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The replacement of a carbonate rock by fluorite: kinetics and microstructure

Elisabete Trindade Pedrosa, Lena Boeck, Christine V Putnis, Andrew Putnis

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26 Mineral replacement reactions may occur in any situation that involves the reequilibration
27 between a solid and a fluid phase and are commonly controlled by an interface-coupled
28 dissolution-precipitation mechanism (Putnis 2002, 2009; Putnis and Putnis 2007). Such reactions
29 occur commonly in the crust of the Earth, where aqueous fluids are ubiquitous, for example,
30 during metamorphism, metasomatism and weathering. These large-scale processes are often
31 characterized by pseudomorphic mineral replacements as seen in albitisation, where Ca or K-rich
32 feldspars are progressively replaced by the Na-rich plagioclase, albite (Hövelmann et al. 2010;
33 Niedermeier et al. 2009; Engvik et al. 2011). During albitisation many elements are mobilized
34 and removed into the fluid phase that may migrate through the rock and ultimately be associated
35 with large-scale ore deposition. Replacement reactions also occur quite commonly in carbonate
36 rocks, promoted by the higher solubility of carbonates compared to other rock-forming minerals.
37 For example, calcite (CaCO_3) may be replaced by other carbonates such as dolomite or siderite
38 (Pearce et al., 2013) or may form other calcium compounds when in contact with appropriate
39 solutions. For example, calcite in contact with PO_4 -bearing solutions is easily replaced by
40 apatite, Ca-phosphate (Yoshimura et al. 2004; Kasiopas et al. 2011; Jonas et al. 2013, 2014;
41 Pedrosa et al. 2016).

42 Replacement reactions are complex reactions controlled by at least three reaction steps:
43 dissolution, mass transfer (including fluid migration through a porous solid phase and element
44 diffusion through a fluid phase) and precipitation (including nucleation and growth). The kinetics
45 of replacement reactions is dependent on the contribution of each of these steps and these may
46 vary during the progression of the reaction. The overall reaction rate is generally dependent on
47 the slowest of these reaction steps. The temperature dependence of the reaction rate is referred to

48 as the empirical activation energy (E_a), without specific reference to the overall rate-controlling
49 step.

50 A study by Xia et al. (2009) has shown that during mineral replacement reactions, when the rate-
51 controlling step is dissolution, there may be perfect preservation of the mineral microstructure
52 inherited from the parent phase (micro and nano-scale pseudomorphism). The relevance of
53 coupled dissolution-precipitation reactions to a wide range of fluid-solid reactions has been
54 recently reviewed by Ruiz-Agudo et al. (2014) and Altree-Williams et al. (2015). As well as
55 describing reequilibration reactions occurring in the Earth, these reactions may be used to design
56 new materials with specific engineered and functionalized properties. Examples of compositional
57 control and designed products include the use of apatite formed from the replacement of a
58 carbonate such as calcite or aragonite (Kasioptas et al. 2010). New bone replacement materials
59 (apatite) need to combine long implant life with compatibility and appropriate mechanical
60 properties and dissolution-precipitation is a process that has been proposed for the synthesis of
61 porous biocompatible material for bone implants (Heness and Ben-Nissan 2004).

62 In this paper we describe the replacement of calcite (Carrara marble) by fluorite (CaF_2).
63 Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has
64 applications in both Earth sciences and engineering. Fluorite (CaF_2) occurs naturally in many
65 types of rocks (igneous, sedimentary, and metamorphic) and its origin is commonly associated
66 with hydrothermal fluids (e.g. Richardson and Holland 1979; Toft 1986; Gagnon 2003; Schwinn
67 and Markl 2005; Pradesh 2013). Fluorite pseudomorphs after calcite are not uncommon in nature
68 as evidenced in museum collections (e.g. from Chihuahua, Mexico). Fluorite is an important
69 industrial mineral. It is used in a wide variety of chemical, metallurgical and ceramic processes.
70 An environmentally important example is the mechanism of interaction of carbonates with

71 fluoride ions in drinking water. Fluoride has been added to town water supplies since the 1950s
72 in Europe, the USA and Australia with the aim of reducing tooth decay. This replacement
73 process results in a hardened surface of fluorapatite at the enamel (apatite) surface of the tooth
74 (Pasteris and Ding 2009). According to the World Health Organization (WHO 2011), fluoride
75 ingestion (through drinking water or a combination with other sources, such as fluoridated
76 toothpaste) gives significant beneficial health effects at low concentrations, but at excessive
77 exposure can result in adverse effects, such as dental and skeletal fluorosis. The WHO (2011)
78 recommends a guideline of a maximum fluoride content of 1.5 mg/L for drinking water.
79 Excessive fluoride exposure has been reported for many years and for a large number of
80 developed and developing countries (Ghosh et al. 2013). This excess results from the
81 accumulation of fluoride in groundwater (principal source of drinking water) from a number of
82 different sources (e.g. fertilizer emission and mineral weathering) depending on the location
83 (Brindha and Elango 2011). Calcite grains have been used as seed material in chemical reactors
84 for the sequestration of fluoride from contaminated waters and wastewaters (Simonsson 1979;
85 Yang et al. 1999; Turner et al. 2005; Aldaco et al. 2007), representing a direct application of the
86 replacement of calcite by fluorite.

87 The aim of the present work is to investigate the kinetics of the replacement of calcium carbonate
88 by fluorite as well as to understand better the mechanism of replacement reactions in general.
89 Carrara marble was chosen as the parent material due to its high purity in calcium carbonate and
90 its uniform grain-size allowing grain-boundary fluid migration to be observed within the
91 experimental sample size. The kinetics of replacement was determined from the amount of
92 fluorite formed as a function of temperature and reaction time, as determined from the Rietveld

93 analysis of X-ray powder diffraction (XRD) patterns. Morphological characteristics of the
94 product phase (studied by scanning electron microscopy, SEM) complement this study.

95 **Materials and Methods**

96 **Starting material**

97 Small cubes ($3 \times 3 \times 3$ mm) of Carrara marble (~ 99.7 wt% of CaCO_3 and ~ 0.3 wt% of Mg,
98 Pedrosa et al. 2016) were cut and reacted with a 4 M ammonium fluoride (NH_4F) solution (Alfa
99 Aesar GmbH 98.0 %). Given that the fluid capacity of the hydrothermal reactor was 2 mL, a
100 concentration of 4 M NH_4F was used to guarantee enough fluoride in solution to fully replace the
101 marble samples by fluorite. The initial pH of the solution was 7.5(2) and the initial weight of the
102 samples averaged 75(2) mg (standard deviation ± 3 %).

103 **Solubilities of calcite and fluorite at experimental conditions**

104 The solubilities of calcite and fluorite in water and at the experimental conditions were estimated
105 using the computer program PHREEQC (Parkhurst and Appelo 1999). The simulations were
106 made for an initial stage of the reaction using the same approach as in Pedrosa et al. (2016). In
107 pure water, with an increase of temperature (60 to 140 °C) the solubility of fluorite increases
108 whilst the solubility of calcite decreases (Table 1, log K). In 4 M NH_4F , given by the saturation
109 index (SI) fluorite is the least soluble phase for all experimental conditions (Table 1). The small
110 difference between the program estimation (Table 1) and the known empirical solubilities of
111 calcite and fluorite in pure water at STP (log K -8.47 and -10.46, respectively) supports the
112 reliability of the simulations.

113 **Hydrothermal experiments**

114 Hydrothermal experiments were performed at different reaction times and temperatures of 60,
115 80, 100, and 140 °C. Each marble cube was inserted into a Teflon[®]-lined reactor together with 2
116 mL of fluid. The Teflon[®] reactor was placed into a steel autoclave and tightly sealed to avoid any
117 fluid loss during reaction. The pressure was autogenous. After reaction, the autoclaves were
118 removed from the furnace and quickly cooled in a flow of compressed air to room temperature (~
119 22 °C). The final pH values of the fluids were measured. The samples were washed with distilled
120 water, left to dry overnight at 40 °C, weighed, and then powdered in an agate mortar. The
121 reactions were repeated for reproducibility and similar results were obtained. The reproduced
122 samples were used for imaging analysis. Calcium contents in the final fluids were measured
123 using inductively-coupled plasma optical emission spectrometry (ICP-OES).

124 **X-ray diffraction (XRD)**

125 A X'Pert PW 3040 PANalytical diffractometer (CuK α 1 radiation, step size = 0.014°, Johansson
126 monochromator with a Ge crystal cut on plane (111)) and the X'Pert Data Collector software
127 were used for the powder XRD measurements. The measurements were performed at room
128 temperature in the range between $5^\circ \leq 2\theta \leq 90^\circ$. Each sample was measured for 128 min. The
129 patterns were analysed qualitatively using PowderCell version 2.4 by comparing the measured
130 peaks visually with the powder patterns for calcite (Maslen et al. 1993) and fluorite (Batchelder
131 et al. 1964) from the Pearson's Crystal database. The fraction of fluorite present in each sample
132 (α) was determined using Rietveld refinements performed with the EdPCR program of the
133 FullProf Suite (version 2.05) and the above mentioned crystal structure data as starting
134 structures.

135 **Calculation of kinetic parameters using complementary methods**

136 The kinetic description of the replacement reaction was made by determining the empirical
137 activation energy (E_a), the pre-exponential factor (A), and the reaction model (more detailed
138 description below). The kinetic parameters of the replacement of calcite by fluorite in a 4 M
139 ammonium fluoride solution were empirically determined by the complementary use of model-
140 fitting and model-free (isoconversional) methods described by Khawam and Flanagan (2005a).
141 The model-free method permitted the calculation of E_a , and a statistical comparison with the E_a
142 values obtained in the model-fitting method permitted the determination of the best fitting
143 reaction model and a value of the pre-exponential factor A .

144 The main difference between these model-fitting and the model-free methods is that the first
145 averages the activation energy over the whole reaction (i.e. it assumes that E_a does not change
146 with time) and the second calculates the activation energy for different extents of reaction. Both
147 methods are based on measuring the amount of fluorite formed as a function of time during
148 isothermal runs at different temperatures (in this case 60, 80, 100, 140 °C). The model-free
149 method allows the calculation of E_a independent of the choice of rate equation and is able to
150 determine if the activation energy varies with the reaction progress (Khawam and Flanagan
151 2005a, 2005b; Hancock and Sharp 1972; Putnis 1992).

152 **Model-fitting method.** In this method the experimental data were fitted to a number of
153 different rate equations (Table 2) to calculate the activation energy (E_a) of the reaction. The
154 goodness of fit of the models was evaluated using the correlation coefficient (r). The
155 mathematical basis of these models can be found in Khawam (2007). The general form of the
156 rate equations is the integral rate law,

157 $g(\alpha) = kt.$ (1)

158 Where α is the fraction of fluorite formed, k (min^{-1}) is the rate constant, and t is the time in
159 minutes. The reaction rate constants (k) are obtained from the slope of the plot of $g(\alpha)$ against the
160 reaction time (t) from equation (1) for each of the four isothermal experiments (performed at 40,
161 60, 80, and 140 °C). E_a was calculated using each of the models listed in Table 2, from the slope
162 of the plot of $\ln k$ against $1/T$ from the natural logarithmic of the Arrhenius equation:

$$163 \quad k = A e^{\left(\frac{E_a}{RT}\right)} \Leftrightarrow \ln k = \ln A - \left(\frac{E_a}{RT}\right). \quad (2)$$

164 Where A (min^{-1}) is the pre-exponential factor (also known as the frequency factor), R is the gas
165 constant (8.341 J/molK), and T is the temperature in K.

166 Additionally, from all fitted models there is one (model An, Table 2), that allows the calculation
167 of an n-value (or Avrami exponent) for each of the isothermal experiments. The value of n has
168 been used to infer a reaction mechanism for solid-state reactions from kinetic data (Hancock and
169 Sharp 1972) and has also been used to infer the mechanism of a replacement reaction (Kasiopas
170 et al. 2010, and references therein). It is calculated from the slope of the plot of $-\ln \ln (1 - \alpha)$
171 against \ln time (details of this method are given in Putnis 1992).

172 **Model-free (isoconversional) method.** In the model-free method E_a values are
173 calculated for different degrees of replacement. The time (t) needed for certain fractions of
174 fluorite to form (we chose $0.01 \leq \alpha \leq 0.99$, with steps of 0.01) were interpolated from the
175 experimental data. In the second step, the Arrhenius equation was substituted in eq. 1 giving,

$$176 \quad g(\alpha) = A e^{\left(\frac{E_a}{RT}\right)} t. \quad (3)$$

177 The natural logarithmic of eq. (3) gives eq. (4),

178
$$-\ln t = \ln \left(\frac{A}{g(\alpha)} \right) - \frac{E_a}{RT} \quad (4)$$

179 E_a values are obtained from the slope of the plot of $-\ln t$ as a function of $1/T$ (in $1/K$). This
180 method does not allow the direct calculation of A (Khawam and Flanagan 2005a). A slightly
181 different formulation of equation 4 is given in Putnis (1992) where the determination of E_a ,
182 independent of the choice of rate equation, is termed the “time to a given fraction” method.

183 **Scanning Electron Microscopy (SEM)**

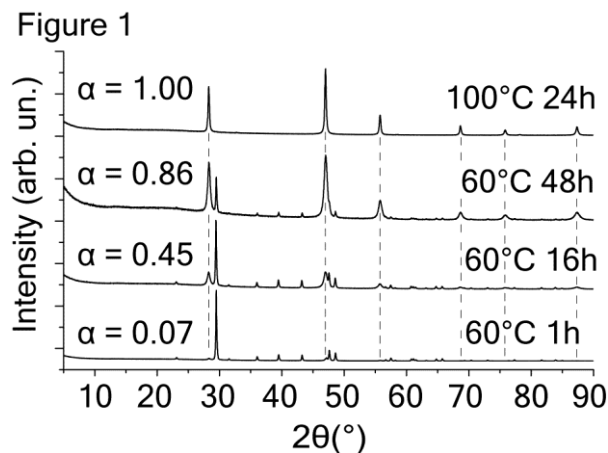
184 For visualization of the replacement microstructures and reaction rims, two sample treatments
185 were made using the previously reacted cubes. A group of samples was sectioned through the
186 center, mounted in epoxy resin, and polished. Other samples were sectioned in different
187 directions and glued onto a glass slide (no polishing was made). All samples were C-coated for
188 imaging in a SEM (JEOL JSM-6610LV) equipped with energy-dispersive X-ray analysis (EDX),
189 and secondary and electron backscattered detectors.

190 **Results**

191 **X-ray diffraction (XRD) analysis**

192 XRD confirmed that the calcium carbonate rock samples were partially transformed into fluorite
193 during the reactions with ammonium fluoride (NH_4F) solutions. The peaks of all powder patterns
194 were identified as either calcite or fluorite. With increasing reaction times the intensity of the

195 calcite peaks decreased whilst the intensity of fluorite peaks increased (e.g. Fig. 1).



196

197 **Figure 1.** X-ray powder diffraction patterns showing the evolution of the parent and product

198 phases from samples reacted at different reaction times and temperatures. The tracing indicates

199 fluorite characteristic peak positions. The fraction of fluorite formed (α) was determined from

200 Rietveld analysis.

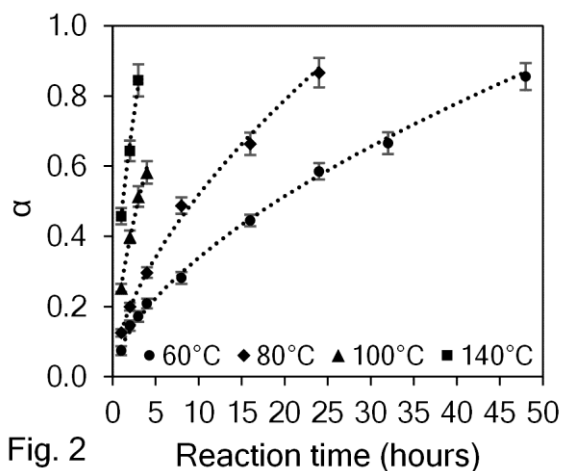
201

202 The fractions of calcite and fluorite in each sample were obtained from Rietveld refinements

203 (Table 3). The fractions of fluorite formed (α) are plotted against the reaction time for each of the

204 isothermal experiments (Fig. 2).

205



206

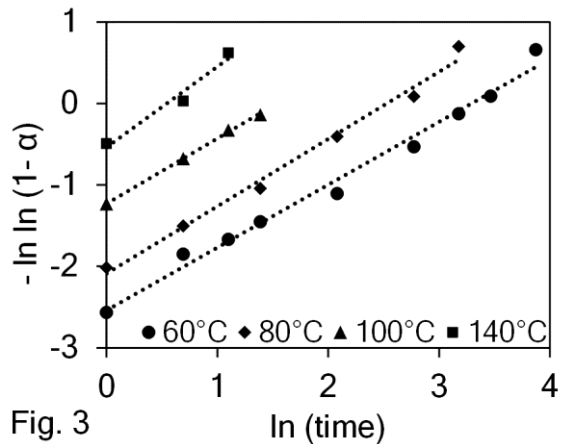
207 **Figure 2.** Calculated fraction of fluorite formed (α), determined from the Rietveld refinements of
 208 X-ray powder diffraction patterns of the mineral products resulting from the hydrothermal
 209 experiments. The fitted lines are non-modelistic power law equations and were used for the
 210 model-free (isoconversional) method.

211

212 Kinetic analysis

213 **Calculation of activation energy (model-fitting method).** With this method an
 214 activation energy E_a was obtained from each model (Table 4). The E_a calculated with the
 215 different models gave very similar results varying between 32 and 46 kJ/mol. Several models
 216 had equivalent fitting coefficients (goodness of fit). If a most appropriate model was to be
 217 selected using the goodness of fit, model D1 would be selected yielding an empirical activation
 218 energy for the reaction of 41 kJ/mol.

219 From model An, ln-ln graphs were constructed for each of the isothermal experiments (Fig. 3).
 220 The slopes of the graphs were 0.77, 0.82, 0.80 and 0.99 for the isothermal experiments
 221 performed at 60, 80, 100 and 140 °C, respectively.



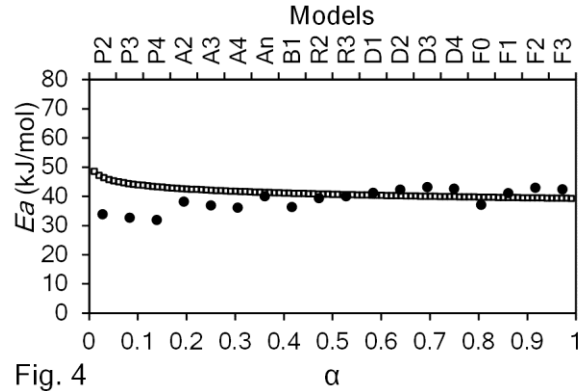
222

223 **Figure 3.** The plot of $-\ln \ln (1-\alpha)$ vs $\ln(\text{time})$ for the replacement of calcite by fluorite that yield
 224 n values of 0.77 (60°C), 0.82 (80°C), 0.80 (100°C) and 0.99 (140°C).

225

226 **Calculation of activation energy (model-free method).** With the model-free method the
 227 E_a values were calculated for different fractions of replacement ($0.01 \leq \alpha \leq 0.99$). The
 228 extrapolation of the time to the given fractions (α) was made using the trend-lines of the α – time
 229 plots shown in Figure 2.

230 The E_a values (Fig. 4) vary between 39 and 49 kJ/mol, however 50 % of this variation occurs at
 231 very low fractions of fluorite formed ($\alpha < 0.1$). This result is most probably an artifact and is
 232 discussed later. For the fraction of fluorite formed between 0.10 and 0.99 E_a averaged 41(1)
 233 kJ/mol.



234

235 **Figure 4.** Activation energies (E_a) for the replacement reaction calculated by: (**empty squares**)
 236 the model-free method; (**circles**) the model-fitting method. Several E_a values of the model-fitting
 237 method intersect the E_a values of the model-free method.

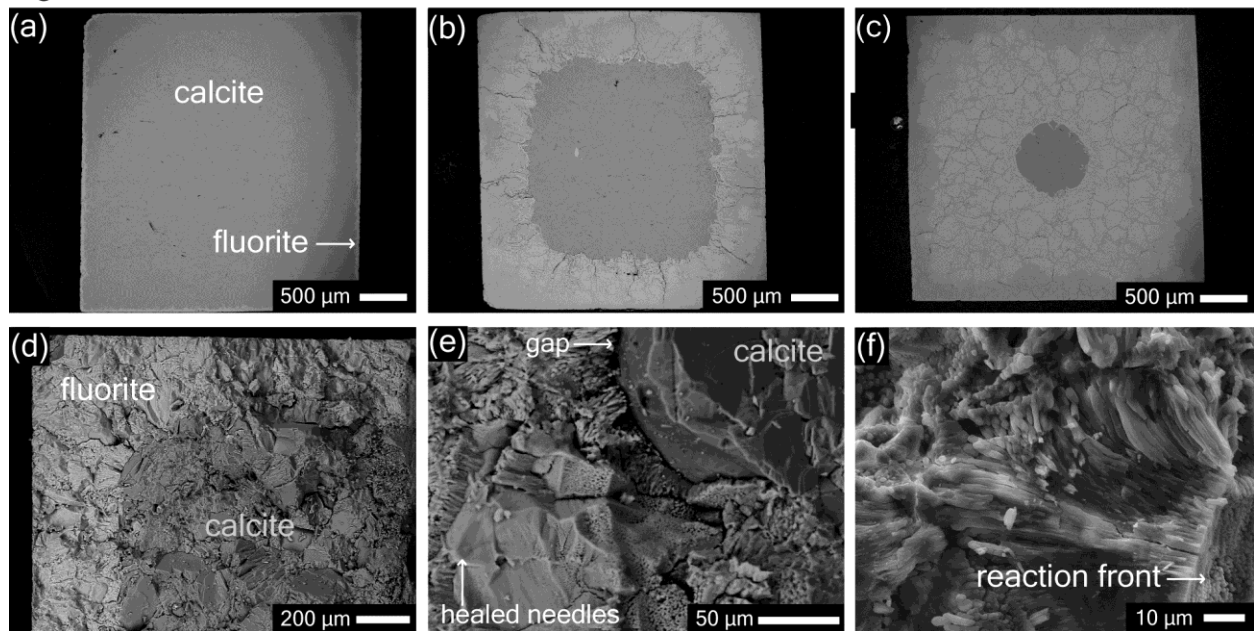
238

239 **Microstructural observations**

240 Hydrothermal treatment of the marble cubes produced perfect pseudomorphs, as measured from
 241 the external dimensions of the reacted cubes. SEM analysis (Fig. 5a to 5e) shows the sharp
 242 interface between the unreacted marble and the replacement product (fluorite). The replacement
 243 reaction occurred homogeneously from the surface of the cubes into the center of the samples
 244 (Fig. 5a to 5c). All samples showed very small amounts of fluorite precipitation adjacent to grain
 245 boundaries ahead of the main reaction front (Fig. 5a to 5b). There is preservation of the grain
 246 boundaries as can be seen in Fig. 5c. The marble and the fluorite have such similar morphologies
 247 that they are almost indistinguishable at low magnification (Fig. 5d). At higher magnifications,
 248 porosity of different sizes is seen in the fluorite rim (Fig. 5e). The pre-existent porosity present in
 249 the marble (mostly grain boundaries) conferred a complex crystal microstructure to the newly
 250 formed product phase (Fig. 5d, e, f). Overall the fluorite rim is composed of differently shaped
 251 grains and the crystals of fluorite exhibit a needle-like morphology (Fig. 5e, f). Fluorite needles

252 do not seem to have any preferred orientation, with the exception of the reaction front, where
253 they are mostly oriented perpendicular to it (Fig. 5f). Away from the reaction front, in many
254 cases the fluorite crystals have healed (Fig. 5e), possibly related to the surface of the previous
255 marble grains. This will be discussed more in the next section. A very small gap that is common
256 to replacement reactions (Putnis 2009; Xia et al. 2009; Kasioptas et al. 2011) appears at the
257 interface between the marble and fluorite (Fig. 5e) and has a variable size of 1.0(4) μm . There is
258 a possibility that the gap could have formed or been widened during the quenching process.
259 SEM-EDX analysis revealed that the low Mg content in the original marble (~ 0.3 wt%) was not
260 included in the product phase (fluorite) crystal structure, but detected inside the pore spaces,
261 where it probably precipitated (as any phase that includes Mg^{2+} , F^- , Na^+ , and/or CO_3^{2-}) from
262 remnant solution remaining in the pores after the reacted samples were cooled.

Figure 5



263
264 **Figure 5.** Images of cross-sections of cubes of Carrara marble reacted with a 4 M NH_4F solution:
265 **a)** for 1 hour at 60 °C; **b)** for 48 hours at 60 °C; **c)** for 4 hours at 140 °C; **d), e),** and **f)** for 16
266 hours at 60 °C. All are BSE images with exception of f) that is SE.

267 **Fluid changes after reaction**

268 After all experiments, the pH of the fluids showed slight increases (Table 3). The increase of the
269 pH was higher for higher reaction times. This is most probably related to the release of
270 carbonates from the dissolution of calcite into the fluid phase. Calcium concentrations in the
271 fluid after experiments were always lower than 0.5 ppm, corresponding to a maximum mass
272 fraction $\text{Ca}_{\text{fluid}}/\text{Ca}_{\text{sample}}$ of 0.0001.

273 **The development of porosity**

274 The development of porosity is an important characteristic of pseudomorphic replacement
275 reactions (Putnis and Mezger 2004; Putnis et al. 2005). The amount of porosity formed in the
276 samples can be calculated from the difference between the expected molar mass change if no
277 porosity was formed and the actual mass change occurring in the samples. The calculated
278 porosity (Table 3) correlates linearly ($R^2 = 98.9\%$) with the fraction of fluorite formed measured
279 with XRD. From this correlation ($\alpha [\%] = 6.2736 \times \text{porosity} [\%] - 97.852$) the calculated
280 porosity for a fully reacted sample would be 31.5 %.

281 **Discussion**

282 In all hydrothermal experiments, known size cubes of Carrara marble (almost pure CaCO_3) were
283 pseudomorphically replaced by fluorite (CaF_2). The degree of reaction was dependent on
284 reaction time and temperature. The general equation that governs the replacement of calcite by
285 fluorite can be written as, $\text{CaCO}_3 (\text{s}) + 2 \text{F}^- (\text{aq}) \leftrightarrow \text{CaF}_2 (\text{s}) + \text{CO}_3^{2-} (\text{aq})$.

286 **Kinetic analysis**

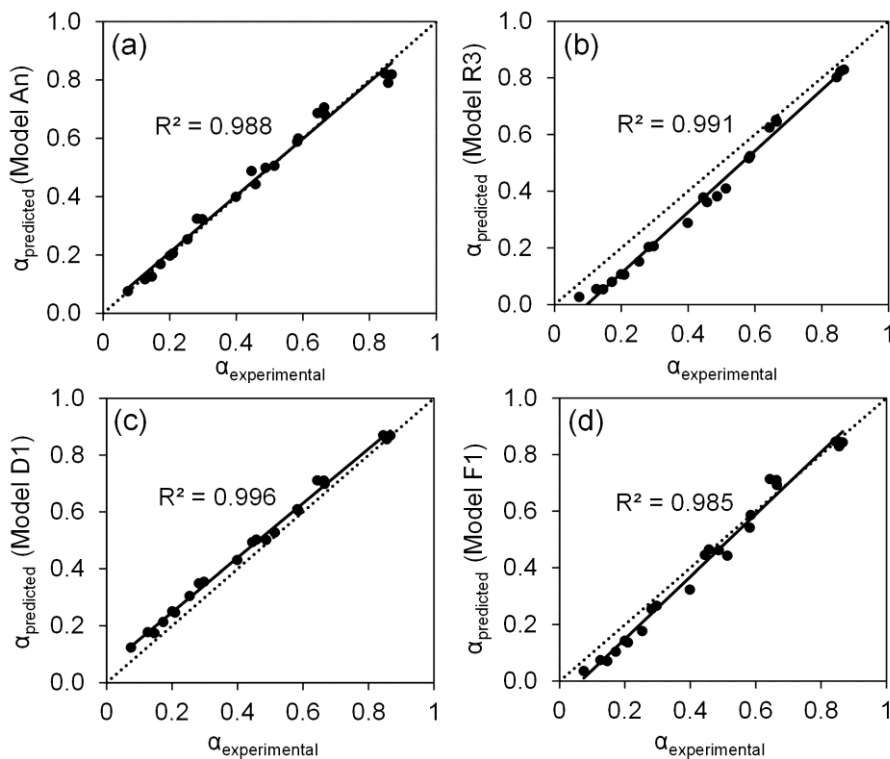
287 **Activation energy from complementary methods.** In this study we used the
288 complementary method proposed by Kawam and Flanagan (2005b) to calculate the activation

289 energy of the replacement reaction. In this method, the most accurate activation energy is the one
290 calculated using the isoconversional (model-free) method and the best model should be the one
291 that results in an activation energy equal to the activation energy calculated with the model-free
292 method.

293 Activation energies calculated from the model-fitting method were very similar (32 to 46
294 kJ/mol). In this case, a statistical approach can be used (see next section) to select the best model
295 from the set of best models that resulted in the same E_a as in the model-free method (Khawam
296 and Flanagan 2005a). The model-free method resulted in an average activation energy of 41(1)
297 kJ/mol for fractions of fluorite (α) above 0.1. For $\alpha < 0.1$ the shape of the model-free
298 (isoconversional) plot (Fig. 4) is consistent with the shape of isoconversional plots of simulations
299 to which small time error shifts (minute-scale) were added (Kawam and Flanagan 2005b),
300 suggesting that the variation is an artifact, possibly caused by the experimental time being
301 controlled on an hour-scale.

302 **Selection of the best model.** Several models (An, R3, D1, and F1) resulted in an E_a
303 (Table 4) equal (41 ± 1 kJ/mol) to that calculated using the model-fitting method (Fig. 4). To
304 evaluate which is the most accurate of the five models, the fraction of fluorite formed (α) was
305 predicted with each of the four model equations. The model that results in the lowest standard
306 error of the estimate (σ_{est}) and lowest bias is considered the best model. Plots of model-predicted
307 versus experimental α values are shown in Fig. 6a to 6d. The model An (Table 2) resulted in the
308 lowest fit ($R^2= 98.8$ %), but had the lowest σ_{est} and the best accuracy (zero bias), therefore it
309 could have been considered the best model (Fig. 6a). However, the model contains a circular
310 argument because it includes n-values that were calculated from the experimental data (from the
311 slope of the graphs in Fig. 3), justifying its accuracy. The second best linear fit ($R^2= 99.1$ %) was

312 made using model R3 (Fig. 6b) but it had a σ_{est} of 0.08, and a negative bias of 50 %, which
 313 means this model could predict well between samples reacted for different reaction times, but the
 314 absolute values could be underestimated by an average of 50 %, making this the least appropriate
 315 model. The most accurate model is D1 with predictions that fitted the experimental data with R^2
 316 of 99.6 %, a σ_{est} of 0.04 and a positive bias of 12 % (Fig. 6c). Model F1 (Fig. 6d) could not be
 317 considered the best model because it had a lower fit (98.5 %), a slightly lower σ_{est} , and a higher
 318 bias (34 %) than that of model D1. The diffusion model D1 is the model of choice for the
 319 replacement of Carrara marble by fluorite, yielding an activation energy of 41 kJ/mol, the same
 320 E_a calculated using the model-free method (for $\alpha > 0.1$), and an A of 732 min^{-1} , resulting in an
 321 integral rate law equation equal to $\alpha^2 = 732e^{(-41/RT)t}$.



322

323 **Figure 6.** Model predicted ($\alpha_{\text{predicted}}$) against measured fractions of fluorite formed ($\alpha_{\text{experimental}}$) in
 324 the experiments: **a)** model An; **b)** model R3; **c)** model D1; **d)** model F1.

325

326 **The Avrami exponential (n-value).** If the mechanism of the reaction is the same for
327 experiments at different temperatures, then they should be characterized by a constant n-value,
328 and if the n-value changes then the rate-controlling kinetic mechanism could have changed
329 (Avrami 1939). Results show very close n-values (0.77, 0.82, and 0.80) for the isothermal
330 experiments carried out at 60, 80, and 100 °C, and these n-values stand between those that
331 Hancock and Sharp (1972) interpreted as being diffusion and first-order kinetic controlled
332 processes. For the 140 °C experiment the higher n-value (0.99) approximates mostly to a first-
333 order kinetic controlled process (Hancock and Sharp 1972). Kasiopas et al. (2010) obtained
334 similar n-values for the replacement of aragonite by apatite under mild hydrothermal conditions
335 and interpreted the combination of these processes as being related to a control of the interfacial
336 reaction. Results from Hancock and Sharp (1972) are based on kinetic studies of solid-state
337 transformations and here we are investigating a fluid-mediated replacement reaction. Therefore
338 we also interpret our results as interfacial reaction controlled, limited by the diffusion of ions
339 through the fluid phase.

340 **Experimental variation.** For the determination of the reaction kinetics, potential
341 experimental variables were held constant (as far as possible) so that any variation was solely
342 due to the temperature change. In our study, the sources of experimental variation could have
343 been due to the slight differences in the size of the samples (3 % variation) and their
344 characteristic internal morphology, and variability in grain sizes (Carrara marble has grains of ~
345 150 µm). The use of identical synthetic calcite samples could avoid such variations, however in
346 this study we wanted to relate as much as possible to natural systems. The reactions were
347 repeated for reproducibility and similar results were obtained.

348 **Replacement reaction mechanism**

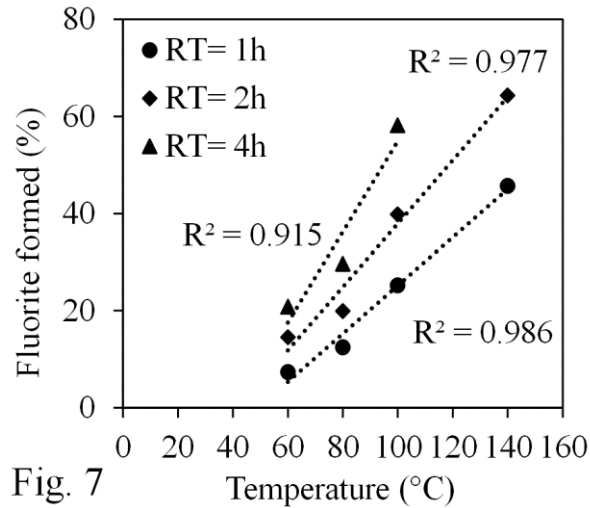
349 Microscopic observations showing pseudomorphism, sharp interfaces between parent and
350 product phases and the generation of porosity, all indicate that the replacement of the Carrara
351 marble by fluorite occurs via an interface-coupled dissolution-precipitation process (Putnis 2009;
352 Putnis and Putnis 2007). The replacement occurs by the coupling of dissolution and precipitation
353 at the reaction interface resulting in the formation of porosity within the newly formed phase. As
354 the reaction moves further into the parent phase, mass transport through the pores in the product
355 becomes an increasingly important factor. Xia et al (2009) suggested that a sharp and narrow
356 (micrometer scale) interface, between reacted and unreacted solids as observed here, suggests
357 that the dissolution of the parent phase is the rate-determining step. However, a decrease in the
358 rate of dissolution might as well be related to the time that ions take to travel through the pores to
359 reach the reaction interface, creating the compositional conditions for further dissolution and
360 precipitation (further discussion below).

361 The successful transformation of calcium carbonate by fluorite using NH_4F solutions has been
362 reported before (Baer and Lewin 1970), and also using HF (Glover and Sippel 1962), NaF
363 (Trautz and Zapanta 1961; Ames 1961), and NH_4HF_2 (Trautz and Zapanta 1961). The
364 precipitation of fluorite at a mineral-fluid boundary layer, enriched in dissolved calcite ions, was
365 also observed by Godinho et al. (2014). The replacement mechanism involves the dissolution of
366 calcite and the precipitation of fluorite. In order to maintain external volume (pseudomorphic
367 replacement), the rate of dissolution must equal the rate of precipitation and this can only be
368 achieved when the reactions are coupled at the parent mineral-fluid interface. As soon as the
369 calcite begins to dissolve in the presence of the F-bearing solution (undersaturated with respect
370 to fluorite), Ca^{2+} ions are released to the solution at the mineral-fluid interface. Immediately this

371 boundary layer fluid becomes supersaturated with respect to the new phase, fluorite, which
372 precipitates. The molar volume of fluorite ($V_m = 24.5 \text{ cm}^3/\text{mol}$) is lower than that of calcite ($V_m =$
373 $36.9 \text{ cm}^3/\text{mol}$). The result is a volume deficit reaction, shown in the high porosity in the fluorite
374 product phase. The formation of an interconnected porosity (permeability) in the product phase
375 enables the solution to penetrate the previously solid parent calcite and so the reaction is able to
376 continue at a moving interface within the rock. The replacement of pure calcite by fluorite
377 corresponds to a molar volume reduction of 33.5 %. This corresponds to the minimum porosity
378 expected in a fully replaced sample of pure calcite. The porosity calculated here for a
379 hypothetical fully reacted sample was slightly lower (31.5 %) but within estimation error. This
380 might indicate that the fluorite density of these samples was slightly lower than that of pure
381 crystalline fluorite, justifying its higher volume. The quantification of porosity will be the focus
382 of a further study. Besides molar volume changes, solubility differences between parent and
383 product phases can result in increased porosity in the product (Pollok et al. 2011). However, the
384 calcium content measured in the fluids after replacement of the marble by fluorite ($< 0.5 \text{ ppm}$),
385 was not in a significant amount for mass balance equations.

386 The large relative change between each isothermal reaction plot (α vs reaction time, Fig. 2)
387 reflects the high sensitivity of the replacement reaction to relatively narrow temperature
388 increases (60, 80, 100, and 140 °C). Thus, temperature is a major driving force for the reaction
389 and it correlates somewhat linearly to the replacement rates (Fig. 7).

390



391

392 **Figure 7.** Fluorite formed as a function of experimental temperatures for different reaction times.

393 The amount of fluorite formed approximates to a linear relationship with the increase in
 394 temperature.

395

396

397 Backscatter SEM images showed that the evolution of the main reaction front (or bulk reaction)

398 is very homogeneous (Fig. 5) forming an almost perfect sphere when it approaches the core of

399 the sample. Fluid movement through grain boundaries can have a significant impact on

400 replacement rates (Jonas et al. 2014), as grain boundaries are faster pathways for fast fluid

401 transport. However, it has also been shown that fast reaction rates can result in replacements that

402 proceed equally through grain boundaries and mineral grains (Pedrosa et al. 2016). In our

403 experiments, replacement reactions were fast (especially at higher temperatures) and only small

404 amounts of fluorite formed ahead of the reaction front next to grain boundaries and fractures, in

405 agreement with Pedrosa et al. (2016).

406 The tight interface ($\sim 1 \mu\text{m}$) between the parent and product phases shows that the degree of
407 coupling between the dissolution and precipitation is very high. From Xia et al. (2009) the
408 interpretation is that dissolution is the rate-controlling step. This results from the fact that if
409 dissolution is much faster than precipitation, the coupling between the two processes would be
410 lost, and thus, for a perfect pseudomorph to be formed, dissolution must be the rate-limiting step.
411 However if the rates of dissolution and precipitation are coupled and approximately equal, both
412 could be ultimately controlled by mass transport to and from the reaction interface. Dissolution
413 and precipitation rates are controlled by the saturation conditions of the interfacial fluid. It can be
414 assumed that the dissolution step is controlled by Ca^{2+} diffusion away from the dissolving calcite
415 surface and this can be caused by small concentration gradients at the narrow reaction front (~ 1
416 μm) caused by its consumption in the precipitation of fluorite (CaF_2). The precipitation of
417 fluorite is, in turn, controlled by the rate at which F^- arrives at the reaction interface, and may
418 control the overall reaction rate. The fact that a diffusion model best fitted the experimental data
419 from the calculated E_a suggests that it is effectively the overall mass transfer within the fluid
420 phase up to the reaction interface (as well as the reequilibration in the opposite direction in both
421 the fluid and solid phases) that dominates the replacement rate.

422 Results of the model-free method to calculate E_a suggest that the mechanism of replacement, and
423 hence the rate-controlling step did not change with the progress of reaction. Nevertheless, in all
424 isothermal experiments, the reaction rate slowed down with the progression of the reaction
425 (Table 3). This would be expected if the rate controlling step was diffusion, in which case the
426 rim thickness would vary as $t^{0.5}$ (Putnis and Mezger 2004). However, another possible cause of a
427 change in the kinetics could be due to morphology changes in the fluorite that affect the porosity.
428 Glover and Sippel (1962) showed that at the very early stages of replacement, the rate differs

429 from the rate after the reaction rim has formed and correlated it to the change in orientation of
430 the newly formed fluorite crystals. SEM images showed that the fluorite needle-like crystals are
431 oriented in many different directions, different from the reaction interface in which they are
432 oriented parallel, and also that the needles often have healed probably as the result of a
433 coarsening process. We hypothesize that this coarsening occurs at the outer edge of the replaced
434 grains, where the porosity is higher (more space for fluid passage) due to the presence of the
435 grain boundaries. This is consistent with textural equilibration where, as well as compositional
436 equilibration, simultaneously porosity begins to coarsen and then disappear in accordance with a
437 lowering of the energy state of the reaction product (Putnis et al. 2005). As soon as the outer
438 edge of the new fluorite grains is healed, no fluid can penetrate in that area leaving behind the
439 needle-like structure plus an impermeable outer surface, seen in Fig. 5e. The rim remained
440 permeable possibly because the grains did not heal completely. This process might have an
441 impact on the permeability of the rim, justifying the slower replacement rates for bigger
442 replacement rims.

443 Jonas et al. (2013) found that changes in the porosity during the replacement of calcite by apatite
444 resulted in kinetic data that could not be successfully fitted to Avrami rate equations. The smaller
445 difference in molar volumes, and hence porosity, and the higher reaction temperatures resulted in
446 more rapid textural equilibration in the reaction rims and hence greater variation in porosity. This
447 was reflected in changes in the rate controlling mechanism and hence activation energy during
448 the course of an isothermal reaction. In our case the consistent kinetics and the good fit between
449 the model-free and the model-dependent methods of determining activation energy suggest that
450 the overall mechanism of the replacement did not change as a function of temperature and time.

451 **Implications**

452 In this study we have determined the activation energy (E_a) for the replacement of calcite (as
453 Carrara marble) by fluorite in F-rich solutions. By comparing different reaction models with the
454 experimental kinetic data as a function of temperature, the best fit gave an activation energy, E_a
455 value of 41 ± 1 kJ/mol. The discussion of the rate-determining step for a coupled dissolution-
456 precipitation reaction has emphasized that dissolution, ion transport and precipitation cannot be
457 simply separated as independent sequential processes in that both dissolution and precipitation
458 depend on the fluid composition at the reaction interface. The conclusion that the overall
459 replacement process is dependent on mass transport through the porous product phase (fluorite)
460 is consistent with the determined value of E_a and the Avrami exponential n-value, and
461 emphasizes the importance of the porosity generation in mineral replacement processes. The
462 study provides data for future work on determining the mechanism of ion transport through
463 micropores, notably the recent discussions on the role of charge gradients in small pores in
464 enhancing transport by diffusioosmosis (Kar et al., 2016).

465 Environmental remediation is an important application of this replacement reaction. The study
466 contributes to the understanding of the mechanism involved in the use of calcite source materials
467 for the removal and/or recovery of fluoride from contaminated waters and wastewaters through
468 the formation of a more stable phase (fluorite). A high calcite surface area and higher
469 temperature will promote a faster replacement reaction and hence a more effective remediation
470 of F-contaminated waters. Moreover, other cations in solution can be captured during this
471 replacement due to the substitution for Ca^{2+} in the crystal structure of fluorite, such as the
472 immobilization of radioactive strontium (Ames, 1960). This replacement can be used as a model
473 system for understanding other geochemical reactions typically occurring in the Earth's crust,
474 such as the partitioning of rare earth elements in fluorite (Schwinn and Markl, 2005). On the

475 other hand, the replacement of calcite by fluorite results in the release of carbonate into the fluid
476 phase, affecting the local and/or global carbon cycle and therefore the redistribution of elements
477 in the Earth's crust.

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606

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Tables

608 **Table 1.** The solubility of calcite and fluorite in water and their saturation indices (SI) in 4 M
 609 NH₄F at 25 °C and at experimental temperatures (PHREEQC calculations).

Pure water			4 M NH ₄ F	
<i>T</i> (°C)	Calcite (log K)	Fluorite (log K)	Calcite (SI)	Fluorite (SI)
25	-8.5	-10.6	0.8	9.8
60	-8.8	-10.3	0.0	9.4
80	-9.0	-10.2	-0.5	9.2
100	-9.3	-10.2	-0.9	9.1
140	-10.0	-10.2	-1.4	8.9

610

611 **Table 2.** Reaction models employed to fit the empirical data (adapted from Khawam and
 612 Flanagan, 2005b).

Model	Integral Rate law $g(\alpha) = kt$
Nucleation and Growth	
Power-law (P2)	$\alpha^{\left(\frac{1}{2}\right)}$
Power-law (P3)	$\alpha^{\left(\frac{1}{3}\right)}$
Power-law (P4)	$\alpha^{\left(\frac{1}{4}\right)}$

Avrami Erofeev (A2)	$[-\ln(1-\alpha)]^{\frac{1}{2}}$
Avrami Erofeev (A3)	$[-\ln(1-\alpha)]^{\frac{1}{3}}$
Avrami Erofeev (A4)	$[-\ln(1-\alpha)]^{\frac{1}{4}}$
Avrami Erofeev (An)	$[-\ln(1-\alpha)]^{\frac{1}{n}}$
Prout–Tompkins (B1)	$\ln\left[\frac{\alpha}{1-\alpha}\right]$

Geometrical contraction

Contracting area (cylinder) (R2)	$[1-(1-\alpha)^{1/2}]$
Contracting volume (sphere) (R3)	$[1-(1-\alpha)^{1/3}]$

Diffusion

1-D diffusion (D1)	α^2
2-D diffusion (D2)	$[(1-\alpha)\ln(1-\alpha)] + \alpha$
3-D diffusion (D3)	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$
Ginstling–Brounshtein (D4)	$1-\left(\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$

Reaction-order

Zero-order (F0)	α
First-order (F1)	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^{-1} - 1$
Third-order (F3)	$0.5\left((1-\alpha)^{-2} - 1\right)$

613

614 **Table 3.** Results of the hydrothermal experiments including, the initial mass of the samples, its
615 mass change (%) after reaction, the porosity (%) calculated from the expected against actual
616 mass change, the percentage of fluorite in each sample, and the overall rate at which fluorite
617 formed in each experiment.

<i>T</i> (°C)	Reaction time (h)	<i>m</i> _{initial} (mg)	<i>m</i> _{decrease} (%)	pH _{final}	Porosity (%)	CaF ₂ (%)	Reaction rate (mg _{CaF2} /h)
60	1	76	1.7	8.1	16.2	7	7
60	2	76	3.3	8.2	17.6	15	7
60	3	73	4.0	8.3	18.2	17	6
60	4	73	5.1	8.3	19.1	21	5
60	8	73	6.3	8.4	20.1	28	4
60	16	76	9.3	8.6	22.7	45	3
60	24	76	11.7	8.7	24.7	59	2
60	32	76	13.2	8.7	26.0	67	2
60	48	76	15.9	8.8	28.3	86	2

80	1	76	2.9	8.1	17.2	13	13
80	2	76	5.2	8.4	19.2	20	10
80	4	76	6.7	8.5	20.5	30	7
80	8	71	10.4	8.6	23.7	49	6
80	16	76	13.4	8.7	26.2	66	4
80	24	76	16.3	8.8	28.7	87	4
100	1	76	5.5	8.4	19.5	25	25
100	2	76	9.0	8.5	22.4	40	20
100	3	73	11.0	8.6	24.2	51	17
100	4	68	12.6	8.6	25.5	58	15
140	1	74	10.0	8.5	23.3	46	46
140	2	75	13.7	8.7	26.4	64	32
140	3	76	16.6	8.8	29.0	84	28

618

619 **Table 4.** Calculated kinetic parameters (pre-exponential factor, A , and activation energy, E_a)
620 using the model-fitting method for the isothermal experiments performed in this study.

Model	A (min^{-1})	E_a (kJ/mol)	r^a
P2	4.88×10^1	34	0.9721
P3	2.46×10^1	33	0.9637
P4	1.58×10^1	32	0.9590
A2	3.65×10^2	38	0.9911 ^b

A3	1.67×10^2	37	0.9860
A4	1.01×10^2	36	0.9824
An ^d	7.29×10^4	40	0.9925 ^b
B1	6.88×10^2	36	0.9814
R2	2.99×10^2	39	0.9952 ^b
R3 ^d	2.86×10^2	40	0.9949
D1 ^{c,d}	7.32×10^2	41	0.9968 ^b
D2	8.06×10^2	42	0.9897
D3	3.96×10^2	43	0.9732
D4	2.38×10^2	43	0.9848
F0	1.88×10^2	37	0.9895
F1 ^d	1.69×10^3	41	0.9906 ^b
F2	8.60×10^3	43	0.9530
F3	2.37×10^4	42	0.9073

621 a) Correlation coefficient $g(\alpha)$ vs t (min).

622 b) Equivalent models based on goodness of fit.

623 c) Model selected based on model-fitting method.

624 d) Models that E_a resulted to be equal to the E_a calculated with the model-free method (41(1)

625 kJ/mol).