

Probing the Electrical Double-Layer Structure
at the Rutile-Water Interface
with X-ray Standing Waves*

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ABSTRACT: We demonstrate that the X-ray standing wave (XSW) technique is a powerful probe of the electrical double-layer (EDL) structure. Measurements were made of Sr adsorption at the rutile (110)-water interface from aqueous solutions. Our results show that Bragg XSW, using small-period standing waves generated by Bragg diffraction from the substrate, precisely probes the location of ions within the condensed layer, and the *in situ* partitioning of ions between the condensed and diffuse layers. Such measurements can provide important constraints for the development and verification of theoretical models that describe ion adsorption at the solid-water interface.

1 INTRODUCTION

The development of mineral surface charge, and the associated distribution of solute ions at solid-water interfaces, generally referred to as the electrical double-layer (EDL), is fundamentally important for a diverse range of natural and industrial processes. Various physical and chemical models have been used to explain and predict the properties of the EDL (Stumm 1992, Dzombak 1990). A conventional schematic diagram of EDL structure, Figure 1, shows ions distributed between the so-called condensed (or "Stern") and diffuse (or "Gouy-Chapman") layers, to balance a fixed charge of a mineral surface. However, there has been a lack of quantitative molecular-scale experimental data that can independently test available EDL models (Brown et al. 1999, Westall and Hohl 1980) and consequently our current understanding of the EDL is incomplete.

Here we demonstrate that the Bragg X-ray standing wave (XSW) technique provides a direct element-specific probe of the *in situ* EDL structure (Fenter et al. 2000) by precisely measuring the location of condensed layer ions and the partitioning of ions between the condensed and diffuse layers. We demonstrate this capability by investigating Sr ion adsorption at the rutile (110)-water interface.

2 EXPERIMENTAL METHODS

The rutile (110) surface was used because it has been studied extensively and is known to be chemically stable over a broad range of pH values (Machesky et al. 1994). Chemomechanically-polished synthetic single crystal rutile (110) substrates were cleaned ultrasonically in methanol to remove any surface organic contamination followed by three ultrasonic baths in nanopure (~18 M Ω /cm) deionized water. Experimental solutions were prepared by dissolving reagent grade RbCl, RbOH, or Sr(NO₃)₂ in nanopure deionized water, and the pH was adjusted using HNO₃ and/or NaOH. The aqueous speciation of Rb and Sr in the solutions was calculated by using the Geochemists

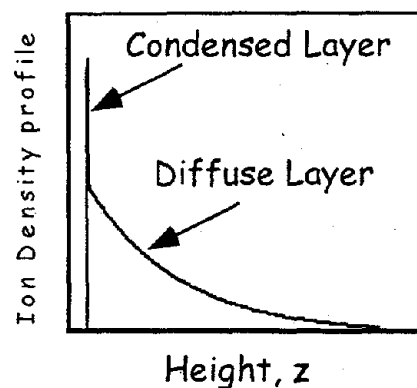


Figure 1. Schematic ion distribution in the EDL.

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Workbench; $[\text{Rb}]_{\text{aq}}$ was exclusively present as Rb^+ in all solutions, and $> 98.5\%$ of $[\text{Sr}]_{\text{aq}}$ was present as Sr^{2+} .

The sample was held in a Kel-F "thin-film" cell using an 8 μm thick Kapton window, in which a thin solution layer is held against the sample surface through capillary action during XSW measurement. The solutions were manually injected into the cell so as to expand the solution layer confined by the Kapton film during reaction to a macroscopic thickness (~ 1 mm). A pump was then used to apply a negative pressure to reduce and maintain the thickness of the solution layer to ~ 2 μm (Bedzyk et al. 1990). Between *in situ* measurements, the sample surface was cleaned by exposure to 1000 μM nitric acid solution. X-ray fluorescence measurements confirmed that the surface was free of any adsorbed Sr or Rb ion with a sensitivity limit of $\sim 5 \times 10^{-4}$ ions/ $\text{\AA}^2$.

3 DESCRIPTION OF THE XSW TECHNIQUE

The Bragg diffraction XSW technique has been described previously (Zegenhagen 1993). Briefly, the substrate Bragg reflection and X-ray fluorescence from EDL constituents are simultaneously measured as the sample is rotated through the Bragg reflection. Due to the nearly perfect reflectivity of the substrate Bragg reflection, an XSW field is generated by a coherent superposition of the incident and reflected X-ray beams during Bragg diffraction (Batterman 1969). The XSW has a period that is equal to the d-spacing of the diffraction planes, and the position of the XSW anti-nodes shifts inward by $d/2$ relative to the diffraction planes as the incident angle, θ , is scanned through the Bragg reflection (see Figure 2). Consequently the fluorescence signal is modulated as the sample is rotated through the substrate Bragg reflection. The atomic position and distribution (characterized by the coherent position, P , and coherent fraction, f , respectively) are determined by monitoring the modulation of the fluorescence yield of a specific atomic species as the crystal is rotated through the Bragg condition. The fluorescence yield, normalized to the off-Bragg yield, varies as

$$Y(\theta) = 1 + R(\theta) + 2[R(\theta)]^{1/2} f_H \cos[v(\theta) - 2\pi P_H] \quad (1)$$

where the reflectivity $R(\theta)$ and the XSW phase $v(\theta)$ are derived from dynamical X-ray diffraction

theory. Each set of XSW data (corresponding to a particular substrate reflection) are fully characterized by two model-independent parameters: the coherent position, P_H , and the coherent fraction, f_H . These parameters are obtained from a χ^2 -fit of Eq. 1 to the XSW data. Uncertainties in f_H and P_H are typically smaller than ± 0.03 , on the basis of counting statistics and a sensitivity analysis of the fitting procedure. In this study, H corresponds to the rutile (110) Bragg diffraction condition, and thus we denote f_{110} and P_{110} simply as f and P . Since the (110) reflection is normal to the surface, this provides a direct measure of the vertical EDL structure.

4 RESULTS

Both *ex situ* and *in situ* XSW measurements of Sr adsorption to rutile(110) are shown in Figure 3. As expected based upon Eq. 1, the Sr fluorescent yield shows a clear enhancement near the rutile(110) Bragg peak position, whose shape is distinct from that of the substrate Bragg reflection. The modulation of the fluorescence yield depends sensitively upon the solution conditions. For instance, the angular variation of the *ex situ* Sr fluorescence data appear to be shifted to larger angles

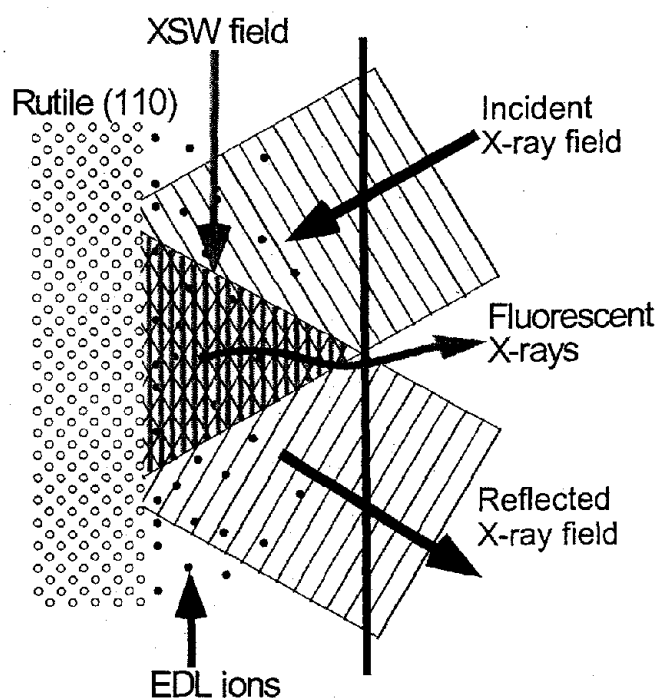


Figure 2. A schematic of the XSW experiment showing the XSW field superimposed on the EDL.

with respect to the TiO_2 reflectivity, and the normalized fluorescent yield, $Y_{\text{Sr}}/Y_{\text{OB}}$, is observed to be less than 1 on the small angle side of the Bragg peak. ($Y_{\text{Sr}}/Y_{\text{OB}} = 1$ corresponds to the fluorescent yield in the absence of a reflected X-ray beam and is noted for each data set as a dashed horizontal line). The *in situ* data also show a distinct, but smaller, modulation. These are unambiguous indications of the standing wave effect which corresponds to the interference term proportional to $f_H \cos[\nu(\theta) - 2\pi P_H]$ in Eq. 1.

We analyze these data using Eq. 1, from which we derive the coherent position, P , and coherent fraction, f , for each set of data. We find that $P = 0.91$ for the *ex situ* data and $P = 0.84$ for the *in situ* data. However, the coherent fraction, f , for the *ex situ* samples is roughly twice the size of that found *in situ*.

To understand the significance of these parameters, we note that there are three distinct contributions to the fluorescent signal in the standing wave data: condensed layer, diffuse layer, and the bulk solution. For condensed layer ions in a unique the solution conditions and derived standing wave adsorption site, the coherent fraction would ideally have the value, $F_c = 1$, and the coherent position,

P_c , will be determined by the height of these ions in units of the substrate lattice spacing ($d_{110} = 3.25 \text{ \AA}$). The actual coherent fraction is typically smaller than this ideal value due to non-specifically adsorbed ions, atomic vibrations, multiple binding sites, etc, all of which tend to reduce the measured coherent fraction. The diffuse layer contribution to the coherent fraction is negligible, e.g., $F_d \sim 0$, as long as the Debye length is large compared with the Bragg plane spacing. For instance, the ionic strengths used in the present measurements are $\leq 4240 \text{ } \mu\text{M}$ corresponding to Debye lengths of $> 50 \text{ \AA}$. The diffuse layer will only contribute significantly to the coherent fraction when the Debye length is comparable to the Bragg plane spacing. Ions in the bulk solution have $F_{\text{bulk}} = 0$ since their locations are, by definition, random with respect to the substrate lattice.

Based upon these considerations only the condensed layer ions contribute to the coherent position. Therefore the measured coherent fraction, f , represents the fraction of ions located in the condensed layer. In other words, the measured coherent position and fractions are given by:

$$P = P_c, \text{ and} \\ f = f_c \theta_c / (\theta_c + \theta_d + \theta_{\text{bulk}}), \quad (2)$$

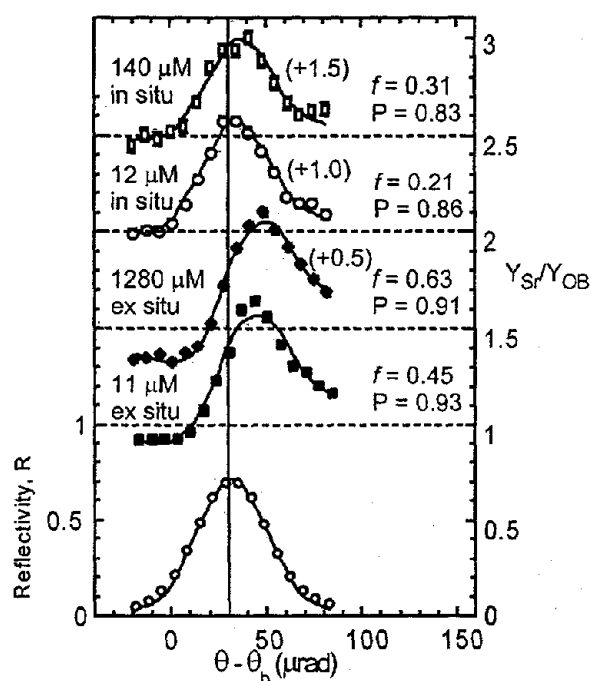


Figure 3. XSW data for Sr adsorption to rutile (110) at pH 10. The substrate 110 Bragg peak is shown at the bottom (open circles), and Sr fluorescence for *in situ* (open symbols) and *ex situ* conditions (closed symbols) are shown. Each set of fluorescence data is offset vertically by 0.5.

where P_c is the coherent position of the condensed layer ions, and θ is the coverage of each layer projected onto the surface plane.

The most precise results are obtained when the coherent fraction is large. Based upon this simple expression, it is easy to see that this is achieved by minimizing θ_{bulk} . Our measurements are therefore performed under conditions where we minimize the bulk solution layer thickness (estimated thickness $\sim 2 \text{ } \mu\text{m}$). Under these conditions θ_{bulk} can be calculated as $\theta_{\text{bulk}}(\text{ML}) = 2.3 \times 10^{-4} [\text{Sr}]_{\text{aq}}(\mu\text{M})$, where the coverage is expressed in units of monolayers [a monolayer (ML) is defined here as $1 \text{ ML} = 5.2 \times 10^{14} \text{ ions/cm}^2$] and the Sr ion concentration is expressed in μM . Since typical ion coverages in these measurements are ~ 0.25 to 0.5 ML , we can expect to be able to use this technique to probe solution ion concentrations as high as $\sim 0.001 \text{ M}$. We can, however, probe the EDL structure at significantly higher ionic strengths, particularly if the ionic strength is determined by an ion whose X-ray fluorescence line does not interfere with the fluorescence line due to the ion of interest.

When the solution concentration is small with respect to the sum of the condensed and diffuse

layer coverages (i.e., $\theta_c + \theta_d \gg \theta_{\text{bulk}}$) the measured coherent fraction becomes independent of the exact solution thickness. In this regime, the measured coherent fraction is equal to the product of the double-layer partition coefficient, $X = \theta_c / (\theta_c + \theta_d)$ and the coherent fraction of the condensed layer ions, F_c . In this way, systematic measurements of the coherent fraction as a function of solution parameters can provide direct insight into the partitioning of ions between the condensed and diffuse ion layers.

The modulation of the *in situ* Sr fluorescence as a function of angle is substantially weaker than that in the *ex situ* data (Figure 3). This indicates that a substantial fraction of Sr ions for the *in situ* measurements are found in the diffuse layer. We also note that we see no significant adsorption of Sr after exposure at pH = 3.2. *In situ* measurements also reveal a negligible coherent fraction at pH 3.2 indicating a random Sr ion location (i.e., Sr ions are not found in the condensed layer). These results suggest that the non-zero f values derived from the *in situ* measurements at pH ~ 11 reflect the *in situ* EDL structure of Sr ions.

Our data show that the coherent fraction increases for both *in situ* and *ex situ* data when the samples are exposed to the highest solution concentrations, $[\text{Sr}]_{\text{aq}}$. This implies that the fraction of double layer ions found in the condensed layer increases with $[\text{Sr}]_{\text{aq}}$.

The coherent position measured *in situ* is ~7% smaller than that measured *ex situ* corresponding to a difference of the ion heights under the respective conditions of 0.23 Å. The overall similarity between the *in situ* and *ex-situ* results, coupled with the high reproducibility of these measurements suggests that the Sr ion location is determined primarily by the ion-substrate interaction, and further suggests a well-defined adsorption site. It also provides confidence in the derived Sr ion location for the *in situ* measurements in spite of the relatively small coherent fractions found in those measurements. However the small but finite difference between these results appears to be significant especially as it is found systematically over a broad range of solution ion concentrations. This suggests that the adsorbed Sr location exhibits some sensitivity to its environment but needs to be confirmed with further measurements.

We have demonstrated the capability to directly probe important aspects of the EDL at mineral-fluid interfaces using the Bragg XSW technique for both *in situ* and *ex situ* measurements.

Aspects of the EDL structure that can be directly probed in this manner include the location of ions in the condensed layer and the partitioning of ions between the condensed and diffuse layers as a function of pH and solution ion concentration. These results suggest that these aspects of the ion distribution near a mineral-water interface can now be measured directly, *in situ*, to yield a truly atomistic understanding of the EDL structure.

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