

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 CaCO_3 - H_2O 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.