



Research papers

Ion-specific effects on the kinetics of mineral dissolution

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ABSTRACT

Specific effects of background electrolytes on mineral growth and dissolution can be interpreted on the basis of the ability of ions to modify solute hydration, in a similar way to the systematic effects of inorganic ions on precipitation, structure and function of organic macromolecules (i.e., the Hofmeister effect). Here, the effect of a range of background electrolytes (sodium and chloride salts) on dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) reactivity was investigated as a model system by measuring dissolution rates using in-situ Atomic Force Microscopy. The systematic trends found for the different ions are interpreted in terms of characteristic parameters of background ions such as effective hydrated radii. Entropic effects associated with the ordering of solvent molecules induced by constituting cations from the crystal ultimately dictate how electrolytes affect dissolution rates. In dilute electrolyte solutions, ion–ion interactions dominate and the stabilisation of the solvation shell of ions constituting the crystal, by counter-ions present in solution enhances the unfavourable entropic effect on dolomite dissolution. The tendency for electrolytes to form ion pairs in solution reduces such an effect, thus leading to an inverse correlation between dissolution rates and background ion separation in solution. On the other hand, in concentrated saline solutions the interaction between background ions and water molecules determines the hydration of a constituent ion immersed in an electrolyte solution. In this case, dissolution rates correlate with the mobility of background ions and, therefore, with their effective hydration radii. The observed effects of background ions on growth and dissolution could be applicable for other inorganic systems where the Hofmeister effect has been reported.

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1. Introduction

It has long been recognised that specific ions at moderate to high concentrations in aqueous solutions can play important but very different roles on the crystallisation, structure and function of proteins (Kunz et al., 2004a; Zhang et al., 2005). It is also well known that most of these effects correlate with water affinity of the respective ions and follow a trend known as the lyotropic or Hofmeister series (Kunz et al., 2004b; Dove and Craven, 2005). Current research in this field suggests that the control that electrolytes exert on water structure is limited to the local environment surrounding the ion and is not related to long-range electric fields emanating from the ions but results from effects associated with the hydration shell(s) of the ions (Collins et al., 2007) and the ions' capacity to “break” or “structure” water (i.e., chaotropic and kosmotropic ions, respectively) (Parsons et al., 2010). Hofmeister effects are ubiquitous and numerous cases in which they apply can be found in biological systems. Examples of

processes following the Hofmeister series include enzyme activity, protein stability, protein–protein interactions, protein crystallisation or optical rotation of sugars and amino acids (see Kunz et al., 2004a; Zhang et al., 2005 and Zhang and Cremer, 2006). Although there is still an on-going debate about the origin of these salt-specific effects (see for instance Cappa et al., 2006), their relation to hydration characteristics of ions is commonly accepted (Collins and Washabaugh, 1985; Collins et al., 2007). However, attempts to relate the Hofmeister effect to thermodynamic solvation properties of ions (e.g., enthalpy and entropy of hydration), generally yield no conclusive results. In fact, no single thermodynamic property associated with the solvation of ions has yet been found to unambiguously explain their hydration characteristics (Marcus, 1994a).

In the case of inorganic solids, the effect of ionic strength on growth and dissolution rates has been traditionally attributed to changes in solubility (i.e. a thermodynamic effect). The strong long-range electric fields emanating from the ions of the background electrolyte reduce the activity of the ions building the crystal due to charge screening, hence increasing its solubility. Nevertheless, several studies have shown that the dependence of growth or dissolution rates of minerals on ionic strength is complex, and is not independent of the ionic species producing it (Dove and Czank, 1995; Weaver et al., 2007; Kowacz and Putnis, 2008; Ruiz-Agudo et al., 2009,

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2010). Ions having different surface charge density exert different effects that cannot be simply explained by continuum electrostatics models (i.e. those considering the ions as point charges). This suggests that purely thermodynamic considerations may not be enough to explain ion specific effects on mineral dissolution and growth and that kinetics may play a key role.

The systematic study of specific ion effects on the growth and dissolution of minerals has so far received little attention. Several experimental and computational studies have shown that crystal growth and dissolution rates of sulphates and carbonates are actually controlled by cation hydration–dehydration dynamics (Dove and Czank, 1995; Pokrovsky and Schott, 2002; Piana et al., 2006). Thus, any factor affecting cation solvation should alter growth and dissolution rates. A few recent studies have proposed that the specific effects of background electrolytes on the kinetics of crystal growth and dissolution can be interpreted on the basis of the ability of such electrolytes to modify hydration of the crystal constituting ions (i.e., the building units) (Kowacz and Putnis, 2008; Ruiz-Agudo et al., 2010). These experiments validate such an approach, and demonstrate the need for the inclusion of specific ion effects in the development of a predictive model that describes crystal growth and dissolution in complex systems, such as those found in nature (e.g., ocean water and rock pore solutions). However, there are several critical aspects that need further clarification in order to ensure the global character of this theory. In the previous studies, calcite (CaCO_3) and barite (BaSO_4) showed opposite trends in reactivity with respect to ion type, thus suggesting that the hydration characteristics of the crystal building units have a dramatic effect on the systematic trends observed for the different background salts. In this sense, with the presence of magnesium, in addition to calcium, in its structure, dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) represents an ideal system to test this hypothesis. The high charge density of Mg^{2+} leads to a very strong solvation, higher than that of other alkali-earth cations (i.e., Ca^{2+} and Ba^{2+}) and may shed light on the ultimate mechanism and factors governing the interactions in solution of background ions with the constituting ions of a mineral. Furthermore, it is important to define relationships between crystal reactivity and fundamental parameters of the background ions that will enable extrapolation of these results to other systems. Here, we address the basic hypotheses that (i) the effect of electrolytes on mineral dissolution is governed by similar principles to those which apply in the case of organic macromolecules (e.g., Hofmeister effect on proteins salting-out) and are related to fundamental properties of the background ions in solution, and (ii) the systematic trends observed in mineral reactivity for the different background salts are determined by the hydration characteristics of the crystal building units.

To test these hypotheses, in-situ flow-through dissolution experiments were conducted using Atomic Force Microscopy (AFM) on dolomite cleavage surfaces in the presence of different 1:1 sodium and chloride salts. In the last 15 years the study of fluid–mineral interactions has experienced a considerable advance, largely due to the use of in-situ AFM. Using this technique, nanoscale real-time observations of crystal surfaces reacting with fluids can be performed, thus representing a valuable tool for precise and representative analysis of fluid–mineral interactions (Hillner et al., 1992; Putnis et al., 1995; Hall and Cullen, 1995; Jordan and Rammensee, 1997; Shtukenberg et al., 2005; Shiraki et al., 2007). Also, it allows quantification of the kinetics of these processes. The reactivity of carbonates can be optimally studied by means of AFM as most carbonate minerals have perfect cleavage, facilitating the study of nearly atomically flat surfaces. Furthermore, the dissolution of carbonates occurs by the retreat of unit-cell high steps and/or formation and spreading of etch pits, processes that are easily observed and quantified by AFM. The experimental approach presented in this study has enabled us to obtain quantitative information on the behaviour of dolomite in a range of solution compositions, with the aim of determining reactivity

trends and ascertaining the principles that define changes in the kinetics of dissolution induced by background ions.

Our results show that the experimentally determined dependence of dolomite dissolution rates on ion type in concentrated solutions is ultimately related to the hydrated volume of the background ion, as an indicator of the strength of the interactions between background ions and the solvent molecules. Moreover, by comparison with other divalent carbonates and sulphates, it seems that the systematic of this dependence is controlled by the hydration characteristics of the cation building the crystal. In dilute solutions, the volume of solvent affected by the electrolytes is reduced and ion–ion interactions dominate.

2. Methodology

Optically transparent dolomite crystals from Eugui (Navarra, Spain) were cleaved in air along $\{10\bar{1}4\}$ planes with a knife blade. Dolomite crystals from Eugui have been commonly used in crystal chemistry studies of dolomite due to its high purity and perfection (Barber et al., 1981; Reeder and Nakajima, 1982; Spinolo and Anselmi-Tamburini, 1984). The crystals, ca. $3 \times 3 \times 1$ mm in size, were examined by optical microscopy to ensure that the cleavage surfaces were free of macroscopic steps and small particles. Crystals were cleaved immediately before each experiment. In-situ AFM dissolution experiments were carried out by passing prepared salt solutions of LiCl, NaCl, KCl, CsCl, NaI, NaF and NaNO_3 at different ionic strengths ($IS = 0.001, 0.01, 0.1$ and 1) over dolomite $\{10\bar{1}4\}$ cleavage surfaces. Na^+ and Cl^- ions are the most suitable counter ions to investigate the effects of different hydration properties of anions and cations on mineral dissolution, as they have been shown to have the least structural effects on the solvent (at room temperature) (Jáklí, 2007). Table 1 shows experimental conditions for each saline solution. The natural pH of concentrated ($IS = 1$) LiCl, KCl, CsCl and NaNO_3 solutions was slightly acidic ($\text{pH} < 5.3$), and it was adjusted to 7 using NaOH. PHREEQC (Parkhurst and Appelo, 1999) was used to calculate the ionic strength of the solutions. Deionised water (resistivity $> 18 \text{ m}\Omega^{-1}$) was passed over the surfaces before each experiment to clean the cleaved surface, as well as to adjust the AFM parameters as in Arvidson et al. (2006). Solutions were prepared immediately before the experiments to avoid the equilibration with CO_2 in the ambient air. Therefore, the amount of carbonate and bicarbonate ions in solutions is considered to be negligible. The absence of calcium and magnesium in the input solutions as well as the constant solution flow during the experiments ensured constant far-from-equilibrium conditions with respect to dolomite.

An Atomic Force Microscope (Digital Instruments Nanoscope III Multimode) equipped with an O-ring sealed fluid cell working in contact mode was used to study dolomite dissolution under ambient conditions ($T = 20^\circ\text{C}$). The scanning frequency was 4 Hz, giving an average time of 1.5 min per scan over $4 (2 \times 2)$ and $9 (3 \times 3) \mu\text{m}^2$ dolomite surfaces. Solution flow rate ($20 \mu\text{L s}^{-1}$) was controlled by syringe injections. AFM images were collected using Si_3N_4 tips (Veeco Instruments, tip model NP-520) and analysed with the Nanoscope software (Version 5.12b48). Measurements of step retreat velocity (or etch pit spreading rate) were made from sequential images scanned in the same direction. The retreat velocity, v_{sum} , was calculated by measuring the length increase per unit time between opposite parallel steps in sequential images.

3. Results

3.1. Dissolution features of etch pits

Dolomite dissolved on $\{10\bar{1}4\}$ cleavage surfaces by the formation and spreading of etch pits after contact with deionised water ($\text{pH} 7$) in the fluid cell. The etch pits were shallow (~ 0.3 nm height) rhombohedral pits at circumneutral pH (Fig. 1). This is the typical

etch pit morphology observed on dolomite surfaces in contact with highly undersaturated solutions (Higgins and Hu, 2005). No significant change in etch pit morphology was observed in the presence of the different background electrolytes tested. Angles between steps defining the etch pits were found to be $\sim 77^\circ$ and $\sim 104^\circ$. The average etch pit density measured in deionised water was $2.25 \times 10^9 \text{ cm}^{-2}$, which is 4 orders of magnitude higher than that observed by Luttgge et al. (2003) at acidic pH (~ 3) using Vertical Scanning Interferometry (VSI). However, their study focussed on deep etch pits (depth up to $2 \mu\text{m}$), most probably nucleated at dislocations (MacInnis and Brantley, 1992). The shallow etch pits considered in our study are nucleated either on point defects or, as the experiments were performed under far-from-equilibrium conditions, on defect-free areas of the surface. At the AFM scale, dolomite dissolution shows characteristics of Type I (Ca, Mn) carbonates, according to the classification of Duckworth and Martin (2004). These authors classified five isostructural carbonate minerals (Ca, Mn, Fe, Mg and Zn carbonates) into three different groups according to similarities in the dissolution behaviour. Type I carbonates show widespread distributed shallow rhombohedral pits, which are densely clustered and seem to be initiated by groups of point defects. However deep, isolated etch pits associated with the presence of line dislocations are observed on a larger scale (Luttge et al., 2003), and are typically reported for Type II (Fe, Mg) carbonates.

3.2. Dissolution kinetics

In flow-through experiments performed in AFM, the very low amount of calcium and magnesium in the outlet solution precludes obtaining reliable macroscopic dissolution rates from measurements of cation concentrations in the output solution (Arvidson et al., 2006). Furthermore, variations and uncertainties related to the reacting surface area contribute to significant error in macroscopic rate determinations, leading to an overestimation of macroscopic dissolution rates (Duckworth and Martin, 2004; Ruiz-Agudo et al., 2010). Thus, etch pit spreading rates determined from measurements of length changes in consecutive AFM images allow a more precise comparison between different solution compositions and, accordingly, comparative etch pit spreading rates have been measured for this study.

Values of the retreat velocity, v_{sum} , reported in this work refer to rate of change in etch pit length along either $[\bar{4}41]$ or $[48\bar{1}]$ directions (Fig. 1). In deionised water, $v_{\text{sum}} = 0.09 \pm 0.01 \text{ nm s}^{-1}$. Table 1 and Fig. 2 show v_{sum} as a function of ionic strength for the electrolytes tested. Although there is some scatter in the published data of dolomite dissolution rates as a function of pH, it seems that under conditions of low pCO_2 (total carbon $< 0.001 \text{ M}$), dolomite dissolution

rates showed, in general, little change with solution pH for $5.4 \leq \text{pH} \leq 8$ (and total carbon $< 0.001 \text{ M}$) (see Pokrovsky et al., 1999 and Pokrovsky and Schott, 2001). For lower pH values, dissolution rates increase with decreasing pH. Most of the electrolyte solutions tested showed $5.6 \leq \text{pH} \leq 7$ (Table 1). The pH of KCl solutions at $\text{IS} = 0.01$ and $\text{IS} = 0.1$ is 5.3 and 5.4, respectively, so pH could have influenced the measured rate to some extent. Nevertheless, the rates in these cases were not faster than those measured in other electrolyte solutions of higher pH at the same IS. This suggests that the differences observed are not due to differences in solution pH. The average etch pit spreading velocity on the dolomite cleavage surface varied according to the nature of the background electrolyte at a low and constant ionic strength ($\text{IS} = 0.001$), increasing in the order $\text{CsCl} < \text{NaNO}_3 < \text{LiCl} \approx \text{NaCl} < \text{NaI} < \text{KCl} < \text{NaF}$. Note that the spreading rate in CsCl and NaNO_3 solution is lower than that observed in pure water, thus suggesting some kind of inhibitory effect on dolomite dissolution. The step retreat rate increased with increasing ionic strength for NaCl, CsCl and NaNO_3 . However, in the case of KCl, LiCl and NaI, spreading rates were observed to remain constant or to slightly decrease when increasing the ionic strength from 0.01 to 1. In concentrated saline solutions ($\text{IS} = 1$), the etch pit spreading rate v_{sum} increased in the order $\text{LiCl} < \text{CsCl} < \text{KCl} < \text{NaCl}$ and $\text{NaI} < \text{NaCl} < \text{NaNO}_3$. Note that in the case of NaF, it was not possible to quantify the etch pit spreading rate at ionic strengths higher than 0.001 as they coalesced faster than the scanning rate. Additionally, extensive formation of precipitates (likely CaF_2 and/or MgF_2) was observed.

4. Discussion

Specific effects of background electrolytes on crystal dissolution can be interpreted on the basis of the ability of ions to modify solute hydration. Hydration of an ion in pure, deionised water is the result of a competition between ion–water (electrostatic) and water–water (hydration forces) interactions. Both can be affected when a background ion is present in solution (Kowacz and Putnis, 2008; Ruiz-Agudo et al., 2010). Solute–water and water–water interactions will determine the relative influence of electrolytes on dissolution rates at low and high ionic strength, respectively. In principle, dissolution should be favoured by a stronger hydration of the constituting ions and thus by increasing affinity of the water solvent to the building units of the dolomite crystal (increasing solute–water interactions) and/or by decreasing solvent affinity to the other solvent molecules (decreasing water–water interactions) in the respective salt solutions. However, as discussed in the next sections, entropic effects associated with the strong hydration of Ca^{2+} and Mg^{2+} dictates how electrolytes affect the kinetics of dolomite dissolution. Information about ion–solvent interactions is usually obtained either

Table 1
Average etch pit spreading rates ($v_{\text{sum}}/\text{nm s}^{-1}$) on dolomite cleavage surfaces for different background electrolytes as a function of ionic strength (IS).

IS	LiCl			KCl			CsCl			NaCl		
	pH	Mean	Std	pH	Mean	Std	pH	Mean	Std	pH	Mean	Std
Water	7.0	0.094	0.006	7.0	0.094	0.006	7.0	0.094	0.006	7.0	0.094	0.006
0.001	6.4	0.088	0.012	6.0	0.129	0.006	6.2	0.037	0.001	5.7	0.089	0.030
0.01	5.7	0.174	0.012	5.4	0.211	0.012	5.8	0.041	0.002	7.0	0.113	0.012
0.1	5.8	0.131	0.014	5.3	0.195	0.013	5.6	0.062	0.002	7.0	0.282	0.029
1	7.0 ^a	0.070	0.039	7.0 ^a	0.085	0.015	7.0 ^a	0.080	0.027	7.2	0.290	0.052
IS	NaI			NaNO ₃			NaF					
	pH	Mean	Std	pH	Mean	Std	pH	Mean	Std			
Water	7.0	0.094	0.006	7.0	0.094	0.006	7.0	0.094	0.006			
0.001	6.0	0.119	0.012	6.2	0.078	0.004	6.9	0.136	0.008			
0.01	7.0	0.194	0.010	6.2	0.145	0.007						
0.1	7.4	0.171	0.020	5.6	0.341	0.018						
1	7.4	0.041	0.013	7.0 ^a	0.430	0.083						

^a pH adjusted using NaOH.

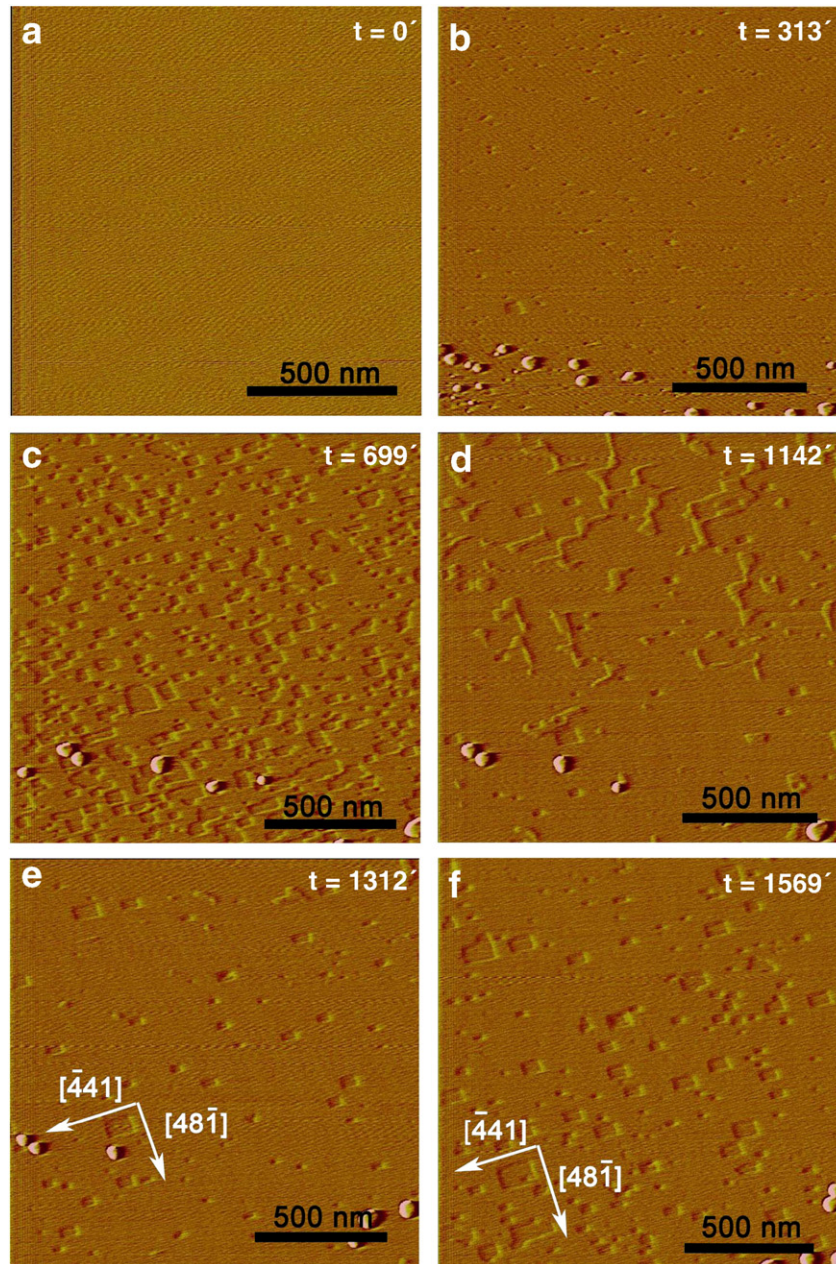


Fig. 1. AFM deflection images of a dolomite ($10\bar{4}$) surface exposed to a highly undersaturated solution for increasing periods of time. Shallow etch pits with edges parallel to $[\bar{4}41]$ and $[48\bar{1}]$ form and spread as dissolution proceeds. Average etch pit depth ~ 0.3 nm. Background electrolyte: NaNO_3 ($IS=0.1$).

from measurements of thermodynamic functions of hydration or from irreversible ionic transport processes such as conductance and ionic mobility (Nightingale, 1959). In the discussion below, we use the data obtained from transport processes in order to derive fundamental relationships between the impact of specific electrolytes on dissolution rates and characteristic properties of these background ions.

4.1. Dissolution at low ionic strength: stabilisation of $\text{Ca}^{2+}/\text{Mg}^{2+}$ hydration shells by background electrolytes

The interaction between a solute ion and the water molecules in its hydration shell is stronger in dilute electrolyte solutions than in pure water, because the water molecules in the hydration shell are stabilised by their electrostatic attraction with the counter-ions in the solution (Samoilov, 1967; Samoilov, 1971). This effect is reduced by the tendency of the background cations and anions to pair in solution. When two ions are close in solution, their combined electric

fields are screened and consequently their electrostatic influence on hydration water diminishes. Differences in the degree of ion pairing of the background salt in solution can be related to differences in diffusion coefficients (ΔD) of the ionic salt constituents in solution: increased ion pairing leads to smaller differences in ionic diffusivity between the cation and anion and should lead to a decrease in dissolution rate (Ruiz-Agudo et al., 2010). This is the trend observed in the dissolution of barite (Kowacz and Putnis, 2008). However, Fig. 3a shows that dolomite dissolution rates at low ionic strength (0.001) decrease with increasing differences in diffusion coefficients (ΔD) i.e. decreasing ion-pairing and thus, with increasing stabilisation of water in the solute-cation hydration shell. Values of ionic diffusion coefficients were taken from Koneshan et al. (1998) (Table 2). Due to the large uncertainties in the published values of ionic diffusion coefficients for Cs^+ and K^+ , in the case of like-hydrated electrolytes such a trend is best observed if we use the solubility of the background salt as a rough “proxy” of ion separation in solution (Fig. 3b). The less

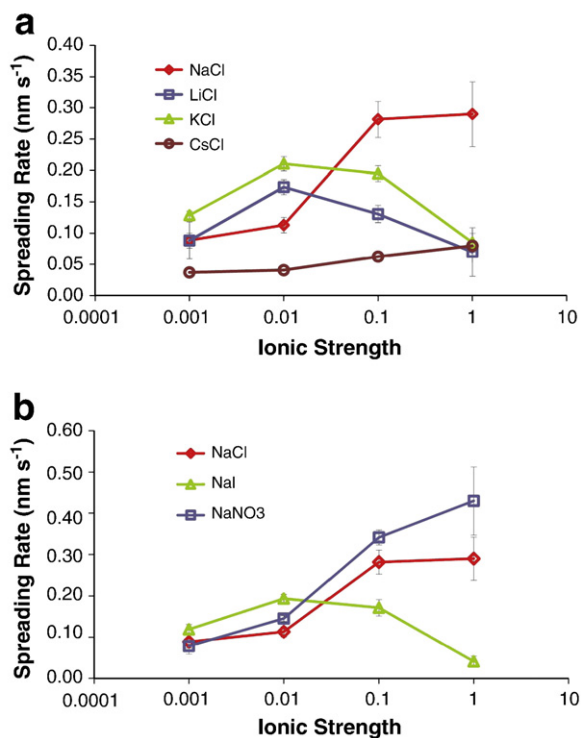


Fig. 2. Etch pit spreading rates ($v_{\text{sum}}/\text{nm s}^{-1}$) on dolomite cleavage surfaces versus ionic strength for a series of (a) chloride and (b) sodium salts.

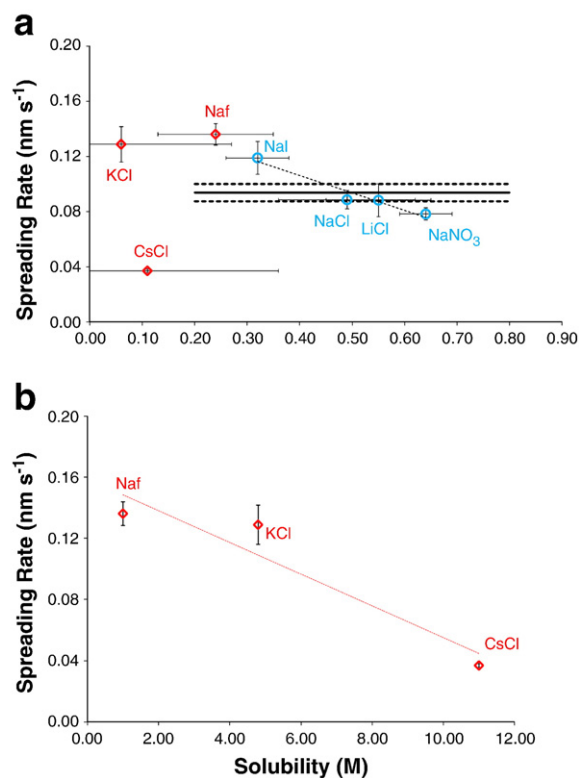


Fig. 3. Etch pit spreading rates ($v_{\text{sum}}/\text{nm s}^{-1}$) on dolomite cleavage surfaces at $IS=0.001$ in different background salts as a function of (a) the difference in the diffusion coefficients (ΔD) of ions composing the respective salt and (b) solubility. The horizontal black line corresponds to etch the pit spreading rate in pure water, and the dotted line represents the standard deviation of this value.

Table 2
Diffusion coefficients (D , $10^{-5} \text{ cm}^2 \text{ s}^{-1}$) for selected ions.
Koneshan et al., 1998.

	$D \cdot 10^{-5} (\text{cm}^2 \text{ s}^{-1})$	
	Mean	Std
F^-	1.04	0.06
Cl^-	1.77	0.08
I^-	1.60	0.01
NO_3^-	1.92 ^a	
Li^+	1.22	0.02
Na^+	1.28	0.05
K^+	1.83	0.13
Cs^+	1.88	0.17

^a Parsons, R. *Handbook of Electrochemical Constants*; Butterworth Scientific Publication: London, 1959; p 79.

paired the salt constituents are in solution, the more soluble is the salt (Collins, 1997). The lower dissolution rates are observed for the less ion-paired electrolytes (CsCl , NaNO_3). This is exactly the opposite trend to that observed during barite dissolution (Kowacz and Putnis, 2008).

The reason for this difference between the effect of background electrolytes on barite dissolution and dolomite dissolution cannot therefore be related to the factors discussed above. As shown for calcite (Ruiz-Agudo et al., 2010), although stabilisation of water molecules on the hydration shells of calcium (and, in the present case, magnesium as well as calcium) by the presence of electrolytes should make dissolution more favourable, there is a strong negative entropic effect due to increased ordering in the water molecules as they arrange in solution around strongly hydrated calcium and magnesium ions, compared to weakly-hydrated Ba^{2+} . The stabilisation of the hydration shell of water molecules around Ca and Mg ions by the presence of background salts augments this negative entropic effect upon calcite and dolomite dissolution relative to barite, thus making the overall process less favourable. This is reflected in the observed decrease in the dissolution rate with increasing ion separation in solution.

4.2. Dissolution at high ionic strength: impact of background anions on water structure dynamics

At high ionic strength, stabilisation of the solute-ion hydration shells by background electrolyte ions will be counterbalanced by the high concentration of like-charges, which increase the potential energy of hydration due to electrostatic repulsion between the like-charge ions and the solvent dipoles. Moreover, the interactions between background ions and solvent molecules will be progressively increased with increasing salt concentration due to the increase in the volume of water affected by the electrolyte. These interactions will change water structure dynamics (i.e. water–water interactions), thus modifying the hydration of solute ions and will become the controlling factor on the resulting dolomite dissolution rates in the different electrolyte solutions.

The strength of the interaction between an ion in solution and the solvent molecules can be related to its intrinsic mobility (μ_0). It is a function of its charge and a frictional drag. To a first approximation, we can consider that the mobility of univalent anions is inversely related to the effective radius of hydrated ions (r_H), according to the Hückel equation

$$\mu_0 = \frac{q}{6\pi\eta r_H}$$

where q is the charge of the ion and η is the viscosity of the solvent (Mbuna et al., 2004). From literature values of r_H (Nightingale, 1959)

Table 3

Effective radii of hydrated ions, r_H (Nightingale, 1959) ionic mobilities, μ_0 (cations: Koneshan et al. (1998); anions: Mbuna et al. (2004)) and Δr (Marcus (1994a)).

	r_H (Å)	$\mu_0 \cdot 10^{-4}$ (cm ² V ⁻¹ s ⁻¹)	Δr (Å)
Fe(CN) ₆ ³⁻	4.22	8.10	0.16
ReO ₄ ⁻	3.52	5.43	0.15
I ⁻	3.31	7.70	0.26
Br ⁻	3.30	7.74	0.35
BrO ₃ ⁻	3.51	5.60	0.38
IO ₃ ⁻	3.74	3.99	0.43
NO ₃ ⁻	3.35	7.14	0.44
Cl ⁻	3.32	7.48 ^a	0.43
Li ⁺	3.82	4.75	1.72
Na ⁺	3.58	4.98	1.16
K ⁺	3.31	7.12	0.74
Rb ⁺	3.29	7.71	0.64
Cs ⁺	3.29	7.32	0.49

^a Value estimated from the linear correlation for other monovalent anions.

and mobilities (Mbuna et al., 2004) (Table 3), Fig. 4a shows that this linear relationship is fulfilled for monovalent anions. The hydrated size of ions specifies the distance over which the electric field of the ion controls solvent behaviour; in other words, identifies the volume of water molecules affected by the presence of the ion (Kiriukhin and Collins, 2002). Low ion mobility is the result of a strong interaction with water molecules (i.e., more water molecules are affected by the ion resulting in a more structured solvent). The competition for hydration water between the bulk and the building units of the dissolving crystal will be higher in a more structured solvent, thus

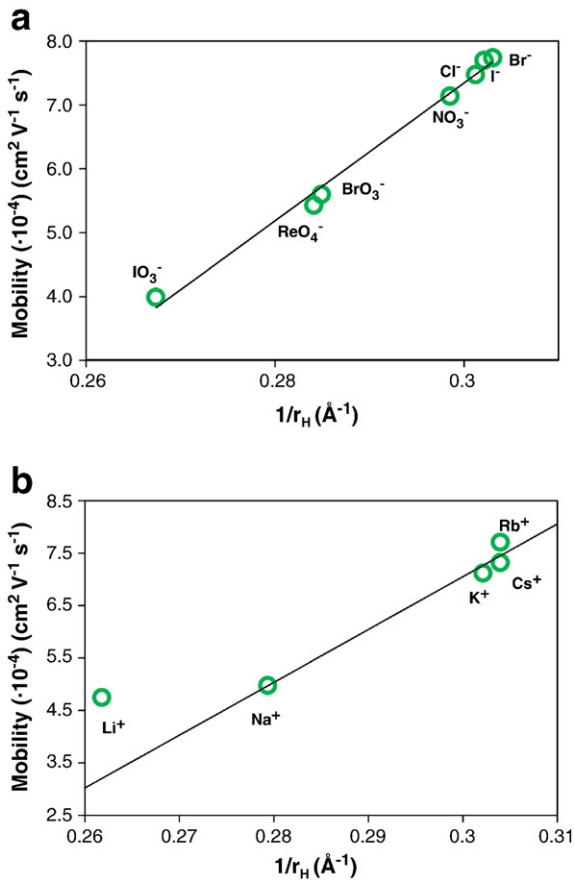


Fig. 4. Mobility (μ_0) of selected (a) anions and (b) cations as a function of effective hydration radius (r_H). Effective hydration radii are taken from Nightingale (1959) and mobilities are those reported by Koneshan et al. (1998) (cations) and Mbuna et al. (2004) (anions). Note the deviation from the linear trend of Li⁺ having higher mobility than expected according to its r_H .

leading to an increase in the frequency of water exchange around the latter. Dissolution will be then more favourable as the above-mentioned unfavourable entropic effect upon calcium and magnesium hydration will be reduced.

Ion mobility in water increases in the order NO₃⁻ < Cl⁻ < I⁻ (Koneshan et al., 1998; Lucy, 1999). Hence, water is less mobile around NO₃⁻ and, thus, more mobile around Ca²⁺ and Mg²⁺. Accordingly, the unfavourable entropic effect on dolomite dissolution is progressively reduced in the order I⁻ < Cl⁻ < NO₃⁻ due to an increasing frequency of water exchange around calcium and magnesium ions, which leads to the observed increase in dissolution kinetics in the same order. From the above discussion, it seems clear that the correlation between ion mobility and the effective radius of the hydrated ions, r_H , (Fig. 4a and Table 3) can be directly related to the dissolution rates (Fig. 5a). Thus the results show that it is possible to correlate the observed dissolution rates with an intrinsic parameter of the ion, such as its effective hydration radius, and in particular the thickness of the hydrated layer, hence representing a valuable tool for establishing predictive trends for other inorganic systems. This trend could not be predicted based solely on thermodynamic properties of the ions in the system. The fact that the effect of different anions on dolomite dissolution rates does not follow the typical Hofmeister series (I⁻ < NO₃⁻ < Cl⁻) (Zhang and Cremer, 2006) may be because the traditional ordering of anions in the Hofmeister series is based only on thermodynamic properties.

4.3. Dissolution at high ionic strength: impact of background cations and the lithium anomaly

The most significant differences in the dissolution kinetics of dolomite should be observed in the presence of different background anions, as they will determine the solvent structure around Ca²⁺ and

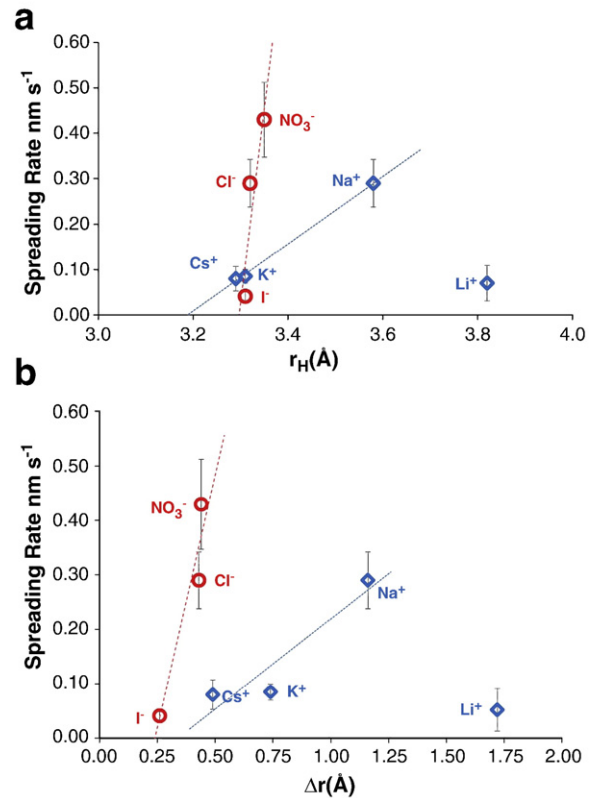


Fig. 5. Etch pit spreading rates ($v_{sum}/nm\ s^{-1}$) on dolomite cleavage surfaces at IS = 1 in different background electrolyte solutions as a function of (a) effective hydration radius (r_H) and (b) thickness of the hydration layer (Δr). Note that sodium and chlorine salts follow different trends with dissolution rates having a weaker dependence for Cl⁻ salts.

Mg^{2+} and solvation of the constituting cation is believed to be the rate limiting step in growth and dissolution of inorganic solids (Dove and Czank, 1995; Pokrovsky and Schott, 2002; Piana et al., 2006). Therefore, chloride salts (LiCl, NaCl, KCl and CsCl) should have a similar effect on the dissolution rates of carbonates at high ionic strengths. This has been observed for example for calcite (Ruiz-Agudo et al., 2010). However, in the case of dolomite, the nature of the background counter cation also appears to have an impact on the dissolution rate, which was not clearly appreciated in the case of calcite. This is reasonable as Mg^{2+} hydration is even higher than Ca^{2+} , and therefore solvent structuring effects induced by the cation building the crystal are expected to be more important.

As in the case of anions, cations with the larger effective hydration radius are expected to show the strongest interaction with water dipoles. Therefore, dissolution rates should be expected to increase with r_H , and hence in the order $CsCl < KCl < NaCl < LiCl$ (i.e. following a reverse Hofmeister series). With the exception of LiCl, this series is followed here as shown by Fig. 5a. A similar relationship was found between dissolution rates and Δr , which is the thickness of the region surrounding an ion in which the water molecules are translationally immobilised and electrostricted (Fig. 5b). Values of Δr were obtained from Marcus (1994b) (Table 3). Both r_H and Δr refer to similar concepts and in general correlate well with charge density, with higher charge density being associated with higher r_H and Δr values. The correlation of dissolution rates with both parameters clearly shows that the critical parameter controlling the observed behaviour is the volume of water that is affected by the presence of the background ions. The dependence of dissolution rate upon the hydration characteristics of the ions is weaker for cations compared to anions, as expected from the fact that anions will have the stronger influence in the solvation environment of the constituting cations (i.e., Mg and Ca).

Lithium is an exception to this trend. Despite its high effective hydration radius, the water molecules in its solvation shell are less electrostricted than around sodium (Hibrar et al., 2002). Its hydration co-sphere in transport processes is the largest among the alkali cations (Jákli, 2007) (as reflected by its lower ionic mobility compared to the rest of alkali cations) and therefore it should be expected to strongly structure the solvent. However, it always shows the smallest interactions with the solvent (Fortier et al., 1974). The unique hydration properties of lithium are most probably due to its tetrahedral first hydration shell, which fits well into the water structure thus resulting in only weak structural perturbations (Hibrar et al., 2002; Jákli, 2007). This may explain why LiCl does not follow the Hofmeister series observed for dolomite dissolution rates in the presence of other alkali chlorides, showing lower dissolution rates than NaCl or KCl. Also, as shown in Fig. 4b, this may explain the deviation of lithium from the linear relationship between mobility and r_H , with lithium having higher mobility (and, thus, weaker ion–water interactions) than expected from its hydrated radius.

Finally, K^+ , Li^+ and I^- weaken the structure of the solvent (overwhelming the effect of the respective counter ions, Cl^- and Na^+). In this case, the competition for water of hydration between the bulk and the solute ions will be lower than in a strongly structured solvent, resulting in a decrease in the frequency of water exchange around the solution ion. This will result in a less positive entropy upon ion hydration and, therefore, a less favourable process. Such an effect seems to be more important in dolomite than in calcite, leading to the observed decrease in dissolution rate in these salts when increasing the ionic strength from 0.01 to 1. As mentioned above, the stronger hydration of Mg^{2+} compared to Ca^{2+} may explain the observation that water structuring effects have a higher impact on dissolution rates.

5. Conclusions

Although it has been known for more than a century that the behaviour of organic macromolecules in aqueous solutions is affected

by background ions in a systematic sequence (lyotropic or Hofmeister series) based on ion hydration characteristics, similar effects on the growth and dissolution of inorganic solids are still not well documented. Here, the dissolution of dolomite has been studied as a model system to obtain insights into the principles governing ion specific effects in crystal reactivity, representing a relatively simple test of systematic trends in dissolution rates upon ion type. Pairing of background ions reduces the electrostatic stabilisation of water molecules in the hydration shells of a solute ion induced by the background electrolyte. This effect is thought to control ion-specific effects in dilute solutions. The role of background ions in crystal dissolution at high ionic strength is proposed to be determined by their affinity for water, the effective radius of the hydrated ions being a measure of such affinity. Furthermore, our results support the hypothesis that the response of the system to changes in hydration being induced by specific background ions depends on the hydration characteristics of the cations building the crystal (here calcium and magnesium). To our knowledge, this is one of the few systematic studies which provides a conceptual model that correlates dissolution rates of ionic inorganic solids with a fundamental property of the background ions, that is, the effective hydration radius. The volume of water affected by the background ions is the critical parameter to understand their effects on crystal dissolution in concentrated saline solutions, and the observed trends cannot be predicted or explained only in terms of the thermodynamic properties of ion solvation. It is likely that this model will be suitable for other inorganic systems where the Hofmeister effect occurs. Similar correlations have been shown for oxide minerals (Dove and Nix, 1997), therefore supporting the validity of our qualitative model for general dissolution processes. This study extends our ability to predict crystal reactivity in the fluids of both engineering and natural systems. As an example, from our conclusions we can hypothesise that ion-assisted dehydration of relevant cations could occur in biological systems thus affecting growth and weathering rates of biominerals as well as trace metal incorporation.

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References

- Arvidson, R.S., Collier, M., Davis, K.J., Vinson, M.D., Amonette, J.E., Luttge, A., 2006. Magnesium inhibition of calcite dissolution kinetics. *Geochimica et Cosmochimica Acta* 70, 583–594.
- Barber, D.J., Heard, H.C., Wenk, H.R., 1981. Deformation of dolomite single crystals from 20–800 °C. *Physics and Chemistry of Minerals* 7, 271–286.
- Cappa, C.D., Smith, J.D., Messer, B.M., Cohen, R.C., Saykally, R.J., 2006. Effects of cations on the hydrogen bond structure of liquid water. *The Journal of Physical Chemistry, B* 110, 5301–5309.
- Collins, K.D., 1997. Charge density-dependent strength of hydration and biological structure. *Biophysical Journal* 72, 65–76.
- Collins, K.D., Washabaugh, M.W., 1985. The effect and behaviour of water interfaces. *Quarterly Review of Biophysics* 18, 323–422.
- Collins, K.D., Neilson, G.E., Enderby, J.E., 2007. Ions in water: characterizing the forces that control chemical processes and biological structure. *Biophysical Chemistry* 128, 95–104.
- Dove, P.M., Craven, C.M., 2005. Silica surface charge in alkali chloride solutions reveals roots of ionic specificity. *Geochimica et Cosmochimica Acta* 69, 4963–4970.

- Dove, P.M., Czank, C.A., 1995. Surface chemical controls on the dissolution kinetics of the isostructural sulfates: barite, celestite and anglesite. *Geochimica et Cosmochimica Acta* 59, 1907–1915.
- Dove, P.M., Nix, C.J., 1997. Role of solvent-surface interactions in the electrolyte catalyzed kinetics of quartz dissolution. *Geochimica et Cosmochimica Acta* 61, 3329–3340.
- Duckworth, O.W., Martin, S.T., 2004. Dissolution rates and pit morphologies of rhombohedral carbonate minerals. *American Mineralogist* 89, 554–563.
- Fortier, J.-L., Philip, P.R., Desnoyers, J.E., 1974. Thermodynamic properties of alkali halides. III. Volumes and heat capacities of transfer from H₂O to D₂O at 25 °C. *Journal of Solid State Chemistry* 3, 523–538.
- Hall, C., Cullen, D.C., 1995. Scanning force microscopy of gypsum dissolution and crystal growth. *AIChE Journal* 42, 232–238.
- Hibrar, B., Southall, N.T., Vlachy, V., Dill, K.A., 2002. How ions affect the structure of water. *Journal of the American Chemical Society* 124, 12,302–12,311.
- Higgins, S.R., Hu, X., 2005. Self-limiting growth on dolomite: experimental observations with in situ atomic force microscopy. *Geochimica et Cosmochimica Acta* 69, 2085–2094.
- Hillner, P.E., Gratz, A.J., Manne, S., Hansma, P.K., 1992. Atomic-scale imaging of calcite growth and dissolution in real time. *Geology* 20, 359–362.
- Jákli, G., 2007. The H₂O–D₂O solvent isotope effects on the molar volumes of alkali-chloride solutions at T = (288.15, 298.15, and 308.15) K. *The Journal of Chemical Thermodynamics* 39, 1589–1600.
- Jordan, G., Rammensee, W., 1997. Growth and dissolution on the CaF₂ (111) surface observed by scanning force microscopy. *Surface Science* 371, 371–380.
- Kiriukhin, M.Y., Collins, K.D., 2002. Dynamic hydration numbers for biologically important ions. *Biophysical Chemistry* 99, 155–168.
- Koneshan, S., Rasaiah, J.C., Lynden-Bell, R.M., Lee, S.H., 1998. Solvent structure, dynamics, and ion mobility in aqueous solutions at 25 °C. *The Journal of Physical Chemistry. B* 102, 4193–4204.
- Kowacz, M., Putnis, A., 2008. The effect of specific background electrolytes on water structure and solute hydration: consequences for crystal dissolution and growth. *Geochimica et Cosmochimica Acta* 72, 4476–4487.
- Kunz, W., Henle, J., Ninham, B.W., 2004a. Zur Lehre von der Wirkung der Salze' (about the science of the effect of salts): Franz Hofmeister's historical papers. *Current Opinion in Colloid and Interface Science* 9, 19–37.
- Kunz, W., Lo Nostro, P., Ninham, B.W., 2004b. The present state of affairs with Hofmeister effects. *Current Opinion in Colloid and Interface Science* 9, 1–18.
- Lucy, C.A., 1999. Factors affecting selectivity of inorganic anions in capillary electrophoresis. *Journal of Chromatography A* 850, 319–337.
- Luttge, A., Winkler, U., Lasaga, A.C., 2003. Interferometric study of the dolomite dissolution: a new conceptual model for mineral dissolution. *Geochimica et Cosmochimica Acta* 67, 1099–1116.
- MacInnis, I.N., Brantley, S.L., 1992. The role of dislocations and surface morphology in calcite dissolution. *Geochimica et Cosmochimica Acta* 56, 1113–1126.
- Marcus, Y., 1994a. A simple empirical model describing the thermodynamics of hydration of ions of widely varying charges, sizes, and shapes. *Biophysical Chemistry* 51, 111–127.
- Marcus, Y., 1994b. Viscosity B-coefficients, structural entropies and heat capacities, and the effects of ions on the structure of water. *Journal of Solid State Chemistry* 23, 831–848.
- Mbuna, J., Takayanagi, T., Oshima, M., Motomizu, S., 2004. Evaluation of weak ion association between tetraalkylammonium ions and inorganic anions in aqueous solutions by capillary zone electrophoresis. *Journal of Chromatography A* 1022, 191–200.
- Nightingale Jr., E.R., 1959. Phenomenological theory of ion solution. Effective radii of hydrated cations. *The Journal of Physical Chemistry* 63, 1381–1387.
- Parkhurst, D.L., Appelo, C.A.J., 1999. Users Guide to PHREEQC (version 2) – A Computer Program for Speciation, Batch Reaction, One Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigation Report 99-4259. 312 pp.
- Parsons, D.F., Boström, M., Maceina, T.J., Salis, A., Ninham, B.W., 2010. Why direct or reversed Hofmeister Series? Interplay of hydration, non-electrostatic potentials, and ion size. *Langmuir* 26, 3323–3328.
- Piana, S., Jones, F., Gale, J.D., 2006. Assisted desolvation as a key kinetic step for crystal growth. *Journal of the American Chemical Society* 128, 13,568–13,574.
- Pokrovsky, O.S., Schott, J., 2001. Kinetics and mechanism of dolomite dissolution in neutral to alkaline solutions revisited. *American Journal of Science* 301, 597–626.
- Pokrovsky, O.S., Schott, J., 2002. Surface chemistry and dissolution kinetics of divalent metal carbonates. *Environmental Science & Technology* 36, 426–432.
- Pokrovsky, O.S., Schott, J., Thomas, F., 1999. Dolomite surface speciation and reactivity in aquatic systems. *Geochimica et Cosmochimica Acta* 63, 3133–3143.
- Putnis, A., Junta-Rosso, J.L., Hochella Jr., M.F., 1995. Dissolution of barite by a chelating ligand: an atomic force microscopy study. *Geochimica et Cosmochimica Acta* 59, 4623–4632.
- Reeder, R.J., Nakajima, Y., 1982. The nature of ordering and ordering defects in dolomite. *Physics and Chemistry of Minerals* 8, 29–35.
- Ruiz-Agudo, E., Putnis, C.V., Jiménez-López, C., Rodríguez-Navarro, C., 2009. An atomic force microscopy study of calcite dissolution in saline solutions: the role of magnesium ions. *Geochimica et Cosmochimica Acta* 73, 3201–3217.
- Ruiz-Agudo, E., Kowacz, M., Putnis, C.V., Putnis, A., 2010. Role of background electrolytes on the kinetics and mechanism of calcite dissolution. *Geochimica et Cosmochimica Acta* 74, 1256–1267.
- Samoilov, O.Ya., 1967. The theory of salting out from aqueous solutions – I. General problems. *Journal of Structural Chemistry* 7, 12–19.
- Samoilov, O.Ya., 1971. Theory of salting out from aqueous solutions. *Journal of Structural Chemistry* 11, 929–931.
- Shiraki, R., Rock, P.A., Casey, W.H., 2007. Dissolution kinetics of calcite in 0.1 M NaCl solution at room temperature: an atomic force microscopic (AFM) study. *Aquatic Geochemistry* 6, 87–108.
- Shtukenberg, A.G., Astilleros, J.M., Putnis, A., 2005. Nanoscale observations of epitaxial growth of hashemite on barite (001). *Surface Science* 590, 212–223.
- Spinolo, G., Anselmi-Tamburini, U., 1984. Dolomite decomposition to (Ca,Mg)O solid solutions: an X-ray diffraction study, part I. *Naturforsch Pt A* 39a, 975–980.
- Weaver, M.L., Qiu, S.R., Hoyer, J.R., Casey, W.H., Nancollas, G.H., De Yoreo, J.J., 2007. Inhibition of calcium oxalate monohydrate growth by citrate and the effect of the background electrolyte. *Journal of Crystal Growth* 306, 135–145.
- Zhang, Y., Cremer, P.S., 2006. Interactions between macromolecules and ions: the Hofmeister Series. *Current Opinion in Chemical Biology* 10, 658–663.
- Zhang, Y., Furyk, S., Bergbreiter, D.E., Cremer, P.S., 2005. Specific ion effects on the water solubility of macromolecules: PNIPAM and the Hofmeister Series. *Journal of the American Chemical Society* 127, 14,505–14,510.