



A unified approach to model uptake kinetics of trace elements in complex aqueous – solid solution systems



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ABSTRACT

Thermodynamics alone is usually not sufficient to predict growth-rate dependencies of trace element partitioning into host mineral solid solutions. In this contribution, two uptake kinetic models were analyzed that are promising in terms of mechanistic understanding and potential for implementation in geochemical modelling codes. The growth Surface Entrapment Model (Watson, 2004) and the Surface Reaction Kinetic Model (DePaolo, 2011) were shown to be complementary, and under certain assumptions merged into a single analytical expression. This Unified Uptake Kinetics Model was implemented in GEMS3K and GEM-Selektor codes (<http://gems.web.psi.ch>), a Gibbs energy minimization package for geochemical modelling. This implementation extends the applicability of the unified uptake kinetics model to accounting for non-trivial factors influencing the trace element partitioning into solid solutions, such as the changes in aqueous solution composition and speciation, or the depletion effects in closed geochemical systems.

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1. Introduction

The prediction of trace element partitioning in growing minerals is considered to be a key issue in water–rock interaction processes related to environmental issues like the disposal of radioactive waste (Curti, 1999; Duro et al., 2010), the remediation of polluted soils (Garcia Delgado et al., 1996; Plassard et al., 2000), and also to geological problems like paleo-thermometry (Gaetani and Cohen, 2006). Modelling trace element uptake by minerals in thermodynamic equilibrium with aqueous solution is possible by accounting for the solid solution (Kulik et al., 2010) or surface adsorption (Barrow and Bowden, 1987; Fischer et al., 2007; Kulik, 2002; Kulik, 2006; Zachara et al., 1991) mechanisms. However, there is ample evidence that kinetic effects may lead to considerable deviations from the equilibrium partitioning.

Co-precipitation experiments showed that the relative amount of trace element taken up depends on the mineral precipitation rate. For instance, the relative content of Sr in calcite was found to increase with the growth rate (Gabitov and Watson, 2006; Huang and Fairchild, 2001; Lorens, 1981; Nehrke et al., 2007; Tang et al., 2008a; Tesoriero and Pankow, 1996). A similar behaviour was observed for Ba (Tesoriero and Pankow, 1996; Yoshida et al., 2008) and Ra (Yoshida et al., 2008) in the same mineral, whereas the relative content of Cd decreased with increasing calcite growth rate (Lorens, 1981; Tesoriero and Pankow, 1996). A similar dependency

was found for uptake of Ni (Lakshtanov and Stipp, 2007), Co (Lorens, 1981), Mn (Dromgoole and Walter, 1990; Lorens, 1981) and Fe (Dromgoole and Walter, 1990) in calcite, and for U in aragonite (Meece and Benninger, 1993). For lanthanides (i.e. Eu^{3+}) in calcite, the relative content seems to remain the same whatever the precipitation rate (Zhong and Mucci, 1995; Lakshtanov and Stipp, 2004). For Mg and U^{6+} in aragonite, the direction of the growth-rate dependency depends on temperature (Gabitov et al., 2008). For ^{44}Ca in calcite it was observed that the enrichment in this isotope in the mineral increases with the growth rate (Lemarchand et al., 2004) but also the contrary trend was observed (Tang et al., 2008b).

These experimental results cannot be predicted using conventional thermodynamic aqueous – solid-solution models because the observed trace element concentrations deviate from equilibrium. A suitable model has to account for this deviation and its dependency on the growth kinetics. In order to succeed in predicting trace elements uptake in (growing) minerals, some key issues must be resolved. It is necessary to understand what mechanisms on the microscopic (atomistic) scale are responsible for the observed trace element uptake in host minerals, and how they depend on growth rate. Further, one must define equilibrium distribution and find the laws and parameters necessary for quantifying the deviations from equilibrium values. Recently, several models have been developed to predict quantitatively the effect of growth kinetics on trace element uptake, based on different premises and approaches. Those models are rather simple to use and satisfactorily describe many experimental results. Nevertheless, some input parameters (e.g. mineral growth rate) depend on

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solution composition and speciation, and are likely to change over time, especially considering long times. To account for such dependencies, the uptake kinetics model suitable for complex geochemical systems must be coupled to a geochemical speciation code. This task is non-trivial.

We chose two models that appear to be most promising in terms of mechanistic insight and potential for implementation in geochemical modelling codes: the (growth) Surface Entrapment Model (SEMO) (Watson, 2004), and the Surface Reaction Kinetics Model (SRKM) (DePaolo, 2011). We examined the underlying hypotheses, limiting assumptions, assumed driving mechanisms, ranges of required parameters, and results of applications to available experimental data. On this basis, under certain assumptions, we derived a Unified Uptake Kinetics Model (UUKM) in a form appropriate for implementation in geochemical speciation codes, and implemented it in the in-house GEM-Selektor/GEMS3K codes (Kulik et al., 2013; Wagner et al., 2012). This implementation would allow predictions of the non-equilibrium trace element uptake in complex aqueous – solid solution systems while considering chemical effects such as speciation changes, depletion, that cannot be taken into account by either of the two mentioned models alone. The potential of UUKM embedded in the GEM-Selektor code is illustrated on modelling selected experimental data and their extrapolations.

Note that our model assumes the presence of pre-existing solid acting as “seed crystals” for the incremental growth of a dilute solid solution. Accordingly, the experimental data used to test the model involved the formation of overgrowths around seed particles. Formation of solid solutions via homogeneous or heterogeneous nucleation was not considered because such processes demand relatively high supersaturation, which is unlikely for the specific systems of our interest, such as slowly evolving radioactive waste repository systems. Moreover, nucleation is still too complex to model, notwithstanding recent advances (Noguera et al., 2010; 2012).

2. Theoretical background and methods

2.1. Fractionation coefficient

The distribution of a trace element Tr between the aqueous solution (or melt) and the mineral (crystalline solid solution) relative to the host component Hc is usually described by the fractionation coefficient $\Delta_{\text{Tr,Hc}}$, which is the ratio of two distribution ratios R_d :

$$\Delta_{\text{Tr,Hc}} = \frac{R_d(\text{Tr})}{R_d(\text{Hc})} \quad (2.1)$$

The distribution ratio is defined as the ratio of component concentration in the solid to that in the aqueous phase. Taking mole fraction x for the solid and molarity $[\]$ or molality for the aqueous part, Eq. (2.1) can be rewritten as follows:

$$\Delta_{\text{Tr,Hc}} = \left(\frac{x_{\text{Tr}}}{[\text{Tr}]} \right) / \left(\frac{x_{\text{Hc}}}{[\text{Hc}]} \right) \quad (2.2.a)$$

This equation is most frequently used in the re-arranged form:

$$\Delta_{\text{Tr,Hc}} = \frac{x_{\text{Tr}}}{x_{\text{Hc}}} \cdot \frac{[\text{Hc}]}{[\text{Tr}]} \quad (2.2.b)$$

$\Delta_{\text{Tr,Hc}}$ can be related to a thermodynamic constant of an exchange reaction, for instance Sr incorporation in calcite:



The equilibrium fractionation (exchange) constant of this reaction is:

$$\Delta K_{\text{Sr,Ca,eq}} = \frac{x_{\text{SrCO}_3} \gamma_{\text{SrCO}_3}}{x_{\text{CaCO}_3} \gamma_{\text{CaCO}_3}} \cdot \frac{[\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}}{[\text{Sr}^{2+}] \cdot \gamma_{\text{Sr}^{2+}}} \quad (2.4)$$

where γ stands for the activity coefficients. Comparing Eqs. (2.2) and (2.4), one can see that, assuming the same extent of aqueous complexation of Ca^{2+} and Sr^{2+} aqueous ions,

$$\Delta K_{\text{Sr,Ca}} \approx \Delta_{\text{Sr,Ca}} \frac{\gamma_{\text{Sr,ss}}}{\gamma_{\text{Ca,ss}}} \frac{\gamma_{\text{Ca,aq}}}{\gamma_{\text{Sr,aq}}} \quad (2.5)$$

both in equilibrium and in a metastable state. In the case of very dilute aqueous electrolyte and ideal solid solution (ss), Eq. (2.5) further simplifies to $\Delta K_{\text{Tr,Hc}} \approx \Delta_{\text{Tr,Hc}}$.

There is no consensus on the terminology of distribution in the literature. The fractionation coefficient described in this section is often called “distribution coefficient” (Lorens, 1981; Mucci and Morse, 1983; Tang et al., 2008a; Zhong and Mucci, 1995), or “partition coefficient” (Curti, 1999; Lakshatanov and Stipp, 2007; McIntire, 1963; Morse and Bender, 1990), or “fractionation factor” (Fantle and DePaolo, 2007); it is also denoted with different symbols: D (Gaetani and Cohen, 2006; Katsikopoulos et al., 2008; Tesoriero and Pankow, 1996), K_d (DePaolo, 2011; Gabitov and Watson, 2006; Rimstidt et al., 1998; Zhu, 2004), K_{ex} (Zachara et al., 1991), or λ_{Tr} (Curti, 1999; Doerner and Hoskins, 1925).

2.2. Gibbs energy minimization (GEM)

Geochemical modelling of (time-dependent) metastable systems is usually based on the principle of partial equilibrium, which occurs if, upon the speciation calculation, some components in some phases cannot reach their equilibrium amounts because of the input *additional metastability restrictions* (AMR). All phases and components without AMR take part in the achievement of the partial equilibrium state under the mass balance common to the whole system.

The GEM IPM (Interior Points Method) algorithm (Kulik et al., 2013; Karpov et al., 2001), implemented in GEM Software (GEMS), has a great potential for thermodynamic modelling of mineral–water reaction kinetics because it can directly handle the AMRs. In GEM IPM, the chemical system is defined by a bulk composition vector, $n^{(b)}$, specifying the input amounts of chemical elements and charge; the standard molar Gibbs energies of all dependent components (species), g^0 , at T, P of interest; the parameters of (non)ideal models of mixing in solution phases (Wagner et al., 2012), needed to calculate activity coefficients λ_j of species indexed with j ; and the optional AMRs. After each run, the GEM *primal* (speciation vector $\hat{n}^{(x)}$) and the *dual* (vector $\hat{u}^{(b)}$ of chemical potentials of chemical elements and charge) results provide concentrations and activities of all aqueous species, as well as activities and amounts of all components in all other phases. The stability index Ω_k of any phase, even of that absent from the mass balance, is found as a *dual-thermodynamic* estimate of the sum of anticipated mole fractions \hat{x}_j of all phase components:

$$\Omega_k = \sum_j \hat{x}_j = \sum_j \exp(\hat{\eta}_j - g_j^0/RT - \ln \lambda_j - \Xi_k) \quad (2.6)$$

where the index j runs over all components in the phase; R is the universal gas constant; Ξ_k is a term for converting species concentration into the common mole fraction scale (e.g. $\ln P$ for gases; $\ln 55.5085$ for aqueous species); and $\hat{\eta}_j$ stands for the *dual-solution chemical potential*

$$\hat{\eta}_j = \sum_i a_{ij} \hat{u}_i^{(b)} \quad (2.7)$$

where index i runs over all chemical elements and charge, and a_{ij} is the formula stoichiometry coefficient of i -th element in j -th species (e.g. 2 for O in SiO_2).

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