

Modeling dolomite-brine interaction in the context of geological CO₂ sequestration.

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INTRODUCTION

The repository rocks to inject CO₂ at the Hontomín test site (northern Spain) are dominantly limestones and dolostones (Fig. 1). Interaction between dissolved CO₂-rich brine and the rocks will induce dissolution of carbonate minerals. Since the Hontomin brine contains sulfate, gypsum (or anhydrite at depth) can precipitate, resulting in a gypsum coating on the dissolving carbonate minerals' surface to cause its passivation. These reactions may change the porosity, permeability and storage capacity of the reservoir. In this study, laboratory column experiments under atmospheric pCO₂ are performed to quantify these processes. 1-D numerical simulations of the experimental results using the reactive transport code CrunchFlow (Steeffel, 2009) are suitable to validate kinetic parameters, such as the mineral reactive surface area values and kinetic rate laws) used to predict the geochemical evolution in experiments run under supercritical CO₂ conditions (pCO₂ of 80 bar and 60 °C).

METHODOLOGY

A column experiment was conducted under atmospheric pCO₂ (Fig. 2). The input solution circulated through the column (V = 39 mL) packed with dolomite fragments (1-2 mm in size) (Fig. 2) at 8.3x10⁻¹⁰ m³/s, i.e., Darcy velocity (V_D) of 1.5x10⁻⁶ m³/m²/s, which is similar to the flux at the vicinity of the injection borehole at Hontomin. The input solution was rich in calcium and nearly equilibrated with respect to gypsum with an initial pH of 2.5. The initial porosity is 0.46. For the 1-D simulations the column is discretized in 20 nodes. The code couples the transport equation with the kinetic rate laws, and the reactive surface areas are updated according to the equations shown in Fig. 3.

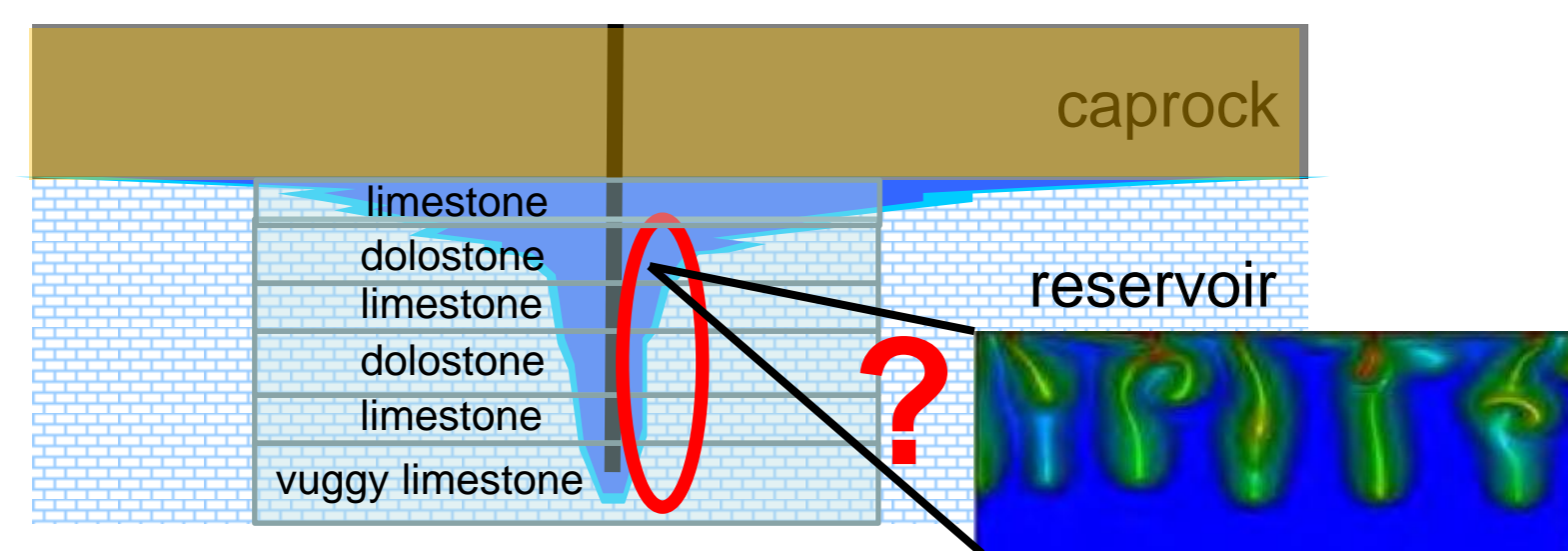


Fig. 1 About 2-3 % of the supercritical CO₂ will be dissolved in the reservoir brine (fingering formation). The dissolved CO₂-rich brine will interact with the reservoir rocks (limestones and dolostones in Hontomín).

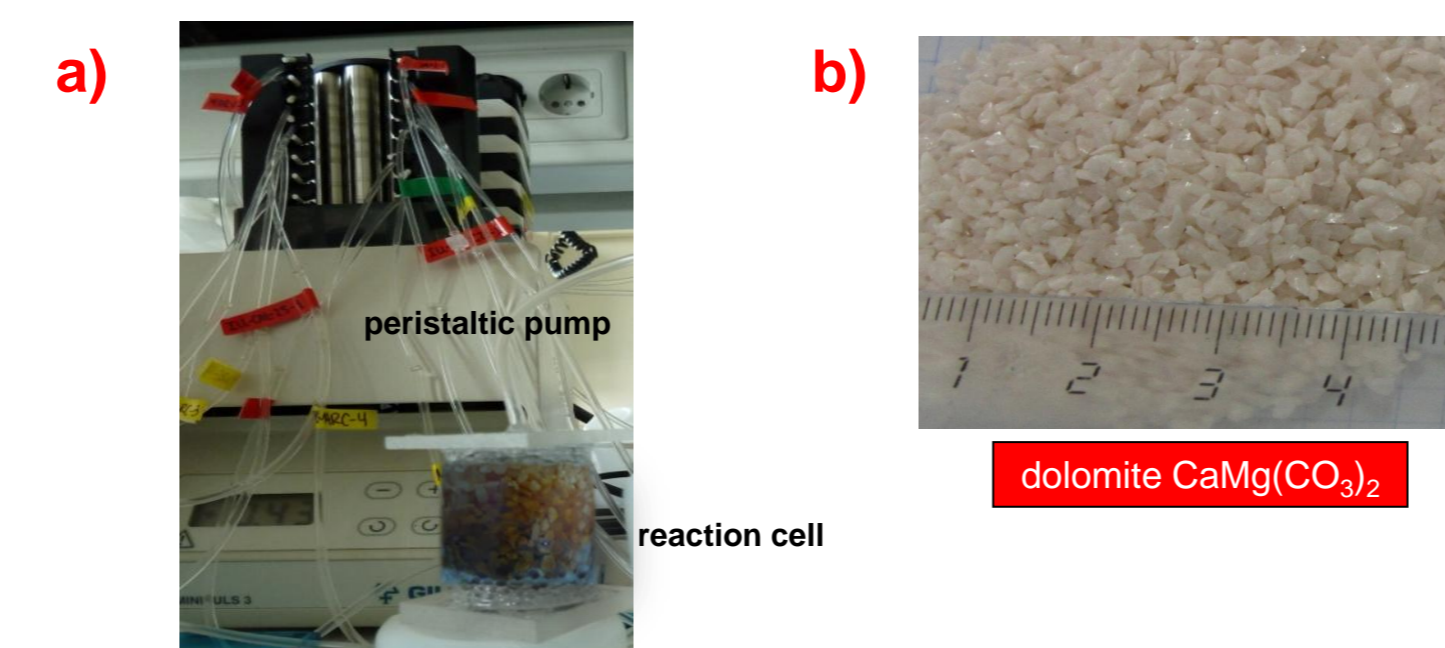


Fig. 2 (a) Flow-through column packed with dolomite fragments shown in (b).

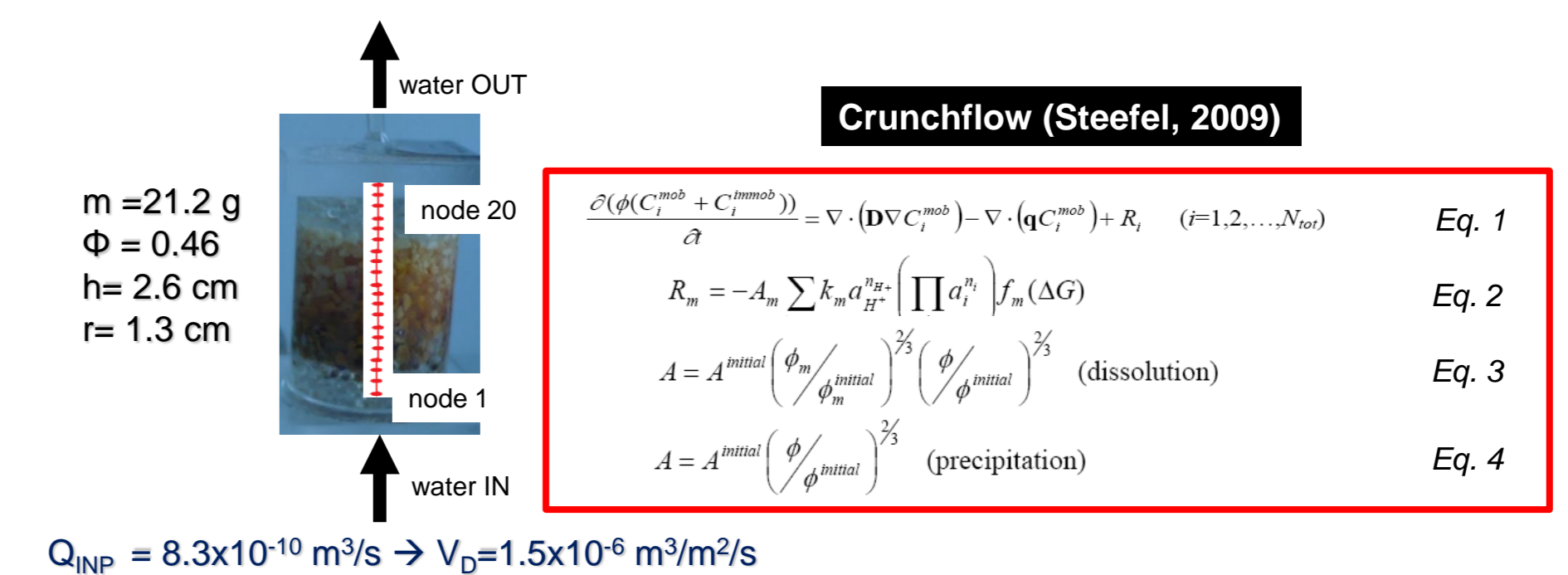


Fig. 3. Conceptual model and reactions that are considered in the reactive transport code CrunchFlow.

RESULTS AND DISCUSSION

Variation of Ca, Mg and S concentrations and pH with time is shown in Fig. 4. With time, calcium concentration is higher than the initial one (dolomite dissolution), magnesium is released (dolomite dissolution), and the concentration of sulfate is lower than the initial one (gypsum precipitation). The simulations match the experimental data (Fig. 4). Reactive surface area values were adjusted to match the experimental results. After 3 months, the calcite precipitate at the end of the column (before 0.015m), anhydrite precipitate at the beginning of the column (first 0.005m) and dolomite dissolves, causing an increase in porosity of the beginning of the column is observed (Fig. 4). The simulated pH is lower than the measured one likely due to CO₂ degassing. Dedolomitization (mole per mole replacement of dolomite by calcite) is a negligible process in these experiments (Fig. 5). Based on the reactive surface area values obtained and considering that the column is run under supercritical conditions (pCO₂ of 150 bar and 70°C), simulations predict significant dissolution of dolomite that causes very high increase in porosity along the entire column (Fig. 6).

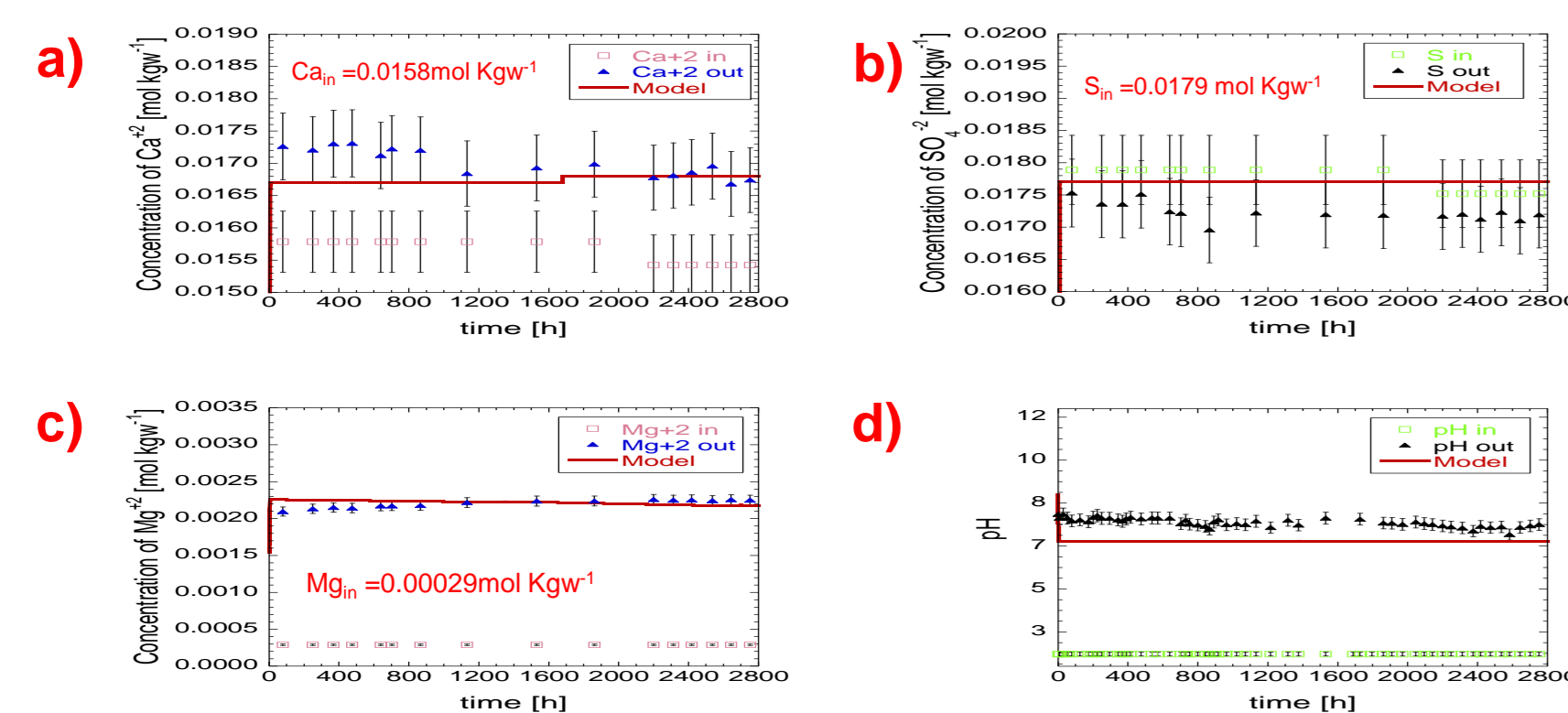


Fig. 4 Variation of output solution concentration with time under atmospheric pCO₂: (a) Ca²⁺, (b) Mg²⁺, (c) SO₄²⁻ and (d) pH.

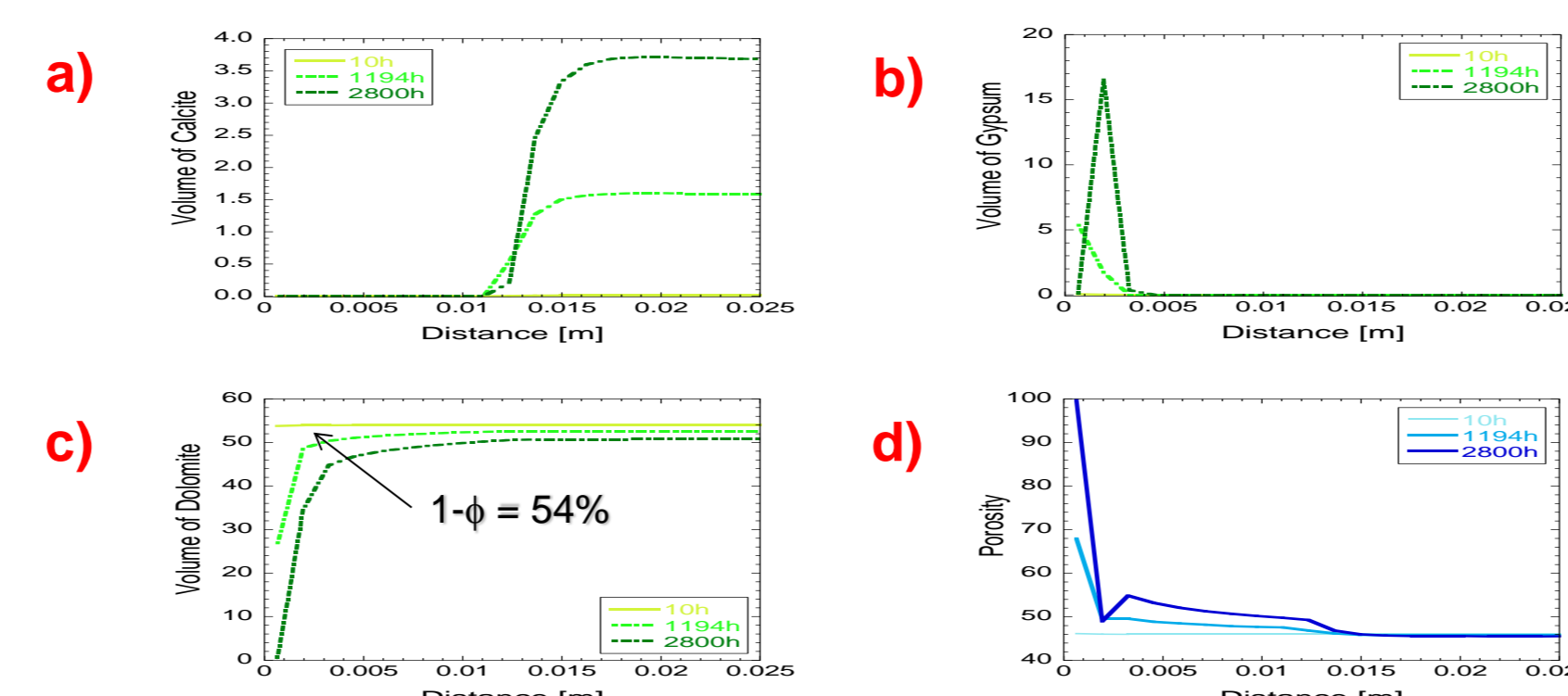


Fig. 5 Variation of the simulated volumetric fraction of minerals along the column at atmospheric pCO₂ and 25°C: (a) calcite, (b) gypsum, and (c) dolomite and porosity variation (d).

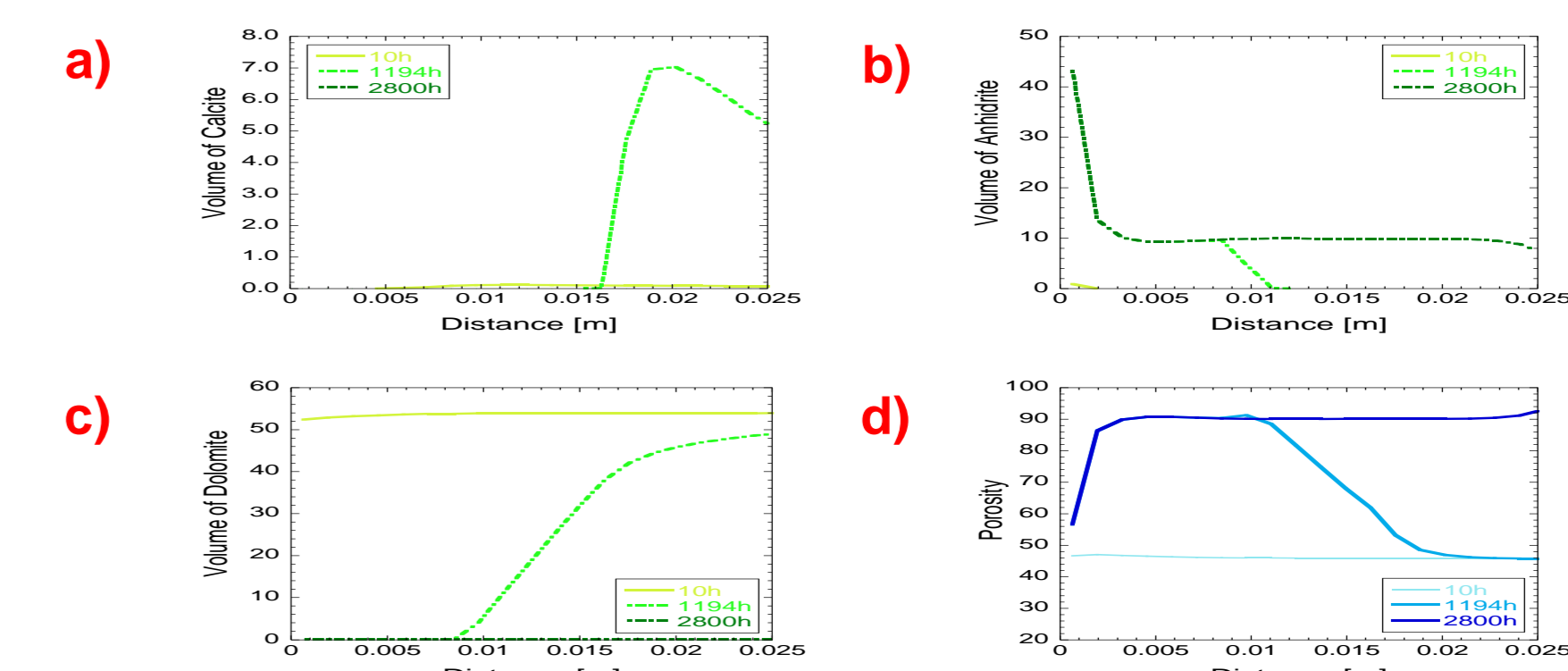


Fig. 6 Variation of the simulated mineral volumetric fraction along the column at pCO₂ of 150 bar and 70°C: (a) calcite, (b) gypsum, (c) dolomite and variation of porosity (d).

PASSIVATION
clear trend: ↑ T
and ↑ P ⇒ ↑
porosity along the
whole column

SUMMARY

The 1-D numerical simulations of the experimental results of dolomite dissolution at atmospheric pCO₂ and 25 °C show that:

- Values of the adjusted reactive surface areas are similar to those calculated based on the geometric surface area. These values are used to predict the geochemical behavior of the column run at supercritical CO₂ conditions.
- The main processes that take place are dissolution of dolomite and gypsum formation at the entrance of the column. Calcite precipitation and dedolomitization are negligible. Consequently, initial porosity increases up to 90% at the entrance of the column.

Simulations under supercritical CO₂ conditions (similar to the ones at the injection site of Hontomin) show a significant increase in the initial porosity along the column. Future experimental results under these conditions will be used to validate the resulting simulations.

ACKNOWLEDGMENTS

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