Revision 3 **The replacement of a carbonate rock by fluorite: kinetics and microstructure**

Elisabete Trindade Pedrosa[1], Lena Boeck[1], Christine V. Putnis[1,2], Andrew Putnis[1,3]

[1]Institut für Mineralogie, University of Münster, Corrensstrasse 24, 48149 Münster, Germany
[2]Department of Chemistry, Curtin University, 6845 Perth, Australia
[3]The Institute for Geoscience Research (TIGeR), Curtin University, 6845 Perth, Australia

Abstract

Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has application in Earth sciences and engineering. Samples of Carrara marble were reacted with an ammonium fluoride (NH_4F) solution for different reaction times and temperatures. The microstructure of the product phase (fluorite) was analyzed using SEM. The kinetics of replacement was monitored using Rietveld analysis of X-ray powder diffraction patterns of the products. After reaction, all samples preserved their size and external morphology (a pseudomorphic replacement). The grain boundaries of the original marble were preserved although each calcite grain was replaced by multiple fine crystals of fluorite creating inter-crystal porosity. The empirical activation energy E_a (kJ/mol) of the replacement reaction was determined by both model-fitting and model-free methods. The isoconversional method yielded an empirical activation energy of 41 kJ/mol, and a statistical approach applied to the model-fitting method revealed that the replacement of Carrara marble by fluorite is better fitted to a diffusion-controlled process. These results suggest that the replacement reaction is dependent on the ion diffusion rate in the fluid phase through the newly formed porosity.

Keywords: Calcite, fluorite, replacement, dissolution-precipitation, kinetics, porosity

Introduction

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

Replacement reactions are complex reactions controlled by at least three reaction steps: dissolution, mass transfer (including fluid migration through a porous solid phase and element diffusion through a fluid phase) and precipitation (including nucleation and growth). The kinetics of replacement reactions is dependent on the contribution of each of these steps and these may vary during the progression of the reaction. The overall reaction rate is generally dependent on the slowest of these reaction steps. The temperature dependence of the reaction rate is referred to as the empirical activation energy (E_a), without specific reference to the overall rate-controlling step.

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

In this paper we describe the replacement of calcite (Carrara marble) by fluorite (CaF_2). Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has applications in both Earth sciences and engineering. Fluorite (CaF_2) occurs naturally in many types of rocks (igneous, sedimentary, and metamorphic) and its origin is commonly associated with hydrothermal fluids (e.g. Richardson and Holland 1979; Toft 1986; Gagnon 2003; Schwinn and Markl 2005; Pradesh 2013). Fluorite pseudomorphs after calcite are not uncommon in nature as evidenced in museum collections (e.g. from Chihuahua, Mexico). Fluorite is an important industrial mineral. It is used in a wide variety of chemical, metallurgical and ceramic processes. An environmentally important example is the mechanism of interaction of carbonates with fluoride ions in drinking water. Fluoride has been added to town water supplies since the 1950s in Europe, the USA and Australia with the aim of reducing tooth decay. This replacement process results in a hardened surface of fluorapatite at the enamel (apatite) surface of the tooth (Pasteris and Ding 2009). According to the World Health Organization (WHO 2011), fluoride ingestion (through drinking water or a combination with other sources, such as fluoridated toothpaste) gives significant beneficial health effects at low concentrations, but at excessive exposure can result in adverse effects, such as dental and skeletal fluorosis. The WHO (2011) recommends a guideline of a maximum fluoride content of 1.5 mg/L for drinking water. Excessive fluoride exposure has been reported for many years and for a large number of developed and developing countries (Ghosh et al. 2013). This excess results from the accumulation of fluoride in groundwater (principal source of drinking water) from a number of different sources (e.g. fertilizer emission and mineral weathering) depending on the location (Brindha and Elango 2011). Calcite grains have been used as seed material in chemical reactors for the sequestration of fluoride from contaminated waters and wastewaters (Simonsson 1979; Yang et al. 1999; Turner et al. 2005; Aldaco et al. 2007), representing a direct application of the replacement of calcite by fluorite.

The aim of the present work is to investigate the kinetics of the replacement of calcium carbonate by fluorite as well as to understand better the mechanism of replacement reactions in general. Carrara marble was chosen as the parent material due to its high purity in calcium carbonate and its uniform grain-size allowing grain-boundary fluid migration to be observed within the experimental sample size. The kinetics of replacement was determined from the amount of fluorite formed as a function of temperature and reaction time, as determined from the Rietveld analysis of X-ray powder diffraction (XRD) patterns. Morphological characteristics of the product phase (studied by scanning electron microscopy, SEM) complement this study.

Materials and Methods

Starting material

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

Solubilities of calcite and fluorite at experimental conditions

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

Hydrothermal experiments

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

X-ray diffraction (XRD)

A X'Pert PW 3040 PANalytical diffractometer (CuKα1 radiation, step size = 0.014°, Johannson monochromator with a Ge crystal cut on plane (111)) and the X'Pert Data Collector software were used for the powder XRD measurements. The measurements were performed at room temperature in the range between $5° \leq 2\theta \leq 90°$. Each sample was measured for 128 min. The patterns were analysed qualitatively using PowderCell version 2.4 by comparing the measured peaks visually with the powder patterns for calcite (Maslen et al. 1993) and fluorite (Batchelder et al. 1964) from the Pearson's Crystal database. The fraction of fluorite present in each sample (α) was determined using Rietveld refinements performed with the EdPCR program of the FullProf Suite (version 2.05) and the above mentioned crystal structure data as starting structures.

Calculation of kinetic parameters using complementary methods

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

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

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

$$g(\alpha) = kt. \tag{1}$$

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

$$k = A\mathrm{e}^{\left(-\frac{Ea}{RT}\right)} \Leftrightarrow \ln k = \ln A - \left(\frac{Ea}{RT}\right). \tag{2}$$

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

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

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

$$\mathrm{g}(\alpha) = Ae^{\left(-\frac{Ea}{RT}\right)}t. \tag{3}$$

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

$$-\ln t = \ln\left(\frac{A}{g(\alpha)}\right) - \frac{Ea}{RT} \tag{4}$$

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

Scanning Electron Microscopy (SEM)

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

Results

X-ray diffraction (XRD) analysis

XRD confirmed that the calcium carbonate rock samples were partially transformed into fluorite during the reactions with ammonium fluoride (NH_4F) solutions. The peaks of all powder patterns were identified as either calcite or fluorite. With increasing reaction times the intensity of the calcite peaks decreased whilst the intensity of fluorite peaks increased (e.g. Fig. 1).

The fractions of calcite and fluorite in each sample were obtained from Rietveld refinements (Table 3). The fractions of fluorite formed (α) are plotted against the reaction time for each of the isothermal experiments (Fig. 2).

Kinetic analysis

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

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

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

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

Microstructural observations

Hydrothermal treatment of the marble cubes produced perfect pseudomorphs, as measured from the external dimensions of the reacted cubes. SEM analysis (Fig. 5a to 5e) shows the sharp interface between the unreacted marble and the replacement product (fluorite). The replacement reaction occurred homogeneously from the surface of the cubes into the center of the samples (Fig. 5a to 5c). All samples showed very small amounts of fluorite precipitation adjacent to grain boundaries ahead of the main reaction front (Fig. 5a to 5b). There is preservation of the grain boundaries as can be seen in Fig. 5c. The marble and the fluorite have such similar morphologies that they are almost indistinguishable at low magnification (Fig. 5d). At higher magnifications, porosity of different sizes is seen in the fluorite rim (Fig. 5e). The pre-existent porosity present in the marble (mostly grain boundaries) conferred a complex crystal microstructure to the newly formed product phase (Fig. 5d, e, f). Overall the fluorite rim is composed of differently shaped grains and the crystals of fluorite exhibit a needle-like morphology (Fig. 5e, f). Fluorite needles do not seem to have any preferred orientation, with the exception of the reaction front, where they are mostly oriented perpendicular to it (Fig. 5f). Away from the reaction front, in many cases the fluorite crystals have healed (Fig. 5e), possibly related to the surface of the previous marble grains. This will be discussed more in the next section. A very small gap that is common to replacement reactions (Putnis 2009; Xia et al. 2009; Kasioptas et al. 2011) appears at the interface between the marble and fluorite (Fig. 5e) and has a variable size of 1.0(4) µm. There is a possibility that the gap could have formed or been widened during the quenching process. SEM-EDX analysis revealed that the low Mg content in the original marble (~ 0.3 wt%) was not included in the product phase (fluorite) crystal structure, but detected inside the pore spaces, where it probably precipitated (as any phase that includes Mg^{2+}, F^{-}, Na^{+}, and/or CO_3^{2-}) from remnant solution remaining in the pores after the reacted samples were cooled.

Fluid changes after reaction

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

The development of porosity

The development of porosity is an important characteristic of pseudomorphic replacement reactions (Putnis and Mezger 2004; Putnis et al. 2005). The amount of porosity formed in the samples can be calculated from the difference between the expected molar mass change if no porosity was formed and the actual mass change occurring in the samples. The calculated porosity (Table 3) correlates linearly (R^2= 98.9 %) with the fraction of fluorite formed measured with XRD. From this correlation (α [%] = 6.2736 × porosity [%] – 97.852) the calculated porosity for a fully reacted sample would be 31.5 %.

Discussion

In all hydrothermal experiments, known size cubes of Carrara marble (almost pure $CaCO_3$) were pseudomorphically replaced by fluorite (CaF_2). The degree of reaction was dependent on reaction time and temperature. The general equation that governs the replacement of calcite by fluorite can be written as, $CaCO_3\ (s) + 2\ F^-\ (aq) \leftrightarrow CaF_2\ (s) + CO_3^{2-}\ (aq)$.

Kinetic analysis

Activation energy from complementary methods. In this study we used the complementary method proposed by Kawam and Flanagan (2005b) to calculate the activation energy of the replacement reaction. In this method, the most accurate activation energy is the one calculated using the isoconversional (model-free) method and the best model should be the one that results in an activation energy equal to the activation energy calculated with the model-free method.

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

Selection of the best model. Several models (An, R3, D1, and F1) resulted in an E_a (Table 4) equal (41 ± 1 kJ/mol) to that calculated using the model-fitting method (Fig. 4). To evaluate which is the most accurate of the five models, the fraction of fluorite formed (α) was predicted with each of the four model equations. The model that results in the lowest standard error of the estimate (σ_{est}) and lowest bias is considered the best model. Plots of model-predicted versus experimental α values are shown in Fig. 6a to 6d. The model An (Table 2) resulted in the lowest fit (R^2= 98.8 %), but had the lowest σ_{est} and the best accuracy (zero bias), therefore it could have been considered the best model (Fig. 6a). However, the model contains a circular argument because it includes n-values that were calculated from the experimental data (from the slope of the graphs in Fig. 3), justifying its accuracy. The second best linear fit (R^2= 99.1 %) was made using model R3 (Fig. 6b) but it had a σ_{est} of 0.08, and a negative bias of 50 %, which means this model could predict well between samples reacted for different reaction times, but the absolute values could be underestimated by an average of 50 %, making this the least appropriate model. The most accurate model is D1 with predictions that fitted the experimental data with R^2 of 99.6 %, a σ_{est} of 0.04 and a positive bias of 12 % (Fig. 6c). Model F1 (Fig. 6d) could not be considered the best model because it had a lower fit (98.5 %), a slightly lower σ_{est}, and a higher bias (34 %) than that of model D1. The diffusion model D1 is the model of choice for the replacement of Carrara marble by fluorite, yielding an activation energy of 41 kJ/mol, the same E_a calculated using the model-free method (for $\alpha > 0.1$), and an A of 732 min^{-1}, resulting in an integral rate law equation equal to $\alpha^2 = 732e^{(-41/RT)}t$.

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

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

Replacement reaction mechanism

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

The successful transformation of calcium carbonate by fluorite using NH_4F solutions has been reported before (Baer and Lewin 1970), and also using HF (Glover and Sippel 1962), NaF

(Trautz and Zapanta 1961; Ames 1961), and NH_4HF_2 (Trautz and Zapanta 1961). The precipitation of fluorite at a mineral-fluid boundary layer, enriched in dissolved calcite ions, was also observed by Godinho et al. (2014). The replacement mechanism involves the dissolution of calcite and the precipitation of fluorite. In order to maintain external volume (pseudomorphic replacement), the rate of dissolution must equal the rate of precipitation and this can only be achieved when the reactions are coupled at the parent mineral-fluid interface. As soon as the calcite begins to dissolve in the presence of the F-bearing solution (undersaturated with respect to fluorite), Ca^{2+} ions are released to the solution at the mineral-fluid interface. Immediately this boundary layer fluid becomes supersaturated with respect to the new phase, fluorite, which precipitates. The molar volume of fluorite (V_m= 24.5 cm^3/mol) is lower than that of calcite (V_m= 36.9 cm^3/mol). The result is a volume deficit reaction, shown in the high porosity in the fluorite product phase. The formation of an interconnected porosity (permeability) in the product phase enables the solution to penetrate the previously solid parent calcite and so the reaction is able to continue at a moving interface within the rock. The replacement of pure calcite by fluorite corresponds to a molar volume reduction of 33.5 %. This corresponds to the minimum porosity expected in a fully replaced sample of pure calcite. The porosity calculated here for a hypothetical fully reacted sample was slightly lower (31.5 %) but within estimation error. This might indicate that the fluorite density of these samples was slightly lower than that of pure crystalline fluorite, justifying its higher volume. The quantification of porosity will be the focus of a further study. Besides molar volume changes, solubility differences between parent and product phases can result in increased porosity in the product (Pollok et al. 2011). However, the calcium content measured in the fluids after replacement of the marble by fluorite (< 0.5 ppm), was not in a significant amount for mass balance equations.

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

Backscatter SEM images showed that the evolution of the main reaction front (or bulk reaction) is very homogeneous (Fig. 5) forming an almost perfect sphere when it approaches the core of the sample. Fluid movement through grain boundaries can have a significant impact on replacement rates (Jonas et al. 2014), as grain boundaries are faster pathways for fast fluid transport. However, it has also been shown that fast reaction rates can result in replacements that proceed equally through grain boundaries and mineral grains (Pedrosa et al. 2016). In our experiments, replacement reactions were fast (especially at higher temperatures) and only small amounts of fluorite formed ahead of the reaction front next to grain boundaries and fractures, in agreement with Pedrosa et al. (2016).

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

Results of the model-free method to calculate E_a suggest that the mechanism of replacement, and hence the rate-controlling step did not change with the progress of reaction. Nevertheless, in all isothermal experiments, the reaction rate slowed down with the progression of the reaction (Table 3). This would be expected if the rate controlling step was diffusion, in which case the rim thickness would vary as $t^{0.5}$ (Putnis and Mezger 2004). However, another possible cause of a change in the kinetics could be due to morphology changes in the fluorite that affect the porosity. Glover and Sippel (1962) showed that at the very early stages of replacement, the rate differs from the rate after the reaction rim has formed and correlated it to the change in orientation of the newly formed fluorite crystals. SEM images showed that the fluorite needle-like crystals are oriented in many different directions, different from the reaction interface in which they are oriented parallel, and also that the needles often have healed probably as the result of a coarsening process. We hypothesize that this coarsening occurs at the outer edge of the replaced grains, where the porosity is higher (more space for fluid passage) due to the presence of the grain boundaries. This is consistent with textural equilibration where, as well as compositional equilibration, simultaneously porosity begins to coarsen and then disappear in accordance with a lowering of the energy state of the reaction product (Putnis et al. 2005). As soon as the outer edge of the new fluorite grains is healed, no fluid can penetrate in that area leaving behind the needle-like structure plus an impermeable outer surface, seen in Fig. 5e. The rim remained permeable possibly because the grains did not heal completely. This process might have an impact on the permeability of the rim, justifying the slower replacement rates for bigger replacement rims.

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

Implications

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

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

Acknowledgements

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Figure captions

Figure 1. X-ray powder diffraction patterns showing the evolution of the parent and product phases from samples reacted at different reaction times and temperatures. The tracing indicates fluorite characteristic peak positions. The fraction of fluorite formed (α) was determined from Rietveld analysis.

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

Figure 3. The plot of -ln ln (1-α) vs ln (time) for the replacement of calcite by fluorite that yield n values of 0.77 (60°C), 0.82 (80°C), 0.80 (100°C) and 0.99 (140°C).

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

Figure 5. Images of cross-sections of cubes of Carrara marble reacted with a 4 M NH_4F solution: **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 hours at 60 °C. All are BSE images with exception of f) that is SE.

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

Figure 7. Fluorite formed as a function of experimental temperatures for different reaction times. The amount of fluorite formed approximates to a linear relationship with the increase in temperature.

Tables

Table 1. The solubility of calcite and fluorite in water and their saturation indices (SI) in 4 *M* NH_4F at 25 °C and at experimental temperatures (PHREEQC calculations).

	Pure water		**4 *M* NH_4F**	
***T* (°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

594 **Table 2.** Reaction models employed to fit the empirical data (adapted from Khawam and
595 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)	$\left[-\ln(1-\alpha)\right]^{\frac{1}{2}}$
Avrami Erofeev (A3)	$\left[-\ln(1-\alpha)\right]^{\frac{1}{3}}$
Avrami Erofeev (A4)	$\left[-\ln(1-\alpha)\right]^{\frac{1}{4}}$
Avrami Erofeev (An)	$\left[-\ln(1-\alpha)\right]^{\frac{1}{n}}$
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)	$\left[(1-\alpha)\ln(1-\alpha)\right]+\alpha$
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)	$0.5\left((1-\alpha)^{-2}-1\right)$

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

T **(°C)**	**Reaction time (h)**	m_{initial} **(mg)**	m_{decrease} **(%)**	$\mathrm{pH_{final}}$	**Porosity (%)**	$\mathrm{CaF_2}$ **(%)**	**Reaction rate** $(\mathrm{mg_{CaF2}/h})$

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

Table 4. Calculated kinetic parameters (pre-exponential factor, *A*, and activation energy, $\boldsymbol{E_a}$) 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

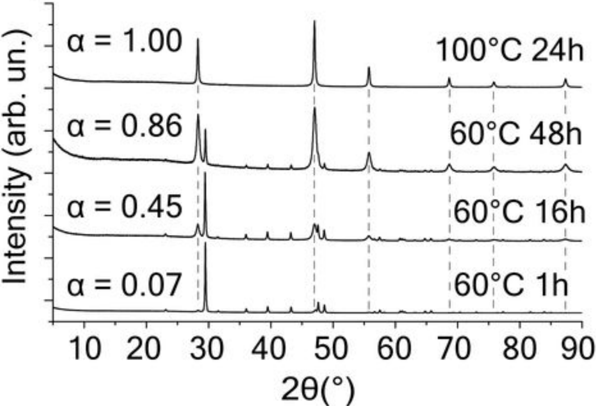
a) Correlation coefficient g(α) vs *t* (min).

b) Equivalent models based on goodness of fit.

c) Model selected based on model-fitting method.

d) Models that E_a resulted to be equal to the E_a calculated with the model-free method (41(1) kJ/mol).

Figure 1


α = 1.00
100°C 24h
α = 0.86
60°C 48h
α = 0.45
60°C 16h
α = 0.07
60°C 1h
Intensity (arb. un.)
10
20
30
40
50
60
70
80
90
2θ(°)

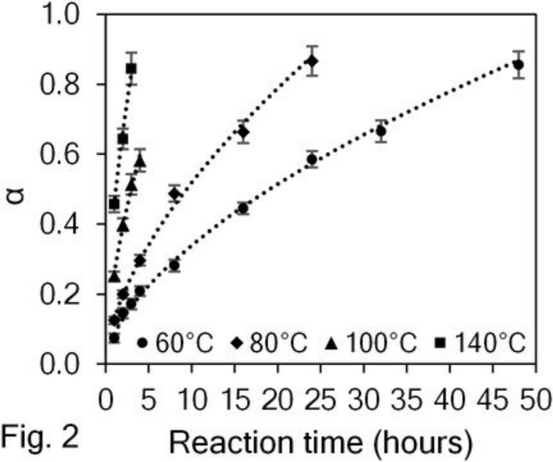

1.0
0.8
0.6
0.4
0.2
0.0
α
0
5
10
15
20
25
30
35
40
45
50
Reaction time (hours)
● 60°C
◆ 80°C
▲ 100°C
■ 140°C

Fig. 2

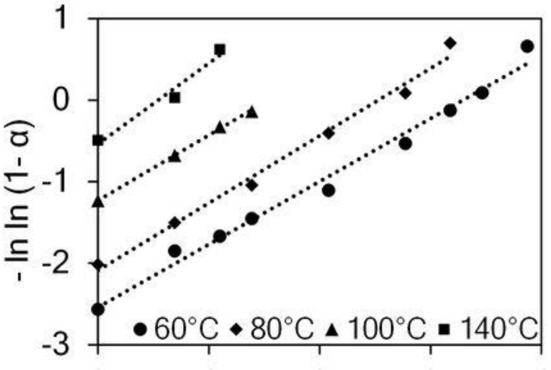


Fig. 3

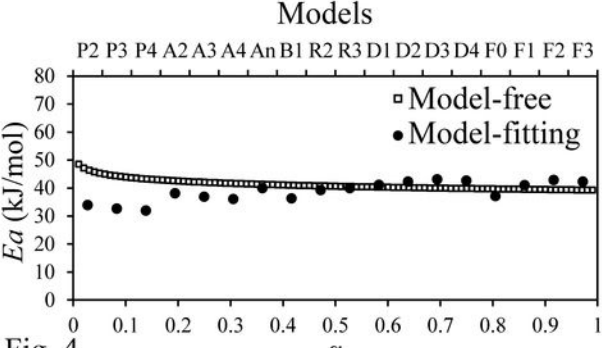
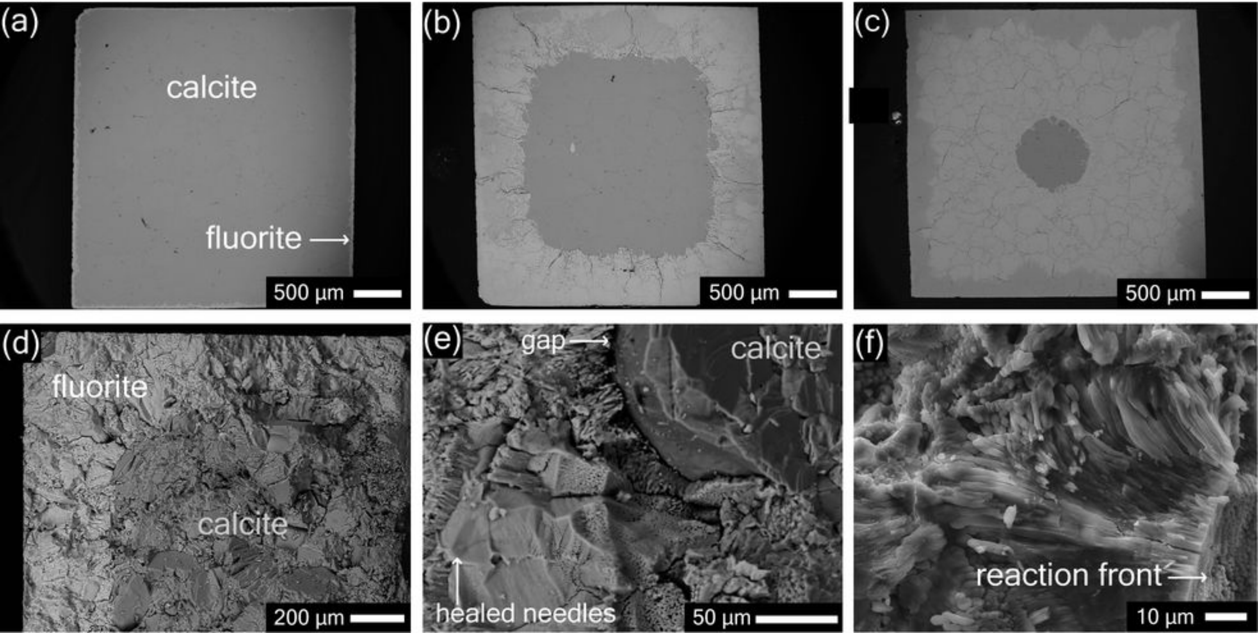

Models
P2
P3
P4
A2
A3
A4
An
B1
R2
R3
D1
D2
D3
D4
F0
F1
F2
F3
80
70
60
50
40
30
20
10
0
Ea (kJ/mol)
□ Model-free
● Model-fitting
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
α

Fig. 4

Figure 5


(a)
calcite
fluorite
500 µm
(b)
500 µm
(c)
500 µm
(d)
fluorite
calcite
200 µm
(e)
gap
calcite
healed needles
50 µm
(f)
reaction front
10 µm

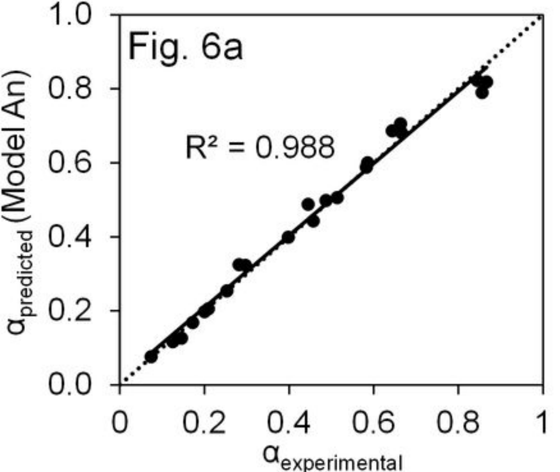


Fig. 6a

R² = 0.988
αpredicted (Model An)
αexperimental
0.0
0.2
0.4
0.6
0.8
1.0
0
0.2
0.4
0.6
0.8
1

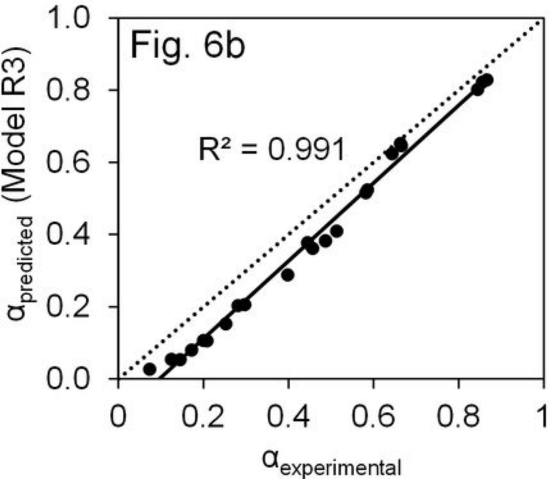


Fig. 6b
R² = 0.991
$\alpha_{predicted}$ (Model R3)
$\alpha_{experimental}$
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1

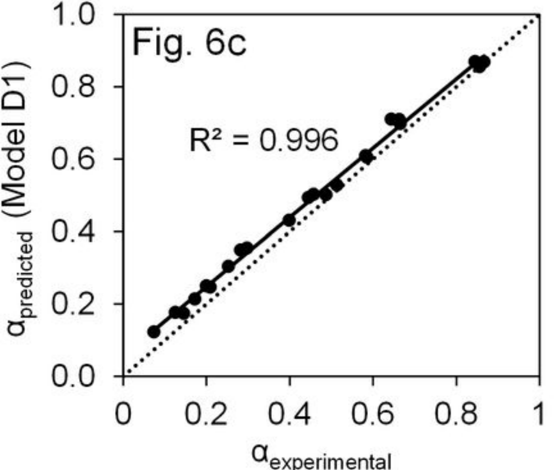


Fig. 6c
R² = 0.996
$\alpha_{predicted}$ (Model D1)
$\alpha_{experimental}$
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1

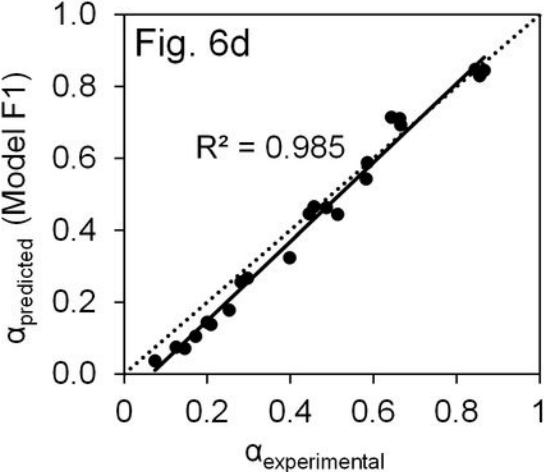
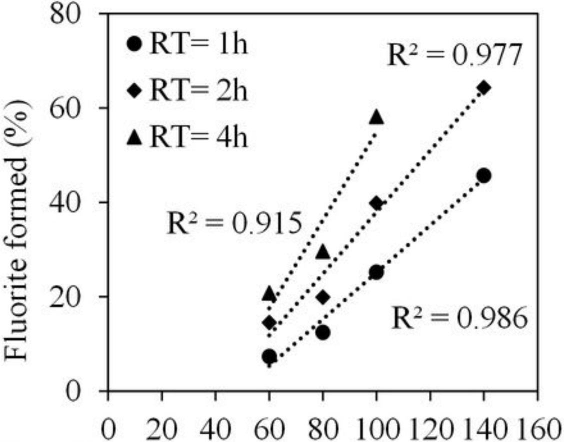


Fig. 6d
R² = 0.985
$\alpha_{predicted}$ (Model F1)
$\alpha_{experimental}$
0.0
0.2
0.4
0.6
0.8
1.0
0
0.2
0.4
0.6
0.8
1



80
60
40
20
0
Fluorite formed (%)
● RT= 1h
◆ RT= 2h
▲ RT= 4h
R² = 0.977
R² = 0.915
R² = 0.986
0
20
40
60
80
100
120
140
160
Temperature (°C)

Fig. 7