

Interfacial tension and nucleation behaviour of minerals (revisited)

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According to the classical nucleation theory (CNT), the nucleation rate depends strongly on the interfacial tension (σ), which in aqueous systems is related to the solubility by the rule that the higher the solubility, the lower σ . Indirect estimations of σ from nucleation experiments [1] are typically used to account for crystallization in natural aqueous systems [2] and to model the precipitation in sequential order of lesser and lesser soluble isochemical mineral phases according to the Ostwald step rule. In a related way, when solid solutions crystallize from supersaturated aqueous solutions the distribution of the substituting ions between the solid and the fluid phase usually differs from the equilibrium values [3]. “More soluble” solid solution compositions are kinetically favoured and tend to nucleate even though the aqueous solution is less supersaturated for these compositions than for less soluble members. This effect has been modelled by considering a linear variation of σ with composition [4]. However, to the authors knowledge, there is no empirical study on the compositional evolution of σ in solid solution systems.

In this work we revisit the concept of interfacial tension in the light of recent findings that challenge the traditional picture of crystal nucleation, at least in the case of the $\text{CaCO}_3\text{-H}_2\text{O}$ system [5]. Our point is that, in the CNT framework, the interfacial tension must be considered more an “artificial” fitting parameter than a measurable magnitude with a precise physical meaning. We show the dependence of CNT-derived σ values on the speciation model, the expression chosen for the driving force, and the shape chosen for the nuclei. Special attention is paid to the polymorphic precipitation of CaCO_3 phases. Finally, we determine the CNT- σ parameters for intermediate members of a number of binary (virtually ideal and non-ideal) solid solutions. Our results show a good correlation between the deviations from the ideal mixing behaviour, the solubility, and the obtained CNT- σ values. Positive deviations from ideality (positive enthalpy of mixing) correlate with negative deviations of σ from a linear trend, whereas negative deviations (tendency to ordering) correlate with positive deviations of σ . In each case, the obtained σ values are used to model non-equilibrium distribution coefficients, the results being in good agreement with experimental measurements reported in the literature.

[1] Söhnel (1982) *J. Cryst. Growth* **57**, 101-108. [2] Fritz & Noguera (2009) *Rev. Min. Geochem.* **70**, 371-410. [3] Prieto (2009) *Rev. Min. Geochem.* **70**, 47-85. [4] Pina & Putnis (2002) *Geochim. Cosmochim. Acta* **66**, 185-192. [5] Gebauer, Völkel & Cölfen (2008) *Science* **322**, 1819-1822.

Precipitation of MgCO_3 at elevated temperature and CO_2 pressure

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Introduction and methods

Mineral carbonation is a Carbon Capture and Storage (CSS) technology that consists in fixing CO_2 into stable carbonates, e.g., magnesite (MgCO_3) which can be either disposed of or reused [1]. Hydrated phases can initially form which then transform into the stable carbonate [2]. If carbonates are designed to be reused, the precipitation process must be carried out under well-constrained conditions which are still unknown or not fully defined [3,4,5]. Here, we present the results from a MgCO_3 precipitation study at 90°C, 120°C, and 150°C and at 100 bar of CO_2 [6]. Batch experiments were performed using a $\text{MgCl}_2\text{-CO}_2\text{-Na}_2\text{CO}_3$ aqueous system and monitored with online Raman spectroscopy. Precipitation was modeled using a population balance equation (PBE) [7] coupled with a geochemical model. Nucleation and growth rates were described by empirical equations based on classical nucleation theory and the birth-and-spread growth mechanism and the kinetic parameters were estimated by fitting Raman spectroscopy measurements using multivariate kinetics modeling [8].

Results and conclusions

Two types of mechanisms were verified. At all investigated temperatures and at low magnesium concentration (C_{Mg}) MgCO_3 precipitated directly (Fig. 1.a). At 120 and 150°C and at high C_{Mg} , MgCO_3 formed simultaneously with hydromagnesite which then transformed into MgCO_3 (Fig. 1.b). The kinetics showed no sensitivity to C_{Mg} , small sensitivity to temperature, and a significant sensitivity to supersaturation with respect to MgCO_3 (S_M). This allowed the formulation of general rate equations for nucleation and growth given by, respectively,

$$J = 4 \times 10^8 e^{(-19/\ln^2 S_M)}, \quad (1)$$

$$G = 29 \times 10^{-9} (S_M - 1)^{2/3} \ln^{1/6} S_M e^{(-19/\ln^2 S_M)}, \quad (2)$$

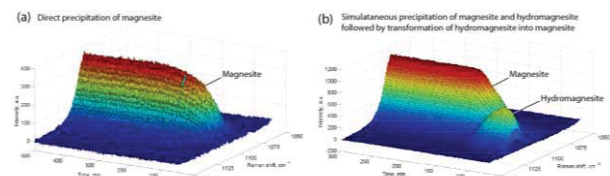


Figure 1: Online Raman spectroscopy measurements.

[1] IPCC (2005). IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, 442 pp. [2] Hänchen, Prigobbe, Baciocchi, Mazzotti (2008). *Chem. Eng. Sci.* **63**, 1012-1028. [3] Sayles, Fyfe (1973) *Geochim. Cosmochim. Acta* **37**, 87-99. [4] Zhang *et al.* (2000) Sandia Nat. Lab. **NM 87185-0750**. [5] Saldi *et al.* (2009) *Geochim. Cosmochim. Acta* **73**, 5646-5657. [6] Prigobbe, Mazzotti (2012) *in preparation*. [7] Randolph, Larson (1988) *Theory of particulate processes* Academic Press. [8] Cornet, Mazzotti (2008) *Anal. Chem.* **80**, 9240-9249.