# From mixed flow reactor to column experiments and modeling: Upscaling of calcite dissolution rate

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## ARTICLE INFO

## ABSTRACT

The objective of this work was to assess the extent to which calcite dissolution rate ($R_{calcite}$) measured at controlled saturation state in mixed flow set-ups could be upscaled to column experiments, where the solution composition was variable in space and time. The dissolution rate of the (104) calcite face was investigated in mixed flow reactor set-ups at room temperature and pH 8. Various saturation conditions were studied by changing the composition of the inlet solution, enabling the determination of an empirical relation between $R_{calcite}$ and the Gibbs free energy of calcite dissolution ($\Delta G$) by measuring the surface topography with vertical scanning interferometry (VSI). The prevalent dissolution mode (i.e., etch pit nucleation or homogeneous surface retreat) was assessed with the same method. A dramatic decrease of the dissolution rate was observed for $-8 < \Delta G < -3$ kJ/mol, correlated with a switch in the dissolution regime (inhibition of etch pit nucleation). The resulting $R_{calcite}$-$\Delta G$ relation, which is at odds with that derived from transition state theory (TST), was successfully fitted using the stepwave model (SWM). These experiments were supplemented with plug-flow column experiments, consisting of a chemically inert porous medium and oriented rhombohedral calcite single-crystals ($0.4 \times 0.4$ cm$^2$) regularly distributed in the column. The dissolution rates of calcite single crystals all along the column were retrieved using VSI on the recovered crystals at the end of the experiments. These latter experiments were compared with 1D and 2D reactive transport simulations, using either the TST- or the SWM-derived rate equation determined from our mixed-flow reactor experiments. The reactive transport simulations revealed that (i) 1D-simulations overestimated the dissolution rate of upstream and downstream calcite faces by a ~3- and ~20-fold factor, (ii) 2D-simulations satisfactorily reproduced the dissolution rates of all faces without any fitting parameter, within experimental uncertainties and (iii) both models slightly overestimated the steady-state concentration of calcium at the outlet of the column. Overall, this study can be considered as one of the multiple intermediate steps between chemostatic experiments and field measurements to assess the validity of the classical bottom-up upscaling approach. It also provides insight into our ability to model fluid flow and solution composition in the vicinity of dissolving single crystals.

## 1. Introduction

Considerable advances concerning our understanding of chemical weathering processes and their impact on water chemistry or Earth's climate occurred over the last decades. Various processes impact weathering, but one of the most significant is the chemical weathering (dissolution or precipitation) of minerals. The kinetics of these reactions contribute to (bio)geochemical cycles as important as the C cycle, as the chemical weathering of silicate and carbonate minerals represents a net sink for $CO_2$ over long (Berner, 1990) and short (Beaulieu et al., 2012) timescales, respectively. As a consequence, a significant body of experimental and theoretical studies was dedicated to the development of kinetic rate laws of mineral dissolution and precipitation (Brantley and

Olsen, 2014). However, bridging the gap between laboratory experiments and field data remains an elusive goal, as mineral dissolution/precipitation rates measured in the laboratory generally remain orders of magnitude greater than those measured in the field (Fischer et al., 2014; White and Brantley, 2003). A common way to circumvent this upscaling issue is to tune several modeling parameters (e.g., Aradóttir et al., 2012; Montes-H et al., 2005), albeit this strategy is not devoid of risks, because it does not account for the mechanistic origins of the so-called "field-lab" discrepancy.

Several non-exclusive explanations have been proposed to account for such discrepancies, which can be divided into intrinsic and extrinsic factors (White and Brantley, 2003). Intrinsic factors are related to the physicochemical properties of the reacting mineral itself, such as the

density of line defects (e.g., screw dislocations) outcropping at the mineral surface (Fischer et al., 2012; Macinnis and Brantley, 1992; MacInnis and Brantley, 1993; Pollet-Villard et al., 2016b; Smith et al., 2013; Teng, 2004), which represent favorable surface energy sites that promote the nucleation of etch pits (Lasaga and Blum, 1986; Pollet-Villard et al., 2016b), or the distribution of crystal morphologies, which results in a wide range of crystal reactivities due to dissolution anisotropy (Daval et al., 2013; Godinho et al., 2012; Pollet-Villard et al., 2016a; Smith et al., 2013). Extrinsic factors encompass all processes and parameters that are not derived from the nature of the dissolving mineral, such as the microbial activity or the chemical composition of the aqueous phase and, in particular, the saturation state of the solution with respect to the considered mineral (Schott et al., 2009; Smith et al., 2013; Teng, 2004). In that respect, it has been suggested that the effect of the driving force of the reaction (i.e., the Gibbs free energy of reaction, $\Delta G$) on the dissolution rate ($R$), often implemented in reactive transport codes by using a relation derived from transition state theory (TST; Eyring, 1935; Lasaga, 1995), fails to account for the actual $R$–$\Delta G$ relations (e.g., Burch et al., 1993; Lasaga and Luttge, 2001; Pollet-Villard et al., 2016a; Smith et al., 2013), and that the use of alternative relations such as the stepwave model (Lasaga and Luttge, 2001) helps to improve the agreement between modeled and measured weathering rates (Maher et al., 2009). Hence, a possible improvement of the reliability of reactive transport simulations (at least partly) relies on the implementation of the actual dependence of mineral dissolution rates on the solution saturation state.

Closely related to the issue of $R$–$\Delta G$ relations, other critical extrinsic factors that may contribute to bridging the gap between laboratory- and field-derived chemical weathering rates are the knowledge of the local fluid composition surrounding the dissolving minerals that impacts their dissolution rates (Molins et al., 2014; Noiriel and Daval, 2017), and the existence of diffusive boundary layers (Ruiz-Agudo et al., 2016).

In general, flow and solute transport in a porous medium are modeled at the scale of a representative elementary volume (REV) where the porous medium is described as continuous. Depending on the spatial discretization of the domain (1D to 3D, size of the control volume used to compute the numerical solution), the computation of the fluid velocity will show different kinds of variability. Conversely, at the pore scale, flow paths are complex and might have a significant impact on the reactivity of a given geological formation. In that respect, the use of geochemical models in a simplified 1D geometry (e.g., WITCH model, Godderis et al., 2006) allows for fast computation, but may miss important issues related to the complex fluid velocity around minerals and to the mixing due to lateral dispersion/diffusion in case of concentration gradients.

The objective of this work was to quantify the dissolution rate of calcite using mixed flow reactor (MFR) experiments performed on cleaved and polished {104} calcite surfaces and to use the corresponding model and parameters to evaluate the dissolution of calcite under different flow conditions, i.e. in a column filled with an inert material. The key question that we aimed to tackle can be summarized as follows: can we use the dissolution rate law defined by experiments performed in MFR in turbulent flow conditions to model the dissolution rate of calcite measured in a porous medium under laminar flow and in cylindrical configuration? Furthermore, because column experiments are usually described in one dimension, we also analyzed the effects of this additional simplification on the modeling of the dissolution processes. This comparison can be considered as one of the many intermediate steps between chemostatic experiments and field tests to assess the validity of the classical bottom-up upscaling approach (see e.g. Galeczka et al., 2014; Molins et al., 2014 for similar attempts). It also provides insights into our ability to model fluid flow and solution composition in the vicinity of dissolving single crystals.

**Table 1**

Chemical composition of calcite used in experiments. Concentrations are determined from 3 g of calcite by loss on ignition and alkaline fusion.

| Elements | Loss 1000 °C | CaO | MgO | MnO | Sr |
|---|---|---|---|---|---|
| | % | % | ‰ | ‰ | ppm |
| Calcite | 42.3 | 57.2 | 2 | 0.08 | 475 |

## 2. Materials and experimental methods

### 2.1. Sample preparations

A decimeter-sized calcite sample (see Table 1 for chemical composition) optically transparent coming from the Massif des Ecrins (Alpes, France) was cleaved following the natural {104} calcite plane to obtain several single crystals of calcite with a size ranging from 0.3 to 0.6 cm. The crystallographic orientation was verified over the entire surface of each sample using electron backscatter diffraction (EBSD) on a Tescan Vega 2 scanning electron microscope (SEM). Each sample was subsequently polished down to the nanometer-scale in aqueous solution saturated with respect to calcite to avoid etching of the surface through a multi-step abrasive sequence. The obtained samples had a similar initial average arithmetic roughness ($Ra$), defined as the arithmetic average of the absolute values of the roughness profile, ranging between 43 and 100 nm, enabling us to minimize the effect on the dissolution rate of various step densities on the mineral surfaces. This initial roughness parameter was measured on $350 \times 85 \, \mu m^2$ images collected using vertical scanning interferometry (VSI, see below).

Two types of experiments were conducted: mixed-flow reactor experiments and a flow-through column experiment. Regarding mixed-flow reactor experiments, only one face was polished whereas for the column experiment, both the front (upstream) and back (downstream) faces of each crystal were polished (see Sections 2.3 and 2.4).

Finally, for each sample, a portion of the surface was masked with either RTV glue or CrystalBond™ (CB) for mixed flow or column experiments, respectively. This protocol prevented interactions between the portion of the mineral underneath the mask and the fluid and, thus, provided a non-reacted reference surface to measure the height difference between the masked and unmasked portions (that is, the dissolution rate) using VSI.

### 2.2. Aqueous solution preparations

Reagent-grade NaCl, NaHCO$_3$ and CaCl$_2$ were added to ultra-pure water (18 MΩ·cm) in different concentrations similar to Smith et al. (2013). NaCl (5.85 g/L) was added to fix the ionic strength to approximately 0.1 molal. The addition of 0.086 g/L of NaHCO$_3$ fixed the alkalinity and various concentrations of CaCl$_2$ were used to vary the saturation index of the solution with respect to calcite (see Table 2). Before experiments, the solutions were left at rest for a day to allow equilibration with atmospheric CO$_2$. The measured pH of these solutions was $8.0 \pm 0.1$.

### 2.3. Mixed flow reactor experiments

Classical mixed-flow reactor experiments such as described in, e.g., Pokrovsky and Schott (2000) were conducted on calcite single crystals as a function of the solution saturation state. In brief, a 50 mL Teflon reactor containing the single-faced polished calcite samples placed on a Teflon tripod with a Teflon-coated stir bar was connected with Tygon tubing to a Gilson Minipuls 3 peristaltic pump running at a constant flow rate (0.25 mL/min). The aqueous solution at the outlet of the reactor was regularly sampled for pH and calcium measurements. All