Solubility of the hydrated Mg-carbonates nesquehonite and dypingite from 5 to 35°C:

Implications for CO₂ storage and the relative stability of Mg-carbonates

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1 **Abstract**

2   Hydrated Mg-carbonate minerals form during the weathering of ultramafic rocks, and

3 can be used to sequester atmospheric CO_2 to help combat greenhouse gas-fueled climate

4 change. Optimization of engineered CO_2 sequestration and prediction of the composition and

5 stability of Mg-carbonate phase assemblages in natural and engineered ultramafic

6 environments requires knowledge of the solubility of hydrated Mg-carbonate phases, and the

7 transformation pathways between these metastable phases. In this study, we evaluate the

8 solubility of nesquehonite [$MgCO_3 \cdot 3H_2O$] and dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot (5 \text{ or } 8)H_2O$] and

9 the transformation from nesquehonite to dypingite between 5°C and 35°C, using constant-

10 temperature, batch-reactor experimentals.. The logarithm of the solubility product of

11 nesquehonite was determined to be: -5.03±0.13, -5.27±0.15, and -5.34±0.04 at 5°C, 25°C,

12 and 35°C, respectively. The logarithm of the solubility product of dypingite, never reported

13 before, was determined to be: -34.95±0.58 and -36.04±0.31 at 25°C and 35°C, respectively,

14 with eight waters of hydration. The transformation from nesquehonite to dypingite was

15 temperature-dependent, and was complete within 57 days at 25°C, and 20 days at 35°C, but

16 did not occur during experiments of 59 days at 5°C. This phase transformation appeared to

17 occur via a dissolution-reprecipitation mechanism; external nesquehonite crystal morphology

18 was partially maintained during the phase transformation at 25°C, but was eradicated at 35°C.

19 Together, our results facilitate the improved evaluation of Mg-carbonate mineral precipitation

20 during natural and engineered ultramafic mineral weathering systems that sequester CO_2, and

21 for the first time allow assessment of the saturation state of dypingite in aqueous solutions.

22

23 **Keywords:** Mg-carbonates; CO_2 sequestration; mineral solubility; ultramafic mineral

24 weathering; mineral phase transformation; dissolution-reprecipitation; dypingite;

25 nesquehonite

1. Introduction

The largest proportion of carbon on Earth's crust is bound in carbonate minerals, where it is stable over millennia (Sundquist, 1993; Lackner, 2003). The engineered storage of anthropogenic CO_2 in carbonate minerals is therefore sought to offset greenhouse gas emissions and mitigate climate change (Lackner et al., 1995; Kelemen and Matter, 2008; Oelkers and Cole, 2008; Power et al., 2013a, b; Matter et al., 2016). Carbonate mineral formation during the weathering of silicates and hydroxides is a naturally occurring process, known as carbon mineralization; this process can be enhanced artificially to sequester CO_2. Several engineered carbon mineralization approaches have been studied at the laboratory and/or pilot-scale, including injection of CO_2 into subsurface basaltic or ultramafic rock (Kelemen and Matter, 2008; Power et al., 2013a, b; Gislason and Oelkers, 2014; Matter et al., 2016), passive or accelerated carbonation of ultramafic mine waste rock and tailings (Wilson et al., 2006, 2009, 2011, 2014; Power et al., 2010, 2014a; Pronost et al., 2011, 2012; Bea et al., 2012; Beinlich and Austrheim, 2012; Harrison et al., 2013a, b, 2015, 2016; Oskierski et al., 2013; Assima et al., 2012, 2014a, b, c; McCutcheon et al., 2015, 2017; Gras et al., 2017), and accelerated mineralization in high pressure/high temperature *ex situ* reactors (Lackner et al., 1995; Gerdemann et al., 2007). Enhanced weathering is a related approach that aims primarily to sequester CO_2 in dissolved form, but can also induce carbonate precipitation. It entails spreading fine-grained mafic or ultramafic rock in natural weathering environments to artificially enhance natural weathering (Schuiling and Boer, 2010; Renforth, 2012; Hartmann et al., 2013; Montserrat et al., 2017; Rigopoulos et al., 2018). Estimation of the CO_2 storage security of these approaches requires knowledge of the stability, solubility, and formation pathways of the carbonate mineral products that store the CO_2. The relative stability and solubility of several Mg-carbonates has been investigated (Langmuir, 1965; Canterford et al.,

51   1984; Königsberger et al., 1999; Zhang et al., 2006; Hopkinson et al., 2008, 2012; Hänchen

52   et al., 2008; Xiong and Lord, 2008; Bénézeth et al., 2011; 2018; Xiong, 2011; Ballirano et al.,

53   2013; Berninger et al., 2014; Kristova et al., 2014; Gautier et al., 2014). In general, the

54   stability of Mg-carbonates increases from more to less hydrated phases, in the order:

55   lansfordite < nesquehonite < dypingite < hydromagnesite < magnesite (Langmuir, 1965;

56   Canterford et al., 1984). Due to the strong hydration of aqueous Mg, the formation of

57   anhydrous magnesite [$MgCO_3$], is kinetically inhibited at low temperatures, and is rarely

58   observed to form on laboratory timescales at temperature less than 60°C (Hänchen et al.,

59   2008; Saldi et al., 2009, 2012; Power et al., 2017). For example, Gautier et al. (2014)

60   demonstrate a 2.5-fold greater growth rate constant for hydromagnesite

61   [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] compared to magnesite at 90°C. Thus, ultramafic weathering at the

62   Earth's near-surface is dominated by hydrated Mg-carbonate formation (Shirokova et al.,

63   2013; Power et al., 2014b; Lin et al., 2017), and engineered CO_2 sequestration efforts at near-

64   Earth's surface temperatures will also tend to form hydrated Mg-carbonates. However,

65   observed mineral assemblages in the field and in laboratory experiments reveal that multiple

66   hydrated magnesium carbonate phases often co-exist, with the more-hydrated phases

67   frequently acting as transient precursors to the more stable, less-hydrated phases (Davies and

68   Bubela, 1973; Hopkinson et al., 2008, 2012; Wilson et al., 2009; Ballirano et al., 2013; Power

69   et al., 2014b; Harrison et al., 2015, 2016). The multitude of potential metastable hydrated

70   phases complicates prediction of Mg-carbonate formation and thus the stability of the CO_2-

71   storing phase (Königsberger et al., 1999; Hopkinson et al., 2008, 2012; Hänchen et al., 2008;

72   Montes-Hernandez et al., 2012; Kristova et al., 2014). To reduce some of the ambiguity in

73   the prediction of Mg-carbonate mineral formation under various conditions, in this study we

74   determine the solubility of nesquehonite [$MgCO_3 \cdot 3H_2O$] and dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot (5$

75   or)$8H_2O$], two commonly observed products of carbon mineralization in ultramafic materials

4

76   (Wilson et al., 2006, 2009, 2011, 2014; Boschi et al., 2009; Zhao et al., 2010; Pronost et al.,

77   2011; Schaef et al., 2011; Bea et al., 2012; Loring et al., 2012; Montes-Hernandez et al., 2012;

78   Assima et al., 2012, 2014c; Hövelmann et al., 2012; Felmy et al., 2012; Beinlich and

79   Austrheim, 2012; Schaef et al., 2013; Harrison et al., 2013a, 2015, 2016, 2017; Power et al.,

80   2013a, b, c, 2014b; Kristova et al., 2014; McCutcheon et al., 2016; Chaka et al., 2016; Garcia

81   del Real et al., 2016; Highfield et al., 2016; Gras et al., 2017; McCutcheon et al., 2017), and

82   the transformation process that converts nesquehonite to dypingite. Both nesquehonite and

83   dypingite are readily formed during reaction of Mg-rich minerals with CO_2 at ambient

84   temperatures, with nesquehonite tending to form at greater than atmospheric pCO_2 or

85   evaporative conditions (Königsberger et al., 1999; Power et al., 2007; Xiong and Lord, 2008;

86   Zhao et al., 2010; Schaef et al., 2011; Harrison et al., 2013a), and dypingite favored under

87   atmospheric pCO_2 (~400 ppm) and microbially-mediated conditions (Power et al., 2007;

88   Wilson et al., 2010; Mavromatis et al., 2012; Shirokova et al., 2013; Harrison et al., 2013a;

89   McCutcheon et al., 2016). In addition to their natural occurrence and use for CO_2 storage,

90   hydrated Mg-carbonates have prompted interest due to their potential formation in engineered

91    $Mg(OH)_2$/MgO barriers for nuclear waste storage (Xiong and Lord, 2008; Xiong, 2011), and

92   the precipitation of nesquehonite from $MgCl_2$ brines has been investigated as a way to exploit

93   Mg resources from salt lakes (Dong et al., 2008; Wang et al., 2008; Cheng et al., 2009;

94   Cheng and Li, 2009), and as a precursor for high purity MgO production (Cheng et al., 2009;

95   Wang and Li, 2012). This broad interest in nesquehonite has inspired a number of studies

96   regarding its thermal stability (Lanas and Alvarez, 2004; Hales et al., 2008; Vágvölgyi et al.,

97   2008; Ballirano et al., 2010; Jauffret et al., 2015; Morgan et al., 2015), nucleation kinetics

98   (Cheng and Li, 2010; Zhao et al., 2013), its tendency for solid-solution with transition metals

99   (Hamilton et al., 2016), and the impacts of temperature, saturation state, and fluid

100   composition on nucleation and crystal morphology and size (Zhang et al., 2006; Wang et al.,

101 2008; Cheng et al., 2009; Ding et al., 2016). Robie and Hemingway (1972; 1973) determined

102 its standard heat capacity, standard entropy, and standard enthalpy of formation. Although

103 several solubility studies of nesquehonite have been conducted both experimentally and

104 theoretically, they report differing results, or in some cases do not report a solubility product,

105 instead reporting total aqueous Mg or C concentrations (*c.f.*, Kline, 1929; Kazakov et al.,

106 1959; Hostetler, 1964; Langmuir, 1965; Königsberger et al., 1999; Dong et al., 2008, 2009;

107 Wang and Li, 2012). On the other hand, dypingite solubility remains undetermined, despite

108 its common occurrence in natural and engineered ultramafic weathering environments

109 (Power et al., 2013a and references therein). Dypingite can be a precursor for the formation

110 of hydromagnesite (Davies and Bubela, 1973; Hopkinson et al., 2008, 2012; Sutradhar et al.,

111 2011), a mineral that securely stores CO_2 over tens of thousands of years at Earth's surface

112 conditions (e.g., Power et al., 2009; 2014). The process by which the metastable hydrous Mg-

113 carbonates transform from less to more stable phases is also an important control on the

114 isotopic signature of the carbonate minerals, which can be used to trace CO_2 cycling and

115 sequestration processes (Power et al., 2007, 2014b; Wilson et al., 2009, 2010, 2011, 2014;

116 Beinlich and Austrheim, 2012; Shirokova et al., 2013; Harrison et al., 2013a, 2016; Oskierski

117 et al., 2013; Mervine et al., 2014; Falk et al., 2016; Oskierski et al., 2016; Gras et al., 2017).

118 Similarly, the mobility of toxic metals that can be incorporated in nesquehonite (Hamilton et

119 al., 2016) will be controlled in part by the efficiency and mechanism of Mg-carbonate phase

120 transformations.

121   The goals of the present study were to 1) determine the solubility of nesquehonite and

122 dypingite at conditions relevant to natural and engineered CO_2-driven weathering, and 2)

123 assess the nesquehonite-dypingite transformation pathway and the implications for CO_2

124 storage.

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126

2. Methods

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2.1. Nesquehonite and dypingite synthesis

Nesquehonite was synthesized according to a modified method of Robie and

Hemingway (1972), whereby 200 mL of an aqueous 1.8 M K_2CO_3 solution (reagent grade

K_2CO_3) was slowly added to a 1000 mL glass beaker containing 200 mL of 1.8 M aqueous

$MgCl_2$ (NormaPur $MgCl_2 \cdot 6H_2O$). The beaker was then covered with a watch glass to permit

some exchange with laboratory air but limit evaporation and dust inputs. A white gel-like

precipitate was formed immediately upon mixing of the two solutions. This precipitate was

allowed to age in the solution for five days at ambient temperature (~22°C) after which the

slurry was vacuum-filtered and rinsed multiple times with distilled, de-ionized water. The

precipitate was then dried at ambient temperature for ~3 days. Once dry, the precipitate was

gently disaggregated using an agate mortar and pestle, and stored in a desiccator prior to

analysis and use in experiments. The nesquehonite was made in two separate batches due to

the large quantity required, and each was used in separate experimental runs; a short-term

experiment (nesquehonite batch 1), and a long-term experiment (nesquehonite batch 2). The

long-term experiment was conducted subsequent to the short-term experiment to capture the

complete conversion of nesquehonite to dypingite. Dypingite was synthesized via

transformation of the synthetic nesquehonite within the experiments. The experimental

conditions are described in more detail in Section 2.2.

The synthetic nesquehonite was characterized using X-ray diffraction (XRD) and

Fourier transform infrared spectroscopy (FTIR), which confirmed the presence of only

nesquehonite in the initial solids used in the experiments (Figures 1 and 2). The empirical

formula of nesquehonite has been debated, and is sometimes reported as

151      $[Mg(OH)(HCO_3) \cdot 2H_2O]$ (Frost and Palmer, 2011). However, the FTIR spectra were more

152   consistent with the formula $[MgCO_3 \cdot 3H_2O]$, as the bicarbonate-derived band at 985 cm^{-1}

153   (Zhang et al., 2006) was not present (Figure 1). Scanning electron microscopy (SEM) images

154   (Figure 3) revealed a needle-like morphology typical of nesquehonite (*c.f.*, Power et al., 2009;

155   Zhao et al., 2010; Schaef et al., 2011; Harrison et al., 2013a, 2017). Neither XRD nor FTIR

156   data revealed significant differences between the two batches of synthetic nesquehonite

157   (Figures 1 and 2), though SEM revealed a slightly higher proportion of fine particles in the

158   second synthesized batch, which was used for the longer-term experiments.

159

160   *2.2. Experimental methods*

161   Experiments to determine the solubility product of nesquehonite were conducted at

162   constant temperatures of 5°C, 25°C, and 35°C. A single experiment was conducted at 5°C,

163   whereas duplicate experiments were conducted at 25°C and 35°C. The duplicate experiments

164   ran subsequently to the originals, and for a longer duration, to ensure the complete

165   conversion of nesquehonite to dypingite. Each experiment consisted of a suite of nine to

166   eleven sealed, closed system reactors. The starting aqueous solution and solid were first

167   added to the individual reactors (Nalgene bottles) in identical amounts. Each bottle contained

168   0.06 g of nesquehonite and ~73.4 g of an aqueous solution containing 0.10 M NaCl and 0.06

169   M NaHCO$_3$. At various selected times, an individual reactor was sampled in its entirety

170   (liquid and solid). This approach was taken to ensure the solid and its contemporaneous fluid

171   were collected, and to avoid generation of headspace due to sampling, as would occur by

172   sampling fluids from a single reactor. The individual reactors were filled with minimal

173   headspace to inhibit loss of $CO_{2(g)}$ from solution. To avoid precipitation due to temperature

174   changes, the experimental solutions were prepared by first heating or cooling distilled, de-

175   ionized water (18.2 MΩ cm^{-1}) to the desired experimental temperature, followed by the

176   addition of reagent-grade NaCl and $NaHCO_3$ to reach the desired concentration. This aqueous

177   solution was then poured into the individual reactors, which already contained nesquehonite,

178   and the reactors were rapidly sealed, weighed, and placed at the experimental temperature.

179   Experiments conducted at 5°C were placed on an orbital shaker in a thermostatic refrigerator,

180   whereas experiments conducted at 25°C and 35°C were conducted in shaking water baths at

181   constant temperature.

182   Individual reactors were sampled one at the time to track the chemical composition of

183   the reactive aqueous solution, as well as changes in the mineral composition of the solids.

184   Upon sampling, reactors were weighed to assess evaporative losses and the solution

185   temperature was measured using a thermometer. The solution was then removed via a syringe

186   and needle, and filtered with a 0.22 µm polyethersulfone (PES) syringe filter. Two aliquots

187   were immediately acidified to 2% HNO_3 for subsequent analysis of Mg concentrations, and a

188   single aliquot was used for immediate pH measurements, and later alkalinity measurements.

189   Fluid pH was measured using a Metrohm 913 pH-meter and a Metrohm combined electrode

190   (6.0234.1000) that was calibrated using NIST traceable $pH_{25°C}$ 4.01, 7.00, and 9.18 buffer

191   solutions at each experimental temperature, with an uncertainty of approximately ±0.03 pH

192   units. Dissolved inorganic carbon concentration was calculated using PHREEQC V3

193   (Parkhurst and Appelo, 2013) and a modified LLNL database, based on the measured fluid

194   compositions. Geochemical modeling methods are discussed in further detail in Section 2.4.

195   The solids were separated from any remaining solution via vacuum filtration, and

196   were rinsed with distilled, de-ionized water to prevent NaCl precipitation. They were then

197   dried at room temperature for ~48 h and stored in a desiccator prior to analysis. Note that

198   hydrated Mg-carbonate minerals must be stored under dry conditions to prevent their

199   transformation in humid air (Davies and Bubela, 1973; Power et al., 2016), therefore care

200   was taken to minimize exposure to laboratory air at all times.

201   Dypingite was formed *in situ* within the reactors at 25°C and 35°C, with longer-term

202   experiments designed to allow the complete transformation from nesquehonite to dypingite

203   and to capture a period of stable solution chemistry representative of equilibrium between the

204   dypingite and the reactive aqueous solution. The phase transformation was tracked via

205   changes in aqueous solution composition and mineralogical data collected using XRD

206   complemented with FTIR for some samples.

207

208   *2.3. Analytical techniques*

209   The alkalinity of all fluid samples was determined by HCl titration using an

210   automated Schott Titroline Alpha Plus titrator. Long term reproducibility, determined from

211   repeated analysis of a standard, was better than $\pm0.36 \times 10^{-2}$ mol/L (3σ), and the detection

212   limit was 5×10^{-5} mol/L. Dissolved inorganic carbon (DIC) concentrations were calculated

213   using the measured fluid composition and PHREEQC V3 (Parkhurst and Appelo, 2013) with

214   a modified LLNL database, as described in further detail in Section 2.4. The uncertainty

215   introduced via the calculation of DIC is unknown; a minimum uncertainty equal to that of the

216   alkalinity measurement is assumed ($\pm0.36 \times 10^{-2}$ mol/L). Aqueous Mg concentrations were

217   measured by atomic absorption spectroscopy (AAS) using a Perkin Elmer AAnalyst 400.

218   Samples and standards were matrix-matched in 0.01 mol/L HNO_3. All samples were

219   measured in triplicate and reported concentrations represent averages of these measurements,

220   the standard deviation (3σ) is smaller than the symbols employed in figures, unless otherwise

221   shown. Reproducibility was better than 2%, and the quantification and detection limits were

222   2.3×10^{-3} ppm and 7.0×10^{-4} ppm, respectively. Quantification and detection limits were

223   defined as 10σ and 3σ over background variation.

224   The mineralogical compositions of the solids were determined using powder XRD

225   with a Bruker D2 Phaser with Cu radiation. The scan speed was 0.5 s/step, and a step size of

226 0.02°/step was used. To complement the XRD data, FTIR analysis was conducted on select

227 samples using a ThermoScientific Nicolet iN 10 MX infrared imaging microscope.

228 Morphological characteristics were examined via scanning electron microscopy using a

229 JEOL JSM 6360LV or a JEOL JSM 6480LV.

230

231 *2.4. Geochemical modeling*

232   The standard state adopted in this study is that of unit activity at any temperature and

233 pressure for pure minerals. The standard state for aqueous species at any temperature and

234 pressure is unit activity of a hypothetical 1 molal solution referenced to infinite dilution.

235 Aqueous speciation and mineral saturation states were calculated using PHREEQC V3

236 (Parkhurst and Appelo, 2013) and its LLNL database, which was modified to include the

237 carbonic acid dissociation constants of Patterson et al. (1982; 1984), the Mg^{2+} hydrolysis

238 constant from Palmer and Wesolowski (1997), the formation constants of $MgHCO_3^+$ and

239 $MgCO_3°$ ion pairsfrom Stefansson et al. (2014), the magnesite solubility product from

240 Bénézeth et al. (2011), the hydromagnesite solubility product from Gautier et al. (2014), and

241 the brucite solubility product from Brown et al. (1996). Activity coefficients are calculated

242 using the b-dot model (Helgeson, 1969).

243

244 **3. Results**

245 *3.1 Phase transformations*

246 *3.1.1 Phase transformation at 25°C*

247   The measured Mg concentration, pH, alkalinity, mineralogical composition, the

248 calculated DIC concentration, and determined aqueous Mg^{2+}, CO_3^{2-}, and H_2O activities with

249 time in all experiments are listed in Table 1. At 5°C, nesquehonite did not transform into a

250 different phase throughout the 1420 h (59 d) experiment as confirmed by XRD (Electronic

251   Supplement (ES) -Figure 1). Similarly, SEM micrographs revealed that the solid phase

252   maintained the needle-like nesquehonite morphology throughout the experiment (Figure 3).

253   At 25°C, minor dypingite was first detected with XRD at 359 h in the long-term

254   experiment, and dypingite formed between 367 h and 1086 h during the short-term

255   experiment (ES-Figures 2 and 3). Trace dypingite was also detected in the 22 h sample in the

256   long-term 25°C experiment, however, the lack of change in solution composition at this time,

257   its non-existence in the solids collected from the subsequent sample, and the lack of

258   dypingite over this timeframe in the short-term 25°C experiment suggest that its presence in

259   the 22 h sample from the long-term experiment is an artifact of improper sample storage, not

260   dypingite formation in the experiment. The sample collected at 359 h in the long-term

261   experiment exhibits particles with needle-like external morphology, similar to the initial

262   nesquehonite, but with rounded edges, and a flakey, porous surface (Figure 3c). This flakey

263   morphology is typical of dypingite (e.g., Canterford et al., 1984; Power et al., 2007;

264   Mavromatis et al., 2012), and suggests the precipitation of dypingite is closely coupled to the

265   dissolution of nesquehonite at the mineral-fluid interface, as has been observed for several

266   mineral replacement reactions (e.g., Ruiz-Agudo et al., 2012 and references therein). Within

267   1367 h, nesquehonite was completely replaced by dypingite, and no other phase was

268   observed for the remainder of the 2043 h (85 d) long-term experiment (ES-Figure 3).

269   Dypingite is normally reported in the literature to have the chemical formula

270    $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O]$, but has also been reported to have the formula

271    $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$, and more rarely $[Mg_5(CO_3)_4(OH)_2 \cdot 6H_2O]$ (Raade, 1970;

272   Canterford et al., 1984; Xiong and Lord, 2008; Hopkinson et al., 2012; Kristova et al., 2014).

273   The XRD pattern of the dypingite in our experiments was consistent with

274    $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ (International center for diffraction data, pattern PDF-00-029-

275   0857; ES-Figures 3-5), which differs from that of $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O]$ (International

276   center for diffraction data, pattern PDF-00-023-1218), by the presence of a low angle peak at

277   2.659° 2θ (d = 33.200). Other than this peak, the similarity of the XRD patterns for dypingite

278   with 5 or 8 hydration waters means the presence of $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O]$ in addition to

279    $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ cannot be excluded.

280   An additional phase was observed in the long-term experiment from 599 h until the

281   end of the experiment; this additional phase is characterized by two small, low-angle peaks

282   (labeled "d-1" in ES-Figure 3). Dypingite-like phases with varying degrees of hydration and

283   similar structures, which exhibit low-angle XRD peaks, have been observed in several studies

284   (Davies and Bubela, 1973; Hopkinson et al., 2008; Hopkinson et al., 2012; Ballirano et al.,

285   2013; Kristova et al., 2014). For example, during the degassing of a Mg-CO_3 solution at 58°C,

286   Hopkinson et al. (2012) observed what they referred to as several "dypingite-type" phases

287   with similar crystal structures but different cell volumes and varying numbers of waters of

288   hydration, including $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$. Additional peaks not reported in the

289   established dypingite XRD patterns were also observed at ~3.5° and ~6° by Ballirano et al.

290   (2013) during the phase transformation of nesquehonite at room temperature. These low

291   angle peaks and their inconsistent appearance are attributed to the large and varied cell-

292   volume of dypingite-like phases, different stacking-sequences of the layers of MgO_6 and

293   carbonate groups, or different water contents (Ballirano et al., 2013). As such, the low angle

294   peaks observed from 599 h until the end of the experiment, are attributed to an additional

295   dypingite-like phase, potentially differing in cell volume and/or number of hydration waters.

296   To further evaluate the dypingite-like phase documented at 25°C, the FTIR spectrum of a

297   sample containing this phase (25°C, 1607 h) was compared to the FTIR spectrum of a sample

298   from the long-term 35°C experiment, which contained only XRD-identifiable dypingite

299   (35°C, 560 h). The FTIR spectra are close to identical (Figure 1), consistent with the

300   interpretation that the unnamed phase documented in the 25°C experiments is likely another

301   dypingite-like phase.

302   Changes in fluid composition were coincident with the phase transformation

303   documented with XRD. During the phase transformation, pH decreased from ~9.2 to ~8.8

304   between 120 h and 599 h before stabilizing at ~8.8 for the remainder of the experiment

305   (Figures 4a and 4d). This suggests that the phase transformation consumes protons despite

306   forming a hydroxyl-bearing phase. The Mg concentration exhibited a minor decrease during

307   the phase transformation (Figures 4b and 4e), whereas the DIC exhibited a slight increase

308   (Figures 4c and 4f). After 599 h, DIC and Mg concentration again remained stable for the

309   remainder of the experiment (Figures 4b and 4c).

310

311   *3.1.2. Phase transformation at 35°C*

312   At 35°C, the transformation from nesquehonite to dypingite was more rapid than at

313   25°C. Dypingite was first detected at trace levels by XRD in the 75 h sample from the short-

314   term experiment (ES-Figure 4), and in the 123 h sample from the long-term experiment (ES-

315   Figure 5). Similar to the 25°C experiment, the dypingite XRD pattern was consistent with

316   that of $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ (International center for diffraction data, pattern PDF-00-

317   029-0857; ES-Figures 4 and 5). The additional dypingite-like phase observed at 25°C was not

318   evident in the 35°C experiments, however, a different unidentified phase was recorded in the

319   sample at 718 h in the long-term experiment (identified as "unknown" in ES-Figure 5),

320   evidenced by additional peaks at ~27° and ~33° and the disappearance of the ~11° peak. It is

321   not clear whether this was an additional phase, or representative of a change in the dypingite

322   structure. This phase was not present before or after 718 h, nor was it traced in the short-term

323   experiment. It may be an artifact of imperfect sample storage, rather than reflecting an *in situ*

324   mineralogical change in the reactors. However, if it was the case, that would affect solubility

325   calculations. In doubt, this sample was not included in calculation of the solubility product.

326   Nesquehonite was no longer present within 482 h at 35°C (ES-Figure 5), compared to 1367 h

327   for complete conversion of nesquehonite at 25°C.

328   SEM images revealed a different evolution of crystal morphology between the 25°C

329   and 35°C experiments; unlike at 25°C, the external crystal morphology of nesquehonite was

330   not maintained. Rather, over a similar time-frame, the needle-like morphology was replaced

331   by flakey aggregates with typical dypingite morphology (Figure 3d) (*e.g.*, Canterford et al.,

332   1984; Power et al., 2007; Mavromatis et al., 2012). This difference in morphological

333   evolution may be a consequence of the different reaction rates. In both cases, the morphology

334   change suggests the mineral phase transformation occurs via dissolution-reprecipitation.

335   However, the slower rate of nesquehonite dissolution at 25°C coupled to the rapid re-

336   precipitation as dypingite could result in the observed pseudo-morphic replacement at this

337   temperature. Conversely, a relatively high nesquehonite dissolution rate compared to

338   dypingite precipitation rate at 35°C, would allow a spatial and thus morphological separation

339   of the two phases.

340   Similar to the fluid composition change observed during the phase transformation at

341   25°C, the pH, Mg concentration, and DIC concentration evolved during the nesquehonite-

342   dypingite transformation at 35°C (Figure 4). A decrease in pH from ~9.15 to ~8.66 occurred

343   between ~74 h and 482 h (Figures 4a and 4d), while a slight decline in Mg concentration was

344   observed after 310 h (Figures 4b and 4e). The decline in Mg concentration occurred when the

345   solids became dominated by dypingite, rather than by nesquehonite (Table 1). A slight

346   decrease in Mg concentration continued for the remainder of the 35°C experiment, suggesting

347   either a slow approach to dypingite equilibrium, or perhaps the beginning of a transformation

348   to a less hydrated Mg-carbonate, though no further mineralogical changes were detected with

349   XRD or FTIR. A minor increase in DIC concentration was observed after 75 h (Figures 4c

350 and 4f), but DIC was again constant from ~243 h to the end of the short- and long-term

351 experiments. The short-term experiments were too brief for completion of the nesquehonite-

352 dypingite transformation, but the trends in fluid composition were consistent with the early

353 stages of the transformation documented in the longer-term experiments.

354

355 *3.2 Retrieval of the nesquehonite solubility product*

356   The dissolution of nesquehonite to a constant fluid composition was rapid in all

357 experiments, with pH, Mg, and alkalinity increasing to constant values within 120 h, 24 h,

358 and 3 h in the 5°C, 25°C, and 35°C experiments, respectively (Table 1; Figure 4). The values

359 used for the calculation of nesquehonite and dypingite solubility products at all temperatures

360 are indicated in Table 1. Brucite [$Mg(OH)_2$], which can form at room temperature from Mg-

361 rich solutions, remained undersaturated in all experiments. Nesquehonite was the only phase

362 detected with XRD throughout the 5°C experiment (ES-Figure 1), therefore all samples taken

363 from 120 h, when the fluid composition stabilized, up to the end of the experiment (1420 h)

364 were included in the calculation of its solubility product (K_{sp}^{nsq}). In the 25°C experiment,

365 nesquehonite was the only phase detectable with XRD for 367 h in the short-term experiment

366 (ES-Figure 2), though minor dypingite was detected at 359 h in the long-term experiment

367 (ES-Figure 3). Solution compositions remained constant over these time periods, therefore

368 samples from between 24 h and 367 h in the short-term experiment, and less than 359 h in the

369 long-term experiment were used for the calculation of $K_{sp,25}^{nsq}$, providing a total of six distinct

370 points for which the solubility product was calculated and averaged.

371   In the 35°C experiment, the solubility product was calculated using the aqueous

372 solution composition between 3 h and 24 h in the short-term experiment, and 26 h and 74 h in

373 the long-term experiment (seven time points in total), representing time points that had

374 constant fluid composition and no detectable dypingite (Table 1).

375   The nesquehonite solubility product was determined using the average of the

376   calculated Mg^{2+} and CO_3^{2-} aqueous activities according to the reaction

377                     $$MgCO_3 \cdot 3H_2O \leftrightharpoons Mg^{2+} + CO_3^{2-} + 3H_2O \qquad\qquad \text{Eq. 1}$$
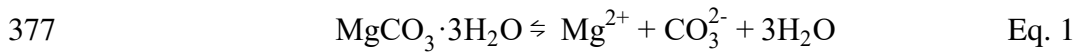
378   and its law of mass action

379                     $$K_{sp}^{nsq} = a_{Mg^{2+}} \, a_{CO_3^{2-}} \, a_{H_2O}{}^3 \qquad\qquad \text{Eq. 2}$$

380

381   The aqueous activities in Eq. 2 were calculated using PHREEQC V3 with the modified

382   LLNL database, as described in section 2.4, and are listed in Table 1. The nesquehonite

383   solubility products are reported in Table 2.

384

385

386   Based on the solubility product determined in this study, the standard molar Gibbs

387   free energy of formation of nesquehonite was also calculated. The standard state properties of

388   the aqueous species involved in equation 1 were used, and are listed in Table 3. The enthalpy

389   of the nesquehonite dissolution reaction (equation 1) was estimated by plotting the natural

390   logarithm of the solubility product versus reciprocal temperature (Figure 5, as shown with

391   base 10 logarithm), with the slope of the line equated to $-\Delta H_r^\circ/R$, where ΔH_r° is the enthalpy

392   of reaction, and R is the ideal gas constant (Table 3). The standard enthalpy of formation of

393   nesquehonite was then calculated using the standard state properties of the aqueous species

394   involved in equation 1, as listed in Table 3.

395

396   *3.3 Retrieval of the dypingite solubility product*

397   The solubility product of dypingite (K_{sp}^{dyp}) was estimated from the long-term 25°C

398   and 35°C experiments in which complete transformation to dypingite was achieved.

399   Dypingite was not formed at 5°C, likely due to slower kinetics of the transformation reaction,

400   thus its solubility product was not determined at this temperature. At 25°C, nesquehonite was

401   no longer detected after 1367 h (Table 1; ES-Figure 3), and the fluid composition was

402   relatively constant for the remainder of the experiment. This period is therefore taken to

403   reflect equilibrium between the dypingite and the aqueous solution, and the solubility product

404   was calculated from the final three samples from this experiment (Table 1). At 35°C,

405   nesquehonite was no longer detected after 482 h (Table 1; ES-Figure 5); the fluid

406   composition also remained relatively constant for the remainder of the experiment. The fluid

407   composition from 482 h until the end of the experiment was therefore used to calculate K_{sp}^{dyp}

408   (Table 1), except for the sample taken at 718 h, due to the presence of an unidentified phase

409   in the solid sample as previously described. A total of five distinct points were used for the

410   solubility product calculation at 35°C. Aqueous activities of Mg^{2+} and CO_3^{2-} were calculated

411   using PHREEQC V3 and the modified LLNL database, and OH^- activity was calculated from

412   pH measurements. The K_{sp}^{dyp} was calculated using these values and equations 3 and 4.

413   $$Mg_5(CO_3)_4(OH)_2 \cdot {\sim}nH_2O \leftrightharpoons 5Mg^{2+} + 4CO_3^{2-} + 2OH^- + nH_2O \qquad \text{Eq. 3}$$
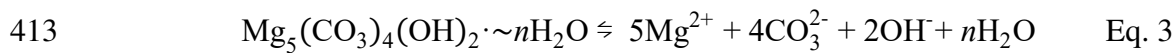
414

415   $$K_{sp}^{dyp} = a_{Mg^{2+}}{}^5 \, a_{CO_3^{2-}}{}^4 a_{OH^-}{}^2 \, a_{H_2O}{}^n \qquad\qquad \text{Eq. 4}$$

416   where the variable, n, was 5 or 8. The presence of at least two dypingite-like phases in the

417   25°C experiments, and potentially both $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O]$ and

418   $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ in the 35°C experiments means that the value calculated for the

419   dypingite solubility product likely represents a mixture of dypingite-like phases of varying

420   degrees of hydration. Due to the uncertainty in the exact hydration state of dypingite, and the

421   presence of an additional dypingite-like phase at 25°C, the K_{sp}^{dyp} was calculated in three

422   ways. Either the activity of water was assumed to be unity, or the activity of water was

423   calculated based on the solution composition using PHREEQC V3, and K_{sp}^{dyp} was

424   determined using eight or five waters of hydration and the aid of equation 4. These are the

425   most commonly reported stoichiometries for dypingite and have XRD patterns that are

426   consistent with our experimental data. The K_{sp}^{dyp} values calculated in each case were

427   equivalent within error (Table 2), demonstrating that uncertainty in the hydration state of

428   dypingite does not strongly affect the K_{sp}^{dyp} retrieved at the experimental ionic strength. The

429   solubility product (Table 2) decreased slightly with increasing temperature, consistent with

430   the behavior of nesquehonite (this study) and hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$]

431   (Gautier et al., 2014).

432

433

434   **4. Discussion**

435   *4.1 Nesquehonite and dypingite solubility products*

436   The standard molar Gibbs free energy of formation of nesquehonite calculated from

437   our data was in very good agreement with that determined by Robie and Hemingway (1973),

438   and Langmuir (1965), and the standard molar enthalpy of formation calculated from our data

439   was in very good agreement with Robie and Hemingway (1973) (Table 3). The nesquehonite

440   solubility product calculated from our data decreases slightly with increasing temperature,

441   consistent with the solubility of other Mg- and Ca-carbonate minerals (Table 2) (e.g.,

442   Königsberger et al., 1999; Marion, 2001; Bénézeth et al., 2011, 2018; Gautier et al., 2014),

443   and temperature dependence reported for nesquehonite solubility in previous studies (Dong et

444   al., 2008; Wang and Li 2012). However, the temperature dependence is not signficant outside

445   3σ uncertainty (Table 2; Figure 5). Our values are in good agreement with those reported in

446   the modeling study of Wang and Li (2012), which considered the impact of aqueous

447   speciation on nesquehonite solubility in saline solutions (Table 2). However, discrepancies

448   are evident between our values and some of the corresponding values at 25°C reported in the

449 literature; values in the present study fall between those of Kline (1929), Langmuir (1965),

450 and Hostetler (1964) (Table 2; Figure 5); such differences could be attributed to differences

451 in the calculation of aqueous speciation. The $log\,K_{sp}^{nsq}$ in both the LLNL and minteqv4

452 PHREEQC databases are most similar to that of Kline (1929), and are considerably larger

453 than those measured in this study as well as the values reported by Langmuir (1965) and

454 Hostetler (1964) (Table 2; Figure 5). In addition, the temperature extrapolation employed in

455 both of these databases exhibits a stronger temperature dependence than that measured in the

456 present study, or that indicated by Wang and Li (2012) (Figure 5). The neglect of aqueous

457 speciation in the calculation of the solubility product of Kline (1929) likely explains the

458 discrepancy between this value and that calculated in our study, as also suggested by

459 Langmuir (1965) to explain differences between reported nesquehonite solubility products.

460 The reason for the discrepancy between our measured values and those reported by Hostetler

461 (1964) and Langmuir (1965) is less clear, but may again relate to differences in the treatment

462 of aqueous speciation. Robie and Hemingway (1973) suggest that the calorimetric data from

463 their study are only in agreement with the solubility data of Langmuir (1965) if the aqueous

464 complexation of Mg by carbonate species assumed by Langmuir (1965) is overestimated.

465 This could also account for the discrepancy between the Langmuir (1965) value and that

466 calculated here, but mainly beacause thepresent study used recent data for the complexation

467 of aqueous Mg-carbonate species (Stefansson et al., 2014), which were not available at the

468 time of the Hostetler (1964) and Langmuir (1965) studies and much of the data regarding

469 aqueous Mg-carbonate complex stability came after these studies (Stefansson et al., 2014 and

470 references therein). In addition, the reported stability of $MgCO_3^\circ$ and $MgHCO_3^+$ aqueous

471 complexes at 25°C reported in early literature was highly variable (Stefansson et al., 2014). It

472 is therefore unsurprising that solubility products determined for magnesium carbonates like

473 nesquehonite differ between studies that used different thermodynamic data for aqueous

474 speciation. The similarity between the Kline (1929) value and those used in the LLNL and

475 minteqv4 databases suggests they may also lack consideration of aqueous complexation, thus

476 we propose that values reported in the present study and by Wang and Li (2012) are more

477 appropriate for calculating nesquehonite saturation state.

478   The dypingite solubility product has not previously been reported, therefore our

479 calculated K_{sp}^{dyp} cannot be compared with other dypingite values. Instead, we compare our

480 K_{sp}^{dyp} values to those of hydromagnesite, a structurally similar but less hydrated Mg-

481 carbonate. Our calculated K_{sp}^{dyp} is higher than those reported for hydromagnesite at 25°C:

482 $K_{sp,25}^{hmg} = 10^{-37.08}$ (Gautier et al., 2014), and $10^{-41.56}$ (Xiong, 2011), compared to $K_{sp,25}^{dyp,8H2O} =$

483 $10^{-34.95 \pm 0.58}$. This is consistent with previous observations of dypingite behavior, as it is

484 commonly observed to transform to hydromagnesite over time (Davies and Bubela, 1973;

485 Hopkinson et al., 2008,. 2012; Sutradhar et al., 2011; Ballirano et al., 2013), reflecting its

486 instability compared to hydromagnesite and therefore its higher solubility product. Using our

487 dypingite and nesquehonite solubility products, it can be shown that hydromagnesite is more

488 stable than both of these phases across a broad range of pH and pCO_2 conditions (Figure 6).

489 However, the relative stability of dypingite and nesquehonite is sensitive to pH for a fixed

490 DIC concentration (Figure 6). At higher pH there is a greater difference in their relative

491 stability, with dypingite being more stable than nesquehonite, whereas a smaller difference is

492 predicted at low pH, owing to the sensitivity of the dypingite solubility product to the activity

493 of OH^- (Figure 6).

494

495 *4.2 Implications*

496   Dypingite and nesquehonite are common weathering products of ultramafic rocks

497 (Wilson et al., 2006, 2009, 2014; Power et al., 2007; Beinlich and Austrheim, 2012; Garcia

498 del Real et al., 2016; Lin et al., 2017), and are documented CO_2 sinks that can be used to

499   store CO_2 (Power et al., 2007, 2013a, b, c, 2016; Pronost et al., 2011; Bea et al., 2012;

500   Assima et al., 2012, 2014c ; Harrison et al., 2013a, 2015, 2016, 2017; Wilson et al., 2014;

501   McCutcheon et al., 2014; Morgan et al., 2015; Hamilton et al., 2016, 2018; Gras et al., 2017).

502   Yet, a lack of dypingite solubility data has hindered the ability to evaluate and predict its

503   formation (Power et al., 2007, 2013c, 2014b; Wilson et al., 2010; Mavromatis et al., 2012;

504   Harrison et al., 2013a; McCutcheon et al., 2014). The results presented in this study allow

505   better estimation of dypingite stability in aqueous solution. For example, the solubility

506   products determined in this study were added to PHREEQC V3 and used to calculate the

507   dypingite saturation state in a previous experimental study in which it formed (Mavromatis et

508   al., 2012), and in a natural wetland in Atlin, Canada, where it has been observed to form in

509   microbial mats (Power et al., 2007, 2009, 2014b). In the experimental study (Mavromatis et

510   al., 2012), dypingite was somewhat supersaturated, suggesting that despite forming more

511   readily at low temperature than hydromagnesite, its precipitation is nevertheless somewhat

512   kinetically inhibited (Table 4). In the natural wetlands, where dypingite has both been

513   directly observed, as well as precipitated in experiments using water from the wetlands

514   (Power et al., 2007, 2014b), dypingite was very close to equilibrium (Table 4), providing

515   confidence in our K_{sp}^{dyp}. The K_{sp}^{dyp} determined in the present study can therefore be used to

516   better constrain the possibility of dypingite precipitation in natural environments, and during

517   engineered CO_2 storage operations. Note also that the nesquehonite solubility products in the

518   PHREEQC databases appear to underestimate the stability of this mineral compared to the

519   results of recent studies (this study; Wang and Li, 2012), and may thus underestimate its

520   likelihood to form.

521   The main goal of engineered CO_2 storage operations is to ensure CO_2 is stored in a

522   stable form and will not be substantially released over thousand-year timescales. Therefore,

523   the design of CO_2 storage strategies to produce stable carbonate minerals is a key

524   consideration, and has motivated numerous studies on the relative stability of Mg-carbonate

525   minerals (Königsberger et al., 1999; Lanas and Alvarez, 2004; Hales et al., 2008; Hopkinson

526   et al., 2008, 2012; Vágvölgyi et al., 2008; Hänchen et al., 2008; Frost et al., 2008; Ballirano

527   et al., 2010; Ballirano et al., 2013; Kristova et al., 2014; Jauffret et al., 2015; Morgan et al.,

528   2015). The stoichiometry of minerals in terms of their Mg:C ratios and Mg:H_2O ratios also

529   governs the efficiency of CO_2 sequestration; a Mg:C of 1:1 such as provided by nesquehonite,

530   lansfordite [$MgCO_3 \cdot 5H_2O$], and magnesite is most efficient. In dry conditions, such as in

531   subaerially stored ultramafic mining wastes (Bea et al., 2012; Wilson et al., 2014), or near the

532   injection of supercritical CO_2 in the subsurface (Schaef et al., 2011, 2013; Chaka et al., 2016),

533   the availability of water may be a limiting factor for carbonate precipitation (Schaef et al.,

534   2011, 2013; Harrison et al., 2015, 2016), therefore carbonates that consume less water during

535   their formation, such as dypingite, hydromagnesite, and magnesite, are desirable. The

536   anhydrous carbonate, magnesite, is the ideal carbon sink in terms of stability, water

537   requirements, and efficiency (Power et al., 2017). However, as it does not tend to form at low

538   temperatures (Hänchen et al., 2008; Saldi et al., 2012), the hydrated carbonates are the targets

539   for near Earth's surface temperature carbon storage. Although nesquehonite tends to

540   precipitate from CO_2-rich solutions and under evaporative conditions (Königsberger et al.,

541   1999; Power et al., 2007; Zhao et al., 2010; Harrison et al., 2013a), it readily transforms on

542   hour- to month-long time scales to either dypingite or hydromagnesite, depending on the

543   temperature. This transformation is accompanied by a slight loss of CO_2 to solution, as

544   documented in the experiments at 25°C and 35°C (Figure 4c and 4f), which is less ideal for

545   CO_2 storage. On the other hand, the transformation from dypingite to the more stable phase,

546   hydromagnesite, does not result in a loss of CO_2 (Ballirano et al., 2013), therefore this

547   mineral phase transformation minimizes loss of stored CO_2. This suggests dypingite is a good

548   target mineral for CO_2 sequestration at low temperatures. The tendency for dypingite to form

549 over nesquehonite at atmospheric pCO$_2$ (~400 ppm), suggests that air capture coupled with

550 carbonate mineral precipitation inherently produces a CO$_2$ sink of higher stability, though the

551 relatively low concentration of CO$_2$ in ambient air compared to CO$_2$ point sources means that

552 carbon mineralization rates can be limited by the availability of CO$_2$ (Wilson et al., 2010; Bea

553 et al., 2012; Pronost et al., 2012; Harrison et al., 2013b; Wilson et al., 2014). Microbially-

554 mediated carbonate precipitation also tends to favor dypingite precipitation (Power et al.,

555 2007; Mavromatis et al., 2012; McCutcheon et al., 2016), highlighting that microbially-

556 mediated carbonation is a highly promising strategy for carbon mineralization at near Earth's

557 surface conditions.

558 Ultramafic rock such as serpentinite contributes disproportionately to the release of

559 chromium globally during natural weathering processes compared to other rock-types, owing

560 to its high reactivity and high chromium content (McClain and Maher, 2016; Beinlich et al.,

561 2018). It has recently been observed that secondary Mg-carbonate minerals formed during the

562 weathering of ultramafic rock can help to mitigate the release of metals such as chromium,

563 due both to incorporation of the metals into the carbonate minerals, and trapping of

564 particulates within carbonate cement (Hamilton et al., 2016; Hamilton et al., 2018). The

565 relative stability and mechanism of phase transformations is highly relevant to the cycling of

566 potential contaminants like chromium in both natural and engineered ultramafic weathering

567 environments. The change in mineral structure between nesquehonite and dypingite, and the

568 alteration of crystal morphology during the phase transformation is indicative of a

569 dissolution-reprecipitation process. This implies that metals initially stored in nesquehonite

570 may be released to solution, and may or may not be equally reincorporated into dypingite,

571 depending on the relative affinity for metals between the two phases. Similarly, isotopic

572 signatures, which can be used as tracers for CO$_2$ cycling in natural ultramafic environments

573 and mine wastes (Power et al., 2007; Wilson et al., 2009, 2010, 2011, 2014; Beinlich and

574   Austrheim, 2012; Shirokova et al., 2013; Harrison et al., 2013a, 2016; Oskierski et al., 2013,

575   2016; Mervine et al., 2014; Mavromatis et al., 2015; Falk et al., 2016; Gras et al., 2017;

576   Oelkers et al., 2018), may be reset during mineral phase transformations that occur via

577   dissolution-reprecipitation, complicating their interpretation.

578

579   **5. Conclusions**

580   The hydrated Mg-carbonate minerals nesquehonite and dypingite are common

581   products of natural and engineered ultramafic rock weathering, and are of interest owing to

582   their capacity to securely store atmospheric CO_2. Knowledge of their stability, longevity, and

583   consequences of transformations will aid in our ability to ascertain the longevity and capacity

584   of engineered carbon storage operations. In this study, the solubility of nesquehonite was re-

585   examined, and the solubility of dypingite was measured for the first time. Our nesquehonite

586   solubility product is in good agreement with the recent modeling study of Wang and Li

587   (2012), which considered aqueous speciation. Our dypingite solubility product, though

588   complicated by the presence of multiple dypingite-like phases, nevertheless allows estimation

589   of dypingite saturation state in natural waters and engineered CO_2 storage operations. A

590   natural wetland where dypingite has been observed (Power et al., 2007, 2009, 2014) is

591   demonstrated to be close to equilibrium with respect to dypingite, providing confidence in

592   our values. Finally, our experimental results indicate that nesquehonite, which tends to form

593   at greater than atmospheric pCO_2, can rapidly transform to dypingite at 25°C and 35°C,

594   resulting in greater security of CO_2 storage due the higher stability of this phase, but

595   accompanied by a slight loss of CO_2 to solution. This phase transformation apparently occurs

596   via a dissolution re-precipitation mechanism, altering external crystal morphology,

597   potentially releasing trace metals, and likely resetting isotopic signatures.

598

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Tables

Table 1. Aqueous composition, aqueous activities, and mineralogical composition measured

over time for all experiments.

Experiment	Time (h)[a]	pH (±0.03)	Alkalinity (× 10^{-2} mol/L; ±0.36 × 10^{-2})	DIC[b] (× 10^{-2} mol/L; ±0.36× 10^{-2})	Mg (× 10^{-2} mol/L)	Mg error (3σ × 10^{-2})	$a_{Mg^{2+}}$[c] (× 10^{-3})	$a_{CO_3^{2-}}$[c] (× 10^{-3})	a_{H_2O}[c]	Mineralogy[d]
5	0	8.25	5.95	6.00				0.19	0.995	nsq
	6	9.44	9.04	7.54	1.214	0.005	2.431	2.88	0.994	nsq
	9	9.40	8.90	7.54	1.157	0.004	2.381	2.65	0.994	nsq
	12	9.41	8.94	7.49	1.290	0.012	2.641	2.71	0.994	nsq
	24	9.39	9.17	7.75	1.269	0.010	2.586	2.70	0.994	nsq
	49	9.43	9.16	7.65	1.278	0.017	2.558	2.87	0.994	nsq
	120 (nsq)	9.47	9.66	7.91	1.510	0.006	2.915	3.15	0.994	nsq
	367 (nsq)	9.59	9.71	7.66	1.505	0.006	2.734	3.76	0.994	nsq
	1085 (nsq)	9.39	9.68	8.14	1.498	0.016	3.001	2.78	0.994	nsq
	1420 (nsq)	9.59	9.67	7.62	1.502	0.014	2.732	3.75	0.994	nsq
25_short	0	8.15	5.94	5.97				0.25	0.995	nsq
	4	9.20	8.99	7.52	1.167	0.015	1.976	2.85	0.994	nsq
	6	9.20	8.99	7.55	1.094	0.011	1.847	2.86	0.994	nsq
	8	9.19	8.87	7.47	1.119	0.003	1.926	2.75	0.994	nsq
	10	9.18	8.61	7.27	1.075	0.019	1.882	2.67	0.994	nsq
	12	9.20	8.72	7.31	1.114	0.008	1.920	2.76	0.994	nsq
	24 (nsq)	9.19	8.95	7.50	1.197	0.013	2.048	2.79	0.994	nsq
	49 (nsq)	9.19	8.97	7.52	1.183	0.002	2.022	2.79	0.994	nsq
	120 (nsq)	9.20	9.02	7.54	1.192	0.011	2.019	2.85	0.994	nsq
	367 (nsq)	9.19	9.05	7.59	1.216	0.015	2.076	2.79	0.994	nsq
	1086	8.97	8.99	8.00	1.113	0.006	2.158	1.95	0.994	nsq+dyp
25_long	0	8.23	5.92	5.92	0.006	0.001	0.002	0.30	0.995	nsq
	22 (nsq)	9.27	8.68	7.12	1.105	0.011	1.821	3.08	0.994	nsq (minor dyp)
	122 (nsq)	9.23	8.69	7.23	1.098	0.009	1.861	2.88	0.994	nsq
	359	8.94	8.69	7.77	1.119	0.012	2.249	1.78	0.994	nsq+dyp
	599	8.82	8.66	7.95	1.075	0.001	2.296	1.42	0.994	nsq+dyp
	843	8.88	8.69	7.87	1.104	0.007	2.288	1.59	0.994	nsq+dyp
	987	8.86	8.09	7.38	1.011	0.020	2.187	1.43	0.994	nsq+dyp
	1157	8.82	8.49	7.80	1.065	0.012	2.303	1.38	0.994	dyp+nsq
	1367 (dyp)	8.81	8.49	7.81	1.069	0.010	2.325	1.35	0.994	dyp+dyp-like
	1607 (dyp)	8.81	8.61	7.93	1.051	0.062	2.265	1.38	0.994	dyp+dyp-like
	2043 (dyp)	8.90	8.49	7.68	1.036	0.008	2.148	1.62	0.994	dyp+dyp-like

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Table 1 (continued). Aqueous composition, aqueous activities, and mineralogical

composition measured over time for all experiments.

Experiment	Time (h)[a]	pH ($\pm$0.03)	Alkalinity ($\times$ 10^{-2} mol/L; $\pm 0.36 \times 10^{-2}$)	DIC[b] ($\times 10^{-2}$ mol/L; $\pm 0.36 \times 10^{-2}$)	Mg ($\times 10^{-2}$ mol/L)	Mg error ($3\sigma \times 10^{-2}$)	a_{Mg2+}[c] ($\times 10^{-3}$)	a_{CO32-}[c] ($\times 10^{-3}$)	a_{H2O}[c]	Mineralogy[d]
35_short	0	8.11	5.94	5.96	0.004	nd[e]	0.001	0.28	0.995	nsq
	3 (nsq)	9.12	8.77	7.35	1.051	0.008	1.629	2.82	0.994	nsq
	5 (nsq)	9.12	8.64	7.24	1.063	0.018	1.670	2.75	0.994	nsq
	7 (nsq)	9.14	8.63	7.21	1.047	0.015	1.625	2.83	0.994	nsq
	11 (nsq)	9.11	8.65	7.27	1.050	0.016	1.654	2.73	0.994	nsq
	24 (nsq)	9.22	8.74	7.11	1.048	0.010	1.519	3.26	0.994	nsq
	75	9.19	8.75	7.18	1.062	0.004	1.573	3.12	0.994	nsq (trace dyp)
	122	9.12	8.74	7.33	1.054	0.007	1.647	2.78	0.994	nsq+dyp
	191	9.04	8.78	7.52	1.080	0.008	1.778	2.45	0.994	nsq+dyp
	243	9.02	8.65	7.46	1.048	0.011	1.767	2.32	0.994	nsq+dyp
	432	8.84	8.43	7.61	0.900	0.004	1.705	1.70	0.994	dyp+nsq
35_long	0	8.08	5.93	5.96	0.001	0.0001	0.004	0.26	0.995	nsq
	26 (nsq)	9.17	8.54	7.06	1.044	0.002	1.596	2.95	0.994	nsq
	74 (nsq)	9.20	8.57	7.02	1.056	0.009	1.577	3.10	0.994	nsq
	123	9.09	8.60	7.26	1.057	0.015	1.697	2.64	0.994	nsq (trace dyp)
	244	8.90	8.66	7.66	1.138	0.011	2.082	1.89	0.994	nsq+dyp
	311	8.80	8.14	7.37	1.048	0.002	2.087	1.50	0.994	dyp+nsq
	482 (dyp)	8.65	8.36	7.80	0.951	0.007	2.018	1.16	0.994	dyp
	552 (dyp)	8.64	7.58	7.09	0.922	0.009	2.057	1.03	0.994	dyp
	600 (dyp)	8.63	8.29	7.77	0.930	0.007	1.999	1.10	0.994	dyp
	718	8.63	8.18	7.67	0.915	0.007	1.977	1.10	0.994	dyp+ unknown phase

979   [a](nsq) indicates time points used for the calculation of K_{sp}^{nsq}, and (dyp) indicates timepoints used for the calculation of K_{sp}^{dyp}

980   [b]DIC = dissolved inorganic carbon; calculated using PHREEQC V3

981   [c]Aqueous activity calculated using PHREEQC V3

982   [d]determined with X-ray diffraction

983   [e]No data

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Table 2. Solubility products for nesquehonite and dypingite from this study and previous

works including the PHREEQC databases.

Temperature (°C)	Nesquehonite log K_{sp}^{nsq}							Dypingite log K_{sp}^{dyp}		
	this study ±3σ	PHREEQC		Wang and Li (2012)	Kline (1929)	Langmuir (1965)	Hostetler (1964)	this study		
		Minteqv4	LLNL					$a_{H2O}=1$ ±3σ	a_{8H2O} ±3σ	a_{5H2O} ±3σ
5	-5.03±0.13	-4.36	-4.53	-4.99						
25	-5.27±0.15	-4.67	-5.06	-5.27	-4.96	-5.59±0.1 -5.42*	-5.51	-34.93±0.58	-34.95±0.58	-34.94±0.58
35	-5.34±0.04	-4.81	-5.23	-5.40				-36.02±0.31	-36.04±0.31	-36.03±0.31

* considering the $MgHCO_3^+$ and/or $MgCO_3°$ aqueous complexes (reported by Robie and

Hemingway (1973) based on the data of Langmuir (1965)).

996   Table 3. Standard state properties (25°C, 1 bar) of nesquehonite reported in the literature and

997   determined in this study, and standard state properties of dypingite determined in this study.

998   The standard state properties of aqueous species used to calculate the Gibbs free energy of

999   formation of nesquehonite and dypingite in the present study are reported in the lower table,

1000   as are the equilibrium constants of the considered aqueous Mg complexes at 25°C.

Nesquehonite [$MgCO_3 \cdot 3H_2O$]				
Source	ΔG_r° (kJ/mol)	ΔG_f° (kJ/mol)	ΔH_r° (kJ/mol)	ΔH_f° (kJ/mol)
this study	30.1±0.8	-1723.5±0.8	-17.17	-1981.5
Robie and Hemingway (1973)		-1723.8±0.5		-1977.3±0.5
Langmuir (1965)		-1726.6±2.1		
Dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O$]				
this study	199.4±1.3	-6792.7±1.3		
Aqueous Species				
Source	Species	ΔG_f° (kJ/mol)	S (J/mol/K)	ΔH_f° (kJ/mol)
Wagman et al (1982)	H_2O	-237.13	69.95	-285.83
Shock and Helgeson (1988), Shock et al (1997)	Mg^{2+}	-453.98	-138.07	-465.96
Shock and Helgeson (1988)	CO_3^{2-}	-527.98	-50.00	-675.24
Wagman et al (1982)	HCO_3^-	-586.77	91.20	-691.99
Wagman et al (1982)	OH^-	-157.24	-10.75	-229.99
Aqueous Complexes				
Source	Species	log K	Reaction	
Stefansson et al (2014)	$MgHCO_3^+$	1.1	$Mg^{2+} + HCO_3^- \leftrightarrows MgHCO_3^+$	
Stefansson et al (2014)	$MgCO_3^\circ$	3.0	$Mg^{2+} + CO_3^{2-} \leftrightarrows MgCO_3^\circ$	
Palmer and Wesolowski (1997)	$Mg(OH)^+$	-11.7	$Mg^{2+} + H_2O \leftrightarrows MgOH^+ + H^+$	
PHREEQC V3 LLNL database	$MgCl^+$	-0.1	$Mg^{2+} + Cl^- \leftrightarrows MgCl^+$	

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1003   Table 4. Calculated saturation indices for nesquehonite and dypingite from an experimental

1004   study (Mavromatis et al., 2012) and a natural Mg-rich wetland (Power et al., 2014).

Mg-carbonate precipitation experiments (data from Mavromatis et al. 2012)				
			Saturation index	
Experiment	Experiment type	Precipitated mineral	nesquehonite	dypingite
Abio-A-1	Abiotic	Nesquehonite	-0.52	-2.10
Abio-A-5	Abiotic	Dypingite	0.06	2.19
Abio-A-10	Abiotic	Dypingite	-0.05	1.67
Abio-A-13	Abiotic	Dypingite	-0.16	1.09
Abio-B-18	Abiotic	Nesquehonite	-0.16	1.16
Abio-C-7	Abiotic	Nesquehonite	-0.16	1.31
Abio-C-9	Abiotic	Nesquehonite	-0.22	0.91
Abio-C-11	Abiotic	Nesquehonite	-0.16	1.28
Abio-C-12	Abiotic	Nesquehonite	-0.18	1.12
Abio-D1-8	Abiotic	Nesquehonite	-0.34	0.39
Abio-D1-18	Abiotic	Nesquehonite	-0.21	1.20
Abio-D2-8	Abiotic	Dypingite	-0.26	0.96
Abio-D2-23	Abiotic	Dypingite	-0.17	1.26
Abio-E-7	Abiotic	Nesquehonite	0.11	1.84
Abio-E-10	Abiotic	Nesquehonite	0.34	3.61
Abio-E-11	Abiotic	Nesquehonite	0.35	3.83
Abio-E-13	Abiotic	Nesquehonite	0.27	3.42
Bio-A-1	Biotic	Nesquehonite	-0.45	-1.62
Bio-A-5	Biotic	Dypingite	-0.03	1.05
Bio-A-8	Biotic	Dypingite	0.26	3.20
Bio-A-12	Biotic	Dypingite	0.30	3.78
Bio-A-15	Biotic	Dypingite	0.13	3.13
Bio-B-4	Biotic	Nesquehonite	0.08	3.11
Bio-B-6	Biotic	Nesquehonite	0.02	2.86
Bio-B-8	Biotic	Nesquehonite	-0.19	1.78
Bio-B-9	Biotic	Nesquehonite	-0.31	1.43
Bio-B-10	Biotic	Nesquehonite	-0.46	1.64
Bio-B-11	Biotic	Dypingite	-0.49	2.00

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1007   Table 4 (continued). Calculated saturation indices for nesquehonite and dypingite from an

1008   experimental study (Mavromatis et al., 2012) and a natural Mg-rich wetland (Power et

1009   al., 2014).

Mg-carbonate precipitation experiments (data from Mavromatis et al. 2012)				
Experiment	**Experiment type**	**Precipitated mineral**	**Saturation index**	
			nesquehonite	**dypingite**
Bio-C-5	Biotic	Dypingite	-0.39	1.65
Bio-C-5	Biotic	Dypingite	-0.37	1.75
Bio-D-3	Biotic	Dypingite	-0.32	1.59
Bio-E-7	Biotic	Nesquehonite+Dypingite	-0.30	1.96
Bio-E-9	Biotic	Nesquehonite+Dypingite	-0.24	1.60
Bio-F-9	Biotic	Nesquehonite	-0.18	2.02
Bio-G-2	Biotic	Nesquehonite	-0.35	-1.01
Bio-G-6	Biotic	Nesquehonite	0.40	4.90
Bio-I-5	Biotic	Nesquehonite	-0.49	1.59
Natural wetland (data from Power et al., 2014)				
Location	**Precipitation circumstances**	**Precipitated mineral**	**Saturation index**	
			nesquehonite	**dypingite[a]**
Atlin, North lobe of main wetland	microbial mats	Dypingite	-0.06	0.32
Atlin, South lobe of main wetland	microbial mats	Dypingite	-0.11	0.01

1010   [a]temperature of wetland water was 10°C, but dypingite K_{sp} used was for 25°C

1011

Figure Captions

Figure 1. Fourier transform infrared spectroscopy (FTIR) data for selected samples. Spectra

are offset along y-axis. Intensities on the y-axis are in arbitrary units (a.u.).

Figure 2. X-ray diffraction patterns of initial nesquehonite used in the short-term (blue line)

and long-term (purple line) experiments. The location of peaks in the nesquehonite reference

pattern are indicated by black circles.

Figure 3. Scanning electron micrographs of solids. A) initial nesquehonite. B) Solid sample

after 1420 h at 5°C. C) Solid sample after 359 h at 25°C. D) Solid sample after 311 h at 35°C.

Figure 4. Fluid composition over time in all experiments. Fluid composition evolution for the

entire experimental duration: A) pH, B) Mg concentration, C) dissolved inorganic carbon

concentration (DIC). Fluid composition evolution for the first 600 h of each experiment: D)

pH, E) Mg concentration, F) DIC. Data from the 5°C, 25°C, and 35°C experiments are

indicated by gray triangles, black diamonds, and blue squares, respectively, and short- and

long-term experiments are indicated by filled and open points, respectively. Error is smaller

than symbols unless otherwise shown.

Figure 5. Logarithm of nesquehonite solubility products (K_{sp}^{nsq}) versus reciprocal of

temperature (in Kelvin).

Figure 6. Relative stability of hydrated Mg-carbonates at 25°C. A) Mg^{2+} activity in

equilibrium with magnesite, hydromagnesite, dypingite, and nesquehonite as a function of pH.

1037   The total dissolved inorganic carbon concentration was fixed at 0.06 M, the Na concentration

1038   was fixed at 0.16 M, and the Cl concentration was fixed at 0.10 M to reflect the conditions in

1039   the experiments. B) Mg^{2+} activity in equilibrium with magnesite, hydromagnesite, dypingite,

1040   and nesquehonite as a function of pCO_2. The pH was fixed at 9, Na concentration was fixed

1041   at 0.16 M, and Cl concentration fixed at 0.10 M to reflect the conditions in the experiments.

1042   Calculations were done using PHREEQC V3 and the modified LLNL database, as described

1043   in section 2.4.

1044

1045   **ES-Figure 1.** X-ray diffraction patterns of reacted solids in the 5°C experiment over time.

1046   Major nesquehonite peaks are indicated by the letter "n."

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1048   **ES-Figure 2.** X-ray diffraction patterns of reacted solids in the short-term 25°C experiment

1049   over time. Major nesquehonite peaks are indicated by the letter "n," and dypingite peaks by

1050   the letter "d."

1051

1052   **ES-Figure 3.** X-ray diffraction patterns of reacted solids in the long-term 25°C experiment

1053   over time. Major nesquehonite peaks are indicated by the letter "n," and dypingite peaks by

1054   the letter "d." The peak indicative of the dypingite stoichiometry of

1055 $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ is indicated by the label "d(8H$_2$O)." The peaks of the unidentified

1056   dypingite-like phase are indicated by the label "d-l." The appearance of more noise in some

1057   patterns is attributed to lower maximum intensities for those data.

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1059   **ES-Figure 4.** X-ray diffraction patterns of reacted solids in the short-term 35°C experiment

1060   over time. Major nesquehonite peaks are indicated by the letter "n," and dypingite peaks by

1061   the letter "d." The peak indicative of the dypingite stoichiometry of

1062 $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ is indicated by the label "d($8H_2O$)."

1063

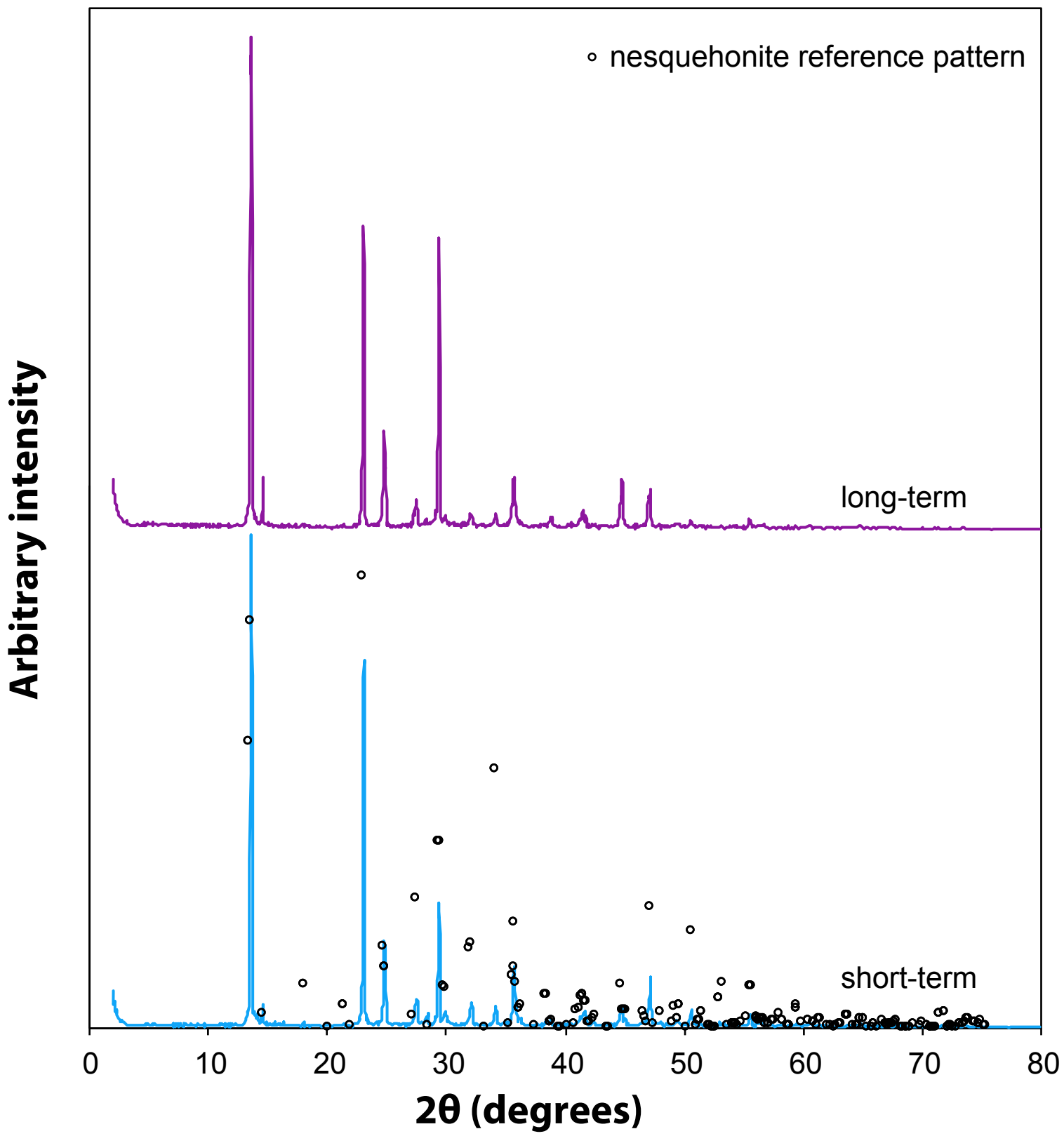1064   **ES-Figure 5.** X-ray diffraction patterns of reacted solids in the long-term 35°C experiment

1065   over time. Major nesquehonite peaks are indicated by the letter "n," and dypingite peaks by

1066   the letter "d." The peak indicative of the dypingite stoichiometry of

1067 $[Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O]$ is indicated by the label "d($8H_2O$)." The appearance of more

1068   noise in some patterns is attributed to lower maximum intensities for those data.

a) initial nsq

50 μm

b) 5°C, 1420 h

100 μm

c) 25°C, 359 h

20 μm

d) 35°C, 311 h

50 μm

35°C long-term experiment