

Growth kinetics of siderite at 298.15 K and 1 bar

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Abstract

The widespread occurrence of siderite at the Earth's surface has motivated investigations into the thermodynamic factors controlling its stability for most of the last century. However, despite a new appreciation for multiple Fe(II)-carbonate mineralisation pathways, the rates of siderite growth have not been accurately predicted as a function of solution chemistry. This has impeded a quantitative understanding of myriad geochemical systems, both modern and ancient. To address this issue, we investigated the growth kinetics of synthetic siderite seeds in anoxic closed-system conditions at 298.15 K and 1 bar. On the basis of monitoring the chemical evolution of the bulk solutions over the course of 46 days, our results demonstrate two distinct relationships between kinetic behaviour and solution saturation (Ω) with respect to siderite. These relationships are best explained by chemical affinity-based rate laws that have been extensively applied to the growth kinetics of calcite (a mineral isostructural with siderite). More specifically, the surface area-normalised siderite growth rates ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) display a linear correlation with supersaturation ($\Omega - 1$) when $\Omega \gtrsim 5$, suggesting a growth rate controlled by the transport of ions to the mineral surface (r_{tr}):

$$r_{tr} = 10^{-12.60 \pm 0.16} (\Omega - 1)^{1.057 \pm 0.112}.$$

At low solution saturation, growth rates are consistent with spiral mechanism-dominated surface reactions (r_{sr}), exhibiting a parabolic correlation with ($\Omega - 1$):

$$r_{sr} = 10^{-13.42 \pm 0.14} (\Omega - 1)^{1.868 \pm 0.307}.$$

These data show that at comparable solution saturation at 25 °C, siderite growth is nearly 7-orders of magnitude slower than that of calcite. These kinetic behaviours imply that most examples of natural Fe(II) supply fluxes (e.g., dissimilatory iron reduction, hydrothermal activity, or dissolution of other Fe(II)-minerals) would only be balanced by siderite precipitation rates at very high supersaturation, or, if the barrier to Fe(II)-carbonate nucleation is surpassed, balanced by episodic fluctuations in precipitation rate in response to Fe(II) accumulation. In combination with kinetic barriers influencing nucleation, this slow growth rate provides a straightforward explanation for the common observation that many anoxic water bodies are persistently supersaturated with respect to siderite, and implies that the precipitation of siderite may be more dynamic than previously appreciated.

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1. INTRODUCTION

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Detailed knowledge of Fe(II)-carbonate crystallisation is crucial in understanding and predicting the behaviour of a

wide variety of natural and engineered geochemical systems. For example, because it is essentially ubiquitous in ancient sedimentary rocks (in particular of Precambrian age), siderite is thought to have strongly influenced the biogeochemical cycling of Fe and C throughout much of Earth's history (e.g., Holland, 1984; Kaufman et al., 1990; Klein, 2005; Holland, 2007; Beukes and Gutzmer, 2008; Heimann et al., 2010; Raiswell et al., 2011; Bachan and Kump, 2015; Rasmussen and Muhling, 2018; Tosca et al., 2019). Beyond the Earth, siderite is a common component in pre-terrestrial mineral assemblages found in Martian meteorites (Bridges et al., 2018), and appears locally abundant in ancient sedimentary rocks exposed at the Martian surface (Wray et al., 2016). The formation and dissolution of siderite strongly influence corrosion processes (Ogundele and White, 1986), as well as nutrient availability and crop production in modern environmental and agricultural systems (Schwab and Lindsay, 1983). More recently, Fe-carbonate crystallisation has assumed a central role in efforts to reduce anthropogenic carbon emissions. These include, for example, the application of basaltic rocks rich in Ca, Mg, and Fe(II) at source point (e.g., power plants) to capture CO₂ via carbonate mineralisation (e.g., Oelkers et al., 2008; Gislason, 2010; Callow et al., 2018), as well as the injection of CO₂ saturated-fluids into depleted oil and gas reservoirs (e.g., Xu et al., 2004, 2005).

Although the widespread occurrence of siderite has motivated thermodynamic studies for most of the last century (since Smith, 1918), the rates and pathways of Fe(II)-carbonate crystallisation remain poorly understood. For example, geochemists have only recently appreciated that Fe(II)-carbonate precipitation commonly involves multiple solid phases and, as a consequence, various precipitation pathways. Recent experimental studies have shown that homogeneous Fe(II)-carbonate precipitation is commonly initiated by the nucleation of amorphous iron carbonate (AFC) at high supersaturation (e.g., Sel et al., 2012; Dideriksen et al., 2015; Montes-Hernandez and Renard, 2016; Jiang and Tosca, 2019). Once formed, AFC appears to provide a favourable surface promoting the secondary growth of more stable crystalline phases, including chukanovite (which is metastable with respect to siderite) and/or siderite depending on solution chemistry (Sel et al., 2012; Dideriksen et al., 2015; Montes-Hernandez and Renard, 2016; Jiang and Tosca, 2019).

However, even though recent work has shown that siderite may be produced through multiple pathways, its growth rate has not been accurately predicted as a function of solution saturation. This has impeded a quantitative understanding of myriad geochemical systems, both modern and ancient. While numerous experimental studies have documented the formation of siderite films on corroding steel (i.e., Burkle et al., 2017), few experiments have derived phenomenological rate laws for seeded siderite growth as a function of solution saturation. Of the handful of studies reporting kinetic data, Wajon et al. (1985) reported Fe(II) removal rates through siderite precipitation on to Ca- and Mg-containing carbonate minerals, and Greenberg and Tomson (1992) reported the results of seeded siderite precipitation experiments as a function of temperature, but

both studies reported insufficient data to constrain the effect of solution saturation at a given temperature. Jimenez-Lopez and Romanek (2004) examined seeded Fe(II)-carbonate growth at room temperature on uncharacterised solids which were homogeneously precipitated from solution before constant chemical conditions were established. However, data are reported only across a high but narrow range of supersaturation. One recent study, Ma et al. (2018), measured heterogeneous siderite growth on an electrochemical quartz crystal microbalance coated with Fe or Au from 50 to 80 °C, and fitted their data with a temperature- and surface activation energy-dependent kinetic model. The Ma et al. (2018) model, however, if extrapolated to room temperature, yields precipitation rates that diverge from those reported in Jimenez-Lopez and Romanek (2004) by more than 5 orders of magnitude at the same solution saturation. The scarcity of room temperature kinetic data also leaves the dominant crystal growth mechanisms of siderite, and the ranges in saturation state over which they operate, largely unknown. This, in turn, prevents a detailed understanding of the links between solution chemistry, crystalline morphology, and isotope/trace element incorporation.

To address these issues, we investigated the growth kinetics of siderite at room temperature and pressure across a wide range of saturation state. In what follows, we present the experimental procedure, observations on solution chemistry, characterisations of solids, and development of kinetic expressions correlating siderite growth rate with solution saturation.

2. METHODOLOGY

2.1. Apparatus and reagent preparation

Closed-system siderite syntheses were conducted at 298.15 K within a strictly anoxic Coy polymer glovebox filled with 4% H₂/96% N₂ gas and maintained at anoxic conditions by two pairs of palladium catalysts and anhydrous CaSO₄ desiccants. The palladium catalysts scrubbed O₂(g) in the glovebox by continuously reacting trace O₂(g) with available H₂(g) to form H₂O(l), which was subsequently removed by CaSO₄ desiccants. The O₂ and H₂ contents in the glovebox were continuously monitored by a Coy gas analyser to ensure an atmosphere of <1 ppm O₂ throughout the preparation and storage of stock solutions and samples.

All solutions were prepared using de-ionised water (resistivity 18.2 MΩ·cm) that was first deoxygenated by purging with O₂-free N₂ gas for at least 2 h (Butler, 1964), then placed on a stir plate for 24 h in the glovebox to allow any residual O₂ to escape and be removed by the catalysts and desiccants. Metal-stock solutions (1 molal) were prepared by dissolving analytical grade metal-chloride powders in the deoxygenated de-ionised water. FeCl₂ stock solution was treated with Fe⁰ powder (≥99%; Sigma-Aldrich) and HCl (pH < 2) for 24 h to remove any Fe(III) in the stock FeCl₂·4H₂O powder (≥99%; Sigma-Aldrich). The Fe⁰ was then removed by running the stock solution through a polymer container with a high-strength Nd magnet

inserted in the wall. NaHCO_3 stock solutions (0.5 molal; powder $\geq 99.7\%$; Sigma-Aldrich) were freshly prepared for each batch of experiments to ensure the total dissolved inorganic carbon (DIC) across experiments was not affected by degassing of the stock solution over time. KCl was added to all growth experiments as a reference element to ensure the internal consistency of elemental analyses. NaCl powder was added to the experiment to balance the stoichiometric ionic strength for each solution composition.

2.2. Siderite seed synthesis

Siderite seed was generated in a sealed Teflon reactor constructed outside of the glovebox for the ease of handling and cleaning (Fig. 1). NaHCO_3 solution (250 mL, 0.2 molal with 0.01 molal NaOH, pH ≈ 10) and the FeCl_2 solution (250 mL, 0.1 molal, pH ≈ 3) were prepared within the glovebox and sealed with three-way stopcocks prior to being taken out of the glovebox. The Teflon reactor and all the tubing were purged with O_2 -free N_2 gas for 10 min and 2 min, respectively, before the reagents were connected. A strictly anoxic interior atmosphere was achieved by constantly purging the head-space in the system with N_2 gas throughout the 3-h synthesis. As illustrated in Fig. 1, through a combination of stopcocks and unidirectional check valves, FeCl_2 solution was first introduced into the Teflon reactor by N_2 gas, and the synthesis was initiated by titrating NaHCO_3 solution via a Metrohm 848 Titrino plus autotitrator. The NaHCO_3 solution was titrated at $0.025 \text{ mL}\cdot\text{s}^{-1}$, a rate low enough for the nucleated AFC precursor to start crystallising into siderite, but not too low where the solution $\text{CO}_3^{2-}/\text{Fe}^{2+}$ ratio would favour the crystallisation of chukanovite instead of siderite (Jiang and Tosca, 2019). A typical pH profile of seed synthesis increased from pH 3 to near-neutral within 1 h and plateaued at pH ≈ 7.5 due to the pH-dependent nucleation of

AFC. Upon the completion of seed synthesis, solution in the Teflon reactor was pressed back into the FeCl_2 container by N_2 gas, sealed and transferred into the glovebox for filtration. A volume of 550 mL of 5% HNO_3 acid was introduced into the reactor (in the same manner as FeCl_2 reagent) prior to any exposure to the atmosphere for effective removal of residual reagents, the reactor was then flushed with de-ionised water three times. This method allows a reliable and consistent production of a large quantity of siderite seed; $\approx 1.5 \text{ g}$ every 4 h.

2.3. Growth and reprecipitation experiments

Two sets of closed-system experiments were conducted using freshly prepared siderite seed (0.5 g each): growth experiments (G-series) and reprecipitation experiments (RP-series). Growth experiments were carried out in 1 L borosilicate glass reaction vessels wrapped in Al-foil to prevent photo-oxidation within the glovebox. After the establishment of initial solution chemistry (Table 1), all solutions were allowed to react over the course of 46 days and gently hand-shaken twice a day. Reprecipitation experiments (RP-series) were designed to replicate growth experiments apart from having no dissolved Fe(II) in the matrices, and allowed to react over the course of 288 days.

The pH of both growth and reprecipitation experiments was held constant by a combination of MOPS (3-(N-morpholino) propanesulfonic acid; 0.05 molal) pH buffer and large DIC pools (up to 0.084 molal). MOPS features significant steric hindrance of acid-base functional groups and therefore exhibits negligible metal complexation (Kandegedara and Rorabacher, 1999). MOPS was first added to deoxygenated de-ionised water, and the solution pH was raised to within 0.5 unit of the target value by manual addition of NaOH solution (1 molal), followed by the addition of KCl and NaCl and left for 24 h to homogenise.

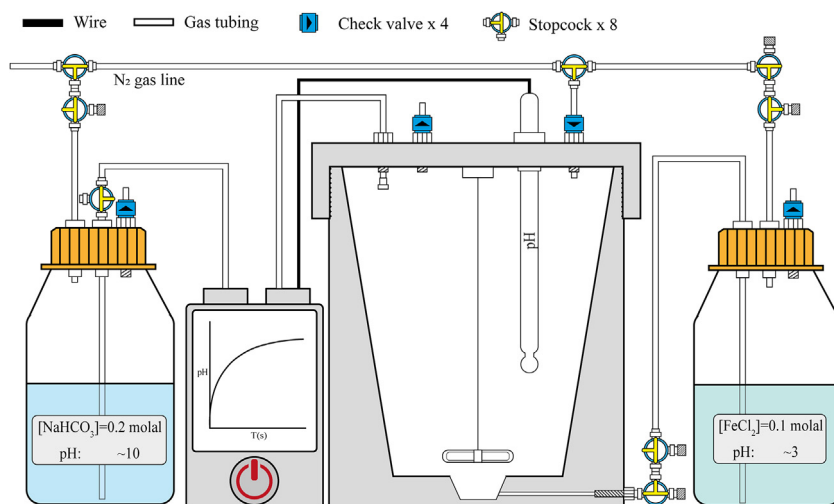


Fig. 1. Experimental apparatus for siderite seed synthesis. Reagents were prepared and sealed within an anoxic glovebox. All tubing was purged with N_2 gas for 2 min and the Teflon reactor (600 mL) for 10 min before being connected to reagents. FeCl_2 solution (250 mL) was pressed into the Teflon reactor by N_2 gas, whereas NaHCO_3 solution (250 mL) was titrated at a rate of $0.025 \text{ mL}\cdot\text{s}^{-1}$. Upon the termination of synthesis, precipitates and solution were pressed back (by N_2 gas) into the FeCl_2 container and transferred into the glovebox for filtration.

Table 1

Starting solution compositions of growth (G) and reprecipitation (RP) experiments. Concentrations of all reagents calculated from added powders and analysed (ICP-MS) stock solutions. Ionic strength calculation includes pH buffer MOPS; $I_{\text{MOPS}} = 0.04$ molal (Buffer Calculator: <http://www.liv.ac.uk/buffers>). Reagents were added to deoxygenated de-ionised water in the order listed in the table (left→right).

$T = 298.15$ K and 1 bar

Ex.No	pH	MOPS molal $\times 10^3$	KCl molal $\times 10^3$	NaCl molal $\times 10^3$	NaHCO ₃ molal $\times 10^3$	FeCl ₂ molal $\times 10^3$	Ionic strength molal	Initial Ω
G-1	7.515	50.183	2.013	125.617	6.366	0.502	0.176	22
G-2	7.496	50.183	2.009	111.849	20.090	0.502	0.176	66
G-3	7.752	50.009	2.009	120.887	11.071	0.502	0.176	67
G-4	7.378	50.184	2.014	83.491	48.444	0.502	0.176	120
G-5	7.760	50.183	2.024	97.116	35.035	0.502	0.176	217
G-6	7.638	50.184	2.148	48.231	83.739	0.502	0.176	389
RP-1	7.478	50.003	2.000	125.152	6.332	0.000	0.173	–
RP-2	7.496	50.020	2.001	111.499	20.031	0.000	0.174	–
RP-3	7.770	50.009	2.000	120.464	11.036	0.000	0.174	–
RP-4	7.363	50.056	2.002	83.305	48.318	0.000	0.174	–
RP-5	7.742	50.039	2.001	96.658	34.921	0.000	0.174	–
RP-6	7.622	50.100	2.004	48.136	83.604	0.000	0.174	–

Predetermined amounts of NaHCO₃ stock solution were then added to the homogenised solution, followed by pH adjustments using a Metrohm 902 Titrando autotitrator (within the glovebox) with NaOH solution (0.5 molal). This procedure was to minimise changes to carbonate speciation associated with pH adjustment. For example, a high proportion of CO₂(aq) in low pH solution would lead to CO₂(g) escape during preparation. To avoid instantaneous nucleation on the entry of the concentrated FeCl₂ solution, the stock solution was first diluted to 0.05 molal before being pipetted into the matrices and gently mixed immediately. In order to minimise CO₂(g) degassing over time, the head-space in the reaction vessels were essentially eliminated (i.e., < 1 mL), and sealed with gas-tight septum caps to facilitate solution sampling. Both the growth and reprecipitation experiments were initiated by the addition of 0.5 g of seed.

Complete starting solution compositions of all experiments are provided in Table 1. Solution saturations of growth experiments with respect to siderite equilibrium (Singer and Stumm, 1970) and the critical supersaturation for homogeneous nucleation of precursor amorphous Fe (II)-carbonate (Jiang and Tosca, 2019) are illustrated in Fig. 2.

2.4. Analytical procedures

Solution samples (≈ 1.5 mL) were withdrawn through the septum caps of the reaction vessels. To further assure minimum CO₂ degassing into the vacuum caused by solution-extraction, a O₂-free N₂ gas-filled syringe was inserted alongside the sampling syringe to replace the extracted solution volume. The solution samples were then syringe-filtered (0.22 μ m), and an aliquot of 0.5 mL was pipetted into a metal-free polypropylene centrifuge tube with 10 mL of 2% HNO₃ solution for in-house ICP-MS elemental analysis. All stock solutions were analysed alongside the samples in order to recalibrate the thermodynamic cal-

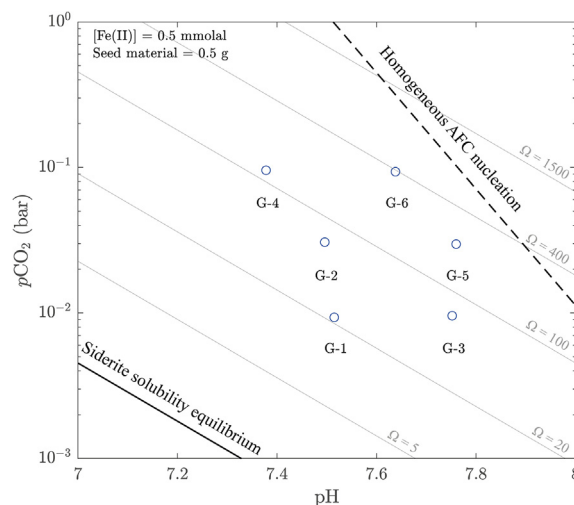


Fig. 2. $p\text{CO}_2$ -pH space illustrates the initial solution saturations (Ω) of growth experiments with respect to siderite solubility equilibrium ($\log K_{sp} = -10.24$; Singer and Stumm, 1970; solid line) and the critical supersaturation for homogeneous nucleation of precursor amorphous Fe(II)-carbonate ($\log IAP_{AFC} = 2.20$; Jiang and Tosca, 2019; dashed line; IAP: ionic activity product). Complete solution compositions are provided in Table 1. Thermodynamic calculations are provided in Supplementary information.

culations of the actual solution chemistry. The terminal pH measurements indicate < 0.1-unit change over the course of the reaction.

All solids, including the seeds, were filtered out the parent solutions through 0.22 μ m nylon filter membranes and left to dry under the low-humidity anoxic atmosphere in the glovebox for 24 h. Solids harvested from growth experiments were analysed by powder X-ray diffraction (XRD) using a PANalytical Empyrean Series 2 X-ray diffractometer with a Co K α source, operated at 40 kV and 40 mA, and scanned between 5 and 80 deg 2 θ at a step size of 0.026 deg.

Powders were loaded on single-crystal silicon sample holders and sealed with Kapton film within the glovebox to minimise oxidation during XRD analysis. Final X-ray diffractograms are shown with background patterns removed (subtracting patterns obtained on Kapton film).

Fourier transform infrared spectroscopy (FT-IR) analyses were performed on powdered products and were acquired in transmission mode using a PerkinElmer Frontier mid-IR spectrometer. FT-IR transmission measurements were collected on optically transparent KBr pellets with a sample: KBr ratio of $\approx 1:200$. KBr powder and sample were ground and compressed into pellets at 7 tons and analysed within 30 min of exposure to air (Fe(III)-O vibrations were closely monitored to ensure minimal oxidation had taken place). Measurements were collected from 400 to 4000 cm^{-1} at 1 cm^{-1} resolution using a deuterated triglycine sulphate (DTGS) detector with a KBr window and beam-splitter.

After identifying oxidation of the solids from growth experiments during sample preparation and analyses (but not during growth experiments), subsequent modifications were made to both XRD and FT-IR procedures for reprecipitation experiments; discussed in Section 3.2.1.

In-house scanning electron microscopy (SEM) was performed on all samples to characterise the morphology of the seed and harvested solids. Imaging was conducted using an FEI Quanta 650 FEG SEM in high vacuum mode. To minimise oxidation during sample preparation, small amounts of solid were mounted on adhesive carbon layers on aluminium stubs within the glovebox, then transported to a gold-coating unit in a parafilm-sealed container; sample exposure to air was < 1 min. Once gold-coated (9 nm Au), samples were immediately transferred into the evacuated SEM-EDS chamber.

The BET-surface area of seed and three harvested solids were measured using a Micromeritics TriStar II Plus surface area and porosity analyser with N_2 gas at a bath temperature of -195.850°C . BET-surface area analysis was conducted at the Surface Analysis Facility, Department of Chemistry, University of Oxford.

3. RESULTS

3.1. Solution chemistry evolution

ICP-MS analyses show monotonic decreases in solution Fe(II) concentrations from all growth experiments (Fig. 3A). A higher initial solution saturation (Ω) corresponds to a higher rate of Fe(II) consumption, and the rate decreases as the solution and solid approach siderite equilibrium (Fig. 4). Importantly, experiments with similar siderite saturations show similar rates of Fe(II) consumption (e.g., G-2 and G-3; Fig. 3A), despite different initial pH- $p\text{CO}_2$ conditions (Fig. 2). Cumulative Fe(II) consumption (in moles) as solution saturation evolved is presented in Fig. 4.

The solution chemistry of reprecipitation experiments (first 46 days; Fig. 3B) shows initial increases in Fe(II) concentrations corresponding to rapid dissolution of nanocrystalline siderite seed (see solid characterisation below),

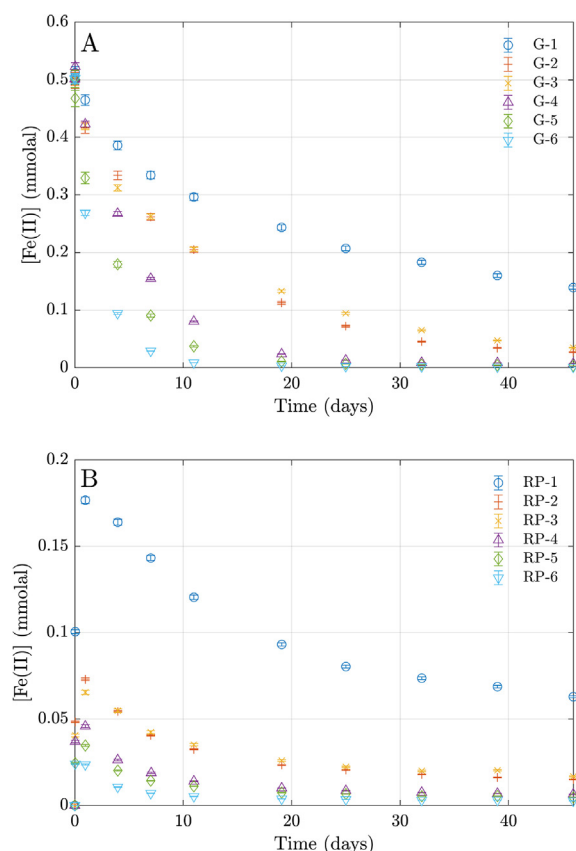


Fig. 3. Evolution of solution [Fe(II)] (ICP-MS analysis) in (A) the growth experiments (G series) and (B) the reprecipitation experiments (RP series; first 46 days). The reprecipitation experiments are exact replica of the growth experiments except that their initial [Fe(II)] = 0 mmolal. Analytical errors (3σ) are $< 3\%$ of measurements.

followed by gradual decreases that, though at much lower concentrations, imitate the saturation-correlated growth kinetics of siderite (Fig. 3A). Although the sampling frequency was too low to constrain the dissolution kinetics of nanocrystalline siderite (completely dissolved in ≤ 3 days), the maximum solution saturation with respect to siderite reached via dissolution was confined to $7 < \Omega < 18$ (Table 3); at this point in the experiments, the dissolution of nanocrystalline siderite, once complete, was overtaken by the secondary growth of coarsely crystalline siderite.

3.2. Solid characterisations

3.2.1. XRD and FT-IR characterisation

The siderite seed yields a monomineralic X-ray diffractogram and an FT-IR spectrum corresponding to siderite (Fig. 5 & 6). This indicates the initially nucleated AFC rapidly crystallised to siderite during seed synthesis; XRD and FT-IR characterisations of the precursor AFC are provided in Jiang and Tosca (2019). In addition to XRD and FT-IR patterns corresponding to siderite, solids harvested from growth experiments show weak diffraction and

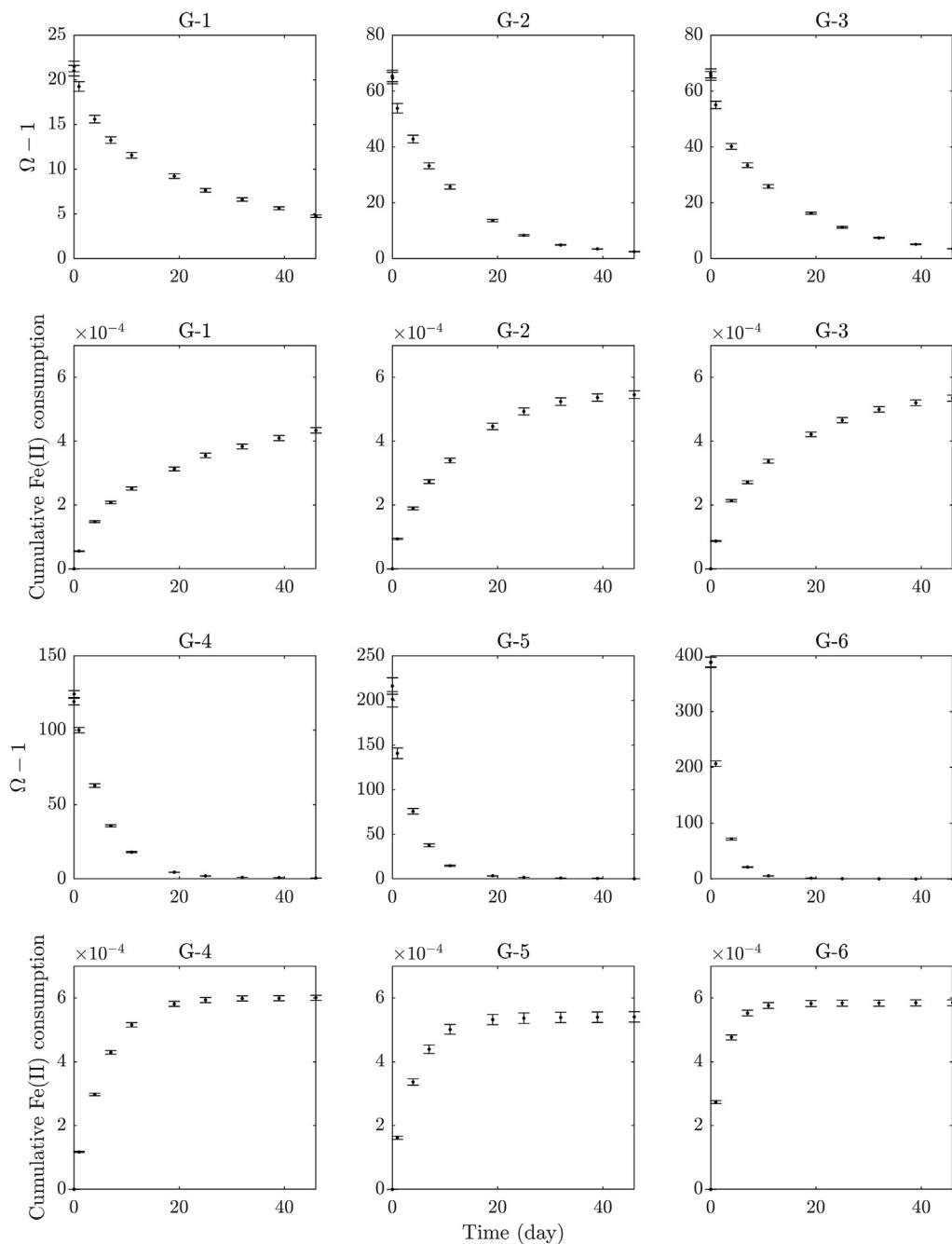


Fig. 4. The evolution of solution saturation (Ω) and the cumulative Fe(II) consumption (in moles) of growth experiments. Error bars are 3σ ; σ_{Ω} is calculated by assuming $\sigma_{[\text{CO}_3^{2-}]} = \sigma_{[\text{Fe}^{2+}]}$; calculations shown in Supplementary information.

absorption peaks that correspond to minor amounts of goethite ($\text{FeO}(\text{OH})$); its peak intensities appear to increase in the order that the samples were analysed (G-1 to G-6).

As described in the analytical procedure (Section 2.4), harvested solids from growth experiments were sealed with Kapton film within the glovebox to minimise oxidation. However, due to the scattering of X-rays by Kapton film, the scanning time of each sample was extended to 50 min to obtain a clear diffractogram. This procedure resulted in up to 4 h and 10 min exposure to the atmosphere when G-6 was analysed. Pervasive oxidation of solids under Kap-

ton film is observed by the colour change from grey-green to orange-red of the solids at the end of XRD analysis. Kapton film's inability to prevent oxidation has also been reported in the characterisation of synthetic amorphous Fe(II)-carbonate by [Dideriksen et al. \(2015\)](#). Similarly, after mixing with KBr powder in the glovebox, grinding and preparing KBr pellet, and FT-IR analysis accounted for ≈ 30 min exposure to the atmosphere for each sample, cumulatively 2 h and 30 min when G-6 was analysed.

To test the hypothesis that siderite oxidation occurred during sample analysis and not in the glovebox during crys-

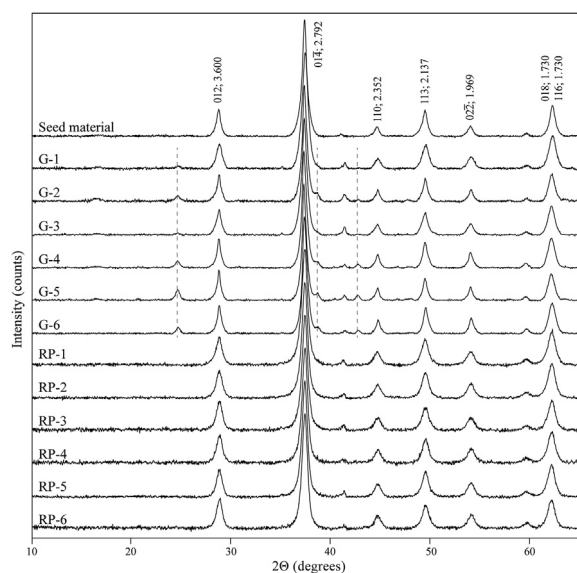


Fig. 5. Powder X-ray diffractograms (Co K α source) of siderite seed and the growth experiments (G-series) harvested after 46 days (Kapton film background removed; 50 min scanning time) and reprecipitation experiments (RP-series) harvested after 288 days (no Kapton film, 19 min scanning time). All solids show diffraction peaks corresponding to siderite, labelled with Miller indices and d -spacing (Å). Dashed lines indicate the minor occurrence of goethite (FeO(OH)) in the harvested solids from growth experiments but absent in reprecipitation experiments. The origin of goethite is discussed in Section 3.2.1.

tal growth experiments, solids from reprecipitation experiments (RP series) were treated with extra precaution. For both XRD and FT-IR analyses, only one sample was taken out of the glovebox each time. Individual XRD analysis was conducted without Kapton film, which allowed a significantly reduced scanning time (19 min). KBr-sample mixture was ground within the glovebox before individually taken out for pellet preparation and analysis. All reprecipitation experiments show X-ray diffractograms and FT-IR spectra corresponding to pure siderite (Fig. 5 & 6).

The absence of goethite in the reprecipitation experiments rules out the possibility of goethite formation by (1) residual $O_2(aq)$ in the matrix solution, and (2) trace $O_2(g)$ in the glovebox atmosphere that diffused through the septum cap over the course of experiments, because (1) growth and reprecipitation were prepared with same deoxygenated matrix solutions and reagents and (2) reprecipitation experiments resided in the glovebox over a period of 288 days, compared to 46 days of growth experiments. Importantly, the cumulative Fe(II) consumption in all growth experiments was governed by solution saturation with respect to siderite (Fig. 4). Therefore, we reason that the kinetic constraints obtained from the evolution of solution chemistry can be solely attributed to the precipitation of siderite, and the formation of goethite likely occurred during solid sample drying, preparation, and analyses.

3.2.2. SEM imaging

The unreacted siderite seed is dominated by spherical particles of $\approx 2 \mu m$ in diameter, with a minor occurrence

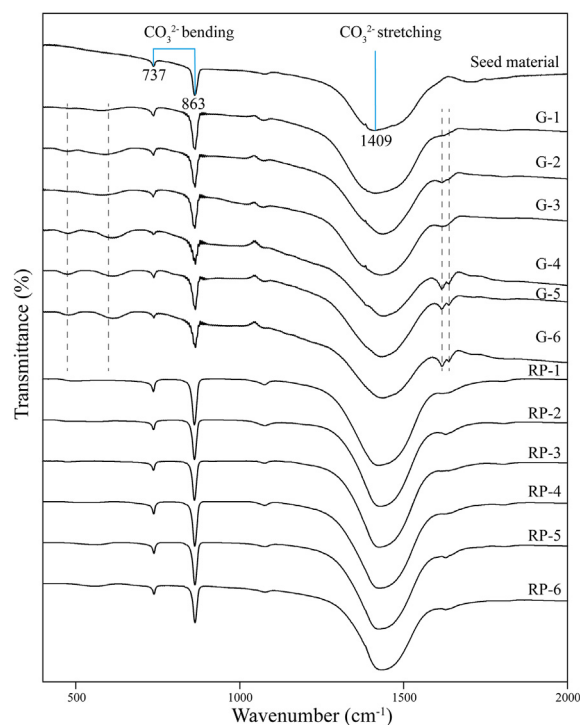


Fig. 6. FT-IR transmittance spectra of seed and harvested solids. Solids from growth experiments (G) show the absorption peaks corresponding minor occurrences of goethite (dashed lines) that is absent in the reprecipitation experiments (RP). The origin of goethite is discussed in Section 3.2.1.

(<5%) of ≈ 10 – $15 \mu m$ larger population (Fig. 7A&B). Neither of the two populations displays discernible crystal morphology, suggesting the seed particles are aggregates of nanocrystalline siderite nuclei. The surface of some $\approx 10 \mu m$ spheres shows partially formed globules ($\approx 2 \mu m$; Fig. 7A), indicating an early stage of rhomb formation.

After 46 days, solids from growth experiments show two types of crystalline siderite. (1) Interlocking siderite rhombs that are ≤ 50 nm in edge length; these are observed on all harvested solids (e.g., Fig. 7F&H). The formation of the interlocking small siderite rhombs can be attributed to the crystallisation of seed particles themselves. (2) Overgrown siderite rhombs of edge length ≤ 200 nm on the surface of seed particles. This population is interpreted to result from localised growth from the oversaturated solutions. The degree of siderite overgrowth is qualitatively consistent with the initial solution saturation. At the lowest initial saturation, G-1 is dominated by interlocking small siderite rhombs (Fig. 7C&D). With increasing initial saturations, G-2 (Fig. 7E&F), G-3 (Fig. 7G&H), G-4 (Fig. 7I&J), and G-5 (Fig. 7K&L) show the overgrown siderite crystals increase both in size and abundance, as well as a better-developed rhombohedral morphology. Finally, G-6 (Fig. 7M&N) shows complete encrustation of overgrown siderite rhombs of ≈ 200 nm in edge length.

Similar observations can be made from the reprecipitation experiments (288 days), that the seed particles crystallised into interlocking small siderite rhombs (≤ 10 nm)

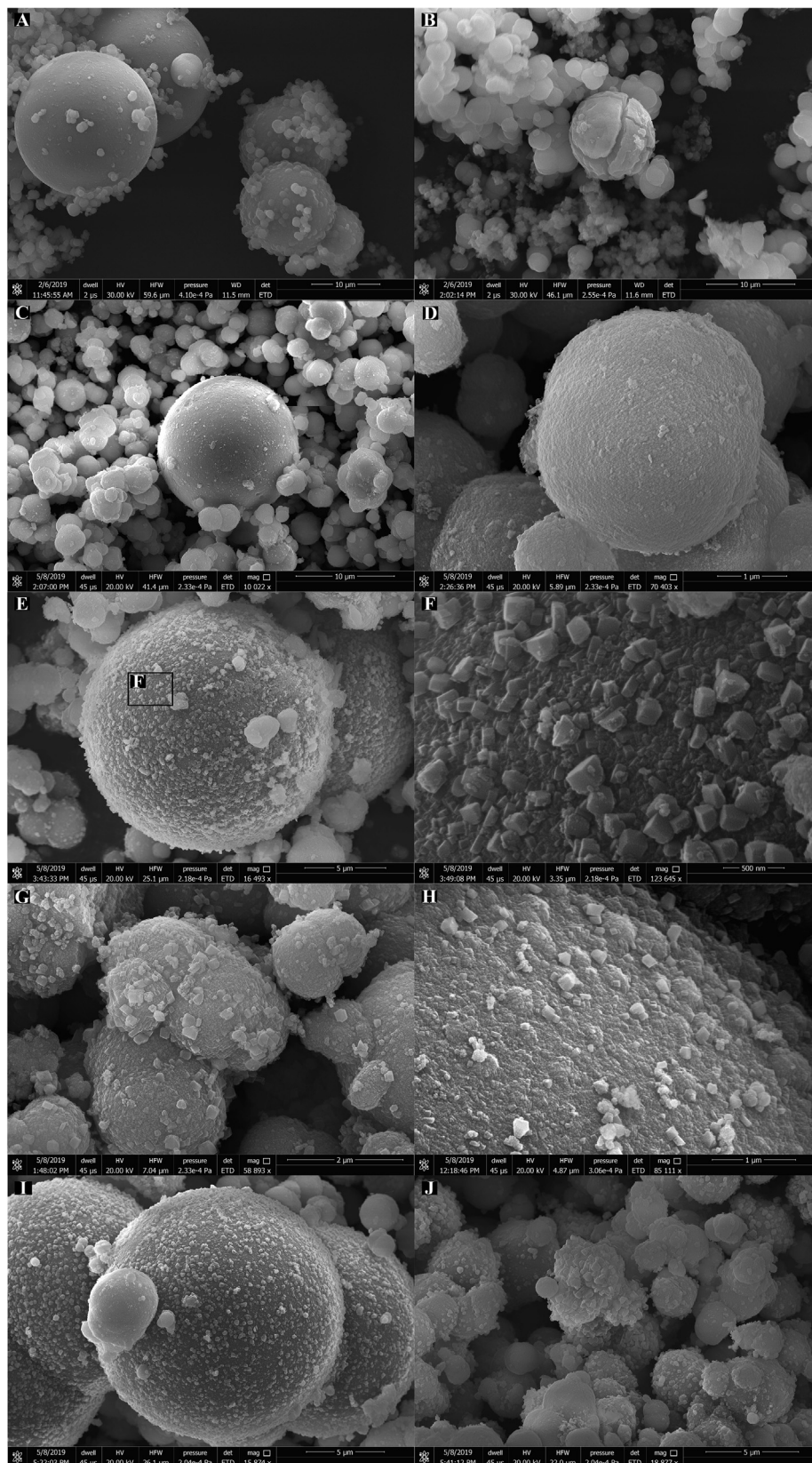


Fig. 7. SEM images of siderite seed and harvested solids from growth experiments (46 days). (A&B) Siderite seeds, predominantly composed of spherical particles of $\approx 2 \mu\text{m}$ in diameter with a minor occurrence ($\leq 5\%$) of larger particles of $\approx 10\text{--}15 \mu\text{m}$ in diameter. (C&D) G-1 shows minor siderite encrustation ($\leq 20 \text{ nm}$ in edge length). With increasing initial solution saturation, G-2 (E&F), G-3 (G&H), G-4 (I&J), and G-5 (K&L) show siderite encrustation increases both in size and abundance, as well as a better-developed rhombohedral morphology. (M&N) G-6 shows complete encrustation of siderite rhombs of $\approx 200 \text{ nm}$ in edge length.

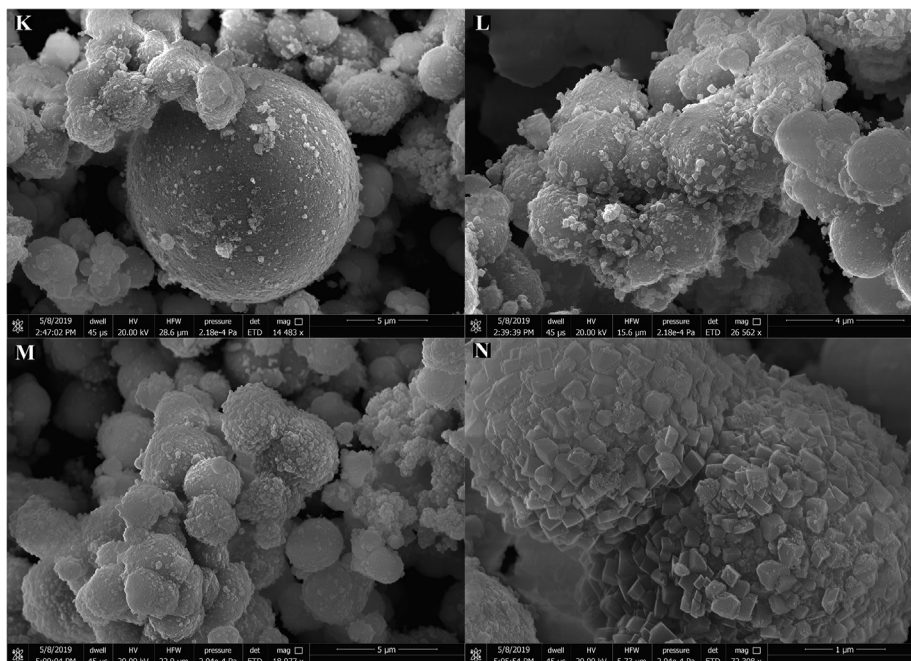


Fig 7. (continued)

with various degrees of siderite overgrowth (≤ 200 nm) from oversaturated solutions (Fig. 8). However, as indicated by solution chemistry (Fig. 3B), reprecipitation experiments first underwent dissolution of nanocrystalline siderite seeds and followed by secondary growth. Therefore, the degree of siderite overgrowth on the seed particles was not only tied to the supersaturation but also the amount of Fe(II) released via dissolution. For example, because of the high solution pH and DIC, RP-6 reached the highest solution saturation ($\Omega = 18$) with the least amount of seed dissolution ($d[\text{Fe(II)}] = 0.0241 \times 10^{-3}$ molal; Table 3); SEM imaging of RP-6 show interlocking small siderite but an insignificant amount of overgrowth (Fig. 8F).

It is important to note that the diameters of both size-populations (≈ 2 μm and ≈ 10 – 15 μm) of seed particles were retained after growth and reprecipitation experiments, and the acicular needle morphology that is typical of water-column goethite precipitation was not observed in all harvested solids (a total of 50 SEM images).

3.2.3. BET-surface area

Surface analyses show the unreacted siderite seed has a BET surface area (A_{BET}) of $109.75 \text{ m}^2 \cdot \text{g}^{-1}$ and a micropore volume (v_{pore} ; t-Plot) of $1.788 \text{ mm}^3 \cdot \text{g}^{-1}$. Three solids harvested from growth experiments show reductions in both surface area and micropore volume; G-2: $A_{\text{BET}} = 82.48 \text{ m}^2 \cdot \text{g}^{-1}$, $v_{\text{pore}} = 0.036 \text{ mm}^3 \cdot \text{g}^{-1}$, G-4: $A_{\text{BET}} = 81.12 \text{ m}^2 \cdot \text{g}^{-1}$, $v_{\text{pore}} = 0.074 \text{ mm}^3 \cdot \text{g}^{-1}$, and G-6: $A_{\text{BET}} = 81.39 \text{ m}^2 \cdot \text{g}^{-1}$, $v_{\text{pore}} = 0.076 \text{ mm}^3 \cdot \text{g}^{-1}$. Though lacking measurements on the evolution of the surface area during growth experiments, the changes in the surface area can be correlated with the amounts of siderite growth, which themselves were stoichiometrically equivalent to the

changes in solution Fe(II) concentrations: $\Delta A_{\text{BET}} \propto \Delta[\text{Fe(II)}]$. By fitting the BET-surface area of siderite seed and the end values of three harvested solids, scaling to the ratio of the mass of precipitated siderite (m_{ppt}) over the mass of siderite seed (m_{seed}), the following relation can be established:

$$A_{\text{BET}} = -211.39 \left(\frac{m_{\text{ppt}}}{m_{\text{seed}}} \right) + 109.41, \quad (1)$$

with $R^2 = 0.97$ ($n = 3$). Eq. (1) is used to estimate the BET-surface area of all the solids at each sampling time, against which the growth rates are normalised (Table 2).

The same approximation, however, cannot be applied to the reprecipitation experiments as they underwent both dissolution and growth. These processes complicate the evolution of the surface area and its correlation with solution chemistry. Therefore, the secondary growth rates from reprecipitation experiments are only normalised against the initial surface area of the siderite seed $A_{\text{BET}} = 109.75 \text{ m}^2 \cdot \text{g}^{-1}$ (Table 3).

4. DISCUSSION

4.1. Chemical affinity-based rate laws

Since the publication of the influential Burton, Cabrera, and Frank crystal growth theory (Burton et al., 1951), numerous mechanistic models have been further developed to correlate the kinetic behaviour of mineral-water interactions with solution chemistry. The most widely applied are the chemical affinity-based rate laws (e.g., Nancollas and Reddy, 1971; House, 1981; Aagaard and Helgeson, 1982; Lasaga, 1984; Nielsen, 1984), which generalise growth and

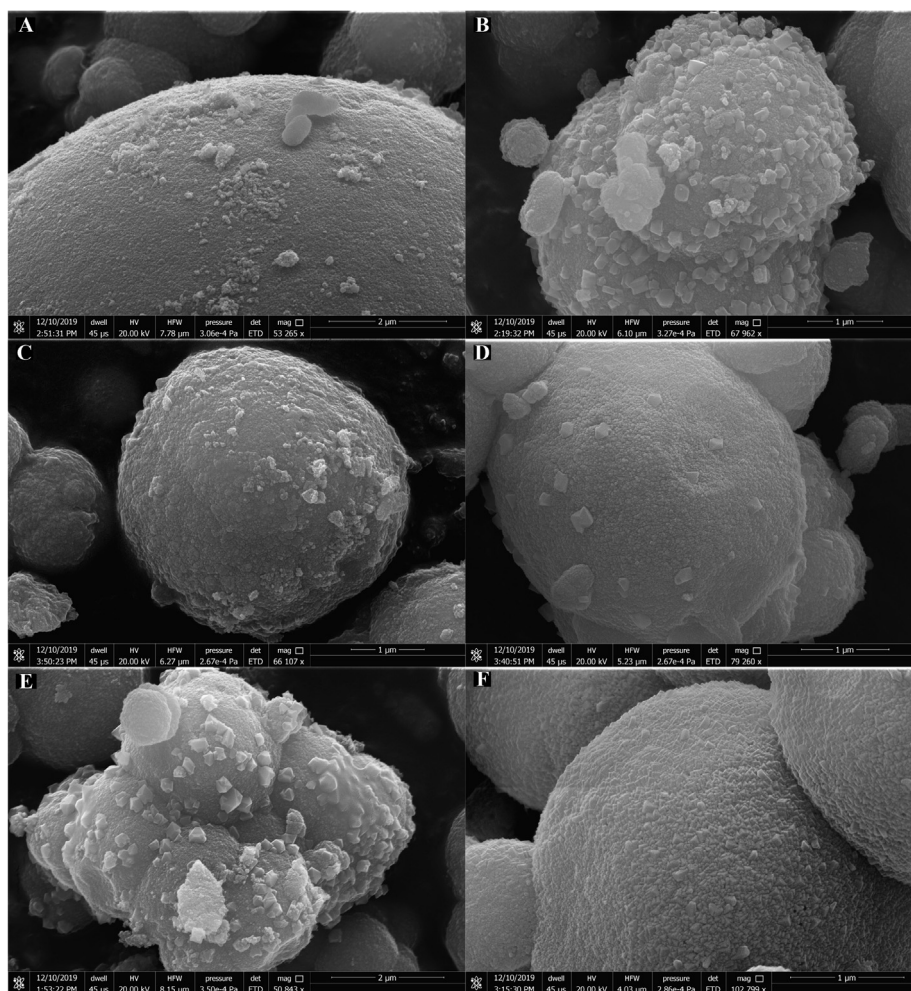


Fig. 8. SEM images of harvested solids from reprecipitation experiments (288 days). RP-1 (A) and RP-6 (F) show crystallised seed particles of interlocking small siderite rhombs that are ≤ 10 nm in edge length. RP-2 (B), RP-3 (C), RP-4 (D), and RP-5 (E) show various degrees of localised growth of rhombohedral siderite crystals of edge length ≤ 200 nm, in addition to the crystallised surface of the seed particles.

dissolution kinetics as a function of energetics (free energy of reaction ΔG_r , or as $\Omega = \exp \frac{\Delta G_r}{RT}$), and can be cast in the following general formalism (e.g., [Nielsen, 1984](#)):

$$\text{rate} = k(\Omega - 1)^n / (1 - \Omega)^n, \quad (2)$$

where k is the rate constant, and n indicates the reaction order of growth rate on supersaturation ($\Omega - 1$), or dissolution rate on undersaturation ($1 - \Omega$). The following discussion focuses on crystal growth.

Experimentally derived reaction orders (n) from macroscopic precipitation (i.e., solution chemistry) have been ascribed to the following rate-determining microscopic processes associated with the transfer of the constituent ions (summarised from [Nielsen, 1981](#); [Nielsen and Toft, 1984](#); [Van Cappellen, 1991](#); [Lasaga, 1998](#)):

1. From the bulk solution to the mineral-water interface.
2. From the solution into an adsorption layer.
3. From the solution or an adsorption layer to surface defects and subsequent integration into the crystal lattice.

4. From the solution or an adsorption layer to or to form surface nuclei.

These processes are thought to contribute to overall reaction rates in the following ways:

1. Transport-controlled growth rates are linearly dependent on diffusion: $\text{rate} \propto (\Omega - 1)$ ([Nielsen, 1964](#); [Mullin, 1972](#)).
2. Surface-controlled growth by adsorption, with rates linearly dependent on diffusion: $\text{rate} \propto (\Omega - 1)$ ([Nancollas and Reddy, 1971](#); [Nielsen and Christoffersen, 1982](#); [Nielsen, 1983](#); [Nielsen, 1984](#); [Shiraki and Brantley, 1995](#)).
3. Surface-controlled growth at crystal defects dominated by spiral growth, which follows a parabolic rate law: $\text{rate} \propto (\Omega - 1)^2$ ([Nancollas, 1979](#); [Nielsen, 1981](#); [Shiraki and Brantley, 1995](#)).
4. Surface nucleation that follows an exponential dependence on saturation: $\text{rate} \propto \exp(-\frac{U}{\ln \Omega})$, where U incorporates the molar properties and the geometry of nuclei

Table 2

Evolution of solution chemistry of growth experiments. [Fe(II)] measured via ICP-MS, the initial DIC determined from added NaHCO_3 powder, whereas the subsequent evolutions of DIC, $[\text{CO}_3^{2-}]$, BET-surface area, and solution saturation are calculated via methods detailed in Supplementary information and Section 3.2.3. Change in ionic strength due to siderite growth is $\lesssim 1\%$. Growth rates between the designed [Fe(II)] and the first measurement are discarded.

$I = 0.175$ molal; $T = 298.15$ K and 1 bar

Ex.No	Time h	[Fe(II)] molal $\times 10^3$	[DIC] molal $\times 10^3$	$[\text{CO}_3^{2-}]$ molal $\times 10^6$	BET surface area $\text{m}^2\cdot\text{g}^{-1}$	Ω	Growth rate $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ $\times 10^{12}$
G-1 pH = 7.515	0.77	0.5127	6.366	23.595	109.75	22.5	–
	22.95	0.4650	6.318	23.419	109.41	20.3	12.984
	94.70	0.3858	6.239	23.125	107.24	16.6	6.952
	167.98	0.3340	6.188	22.933	102.69	14.3	4.577
	263.38	0.2962	6.150	22.793	99.71	12.6	2.621
	457.72	0.2433	6.097	22.597	97.53	10.2	1.854
	599.68	0.2069	6.060	22.462	94.51	8.6	1.789
	767.48	0.1829	6.036	22.373	92.42	7.6	1.009
	935.25	0.1599	6.013	22.288	91.05	6.6	0.980
	1103.07	0.1390	5.992	22.210	89.73	5.7	0.902
G-2 pH = 7.496	0.83	0.4964	20.084	71.107	109.75	65.6	–
	23.02	0.4160	20.004	70.822	109.06	54.8	22.489
	94.73	0.3338	19.922	70.531	104.43	43.9	7.429
	168.05	0.2617	19.850	70.276	99.72	34.2	6.648
	263.42	0.2049	19.793	70.075	95.58	26.7	4.169
	457.75	0.1126	19.701	69.748	92.33	14.6	3.515
	599.72	0.0721	19.660	69.605	87.07	9.3	2.166
	767.55	0.0454	19.633	69.510	84.76	5.9	1.225
	935.32	0.0345	19.623	69.472	83.25	4.5	0.507
	1103.13	0.0269	19.615	69.445	82.63	3.5	0.351
G-3 pH = 7.752	0.73	0.4951	11.064	72.088	109.75	66.4	–
	22.92	0.4206	10.990	71.602	109.00	56.0	20.776
	94.68	0.3120	10.881	70.895	104.70	41.1	9.938
	167.95	0.2622	10.831	70.570	98.48	34.4	4.596
	263.37	0.2054	10.774	70.200	95.62	26.8	4.161
	457.70	0.1328	10.702	69.727	92.36	17.2	2.729
	599.67	0.0946	10.664	69.478	88.22	12.2	2.010
	767.45	0.0654	10.634	69.288	86.05	8.4	1.324
	935.22	0.0474	10.616	69.171	84.39	6.1	0.827
	1103.03	0.0350	10.604	69.090	83.36	4.5	0.574
G-4 pH = 7.378	0.90	0.5231	48.444	128.728	109.75	125.3	–
	23.08	0.4226	48.343	128.461	109.41	100.9	28.032
	94.77	0.2676	48.188	128.049	104.81	63.7	14.591
	168.12	0.1547	48.075	127.749	95.93	36.7	11.127
	263.45	0.0804	48.001	127.551	89.47	19.1	5.903
	457.78	0.0237	47.944	127.401	85.23	5.6	2.296
	599.75	0.0131	47.934	127.373	82.00	3.1	0.587
	767.62	0.0089	47.930	127.361	81.40	2.1	0.201
	935.38	0.0084	47.929	127.360	81.16	2.0	0.022
	1103.20	0.0071	47.928	127.357	81.13	1.7	0.061
G-5 pH = 7.760	0.80	0.4679	35.001	232.382	109.75	202.3	–
	22.98	0.3291	34.862	231.461	107.44	141.6	40.771
	94.72	0.1792	34.712	230.466	99.47	76.9	14.876
	168.02	0.0906	34.624	229.877	90.89	38.7	9.103
	263.40	0.0374	34.570	229.524	85.83	16.0	4.354
	457.73	0.0109	34.544	229.348	82.79	4.6	1.081
	599.70	0.0067	34.540	229.320	81.28	2.9	0.232
	767.52	0.0051	34.538	229.309	81.05	2.2	0.079
	935.28	0.0042	34.537	229.303	80.95	1.8	0.042
	1103.10	0.0033	34.536	229.298	80.90	1.4	0.042

(continued on next page)

Table 2 (*continued*) $I = 0.175$ molal; $T = 298.15$ K and 1 bar

Ex.No	Time h	[Fe(II)] molal $\times 10^3$	[DIC] molal $\times 10^3$	[CO ₃ ²⁻] molal $\times 10^6$	BET surface area m ² ·g ⁻¹	Ω	Growth rate mol·m ⁻² ·s ⁻¹ $\times 10^{12}$
G-6 pH = 7.638	0.87	0.5028	83.739	416.588	109.75	389.9	–
	23.05	0.2687	83.505	415.423	109.41	207.5	71.350
	94.75	0.0944	83.330	414.556	96.00	72.8	18.312
	168.08	0.0290	83.265	414.231	86.02	22.4	7.007
	263.43	0.0087	83.245	414.130	82.29	6.7	1.702
	457.77	0.0033	83.239	414.103	81.12	2.5	0.220
	599.73	0.0022	83.238	414.098	80.82	1.7	0.059
	767.58	0.0019	83.238	414.096	80.76	1.5	0.017
	935.35	0.0014	83.237	414.094	80.74	1.1	0.021
	1103.17	0.0012	83.237	414.093	80.71	–	–

Table 3

Evolution of solution chemistry (first 46 days) of reprecipitation experiments. Secondary growth rates are normalised against BET-surface area of the seed material (109.75 m²·g⁻¹). DIC and [CO₃²⁻] are calculated as a function of siderite dissolution and precipitation (Supplementary information). Note that siderite dissolution kinetics are excluded from this table.

 $I = 0.175$ molal; $T = 298.15$ K and 1 bar

Ex.No	Time h	[Fe(II)] molal $\times 10^3$	[DIC] molal $\times 10^3$	[CO ₃ ²⁻] molal $\times 10^6$	Ω	Secondary growth rate mol·m ⁻² ·s ⁻¹ $\times 10^{12}$
RP-1 pH = 7.478	1.03	0.1005	6.433	21.807	4.1	–
	23.27	0.1767	6.510	22.066	7.3	–
	95.00	0.1640	6.497	22.023	6.7	0.948
	168.18	0.1432	6.476	21.952	5.8	1.523
	263.63	0.1205	6.453	21.875	4.9	1.269
	457.97	0.0932	6.426	21.783	3.8	0.750
	600.03	0.0803	6.413	21.739	3.3	0.481
	767.87	0.0736	6.407	21.716	3.0	0.213
	935.47	0.0687	6.402	21.700	2.8	0.155
	1103.28	0.0629	6.396	21.680	2.5	0.185
RP-2 pH = 7.496	1.03	0.0484	20.075	71.073	6.4	–
	23.27	0.0729	20.099	71.160	9.7	–
	95.00	0.0543	20.081	71.094	7.2	1.391
	168.15	0.0405	20.067	71.045	5.4	1.005
	263.60	0.0324	20.059	71.016	4.3	0.454
	457.97	0.0233	20.050	70.984	3.1	0.249
	600.00	0.0205	20.047	70.974	2.7	0.107
	767.83	0.0179	20.044	70.965	2.4	0.081
	935.43	0.0162	20.043	70.959	2.1	0.055
	1103.25	0.0150	20.041	70.955	2.0	0.037
RP-3 pH = 7.770	1.03	0.0405	11.077	75.294	5.7	–
	23.27	0.0654	11.102	75.464	8.2	–
	95.00	0.0549	11.091	75.392	7.7	0.789
	168.20	0.0423	11.079	75.307	5.9	0.914
	263.65	0.0351	11.072	75.258	4.9	0.402
	457.97	0.0260	11.062	75.195	3.6	0.252
	600.05	0.0223	11.059	75.170	3.1	0.138
	767.88	0.0200	11.056	75.155	2.8	0.073
	935.48	0.0203	11.057	75.157	2.8	–
	1103.30	0.0167	11.053	75.133	2.3	0.114
RP-4 pH = 7.363	1.03	0.0370	48.310	123.733	8.5	–
	23.27	0.0458	48.319	123.755	10.5	–
	95.00	0.0263	48.299	123.705	6.1	1.453
	169.10	0.0188	48.292	123.686	4.3	0.542
	263.57	0.0140	48.287	123.674	3.2	0.273

(continued on next page)

Table 3 (continued)

 $I = 0.175$ molal; $T = 298.15$ K and 1 bar

Ex.No	Time h	[Fe(II)] molal $\times 10^3$	[DIC] molal $\times 10^3$	[CO ₃ ²⁻] molal $\times 10^6$	Ω	Secondary growth rate mol·m ⁻² ·s ⁻¹ $\times 10^{12}$
	457.97	0.0100	48.283	123.664	2.3	0.109
	599.97	0.0085	48.281	123.660	2.0	0.056
	767.80	0.0075	48.280	123.657	1.7	0.033
	935.40	0.0069	48.280	123.656	1.6	0.020
	1103.22	0.0065	48.279	123.655	1.5	0.013
RP-5	1.03	0.0245	34.925	222.251	10.1	–
pH = 7.742	23.27	0.0347	34.935	222.317	14.4	–
	95.00	0.0202	34.920	222.224	8.3	1.084
	168.17	0.0143	34.915	222.187	5.9	0.429
	263.62	0.0112	34.911	222.167	4.6	0.176
	457.97	0.0074	34.908	222.143	3.1	0.103
	600.02	0.0066	34.907	222.138	2.7	0.032
	767.85	0.0054	34.906	222.130	2.2	0.039
	935.45	0.0054	34.906	222.130	2.2	–
	1103.27	0.0046	34.905	222.125	1.9	0.026
RP-6	1.03	0.0241	83.476	399.761	17.9	–
pH = 7.622	23.27	0.0236	83.475	399.759	17.6	0.108
	95.00	0.0107	83.462	399.697	7.9	0.966
	168.13	0.0070	83.459	399.679	5.2	0.269
	263.58	0.0052	83.457	399.671	3.9	0.101
	457.97	0.0038	83.455	399.664	2.8	0.039
	599.98	0.0035	83.455	399.662	2.6	0.012
	767.82	0.0031	83.455	399.660	2.3	0.013
	935.42	0.0031	83.455	399.661	2.3	–
	1103.23	0.0026	83.454	399.658	1.9	0.015

(Hillig, 1966; Nielsen, 1984; Van Cappellen, 1991; Christoffersen and Christoffersen, 1992; Shiraki and Brantley, 1995).

Process (1) is a transport process, and (2–4) can be grouped as surface reaction mechanisms. Typically, the kinetic behaviour of crystal growth is simultaneously influenced by two or more of these processes. An important distinction is that those surface reactions are parallel mechanisms—their individual rates are added, and the faster is the rate-determining mechanism. In contrast, transport and surface reactions are consecutive processes—the slower one is the rate-determining process (e.g., Nielsen, 1984).

At low supersaturation, surface reactions proceed at defect sites including step edges, kink, ledge, and hillock/adatom, where the adsorbed ions are preferentially integrated into crystal lattice (e.g., Burton et al., 1951; Nielsen, 1984; Van Cappellen, 1991; Lasaga, 1998; Watkins et al., 2017). Because step and kink sites are the most abundant defect sites on crystal surface (Burton et al., 1951; Zhang and Nancollas, 1990; Zhang and Nancollas, 1998), growth at defects is commonly observed to be dominated by a spiral growth spiral mechanism ($n \approx 2$) (Nancollas, 1979; Nielsen, 1981; van Enckevort et al., 1981; Shiraki and Brantley, 1995; Teng et al., 2000; Saldi et al., 2009). In the absence of favourable surface structure, or if the energetics of the system do not favour

growth at defects, growth by adsorption ($n = 1$) may become the dominant mechanism (Nielsen, 1983; Nielsen, 1984). Growth by adsorption has been used to successfully model quartz dissolution and precipitation across a wide range of solution saturation and temperature (Rimstidt and Barnes, 1980), but has only been documented for calcite precipitation near-equilibrium (Nancollas and Reddy, 1971; Shiraki and Brantley, 1995). As supersaturation increases, surface nucleation will, from a certain point on, become the more efficient growth mechanism (e.g., calcite growth; Shiraki and Brantley, 1995; Teng et al., 2000).

Because surface reaction rates (apart from adsorption) are high-power functions of supersaturation, deviation from equilibrium increases reaction rates drastically; this consumes ions in the surface fluid faster than they can be homogenised with the bulk solution. This process establishes a diffusive zone where the surface fluid is maintained at equilibrium by fast surface reactions, and the saturation state in the diffusive zone increases towards the bulk solution (Fig. 9). In this scenario, the rate of surface reactions is capped by the transport of the ions through the diffusive zone, and the overall kinetic behaviour of the system becomes transport-controlled (e.g., Mullin, 1972; Nielsen, 1984; Van Cappellen, 1991; Shiraki and Brantley, 1995; DePaolo, 2011; Watkins et al., 2017). This phenomenon can be illustrated by plotting $\text{rate} \propto (\Omega - 1)$ and $\text{rate} \propto (\Omega - 1)^2$ in Fig. 9, indicating that transport-controlled kinetic behaviour is expected in conditions far from equilibrium.

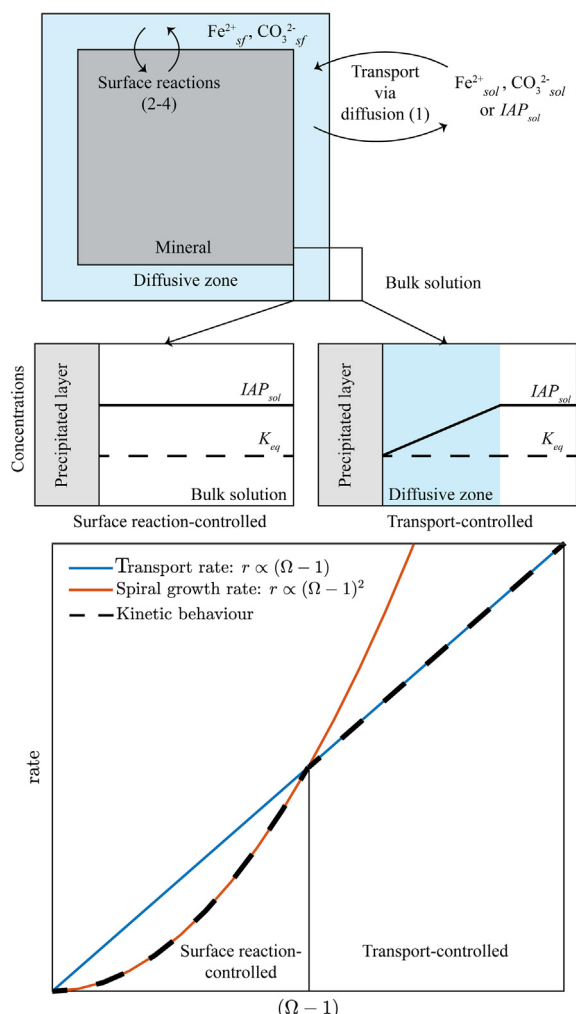


Fig. 9. An illustration of microscopic processes at the mineral-water interface (above) and a schematic of the overall kinetic behaviour of the system (below). Water-mineral interactions (exemplified here is crystal growth) follows the surface reaction kinetic model summarised by DePaolo (2011). At low supersaturation, the kinetic behaviour is determined by surface reactions rate, while the solution is sufficiently homogenised (left column). At high supersaturation, a fast surface reaction rate drives the surface fluid (sf ; in blue) in proximity to the mineral surface to equilibrium, creates a diffusive zone where the transport of dissolved species from the bulk solution (sol) becoming the slowest process (right column). The overall kinetic behaviour (dashed line) is dictated by the slowest process, thus, can be cast as surface reaction-controlled versus transport-controlled as a function of supersaturation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.2. Siderite growth kinetics

The growth rate (r ; $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) of siderite is calculated here as the difference in $[\text{Fe(II)}]$ divided by the time lapse between sampling and normalised against the BET-surface area. To calculate the evolving solution saturation during siderite precipitation, a stoichiometrically equivalent amount (to $\Delta[\text{Fe(II)}]$) of carbon is subtracted from the total DIC, followed by calculation of the remaining $[\text{CO}_3^{2-}]$ and

supersaturation (Supplementary information, S.2); assuming relatively rapid re-equilibration of carbonate species and no $\text{CO}_2(g)$ exchange. These calculations permit us to assign an average growth rate over the sampling interval to the solution saturation at the time of sampling. All measured and calculated values for growth and reprecipitation experiments are listed in Tables 2 and 3, respectively.

Taking the logarithmic form of the general chemical affinity-based rate law (Eq. (2)):

$$\log \text{rate} = \log k + n \log(\Omega - 1),$$

kinetic data from growth experiments (53 data; Table 2) can be fitted to obtain n as the gradient, and k as the intercept:

$$r = 10^{-12.92 \pm 0.10} (\Omega - 1)^{1.223 \pm 0.10}, \quad (3)$$

with 95% confidence bound, $R^2 = 0.94$, and the sum of squared errors of prediction (SSE) of 2.386. The fitted equation indicates an overall mixed transport- and surface reaction-controlled kinetic behaviour, with the former being the dominant.

It is, however, noticeable that the growth rate deviates from the Eq. (3) at low supersaturation (e.g., $\Omega \leq 5$; Fig. 10A). Such deviation may reflect a transition from transport-controlled growth to surface reaction-controlled as the system approaches equilibrium. However, due to the sparsity of low-supersaturation kinetic data from the growth experiments, a rate law in this growth region can not be established with confidence (i.e., 16 data at $\Omega \leq 5$ yield a $R^2 = 0.76$).

Given the theoretical derivation summarised above and the observations that the reprecipitation experiments were capped to a confined range of low supersaturation ($7 < \Omega < 18$; Table 3), we reason that the secondary growth in reprecipitation experiments was controlled by surface reactions (r_{sr} ; $n \approx 2$) instead of transport. This interpretation is supported by the fitted equation (Fig. 10B; 48 data):

$$r_{sr} = 10^{-13.42 \pm 0.14} (\Omega - 1)^{1.868 \pm 0.307}, \quad (4)$$

with 95% confidence bounds, $R^2 = 0.78$, and $SSE = 3.994$. This kinetic-saturation correlation ($n = 1.868$) indicates that siderite growth at low supersaturation is likely dominated by spiral mechanism. A further differentiation among growth by adsorption, at defect sites, and by surface nucleation will require direct microscopic observation employing, for example, atomic force microscopy (Teng et al., 2000; Duckworth and Martin, 2004; Saldi et al., 2009). The effect on DIC and Ω during nanocrystalline siderite dissolution is taken into account in the calculations; DIC increase due to dissolution was $\leq 1.2\%$ (Table 3).

If the kinetic behaviour from the growth experiments at low supersaturation was surface reaction-controlled, by excluding them from fitting (e.g., $\Omega \leq 5$; Fig. 10A), a correlation can be obtained that is consistent with a transport-controlled growth rate (r_{tr} ; 37 data):

$$r_{tr} = 10^{-12.68 \pm 0.16} (\Omega - 1)^{1.057 \pm 0.112}, \quad (5)$$

with 95% confidence bounds, $R^2 = 0.90$, and $SSE = 0.880$. It is important to note that the choice of the cut-off satura-

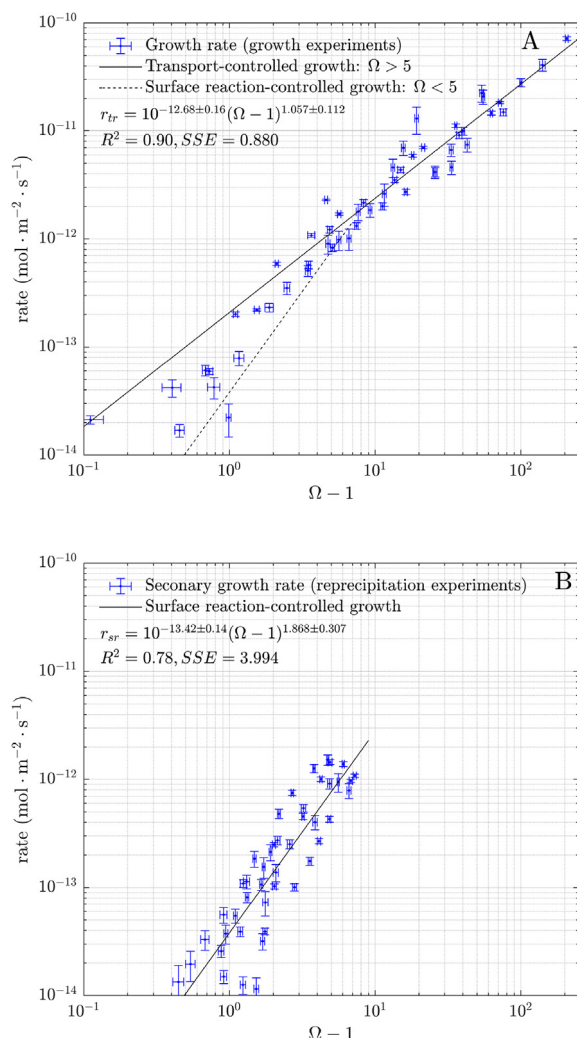


Fig. 10. Kinetic data of (A) growth experiments and (B) secondary growth of reprecipitation experiments plotted against supersaturation with respect to siderite. The secondary growth rate (B) is in a good agreement with surface reaction-controlled kinetic behaviour: $r_{sr} \propto (\Omega - 1)^2$. By excluding the deviation at lower supersaturation ($\Omega < 5$; 16 data), the growth experiments (A) are consistent with a transport-controlled kinetic behaviour: $r_{tr} \propto (\Omega - 1)$. Error (3σ) propagation for growth and reprecipitation rate are calculated from $\sigma_{d[\text{Fe}^{2+}]}$, σ_{Ω} is based on $\sigma_{[\text{Fe}^{2+}]}$, assuming $\sigma_{[\text{CO}_3^{2-}]} = \sigma_{[\text{Fe}^{2+}]}$, and only considers the uncertainty in calculating Ω at the time of sampling.

tion level $\Omega = 5$ is specific to the conditions (temperature, pressure, and ionic strength) and the nature of the siderite seed used in this study.

Transport-controlled kinetic behaviour is subject to the thickness of the diffusive layer, which itself can be a function of fluid dynamics (e.g., stirring speed). Effect of fluid dynamics on transport-controlled kinetic behaviour has been discussed in detail by Mullin (1972), Nielsen (1964, 1984), Plummer et al. (1979) and Watkins et al. (2017). Nielsen (1964, 1984) and Nielsen and Toft (1984) argued that for crystals smaller than $\approx 5 \mu\text{m}$ (siderite seeds in this study are predominantly $\approx 2 \mu\text{m}$ spherical particles; Sec-

tion 3.2.2), the thickness of the diffusive layer is apparently independent of stirring speed; such small particles are carried with the solution and they sediment so slowly that the liquid flow over their surface is too weak to influence diffusion rate. The stirring speed was not examined as a variable here, but experiments were gently agitated twice a day. We, therefore, predict the observed growth rates have little to no dependence on stirring speed.

4.3. Comparison with previous siderite kinetic studies

A number of studies have conducted siderite precipitation experiments at surface temperature, with the purpose of deriving siderite solubility (Singer and Stumm, 1970; Greenberg and Tomson, 1992; Jensen et al., 2002), constraining isotopic fractionation (Jimenez-Lopez and Romanek, 2004; Wiesli et al., 2004; van Dijk et al., 2018), understanding trace metal incorporation (Romanek et al., 2009), and the recent efforts in characterising the amorphous Fe(II)-carbonate precursor (AFC) and its subsequent mineralisation pathways (Azoulay et al., 2012; Sel et al., 2012; Dideriksen et al., 2015; Montes-Hernandez and Renard, 2016; Jiang and Tosca, 2019). To our knowledge, only Jimenez-Lopez and Romanek (2004) provided the necessary constraints on experimental conditions for a direct comparison of growth kinetics at 25 °C. Jimenez-Lopez and Romanek (2004) conducted two sets of experiments, (1) closed-system/free-drifting syntheses and (2) controlled-chemistry experiments where a constant chemical condition was maintained by an autotitrator. They reported multiple metastable precursor phases in their harvested solids, and as the important roles of AFC and chukanovite were not known at the time, they chose to report only the precipitation rate of samples that contained $>50\%$ siderite (determined by XRD). The mixture of multiple phases may have led to the scattering of kinetic data when plotted against supersaturation with respect to pure siderite. This can be demonstrated by refitting their results with the speciation scheme used in this study (Fig. 11). Importantly, our kinetic data are 2 orders of magnitude lower than those reported by Jimenez-Lopez and Romanek (2004) at a comparable supersaturation.

There are a number of factors behind this discrepancy. First, the reported mixtures of multiple phases indicate that the high supersaturation in Jimenez-Lopez and Romanek (2004) experiments might have surpassed and perhaps maintained above the critical supersaturation threshold for homogeneous AFC nucleation (Fig. 2; Jiang and Tosca, 2019). If so, two or more mineralisation processes may have withdrawn solution $[\text{Fe}(\text{II})]$, from which the precipitation rate was calculated by Jimenez-Lopez and Romanek (2004). Secondly, the siderite seed used in their study were crystalline siderite with a BET-surface area of $\leq 1.86 \text{ m}^2 \cdot \text{g}^{-1}$ (where rates were calculated), compared to the $109.75 \text{ m}^2 \cdot \text{g}^{-1}$ of the synthetic seeds used in this study. Aside from the difference in the surface area, the surface activation energy between crystalline and nanocrystalline siderite seeds are no doubt different. Unfortunately, there is insufficient information to conduct a numerical compar-

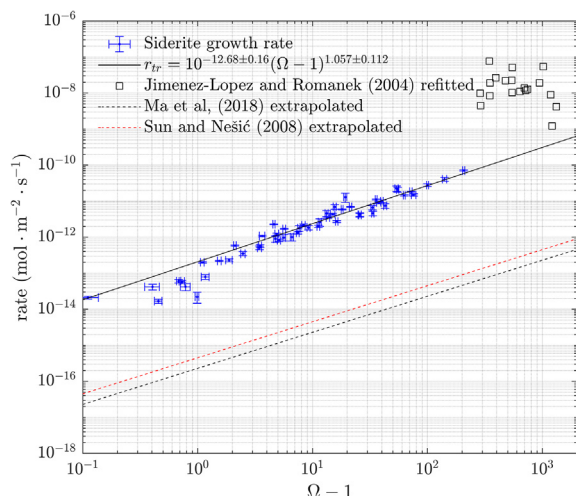


Fig. 11. Comparison of siderite growth rates with previous kinetic studies. Jimenez-Lopez and Romanek (2004) experimental results at 25 °C are refitted with the speciation scheme used in this study (squares), ionic strength correction is calculated based on their measured $[\text{Fe}^{2+}]$, pH, and alkalinity. Ma et al. (2018) and Sun and Nešić (2008) used same kinetic model based on high-temperature experiments, and are both extrapolated to 25 °C using the temperature corrections provided in their models. (dashed lines).

ison between the surface activation energy of the siderite seed between this investigation and theirs.

Siderite precipitation kinetics has been a core interest of corrosion sciences, particularly concerning the corrosion of mild steel in carbonated media (e.g., Johnson and Tomson, 1991; Saheb et al., 2008; Sun and Nešić, 2008; Saheb et al., 2010; Ma et al., 2018; Sk et al., 2017; Burkle et al., 2017; Barker et al., 2018). Though focused on elevated temperature, multiple studies reported transport-controlled kinetic behaviour across a wide range of physico-chemical conditions (Sun and Nešić, 2008; Sk et al., 2017; Ma et al., 2018). For example, Ma et al. (2018) carefully conducted a series of siderite precipitation experiments at a temperature range of 50–80 °C, in which the growth of siderite was measured as weight-gain on an electrochemical quartz crystal micro-balance coated with either $\approx 1 \mu\text{m}$ of iron or $\approx 0.5 \mu\text{m}$ of gold. The *in-situ* micro-balance allowed real-time recording of solid mass on the coated quartz plate, enabled Ma et al. (2018) to differentiate between the initial surface nucleation of Fe(II)-carbonate on the coated plate and the continued growth of the nuclei. They fitted the growth rate to a temperature- and surface activation energy-dependent kinetic model originally proposed by Johnson and Tomson (1991) and modified by Sun and Nešić (2008):

$$\text{rate} = k_r e^{-\frac{\Delta G_a}{RT}} K_{sp,T,I} (\Omega - 1), \quad (6)$$

where k_r is kinetic constant: $3.32 \times 10^7 \text{ m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, ΔG_a is surface activation energy for growth on siderite nuclei: $73739 \text{ J} \cdot \text{mol}^{-1}$, R is the gas constant $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. In the Ma et al. (2018) model, solution saturation (Ω) with respect to siderite is calculated as the product of concentrations instead of activities, and the effects of temperature (T ;

in K) and stoichiometric ionic strength (I) are taken into account in the solubility product $K_{sp,T,I}$ in the following empirical equation summarised by Sun et al. (2009):

$$\log K_{sp,T,I} = -59.3498 - 0.041377T - \frac{2.196}{T} + 24.5724 \log T + 2.518\sqrt{I} - 0.657I. \quad (7)$$

It should be noted that the temperature-dependent terms in Eq. (7) are based on the relationship proposed by Greenberg and Tomson (1992, and Eq. 2 therein), and the stoichiometric ionic strength-dependent terms are taken from Silva et al. (2002), with the constant in Eq. (7) modified to fit with the average of selected siderite solubility values. The average solubility value concluded by Sun et al. (2009) is identical to the crystalline siderite solubility proposed by Nordstrom et al. (1990): $\log K_{sp,T,I} = -10.89$ at 298.15 K and $I = 0$ molal. This value, in fact, was based on the dissolution experiments conducted by Smith (1918), refitted with a speciation scheme that included FeHCO_3^+ , $\text{FeCO}_3(aq)$, and FeOH^+ (Nordstrom et al., 1990). The apparent concordance reached between Greenberg and Tomson (1992) and Nordstrom et al. (1990) can be partially attributed to the adaptation of speciation scheme and equilibrium constants from the latter by the former. In fact, Nordstrom et al. (1990) also proposed $\log K_{sp} = -10.45$ for precipitated siderite solubility, refitted from the work by Singer and Stumm (1970); a more suitable value for siderite precipitation experiments but nevertheless not used. We, therefore, reason that the difference between siderite solubility calculated from Eq. (7) and the value adopted in this study is largely an artefact between calculation schemes instead of a matter of accuracy.

Because this study considers the effect of stoichiometric ionic strength in the calculation of solution saturation and adopts a basic speciation scheme (no Fe(II)-compound; Supplementary information. S.1), we may implement the temperature dependence proposed by Greenberg and Tomson (1992), and modify the constant to yield a $\log K_{sp} = -10.24$ at 298.15 K:

$$\log K_{sp,T} = -58.6989 - 0.041377T - \frac{2.196}{T} + 24.5724 \log T.$$

In so doing, the kinetic model by Ma et al. (2018) (Eq. (6)) and Sun and Nešić (2008) can be extrapolated to 298.15 K for comparison (Fig. 11). Note that a different temperature dependence has been proposed by Bénédeth et al. (2009) for temperature range of 25–250 °C, but the difference in the temperature range of 25–80 °C from that of Greenberg and Tomson (1992) is minor.

The similarity between our kinetic data and that extrapolated from Ma et al. (2018) and Sun and Nešić (2008) does not extend beyond the transport-controlled growth kinetic behaviour (linear correlation with supersaturation); our results are more than 2 orders of magnitude higher than the extrapolated constraints (Fig. 11). This exercise underscores the need for more thermodynamic and kinetic data between 25 °C and 80 °C. For example, Stefánsson et al. (2013) demonstrated the importance of $\text{NaCO}_3^-(aq)$ and $\text{NaHCO}_3(aq)$ complexes in carbonate speciation at elevated

temperature. Not including these carbonate species in high-temperature experiments might have led to overestimations of solution saturation with respect to siderite, thus, potentially contributing to underestimations of kinetic behaviour when extrapolated to 25 °C.

4.4. Comparison with Ca- and Mg-carbonate growth

To compare siderite growth kinetics with the well-documented process of calcite precipitation, calcite growth kinetics are refitted from a comprehensive investigation by [Busenberg and Plummer \(1986, and Table 10 therein\)](#) at 25 °C in solutions stirred at 260 rpm. [Busenberg and Plummer \(1986\)](#) recognised two distinct precipitation regions of calcite (*cal*): (1) near-equilibrium, where growth rate is very low and (2) from $\Omega_{cal} = 1.45$ and higher, where growth rate is proportional to the activity product of dissolved species ([Fig. 12A](#); a similar conclusion was reached in a review by [Shiraki and Brantley, 1995](#)).

In inhibitor-free aqueous conditions at surface temperature and pressure, the growth rate of siderite is nearly 7-orders of magnitude slower than that of calcite at their respective supersaturation ([Fig. 12B](#)). If extrapolated from the observed transport-controlled kinetic behaviour (Eq. (5)), for siderite to achieve a comparable growth rate with that of calcite near-equilibrium, Ω_{sid} needs to exceed 10^5 ([Fig. 12B](#)). Such a supersaturated condition is unrealistic in a natural system, as it is far above the critical supersaturation for homogeneous nucleation of precursor AFC phase ($\Omega_{sid} \approx 600$; [Jiang and Tosca, 2019](#)); pervasive and rapid nucleation of AFC acts as a ceiling for the maximum solution saturation in a natural system.

The significant difference in calcite and siderite growth kinetics has been attributed to the difference in the average surface charge density of Fe^{2+} versus Ca^{2+} ([Jimenez-Lopez and Romanek, 2004](#)). Due to the smaller ionic radius of Fe^{2+} (0.078 nm) than that of Ca^{2+} (0.1 nm; ionic radii taken from [Marcus, 1988](#)), a higher activation energy is required to dehydrate the more densely charged Fe^{2+} ion on the crystal surface to form siderite—which can also be conceptualised as a lower dehydration frequency (e.g., [Nielsen, 1984](#)) or a lower exchange rate of the solvation shell (e.g., [Pokrovsky and Schott, 2002](#)) associated with smaller cations.

If cation charge density is the main contributor behind the slower growth rate of siderite compared to calcite, one may speculate an even slower growth rate of magnesite (MgCO_3) due to the even lower dehydration frequency of Mg^{2+} (0.072 nm) ([Nielsen, 1984](#); [Pokrovsky and Schott, 2002](#)). Indeed, it has long been hypothesised that high dehydration energy for Mg^{2+} prohibits the formation of magnesite at surface conditions (e.g., [Christ and Hostetler, 1970](#); [Sayles and Fyfe, 1973](#); [Kowacz et al., 2007](#)). Instead, low-temperature Mg-carbonate precipitation involves the formation of metastable nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$).

Abiotic magnesite growth kinetics have only been documented from high-temperature experiments, and the most complete data set to date (e.g., [Saldi et al., 2009](#); [Saldi,](#)

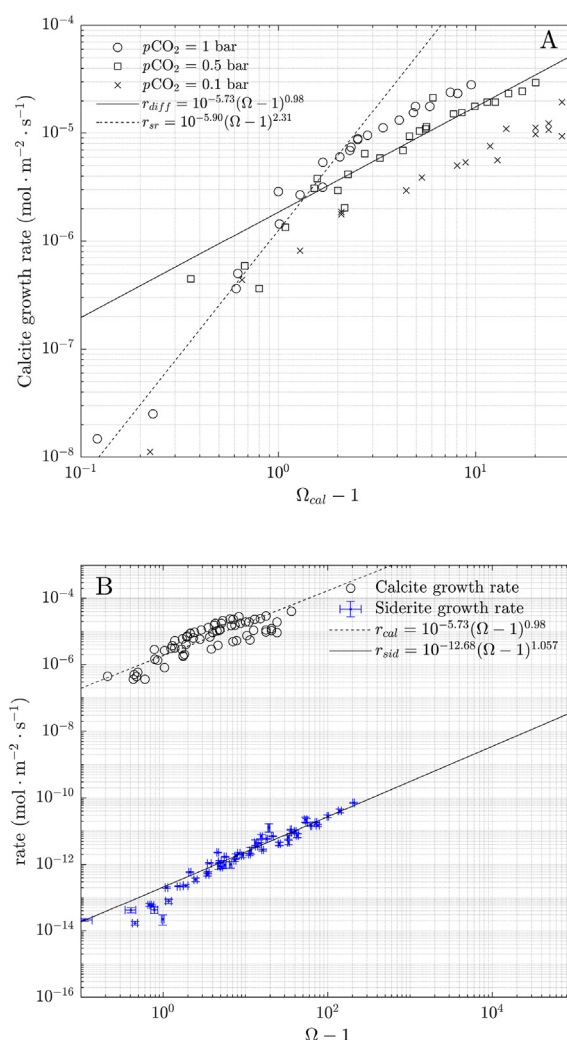


Fig. 12. Comparison of growth kinetics between siderite and calcite. (A) Calcite growth kinetics under different $p\text{CO}_2$ levels at 25 °C, recalculated from measurements by [Busenberg and Plummer \(1986\)](#). Though the absolute kinetic behaviours of calcite growth are different under different $p\text{CO}_2$ conditions, two precipitation regions can be identified: a linear correlation with supersaturation at $\Omega_{cal} \geq 2$, but a higher-order correlation near-equilibrium. Exemplary fitted-lines of two separate precipitation regions are plotted for kinetic behaviour under $p\text{CO}_2 = 0.5$ bar. Calcite solubility $\log K_{sp,cal} = -8.48$ ([Mucci, 1983](#)). (B) Siderite growth rate compared to that of calcite (r_{cal}) ([Busenberg and Plummer, 1986](#)) at their respective supersaturations.

[2009](#)) indicates the growth behaviour of magnesite is controlled by extremely slow surface reactions that involve the desolvation of Mg^{2+} for Ω_{mag} up to 100 in a temperature range of 80–200 °C. [Saldi et al. \(2009\)](#) presented an experimental investigation employing a self-constructed hydrothermal atomic force microscope, which allowed direct measurements of the microscopic propagation velocity of the 2.7 Å-high monomolecular steps on magnesite crystal surface, as well as the frequencies of new steps generation, both as functions of supersaturation. Their diligent examination demonstrated that at elevated temperature (1

step propagation velocity is linearly proportional to supersaturation ($n = 1$) and (2) step generation show a parabolic correlation with supersaturation that is consistent with spiral growth at screw dislocation ($n = 2$). Based on their estimation of activation energies as a function of temperature, Saldi et al. (2009) concluded that spiral growth mechanism for magnesite is prohibited by the much slower step propagation velocity at 25 °C. As such, despite the importance of magnesite growth kinetics, a comparison with siderite growth can not be achieved through temperature extrapolation alone.

5. CONCLUSION

Experimentation on siderite crystal growth at 25 °C yields important constraints on growth kinetics as a function of solution saturation; analogous to calcite growth mechanisms but orders of magnitude slower at comparable saturation. The observed kinetic behaviour of siderite growth is best explained by a chemical affinity-based kinetic model, which predicts a linear correlation with supersaturation ($\Omega - 1$) for growth controlled by transport of dissolved species from the parent solution to the surface fluid (Eq. 5), and a parabolic correlation for growth controlled by spiral mechanism-dominated surface reactions (Eq. (4)). Though the differentiation between these two kinetic behaviours with respect to supersaturation is likely sample- and condition-specific, it lays the foundation for further theoretical and experimental exploration on the kinetic isotope fractionation and trace element incorporation during the precipitation of Fe(II)-carbonate; especially in light of the growing understanding of the thermodynamic properties and mineralisation pathways of this group of carbonates.

The slow kinetics of siderite growth explains the commonly reported siderite supersaturation in anoxic water bodies that are either (1) lacking a suitable surface for heterogeneous siderite precipitation, or (2) open-systems with influxes of Fe(II). In the absence of a suitable surface, siderite precipitates via homogeneous nucleation of the precursor phase amorphous Fe(II)-carbonate, where solution saturation has to surpass a critical threshold that is significantly higher than siderite equilibrium solubility (Fig. 2; Jiang and Tosca, 2019). Because the near-equilibrium growth rate of siderite is extremely slow, any Fe(II) influxes (e.g., microbial Fe(III) reduction, hydrothermal activity, or dissolution of other Fe(II)-minerals) would outpace the slow growth of siderite and lead to the accumulation of Fe^{2+} in the solution, which in turn, increases the solution saturation. This is expected to continue until solution saturation builds to support an appreciable growth/nucleation rate (at high Ω) that balances the Fe(II) influx. In this light, siderite precipitation may be more dynamic and episodic than previously understood, potentially involving multiple mineralisation pathways if nucleation barriers are crossed. This knowledge has important implications for engineering efforts in wetland management, steel corrosion, carbon capture and storage, and long-term nuclear waste storage plan.

Further experimentation is, of course, pivotal in filling the knowledge gap between low- and high-temperature precipitation kinetics and differentiating different surface reac-

tion mechanisms. A complete kinetic framework for Fe(II)-carbonate precipitation holds the key to the genesis of the siderite-rich sedimentary rocks that are fundamental to our understanding of the biogeochemical evolution in the distant past (e.g., Beukes and Gutzmer, 2008; Raiswell et al., 2011; Rasmussen and Muhling, 2018; Jiang and Tosca, 2019; Tosca et al., 2019). More importantly, such knowledge will make a crucial contribution to the Mars 2020 Mission, where the rover will land at Jezero Crater—the only regionally expansive Fe(II)-Mg-carbonate deposit on Mars (Wray et al., 2016; Bridges et al., 2018)—and study these sedimentary formations *in-situ*. Our interpretations of the mineralogical observations from more than 54 million kilometres away, however, will be hindered by the lack of kinetic constraints.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2020.01.047>.

REFERENCES

- Aagaard P. and Helgeson H. C. (1982) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions; I. Theoretical considerations. *Am. J. Sci.* **282**(3), 237–285. <https://doi.org/10.2475/ajs.282.3.237>, issn: 0002-9599.
- Azoulay I., Rémaizeilles C. and Refait Ph. (2012) Determination of standard Gibbs free energy of formation of chukanovite and Pourbaix diagrams of iron in carbonated media. *Corros. Sci.* **58**, 229–236. <https://doi.org/10.1016/j.corsci.2012.01.033>, issn: 0010938X.
- Bachan Avi and Kump Lee R. (2015) The rise of oxygen and siderite oxidation during the Lomagundi Event. *Proc. Nat. Acad. Sci.* **112**(21), 6562–6567. <https://doi.org/10.1073/pnas.1422319112>, issn: 0027-8424.
- Barker Richar, Burkle Danie, Charpentier Thibau, Thompson Harve and Neville Ann (2018) A review of iron carbonate (FeCO_3) formation in the oil and gas industry. *Corros. Sci.* **142**, 312–341. <https://doi.org/10.1016/j.corsci.2018.07.021>, issn: 0010938X.
- Bénézech P., Dandurand J. L. and Harrichoury J. C. (2009) Solubility product of siderite (FeCO_3) as a function of

- temperature (25–250°C). *Chem. Geol.* **265**(1–2), 3–12. <https://doi.org/10.1016/j.chemgeo.2009.03.015>, issn: 00092541.
- Beukes N. J. and Gutzmer J. (2008) Origin and paleoenvironmental significance of major iron formations at the Archean-Paleoproterozoic boundary. *Soc. Econ. Geol. Rev.* **15**, 5–47. <https://doi.org/10.5382/Rev.15.01>, issn: 07410123.
- Bridges John C., Hicks Leon J. and Treiman Allan H. (2018) Carbonates on mars, vol. 5. Elsevier Inc., pp. 89–118. doi: 10.1016/B978-0-12-804191-8.00005-2. isbn: 9780128041918.
- Burkle D., De Motte R., Taleb W., Kleppe A., Comyn T., Vargas S. M., Neville A. and Barker R. (2017) In situ SR-XRD study of FeCO₃ precipitation kinetics onto carbon steel in CO₂-containing environments: The influence of brine pH. *Electrochim. Acta* **255**, 127–144. <https://doi.org/10.1016/j.electacta.2017.09.138>, issn: 00134686.
- Burton W. K., Cabrera N. and Frank F. C. (1951) The growth of crystals and the equilibrium structure of their surfaces. *Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci.* **243**(866), 299–358. <https://doi.org/10.1098/rsta.1951.0006>, issn: 1364-503X.
- Busenberg E. and Plummer L. N. (1986). A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. In *Studies in Diagenesis*. U.S. Geological Survey Bulletin 1578 January 1986. pp. 139–168. issn: 00831093.
- Butler James Newto (1964) *Ionic Equilibrium: A Mathematical Approach*. Addison-Wesley Pub. Co., Reading MA, p. 547.
- Callow Be, Falcon-Suarez Ismae, Ahmed Shari and Matter Juer (2018) Assessing the carbon sequestration potential of basalt using X-ray micro-CT and rock mechanics. *Int. J. Greenhouse Gas Control* **70**, 017 146–156. <https://doi.org/10.1016/j.ijggc.2017.12.008>, issn: 17505836.
- Christ C. L. and Hostetler P. B. (1970) Studies in the system MgO-SiO₂-CO₂-H₂O (II); the activity-product constant of magnesite. *Am. J. Sci.* **268**(5), 439–453. <https://doi.org/10.2475/ajs.268.5.439>, issn: 0002-9599.
- Christoffersen Jørg and Christoffersen Margaret R. (1992) A revised theory for the growth of crystals by surface nucleation. *J. Cryst. Growth* **121**(4), 608–616. [https://doi.org/10.1016/0022-0248\(92\)90568-4](https://doi.org/10.1016/0022-0248(92)90568-4), issn: 00220248.
- DePaolo Donald J. (2011) Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions. *Geochim. Cosmochim. Acta* **75**(4), 1039–1056. <https://doi.org/10.1016/j.gca.2010.11.020>, issn: 00167037.
- Dideriksen Knu, Frandsen Cathrin, Bovet Nicola, Wallace Adam F., Sel Ozle, Arbour Tyle, Navrotsky Alexandr, De Yoreo James J. and Banfield Jill-ian F. (2015) Formation and transformation of a short range ordered iron carbonate precursor. *Geochim. Cosmochim. Acta* **164**, 53–70. <https://doi.org/10.1016/j.gca.2015.05.005>, issn: 00167037.
- van Dijk Joe, Fernandez Alvar, Müller Inigo A., Lever Mar and Bernasconi Stefano M. (2018) Oxygen isotope fractionation in the siderite-water system between 8.5 and 62°C. *Geochim. Cosmochim. Acta* **220**, 535–551. <https://doi.org/10.1016/j.gca.2017.10.009>, issn: 00167037.
- Duckworth Owen W. and Martin Scot T. (2004) Role of molecular oxygen in the dissolution of siderite and rhodochrosite. *Geochim. Cosmochim. Acta* **68**(3), 607–621. [https://doi.org/10.1016/S0016-7037\(00\)00464-2](https://doi.org/10.1016/S0016-7037(00)00464-2), issn: 00167037.
- Gislason Sigurdur Reyni et al. (2010) Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *Int. J. Greenhouse Gas Control* **4**(3), 537–545. <https://doi.org/10.1016/j.ijggc.2009.11.013>, issn: 17505836.
- Greenberg Jane and Tomson Maso (1992) Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature. *Appl. Geochem.* **7**(2), 185–190. [https://doi.org/10.1016/0883-2927\(92\)90036-3](https://doi.org/10.1016/0883-2927(92)90036-3), issn: 08832927.
- Heimann Adrian, Johnson Clark M., Beard Brian L., Valley John W., Roden Eric E., Spicuzza Michael J. and Beukes Nicolas J. (2010) Fe, C, and O isotope compositions of banded iron formation carbonates demonstrate a major role for dissimilatory iron reduction in ~2.5Ga marine environments. *Earth Planet. Sci. Lett.* **294**(1–2), 8–18. <https://doi.org/10.1016/j.epsl.2010.02.015>, issn: 0012821X.
- Hillig W. B. (1966) A derivation of classical two-dimensional nucleation kinetics and the associated crystal growth laws. *Acta Metall.* **14**(12), 1868–1869. [https://doi.org/10.1016/0001-6160\(66\)90046-0](https://doi.org/10.1016/0001-6160(66)90046-0), issn: 00016160.
- Holland H. D. (2007) The geologic history of seawater. In *Treatise on Geochemistry*, vol. 6, pp. 1–46. Treatise on Geochemistry. <https://doi.org/10.1016/B0-08-043751-6/06122-3>. Elsevier, isbn: 0-08-043751-6.
- Holland Heinrich D. (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, p. 598.
- House William A. (1981) Kinetics of crystallisation of calcite from calcium bicarbonate solutions. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **77**(2), 341–359. <https://doi.org/10.1039/F19817700341>, issn: 03009599.
- Jensen Dorth, Boddum Jens, Tjell Jens Christia and Christensen Thomas (2002) The solubility of rhodochrosite (MnCO₃) and siderite (FeCO₃) in anaerobic aquatic environments. *Appl. Geochem.* **17**(4), 503–511. [https://doi.org/10.1016/S0883-2927\(01\)00118-4](https://doi.org/10.1016/S0883-2927(01)00118-4), issn: 08832927.
- Jiang Clancy Zhijia and Tosca Nicholas J. (2019) Fe(II)-carbonate precipitation kinetics and the chemistry of anoxic ferruginous seawater. *Earth Planet. Sci. Lett.* **506**, 231–242. <https://doi.org/10.1016/j.epsl.2018.11.010>, issn: 0012821X.
- Jimenez-Lopez Concepció and Romanek Christopher S. (2004) Precipitation kinetics and carbon isotope partitioning of inorganic siderite at 25°C and 1 atm. *Geochim. Cosmochim. Acta* **68**(3), 557–571. [https://doi.org/10.1016/S0016-7037\(03\)00460-5](https://doi.org/10.1016/S0016-7037(03)00460-5), issn: 00167037.
- Johnson M. L. and Tomson M. B. (1991) Ferrous Carbonate Precipitation Kinetics and its Impact CO₂ Corrosion. *Corros. Houston T.* **268**.
- Kandegeedara Ashok and Rorabacher David B. (1999) Noncomplexing tertiary amines as better buffers covering the range of pH 3–11. Temperature Dependence of Their Acid Dissociation Constants. *Analyt. Chem.* **71**(15), 3140–3144. <https://doi.org/10.1021/ac9902594>, issn: 0003-2700.
- Kaufman Alan J., Hayes J. M. and Klein C. (1990) Primary and diagenetic controls of isotopic compositions of iron-formation carbonates. *Geochim. Cosmochim. Acta* **54**(12), 3461–3473. [https://doi.org/10.1016/0016-7037\(90\)90298-Y](https://doi.org/10.1016/0016-7037(90)90298-Y), issn: 00167037.
- Klein Corneli (2005) Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. *Am. Mineral.* **90**(10), 1473–1499. <https://doi.org/10.2138/am.2005.1871>, issn: 0003004X.
- Kowacz M., Putnis C. V. and Putnis A. (2007) The effect of cation: anion ratio in solution on the mechanism of barite growth at constant supersaturation: Role of the desolvation process on the growth kinetics. *Geochim. Cosmochim. Acta* **71**(21), 5168–5179. <https://doi.org/10.1016/j.gca.2007.09.008>, issn: 00167037.
- Lasaga Antonio C. (1984) Chemical kinetics of water-rock interactions. *J. Geophys. Res.: Solid Earth* **89**(B6), 4009–4025. <https://doi.org/10.1029/JB089iB06p04009>, issn: 01480227.
- Lasaga, Antonio C. (1998) 7. Theory of Crystal Growth and Dissolution. In *Kinetic Theory in the Earth Sciences* (ed. H.D. Holland). Princeton University Press, Princeton. pp. 581–618. isbn: 0-691-03748-5.

- Ma, Zheng, Yang Yang, Bruce Brown, Srdjan Nesic and Marc Singer (2018) Investigation of precipitation kinetics of FeCO_3 by EQCM. In *Corrosion Science* 141. June, pp. 195–202. doi: 10.1016/j.corsci.2018.06.017. issn: 0010938X.
- Marcus Yizha (1988) Ionic radii in aqueous solutions. *Chem. Rev.* **88**, 1475–1498. <https://doi.org/10.1007/BF00646201>, arXiv: 1402.6991v1. issn: 00959782.
- Montes-Hernandez Germa and Renard François (2016) Time-resolved in situ raman spectroscopy of the nucleation and growth of siderite, mag-nesite, and calcite and their precursors. *Cryst. Growth Des.* **16**(12), 7218–7230. <https://doi.org/10.1021/acs.cgd.6b01406>, issn: 15287505.
- Mucci A. (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Am. J. Sci.* **283**(7), 780–799. <https://doi.org/10.2475/ajs.283.7.780>, issn: 0002–9599.
- Mullin, J. W. (1972) Crystallization. 2nd. London: Butterworths, p. 600. isbn: 0408703490.
- Nancollas George H. (1979) The growth of crystals in solution. *Adv. Colloid Interface Sci.* **10**(1), 215–252. [https://doi.org/10.1016/0001-8686\(79\)87007-4](https://doi.org/10.1016/0001-8686(79)87007-4), issn: 00018686.
- Nancollas George H. and Reddy Michael M. (1971) The crystallization of calcium carbonate. II. Calcite growth mechanism. *J. Colloid Interface Sci.* **37**(4), 824–830. [https://doi.org/10.1016/0021-9797\(71\)90363-8](https://doi.org/10.1016/0021-9797(71)90363-8), issn: 00219797.
- Nielsen Arne Eri (1964) *Kinetics of precipitation*. Pergamon Press, New York.
- Nielsen Arne Eri (1981) Theory of electrolyte crystal growth. The parabolic rate law. *Pure Appl. Chem.* **53**(11), 2025–2039. <https://doi.org/10.1351/pac198153112025>, issn: 1365-3075.
- Nielsen, Arne Erik (1983). Precipitates: formation, coprecipitation, and aging. In *Treatise on Analytical Chemistry* (ed. by I.Mtff and P.J. Elving). Wiley. pp. 269–347.
- Nielsen Arne Eri (1984) Electrolyte crystal growth mechanisms. *J. Cryst. Growth* **67**(2), 289–310. [https://doi.org/10.1016/0022-0248\(84\)90189-1](https://doi.org/10.1016/0022-0248(84)90189-1), issn: 002202.
- Nielsen, Arne Erik and Christoffersen J. (1982) The Mechanisms of Chrystal Growth and Dissolution. In *Biological Mineralization and Demineraliza-tion* (ed. by G H Nancollas). Springer, Berlin, Heidelberg. pp. 37–77. isbn: 978-3-642-68574-3.
- Nielsen Arne Eri and Toft Jens M. (1984) Electrolyte crystal growth kinetics. *J. Cryst. Growth* **67**(2), 278–288. [https://doi.org/10.1016/0022-0248\(84\)90188-X](https://doi.org/10.1016/0022-0248(84)90188-X), issn: 00220248.
- Nordstrom Darrell Kir, Niel Plummer L., Langmuir Donal, Busenberg Eurybiade, May Howard M., Jones Blair F. and Parkhurst David L. (1990) Revised chemical equilibrium data for major water—mineral reactions and their limitations. *Chem. Model. Aqueous Syst. II*, 398–413. <https://doi.org/10.1021/bk-1990-0416.ch031>.
- Oelkers E. H., Gislason S. R. and Matter J. (2008) Mineral Carbonation of CO_2 . *Elements* **4**(5), 333–337. <https://doi.org/10.2113/gselements.4.5.333>, issn: 1811-5209.
- Ogundele G. I. and White W. E. (1986) Some observations on corrosion of carbon steel in aqueous environments containing carbon dioxide. *Corrosion* **42**(2), 71–78. <https://doi.org/10.5006/1.3584888>, issn: 0010-9312.
- Plummer L. N., Parkhurst D. L. and Wigley T. M. L. (1979) Critical Review of the Kinetics of Calcite Dissolution and Precipitation In pp. 537–573. doi: 10.1021/bk-1979-0093.ch025.
- Pokrovsky O. S. and Schott J. (2002) Surface chemistry and dissolution kinetics of divalent metal carbonates. *Environ. Sci. Technol.* **36**(3), 426–432. <https://doi.org/10.1021/es010925u>, issn: 0013936X.
- Raiswell Rob, Reinhard Christopher T, Derkowski Arkadiusz, Owens Jeremy, Bottrell Simon H, Anbar Ariel D, Lyons Timothy W (2011). Formation of syngenetic and early diagenetic iron minerals in the late Archean Mt. McRae Shale, Hamersley Basin, Australia: New insights on the patterns, controls and paleoenvironmental implications of authigenic mineral formation. *Geochim. Cosmochim. Acta* **75**(4), 1072–1087. doi: 10.1016/j.gca.2010.11.013. issn: 00167037.
- Rasmussen, Birger and Muhling Janet R. (2018). Making magnetite late again: Evidence for widespread magnetite growth by thermal decomposition of siderite in Hamersley banded iron formations. *Precambrian Res.* **306**(June 2017), 64–93. doi: 10.1016/j.precamres.2017.12.017. issn: 03019268.
- Rimstidt J. D. and Barnes H. L. (1980) The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta* **44**(11), 1683–1699. [https://doi.org/10.1016/0016-7037\(80\)90220-3](https://doi.org/10.1016/0016-7037(80)90220-3), issn: 00167037.
- Romanek Christopher S., Jiménez-López Concepción, Navarro Alejandro Rodrigue, Sánchez-Román Monic, Sahai Nit and Coleman Ma (2009) Inorganic synthesis of Fe-Ca-Mg carbonates at low temperature. *Geochim. Cosmochim. Acta* **73**(18), 5361–5376. <https://doi.org/10.1016/j.gca.2009.05.065>, issn: 00167037.
- Saheb M., Descostes M., Neff D., Matthiesen H., Michelin A. and Dillmann P. (2010) Iron corrosion in an anoxic soil: Comparison between thermody-namic modelling and ferrous archaeological artefacts characterised along with the local in situ geochemical conditions. *Appl. Geochem.* **25**(12), 1937–1948. <https://doi.org/10.1016/j.apgeochem.2010.10.010>, issn: 08832927.
- Saheb M., Neff D., Dillmann P, Matthiesen H. and Foy E. (2008) Long-term corrosion behaviour of low-carbon steel in anoxic environment: Characterisation of archaeological artefacts. *J. Nucl. Mater.* **379**(1–3), 118–123. <https://doi.org/10.1016/j.jnucmat.2008.06.019>, issn: 00223115.
- Saldi, Giuseppe (2009). Les cinétiques de dissolution et précipitation de la magnesite aux conditions hydrothermales. PhD thesis. Thèse de l'Université Paul-Sabatier, Toulouse, p. 184.
- Saldi Giuseppe D., Jordan Guntra, Schott Jacques and Oelkers Eric H. (2009) Magnesite growth rates as a function of temperature and saturation state. *Geochim. Cosmochim. Acta* **73**(19), 5646–5657. <https://doi.org/10.1016/j.gca.2009.06.035>, issn: 00167037.
- Sayles F. L. and Fyfe W. S. (1973) The crystallization of magnesite from aqueous solution. *Geochim. Cosmochim. Acta* **37**(1), 87–99. [https://doi.org/10.1016/0016-7037\(73\)90246-9](https://doi.org/10.1016/0016-7037(73)90246-9), issn: 00167037.
- Schwab A. P. and Lindsay W. L. (1983) Effect of redox on the solubility and availability of iron. *Soil Sci. Soc. Am. J.* **47**(2), 201. <https://doi.org/10.2136/sssaj1983.03615995004700020005x>, issn: 0361-5995.
- Sel Ozle, Radha A. V., Dideriksen Knu and Navrotsky Alexandr (2012) Amorphous iron (II) carbonate: Crystallization energetics and comparison to other carbonate minerals related to CO_2 sequestration. *Geochim. Cosmochim. Acta* **87**, 61–68. <https://doi.org/10.1016/j.gca.2012.03.011>, issn: 00167037.
- Shiraki Ryoj and Brantley Susan (1995) Kinetics of near-equilibrium cal-cite precipitation at 100C: An evaluation of elementary reaction-based and affinity-based rate laws. *Geochim. Cosmochim. Acta* **59**(8), 1457–1471. [https://doi.org/10.1016/0016-7037\(95\)00055-5](https://doi.org/10.1016/0016-7037(95)00055-5), issn: 00167037.
- Silva Carlos A , Liu Xuew and Millero F. J. (2002) Solubility of Siderite (FeCO_3) in NaCl Solutions. *J. Solution Chem.* **31**(2), 97–108. <https://doi.org/10.1023/A:1015275618138>, issn: 0095-9782.
- Singer Philip C. and Stumm Werne (1970) The solubility of ferrous iron in carbonate-bearing waters. *J. Am. Water Works Assoc.* **62**(3), 198–202. <https://doi.org/10.1002/j.1551-8833.1970.tb03888.x>, issn: 0003150X.
- Sk Mobbassar Hassan, Abdullah Aboubakr M, Ko Monika, Ingham Bridget, Laycock Nick, Arul Rakesh and Williams

- David E. (2017). Local super-saturation and the growth of protective scales during CO₂ corrosion of steel: Effect of pH and solution flow. *Corrosion Sci.* 126(January), 26–36. doi: 10.1016/j.corsci.2017.05.026. issn: 0010938X.
- Smith, Herbert J. (1918) On equilibrium in the system: ferrous carbonate, carbon dioxide and water.1. *J. Am. Chem. Soc.* 40 (6), 879–883. doi: 10.1021/ja02239a002. issn: 0002-7863.
- Stefánsson Andr, Bénézeth Pascal and Schott Jacque (2013) Carbonic acid ionization and the stability of sodium bicarbonate and carbonate ion pairs to 200C - A potentiometric and spectrophotometric study. *Geochimica et Cosmochimica Acta* 120, 600–611. <https://doi.org/10.1016/j.gca.2013.04.023>, issn: 00167037.
- Sun W. and Nešić S. (2008) Kinetics of corrosion layer formation: part I—iron carbonate layers in carbon dioxide corrosion. *Corrosion* 64(4), 334–346. <https://doi.org/10.5006/1.3278477>, issn: 0010-9312.
- Sun We, Nešić Srdja and Woollam Richard C. (2009) The effect of temperature and ionic strength on iron carbonate (FeCO₃) solubility limit. *Corros. Sci.* 51(6), 1273–1276. <https://doi.org/10.1016/j.corsci.2009.03.009>, issn: 0010938X.
- Teng H. Henr, Dove Patricia M. and De Yoreo James J. (2000) Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws. *Geochim. Cosmochim. Acta* 64(13), 2255–2266. [https://doi.org/10.1016/S0016-7037\(00\)00341-0](https://doi.org/10.1016/S0016-7037(00)00341-0), issn: 00167037.
- Tosca Nicholas J, Jiang Clancy Zhijian, Rasmussen Birger and Muhling Janet (2019). Products of the iron cycle on the early Earth. *Free Radic. Biol. Med.* 140(December 2018), 138–153. doi: 10.1016/j.freeradbiomed. 2019.05.005. issn: 08915849.
- Van Cappellen P. (1991) *The Formation of Marine Apatite: A Kinetic Study* PhD thesis. Yale University, p. 240.
- van Enckevort W. J. P., Bennema P. and van der Linden W. H. (1981) On the observation of growth spirals with very low step heights on potash alum single crystals. *Z. Phys. Chem.* 124(2), 171–191. <https://doi.org/10.1524/zpch.1981.124.2.171>, issn: 0942-9352.
- Wajon Johannes Edmun, Ho Goen-En and Murphy Peter J. (1985) Rate of precipitation of ferrous iron and formation of mixed iron-calcium carbonates by naturally occurring carbonate materials. *Water Res.* 19(7), 831–837. [https://doi.org/10.1016/0043-1354\(85\)90140-X](https://doi.org/10.1016/0043-1354(85)90140-X), issn: 00431354.
- Watkins James M., DePaolo Donald J. and Bruce Watson E. (2017) Kinetic fractionation of non-traditional stable isotopes by diffusion and crystal growth reactions. *Rev. Mineral. Geochem.* 82(1), 85–125. <https://doi.org/10.2138/rmg.2017.82.4>, issn: 1529-6466.
- Wiesli René A., Beard Brian L. and Johnson Clark M. (2004) Experimental determination of Fe isotope fractionation between aqueous Fe(II), siderite and green rust in abiotic systems. *Chem. Geol.* 211(3-4), 343–362. <https://doi.org/10.1016/j.chemgeo.2004.07.002>, issn: 00092541.
- Wray James , Murchie Scott , Bishop Janice , Ehlmann Bethany , Milliken Ralph , Wilhelm Mary Bet, Seelos Kimberly and Chojnacki Matthe (2016) Orbital evidence for more widespread carbonate-bearing rocks on Mars. *J. Geophys. Res.: Planets* 121(4), 652–677. <https://doi.org/10.1002/2015JE004972>, issn: 21699097.
- Xu Tianf, Apps John A. and Pruess Karste (2004) Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Appl. Geochem.* 19(6), 917–936. <https://doi.org/10.1016/j.apgeochem.2003.11.003>, issn: 08832927.
- Xu Tianf, Apps John A. and Pruess Karste (2005) Mineral sequestration of carbon dioxide in a sandstone-shale system. *Chem. Geol.* 217(3-4), 295–318. <https://doi.org/10.1016/j.chemgeo.2004.12.015>, issn: 00092541.
- Zhang Jingw and Nancollas George H. (1990) Kink densities along a crystal surface step at low temperatures and under nonequilibrium conditions. *J. Cryst. Growth* 106(2-3), 181–190. [https://doi.org/10.1016/0022-0248\(90\)90062-P](https://doi.org/10.1016/0022-0248(90)90062-P), issn: 00220248.
- Zhang Jingw and Nancollas George H. (1998) Kink density and rate of step movement during growth and dissolution of an AB crystal in a nonstoichiometric solution. *J. Colloid Interface Sci.* 200(1), 131–145. <https://doi.org/10.1006/jcis.1997.5357>, issn: 00219797.

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