on the marine Mg isotopic
437 budget may be low, as Mg is almost quantitatively removed from the seawater during
438 hydrothermal reactions (e.g., Mottl and Holland, 1978; Elderfield et al., 1999; Coggon et al.,
439 2004; German and Seyfried, 2014). Using the mean of our best fit fraction factor, the isotopic
440 difference between seawater and clays due to irreversible precipitation is approximately
441 $(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}} \approx 0.14 \text{ ‰}$ for an 80 % removal of Mg from seawater (see Fig. 6), which
442 is assumed to be the minimum value for high temperature hydrothermal systems, and it often
443 approaches 100 % (Mottl and Wheat, 1994; German and Seyfried, 2014).

444 Conversely, for low temperature alteration, Mg removal is less complete and reaches
445 down to $f=0$ (Fisher and Wheat, 2010). In their marine Mg budget model, Higgins and Schrag
446 (2015) adopted a value of 0.7 ‰ for the isotopic difference between seawater and Mg-clays,
447 $(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}}$, while Huang et al. (2018) adopted a value of 0.83 ‰ based on the
448 average composition of altered oceanic crust at Site 801. The fractionation factors determined
449 under our experimental conditions are $(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}} < 0.350 \text{ ‰}$ (Fig. 6), which is
450 slightly smaller than the values adopted by Higgins and Schrag (2015) and Huang et al.
451 (2018). However, Mg isotopic fractionation is expected to more pronounced at lower
452 temperatures (e.g., Teng, 2017), thus these values are qualitatively in agreement.

453 In comparison, the influence of carbonate precipitation on the Mg isotopic budget of the
454 oceans is approximately an order of magnitude higher due to its larger isotopic fractionation
455 factor of $\varepsilon_{\text{Carbonate-Liquid}}^{26/24} \approx -2 \text{ ‰}$ (Higgins and Schrag, 2015), even considering a higher Mg
456 flux at mid-ocean ridges compared to that of marine carbonate formation. Nevertheless, both
457 carbonate formation and clay precipitation with incomplete Mg-removal from the seawater

458 are crucial when constraining the global marine Mg cycle using isotopes, as suggested by
459 Higgins and Schrag (2015) and Huang et al. (2018).

460 **5 Conclusions**

461 The evolution of aqueous $\delta^{26/24}\text{Mg}$ was followed during basaltic glass and crystalline
462 basalt-seawater interaction experiments at temperatures of 250 °C and 290 °C under saturated
463 vapour pressure. The solid alteration phases recovered after termination of the experiments
464 mainly consisted of ubiquitous saponite (a trioctahedral Mg-smectite) and minor anhydrite.
465 Trends in the chemical evolution of the fluid composition sampled during the experiments
466 were similar to those observed at marine hydrothermal systems. During the experiments, Mg
467 was released into the liquid phase from basalt dissolution, while the precipitation of alteration
468 minerals such as smectite removed Mg from the liquid, leading to a steady decrease in
469 aqueous Mg concentrations in all experiments.

470 A model of Mg isotopic evolution during the experiments, which assumes irreversible
471 (Rayleigh-type) fractionation during precipitation into smectite concurrent with Mg release
472 from basalt dissolution, can fully explain the trends observed in the experimentally
473 determined fluid $\delta^{26/24}\text{Mg}$ compositions. The retrieved fractionation factors of
474 $\epsilon_{\text{Smectite-Liquid}}^{26/24} = 0.422 \pm 0.065 \text{ ‰}$ at 250 °C and $0.346 \pm 0.016 \text{ ‰}$ at 290 °C indicate
475 that isotopically heavy Mg is preferentially incorporated into the smectite, explaining the drop
476 in liquid $\delta^{26/24}\text{Mg}$ when aqueous Mg concentrations approach zero.

477 The $\epsilon_{\text{Smectite-Liquid}}^{26/24}$ values determined in this study are in agreement with independent
478 field and experimental evidence for similar silicate minerals (Tipper et al., 2006a; Higgins and
479 Schrag, 2010; Teng et al., 2010; Wimpenny et al., 2014), and provide the first constraint on
480 the $\delta^{26/24}\text{Mg}$ composition of smectite forming under hydrothermal conditions. The observation
481 that smectite preferentially incorporates isotopically heavy Mg is opposite to the trend seen in

482 carbonates (Galy et al., 2002; Tipper et al., 2006b; Higgins and Schrag, 2010; Teng et al.,
483 2010; Pearce et al., 2012; Mavromatis et al., 2013; Huang et al., 2018), thus highlights the
484 potential utility of Mg isotopes in fluids as tracers of the formation of these different mineral
485 types (e.g., Oelkers et al., 2018). Furthermore, the magnitude of Mg fractionation observed
486 during clay formation in this study is in good agreement with the previously estimated effects
487 of Mg isotopic fractionation in low-temperature marine hydrothermal systems on the marine
488 Mg budget (Higgins and Schrag, 2015; Huang et al., 2018), significantly reducing
489 uncertainties in the modelling of the Mg isotopic compositional evolution in the marine Mg
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- 699

700 **Appendix A. Details of the mass balance model calculations**

701 The Mg fractionation factors for the formation of smectite from the aqueous fluids
702 were generated from the solutions to a set of simulation differential equations. Solutions to
703 these differential equation system were calculated numerically with the NDSolve function of
704 Wolfram Mathematica, and the maximum likelihood $\alpha_{\text{Smectite-Liquid}}^{26/24}$ (expressed here as
705 $\varepsilon^{26/24} = (\alpha^{26/24} - 1)$) are calculated based on the minimum inverse variance weighted
706 squared errors using the Nelder-Mead method (Nelder and Mead, 1965). The corresponding
707 uncertainties are propagated using Monte Carlo simulations where the 95 % confidence
708 intervals are calculated from the quantiles. As mass balance constraints require inclusion of
709 ^{25}Mg into the equations, $\alpha^{25/24}$ are calculated internally based on $\alpha^{26/24}$ and the kinetic
710 mass-dependent fractionation law (Young et al., 2002), which was used as opposed to the
711 equilibrium mass fractionation law due to the relatively fast kinetics of the involved
712 processes. However, due to the small difference between the two fractionation laws, the
713 choice does not significantly affect the model results. The mean covariance between measured
714 $\delta^{25/24}\text{Mg}$ and $\delta^{26/24}\text{Mg}$, 0.81, was included in the uncertainty propagation calculations. To
715 account for the generation of low-NaCl vapour due to sampling from the reactors towards the
716 ends of the experiments, all mass balance calculations account for the vapour volume
717 estimated using the thermodynamics of the H₂O-NaCl system (Driesner, 2007; Driesner and
718 Heinrich, 2007).

719 The evolution of Mg dissolution and precipitation during the experiments (symbols in
720 Fig. 5a-b) were estimated using the Steffen interpolation method (Steffen, 1990) to establish a
721 smooth trend while preserving the monotonicity. The elemental mass balance model
722 furthermore allows estimation of molar ratios of elements incorporated into secondary phases
723 during the experiment based on the evolution of fluid composition and the inferred amounts
724 of basalt dissolution. We calculated the molar ratio of (Si+Al)/(Mg+Fe) taken up into

725 secondary minerals, which is $4/3 \approx 1.33$ in case of saponite, lower than the mean (weighed by
 726 the inverse of the variance) of the corresponding value in our experiments of 2.37 ± 0.87 .
 727 However, the uncertainty of this parameter is relatively high, as can be seen in Supplementary
 728 Fig. 4, showing its evolution during the experiments. The retrieved (Si+Al)/(Mg+Fe) values
 729 that are greater than expected for saponite can be explained by i) uptake of excess Si and Al
 730 into other phases (such as zeolites, as confirmed in BSW-04 and BSW-06 by XRD
 731 measurements), ii) the fact that calculated amounts of Mg release from basalt dissolution and
 732 thus Mg incorporation into smectite are likely minimum estimates (see section 4.2), or a
 733 combination of the two.

734

735 **Appendix B. Irreversible isotopic fractionation in a closed system**

736 Isotopic fractionation occurring during a reaction where the product is immediately
 737 isolated from the reactant can be described by

$$\alpha_{\text{Product-Reactant}} \equiv (\varepsilon + 1) \equiv \frac{R_{P,i}}{R_R}$$

738 where R_R and $R_{P,i}$ designate the isotopic ratios of the reactant and of an increment of the
 739 product during the reaction, respectively. The reaction progress is commonly expressed as
 740 fractional yield, defined as $f \equiv m_P/m_{R,0}$, where m_P and $m_{R,0}$ are the masses of the product
 741 and of the reactant before the reaction, respectively. The composition of the reactant evolves
 742 according to

$$\ln \left(\frac{R_R}{R_R^0} \right) \approx \varepsilon \ln(1 - f)$$

743 where R_R and R_R^0 designate the isotopic ratios of the reactant after reaction progress f and at
 744 the beginning, respectively, as shown by Bigeleisen and Wolfsberg (1957). Substituting

745 $R_X = (\delta X + 1)R_{\text{Standard}}$ and solving for $\delta_R - \delta_{R,0}$, the change in isotopic composition of the
 746 reactant, gives

$$\delta_R - \delta_{R,0} = (1 + \delta_{R,0})(1 - f)^\varepsilon - 1 \approx (1 - f)^\varepsilon - 1$$

747

748 Conversely, Bothner-By and Bigeleisen (1951) showed that the isotopic composition
 749 of the total accumulated product follows the relationship

$$\ln\left(1 + \frac{R_R^0 - R_{P,\text{Total}}}{R_R^0} \frac{f}{1 - f}\right) \approx \varepsilon \ln(1 - f)$$

750 where $R_{P,\text{Total}}$ designates the isotopic ratios of the accumulated product which can be solved in
 751 a similar way to give the difference $\delta_{P,\text{Total}} - \delta_{R,0}$ as

$$\delta_{P,\text{Total}} - \delta_{R,0} = \frac{(1 + \delta_{R,0})((1 - f)^\varepsilon - 1)(f - 1)}{f} \approx \frac{((1 - f)^\varepsilon - 1)(f - 1)}{f}$$

752 **Tables**753 **Table 1:** Experimental parameters of the basalt-seawater experiments.

| Experiment | T / °C | Basalt type | Starting materials / g | | | Duration / days |
|------------|--------|-------------|------------------------|--------|-----------------------|-----------------|
| | | | Seawater | Basalt | Water/rock mass ratio | |
| BSW04 | 250 | Glassy | 275.0 | 27.50 | 10 | 53 |
| BSW05 | 250 | Crystalline | 275.0 | 27.50 | 10 | 53 |
| BSW06 | 290 | Glassy | 220.0 | 22.01 | 10 | 92 |
| BSW07 | 290 | Crystalline | 220.0 | 22.00 | 10 | 93 |

754

755 **Table 2:** Composition (wt. %) of the basaltic glass and crystalline basalt used as starting
756 materials.

| Sample | SiO ₂ | Al ₂ O ₃ | FeO ^c | MgO | CaO | Na ₂ O | K ₂ O | TiO ₂ | MnO | P ₂ O ₅ | Total |
|--------------------------|------------------|--------------------------------|------------------|------|------|-------------------|------------------|------------------|-----|-------------------------------|-------|
| Glass ^a | 48.1 | 14.6 | 10.8 | 9.1 | 11.8 | 2.0 | 0.3 | 1.6 | 0.2 | 0.2 | 98.7 |
| Crystalline ^b | 47.9 | 13.4 | 11.1 | 10.0 | 12.2 | 1.5 | 0.3 | 1.6 | 0.2 | 0.2 | 97.9 |

757 ^a From Oelkers and Gíslason (2001)758 ^b From Gudbrandsson et al. (2011)759 ^c Most iron is Fe²⁺, Fe²⁺ / Fe³⁺ ≈ 10 (Oelkers and Gíslason, 2001)

760

761 **Table 3:** Measured Mg isotopic composition of standards processed through the column
762 separation protocol in comparison to previously published values.

| Standard | Measured $\delta^{26/24}\text{Mg}$ / ‰ | Literature value / ‰ | Literature references |
|----------|--|----------------------|---|
| IAPSO | -0.93±0.20 -0.82±0.07 | -0.83±0.09 (2SD) | Foster et al. (2010); Ling et al. (2011) |
| DSM-3 | -0.04±0.28 -0.04±0.07 | 0 (by definition) | |
| BCR-2 | -0.29±0.20 | -0.31±0.27 (2SD) | Pearce et al. (2012) |
| SCo-1 | -0.89±0.07 | -0.92±0.06 (2SD) | Li et al. (2010); Ma et al. (Ma et al., 2015) |

763

764

765

766 **Table 4:** Chemical composition of the seawater used as reactant in the experiment and of the liquid samples taken during the experiments. Rows
767 labelled "Quenched" show compositions of the liquid in the reactor after terminating the experiment by quenching. Uncertainties (\pm) designate the
768 95 % confidence interval (~ 2 standard errors) and '< LOD' are values below the detection limits, which are given below the table. Uncertainties for
769 all data are given in Electronic Supplementary Table 1. The major elemental composition was previously reported by Voigt et al. (2018b).

| Experiment | Sample | Duration / days | pH | Fluid mass / g | Concentration / mmol/kg | | | | | | | | $\delta^{25/24}\text{Mg} / \text{‰}$ | | $\delta^{26/24}\text{Mg} / \text{‰}$ | |
|---------------------------------------|----------|--------------------|------|-------------------|-------------------------|-------|------|------|-------|--------|-------|--------------------|--------------------------------------|-------------------|--------------------------------------|-------------------|
| | | | | | Na | Mg | Si | K | Ca | Fe | Cl | SO_4^{2-} | Value | \pm | Value | \pm |
| | Seawater | | 8.14 | 474 | 55 | < LOD | 11.8 | 10.3 | 0.040 | 597.4 | 29.1 | -0.412 | 0.053 | -0.859 | 0.066 | |
| BSW04 250 °C basaltic glass | BSW04-01 | 1.0 | 7.71 | 275 | 489 | 17.0 | 14.4 | 12.9 | 16.8 | 0.27 | 599.9 | 0.604 | -0.54 | 0.10 | -1.02 | 0.19 |
| | BSW04-02 | 3.8 | 8.72 | 257 | 491 | 0.56 | 13.8 | 13.6 | 35.8 | 0.0069 | 606.5 | 0.305 | -0.53 | 0.12 | -1.02 | 0.22 |
| | BSW04-03 | 6.8 | 9.09 | 235 | 493 | 0.106 | 13.4 | 13.7 | 39.7 | 0.0008 | 619.0 | 0.287 | -1.67 | 0.44 ^a | -3.27 | 0.87 ^a |
| | BSW04-04 | 13.9 | 9.48 | 212 | 500 | < LOD | 10.5 | 13.8 | 43.6 | < LOD | 620.4 | 0.295 | | | | |
| | BSW04-05 | 21.0 | 9.58 | 190 | 504 | < LOD | 9.8 | 13.8 | 45.8 | < LOD | 624.5 | 0.289 | | | | |
| | BSW04-06 | 33.9 | 9.65 | 169 | 575 | < LOD | 9.2 | 15.9 | 42.8 | < LOD | 684.6 | 0.345 | | | | |
| | BSW04-07 | 52.9 | 9.52 | 148 | 601 | < LOD | 10.5 | 16.9 | 36.9 | < LOD | 704.1 | 0.350 | | | | |
| | Quenched | | | | 513 | < LOD | 4.25 | 9.6 | 46.9 | < LOD | 621.9 | 4.00 | | | | |
| BSW05 250 °C crystalline basalt | BSW05-01 | 1.0 | 3.74 | 275 | 484 | 46.7 | 18.2 | 14.7 | 1.28 | 1.37 | 608.0 | 14.85 | -0.42 | 0.06 | -0.80 | 0.12 |
| | BSW05-02 | 3.8 | 4.01 | 254 | 479 | 42.9 | 20.4 | 15.2 | 1.43 | 2.0 | 603.8 | 12.45 | -0.44 | 0.06 | -0.85 | 0.13 |
| | BSW05-03 | 6.8 | 4.83 | 232 | 490 | 40.4 | 20.6 | 15.8 | 1.63 | 2.4 | 610.8 | 10.15 | -0.48 | 0.06 | -0.92 | 0.13 |
| | BSW05-04 | 14.0 | 5.89 | 212 | 480 | 20.9 | 17.1 | 16.1 | 10.3 | 1.43 | 597.5 | 0.902 | -0.58 | 0.06 | -1.11 | 0.13 |
| | BSW05-05 | 21.0 | 9.03 | 192 | 489 | 0.84 | 6.0 | 16.7 | 35.7 | 0.014 | 608.3 | 0.291 | -0.41 | 0.07 | -0.79 | 0.14 |
| | BSW05-06 | 33.9 | 9.01 | 172 | 494 | 0.31 | 10.4 | 16.7 | 37.7 | 0.007 | 620.1 | 0.263 | -0.47 | 0.07 | -0.89 | 0.14 |
| | BSW05-07 | 52.9 | 9.08 | 151 | 502 | 0.172 | 9.9 | 17.1 | 40.6 | 0.004 | 628.9 | 0.254 | -0.64 | 0.21 ^a | -1.26 | 0.41 ^a |
| | Quenched | | | | 482 | < LOD | 3.97 | 16.1 | 44.5 | < LOD | 622.0 | 4.00 | | | | |

770 Detection limits (LOD) in mmol/kg were approximately: Mg: 0.026; Si: 0.018; Fe (BSW04 and BSW05): 0.0001; Fe (BSW06 and BSW07): 0.02

771 ^a These uncertainties include the extrapolation of ⁴⁸Ca interference effects

772

Table 4: (continued)

| Experiment | Sample | Duration / days | pH | Fluid mass / g | Concentration / mmol/kg | | | | | | | | $\delta^{25/24}\text{Mg} / \text{‰}$ | | $\delta^{26/24}\text{Mg} / \text{‰}$ | |
|---------------------------------------|----------|--------------------|------|-------------------|-------------------------|--------|------|------|------|-------|-------|--------------------|--------------------------------------|-------|--------------------------------------|-------|
| | | | | | Na | Mg | Si | K | Ca | Fe | Cl | SO_4^{2-} | Value | \pm | Value | \pm |
| BSW06 290 °C basaltic glass | BSW06-01 | 0.8 | 8.36 | 220 | 524 | 6.9 | 23.7 | 12.0 | 28.6 | < LOD | 636.5 | 0.181 | -0.588 | 0.063 | -1.069 | 0.066 |
| | BSW06-02 | 3.0 | 9.20 | 200 | 541 | 0.078 | 19.7 | 12.3 | 42.4 | < LOD | 643.5 | 0.124 | | | | |
| | BSW06-03 | 7.9 | 9.40 | 180 | 545 | 0.0154 | 13.5 | 12.6 | 45.4 | < LOD | 654.6 | 0.120 | | | | |
| | BSW06-04 | 16.0 | 9.41 | 160 | 550 | 0.0080 | 15.7 | 13.5 | 46.3 | < LOD | 667.1 | 0.123 | | | | |
| | BSW06-05 | 33.8 | 9.50 | 141 | 561 | 0.0062 | 13.9 | 14.2 | 44.9 | < LOD | 689.6 | 0.122 | | | | |
| | BSW06-06 | 54.9 | 9.56 | 122 | 582 | 0.0105 | 12.4 | 18.9 | 62.4 | < LOD | 736.3 | 0.141 | | | | |
| | BSW06-07 | 92.0 | 9.50 | 104 | 608 | 0.0200 | 10.6 | 23.9 | 78.8 | < LOD | 806.6 | 0.132 | | | | |
| BSW07 290 °C crystalline basalt | BSW07-01 | 0.9 | 4.93 | 219 | 512 | 30.6 | 25.8 | 14.3 | 2.25 | 4.7 | 631.3 | 3.951 | -0.558 | 0.062 | -1.066 | 0.070 |
| | BSW07-02 | 3.8 | 8.40 | 201 | 516 | 5.0 | 9.8 | 15.5 | 29.9 | 0.50 | 648.0 | 0.175 | -0.531 | 0.061 | -1.011 | 0.066 |
| | BSW07-03 | 8.7 | 8.92 | 183 | 515 | 0.55 | 14.6 | 15.6 | 38.0 | 0.044 | 656.7 | 0.132 | -0.83 | 0.15 | -1.63 | 0.29 |
| | BSW07-04 | 16.9 | 9.01 | 165 | 511 | 0.41 | 15.6 | 15.8 | 39.3 | 0.033 | 660.2 | 0.124 | -0.87 | 0.14 | -1.71 | 0.26 |
| | BSW07-05 | 34.6 | 9.03 | 148 | 528 | 0.29 | 16.6 | 16.4 | 41.7 | 0.032 | 678.0 | 0.062 | -0.888 | 0.063 | -1.746 | 0.077 |
| | BSW07-06 | 55.7 | 9.13 | 128 | 543 | 0.201 | 16.3 | 17.0 | 43.8 | < LOD | 700.5 | 0.057 | | | | |
| | BSW07-07 | 92.8 | 9.22 | 110 | 589 | 0.127 | 14.8 | 18.4 | 48.6 | < LOD | 754.2 | 0.113 | | | | |

774 **Table 5:** Proportions (wt.%) of phases identified by quantitative XRD measurements in the
 775 basaltic glass and crystalline basalt used as reactants in the experiments, as well as in the
 776 solids recovered from the reactors after the experiments were terminated. The last row shows
 777 the total octahedral Fe contents of the smectite, estimated using the position of the d_{060}
 778 reflection and the relationship found by Baldermann et al. (2014).

| | Basaltic glass | BSW04 | BSW06 | Crystalline basalt | BSW05 | BSW07 |
|---|-------------------|-------|-------|-----------------------|-------|-------|
| Amorphous | 95 | 24 | 15 | - | - | - |
| Quartz | 2 | < 1 | < 1 | < 1 | < 1 | < 1 |
| Olivine | 3 | < 1 | 2 | 9 | < 1 | < 1 |
| Anhydrite | - | < 1 | 1 | - | 4 | 2 |
| Zeolite | - | 8 | 5 | - | - | - |
| Plagioclase | - | - | 13 | 43 | 53 | 42 |
| Pyroxene | - | - | - | 47 | 25 | 23 |
| Chlorite-smectite | - | - | 8 | - | - | - |
| Fe-rich saponite | - | 66 | 55 | - | 18 | 33 |
| $^{VI}\text{Fe}_{\text{tot}} / \text{a.p.f.u.}$ | | 0.71 | 0.98 | | 0.46 | 0.67 |

779 Figures

780 **Fig. 1:** Schematic design of Ti-autoclaves used for the experiments in this study. The Ti-
 781 autoclaves were rocked to ensure mixing of the solids with the seawater. The cooling
 782 apparatus attached to the valve allowed fluid samples to be taken during the experimental run.

783 **Fig. 2:** Aqueous concentrations of Ca, Mg, SO_4^{2-} as well as $\delta^{26/24}\text{Mg}$ and pH of seawater
 784 reacting with basaltic glass and crystalline basalt at temperatures of 250 °C (left side) and
 785 290 °C (right side). The errors bars show the 95 % confidence intervals, which are smaller
 786 than the symbol size where no error bars are shown.

787 **Fig. 3:** Scanning electron microscopy images of (a) the basaltic glass used as starting material
 788 and (b)-(d) solids recovered from the experiment reacting basaltic glass with seawater at
 789 250 °C, showing a layer of smectite clay minerals covering the surface of the altered basalt as
 790 well as minor precipitated anhydrite grains. Images of the crystalline basalt are shown in Voigt
 791 et al. (2018b).

792 **Fig. 4:** PXRD patterns of starting materials and reacted solids from experiments with basaltic
 793 glass (a) and crystalline basalt (b). Note the presence of amorphous phases in all samples with
 794 basaltic glass. The hkl -reflections correspond mainly to ferrous saponite. Zincite (20 wt.%;
 795 bars) was used as an internal standard. Fe-sap = ferrous saponite; Chl-Smc = chlorite-
 796 smectite; Zeo = analcime/heulandite; Pl = plagioclase \pm albite; Anh = anhydrite; Qz = quartz;
 797 Ol = olivine; Aug = augite.

799 **Fig. 5:** Estimated mass of Mg released from basalt dissolution and precipitated into alteration
 800 minerals, as calculated by mass balance (a,b, see text for details), (c,d) modelled aqueous
 801 $\delta^{26/24}\text{Mg}$ during the experiments reacting basalt with seawater (dashed curves), (e,f) measured
 802 Mg concentrations in the liquid and (g,h) relative abundance (mol%) of the Mg^{2+} and MgSO_4
 803 species in the fluid samples as calculated with PHREEQC. The errors bars and shaded areas
 804 show the 95 % confidence intervals, which are smaller than the symbol size where no error
 805 bars are shown.

806 **Fig. 6:** Plot of the difference between the Mg isotopic composition of the reacting seawater
807 (SW) and its initial composition, $(\Delta^{26/24}\text{Mg})_{\text{Reacted-SW-SW}}$, blue curve, and between the
808 accumulated clays and the initial SW, $(\Delta^{26/24}\text{Mg})_{\text{Clays-SW}}$, orange curve, during irreversible
809 isotopic fractionation during clays precipitation as function of reaction progress,
810 $f = m_{\text{P}}/m_{\text{R},0}$. Both curves are plotted for $\varepsilon = 0.35$ ‰, the mean (weighed by the inverse of
811 their variance) of our experimental best fit values. The latter value, scaled by the fraction of
812 Mg in the product, f , is shown as well by the green curve in (b) to qualitatively show the effect
813 of Mg isotope fractionation in such a system on the marine budget.).

814 **Supplementary Figures**

815 **Supplementary Fig. 1:** Plot of $\delta^{26/24}\text{Mg}$ vs. $\delta^{25/24}\text{Mg}$ for two of the analysed samples where
816 Ca was not completely removed during the first two purifications before analysis (yellow
817 symbols). The yellow line shows the modelled isobaric Ca interference correction, bringing
818 the compositions to the mass dependent fractionation line (blue line, red symbols). An
819 additional purification of these samples (green symbols) brought the measured compositions
820 closer to the mass dependent fractionation line, consistent with Ca interferences.

821 **Supplementary Fig. 2:** Aqueous concentrations of Na, Cl, Si, and Fe of seawater reacting with
822 basaltic glass and crystalline basalt at temperatures of 250 °C (left side) and 290 °C (right
823 side). The errors bars show the 95 % confidence intervals, which are smaller than the symbol
824 size where no error bars are shown.

825 **Supplementary Fig. 3:** XRD patterns of the clay mineral fraction ($< 2 \mu\text{m}$) of BSW05 and
826 BSW06 obtained under air-dried conditions (black curve), after EG-solvation (blue curve) and
827 heating to 550 °C (red curve). The grey curve shows the best-fit with the Sybilla software.

828 **Supplementary Fig. 4:** Plot of the modelled molar ratio of $(\text{Si}+\text{Al})/(\text{Mg}+\text{Fe})$ taken up into
829 secondary minerals during the experiments at the time of sampling. The horizontal black line
830 shows the theoretical ratio for saponite of $4/3 \approx 1.33$.