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## ABSTRACT

Experimental and numerical simulations dealing with silica and carbonate minerals dissolution/precipitation reactions demonstrated the need to integrate nucleation steps and interfacial mechanisms including surface complexation processes within more comprehensive kinetic approaches. These approaches are successfully applied to amorphous silica (AS) and amorphous calcium carbonate (ACC) precipitation reactions for temperatures of 25°C (ACC) and from 25 to 300°C (AS).

## BACKGROUND

The controlling mechanisms of mineral dissolution - precipitation reactions are complex and interdependent. The current scientific debate includes: i) changes (or not) of the mineral reactive surface area with the progress of the dissolution/precipitation reactions [1]; ii) energy jumps (discontinuity) in the thermodynamic affinity function of some dissolution/precipitation reactions, as highlighted by recent works of Arvidson's team [2,3]; and iii) integration of processes at the "mineral – aqueous solution" interfaces for aluminosilicates, silica and carbonates [4,5,6]. In recent works dealing with the specific case of AS, measurements were performed on nano-metric cross-sections indicating the presence of a surface layer between the bulk solution and the mineral. This thin layer is composed of amorphous silica and hydrated silica "permeable" to the transfer of water and ionic chemical constituents [7].

## MATERIALS & METHODS

Several experiments and numerical simulations were performed to determine the different mechanisms involved in silica and carbonate dissolution/precipitation reactions kinetics [5,8]. The numerical model integrates nucleation steps and interfacial properties [9] with surface complexation reactions [4, 9] for ACC precipitation reactions. For AS precipitation reactions, protonation reactions and Mg surface complexation reactions are taken into account [5]. The ACC precipitation kinetics were studied for a temperature of 25°C and those of AS were studied for temperatures ranging from 25 to 300°C [5]. The kinetic laws were derived from the Transition State Theory (TST) and applied to both silica and carbonate systems.

## RESULTS

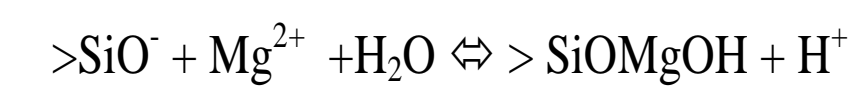
### a. SiO<sub>2</sub>(am) precipitation kinetics

The kinetic of silica precipitation in complex geological and industrial systems is a challenge since many parameters can impact simultaneously this process at progressive steps from oversaturation towards global thermodynamic equilibrium (Fig. 1). Our kinetic approach considers the crucial role of surface complexation reactions of SiO<sub>2</sub> nanoparticles involving magnesium ions. The kinetic law is able to explain the measured evolution of Si and Mg concentrations and pH (Fig. 2).

$$r = k(T) \cdot S \cdot \left( \frac{[SiOMgOH] + [SiOMg^+]}{[H_4SiO_4] + [H_3SiO_4^-]} \right)^{0.5} \cdot \left( 1 - \left( \frac{Q}{K} \right)^{0.5} \right)$$

$$>SiO^- + Mg^{2+} \rightleftharpoons >SiOMg^+$$

$$K_{>SiOMg^+} \cong \left( \frac{a_{>SiOMg^+}}{a_{>SiO^-} \cdot a_{Mg^{2+}}} \right) \cong \left( \frac{\Gamma_{>SiOMg^+}}{\Gamma_{>SiO^-} \cdot a_{Mg^{2+}}} \right) = \left( \frac{\Gamma_{>SiOMg^+}}{\Gamma_{>SiO^-} \cdot a_{Mg^{2+}}^w} \right) \exp \left( -\frac{2e\phi_\beta}{k_b T} \right) \text{ with } \phi_\beta = \phi_d$$



$$K_{>SiOMgOH} \cong \left( \frac{a_{>SiOMgOH} \cdot a_{H^+}}{a_{>SiO^-} \cdot a_{Mg^{2+}} \cdot a_{H_2O}} \right) \cong \left( \frac{\Gamma_{>SiOMgOH} \cdot a_{H^+}}{\Gamma_{>SiO^-} \cdot a_{Mg^{2+}} \cdot a_{H_2O}} \right) = \left( \frac{\Gamma_{>SiOMgOH} \cdot a_{H^+}^w}{\Gamma_{>SiO^-} \cdot a_{Mg^{2+}}^w \cdot a_{H_2O}^w} \right) \exp \left( -\frac{e\phi_\beta}{k_b T} \right)$$

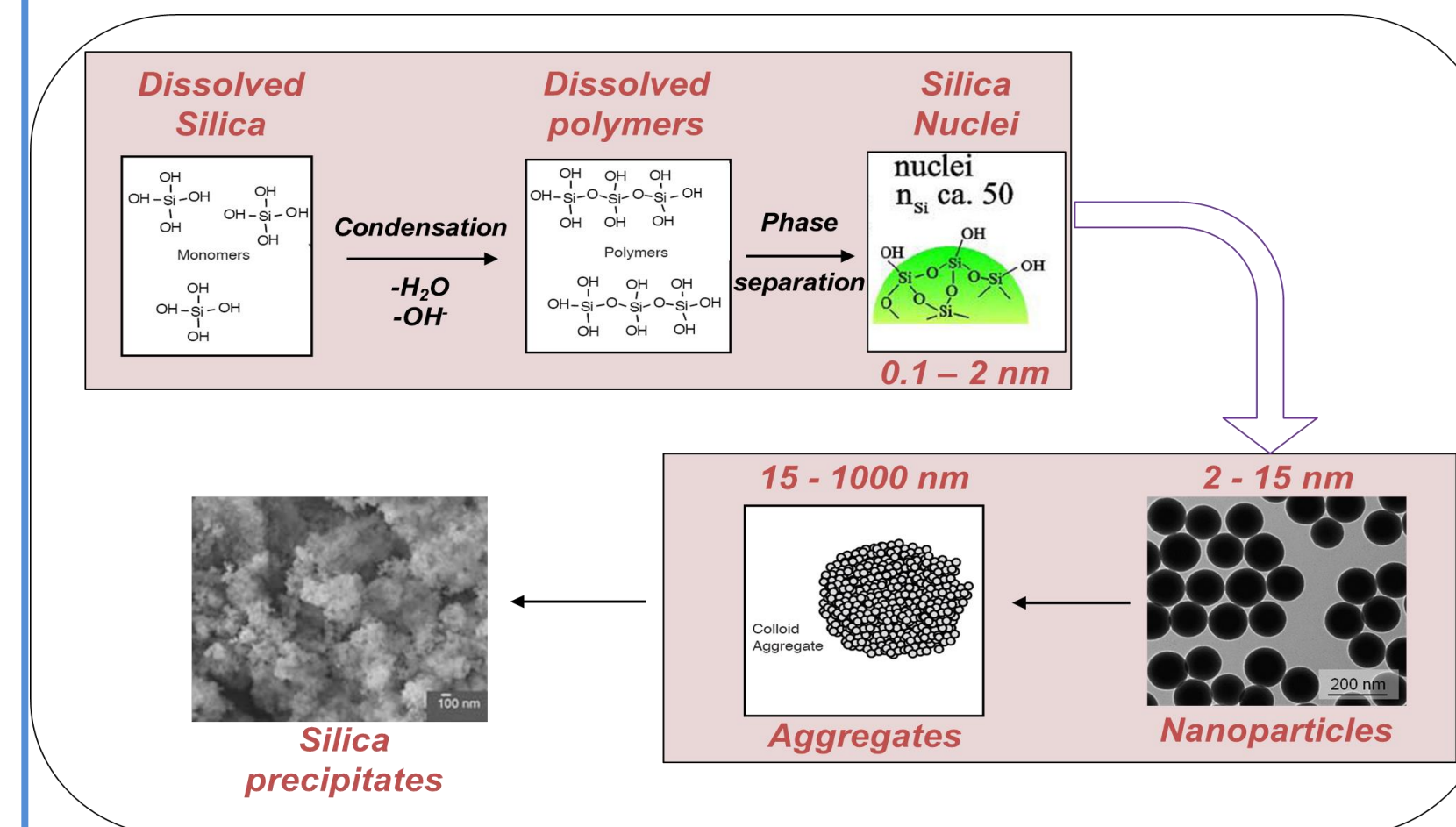


Fig. 1 – Key steps of amorphous silica precipitation. Dissolved silica starts by condensation, polymerization, nucleation, nanoparticles, aggregation before precipitating AS.

The extended kinetic approach was tested and validated on solutions containing silica and MgCl<sub>2</sub> for a large temperature interval (25 – 300°C) with a comprehensive and detailed aqueous and solid surface complexation speciation (including silica, magnesium, calcium), pH and the mass of precipitated minerals.

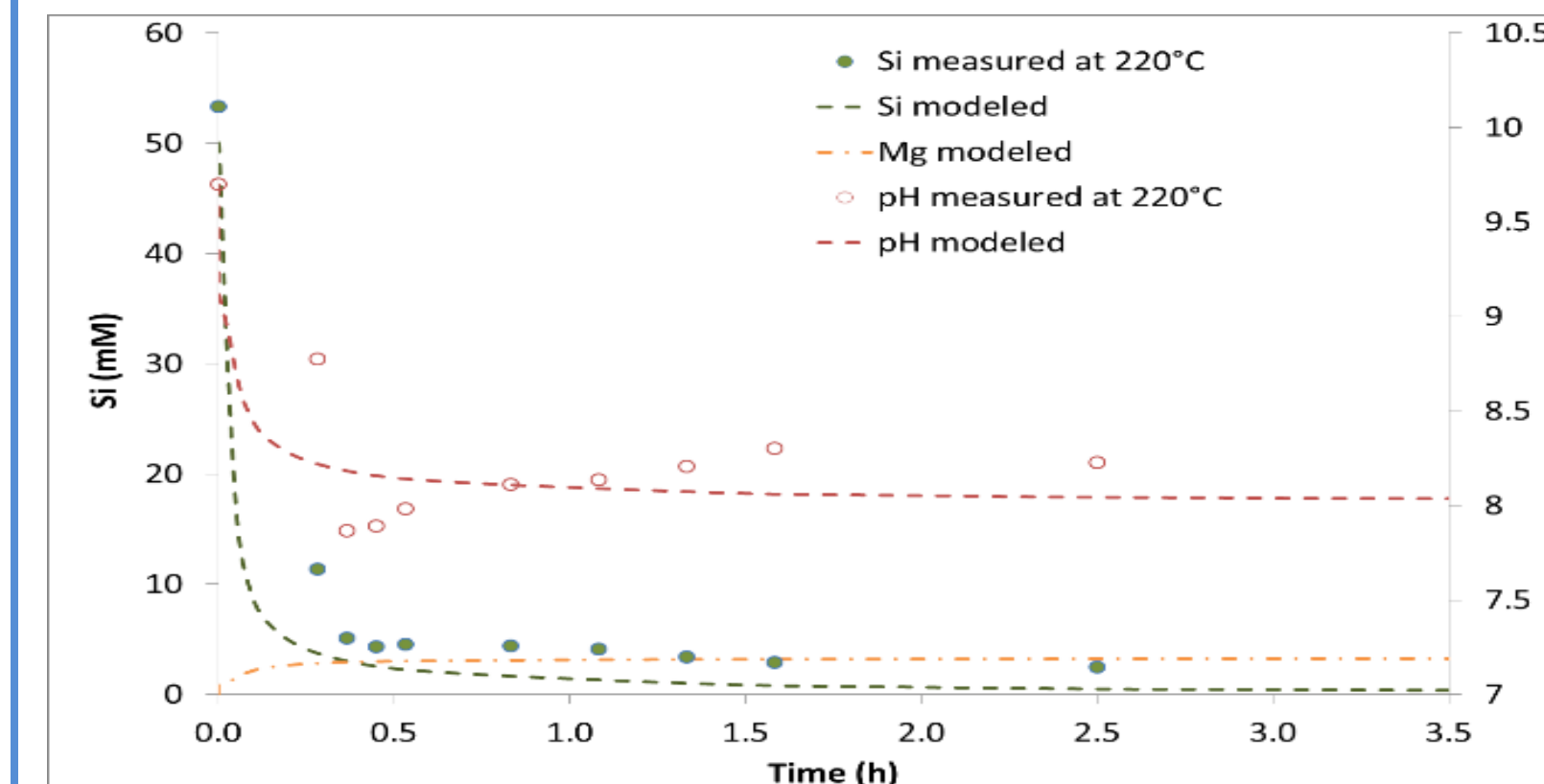


Fig. 2 – Evolution of Si and Mg concentrations and pH during the precipitation of AS in MgCl<sub>2</sub> solutions.

### b. CaCO<sub>3</sub>(s) precipitation kinetics

The ACC precipitation kinetics were studied in batch systems [6] and in a dynamic μchannel [8] designed to approach geological complexities (GLoC: Geological Lab on a Chip; [10]) in which two aqueous solutions (Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub>) were injected. Mixing the two solutions in the μchannel generates highly oversaturated solutions favoring ACC precipitation (Fig. 3). Precisely known flow rate, dimensions with direct observation by in situ X-ray scattering analysis (ESRF) allowed good characterization of the system.

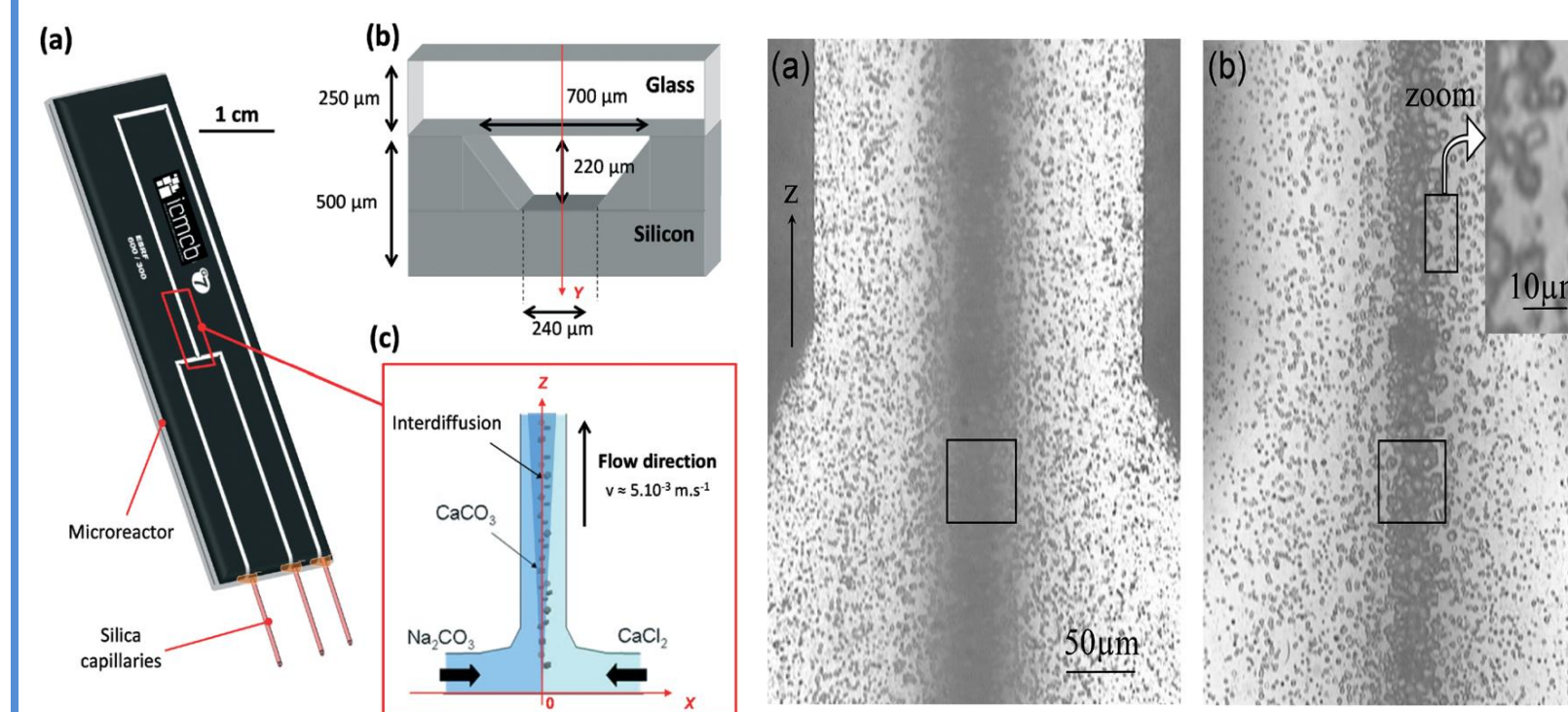


Fig. 3 – GLoC support with detailed dimensions for ACC precipitation kinetics study.

The interpretation of batch and dynamic experimental results is based on the development of a new kinetic law integrating three critical steps: i) "Homogeneous nucleation" of amorphous Ca-carbonate (ACC) + Creation of ≡Ca and ≡CO<sub>3</sub> surface sites on ACC surface; ii) Heterogeneous nucleation of calcite + Creation of ≡Ca and ≡CO<sub>3</sub> surface sites on calcite surface, and iii) Growth of calcite with dissolution of ACC by "cannibalism process" (Fig. 4a,b).

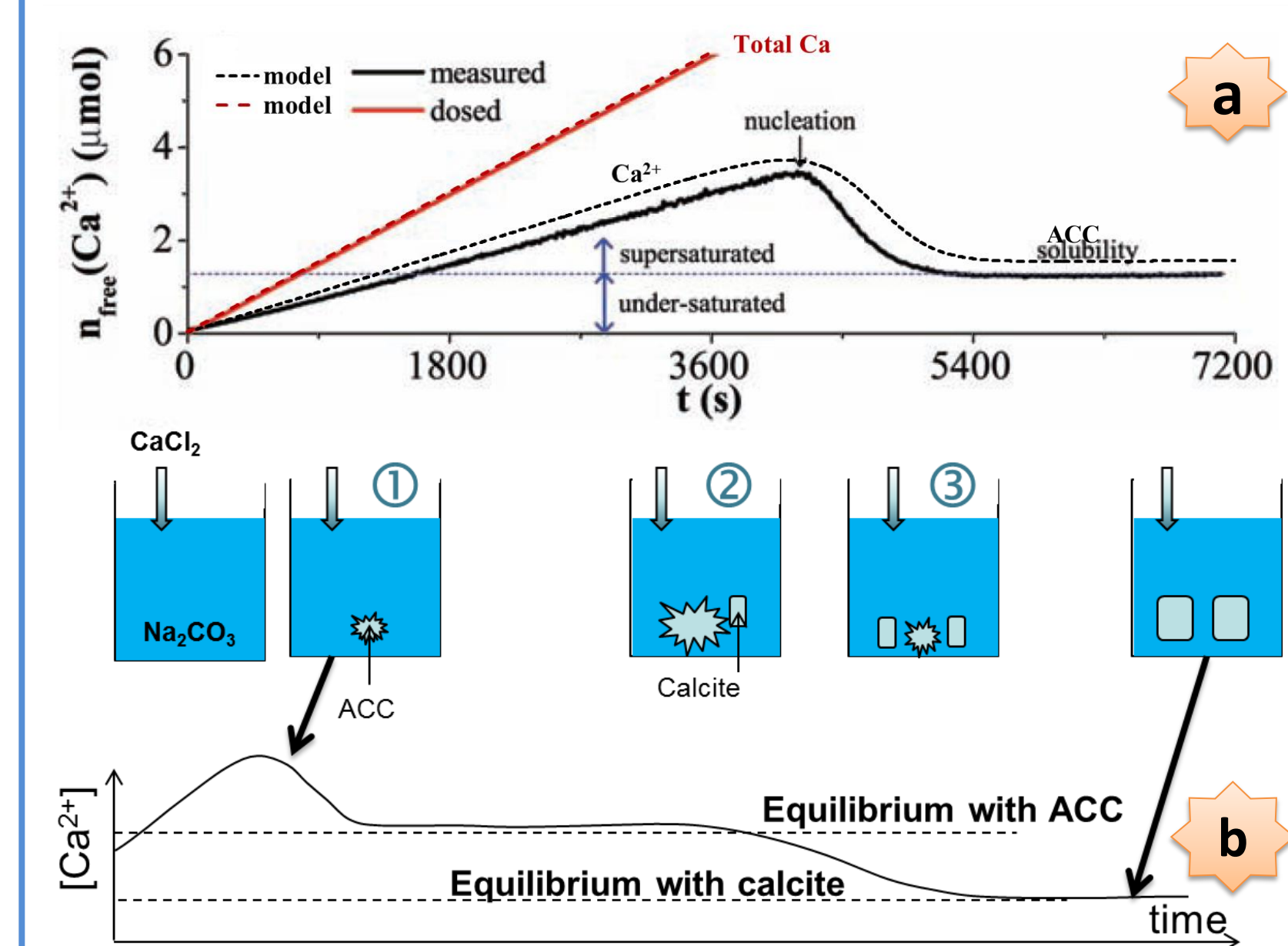


Fig. 4 – CaCO<sub>3</sub>(s) precipitation kinetics: a) Evolution of Ca<sup>2+</sup> content with time, modified after [6]. Full lines: experiments; dashed lines: model; b) Successive 3-steps of precipitation (from ACC to Calcite)

## CONCLUSIONS

This study demonstrates the importance of integrating surface complexation processes, nucleation steps and/or the role of some cations (e.g. Mg<sup>2+</sup>) in the precipitation kinetics of amorphous silica & Ca carbonates. Moreover, the basic thermodynamic and "standard" kinetic approaches are not sufficient to comprehensively describe the properties of the aqueous solution like pH variations.

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## ACKNOWLEDGEMENTS

Presented results were obtained in the framework of different BRGM projects (CIPROGIP), Institute BRGM Carnot project (Transcol), partnership projects: SILICE-HT with TOTAL and the French Agency of Research (ANR) co-funded CGSulLab project.