

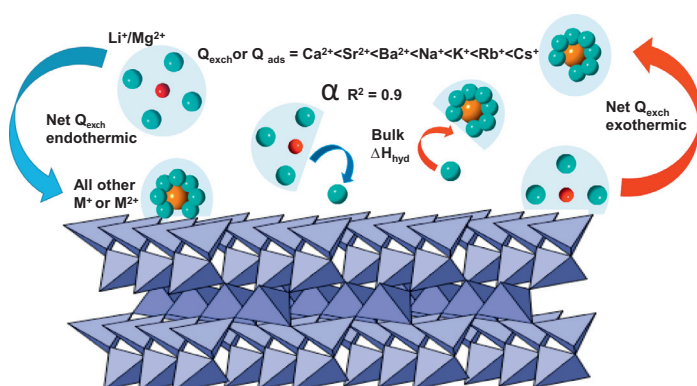


Regular Article

Calorimetric study of alkali and alkaline-earth cation adsorption and exchange at the quartz-solution interface

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GRAPHICAL ABSTRACT



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ABSTRACT

Cations in natural solutions significantly impact interfacial processes, particularly dissolution and surface charge measurements for quartz and silica, which are amongst the most naturally abundant and technologically important solids. Thermodynamic parameters for cation-specific interfacial reactions have heretofore been mostly derived instead of directly measured experimentally. This work investigates the energetics of adsorption and exchange reactions of alkali metal (M^+) and alkaline earth (M^{2+}) cations with the quartz surface by flow adsorption microcalorimetry, in tandem with in-situ pH measurements. The magnitudes of the heats of adsorption and exchange were found to increase along the Hofmeister series i.e., $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, and exhibited strong correlations to bulk cation hydration enthalpies (ΔH_{hyd}). These results suggest inner-sphere adsorption for all studied cations and highlight the role ΔH_{hyd} plays in rationalizing these reactions and controlling their net overall enthalpy. pH measurements demonstrate that quartz surface charge will vary depending on the cation present, as is well known for amorphous forms of silica. Along with calorimetric signals, pH data revealed kinetic differences between the adsorption and desorption reactions of M^+ and M^{2+} , and individual cations within each group.

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1. Introduction

Cations in natural electrolytic solutions significantly impact interfacial mineral/water processes, such as charge development [1–5], particle-particle interactions [6–10], contaminant transport [11–14], mineral dissolution [15–18], and adsorption/desorption [19–22]. The underlying mechanisms by which cations affect surface properties, particularly for silica and quartz, which are amongst the most naturally abundant and technologically important solids [23–24], have been extensively studied over the last few decades.

In particular, cation-specific trends have been observed in surface charge measurements, which are much more prevalent in the literature for amorphous forms of silica [3,25–27] than for quartz [28–29]. In general, surface charge has been found to increase, for a given pH above or below the point of zero charge, in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, and $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$, for the alkali metal and alkaline earth cations, respectively. These trends have been rationalized by Severjenski [4,22] as following hydration energy trends in the case of alkali metals, and hydrated radii size for the alkaline earths (Ba^{2+} smallest), whereas Dove and Craven [27] rationalized both trends in terms of the water structuring ability of the cations.

Cation specific effects have also been noted in dissolution studies. From 1990 to 2010, P.M. Dove and co-workers conducted a systematic study of the effects of cations on quartz dissolution, which was found to increase up to 100 times in the presence of small amounts of some alkali metal (M^+) and alkaline earth (M^{2+}) cations [20,30–32]. Dissolution rates (in logarithmic values) were correlated with the Gibbs free energy of cation solvation (ΔG_{soln}) for M^+ [32], and to solvent exchange rates (K_{exch}) for both M^+ and M^{2+} cations [16], albeit a mechanistic explanation for this relationship was not provided. Furthermore, M^{2+} cations were found to promote the hydrolysis of the Si–O bonds which further enhanced quartz dissolution [17]. Dove et al. [33–34] proposed that cation-free solutions cause dissolution at etch pits while cation-bearing solutions cause a faster stepretreat dissolution mechanism. Kubicki et al. [35] proposed, based on density functional theory calculations, that the role of dissolved alkali and alkaline earth cations on quartz dissolution rates is related to their promotion of intra-surface hydrogen bonds on the hydroxyl-terminated quartz surfaces, which might enhance Si–O–Si surface bond breaking events as the rate limiting step in dissolution. This postulated reaction mechanism is supported by the *ab initio* molecular dynamic (MD) simulations of Dellostritto et al. [36] Furthermore, Wallace et al. [17] used density functional theory (DFT) to show that alkaline earth cations were able to catalyze amorphous silica dissolution through adsorption at bridging oxygen sites.

In addition to cation and solid specific effects, studies have also investigated the role of interfacial water structure. Both Yang et al. [37] and Flores et al. [38] used sum frequency generation spectroscopy to observe the interfacial water structure on fused quartz surfaces and reported a significant perturbation in the presence of adsorbed cations, although again trends and explanations differed. Yang found the perturbation to decrease in the order of $\text{K}^+ > \text{Li}^+ > \text{Na}^+$ and to be related to the effective hydrated radius of the cation and its electrostatic interaction with the surface. However, Flores reported that on quartz perturbations followed mostly a positive lyotropic series ($\text{Li}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+}$), with Li^+ being the anomaly.

Traditionally, M^+ cations were considered as binding non-specifically (or outer-sphere) to oxide surfaces with their hydration shell intact. This assumption was mostly based on the success of surface complexation models in fitting experimental potentiometric surface charge titrations without the need to invoke any specific inner-sphere adsorption mechanism. However, recent experimen-

tal and computational studies have demonstrated that M^+ cations do bind in inner-sphere fashion. Using specular and anomalous X-ray reflectivity, as well as projector-augmented planewave DFT simulations, Bellucci et al. [39] reported Rb^+ adsorption at the quartz (101) surface involved both outer- and inner-sphere configurations. Kroutil et al. [40] employed classical molecular dynamics simulations and found a variety of charge dependent inner- and outer-sphere complexes for Na^+ , Rb^+ , and Sr^{2+} at the (101) quartz surface. Similarly, Pfeiffer-Laplaud and Gaigeot [41] utilizing first-principles DFT-based molecular dynamics simulations (FPMD) reported inner-sphere configurations at the (0001) α -quartz/liquid interface for both Na^+ and K^+ . On the muscovite surface, cation partitioning between inner- and outer-sphere conformations was related to free energies of hydration ($\Delta G_{\text{hyd}}^\circ$), whereby cations with higher $\Delta G_{\text{hyd}}^\circ$ (Na^+ , Li^+) adsorb mostly as outer-sphere complexes, while those with lower $\Delta G_{\text{hyd}}^\circ$ (K^+ , Cs^+ , Li^+) prefer inner-sphere complexation [42–43]. This ion distribution on muscovite was further explored by Kobayashi et al. [44] who showed, based on MD simulations, the presence of three different possible adsorption states for eight different cations (Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}). These are two-inner-sphere, and one outer-sphere surface complexes, and their distribution is correlated to the charge density of the cations. Their results also implied a different hydration structure for the outer-sphere complexes for monovalent and divalent cations.

On silica surfaces, the relative role of enthalpic and entropic factors in governing cation adsorption is still somewhat controversial. Some studies have related cation specificity, for example in developing negative surface charge, to differences in the entropy of hydration (ΔS_{hyd}) related to water arrangement at the interface [2,27,45–47]. This relation assumed a near-zero or a small positive enthalpy of adsorption (ΔH_{ads}). On the other hand, prediction of cation ΔH_{ads} values from the solvation and electrostatic effects found enthalpic effects to dominate entropic effects which were consistently negative and much smaller, except for amorphous silica [48–49].

Despite increasing evidence that cation effects are related to processes involving hydration properties, most previous studies have been done in a non-systematic way, and often involved either a specific quartz surface or a restricted number of cations. This limitation is particularly true for experimental work involving X-ray spectroscopy for which lighter elements (e.g. Li^+ , Na^+) remain difficult to resolve [50]. Furthermore, thermodynamic parameters for cation-specific interfacial reactions have heretofore been mostly derived instead of measured experimentally [45,51–53]. Direct measurements of the energetics of cation adsorption and exchange on quartz remain scarce [14,54].

Here, we utilize flow microcalorimetry in tandem with *in situ* pH measurements to systemically measure the energetics of alkali metal and alkaline earth cation adsorption and exchange reactions with the quartz surface. To our knowledge, this is the first experimental study that encompasses all members of both groups. It will be shown that the thermodynamic information gained through flow microcalorimetry measurements provides valuable insights into the energetics of these interactions, and the role of cation-specific effects, including hydration properties.

2. Experimental section

2.1. Solid and chemicals

The powdered Brazilian quartz (α - SiO_2) used in this study was obtained by grinding large colorless transparent pieces of a single quartz crystal. The quartz, after grinding, was separated from coarser fractions in methanol and then it was centrifuged and dried.

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