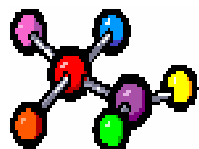


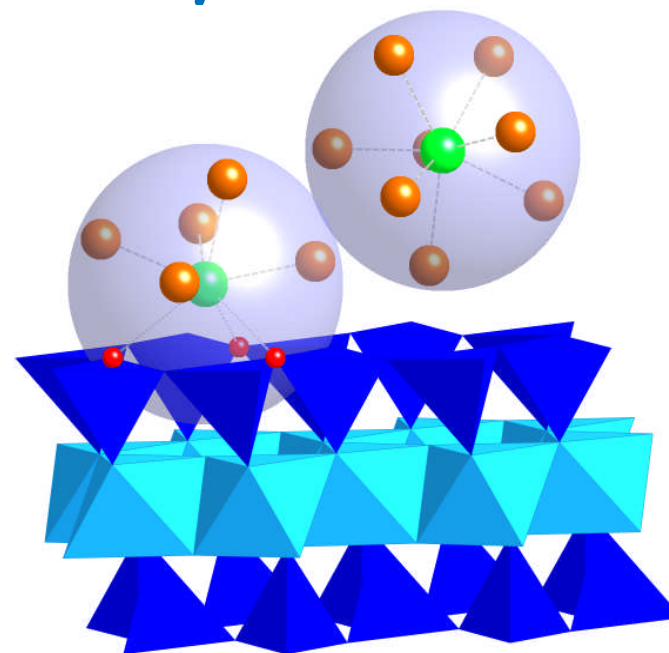
Probing Ion Adsorption at Mineral-Water Interfaces with Resonant Anomalous X-ray Reflectivity

Changyong Park

Interfacial Processes Group, Chemistry Division



Interfacial Processes Group
Argonne National Laboratory



APS/Users Operations Monthly Meeting, July 26, 2006

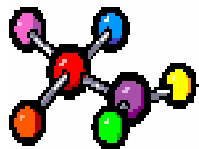


Acknowledgements

Collaborators

Paul A. Fenter (ANL)
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Zhan Zhang (ANL)
Jeffrey G. Catalano (ANL)



Interfacial Processes Group
Argonne National Laboratory

UIC

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Experiments

Advanced Photon Source

The logo for the Advanced Photon Source (APS) features a rainbow-colored triangle pointing upwards and to the right, positioned above a black rectangular box containing the text "BESSRC/XOR" in bright green, glowing, block letters.

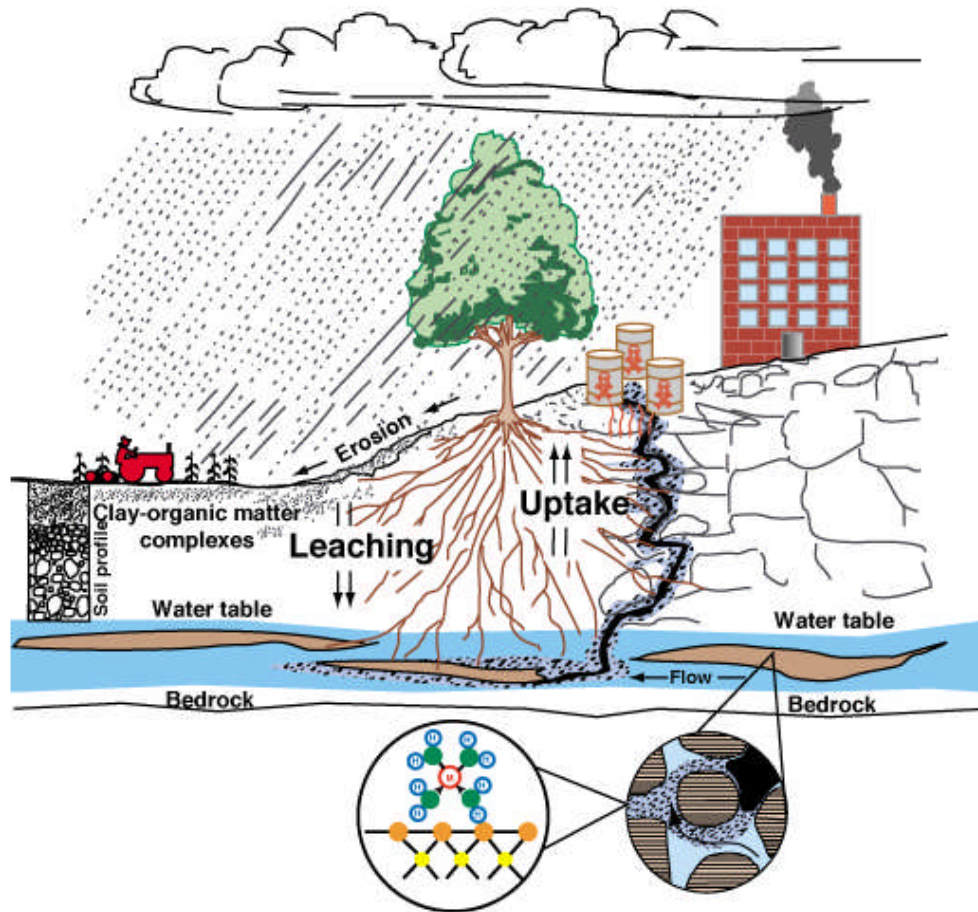
BESSRC/XOR

Ion adsorptions are important in various interfacial processes

- Environmental processes - transport of environmental contaminants in natural water system
- Biomedical processes - ion-mediated macromolecular interactions in physiological environment
- Industrial processes - noble metal catalyst impregnation on oxide supports
- And so on - virtually any interfacial systems immersed in aqueous solutions

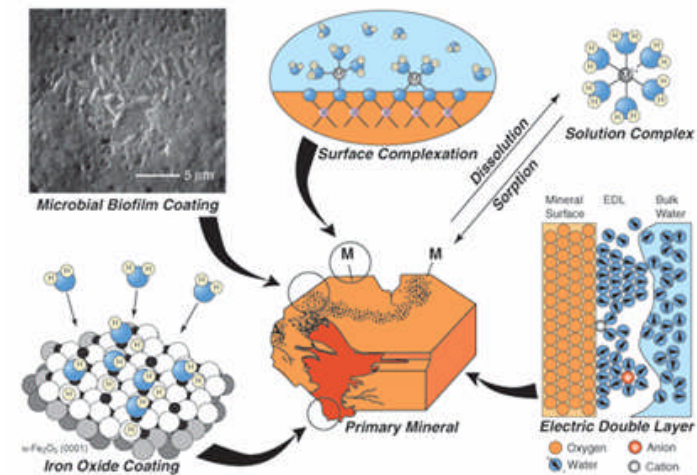
Ion Adsorption as a Fundamental Process: Example. 1.

Transport of environmental contaminants controlled by molecular-scale geochemical processes



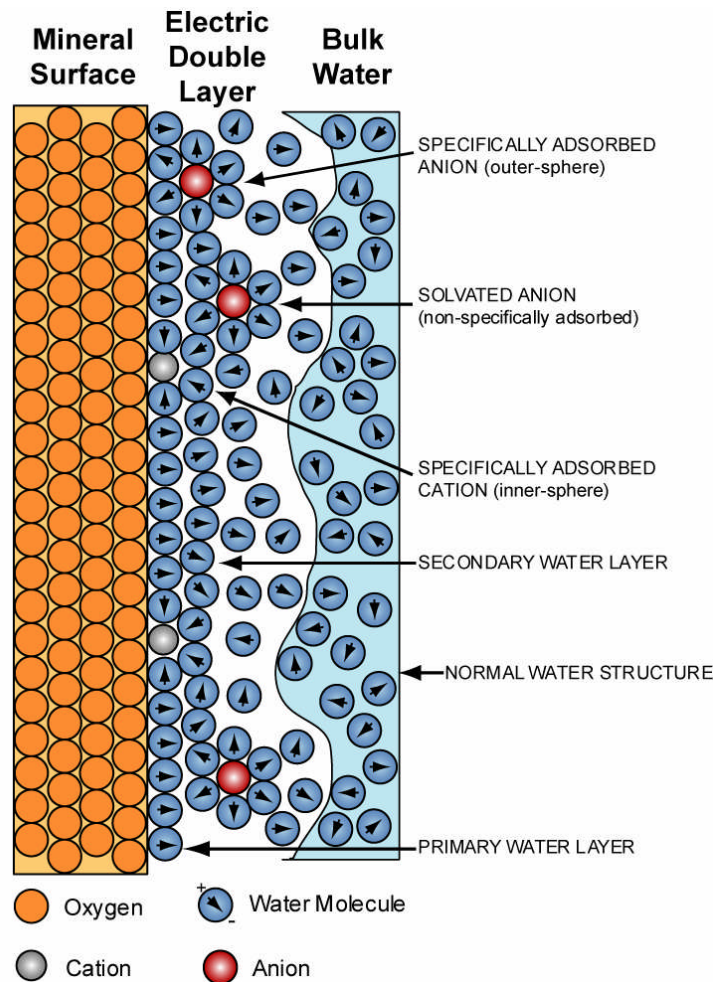
Courtesy of APS

- Our understanding of transport of environmental contaminants is largely limited by knowledge of molecular scale processes.



Brown, G. E. (2001). *Science* **294**, 67-69.

Most fundamental but poorly described phenomenon: Ion interactions at charged solid-liquid interfaces



- Ion-surface, ion-water, and surface-water interactions characterize the inherently complex interfacial structure.
- Classical electrostatic theories do not work in molecular scale since assumptions on point charge distribution and continuous dielectric medium is not valid at the this level.
- Competing role of ion-hydration and its structures in controlling ion adsorption at the interface has been suggested (e.g., from surface force measurements or MD simulations).
- Direct in-situ probe of ion-specific interfacial density distribution has been a long-lasting challenge.

Israelachvili (1992) *Intermolecular and Surface Forces*, Academic Press

Israelachvili and Wennerstrom (1996) *Nature* **379**, 219-225

Luo and Schlossman et al. (2006) *Science* **311**, 216-218

From Brown and Parks (2001) *Int. Geol. Rev.* **43**, 963-1073

Textbook description of ion adsorption: strong inner-sphere vs. weak outer-sphere

CATION SURFACE SPECIES ON 2:1 LAYER TYPE CLAY MINERALS AND THEIR RESIDENCE TIMES BY SPECTRAL METHODOLOGIES

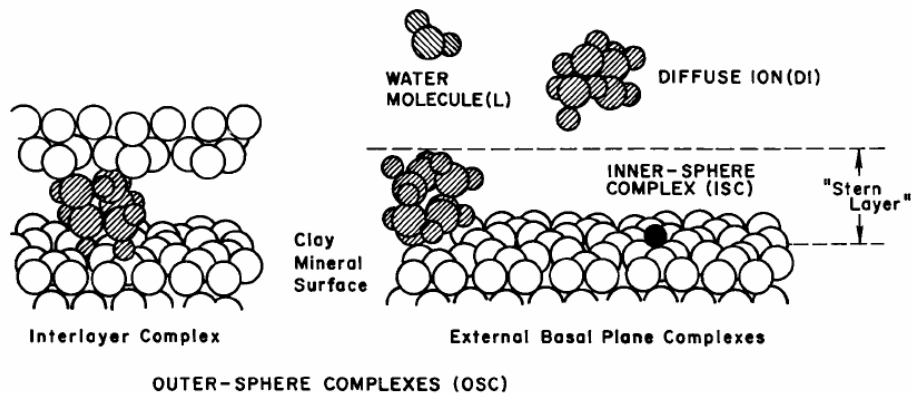
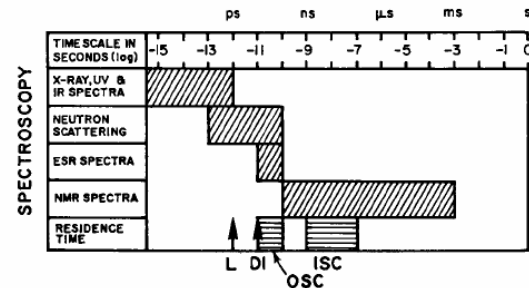


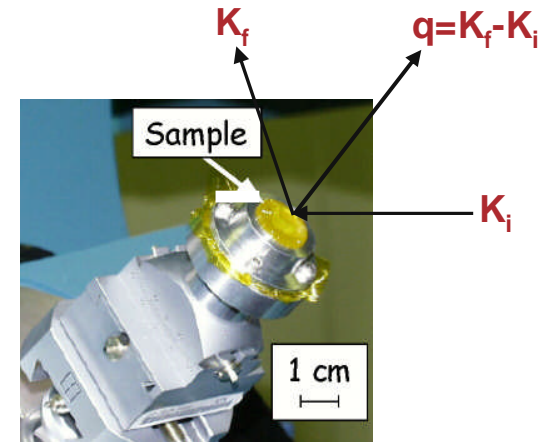
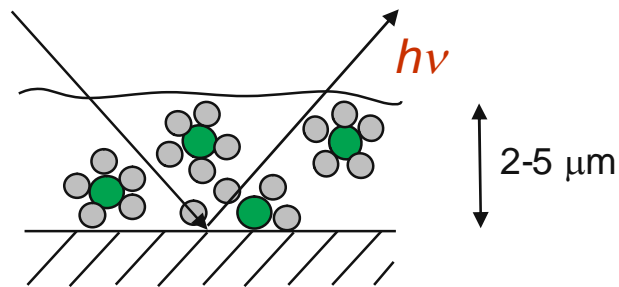
Fig. 2. Cartoon of the three types of small cation adsorption by a 2:1 layer type clay mineral. The “Stern Layer” comprises only surface complexes, which can form in the interlayer region (left) as well as on single siloxane surfaces (right). Characteristic residence time scales of the three adsorbed species are compared at upper right to the time scales of *in situ* spectroscopic methods used to detect them.

From Sposito et al. (1999) *Proc. Natl. Acad. Sci. U.S.A.* **96**, 3358-3364

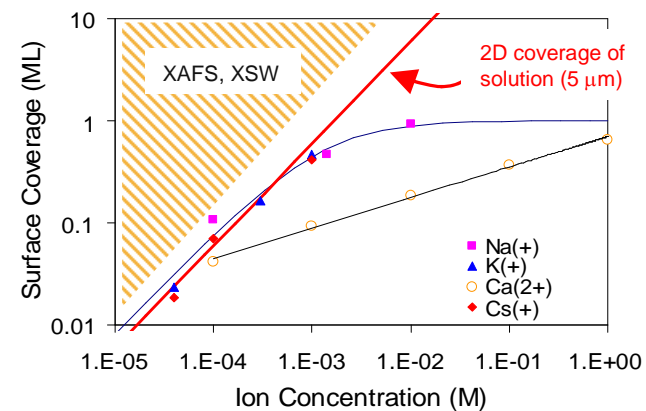
- Two types of ion adsorption
- **Inner-sphere adsorption:** ion removes its hydration shell and directly interact with surface atoms.
- **Outer-sphere adsorption:** ion retains its hydration shell and adsorbs as molecular unit.
- It has been assumed outer-sphere adsorption is inherently (i.e., due its bigger mobility) weaker than inner-sphere adsorption.
- We have empirically known that this oversimplifies the reality.
- Direct observations are desired.

Two challenges

- Direct in-situ determination of the immersed (or buried) interfaces
 - x-ray reflectivity with penetrating hard x-rays

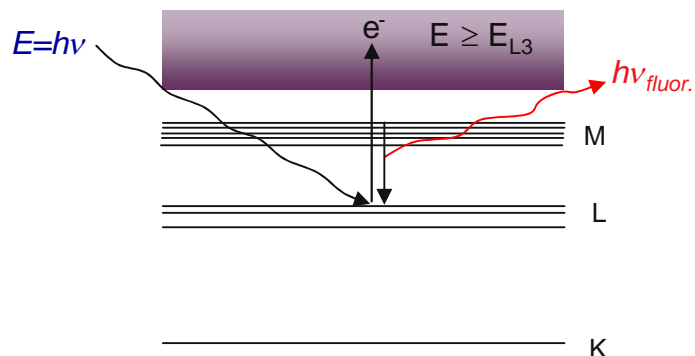


- Ion-specific sub-profiles without ambiguity
 - element-specific method
 - conventional x-ray reflectivity do not have element-specific sensitivity.
 - XSW, XAFS are limited by spectral interference from bulk species.

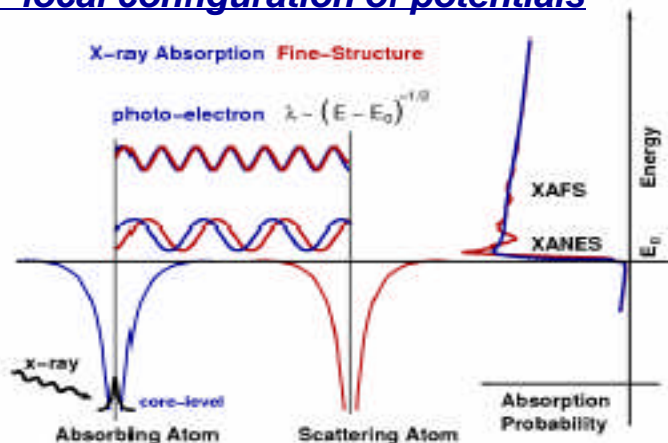


For probing ion-specific sub-profiles: Combine element specificity and surface sensitivity of x-rays

Characteristic absorption

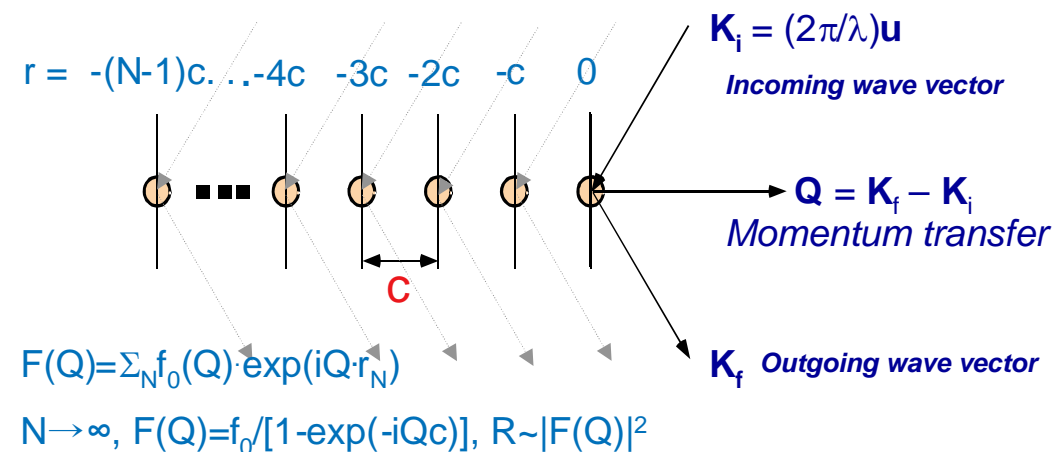


Sensitivity to valence electron state and local configuration of potentials

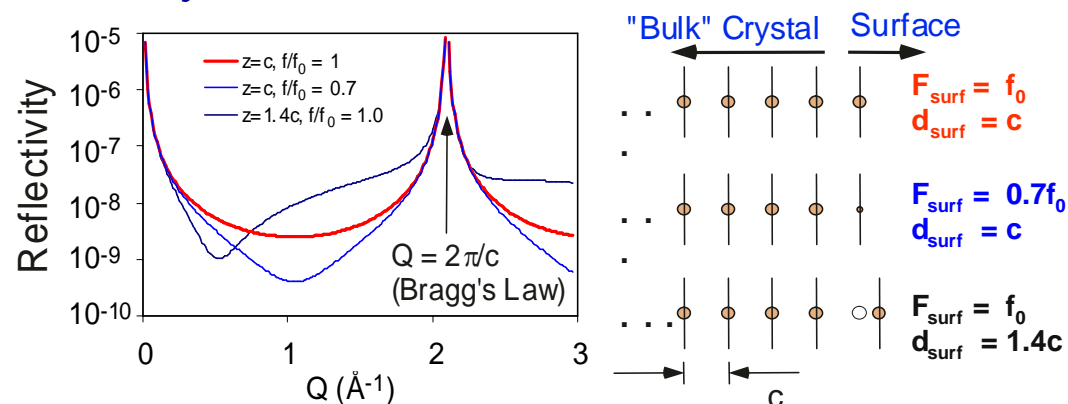


(From "Fundamentals of XAFS" by Matthew Newville)
http://cars9.uchicago.edu/xafs/xas_fun/xas_fundamentals.pdf

Kinematic scattering from a N-Layer Crystal

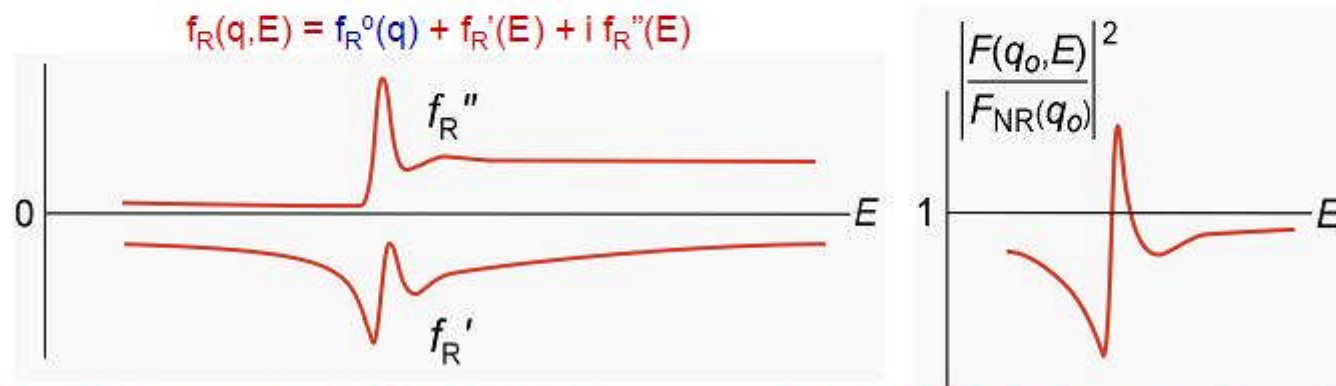
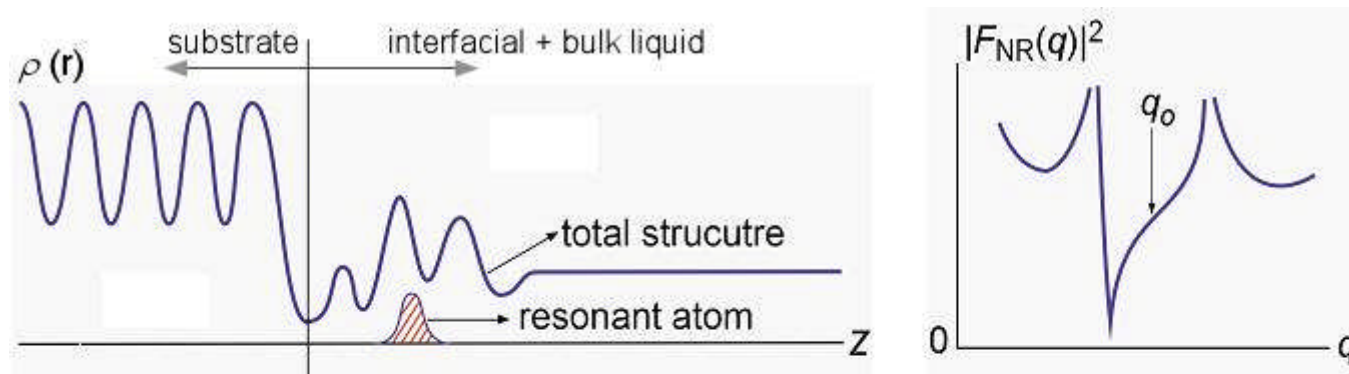


Sensitivity to surface modification



(From "X-ray Reflectivity: A User Guide" by Paul A. Fenter, RMG 49)

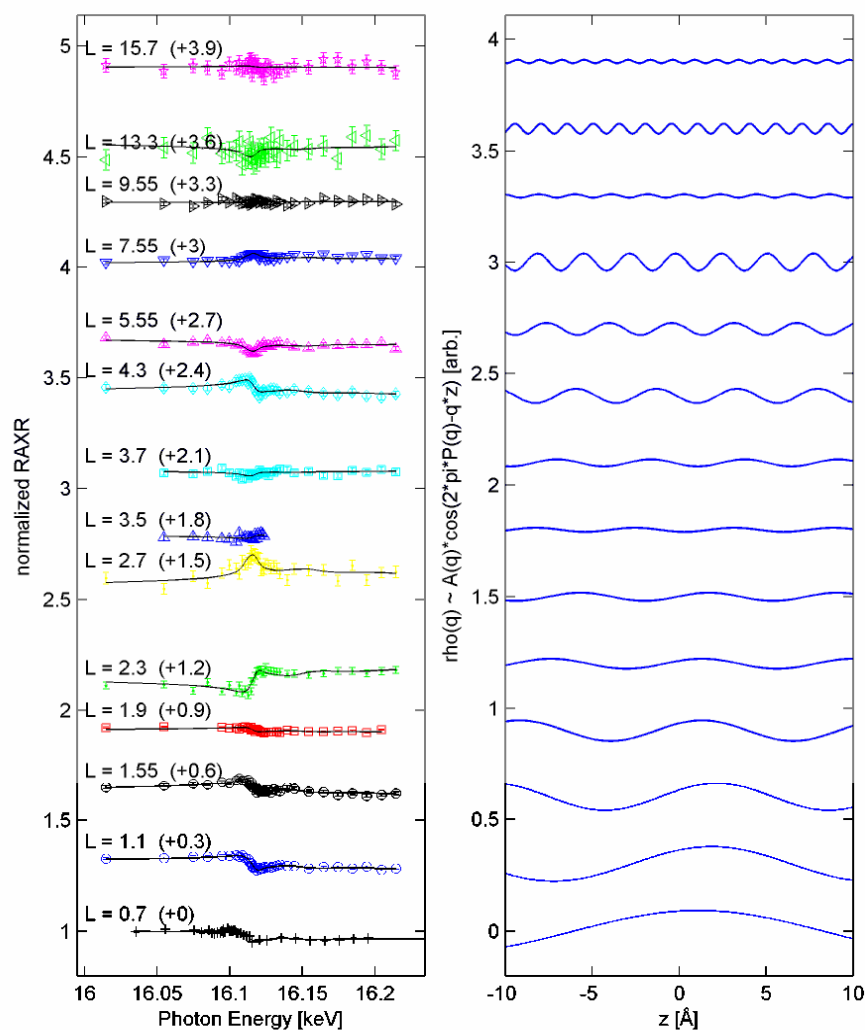
Resonant Anomalous X-ray Reflectivity: X-ray reflectivity measured as function of incident photon energy near an absorption edge at a fixed momentum transfer



$$F(q, E) = F_{NR}(q) + \sum [f_i'(E) + i f_i''(E)] \theta_i \exp(iqz_i) \exp(-q^2 \sigma_i^2 / 2) = F_{NR}(q) + F_R(q, E)$$



Model-independent, unique determination of ion-specific density distribution with discrete Fourier synthesis imaging

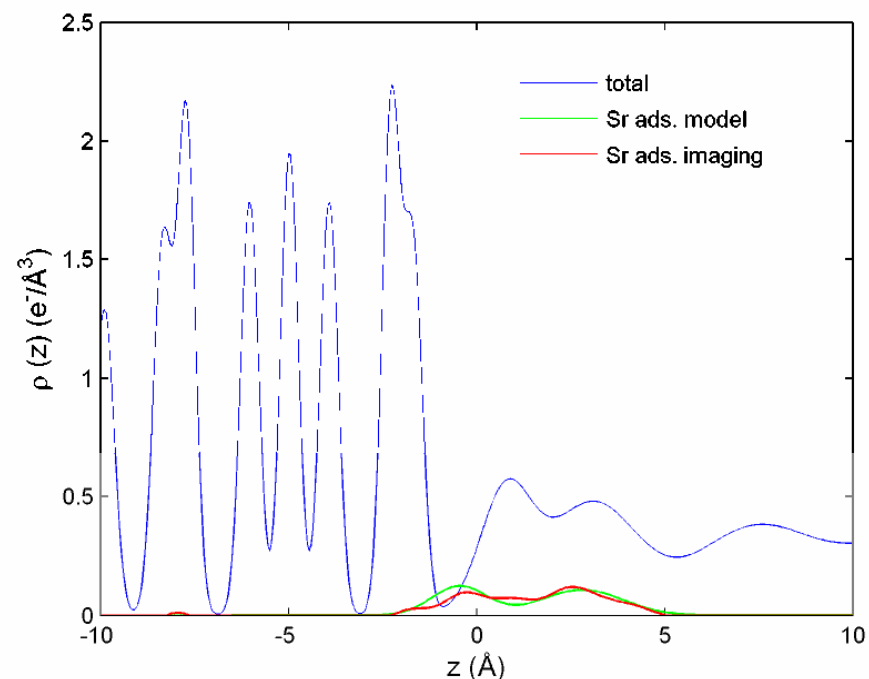


$$F(q,E)=F_{NR}(q) + [f'(E)+if''(E)] A(q) \exp[i \cdot 2\pi \cdot P(q)]$$

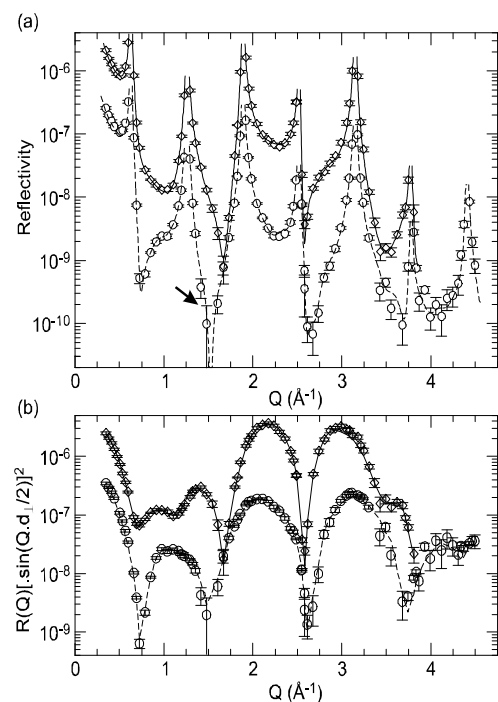
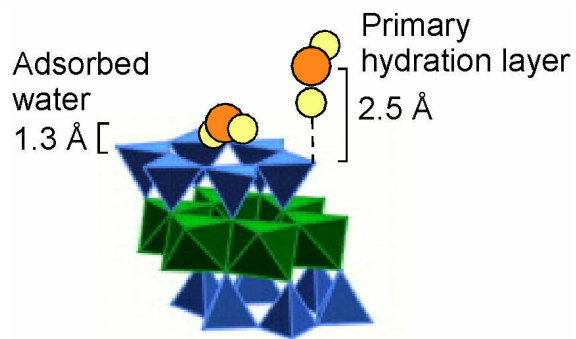
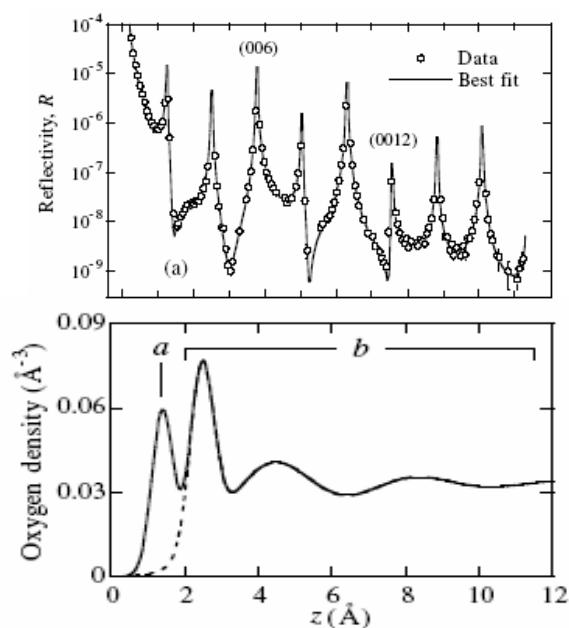
$$\rho_R(z) = (Z_R/A_{uc})(1/2\pi)\sum_q A(q) \cos[2\pi \cdot P(q)-q \cdot z] \Delta q$$

$$\text{where, } A(q) \equiv f_{R,coh}(q) \cdot \theta_{R,total}$$

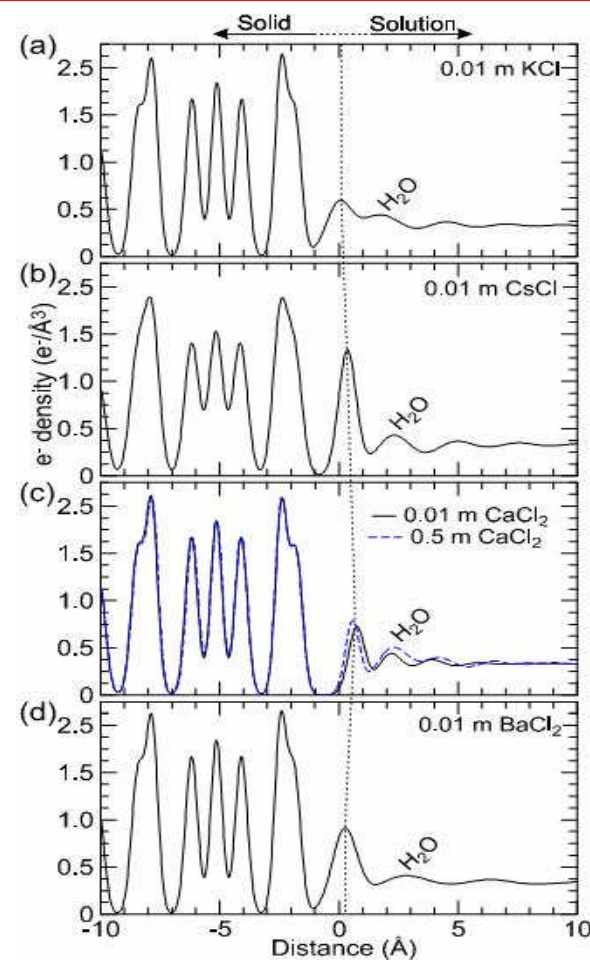
$$2\pi \cdot P(q) = q \cdot z_{avg,coh}(q)$$



Ion adsorption at mica (001)-water interface



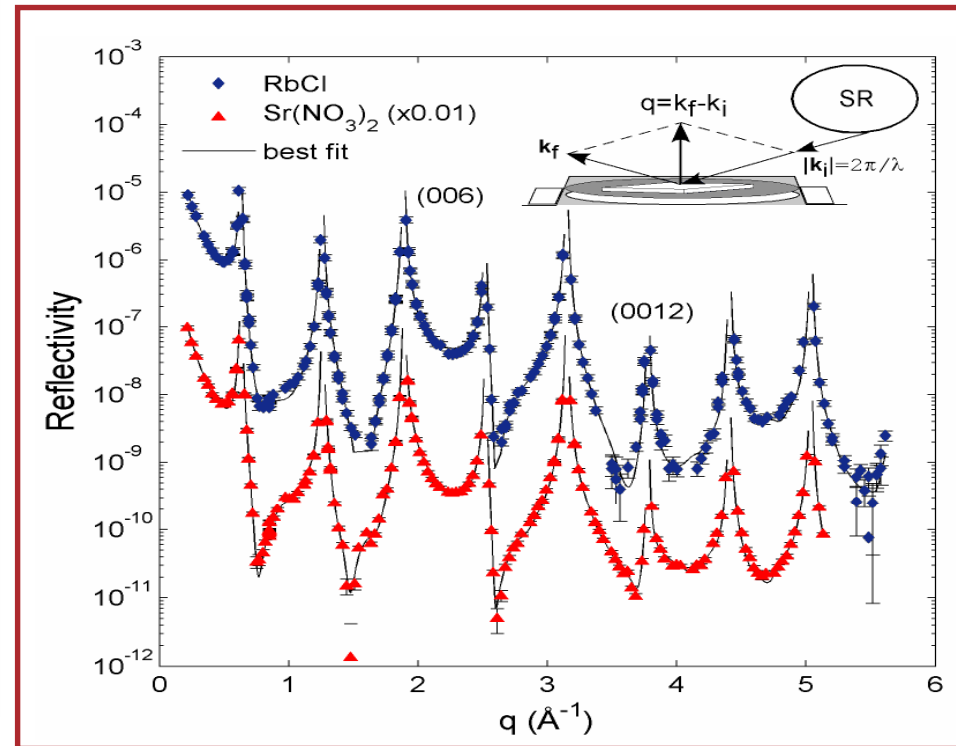
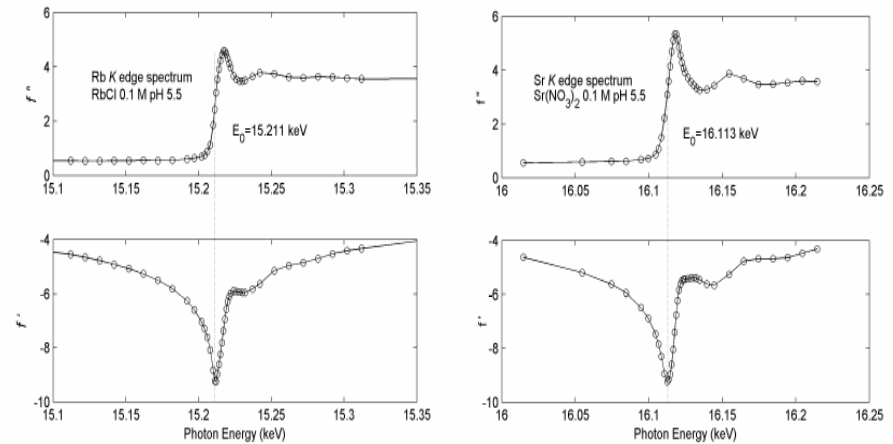
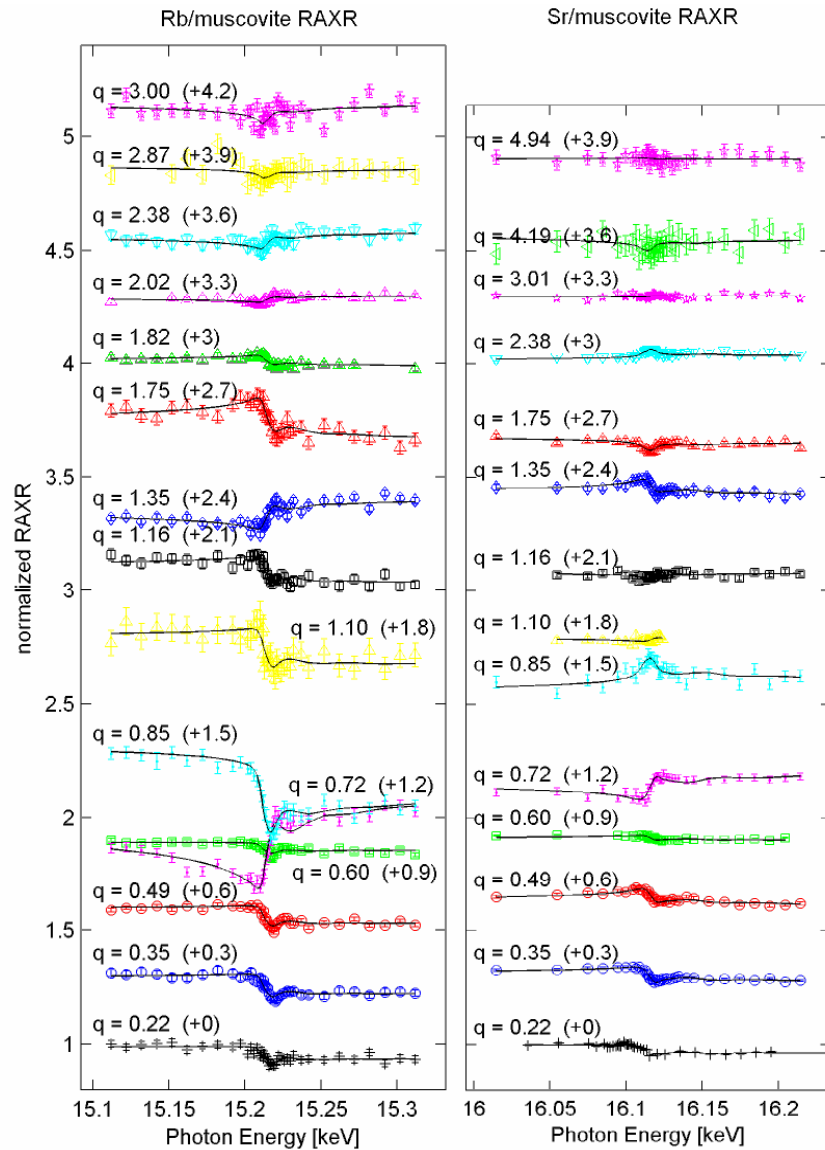
- Ion adsorption substantially alters the interfacial structure.
- Ion-specific profiles are still unknown.



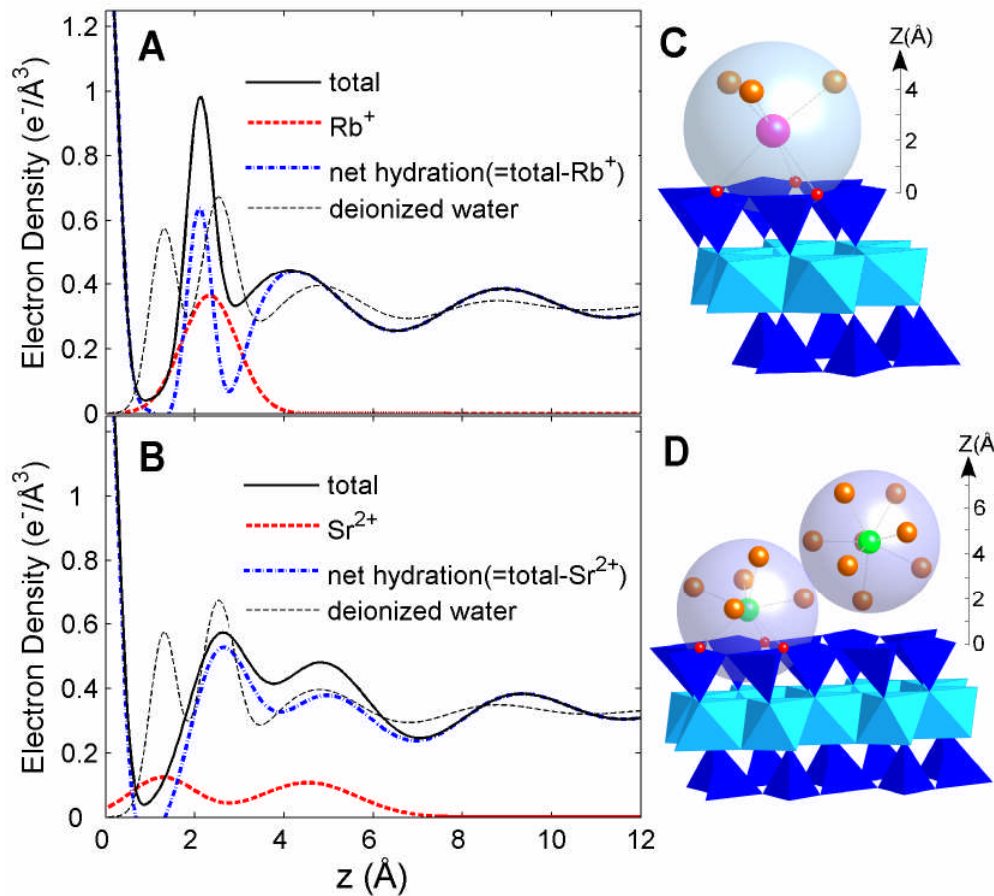
Cheng et al. (2001) *Phys. Rev. Lett.* **87**, 156103

Schlegel et al. (2006) *Geochim. Cosmochim. Acta* **70**, 3549-3565

RAXR of mica(001)-cation solution interface - 0.01M pH 5.5



Rb⁺ vs. Sr²⁺ on mica surface: role of ion-hydration in controlling ion adsorption



Critical difference between Rb⁺ and Sr²⁺

- Rb⁺ : inner-sphere, incomplete charge compensation ($0.72 \pm 0.16 \text{ Rb}^+/\text{A}_{uc}$)
- Sr²⁺: both inner- and outer-sphere, full compensation of surface charge ($0.64 \pm 0.16 \text{ Sr}^{2+}/\text{A}_{uc}$), stronger adsorption than Rb⁺

Contrast Interfacial hydration profiles

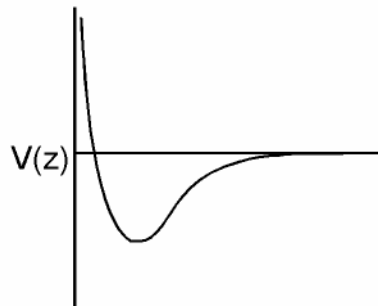
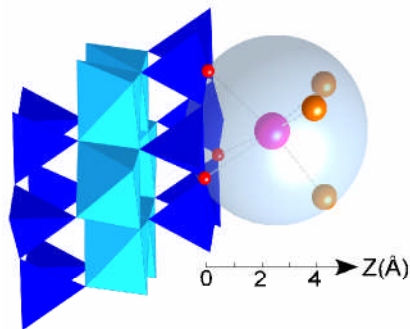
- Dependence on ion-distribution and ion-hydration structure

Energy balance between ion-hydration and electrostatic interaction of cations and water dipoles with charged surface

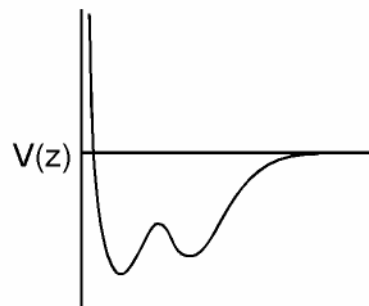
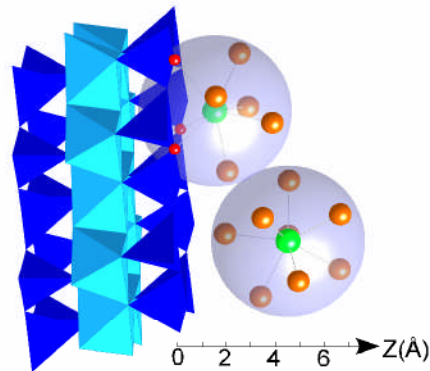
- 1445 kJ/mol for Sr²⁺ hydration
- 296 kJ/mol for Rb⁺ hydration
- ~15 kJ/mol change in electrostatic energy between inner- and outer-sphere Sr²⁺
- low dielectric constant of interfacial water
- strong electrostatic coupling of cations with localized surface charge
- not only energy but also structure is important

New insights into ion adsorption at solid-liquid interfaces

Muscovite/Rb⁺

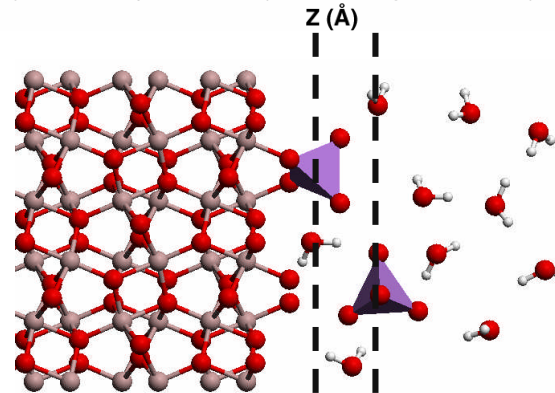
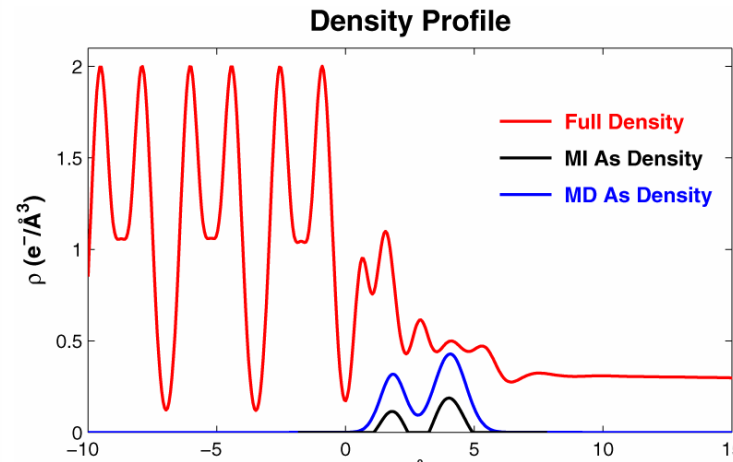
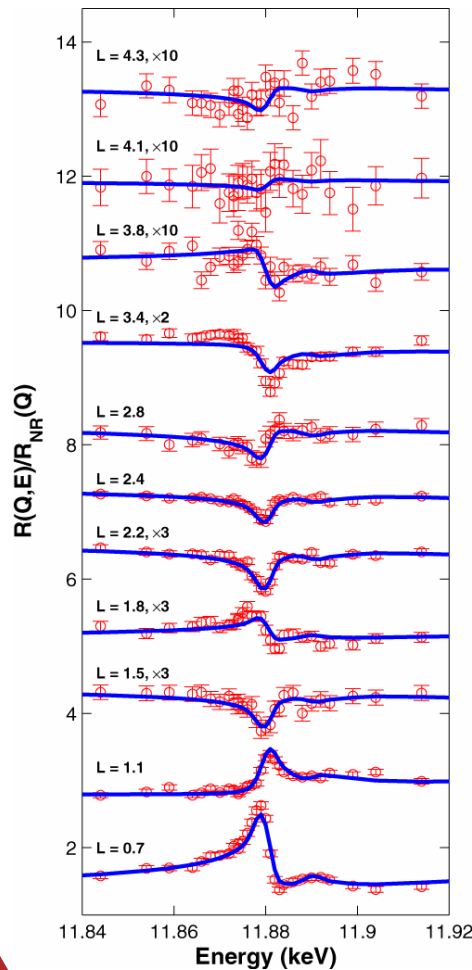


Muscovite/Sr²⁺



- Ion adsorption is not simply described by the black or white type discrimination, but instead there are grey shades of adsorbed states allowing the both inner- and outer-sphere species to coexist.
- New insights are gained about the competing roles of ion hydration and electrostatic attraction on determining the behavior of adsorbed cations at charged aqueous interfaces.

Another example in different sorption mechanism: Simultaneous inner- and outer-sphere As(V) surface complexation



- Adsorbed As(V) occurs at two heights above the surface
 - One consistent with an inner-sphere bidentate complex
 - One consistent only with an outer-sphere complex
- First direct evidence of outer-sphere As(V) adsorption
- Past techniques not sensitive to outer-sphere adsorption if inner-sphere species present
 - Present of OS species would only reduce second shell CN in EXAFS
 - OS would look like As_{aq} in ATR-FTIR

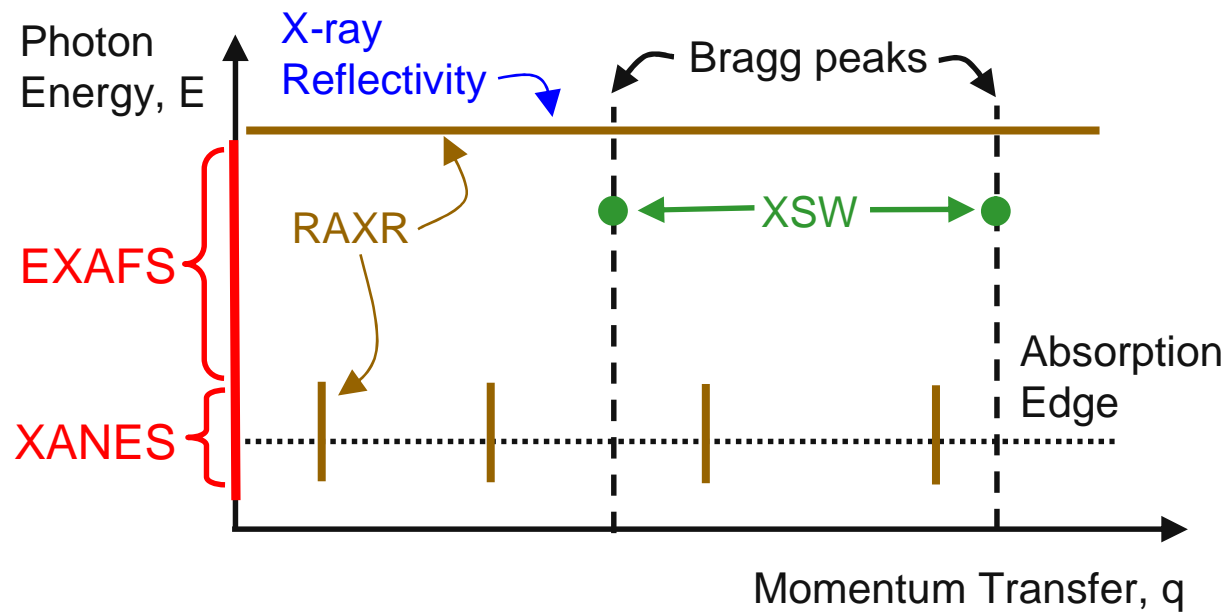
Future technical challenges for better RAXR application in studying ion interactions at solid-liquid interfaces

- To reduce systematic errors inheriting from using natural minerals:
 - micrometer sized beam (maybe by KB mirror or compound refractive lenses)
 - angle-fixed RAXR measurement using broad band of incident photon energy (similar concept of rapid XAFS)
- Toward better sciences
 - new sample cell design for grazing incidence RAXR (direct probe of diffuse ion profile)
 - micro flowing control of solution (direct observation of adsorption kinetics)
- Topics yet untouched with present skills
 - high energy RAXR, non-specular RAXR, interface-specific spectroscopy

Thank you !!



Phase diagram of x-ray utilities



Cation Adsorption on Charged Mineral Surfaces

- Inner-Sphere Adsorption
- Surface Charge due to Surface Speciation – Oxide Minerals

4962 *Langmuir*, Vol. 20, No. 12, 2004

Zhang et al.

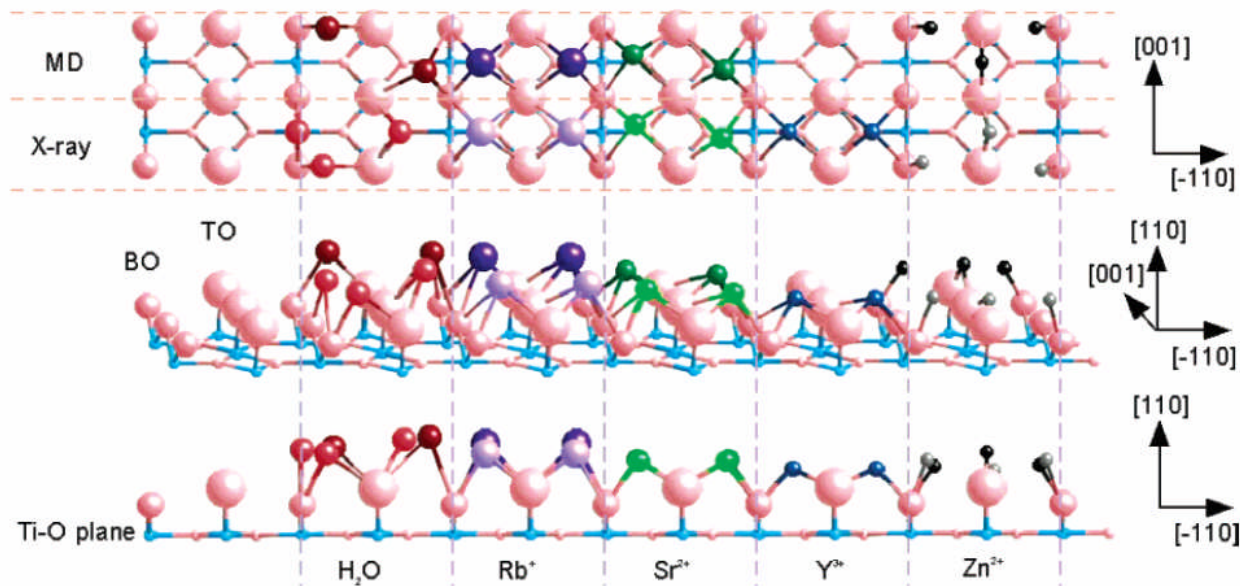


Figure 5. (A) Top, (B) perspective, and (C) side views of the bare rutile (110) surface with bridging and terminal oxygen rows (BO and TO, respectively), and the locations of derived surface hydration and ion adsorption sites, including interfacial water, Rb^+ , Sr^{2+} , Y^{3+} , and Zn^{2+} . X-ray and MD-derived adatom locations are shaded differently as noted in the top view (the MD results correspond to the hydrated rutile (110) surface). Note the close similarity of ion locations between the X-ray and MD derived ion sites.

Cation Adsorption on Charged Mineral Surfaces

- *Outer-Sphere Adsorption*
- *Surface Charge due to Permanent Lattice Charge – Clay Minerals*

3362 Colloquium Paper: Sposito *et al.*

Proc. Natl. Acad. Sci. USA 96 (1999)

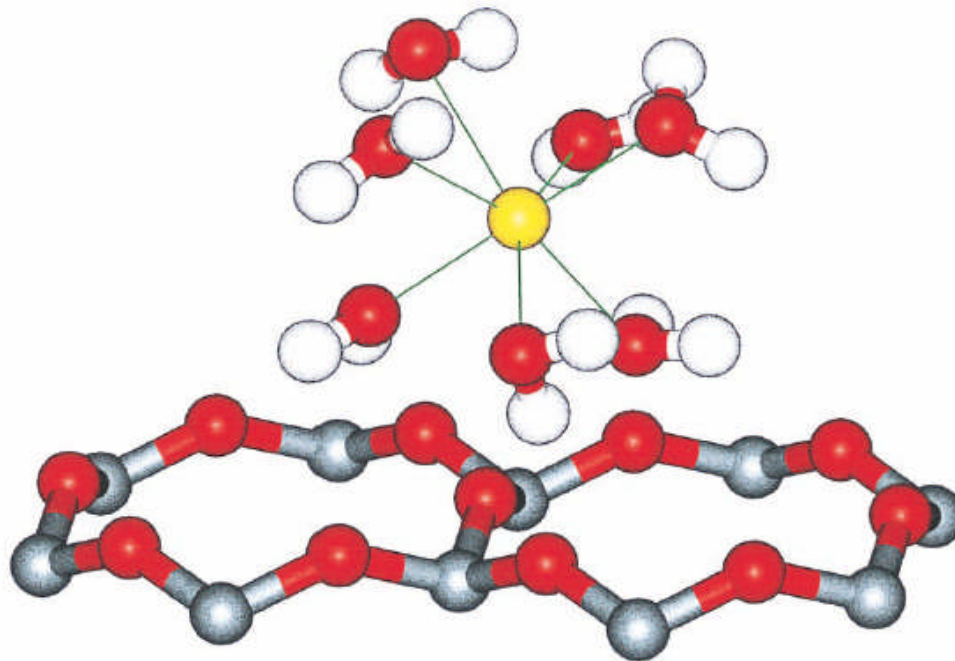


FIG. 4. Visualization of Na^+ bound in an outer-sphere surface complex in the interlayer region of Wyoming montmorillonite, based on MC simulation. A portion of the siloxane surface structure also is shown.

- *Magnitude and location of surface charge is important factors.*
- *Interfacial dielectric constant of water plays a role in electrostatic interactions.*
- *Molecular features are critical for controlling cation adsorption.*