Cation Adsorption and Exchange at the Mineral-Water Interface: The Role of Hydration and Hydrolysis

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CATION ADSORPTION AND EXCHANGE AT THE MINERAL-WATER INTERFACE:
THE ROLE OF HYDRATION AND HYDROLYSIS

by

NICHOLAS ALLEN

Under the Direction of Nadine Kabengi, PhD

ABSTRACT

This work examines the interactions of cations with two mineral surfaces, quartz (SiO$_2$) and corundum (Al$_2$O$_3$) to gain mechanistic insights into those interactions through the use of flow microcalorimetry, quartz crystal microbalance measurements, and density functional theory. The adsorption and exchange of alkali and alkaline earth cations onto the quartz mineral surface was conducted at pH 4.0 and 8.0. The heats of adsorption and exchange were found to increase along the lyotropic series, Li$^+$ < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$ and Mg$^{2+}$ < Ca$^{2+}$ < Sr$^{2+}$ < Ba$^{2+}$, and were strongly correlated with the cation bulk hydration enthalpy. The adsorption of Al$^{3+}$, Cr$^{3+}$, and Mn$^{2+}$ was investigated on the quartz and corundum mineral surfaces at pH 3.8. Adsorption behavior was seen for all cations on both surfaces, with the exception of Mn$^{2+}$ on quartz. The adsorption of these cations was a function of both cation hydration and hydrolysis.

INDEX WORDS: Cation adsorption, Calorimetry, Mineral-water interface, Cation exchange, Cation hydration, Cation hydrolysis
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THE ROLE OF HYDRATION AND HYDROLYSIS

by

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College of Arts and Sciences
Georgia State University
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Figure 23: Fully hydrated models for adsorption onto silica and alumina substrates shows bond of interest for adsorption.

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<tr>
<td>R$_{ion}$</td>
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<td>$\Delta S_{hyd}$</td>
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<td>$\Delta H_{ads}$</td>
<td>Enthalpy of Adsorption</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>Q$_{ads}$</td>
<td>Heat of Adsorption</td>
</tr>
<tr>
<td>Q$_{des}$</td>
<td>Heat of Desorption</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>UV-Vis</td>
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1 INTRODUCTION

The interaction of cations with surfaces at mineral-water interfaces has been and still is a heavily researched area in geochemistry, surface chemistry, material science and many other related disciplines\textsuperscript{1-6}. These interactions control a large number of key biogeochemical processes and technological applications such as contaminant transport\textsuperscript{7-8}, nutrient bioavailability\textsuperscript{9-10}, mineral dissolution\textsuperscript{11-12}, and energy storage\textsuperscript{13-14}. Achieving a mechanistic understanding of these interactions remains a high priority for the geochemistry community as witnessed by the hundreds of papers published yearly on this topic utilizing both experimental and computational approaches, both separately\textsuperscript{15-18} and in combination\textsuperscript{19-20}. Despite this extensive body of work, very few studies have focused on acquiring thermodynamics data for these interfacial interactions despite the fundamental usefulness of this data. This work will use flow microcalorimetry to further develop a mechanistic understanding of cation interactions at mineral surfaces. The work will look at cation interactions with two mineral surfaces, quartz and corundum to explore the different properties of both the cations and the solids that govern the underlying exchange and adsorption processes and more specifically their thermodynamic characteristics.

The cations chosen included alkali (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) alkaline earth (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$), and other multivalent metal cations (Mn$^{2+}$, Al$^{3+}$, Cr$^{3+}$). The choice of cations studied was guided by their relative abundance and prominent role in natural aqueous solutions and biogeochemical processes. They also possess a suite of contrasting cation-specific properties, including ionic radius ($R_\text{ion}$), hydration radius ($R_\text{hyd}$), bulk hydration enthalpy ($\Delta H_\text{hyd}$), and ionic potential ($Z/R$), that allows systematic trends to be evaluated. These cation-specific properties follow one of two trends: properties that increase descending down a group ($R_\text{ion}$) and properties
that decrease descending down a group ($R_{\text{hyd}}, \Delta H_{\text{hyd}}, Z/R$). Furthermore, the inclusion of two transition metal cations, Mn$^{2+}$ and Cr$^{3+}$, allows for the study of cations that have access to the d-orbital, thus potentially increasing the complexity of the interactions.

The minerals chosen for this study, quartz and corundum, are commonly found in the Earth’s crust$^{21}$ and have quite different mineral properties as discussed below.

### 1.1 Minerals and Their Surfaces

The reactivity of mineral surfaces is primarily driven by the surface functional groups present. The pH-dependent protonation and deprotonation of the surface functional groups give rise to surface charge, and an important quantity of which is the point of zero charge is the pH at which the net charge of all the surface functional groups is equal to zero, denoted by $pH_{zpc}^{22}$. At pHs lower than the $pH_{zpc}$, the surface charge is net positive, while at pHs higher than the $pH_{zpc}$, the surface is net negative. These surface charges allow for the electrostatic adsorption of oppositely charged ions in both outer-sphere adsorption (where the cation stays fully solvated) and inner-sphere adsorption (where the cation loses part of the solvation shell to allow for a closer approach the surface). Quartz and corundum are optimal surfaces to study since they exhibit quite different surface groups and zero points of charge as discussed below.

While many forms of silicon dioxide exist in nature, the most common polymorph is $\alpha$-quartz denoted by $\alpha$-SiO$_2^{23}$. The quartz structure consists of a silicon atom connected to four oxygens in a tetrahedral configuration, with each tetrahedron sharing a corner oxygen (Fig 1).
The quartz mineral surface consists primarily of silanol functional groups that can either protonate or deprotonate depending on the solution pH leading to three moieties: Si-O, Si-OH$^0$, and Si-OH$_2^+$. As seen in Figure 2, the speciation of the silanol groups is dominated by the neutral >SiOH$^0$ silanol specie across the pH spectrum while >SiOH$_2^+$ and Si$^-$ become more abundant at pHs below 2.0 and above 4.0 respectively. The pH$_{zpc}$ of quartz has been reported to occur between 1.5 - 2.8\textsuperscript{2, 24-26}.

![Figure 1: Crystal structure of α-quartz (Heaney 1994)](image)

**Figure 1: Crystal structure of α-quartz (Heaney 1994)**

![Figure 2: Quartz surface silanol group speciation as a function of solution pH (Duval 2002)](image)

**Figure 2: Quartz surface silanol group speciation as a function of solution pH (Duval 2002)**
Corundum (α-Al$_2$O$_3$) is the most naturally occurring crystalline aluminum oxide$^{27}$ and is the most thermodynamically stable$^{28-29}$. The corundum structure consists of hexa-coordinated Al$^{3+}$ atoms in an octahedral configuration with face-sharing between individual octahedra$^{30}$ (Figure 3).

![Figure 3: Crystal structure of corundum (Smyth 1988)](image)

The corundum surface consists of AlO, Al$_2$O, and Al$_3$O surface groups$^{31}$ which can protonate and deprotonate to form AlOH$^{1/2}$, AlOH$_2^{+1/2}$, Al$_2$O$^{-1}$, Al$_2$OH$^0$, Al$_2$OH$_2^{+1}$, Al$_3$O$^{-1/2}$, and Al$_3$OH$^{+1/2}$ functional groups$^{32}$ (Figure 4). The accepted pH$_{zpc}$ for corundum ranges between pH 8.0 and pH 9.0$^{33}$.

![Figure 4: Corundum surface groups (Catalano 2010)](image)
1.2 Cations in Solution

When in solution, the positive charge of cations causes surrounding waters to orient in a structured solvation shell with the number of waters incorporated being a function of $R_{\text{ion}}$ of the cation\textsuperscript{34}. The most common coordination among all cations is hexa-coordination\textsuperscript{34}, while smaller cations like Li\textsuperscript{+} exist in tetra-coordination and larger cations like Cs\textsuperscript{+} exist in octa-coordination\textsuperscript{35}.

![Figure 5: Examples of hydrated alkali metal cations with increasing coordination number from left to right (Mahler 2012)](image)

Furthermore, the waters in the hydration shell can hydrolyze depending on the solution pH and the coordination of the cation. These hydrolyzed species have a shorter M-O bond distance for the M-OH bond and longer bond distances for the M-OH\textsubscript{2} bonds\textsuperscript{34}.

$$M(H_2O)_6^{+n} + H_2O \rightarrow MOH(H_2O)_5^{+n-1} + H_3O^+$$

Hence, hydrolysis can have a strong effect on the adsorption of cations to the mineral surface. For instance, the James and Healy model of hydrolyzable metal cation adsorption suggests that, for low dielectric constant mineral surfaces such as quartz, the preferred adsorbate will be the hydrolyzed cation\textsuperscript{36}. 
1.3 Overview

The goal of this work is to examine the interactions of cations with two different mineral surfaces and to use the thermodynamics data obtained from flow microcalorimetry, alone and in combination with other experimental and computational data, to gain mechanistic insights into those interactions. In addition to obtaining unique thermodynamic parameters, flow microcalorimetry is used to study mineral-water interface interactions, due to the in situ nature of the measurements combined with the reproducibility allowed from the flow nature of the system.

This work is divided into two chapters: the first investigates the adsorption of alkali and alkaline earth cations by quartz, and the second examines metal cation adsorption on quartz and corundum. Chapter 2 is a systematic analysis of the adsorption and exchange of cations through the lens of cation specific properties to elucidate how the cations interact with the quartz surface and to evaluate which cation properties play a bigger role in the measured enthalpies. This chapter has been published in the Journal of Colloid and Interface Science. Chapter 3 combines microcalorimetry and quartz crystal microbalance measurements, with density functional theory (DFT) calculations to analyze the interactions of metals on both quartz and corundum in order to investigate the role of cation hydrolysis and cation hydration during adsorption. This multifaceted approach allows for a more thorough investigation of the complex system of metal cation interactions combining in situ experimental data with atomistic computational methods. The quartz crystal microbalance measurements were performed by Chong Dai of the University of Houston and the DFT calculations were conducted by Dr. James Kubicki of the University of Texas at El Paso.
2 EXPERIMENT CALORIMETRIC STUDY OF ALKALI AND ALKALINE-EARTH CATION ADSORPTION AND EXCHANGE AT THE QUARTZ-SOLUTION INTERFACE

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2.1 Introduction

It is generally accepted that cations in natural electrolytic solutions significantly impact interfacial mineral/water processes, such as charge development, particle-particle interactions, contaminant transport, mineral dissolution, and adsorption/desorption. The underlying mechanisms by which cations effect the aforementioned surface properties, particularly for silica and quartz, which are amongst the most naturally abundant and technologically important solids, 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 than for quartz. In general, surface charge has been found to increase, for a given pH above or below
the point of zero charge, in the order Li$^+<$Na$^+<$K$^+<$Rb$^+<$Cs$^+$, and Ba$^{2+}<$Sr$^{2+}<$Ca$^{2+}<$Mg$^{2+}$, for the alkali metal and alkaline earth cations, respectively. These trends have been rationalized by Severjensky$^{40,57}$ 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$^{62}$ 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.$^{55,64-66}$ Dissolution rates (in logarithmic values) were correlated with the Gibbs free energy of cation solvation ($\Delta G_{\text{solv}}$) for M$^+$,$^{66}$ and to solvent exchange rates ($K_{\text{exch}}$) for both M$^+$ and M$^{2+}$ cations,$^{52}$ 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.$^{53}$ Dove et al.$^{12,67}$ proposed that cation-free solutions cause dissolution at etch pits while cation-bearing solutions cause a faster steppretreat dissolution mechanism. Kubicki et al.$^{68}$ 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.$^{69}$

In addition to cation and solid specific effects, studies have also investigated the role of interfacial water structure. Both Yang et al.$^{70}$ and Flores et al.$^{71}$ 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 $K^+ > Li^+ > Na^+$ 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 ($Li^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Zn^{2+}$), 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 experimental 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 density functional theory (DFT) simulations, Bellucci et al. reported $Rb^+$ adsorption at the quartz (101) surface involved both outer- and inner-sphere configurations. Kroutil et al. employed classical molecular dynamics simulations and found a variety of charge dependent inner- and outersphere complexes for $Na^+$, $Rb^+$, and $Sr^{2+}$ at the (101) quartz surface. Similarly, Pfeiffer-Laplaud and Gaigeot utilizing first-principles DFT-based molecular dynamics simulations (FPMD) reported inner-sphere configurations at the (0001) $\alpha$-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 ($\Delta G_{\text{hyd}}^0$), whereby cations with higher $\Delta G_{\text{hyd}}^0$ ($Na^+$, $Li^+$) adsorb mostly as outer-sphere complexes, while those with lower $\Delta G_{\text{hyd}}^0$ ($K^+$, $Cs^+$, $Li^+$) prefer inner-sphere complexation. This ion distribution on muscovite was further explored by Kobayashi et al. 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 (\(\Delta S_{\text{hyd}}\)) related to water arrangement at the interface.\(^{38, 62, 77-79}\) This relation assumed a near-zero or a small positive enthalpy of adsorption (\(\Delta H_{\text{ads}}\)). On the other hand, prediction of cation \(\Delta H_{\text{ads}}\) 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.\(^{80-81}\)

Despite increasing evidence that cation effects are related to processes involving hydration properties, most previous studies has 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.\(^{82}\) Furthermore, thermodynamic parameters for cation-specific interfacial reactions have heretofore been mostly derived instead of measured experimentally.\(^{77, 83-85}\) Direct measurements of the energetics of cation adsorption and exchange on quartz remain scarce.\(^{50, 86}\)

Here, we utilize flow microcalorimetry in tandem with \textit{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.

2.2 Experimental Section

2.2.1 Solids and Chemicals

The powdered Brazilian quartz (α-SiO₂) 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. The general morphology and particle size distribution of the sample were characterized using scanning electron microscopy (SEM; FEI Quanta 600 FEG) and high resolution transmission electron microscopy (HRTEM; JEOL 2100F at 200 kV), both of which revealed variable particle sizes between 40 and 500 nm and the absence of well-defined crystal faces (Figure 14 for SEM and Figure 15 for TEM). BET surface analysis (Quantachrome AS1Win, Quantachrome Instruments) using N₂ gas was performed, and the specific surface area was determined to be 14.49 ± 0.21 m²/g.

All acids, bases and salts used were ACS reagent grade chemicals and were used as received. Solutions were prepared with 18.2 MΩ deionized water. Solutions of M⁺ cations (LiCl, NaCl, KCl, RbCl, and CsCl) were prepared at a concentration of 0.050 M and those of M²⁺ (MgCl₂, CaCl₂, SrCl₂ and BaCl₂) at a concentration of 0.017 M in order to keep the ionic strength (I) constant. Both M⁺ and M²⁺ solutions were adjusted daily to pH 4.00 ± 0.01 using 12.1 M HCl. M⁺ solutions were also adjusted to pH 8.0 ± 0.1 using either 1 M LiOH, 1 M NaOH, 1 M KOH, 1 M RbOH, or 1 M CsOH as needed. pH adjustments led to less than 0.1% change in volume and had no significant effect on ionic strength. The pH of influent and effluent solutions was
monitored to ensure they remained constant. Furthermore, the calorimeter is equipped with a carbonate scrubber to ensure the solutions contained minimal amounts of carbonate.

2.2.2 Flow Microcalorimetry Experiments

All experiments were performed on flow adsorption microcalorimeters (FAMC) that were custom-designed and built in the Kabengi laboratory at Georgia State University. Details concerning the instrumentation and operational procedures have been reported previously and are outlined in section 3 of the SI. The interactions of $M^+$ and $M^{2+}$ with the quartz surface were probed by measuring heats, $Q$ in mJ/mg substrate of two types of reactions. First, adsorption ($Q_{\text{ads}} M^+$ and $Q_{\text{ads}} M^{2+}$) and desorption ($Q_{\text{des}} M^+$ and $Q_{\text{des}} M^{2+}$) reactions to and from the quartz surface, and second, exchange reactions between $Li^+$ and all other $M^+$ ($Q_{\text{exch}} Li^+/M^+$) and between all other $M^+$ and $Li^+$ ($Q_{\text{exch}} M^+/Li^+$), as well as between $Mg^{2+}$ and all other $M^{2+}$ ($Q_{\text{exch}} Mg^{2+}/M^{2+}$) and between all other $M^{2+}$ and $Mg^{2+}$ ($Q_{\text{exch}} M^{2+}/Mg^{2+}$).

Exchange experiments - a known mass of the quartz sample (~ 20.00 -25.00 mg) was homogeneously packed into the sample holder and equilibrated with 0.05M LiCl (or 0.017 M MgCl$_2$ for $M^{2+}$ experiments) solution until a steady baseline was achieved, indicating thermal equilibrium. For $M^+$ experiments, the solution was switched to one differing only by the cation, i.e. either NaCl, KCl, RbCl, or CsCl at the same concentration and pH, and the calorimetric signal corresponding to the displacement of $Li^+$ by $M^+$ (denoted by $[Li^+/M^+]$) on the surface was recorded. Once the reaction had ended as indicated by the return of the calorimetric signal to the original baseline, the solution was reverted back to LiCl and the displacement of $M^+$ by $Li^+$ (denoted $[M^+/Li^+]$) recorded. Once several replicates (~ 4 - 10) of that particular $M^+$ and $Li^+$ exchange reaction were conducted, the process was repeated for another cation, until all $M^+$ were studied. For the $M^{2+}$ experiments, after establishing a thermal baseline in MgCl$_2$, the solution was
switched to either CaCl$_2$, SrCl$_2$, or BaCl$_2$ and a similar process to that described above for the M$^+$
experiments was repeated. The calorimetric signals corresponding to the displacement of Mg$^{2+}$
by M$^{2+}$, denoted by [Mg$^{2+}$/M$^{2+}$], or the displacement of M$^{2+}$ by Mg$^{2+}$, denoted by [M$^{2+}$/Mg$^{2+}$],
were recorded. Again ~ 4 - 10 replicates were obtained for each leg of the exchange cycle. M$^+$
and M$^{2+}$ exchange experiments were conducted at pH values of 4.00 ± 0.01 and 8.0 ± 0.1.

Adsorption experiments - a quartz sample (~ 20 -25 mg) was initially equilibrated with
10$^{-4}$ M HCl solution adjusted to pH 4.00 ± 0.01 until thermal equilibrium was reached. The input
solution was then switched to one of the M$^+$ or M$^{2+}$ containing solutions, and the heat generated
from M$^+$ or M$^{2+}$ adsorption recorded. Upon completion of the adsorption reaction, again as
indicated by the return of the signal to the initial baseline, the solution was reverted back to the
10$^{-4}$ M HCl pH 4.00 solution and any heat associated with the desorption of M$^+$ or M$^{2+}$ from the
surface recorded. Again ~ 4 – 10 replicates were obtained for each M+ or M$^{2+}$ cation studied.

While these experiments are referred to herein as adsorption experiments, it is with the
understanding that the underlying mechanisms may still involve an exchange between H$^+$ and the
M$^+$ or M$^{2+}$ as will be discussed below. The chosen terminology is in part to differentiate between
the exchange experiments conducted whereby the starting point is one where the surface is in
equilibrium with either a M$^+$ or M$^{2+}$ solution, as well as to keep in line with other studies which
referred to a similar interaction with the surface as adsorption. Adsorption experiments
were not performed at pH 8.0 because solutions would have required a pH adjustment using
either the corresponding M$^+$(OH$^-$) or M$^{2+}$(OH$^-$)$_2$ hydroxide solution, and this would have
contaminated the starting solution with the cation of interest.

In-situ pH measurements. During both exchange and adsorption experiments, the pH of
all effluent was continuously monitored to help assess any role H$^+$ might have played in the
reactions studied. To that end, the outflow from the microcalorimeter was connected in-line to a flat surface pH probe (S450CD, Sen sorex; OrionStar A215 pH meter, Fisher Scientific) which continuously recorded the pH as a function of time. The probe was calibrated daily and no drift was observed at pH 4.00. At pH 8.0 pH drifted significantly which led us to abandon recording pH for that condition. pH measurements were integrated and quantified according to the procedure included in section 4 of the SI.

2.3 Results and Discussion

2.3.1 Calorimetric trends of $M^+$ and $M^{2+}$ adsorption

$M^+$ and $M^{2+}$ adsorption on the quartz surface at pH 4.00 was found to be exothermic (Figure 6A and 6B), while $M^+$ and $M^{2+}$ desorption was endothermic and consistently smaller (in absolute magnitude) than the adsorption (Figure 6C and 6D). It is also noteworthy to highlight that the calorimetric signals associated with both the adsorption and desorption of $M^{2+}$ took longer to return to baseline than those associated with the $M^+$ reactions. The $Q_{\text{ads}}$ and $Q_{\text{des}}$ values (mJ/mg substrate) determined from integrating the calorimetric signals depicted in Figure 6 increased in the order Li$^+ <$ Na$^+ <$ K$^+ <$ Rb$^+ <$ Cs$^+$ and Mg$^{2+} <$ Ca$^{2+} <$ Sr$^{2+} <$ Ba$^{2+}$ (Table 1). A closer examination of Table 1 reveals that $Q_{\text{ads}}$ and $Q_{\text{des}}$ were not significantly different between $M^+$ and $M^{2+}$ cations. The adsorption/desorption experiments required alternating between a 10$^{-4}$ M HCl and either 0.05 M $M^+$ solution or 0.017 M $M^{2+}$ solution, meaning a rather substantial change in ionic strength occurred during the adsorption (increasing $I$) and desorption (decreasing $I$) processes.
Figure 6: Representative calorimetric signals for $\text{M}^+$ and $\text{M}^{2+}$ adsorption (A, B) and desorption (C, D) at pH 4.00. An increase in voltage resulting in a positive peak corresponds to a release of energy and hence an exothermic reaction. Conversely, a decrease in voltage resulting in a negative peak corresponds to an energy consumption and hence an endothermic reaction.

Additional experiments were performed to diminish this effect by using $\text{M}^+$ solutions at 10-4 M, i.e. limiting the I change to a factor of 2 instead of 500. However, these experiments were inconclusive since the heats measured were near the calorimeters’ detection limit (~ 4 $\mu$J/mg or 2 $\times 10^{-5}$ K). This could be related to the fact that the negative surface charge for quartz under these concentrations conditions is expected to be very small. Reported surface charge values at pH 4.00 and 0.01-0.1 M I are less than -0.01 C/m$^2$ for both amorphous silica and quartz.\textsuperscript{24, 39}

Nevertheless, since experimental variables were identical for all $\text{M}^+$ and $\text{M}^{2+}$ experiments, any
heats associated with an I change is expected to be a constant, and therefore would not be expected to change the trends observed for both $Q_{\text{ads}}$ and $Q_{\text{des}}$ for $M^+$ and $M^{2+}$. However, changing ionic strength may have contributed to the magnitude and sign of the calorimetric signals, i.e. net exothermicity for $Q_{\text{ads}}$ and net endothermicity for $Q_{\text{des}}$.

**Table 1 Summary of heat of exchange values corresponding to the adsorption (2nd column) and desorption (3rd column) of cations.** Values corresponding to the exchange of monovalent and divalent cations by $Li^+$ and $Mg^{2+}$ respectively at pH 4.00 and pH 8.0 are presented in columns 4 and 5. Values for the exchange $Li^+$ and $Mg^{2+}$ by monovalent and divalent cations respectively at pH 4.00 and pH 8.0 are presented, when available, in columns 6 and 7.

<table>
<thead>
<tr>
<th>Cation</th>
<th>pH 4.00</th>
<th>pH 8.0</th>
<th>$Q_{\text{ads}}$</th>
<th>$Q_{\text{des}}$</th>
<th>$Q_{\text{exch}}$ [$M^+/Li^+$], [$M^{2+}/ Mg^{2+}$]</th>
<th>$Q_{\text{exch}}$ [$Li^+M^+$], [$M^{2+}/ Mg^{2+}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>-0.17 (0.02)$^1$</td>
<td>0.04 (0.01)</td>
<td>n.a.$^2$</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-0.30 (0.04)</td>
<td>0.11 (0.01)</td>
<td>0.055 (0.008)</td>
<td>0.081 (0.009)</td>
<td>-0.054 (0.006)</td>
<td>-0.098 (0.004)</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-0.43 (0.01)</td>
<td>0.12 (0.02)</td>
<td>0.105 (0.019)</td>
<td>0.159 (0.016)</td>
<td>-0.096 (0.019)</td>
<td>-0.173 (0.008)</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>-0.46 (0.02)</td>
<td>0.15 (0.02)</td>
<td>0.148 (0.005)</td>
<td>0.200 (0.012)</td>
<td>n.d.$^3$</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>-0.44 (0.04)</td>
<td>0.14 (0.01)</td>
<td>0.155 (0.003)</td>
<td>0.238 (0.006)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-0.20 (0.04)</td>
<td>0.07 (0.01)</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-0.28 (0.02)</td>
<td>0.09 (0.02)</td>
<td>0.030 (0.003)</td>
<td>0.049 (0.011)</td>
<td>-0.030 (0.003)</td>
<td>-0.064 (0.011)</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>-0.42 (0.05)</td>
<td>0.08 (0.02)</td>
<td>0.047 (0.006)</td>
<td>0.133 (0.018)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>-0.41 (0.05)</td>
<td>0.10 (0.02)</td>
<td>0.101 (0.012)</td>
<td>0.165 (0.006)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

$^1$ Numbers in parenthesis corresponds to ± one standard deviation of all replicates.

$^2$ Not applicable

$^3$ Not determined due to presence of both endothermic and exothermic signals during the cycle.

Directly measured adsorption heats for $M^+$ or $M^{2+}$ adsorption on either quartz or amorphous silica are scarce. Peng et al.\textsuperscript{91} utilized isoperibol solution calorimetry to measure adsorption enthalpies for 9 cations onto amorphous silica. Adsorption enthalpies were exothermic in all cases, and became more exothermic in the order, $Li^+<Na^+<K^+$, and $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$, with values ranging from -4.6 kJ/mol for $Li^+$ to -18.9 kJ/mol for $Ba^{2+}$. These sequences agree with the trends in adsorption heats measured in this study (Table 1).

Indirectly, using the van’t Hoff equation and adsorption equilibrium constants obtained at two
different temperatures, Dugger et al.\textsuperscript{83} and Malati et al.\textsuperscript{84} estimated exothermic heats of adsorption for M\textsuperscript{+} adsorption onto silica. Sahai\textsuperscript{81} calculated standard state enthalpies of adsorption (\(\Delta_{\text{ads}}H^0_{\text{M+}}\)) for quartz and reported them to be exothermic whether the adsorption occurred on negatively charged (>SO\textsuperscript{-}), or neutral (>SOH) sites. However, Kosmulski\textsuperscript{77} determined the \(\Delta_{\text{ads}}H^0\) to silica to be either zero for Na\textsuperscript{+} or slightly endothermic for Cs\textsuperscript{+}, \(\Delta_{\text{ads}}H^0<+10\) kJ/mol. Furthermore, Machesky\textsuperscript{92} predicts adsorption of cations on metal oxides to be endothermic based on temperature dependence measurements. Other calorimetric work on zirconium phosphates with varying degrees of crystallinity has shown that Li\textsuperscript{+} and K\textsuperscript{+} exchange with surface protons (an experimental protocol resembling our adsorption experiments) is either always exothermic or exothermic until a high surface coverage is obtained, wherein it becomes endothermic.\textsuperscript{93-94}

Correlations to cation specific properties - When evaluated against cation-specific properties (bare ionic radius (\(R_{\text{ionic}}\)); hydrated radius (\(R_{\text{hyd}}\)), ionic potential (IP = Z/R), and bulk hydration enthalpy (\(\Delta H_{\text{hyd}}\)) – values compiled in Table 6), the \(Q_{\text{ads}}\) for M\textsuperscript{+} and M\textsuperscript{2+} were found to have a strong correlation to \(\Delta H_{\text{hyd}}\) with R\textsuperscript{2} values of 0.960 and 0.873 for M\textsuperscript{+} and M\textsuperscript{2+} respectively (Figure 7A and 7B). Heats of exchange values, \(Q_{\text{exch}}\), were also strongly correlated to \(\Delta H_{\text{hyd}}\) values (Figures 7C and 7D) as will be further discussed below. Correlations between \(Q_{\text{ads}}\) and other M\textsuperscript{+} and M\textsuperscript{2+} cations properties are shown in Figures 18 and 19, respectively. The strong correlations suggest that both M\textsuperscript{+} and M\textsuperscript{2+} are undergoing processes involving their hydration shells, and that for M\textsuperscript{+} the relationship to hydration properties is stronger than that for M\textsuperscript{2+}. This can be rationalized on the basis that for M\textsuperscript{2+} cations, water molecules are more tightly bound in the first hydration shell than for M\textsuperscript{+}, i.e. dehydrating a M\textsuperscript{2+} is energetically costlier and kinetically slower, as witnessed by both the bulk \(\Delta H_{\text{hyd}}\) values and primary solvation shell water
exchange rate values in Table 6. Slower water exchange rates could also account for the slower return to baseline of the $M^{2+}$ calorimetric signals (Figure 6).

![Graphs showing correlation trends](image)

**Figure 7** Correlation trends between $Q_{ads}$ and bulk $\Delta H_{hyd}$ for $M^+$ (A) and $M^{2+}$ (B), and between $Q_{exch}$ and the difference in bulk $\Delta H_{hyd}$ between Li$^+$ and all other $M^+$ at pH 4.00 and 8.0 (C) and between Mg$^{2+}$ and all other $M^{2+}$ at pH 4.00 and 8.0 (D).

While the higher $\Delta H_{hyd}$ (taken in absolute values) for $M^{2+}$, 1305 to 1921 kJ/mol, versus those for $M^+$, 264 to 519 kJ/mol, may lead to the prediction that heats of adsorption should be greater for $M^{2+}$, another factor to consider is the total amount adsorbed. On silica, Dugger *et al.* report significantly smaller amounts adsorbed for $M^{2+}$ than for $M^+$ (equilibrium constant (pK) for $M^+$ ranged from 7.4 to 6.9, and those for $M^{2+}$ are between 11.9 and 12.5). This also follows simply
from charge considerations in that less $M^{2+}$ than $M^+$ is required to neutralize the same amount of negative surface charge. Thus, the smaller amount of $M^{2+}$ adsorbing would reduce the heat measured, as is observed experimentally (Table 1). Another factor that could have an impact on the measured heats is that of a varying surface charge, as discussed further below.

### 2.3.2 pH effects for adsorption experiments

*In-situ* pH measurements collected during $M^+$ and $M^{2+}$ adsorption (Figure 8A and 8B) and desorption (Figure 8C and Figure 8D) indicate a release of $H^+$ ($+\delta H^+$) from the surface as cations are adsorbing (pH drop from 4.00 to 3.44) and an uptake of $H^+$ onto the surface ($-\delta H^+$) as cations are desorbing (pH rise from 4.00 to 4.37).

![Figure 8: In-situ pH measurements corresponding to $M^+$ and $M^{2+}$ adsorption (A and B) and desorption (C and D) at pH 4.00](image-url)
Proton differential values obtained from integrating the signals in Figure 8 are presented in Table 2. On quartz, M⁺ and M²⁺ adsorption can occur on both protonated (>SiOH) and deprotonated silanols (>SiO⁻) as represented by reactions (1,3) and (2,4), respectively, below:

\[ \text{Si} - \text{OH} + M(H_2O)_x^+ \rightarrow \text{Si} - O - M(H_2O)_{x-y} + H^+ + YH_2O \tag{1} \]
\[ \text{Si} - O^- + M(H_2O)_x^+ \rightarrow \text{Si} - O - M(H_2O)_{x-y} + YH_2O \tag{2} \]
\[ \text{Si} - \text{OH} + M(H_2O)_{x}^{2+} \rightarrow \text{Si} - O - M(H_2O)_{x-y}^+ + H^+ + YH_2O \tag{3} \]
\[ \text{Si} - \text{O}^- + M(H_2O)_{x}^{2+} \rightarrow \text{Si} - O - M(H_2O)_{x-y}^+ + YH_2O \tag{4} \]

At pH 4.00, net negative surface charge is very small (< -0.01 C/m²), implying most surface silanols are protonated and thus that reactions 2 and 4 above dominate the cation adsorption process.

Table 2: Moles of H⁺ and minimum and maximum pH values measured during the adsorption and desorption of M⁺ and M²⁺ cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Proton Differential (moles H⁺) and Min/Max pH Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td>Li⁺</td>
<td>2.9·10⁻⁷ ± 1·10⁻⁸</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.5·10⁻⁷ ± 3·10⁻⁸</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.4·10⁻⁷ ± 6·10⁻⁸</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>2.5·10⁻⁷ ± 1·10⁻⁸</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>2.5·10⁻⁷ ± 1·10⁻⁸</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.6·10⁻⁷ ± 2·10⁻⁸</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.7·10⁻⁷ ± 2·10⁻⁸</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>2.9·10⁻⁷ ± 3·10⁻⁸</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>2.8·10⁻⁷ ± 3·10⁻⁸</td>
</tr>
</tbody>
</table>

Examination of Figure 8 and Table 2 reveals three notable points. First, for both M⁺ and M²⁺ the pH signals retuned to baseline faster moving down the group, i.e. Cs⁺ and Rb⁺, and Ba²⁺ and Sr²⁺ had a faster rate of return to baseline than Li⁺ and Na⁺, and Mg²⁺ and Ca²⁺ respectively.
suggesting these latter cations had overall slower reactions, possibly related to the higher energetic cost of dehydration. To that point, M$^{2+}$ reactions are also slower overall than M$^+$ since they have higher bulk $\Delta H_{\text{hyd}}$ (by approximately a factor of 3). Second, the pH effect accompanying the desorption of M$^{2+}$ took significantly longer to return to baseline than that of M$^+$, and in this case, the higher charge means greater electrostatic forces need to be overcome during the desorption. Another explanation for this observed kinetic effect between M$^{2+}$ and M$^+$ can be related to the distribution of surface complexes formed, i.e. outer- vs. inner-sphere. On muscovite, Kobayashi et al.$^{76}$ found that cations with stronger interactions with water, as reflected by $\Delta G_{\text{hyd}}$, tend to favor one of the two proposed inner-sphere complexes that retained more water molecules. A similar effect might be expected on our quartz sample whereby the kinetics of adsorption and desorption reactions for M$^+$ and M$^{2+}$ may depend on the strength of the cations interactions with water, the charged surface as well as on the distribution of the surface complexes formed (i.e. outer- vs. inner-sphere). Third, the adsorption of M$^{2+}$ released overall more H$^+$ than that of M$^+$ (Table 2). This observation concurs with surface charge density measurements obtained on both amorphous silica and quartz where M$^{2+}$ cations promote greater negative surface development than do M$^+$ cations.$^{62-63}$ With increasing negative surface charge developing as cations adsorb, increasing amounts of H$^+$ are expected to be released, and this is observed experimentally since the pH drops.

2.3.3 Calorimetric trends of M$^+$ and M$^{2+}$ exchange

Representative calorimetric data for [M$^+$/Li$^+$] and [M$^{2+}$/Mg$^+$] exchange at pH values of 4.00 and 8.0 are shown in Figure 9. It was found that Li$^+$ replacing an adsorbed M$^+$ and Mg$^{2+}$ replacing an adsorbed M$^{2+}$ at both pH values of 4.00 and 8.0 were endothermic with the heats consumed in both cases following a direct Hofmeister trend such that $Q_{\text{exch Na}^+/\text{Li}^+} < Q_{\text{exch}}$.
K\(^+\)/Li\(^+\) < Q\(_{\text{exch}}\) Rb\(^+\)/Li\(^+\) < Q\(_{\text{exch}}\) Cs\(^+\)/Li\(^+\) and Q\(_{\text{exch}}\) Ca\(^{2+}\)/Mg\(^{2+}\) < Q\(_{\text{exch}}\) Sr\(^{2+}\)/Mg\(^{2+}\) < Q\(_{\text{exch}}\) Sr\(^{2+}\)/Li\(^+\) (Table 1). At pH 8.0 Q\(_{\text{exch}}\) of M\(^+\)/Li\(^+\) were higher by a factor ranging from 1.35 to 1.54. Values of Q\(_{\text{exch}}\) of M\(^{2+}\)/Mg\(^{2+}\) were also higher by a factor ranging from 1.63 to 2.83. This increase coincides with the increased surface charge that occurs over the same range in pH for M\(^+\) and M\(^{2+}\) respectively.\(^{39,62}\) Additionally, it can be seen that at both pH values of 4.00 and 8.0, the average Q\(_{\text{exch}}\) for [M\(^{2+}\)/Mg\(^+\)] were smaller than those for Q\(_{\text{exch}}\) for [M\(^+\)/Li\(^+\)] by approximately a factor of 2. This is also likely due to the difference in amounts adsorbed, as discussed above for differences in Q\(_{\text{ads}}\) for M\(^+\) and M\(^{2+}\).

**Figure 9:** Representative calorimetric signals for [M\(^+\)/Li\(^+\)] exchange at pH 4.00 (A) and 8.0 (C) and for [M\(^{2+}\)/Mg\(^+\)] exchange at pH 4.00 (B) and 8.0 (D). A decrease in voltage resulting in a negative peak corresponds to an energy consumption and hence an endothermic reaction.
Correlation to cation specific properties - A similar exercise aimed at evaluating $Q_{\text{exch}}$ in terms of cation-specific properties demonstrated the dominant contribution of bulk $\Delta H_{\text{hyd}}$ to the overall energy of the exchange for both $M^+$ and $M^{2+}$. $Q_{\text{exch}}$ values were strongly correlated to the difference between the bulk $\Delta H_{\text{hyd}}$ values for Li$^+$ and the $M^+$ it is replacing ($R^2=0.960$ and $0.987$ at pH values of 4.00 and 8.0 respectively), and for Mg$^{2+}$ and the $M^{2+}$ it is replacing ($R^2=0.922$ and $R^2=0.924$ at pH values of 4.00 and 8.0 respectively) (Figure 7C and 7D). Correlations to other cation specific properties (Figures 19 and 20) indicated that the correlation between $Q_{\text{exch}}$ and the difference in hydrated radii of the exchanging cations at both pH values of 4.00 and 8.0 was weaker for $M^{2+}$ ($R^2=0.823$ and 0.490 respectively) than for $M^+$ ($R^2=0.823$ and 816 respectively), similarly to what have been observed for $Q_{\text{ads}}$. Taking into account the evident role bulk $\Delta H_{\text{hyd}}$ plays, the endothermicity of the $[M^+/Li^+]$ and $[M^{2+}/Mg^+]$ exchange can be understood, as has been suggested by others, as the difference between the endothermic dehydration of the incoming exchanging species and the exothermic rehydration of the desorbed exchanged species. For instance, the $[Na^+/Li^+]$ exchange includes the exothermic rehydration of Na$^+$ as it leaves the surface and enters the bulk solution, and the endothermic dehydration of Li$^+$ as it adsorbs on the surface. Thus, the net endothermic heat of exchange ($Q_{\text{exch}}$) reflects the smaller bulk hydration enthalpy ($\Delta H_{\text{hyd}}$) of Na$^+$ (-409 kJ/mol) compared to the larger (in absolute magnitude) bulk dehydration enthalpy of Li$^+$ (+519 kJ/mol). To our knowledge, there are no other reported directly measured heats of $M^+$ and $M^{2+}$ cations exchanged on quartz. Recently, however, Prelot et al.$^{50}$ also used flow microcalorimetry to measure heats of adsorption of some divalent ($\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Cd}^{2+}$, $\text{Co}^{2+}$ and $\text{Zn}^{2+}$) and trivalent ($\text{Eu}^{3+}$) metals on Spherosil hydrophilic silica in the presence of Na$^+$ on the surface, i.e. corresponding to either a $[\text{Na}^+/M^{2+}]$ or $[\text{Na}^+/M^{3+}]$ reaction. They found the overall displacement to be endothermic, which was attributed to the higher $\Delta H_{\text{hyd}}$ of the
exchanging cations investigated (e.g. -1921 kJ/mol for Mg\(^{2+}\) and -3535 kJ/mol for Eu\(^{3+}\)). On montmorillonite, using isothermal microcalorimetry to measure immersion enthalpies, Rotenberg et al.\(^{20}\) reported exchange enthalpies for the exchange of Na\(^{+}\) by Cs\(^{+}\) in the clay interlayer to be overall exothermic. Since the Monte Carlo molecular simulations conducted by the authors found the clay contributions to the enthalpy of exchange to be endothermic, the net exothermicity was attributed to the replacement of Cs\(^{+}\) by Na\(^{+}\) in the aqueous phase and Cs\(^{+}\) “hydrophobicity” compared to Na\(^{+}\).

\[\text{[Li}^{+}/\text{M}^{+}\text{]}\text{ and [Mg}^{2+}/\text{M}^{2+}\text{]} \text{ exchange} – \text{When adsorbed Li}^{+}\text{ is replaced by an incoming M}^{+}\text{, two different behaviors were observed (Figure 10A). In the case of Na}^{+}\text{ and K}^{+}\text{, an exothermic reaction occurs with } Q_{\text{exch Li}^{+}/\text{K}^{+}} > Q_{\text{exch Li}^{+}/\text{Na}^{+}} \text{, reflecting the higher energy cost associated with dehydrating Na}^{+}\text{ compared to K}^{+}\text{. The calorimetric signals for the endotherms and exotherms correspond in both reactions time and magnitude (Table 1) as expected for a reversible ion exchange reaction. This was true at both pH 4.00 and pH 8.0. In the case of either Rb}^{+}\text{ or Cs}^{+}\text{ replacing Li}^{+}\text{, the calorimetric signals were split whereby the initial exothermic response was followed by a tailing endothermic heat (Figure 10B). The endothermic tail portion was more pronounced for Cs}\text{+ than for Rb}\text{+ and in both cases extended the reaction time past that of the corresponding [M}^{+}/\text{Li}^{+}\text{]} \text{ exchange by 15 and 25 min for Rb}^{+}\text{ and Cs}\text{+, respectively. At pH 8.0, the endothermic tail is greatly reduced in both size and time compared to the exotherm and the tail is completely absent for Rb}^{+}\text{ (Figure 10C). Similarly, different behaviors were observed for M}^{2+}\text{ cations exchanging for Mg}^{2+}\text{ (Figure 10B). [Mg}^{2+}/\text{Ca}^{2+}\text{]} \text{ exchange was exothermic and mirrored that of [Ca}^{2+}/\text{Mg}^{2+}\text{]} \text{ in reaction time and magnitude at both pH values of 4.00 and 8.0. [Mg}^{2+}/\text{Sr}^{2+}\text{]} \text{ and [Mg}^{2+}/\text{Ba}^{2+}\text{]} \text{ exchanges exhibited the split calorimetric signal discussed above (exothermic/endothemic), with Ba}^{2+}\text{ exhibiting a longer endothermic tail than Sr}\text{2+}. For Ba}\text{2+ and} \]
Sr$^{2+}$, the endothermic tail did not change in either size or time at pH 8.0. However, its relative proportion to that of the exothermic part decreased by a factor of 2.

In order to rationalize these experimental results, it is first important to examine potential mechanistic differences that underlie Na$^+$ and K$^+$ versus Rb$^+$ and Cs$^+$ interactions, as well as Ca$^{2+}$ versus Sr$^{2+}$ and Ba$^{2+}$ interactions with the surface. Our calorimetric and pH results from the

Figure 10: Representative calorimetric signals for $[\text{Li}^+ / \text{M}^+]$ exchange at pH 4.00 (A) and 8.0 (C) and for $[\text{Mg}^+ / \text{M}^{2+}]$ exchange at pH 4.00 (B) and 8.0 (D). An increase in voltage resulting in a positive peak corresponds to a release of energy and hence an exothermic reaction. Conversely, a decrease in voltage resulting in a negative peak corresponds to an energy consumption and hence an endothermic reaction. The dotted lines indicating the original baselines are to aid the eye.
adsorption experiments discussed above, in tandem with the previous literature indicate that cations are partially dehydrating and forming inner-sphere complexes with surface silanols. Furthermore, computational studies reviewed earlier suggest that the denticity of each cation and therefore the amount of dehydration is expected to be different.\textsuperscript{72-73} Although no systematic study has been conducted these trends seem to suggest, that at least for the M\textsuperscript{+} cations, dehydration during adsorption increases down the group (i.e., Cs\textsuperscript{+} > Li\textsuperscript{+}). The split in the calorimetric signals can then be further rationalized on the basis of different kinetics and/or configurations associated with that additional dehydration. For Rb\textsuperscript{+} and Cs\textsuperscript{+} this extra step will increase the time needed for the reaction to come to completion. This causes the endothermic dehydration signature to drag, resulting in the observed split of the $Q_{\text{exch}}$ curves. At pH 8.0, this effect is significantly minimized for the M\textsuperscript{+} but remains unchanged for M\textsuperscript{2+}, and we hypothesize that this is related to the total amount of negative charge on the surface, which is very small at pH 4 (<-0.01 C/m\textsuperscript{2}), and considerably larger at pH 8 (> -0.05 C/m\textsuperscript{2}).\textsuperscript{39, 63} For M\textsuperscript{2+}, Kroutil \textit{et al.}\textsuperscript{72} reported that the distribution of surface complexes varied less with the net surface negative charge than that of M\textsuperscript{+} cations. This increase in negative charge translates into a significantly higher electrostatic attraction that causes Rb\textsuperscript{+} and Cs\textsuperscript{+} adsorption to occur at a higher rate. Chorover and Brusseau\textsuperscript{96} reported on different studies in which the rate constant for cation adsorption on hematite varies with surface charge. A similar effect may be at play in this case.

2.3.4 \textit{pH effects for of M\textsuperscript{+} and M\textsuperscript{2+} exchange experiments}

pH measurements collected during M\textsuperscript{+} and M\textsuperscript{2+} exchange cycles (Figure 11 and Table 7) revealed two noteworthy points. First, pH effects accompanying exchange reactions were significantly smaller (± 0.05 pH units) than ones measured during adsorption experiments (± 0.5). The difference arises because as a desorbing cation is leaving the surface and rejoining the
bulk solution, it is replaced by an adsorbing cation, and hence net protonation/deprotonation changes are much smaller. Second, $[\text{Li}^+/\text{M}^+]$ and $[\text{Mg}^{2+}/\text{M}^{2+}]$ were accompanied by a pH drop, and $[\text{M}^+/\text{Li}^+]$ and $[\text{M}^{2+}/\text{Mg}^{2+}]$ by a pH increase, reflecting the difference in surface charge in various cations as discussed above.

![Figure 11: pH effects accompanying $[\text{Li}^+/\text{M}^+]$ and $[\text{Mg}^{2+}/\text{M}^{2+}]$ exchange (A) and $[\text{M}^+/\text{Li}^+]$ and $[\text{M}^{2+}/\text{Mg}^{2+}]$ (B). Each mark on the y-axis corresponds to 0.01 pH units](image)

### 2.4 Conclusion and Significance

We utilized flow microcalorimetry measurements to determine thermodynamic data for the adsorption and exchange reactions of alkali and alkaline earth cations on quartz. These data were analyzed to investigate chemical trends in adsorption and exchange through calculating correlations to relevant cation-specific properties. The adsorption of $\text{M}^+$ and $\text{M}^{2+}$ was found to be exothermic, although a potential confounding effect from an ionic strength change could not be ruled out. Exchange reactions were endothermic for $\text{Li}^+$ replacing all other $\text{M}^+$ and $\text{Mg}^{2+}$ replacing all other $\text{M}^{2+}$. Reverse reactions of an $\text{M}^+$ replacing $\text{Li}^+$ and $\text{M}^{2+}$ replacing $\text{Mg}^{2+}$ were exothermic, although for $\text{Cs}^+$ and $\text{Rb}^+$, and $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$ an endothermic tail was observed, indicating a potential kinetic and/or configurational effects of dehydration.
The magnitudes of the heats of adsorption and exchange reactions (displacement of $M^+$ by $Li^+$ and $M^{2+}$ by $Mg^{2+}$) increased following the positive lyotropic series i.e., $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, and exhibited strong correlations to hydration properties, especially bulk $\Delta H_{hyd}$ and hydrated radii. These correlations indicated that for both alkali and alkaline earth cations, interactions with the quartz surface through either adsorption or exchange reactions implicate processes involving their hydration shell. The correlation to the hydrated radius did not hold as strongly for $M^{2+}$ reactions which were more highly correlated to the bare ionic radius and the ionic potential. Our results highlight the role bulk hydration enthalpies play in these interactions and their net overall enthalpy and, given the considerable energies measured, suggest inner-sphere adsorption for all the cations studied. Combined with other recent X-ray reflectivity and computational studies on cations binding to quartz and muscovite reviewed above, our experimental data extends the evidence for inner-sphere complexation to all alkali and alkaline earth cations.

*In-situ* pH measurements revealed a kinetic difference between the adsorption and desorption reactions of $M^+$ and $M^{2+}$, with the latter being consistently slower. A similar effect was also observed for elements in higher periods within the same group (i.e. $Cs^+$ and $Rb^+$ versus $Li^+ + Na^+$, and $Sr^{2+}$ and $Ba^{2+}$ versus $Ca^{2+}$). Combined with the calorimetric signals and their trends, pH measurements demonstrate that quartz surface charge, of which very studies exist in the literature, will vary depending on the cation present, as is well known for amorphous forms of silica. Hence, taking into account this charge effect is important is rationalizing cation adsorption and desorption reactions. Moreover, even at pH 4.00 where surface charge is very small, and cation specific differences are virtually indistinguishable, calorimetric signals are well resolved which indicates a distinct advantage of the technique over conventional surface charge
titrations in probing surface charge and surficial processes. Finally, any attempt to derive a unified picture of cation interactions with quartz must navigate the complex interplay between hydration (and dehydration) properties as well as the kinetics related to the strength of cation interactions with water, the surface charge and any varying electrostatic effects, as well as the distribution of the surface complexes formed. Future work by our group will apply this approach to oxides with markedly different properties (e.g. rutile) to decipher the effect of surface properties on ion adsorption thermodynamics.

2.5 Acknowledgements

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3 ADSORPTION STUDY OF AL\(^{3+}\), CR\(^{3+}\), AND MN\(^{2+}\) ONTO QUARTZ AND CORUNDUM USING FLOW MICROCALORIMETRY, QUARTZ CRYSTAL MICROBALANCE AND DENSITY FUNCTIONAL THEORY

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3.1 Introduction

Aqueous ion interactions with natural mineral surfaces control numerous interfacial processes, such as mineral dissolution\(^{12,68,97}\), oxidation-reduction\(^{98-99}\), and contaminant transport\(^7,100\), all of which have far-reaching implications for important biogeochemical processes\(^{101-105}\). The mechanisms underlying these interactions have been extensively studied over the last few decades, particularly for silicon and aluminum oxides which are two of the most prevalent crustal mineral constituents\(^{21}\). Of all polymorphs, quartz and corundum are the
most naturally occurring of their respective oxides. Quartz is the primary crystalline structure of silicon oxides and has unique properties as compared to other mineral oxides, in particular, its low zero point of charge reported between pHs of 1.5 to 2.82,24-26,106, the prevalence of the neutral silanol species as the dominant surface functional group across a wide pH range25,107, and a low dielectric constant (ε) of 4.340. Corundum is the most common occurring polymorph27 of the crystalline aluminum oxides and the most thermodynamically stable28-29. The point of zero charge has been reported to occur at pHs of 8 to 9, significantly higher than that of quartz26. The ε of corundum is 10.440, also higher than that of quartz, but still considered in the intermediate ranges of solid dielectric constants.

This work coincides with a study of the effect of impurities during ferrihydrite nucleation and growth on corundum and quartz surfaces (Dai et al, in submission). The cations studied, Al3+, Cr3+, and Mn2+, are thought to substitute into and affect the ferrihydrite structure during precipitation. Therefore, it was important to determine the interactions of these cations with both quartz and corundum in acidic conditions such as those found in acid mine drainage where ferrihydrite precipitation is likely to occur108. These cations are able to hydrolyze in solution, albeit at different pH values, potentially impacting the underlying mechanisms of their interactions with mineral surfaces. Another factor impacting cation adsorption is their hydration properties109, namely their bulk hydration enthalpies110 and hydrated radius111. Finally, the adsorption of these cations has not been examined with a variety of techniques in tandem.

Studies of Al3+ adsorption on mineral surfaces have included those on clays112-114 and silica gel115. Bloom and McBride112-113 used batch adsorption methods to determine that as Al3+ adsorbed to smectite at pH of 4.0 it hydrolyzed to AlOH2+. However, Walker et al114, using a flow-through stirred-cell system, found that no measurable hydrolysis during the adsorption of
Al$^{3+}$ onto clay minerals between pHs 3.0-4.0 and asserted the adsorption to be predominantly an electrostatic outer-sphere exchange. On the other hand, Kuan et al$^{115}$, using a combination of batch adsorption and surface complexation modeling, determined Al$^{3+}$ adsorption on silica to occur predominantly as inner-sphere interaction and that hydrolyzed Al$^{3+}$ was the dominant form interacting with the surface at pHs 3.0 and higher.

The adsorption of Cr$^{3+}$ has been widely studied on δ-aluminum oxide$^{116}$, ferrihydrite$^{117}$, and silica$^{118-120}$. Wehrli et al$^{116}$ determined that Cr$^{3+}$ adsorbed on aluminum oxide as the hydrolyzed species, CrOH$^{2+}$, and formed a bidentate complex with the surface at pH values between 2.5 and 6.0. On ferrihydrite, Charlet and Manceau$^{117}$ found the Cr$^{3+}$ interactions with the surface to depend on surface coverage with inner-sphere CrOH$^{2+}$-complexes dominating at low coverage and chromium oxy-hydroxide precipitation occurring at high surface loadings. Furthermore, Fendorf et al$^{118-119}$ found that CrOH$^{2+}$ formed monodentate inner-sphere complexes on silica at low coverage.

Studies of Mn$^{2+}$ adsorption have included those on iron oxides$^{98,121}$, aluminum oxides$^{98,122-124}$, and silica$^{98,125}$ and have similarly highlighted the important role of cation hydrolysis in these interactions. On the δ-aluminum oxide surface, Davies and Morgan$^{98}$ determined that in basic solutions (pH > 7.5) Mn$^{2+}$ forms both monodentate and bidentate complexes though hydrolysis was not considered during the adsorption process. Hachiya et al$^{122-123}$ concluded that divalent cations including Mn$^{2+}$ adsorbed by the same mechanism described by Bloom and McBride$^{112-113}$ involving hydrolysis after adsorption and further suggested that unhydrolyzed species can also adsorb. Saeki et al$^{125}$ found that Mn$^{2+}$ strongly adsorbs to silica at pHs greater than 6.0 and is nearly completely irreversible when exchanging with Mg$^{2+}$ further demonstrating the strong binding of Mn$^{2+}$ with the surface.
As demonstrated in the above studies, most literature describes metal cation adsorption as a function of hydrolysis, stemming from the James and Healy model of hydrolyzable cation adsorption\textsuperscript{36}. This model suggests that surfaces with a low dielectric constant, such as quartz, preferably adsorb hydrolyzed cations over unhydrolyzed cations while surfaces with higher dielectric constants can adsorb both hydrolyzed and unhydrolyzed cations. It suggests that since a hydrolyzed cation has lower charge and less strongly bound hydration sphere water molecules, adsorption is more favorable because of decreased ion-solvent interactions.

This work seeks to explore the role of the mineral surface, cation hydration, and cation hydrolysis on the adsorption mechanisms of these cations at an acidic pH through the use of flow adsorption microcalorimetry and quartz crystal microbalance with dissipation measurements and density functional theory calculations. To our knowledge, the triangulation of these techniques has never been applied to these adsorption systems before and will undoubtedly offer valuable new insights.

Both flow microcalorimetry and quartz crystal microbalance measurements offer unique and complementary perspectives into the adsorption processes due to the in situ nature of the measurements while density functional theory brings an atomistic perspective.

3.2 Experimental

3.2.1 Chemicals

All reagents and salts used were ACS grade chemicals. Anhydrous NaNO\textsubscript{3} was oven-dried overnight at 85°C and all hydrated salts [Al(NO\textsubscript{3})\textsubscript{3}⋅9H\textsubscript{2}O, Cr(NO\textsubscript{3})\textsubscript{3}⋅9H\textsubscript{2}O, Mn(NO\textsubscript{3})\textsubscript{2}⋅4H\textsubscript{2}O] were used as received. M\textsuperscript{n+}(NO\textsubscript{3})\textsubscript{n} (M = Al\textsuperscript{3+}, Cr\textsuperscript{3+}, or Mn\textsuperscript{2+}) solutions were prepared at a concentration of 1 mM, with a background of 2.9 mM NaNO\textsubscript{3} (Table 8) for
calorimetry experiments and only Mn$^{2+}$ having a 2.9 mM NaNO$_3$ background for quartz crystal microbalance experiments. A NaNO$_3$ solution was also prepared at a concentration of 2.9 mM to be used as control. All solutions were prepared using ultra-pure water ($\Omega > 18.2$ SM) and were carefully adjusted to pH $3.8 \pm 0.1$ using dropwise addition of 1 M HNO$_3$ or 1 M NaOH. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of all solutions confirmed negligible changes to the total aqueous M$^{n+}$ concentration due to this adjustment.

### 3.2.2 Microcalorimetry Experiments

Corundum single crystals were purchased from Wards’ Scientific (Rochester, NY), cleaned and ground as per previously reported procedures$^{126-128}$. The resulting powdered sample was fractionated using a 35 µm sieve and the fine fraction (<35 µm) was collected for all microcalorimetry experiments. The quartz sample used was obtained by grinding large pieces of a single crystal of Brazilian quartz, separating the coarser fractions in methanol and then centrifuging and air drying the finer fraction. The sample was used and well characterized in a previous study$^{109}$.

Experiments were performed using custom-designed flow adsorption microcalorimeters designed and fabricated in the Kabengi laboratories at Georgia State University. The instrument design and basic experimental procedures have been thoroughly discussed in previous works$^{87,109,129-130}$. To obtain the heats of ion exchange, a known mass (~30.0 – 35.0 mg) of either corundum or quartz powder was packed into the sample holder and equilibrated with the NaNO$_3$ solution until a thermal baseline was established. The input solution was then switched to a M$^{n+}$(NO$_3$)$_n$ solution and the calorimetric signal for the M$^{n+}$ reaction with the surface was recorded (denoted [Na/M$^{n+}$]). Once the reaction reached thermal equilibrium as defined by the return of the calorimetric signal to the initial baseline, the solution was returned to the NaNO$_3$
solution. The calorimetric signal associated with $M^{n+}$ displacement from the surface (denoted $[M^{n+}/Na]$) $[Na/M^{n+}]$ and its corresponding $[M^{n+}/Na]$ constituted one cycle, which was repeated 3-5 times for each $M^{n+}(NO_3)_n$ solution to establish statistically representative values. The reproducibility, or lack of, of the calorimetric peaks obtained was further used to assess the reversibility of the complexes formed by each cation. During both $[Na/M^{n+}]$ and $[M^{n+}/Na]$ cycles, effluent samples were collected for chemical analysis. The amount of $M^{n+}$ retained at or exchanged from the surface was determined by a mass balance calculation between the total mass injected and the mass recovered from effluent samples. The total aqueous concentration of $Mn^{2+}$ and $Cr^{3+}$ was determined using inductively coupled plasma optical emission spectroscopy (Varian 730-ES ICP-OES, Varian), and that of $Al^{3+}$ by UV-Vis spectroscopy (GENESYS 10S, Thermo Scientific) using the catechol violet method.

3.2.3 Quartz Crystal Microbalance with Dissipation (QCM-D)

Cation ($Mn^{2+}$, $Al^{3+}$, or $Cr^{3+}$) adsorption onto $SiO_2$ or $Al_2O_3$ substrates was also studied using QCM-D. Quartz sensors coated with $SiO_2$ (QSX 303) or $Al_2O_3$ (QSX 309) were purchased from Q-sense. For each ion adsorption experiment, a clean sensor was placed into the flow module with the $SiO_2$ or $Al_2O_3$ coating facing the solution. Then the flow module was placed on the chamber platform of QCM-D (Biolin Scientific, Paramus, NJ), and the temperature inside the flow module was maintained at $20 \pm 0.1 \,^\circ C$. Initially, ultrapure water was pumped into the flow module with a constant rate of $0.2 \, mL/min$ to establish a stable baseline (Figures 13 and 21). Then the inflow solution was switched (indicated by arrows in Figures 13 and 21) to $1 \, mM \ Al(NO_3)_3$, $Cr(NO_3)_3$, $Mn(NO_3)_2$ (with $2.9 \, mM \ NaNO_3$ added to adjust to the same ionic strength), or $2.9 \, mM \ NaNO_3$ (control experiment) solution with $pH = 3.8 \pm 0.2$. Finally, the solution was switched back to ultrapure water (indicated by arrows in Figures 13 and 21), to test
if the ions adsorbed on each substrate could be desorbed. The changes in resonance frequency ($\Delta f$) and energy dissipation ($\Delta D$) of the sensors were recorded, and the mass changes caused by ion adsorption onto SiO$_2$ or Al$_2$O$_3$ coatings on sensors were calculated using Sauerbrey model\textsuperscript{132}. All data were analyzed by Q-Tools 3.0 from Biolin Scientific, and detailed information can be found in our previous publications\textsuperscript{127-128, 133}.

### 3.2.4 Density Functional Theory Calculations

Density Functional Theory (DFT) calculations using Gaussian 09\textsuperscript{134} were used to calculate the minimum energy structure, vibrational frequencies and bonding of simple molecular clusters representing adsorbed Mn$^{2+}$, Al$^{3+}$, and Cr$^{3+}$ onto silanol and aluminol sites on quartz and corundum. All models were constructed in a monodentate bonding configuration (Figure 22) assuming that Q$^3$ SiOH groups or AlOH$_2$ groups with 5 bonds to the bulk dominate the surfaces under study. This is likely to be the case for silica surfaces\textsuperscript{135} although certain faces can be dominated by Q$^2$ SiOH groups. The AlOH$_2$ surface site is also thought to dominate most alumina surfaces at low pH\textsuperscript{136} compared to geminal sites. Hydroxyl groups bonded to 2 or 3 Al surface atoms are generally considered less reactive towards H$^+$/Me$^{n+}$ exchange.

The structures were drawn manually in the Visualizer module of Materials Studio 2016 (Biovia Inc., San Diego, CA)\textsuperscript{137}. Compositions included: (OH)$_3$SiOSi(OH)$_2$O-(Mn$^{2+}$, Al$^{3+}$, or Cr$^{3+}$)$\cdot$5(H$_2$O) and Al$_2$(OH)$_6$(H$_2$O)$_3$O-(Mn$^{2+}$, Al$^{3+}$, or Cr$^{3+}$)$\cdot$5(H$_2$O) which assumes no hydrolysis of the adsorbed metal ions. Hydrolyzed ion adsorption was modeled with the compositions (OH)$_3$SiOSi(OH)$_2$O-Al(OH)$_3$(H$_2$O)$_2$, (OH)$_3$SiOSi(OH)$_2$O-Mn(OH)$_2$(H$_2$O)$_3$, (OH)$_3$SiOSi(OH)$_2$O-Cr(OH)$_3$(H$_2$O)$_2$, Al$_2$(OH)$_6$(H$_2$O)$_3$O-Al(OH)$_3$(H$_2$O)$_2$, Al$_2$(OH)$_6$(H$_2$O)$_3$O-Mn(OH)$_2$(H$_2$O)$_3$, and Al$_2$(OH)$_6$(H$_2$O)$_3$O-Cr(OH)$_3$(H$_2$O)$_2$ (Figure 23). Spin states of Mn$^{2+}$, Al$^{3+}$, or Cr$^{3+}$ were set to 5, 0, and 3, respectively.
Energy minimizations (i.e., structural optimizations) were performed using the DFT exchange-correlation functionals B3LYP\textsuperscript{138-139} and the 6-311+G(d,p) basis set\textsuperscript{140-141}. Energies were minimized to Gaussian 09 default values, then frequency analyses were performed to ensure that a minimum had been obtained. When the frequency analyses resulted in no imaginary (i.e., negative) frequencies, we concluded the structure was at least in a local potential energy surface minimum (Note: We make no claim that any structure is in the global minimum structure as extensive configurational searches were not performed.) Natural population analyses\textsuperscript{142} were performed on these structures to determine the strength and electron population of bonds in the cluster. The focus was on the metal ion bond to the O atom connecting to the Si or Al of the model surface cluster because this is the key bond that will be involved if a metal ion is adsorbed to a surface.

### 3.3 Results and Discussion

#### 3.3.1 Microcalorimetry Results

![Calorimetric Response](image)

*Figure 12: Calorimetric response to $M^{n+}$ adsorption to corundum and quartz. Positive calorimetric response corresponds to an exothermic process, while negative calorimetric response corresponds to an endothermic process.*
Figure 12 shows the calorimetric signal for the initial exposure of both corundum and quartz surfaces to the \( \text{Mn}^{n+}(\text{NO}_3)_n \) solutions. The reaction of \( \text{Al}^{3+} \) with both surfaces was found to be endothermic as evidenced by the negative peak (voltage decrease corresponding to a decrease in temperature). \( \text{Cr}^{3+} \) adsorption was exothermic on both surfaces while \( \text{Mn}^{2+} \) reaction was endothermic on corundum, albeit significantly smaller, and below detection limit on quartz.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Corundum</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(^{3+})</td>
<td>0.201</td>
<td>0.297</td>
</tr>
<tr>
<td>Initial (mJ/mg)</td>
<td>0.183 (0.006)</td>
<td>0.296 (0.030)</td>
</tr>
<tr>
<td>Subsequent (mJ/mg)</td>
<td>9%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>-0.065</td>
<td>-0.032</td>
</tr>
<tr>
<td>Initial (mJ/mg)</td>
<td>-0.013 (0.006)</td>
<td>-0.011 (0.003)</td>
</tr>
<tr>
<td>Subsequent (mJ/mg)</td>
<td>80%</td>
<td>65%</td>
</tr>
</tbody>
</table>

Note: The values in parenthesis correspond to the standard error for each value. % Change was calculated by the formula \( \frac{\text{Initial} - \text{Subsequent}}{\text{Initial}} \times 100 \). Low values for % change correspond to highly reversible interactions while high values correspond to more irreversible interactions.

The reversibility of the interactions of the cations was also determined from the calorimetric signal as seen in Table 3. The reversibility was determined by comparing the heats of cation adsorption of the initial interaction with those obtained during subsequent cycles. On both quartz and corundum, \( \text{Al}^{3+} \) adsorption and desorption was found to be nearly completely reversible with minimal change in the calorimetric signal over repeated cycles (3-5 cycles; 0.183 – 0.201 mJ/mg for corundum, 0.296 – 0.297 mJ/mg for quartz). \( \text{Cr}^{3+} \) adsorption exhibited a more complex behavior characterized by both reversible and irreversible components. On quartz, the initial \( \text{Cr}^{3+} \) adsorption caused a 65% decrease in the calorimetric signal measured during the second exposure (-0.011 ± 0.003 mJ/mg) as compared to that of the initial exposure (-0.065 mJ/mg). We attribute this reduction to the inability of NaNO\(_3\) to exchange the initial \( \text{Cr}^{3+} \) off the
surface. This could be confirmed by the smaller size of the \([\text{Cr}^{3+}/\text{Na}^+]\) calorimetric peak obtained following the initial \(\text{Cr}^{3+}\) exposure. On corundum, \(\text{Cr}^{3+}\) adsorption was found to be even less reversible, with 80% reduction in the calorimetric signal of the second \([\text{Na}^+/\text{M}^{n+}]\) cycle (from -0.065 mJ/mg to -0.013 ± 0.006 mJ/mg). The reversibility of the \(\text{Mn}^{2+}\) could not be similarly analyzed due to its significantly lower energy on corundum (0.008 ± 0.004 mJ/mg).

The change in the heat, or lack thereof, can be used to gain insights into the strength and mode of binding of the cation with the mineral surface. As discussed in Cao et al\textsuperscript{143} for cations as well as in Sabur et al\textsuperscript{144}, and Kabengi et al\textsuperscript{88, 129} for anions, a change in sequentially repeated heat measurements during ion interaction with mineral surfaces can be attributed to irreversible processes such as complexation or precipitation, while unchanged heats over repeated measurements correspond to reversible reactions that are dominated by electrostatic interactions. As such, the observed \(\text{Cr}^{3+}\) behavior suggests a strong surface interaction similar to those described by Cao et al\textsuperscript{143} (2004) while \(\text{Al}^{3+}\) reversible heats suggest electrostatic interaction with the surface.

It has been recently suggested that most cations undergo a partial dehydration before adsorbing onto a mineral surface\textsuperscript{9, 72-73, 145} through inner-sphere binding mode. Furthermore, the relationship between cation dehydration and the heats of cation interactions was further established\textsuperscript{50, 109, 130} for alkali and alkaline earth, and other multivalent cations (\(\text{Cd}^{2+}\), \(\text{Co}^{2+}\), \(\text{Zn}^{2+}\), \(\text{Eu}^{3+}\)). It was found that the endothermic heats measured during cation adsorption were primarily a function of the bulk dehydration enthalpy. As such, it is a reasonable assertion that the endothermic heats measured for the both \(\text{Mn}^{2+}\) and \(\text{Al}^{3+}\) adsorption would primarily be a function of a partial dehydration step as seen in equation 1.
Equation 1: \[ >S - O^- + M(H_2O)_{n^+} \rightarrow >S - O \cdots M(H_2O)_{n^+} + H_2O \]

Where \( >S \) is a representative surface functional group.

On another hand, the exothermic heat measured during the \( \text{Cr}^{3+} \) adsorption alludes to a different adsorption mechanism. As seen from the reversibility analysis above, \( \text{Cr}^{3+} \) interaction with the surface is partially irreversible suggesting that it is forming a stronger interaction with the surface, potentially as an inner-sphere complex or covalent bond as discussed below in the DFT section. To make such a bond, \( \text{Cr}^{3+} \) would first need to partially dehydrate to attain a point close enough to the surface to form the bond. Hence, the expected measured heat would be the net summation of the dehydration energy (endothermic process) and the bond formation energy (exothermic process). The energy of a Cr-O bond formation is tabulated at -461 kJ/mol\textsuperscript{146} while the bulk hydration enthalpy of \( \text{Cr}^{3+} \) is -4560 kJ/mol\textsuperscript{110}. A water loss from the hydration shell can then be roughly approximated to release +760 kJ/mol (bulk hydration enthalpy / coordination number of 6)\textsuperscript{130}. Therefore, the measured heat should still be a net endothermic reaction. But as seen in Table 4 and Figure 24, under our experimental conditions, a sizable percentage of \( \text{Cr}^{3+} \) exists in a hydrolyzed state, \( \text{Cr(OH)}^{2+} \) and the trimer \( \text{Cr}_3(\text{OH})_{4}^{5+} \), and hence the bonds between the cation and the remaining water molecules are much weaker and have a lower dehydration energy\textsuperscript{34}. In this instance, the net measured heat will be exothermic, as found experimentally.

The precipitation of amorphous chromium hydroxide (\( \text{Cr(OH)}_3 \)) on the mineral surface must be also considered as a possibility to explain the interaction of the \( \text{Cr}^{3+} \) with the mineral surfaces. At our experimental conditions, the \( \text{Cr}^{3+} \) solution is saturated with respect to \( \text{Cr(OH)}_3 \) and precipitation is a possible outcome. However, a precipitation is expected to be endothermic.
in nature and this would have been calorimetrically detected. But since, the net energy measured was exothermic a significant precipitation reaction was ruled out.

3.3.2 Quartz Crystal Microbalance Results

**Metal Ion Adsorption on SiO\(_2\) (QCM-D Measurements)**

**Figure 13:** QCM-D measurements of Mn\(^{2+}\), Cr\(^{3+}\), and Al\(^{3+}\) ion adsorption onto SiO\(_2\) (A1-A3) and Al\(_2\)O\(_3\) sensors (B1-B3) at pH = 3.8 ± 0.2. To establish a stable baseline, measurements were conducted by flowing ultrapure water over SiO\(_2\) and Al\(_2\)O\(_3\) sensors. Then the solution was switched to 1 mM Mn(NO\(_3\))\(_2\) (with 2.9 mM NaNO\(_3\) added to adjust the ionic strength), 1 mM Al(NO\(_3\))\(_3\), and 1 mM Cr(NO\(_3\))\(_3\) test solutions (the arrows indicate the switching point). The decreases in frequency (Δf) indicate the adsorption of ions onto coatings on sensors (ng/cm\(^2\)). Finally, the inlet solution was switched back to ultrapure water, which can wash off the adsorbed ions from substrates (the arrows indicate the switching point).

Under acidic condition (pH = 3.8 ± 0.2), the adsorption of 2.9 mM NaNO\(_3\), 1 mM Al(NO\(_3\))\(_3\), 1 mM Cr(NO\(_3\))\(_3\), and 1 mM Mn(NO\(_3\))\(_2\) (with 2.9 mM NaNO\(_3\) added to adjust the ionic strength) on SiO\(_2\) (Figure 13 A1-A3) and Al\(_2\)O\(_3\) (Figure 13 B1-B3) substrates were measured by QCM-D. The decreases in resonance frequency (Δf) indicated the increases of mass on sensors caused by ion adsorption. For the control experiment with 2.9 mM NaNO\(_3\) solution (Figure 21), no changes in resonance frequency (Δf) were observed on SiO\(_2\) and Al\(_2\)O\(_3\) coated sensors, indicating that no
significant adsorption of Na\(^+\) and NO\(_3^-\) on SiO\(_2\) and Al\(_2\)O\(_3\) substrates occurred. Therefore, the decreases in resonance frequency (\(\Delta f\)) of the sensors (Figure 13), while in contact with Al(NO\(_3\))\(_3\), Cr(NO\(_3\))\(_3\), and Mn(NO\(_3\))\(_2\) + NaNO\(_3\) solutions, must be caused by the adsorption of Al\(^{3+}\), Cr\(^{3+}\), and Mn\(^{2+}\) ions on sensors.

On SiO\(_2\) sensor (pH = 3.8 ± 0.2), no changes in resonance frequency (\(\Delta f\)) were recorded after switching from ultrapure water to 1 mM Mn(NO\(_3\))\(_2\) (with 2.9 mM NaNO\(_3\) added to adjust the ionic strength) solution, indicating no significant adsorption of Mn\(^{2+}\) on SiO\(_2\). However, ~ 1 Hz and ~ 0.5 Hz decreases in resonance frequency (\(\Delta f\)) on SiO\(_2\) sensors were observed after switching to 1 mM Al(NO\(_3\))\(_3\) and 1 mM Cr(NO\(_3\))\(_3\) (pH = 3.8 ± 0.2) solutions, indicating that 18.9 ± 3.3 ng/cm\(^2\) Al\(^{3+}\) and 7.6 ± 3.3 ng/cm\(^2\) Cr\(^{3+}\) ions were adsorbed onto SiO\(_2\) coated sensors. After the inlet solutions were switched back to ultrapure water, the resonance frequency (\(\Delta f\)) went back to the original baseline established by ultrapure water, indicating that the Al\(^{3+}\) and Cr\(^{3+}\) ions adsorbed on SiO\(_2\) substrates can be desorbed from the substrates in ultrapure water.

On Al\(_2\)O\(_3\) sensor, ~ 1 Hz decreases in vibrational frequency (\(\Delta f\)) were detected after switching to Al(NO\(_3\))\(_3\), Cr(NO\(_3\))\(_3\), and Mn(NO\(_3\))\(_2\) +NaNO\(_3\) solutions. This indicated that all three cations (Al\(^{3+}\), Cr\(^{3+}\), and Mn\(^{2+}\)) can adsorb on Al\(_2\)O\(_3\) substrates at pH = 3.8 ± 0.2, with the amounts of 16.4 ± 1.8, 17.6 ± 3.0, and 14.9 ± 2.7 ng/cm\(^2\), respectively. Furthermore, after switching the inlet solution to ultrapure water, the vibrational frequency of sensors went back to the original baseline, indicating that all adsorbed ions were desorbed from Al\(_2\)O\(_3\) substrates.
Table 4: Metal ion adsorption onto substrates measured by QCM-D and DLS and their hydrolysis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>M(OH)$_{n-x}$, a, %</th>
<th>M$^{n+}$, %</th>
<th>M$_{SiO_2}^b$, ng/cm$^2$</th>
<th>M$_{Al_2O_3}^b$, ng/cm$^2$</th>
<th>$\zeta_{SiO_2}$, mV</th>
<th>$\zeta_{Al_2O_3}$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.5</td>
<td>99.5</td>
<td>BDL</td>
<td>16.4 ± 1.8</td>
<td>-25.1 ± 1.9</td>
<td>27.4 ± 6.8</td>
</tr>
<tr>
<td>Al</td>
<td>4.4</td>
<td>95.6</td>
<td>18.9 ± 3.3</td>
<td>17.6 ± 3.0</td>
<td>18.1 ± 3.9</td>
<td>34.3 ± 6.4</td>
</tr>
<tr>
<td>Cr</td>
<td>78.7</td>
<td>21.3</td>
<td>7.6 ± 3.3</td>
<td>14.9 ± 2.7</td>
<td>21.2 ± 1.4</td>
<td>35.1 ± 6.7</td>
</tr>
</tbody>
</table>

Note: M(OH)$_{n-x}$, a, %: Percentages of metal ions in hydrolyzed states (e.g. Al(OH)$^{2+}$, Al(OH)$_2^+$, Al(OH)$_3$), which were calculated using GWB under our experimental conditions. M$_{SiO_2}^b$ and M$_{Al_2O_3}^b$: the amounts of Mn$^{2+}$, Al$^{3+}$, and Cr$^{3+}$ ions adsorbed on SiO$_2$ and Al$_2$O$_3$ coated quartz sensors, measured by QCM-D. No significant adsorption of 2.9 mM NaNO$_3$ on SiO$_2$ and Al$_2$O$_3$ coated quartz sensors was observed. $\zeta_{SiO_2}$ and $\zeta_{Al_2O_3}$: zeta potentials of quartz and corundum powders in the presence of 1 mM Mn$^{2+}$ (2.9 mM NaNO$_3$ was added to adjust IS), Al$^{3+}$, or Cr$^{3+}$, respectively.

The adsorption behaviors of Al$^{3+}$, Cr$^{3+}$, and Mn$^{2+}$ on quartz and corundum were consistent with the zeta potential measurements in another publication (Dai et al, under review).

Under our experimental pH conditions (3.8 ± 0.2), the quartz surfaces in the absence and presence of 1 mM Mn$^{2+}$ were both negatively charged, with similar zeta potential ($\zeta$) values of -22.4 ± 2.6 and -25.1 ± 1.9 mV, consistent with the QCM-D measurements that no Mn$^{2+}$ adsorption onto quartz occurred. Adversely, in the presence of 1 mM Al$^{3+}$ and Cr$^{3+}$ ions, quartz surfaces became positively charged, being 18.1 ± 3.9 and 21.2 ± 1.4 mV, caused by the adsorption of Al$^{3+}$ and Cr$^{3+}$ ions onto quartz as measured by QCM-D. While corundum, the surfaces were more positively charged in the presence of Mn$^{2+}$, Al$^{3+}$, and Cr$^{3+}$, being 27.4 ± 6.8, 34.3 ± 6.4, and 35.1 ± 6.7 mV, than that in the absence of metal ions (20.5 ± 2.8 mV), consistent with the adsorption of Mn$^{2+}$, Al$^{3+}$, and Cr$^{3+}$ onto corundum measured by QCM-D.
3.3.3 Density Functional Theory Results

Each of the clusters resulted in energy minima with no imaginary frequencies. The bond lengths predicted generally follow the observed bond lengths in minerals and aqueous species of the ions in question. Although Gibbs free energies result from the frequency analyses of each cluster, we have no basis for comparison of these surface complex models to produce a $\Delta G$ of adsorption. Such a calculation would require modeling of the aqueous species and the model surface which is outside the scope of the current study. Consequently, we extracted the bond energies for the $\text{Mn}^2+$, $\text{Al}^3+$, and $\text{Cr}-\text{O}$ bonds connecting the $\text{Me}^{n+}\cdot5(\text{H}_2\text{O})$ group to the silica and alumina clusters and compared these to the $\text{Si}-(\text{OH})$ and $\text{Al}-(\text{OH})$ bonds each would be replacing. Lower bond energies than the original $\text{Si}-(\text{OH})$ and $\text{Al}-(\text{OH})$ were considered to favor adsorption.

Table 5: Calculated metal-oxygen bond energies (kJ) for model adsorption complexes in this study.

<table>
<thead>
<tr>
<th>Model</th>
<th>Energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2-\text{OH}$</td>
<td>-85</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-}\text{Al}^{3+}\cdot5(\text{H}_2\text{O})$</td>
<td>-101</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-}\text{Cr}^{3+}\cdot5(\text{H}_2\text{O})$</td>
<td>-96</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-}\text{Mn}^{2+}\cdot5(\text{H}_2\text{O})$</td>
<td>-88</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-}\text{Al(OH)}_3(\text{H}_2\text{O})_2$</td>
<td>-59</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-}\text{Cr(OH)}_3(\text{H}_2\text{O})_2$</td>
<td>-55</td>
</tr>
<tr>
<td>$(\text{OH})_3\text{SiOSi(OH)}_2\text{O-Mn(OH)}_2(\text{H}_2\text{O})_3$</td>
<td>No bond found</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{OH}_2$</td>
<td>-69</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Al}^{3+}\cdot5(\text{H}_2\text{O})$</td>
<td>-77</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Cr}^{3+}\cdot5(\text{H}_2\text{O})$</td>
<td>-85</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Mn}^{2+}\cdot5(\text{H}_2\text{O})$</td>
<td>-92</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Al(OH)}_3(\text{H}_2\text{O})_2$</td>
<td>-49</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Cr(OH)}_3(\text{H}_2\text{O})_2$</td>
<td>-39</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_3-\text{Mn(OH)}_2(\text{H}_2\text{O})_3$</td>
<td>-34</td>
</tr>
</tbody>
</table>
The bond energies are listed in Table 5. For the fully hydrated models, all bond energies are negative and fall in the range of approximately -69 to -101 kJ/mol which is reasonable for these metal ions to O atoms. A negative bond energy does not imply stability of the surface complex, however. For a surface complex to be thermodynamically stable, it should be lower in energy than the O-H bond it replaces (e.g., SiO-H + Me\textsuperscript{n+} \rightarrow SiO-Me\textsuperscript{n+} + H\textsuperscript{+}). Considering conditions where the [H\textsuperscript{+}] is greater than the [Me\textsuperscript{n+}] requires that the Me\textsuperscript{n+}-O bond be stronger (i.e., Le Châtelier’s Principle). In this context, we see that the bond energies in Table 5 for O-H and O-Mn\textsuperscript{2+} in the fully hydrated silica cluster are equivalent within computational error (-85 versus -88 kJ/mol) whereas the O-Al\textsuperscript{3+} and O-Cr\textsuperscript{3+} bonds are significantly lower in energy (-101 and -96 kJ/mol, respectively). These bond energies are consistent with the observation that Mn\textsuperscript{2+} does not adsorb onto silica whereas Al\textsuperscript{3} and Cr\textsuperscript{3+} do.

Comparison of the DFT results to the QCM-D and calorimetry observations of adsorption onto alumina reveals consistent prediction of adsorption. Al\textsuperscript{3+}, Mn\textsuperscript{2+}, and Cr\textsuperscript{3+} are all predicted to have lower energy bonds to the surface O atom than would be formed by an OH\textsubscript{2} leaving group (-69 kJ – Table 5). The Al\textsuperscript{3+} ion is the least favored compared to the OH\textsubscript{2} surface group (-77 versus -69 kJ, respectively), and these values are within computational error of approximately ±10 kJ/mol. Hence, there may be complicating factors on the alumina surface either dealing with the surface groups themselves (e.g., the presence of Al-(OH)\textsubscript{2} sites that allow bidentate, mononuclear bonding) or with the adsorption complex (e.g., hydrolysis and/or coordination change of the adsorbed metal ion). Again, these possible explanations could be better explored with periodic DFT calculations that better account for the mineral-water interface structure.

Because hydrolysis and coordination change may accompany adsorption for ions that undergo hydrolysis in solution\textsuperscript{148}, model hydrolyzed surface complexes (OH)\textsubscript{3}SiOSi(OH)\textsubscript{2}O-
Al(OH)$_3$(H$_2$O)$_2$, (OH)$_3$SiOSi(OH)$_2$O-Mn(OH)$_2$(H$_2$O)$_3$, and (OH)$_3$SiOSi(OH)$_2$O-Cr(OH)$_3$(H$_2$O)$_2$

(Figure 23) were examined. In this case, the metal-O bonds of interest are all less energetically favored (Table 5) as expected because the metal-(OH)$_n$ bonds are stronger than metal-(OH$_2$) bonds which weakens the remaining metal-O bond to the surface. Natural bond orbital analysis$^{142}$ reveals a special case for the Si-O-Mn linkage, however, where no covalent bond is formed when the Mn$^{2+}$ ion is hydrolyzed (Figure 23). These hydrolyzed species (Al(OH)$_3$, Cr(OH)$_3$ and Mn(OH)$_2$) are end-members possible surface complexes in contrast to the other end-member fully hydrated models discussed above. Actual adsorbed species will likely fall between these two end-members and the species will change with pH of the solution. Because both the fully hydrated and fully hydrolyzed Mn$^{2+}$ model surface complexes result in the weakest interactions with the model silica surface, we conclude that bond energetics can explain the lack of Mn$^{2+}$ adsorption onto silica in the QCM-D experiments. This is not the case for the Mn$^{2+}$ surface complex model with the alumina cluster, so adsorption onto alumina should be favored for all the ions considered.

3.3.4 Synthesis of Observations and Significance

Early work in the field of metal cation adsorption, and in particular the James and Healy model, defined adsorption through the lens of hydrolysis, whereas hydrolyzed species adsorb more favorably or species underwent hydrolysis during adsorption. However, as seen in Table 4, two of the cations studies, Al$^{3+}$ and Mn$^{2+}$, do not significantly hydrolyze at the pH studied. The strong interactions of Al$^{3+}$ with the mineral surfaces, seen both by microcalorimetry and QCM-D, suggest that this cation can adsorb to the mineral surface without a significant hydrolysis, at least at pH values at or below 3.8. Furthermore, the DFT results comparing the adsorption of
hydrolyzed and unhydrolyzed cations show a significant preference for the unhydrolyzed ion, albeit only the extreme case of hydrolysis was analyzed.

However, the Cr\(^{3+}\) interactions with the mineral surfaces suggest that Cr\(^{3+}\) is forming a covalent bond with the surface, a significantly different interaction from the electrostatic adsorption for the other cations. It can then be reasoned that the ability of Cr\(^{3+}\) to form this covalent bond with the surface is due, in part, to its hydrolyzed state.

The adsorption of cations in acidic conditions need to take into consideration all cation species, not only the hydrolyzed ones. The adsorption is a spectrum of interactions, dependent of the hydrolyzed state of the cations. Furthermore, no significant difference in cation interactions were seen between the two surfaces, suggesting that the surface properties are not significantly impacting adsorption processes.

### 3.4 Conclusion

This work used the combination of flow microcalorimetry, quartz crystal microbalance measurements, and density functional theory to examine the interactions of three metal cations (Al\(^{3+}\), Cr\(^{3+}\), and Mn\(^{2+}\)) on both quartz and corundum mineral surfaces in an acidic pH. Quartz crystal microbalance and flow microcalorimetry experiments show that the studied cations are able to adsorb onto both mineral surfaces with the exception of Mn\(^{2+}\) onto the quartz surface. The reversibility of the cation adsorption was also explored with the two techniques, with Al\(^{3+}\) being completely reversible by both, while QCM-D found Cr\(^{3+}\) to be reversible and microcalorimetry found it to be mostly irreversible. The difference is most likely a result of either the different desorption solutions used to measure desorption or the use of a powder in calorimetry as compared to a coating in QCM-D. The effect of hydrolysis was examined, both as a function of solution speciation and through density functional theory. This work suggests
that the interactions of the cations with the mineral surfaces is a function of the hydrolysis of the cation, whereas unhydrolyzed cations are able to adsorb to the surface through a weaker electrostatic interaction, whereas hydrolyzed species are able to form covalent bonds with the surface functional groups.
4 CONCLUSION

This work examined the interactions of cations on both quartz and corundum surfaces in a systematic way to gain mechanistic insights about those interactions. This work used flow microcalorimetry data alone in chapter 2, and combined with quartz crystal microbalance measurements and density functional theory in chapter 3 to elucidate the interactions.

Chapter 2 looked at the adsorption and exchange of alkali and alkaline earth cations with the quartz mineral surface using flow microcalorimetry combined with in situ pH measurements. The experiments were conducted in a systematic way so that all stable alkali and alkaline earth cations were examined both through adsorption and exchange using Li\(^+\) as a probe for alkali cations and Mg\(^{2+}\) for alkaline earth cations. During these experiments, it was found that the heats of both adsorption and exchange increase along the lyotropic series on quartz such that Li\(^+\) < Na\(^+\) < K\(^+\) < Rb\(^+\) < Cs\(^+\) and Mg\(^{2+}\) < Ca\(^{2+}\) < Sr\(^{2+}\) < Ba\(^{2+}\). These heats were then analyzed against cation specific properties (ionic radius, hydrated radius, bulk hydration enthalpy, ionic potential) and found to have the strongest correlation with the cation bulk hydration enthalpy. This correlation combined with recent literature suggests that all the cations are partially dehydrating (losing a water from their primary solvation shell) and forming an inner-sphere complex with the surface groups. The heats of exchange offered interesting insights into the kinetics of the interactions. The exchange of probing cations (Li\(^+\), Mg\(^{2+}\)) by larger cations (Rb\(^+\), Cs\(^+\), Sr\(^{2+}\), Ba\(^{2+}\)) exhibited a split calorimetric signal consisting of an initial exothermic energy followed by a tailing endothermic heat. Preliminary computational work has shown that these larger cations experience more dehydration of the primary solvation shell during adsorption and these heats suggest a similar scenario, with extra time needed to complete the dehydration step.
Chapter 3 looked at the interactions of three metal cations, Al$^{3+}$, Cr$^{3+}$, and Mn$^{2+}$ on both the corundum and quartz mineral surfaces using flow microcalorimetry, quartz crystal microbalance measurements, and density functional theory. By combining two different mineral surfaces with distinct mineral surface properties (zero point of charge, surface functional groups speciation and distribution, dielectric constant) and three metal cations with distinguishable characteristics (bulk hydration enthalpy, hydrolyzed species distribution), the important properties of surface-cation interactions were identified. Al$^{3+}$ was found to interact with both surfaces endothermically. The reversibility seen in the calorimetry heats and in the quartz crystal microbalance measurements suggest that the interaction is an inner-sphere electrostatic interaction. Cr$^{3+}$ exhibited a strong interaction with the surface, and the partial irreversibility seen in the calorimetry experiments combined with the exothermic nature of the heat of adsorption suggests a stronger interaction possibly involving a covalent bond with the surface hydroxyl groups. Mn$^{2+}$ was only seen to adsorb on the corundum surface, and not the quartz surface, with an endothermic interaction similar to Al$^{3+}$. Speciation of the cations in solution show that the majority of Cr$^{3+}$ exists in the hydrolyzed state, while both Al$^{3+}$ and Mn$^{2+}$ exist almost exclusively in the unhydrolyzed state. DFT calculations were performed to determine the favorability of the bonding of the cations, both hydrolyzed and unhydrolyzed, to the mineral surfaces. The unhydrolyzed species were found to have strong bond favorability for adsorption while fully hydrolyzed species did not show favorability, generally concurring with the experimental results. However, DFT results do not rule out the possibility of the adsorption of the less hydrolyzed species. The interactions of the both Al$^{3+}$ and Cr$^{3+}$ on the mineral surfaces suggest that the mineral surface properties did not have a significant effect on the adsorption process.
4.1 Future Work

To rationalize the kinetics effect observed during the study of cation exchange on quartz, it was hypothesized that in addition to the time related to the extra dehydration step cation adsorption on the surface may occur on different functional groups, namely Li\(^+\) and Na\(^+\) would adsorb at Si-OH\(^0\) groups while Rb\(^+\) and Cs\(^+\) would adsorb at Si-O\(^-\) groups due to the strength of the hydration shell on the surface hydroxyl group. This explanation stems from initial computational work done by Kroutil et al\(^72\). On-going work is currently exploring this hypothesis using flow microcalorimetry combined with density functional theory to ascertain whether these preferences do indeed occur. The calorimetry experiments consist of two parts, the first being cation exchange using mixed ion solutions (exchange between Li\(^+\) and Li\(^+\) + M\(^+\) solution at different proportions) and the second is using K\(^+\) as a probe to further verify and explore the interactions discussed in chapter 2. Furthermore, time resolved-resonant anomalous x-ray reflectivity studies at the Argonne National Laboratory have similarly focused on cation adsorption on muscovite mineral surface\(^145\). This technique would nicely compliment the quartz-cation interactions studies in that it would offer a detailed atomistic view of the underlying processes, potentially shedding more light on some of the kinetic nuances observed in chapter 2.

Finally, more work is needed to further examine the effect of hydrolysis during cation adsorption on mineral surfaces in acidic conditions. This could be done by including surfaces with markedly different properties including dielectric constant and non-oxide minerals such as rutile and bayerite, as well as other cations such as Cu\(^+\), Zn\(^{2+}\), and Fe\(^{3+}\) to further vary the hydrolysed species distributions. As mentioned in chapter 3, further studies should also be conducted to further determine the effect of the mineral-water interface on the adsorption of hydrolyzable
cations using periodic DFT calculations. Overall, this work would suggest that cation specific properties dominate the interactions that occur at mineral-water interfaces.
REFERENCES


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Gaussian 09, Gaussian, Inc.: Wallingford, CT, 2010.


Figure 14: Representative Scanning Electron Micrograph of the quartz sample showing a variable particle size between 40 and 500 nm.
Figure 15: Representative high-resolution transmission electron micrographs of the quartz sample showing the variable particle sizes as well as the absence of well-defined crystal faces.
Appendix A.1 Instrumentation and basic operational procedure for the flow microcalorimeter.

The flow microcalorimeter consists of a microcolumn assembly containing the sample holder in which a known amount of solid sample is packed. An electrolyte solution containing the species of interest is allowed to flow through the packed micro column at controlled flow rates (between 0.30 and 0.35 ml min$^{-1}$) until thermal equilibrium whence a steady baseline is obtained. A pair of thermistors, one upstream and one downstream from the sample holder, form one half of an electronic bridge and sense temperature changes in the solution as it passes through the column. As the input solution is changed to one with a different composition (e.g., pH, ionic strength or concentration), any changes in solution temperature resulting from heat evolved or consumed as a result of either physical or chemical interactions between the reacting solute and solid produce a calorimetric signal that is displayed graphically and recorded as a function of time. The return of the calorimetric signal to the pre-experiment baseline is taken to indicate the end of the reaction. The heats of reactions ($Q$ in mJ/mg solid) are calculated by integrating the calorimetric peaks to obtain flow rate-averaged peak areas, which are converted to energy units (Joules) by comparison to peaks of known energy input generated from a calibrating resistor located within the flow stream inside the micro-column. Figure S3 shows a series of heat pulses and the associated calibration curve.
Figure 16: (a) Peaks obtained from a series of heat pulses, and (b) the associated calibration curve.
Appendix A.2 Details on the Integration Method

The mass balance for $H^+$ was found by first converting the pH measurements to concentrations and integrating over the time measured. The integrated values were then multiplied by corresponding flow rates. In order to determine the expected number of $H^+$, the same integration was performed for a constant pH of 4.00. The difference between the two values was determined and taken as the $H^+$ differential as shown in the integration equation below.

$$fr \cdot \int_{0}^{t} 10^{-pH} - fr \cdot \int_{0}^{t} 10^{-4.00}$$

### Table 6: Cation specific properties

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Radius (Å)</th>
<th>Ionic Potential (Z/R)</th>
<th>Hydration Radius (Å)</th>
<th>Hydration Enthalpy (kJ/mol)</th>
<th>Primary Solvation Shell Water Exchange Rate (log k, s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.74</td>
<td>1.35</td>
<td>3.82</td>
<td>519</td>
<td>9.1</td>
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<tr>
<td>Na⁺</td>
<td>1.02</td>
<td>0.98</td>
<td>3.58</td>
<td>409</td>
<td>9.1</td>
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<tr>
<td>K⁺</td>
<td>1.38</td>
<td>0.72</td>
<td>3.31</td>
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<tr>
<td>Rb⁺</td>
<td>1.49</td>
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<tr>
<td>Cs⁺</td>
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<tr>
<td>Mg²⁺</td>
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<td>0.74</td>
<td>4.04</td>
<td>1305</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Figure 17: Correlations between the heat of cation adsorption at pH 4.00 for alkali cations and, bare ionic radius (A), hydrated radius (B), and ionic potential (C).
Figure 18: Correlations between the heat of cation adsorption at pH 4.00 for alkaline earth cations and, bare ionic radius (A), hydrated radius (B), and ionic potential (C).
Figure 19: Correlations between the heat of \([\text{Li}^+ / \text{M}^+]\) exchange for alkali cations and, bare ionic radius (A, B), hydrated radius (C, D), and ionic potential (E, F) at pH 4.00 (A, C, E) and pH 8.0 (B, D, F).
Figure 20: Correlations between the heat of \([\text{Mg}^+/\text{M}^{2+}]\) exchange for alkaline earth cations and, bare ionic radius (A, B), hydrated radius (C, D), and ionic potential (E, F) at pH 4.00 (A, C, E) and pH 8.0 (B, D, F).
Table 7: Differences in pH values measured during [Li+/M+] and [Mg2+/M2+] exchange (2nd column) and [M+/Li+] and [M2+/Mg2+] (3rd column).

<table>
<thead>
<tr>
<th></th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M+/Li+]</td>
<td>[M2+/Mg2+]</td>
</tr>
<tr>
<td>Na+</td>
<td>0.00</td>
</tr>
<tr>
<td>K+</td>
<td>0.01</td>
</tr>
<tr>
<td>Rb+</td>
<td>0.01</td>
</tr>
<tr>
<td>Cs+</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.04</td>
</tr>
<tr>
<td>Sr2+</td>
<td>0.02</td>
</tr>
<tr>
<td>Ba2+</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Appendix B: Supplemental Information for Ch. 3

Table 8: Experimental conditions of metal cation adsorption on quartz and corundum

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mn(NO3)2·4H2O, mM</th>
<th>Al(NO3)3·9H2O, mM</th>
<th>Cr(NO3)3·9H2O, mM</th>
<th>NaNO3, mM</th>
<th>pHb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2.9 (2.9)</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0 (2.9)</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0 (2.9)</td>
<td>3.8 ± 0.2</td>
</tr>
</tbody>
</table>

Note: NaNO3⁺: In Mn sample, 2.9 mM NaNO3 was added to Mn(NO3)2·4H2O to remain the same IS as Al(NO3)3·9H2O and Cr(NO3)3·9H2O solutions for quartz crystal microbalance measurements. Values in parantheses indicate values of NaNO3 concentrations used as background for microcalorimetry experiments. pHb: The pH of all solutions was adjusted to 3.8 ± 0.2 using HNO3 or NaOH.
Figure 21: QCM-D control measurements of Na\(^+\) and NO\(_3^-\) ion adsorption onto SiO\(_2\) (A) and Al\(_2\)O\(_3\) sensors (B) at pH = 3.8 ± 0.2. Initially, ultrapure water was pumped through the chamber until a stable baseline was established. Then, the test solution of 2.9 mM NaNO\(_3\) was pumped into the chamber at a flow rate of 0.2 mL/min (the arrows indicate the switching point). Finally, the inlet solution was switched back to ultrapure water (the arrows indicate the switching point). No changes in vibrational frequency or dissipation were observed, indicating no adsorption of Na\(^+\) or NO\(_3^-\) onto SiO\(_2\) and Al\(_2\)O\(_3\) sensors.
Figure 22: Fully hydrated models for adsorption onto silica and alumina substrates shows bond of interest for adsorption. Image was generated using Materials Studio 2016.
Figure 23: Fully hydrated models for adsorption onto silica and alumina substrates shows bond of interest for adsorption. Image was generated using Materials Studio 2016.
Figure 24 Cation Speciation Curves for Al$^{3+}$, Cr$^{3+}$, and Mn$^{2+}$. Cr$^{3+}$ (A) shows complex variation at pH 3.8 with significant amounts of Cr$^{3+}$, Cr(OH)$^{2+}$, and Cr$_3$(OH)$_4^{5+}$ while Al$^{3+}$ (B) and Mn$^{2+}$ (C) exist as single species.