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INTERFACIAL X-RAY SCATTERING FROM SMALL SURFACES: ADAPTING MINERAL-FLUID STRUCTURE METHODS FOR MICROCRYSTALLINE MATERIALS

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Abstract—Crystal truncation rod (CTR) X-ray diffraction is an invaluable tool for measuring mineral surface and adsorbate structures, and has been applied to several environmentally and geochemically important systems. Traditionally, the method has been restricted to single crystals with lateral dimensions >3 mm. Minerals that meet this size criterion represent a minute fraction of those that are relevant to interfacial geochemistry questions, however. Crystal screening, data collection, and CTR measurement methods have been developed for crystals of <0.3 mm in lateral size using the manganese oxide mineral chalcophanite ($ZnMn_3O_7 \cdot 3H_2O$) as a case study. This work demonstrates the feasibility of applying the CTR technique to previously inaccessible surfaces, opening up a large suite of candidate substrates for future study.

Keywords—Birnessite · Crystal truncation rods · Mineral-water interface · Surface structure

INTRODUCTION

Crystal truncation rod (CTR) X-ray scattering probes atomic-level structural details of surfaces and interfaces on single-crystal samples (Fig. 1) (Fenter, 2002; Robinson, 1986). It takes advantage of weak lines or 'rods' of scattered X-ray intensity between Bragg peaks, and perpendicular to crystal surfaces, that encode atom positions and occupancies at interfaces. The technique can be used to determine mineral terminations, the structures of interfacial water layers, and the positions of adsorbates. CTR measurements can be conducted in two geometries. Specular measurements (Fig. 1a) are one-dimensional and probe only the laterally averaged surface-normal electron density, but can determine heights of laterally disordered structures such as layered water. Off-specular measurements (Fig. 1b) allow for the refinement of three-dimensional interfacial structures that are registered with respect to the bulk crystal. Surface scattering signals are many orders of magnitude weaker than bulk Bragg peaks, requiring the use of synchrotron light sources. The University of Chicago GSECARS beamlines 13-BM-C and 13-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory have been optimized for these experiments. The 13-BM-C beamline has a bending magnet source that operates at fixed energy (either 15 or 28.6 keV) and provides larger blocks of beamtime than the 13-ID-C undulator beamline. The greater accessibility to the 13-BM-C beamline makes it an excellent resource for crystal screening and preliminary measurements, while 13-ID-C offers tunable energy and significantly greater X-ray flux.

To date, CTR has been applied to the surfaces of 18 minerals including four silicates, three carbonates, three phosphates, one sulfate, and seven (oxyhydr) oxides at GSECARS beamlines and others (Table 1). These studies used crystals with lateral surface dimensions typically >3 mm. The CTR approach used to measure these systems previously required large, perfect, single-crystal substrates which intercepted the full X-ray beam footprint at small (2–4°) incidence angle (i.e. the angle made by the incident X-ray beam with respect to the surface of the crystal). In a previous study of the hydrated goethite (100) surface (Ghose et al., 2010), a rare 1 mm×1 mm crystal was measured successfully thanks to the unique X-ray optics developed at GSECARS. The mirrors that supply X-rays to the 13-ID-C endstation are capable of focusing the full APS undulator beam to ~30 μm (full width at half maximum; FWHM), corresponding to a beam footprint on the sample surface of 430–840 μm at 2–4°, allowing the beam footprint to remain within the bounds of the goethite surface. Even when the lateral size requirement is reduced to 1 mm, however, much important science is still inaccessible, as it is nearly impossible to find many minerals with single-crystal surfaces this large.

The conventional constraint of preventing the X-ray beam from overfilling the samples is imposed for two reasons: (1) during off-specular CTR measurements the sample must rotate azimuthally. Preventing spill-off during sample rotation keeps the

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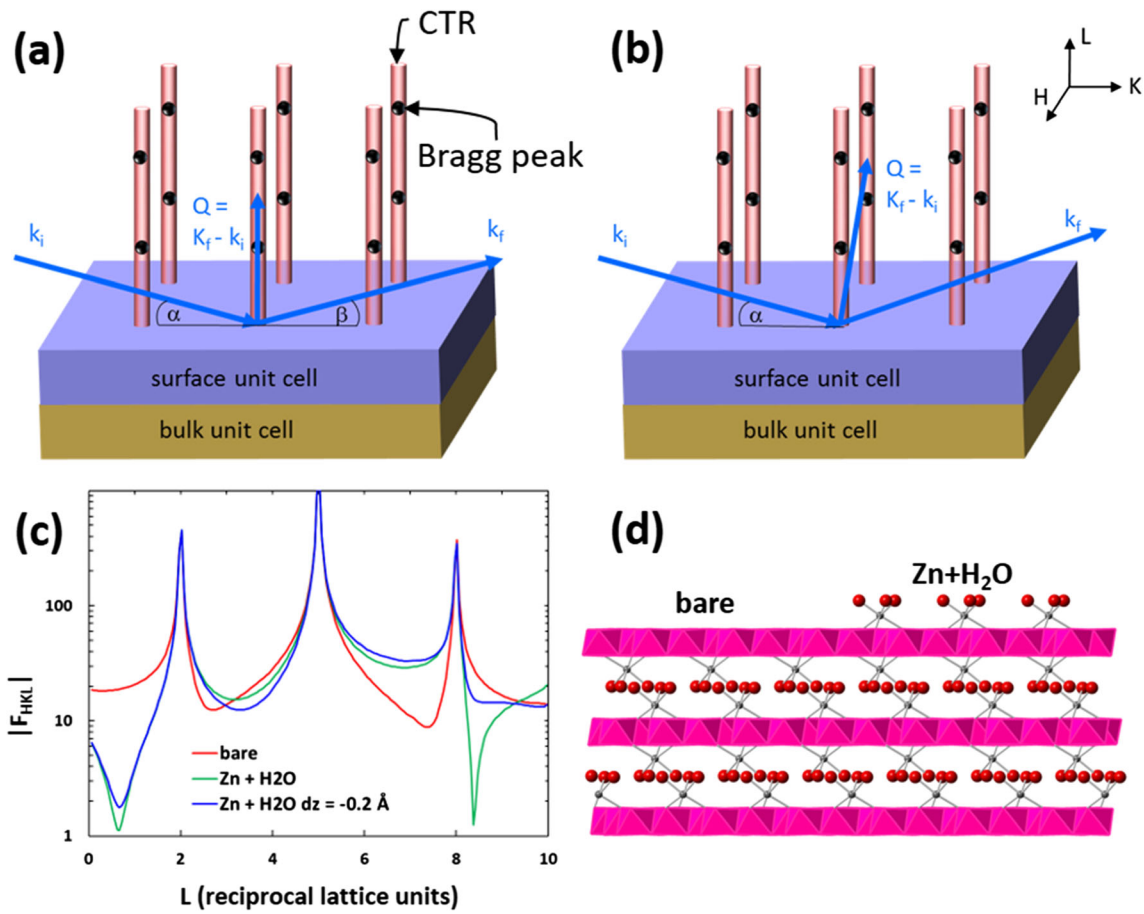


Fig. 1. a, **b**Crystal truncation rods (CTR) are weak lines of X-ray intensity that are perpendicular to the surface and pass through Bragg peaks in reciprocal space. k_i = incident X-ray wave vector; k_f = final scattered wave vector; Q = momentum transfer; α = angle of incidence x-ray beam makes with surface; β = angle of exit; HKL = Miller indices for a surface unit cell with H and K in the surface plane and L normal to it. **a** Specular measurement geometry; α = β, Q ⊥ surface. **b**Off-specular geometry; α fixed, Q has both lateral and surface-normal components. **c** Calculated 20L CTR for chalcophanite ($ZnMn_3O_7{\cdot}3H_2O$) basal plane assuming 'bare' surface (red), surface with Zn and water in bulk positions (green), and surface with Zn and water, as depicted in **d** shifted 0.2 Å toward bulk (blue). CTR profiles are highly sensitive to crystal termination and adsorbate structures

number of surface atoms participating in the scattering constant. (2) Photons that spill off the sample edges will be scattered by the sample holder or other materials. When the number of photons intercepted by the sample surface is comparable to those traversing beyond the sample's edges, the surface diffraction signal becomes difficult to distinguish from the background scattering produced by the sample-support structure.

The present study reports on the development of techniques to measure CTRs from crystals with surfaces a few hundred microns in lateral extent, of sample environments enabling such measurements in the presence of liquids, and of methods for screening microcrystals to identify those of sufficient quality for successful CTR experiments.

METHODS DEVELOPMENT

Methods for Measuring Microcrystals

A method has been pioneered for making CTR measurements from the surfaces of crystals with lateral dimensions as small as 100 μm – an order of magnitude smaller than most previous studies. This is achieved by using the beamline's X-ray optics to adjust the beam footprint so that the entire sample surface is illuminated (thus keeping the number of participating surface atoms fixed). The amount of the beam which 'spills' off the surface is limited to the size needed to illuminate the full sample given eccentricity of the rotation stage, thus minimizing the background scatter from the sample mount. During pilot experiments, background scatter was minimized by attaching samples via electrostatic attraction to high-symmetry, single-crystal substrates composed of low atomic number elements, e.g. diamond or quartz (Fig. 2). The X-ray beam is allowed to spill off of the edges of the microcrystal onto the support crystal, which generates far lower background than typical amorphous or polycrystalline sample cell materials. During specular measurements, the incidence angle varies, and therefore so does the fraction of the beam that spills. Application of a geometric spill-off correction, as is frequently performed for low-angle reflectivity measurements, is relatively straightforward as the crystal does not rotate azimuthally in this measurement mode. The use of single crystals as low-background holders is well established

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Table 1. Minerals investigated to date using CTR

Mineral class	Mineral name	Chemical formula	References
Silicates	Quartz	SiO_2	Bellucci et al. (2015),
			Schlegel et al. (2002)
			Park et al. (2005)
	Orthoclase	$KAlSi_3O_8$	Fenter et al. (2000a, 2003a, 2003b, 2008, 2010a, b, Fenter et al., 2014),
			Teng et al. (2001)
	Forsterite	Mg_2SiO_4	Yan et al. (2014)
	Muscovite	$KAl_3Si_3O_{10}(OH)_2$	Bourg et al. (2017)
			Brugman et al. (2018, 2020)
			Cheng et al. (2001)
			de Poel et al. (2014a, 2014b, 2017)
			Fenter et al. (2010a, b)
			Hellebrandt et al. (2016)
			Lee et al. (2007, 2008, 2009, 2010a, 2010b, 2011, 2012, 2013a, 2013b, 2016, 2017, 2019)
			Pintea et al. (2016, 2018)
			Qiu et al. (2018a)
			Schlegel et al. (2006)
			Schmidt et al. (2012a, 2012b, 2013, 2015)
			Stubbs et al. (2019)
			Yuan et al. (2019a)
Carbonates	Calcite	$CaCO_3$	Callagon et al. (2014, 2017)
			Chiarello and Sturchio (1995)
			Fenter and Sturchio (1999, 2012)
			Fenter et al. (2000b, 2013)
			Geissbuhler (2004)
			Heberling et al. (2011, 2014)
			Hofmann et al. (2016)
			Lee et al. (2016)
			Magdans et al. (2006)
	Dolomite	$CaMg(CO_3)_2$	Callagon et al. (2017)
			Fenter et al. (2007)
			La Plante et al. (2018, 2019)
	Rhodochrosite	$MnCO_3$	Jun et al. (2007)
Phosphates	Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	Pareek et al. (2009)
			Park et al. (2004)
	Archerite	KH_2PO_4	de Vries et al. (1998, 1999)
			Kaminski et al. (2005, 2006)
			Reedijk et al. (2003)
	Xenotime	YPO_4	Stack et al. (2018)
Sulfates	Baryte	$BaSO_4$	Bracco et al. (2017, 2019)
			Fenter et al. (2001)
Oxides	Corundum	Al_2O_3	Catalano (2010, 2011)
			Catalano et al. (2005, 2006a, 2008)
			Eng et al. (2000)

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Table 1. (continued)

Mineral class	Mineral name	Chemical formula	References
			Trainor et al. (2002)
			Xu et al. (2018, 2019)
	Hematite	Fe_2O_3	Catalano (2011)
			Catalano et al. (2008)
			Catalano et al. (2006b, 2007a, 2007b, 2009, 2010)
			Lutzenkirchen et al. (2015)
			McBriarty et al. (2017, 2018, 2019)
			Noerpel et al. (2016)
			Qiu et al. (2018b)
			Tanwar et al. (2007a, 2007b, 2008, 2009)
			Trainor et al. (2004)
			Waychunas et al. (2005)
	Magnetite	Fe_3O_4	Petitto et al. (2010)
	Periclase	MgO	Kim and Baik (1994)
			Kim et al. (1993)
			Robach et al. (1998)
	Rutile	TiO_2	Kohli et al. (2010)
			Zhang et al. (2004, 2006, 2007)
	Uraninite	UO_2	Stubbs et al. (2015, 2017)
Oxyhydroxides	Goethite	FeO(OH)	Ghose et al. (2010)

in powder diffraction but has not, to the authors' knowledge, been extended to CTR. This method of mounting and measuring small crystals enabled CTR measurements of the basal plane of the Mn-oxide, chalcophanite ($ZnMn_3O_7{\cdot}3H_2O$). This sheet-structured mineral (Fig. 1d) is a single-crystal proxy for phyllomanganates of the birnessite group, which are important in both energy storage and environmental applications, and are known to sequester significant quantities of contaminant metals from mining and smelting operations (Post & Appleman, 1988; Morin et al., 1999; Post, 1999; Manceau et al., 2000; Hochella et al., 2005; Shope et al., 2006; Vanek et al., 2008; Bargar et al., 2009; Fuller & Bargar, 2014; Post & Heaney, 2014; Kimball et al., 2016).

Chalcophanite crystals from Sterling Hill, New Jersey, were provided by the National Museum of Natural History (Sample C1814). The first crystals were selected on the basis of size, morphology, and visible light surface reflectivity as viewed with an optical microscope. Once selected, crystals were attached by electrostatic attraction to a thin needle or wire. A droplet of deionized water was deposited on the diamond or quartz substrate that had been pre-mounted with beeswax to a 3 mm brass pin (Fig. 2a), then the chalcophanite crystal was deposited in that droplet. Excess water was wicked away with a cotton-tipped swab. The sample assemblies were next inserted into a holder covered with a Kapton dome through which humid helium gas was allowed to flow during measurements (Fig. 2c). Initial experiments revealed angular instability of the mount that diminished over the course of many minutes to an hour, probably resulting from the slow evaporation of thin water layers trapped between the chalcophanite and substrate. Subsequent samples were allowed to dry for >30 min in a laminar flow hood prior to measurement, eliminating this instability.

CTR data sets collected from several crystals showed excellent agreement (Fig. S1, Supplementary Material), demonstrating the viability of the measurements, and indicating that the chalcophanite growth face has a well-defined, consistent surface structure. These initial, proof-of-concept measurements produced exciting results but were somewhat inefficient, due to the labor-intensive process of evaluating the chalcophanite crystals optically, manipulating them onto diamonds, and screening them one-by-one at the beamline. Crystals that have both bulk and surface qualities that are appropriate for CTR are relatively rare and difficult to identify optically but, once mounted, crystals can be evaluated quickly using fast alignment scans of bulk Bragg peaks and brief snapshots of surface X-ray scattering intensities. Thus, the rate-limiting step is the one-by-one mounting procedure itself.

Screening Procedure

A more efficient method has been developed for semi-automatic screening at the 13-BM-C station (Fig. 3). Numerous crystals are deposited on a 30 mm×30 mm quartz wafer (Fig. 3b). The wafer is mounted on a long travel (25 mm) *x*-*y* sample stage with the wafer surface coincident with the diffractometer's center of rotation (Fig. 3a). Positions of

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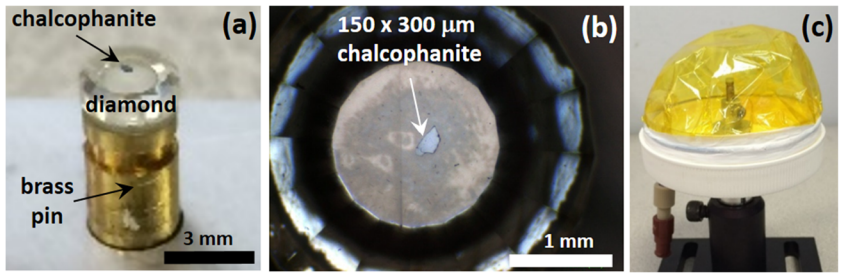


Fig. 2. a Chalcophanite mounted by electrostatic attraction to diamond, which is affixed to a brass pin. **b** Sample crystals <300 µm are mounted readily by this method. **c** Sample is covered by Kapton dome through which humidified helium is allowed to flow during measurement

individual crystals are then mapped using an optical microscope that is centered and focused on the rotation center. The in-plane positions (x, y) are determined using the microscope crosshair (Fig. 3c), and the surface-normal height (z) is determined initially using the depth of focus of the microscope and subsequently refined with X-rays. The sample stage setting (x, y, z) is saved for each crystal. A specular Bragg peak is used for initial alignment. The bulk crystal quality is assessed by measuring the rocking curve of the Bragg peak. In this measurement the crystal is rocked through an angle to determine the width of the diffraction feature with the detector position held fixed. Those with rocking curve FWHM < 0.3° have their alignments refined and CTR intensities are spot-checked at a few points along the specular rod. Crystals are ranked on the basis of bulk and spot-checked surface quality, and those that pass the initial tests undergo three-dimensional alignment and additional CTR measurements. Further observations about crystal and surface quality are recorded, and short CTR data sets, including specular and off-specular data, are collected from the best crystals. These data inform a second ranking scheme that is used to identify candidates for further measurement and experimentation. A typical user experiment at 13-BM-C lasts 3 days, during which >100 crystals may be screened. Roughly 10% of chalcophanite crystals examined in this manner are suitable for further study.

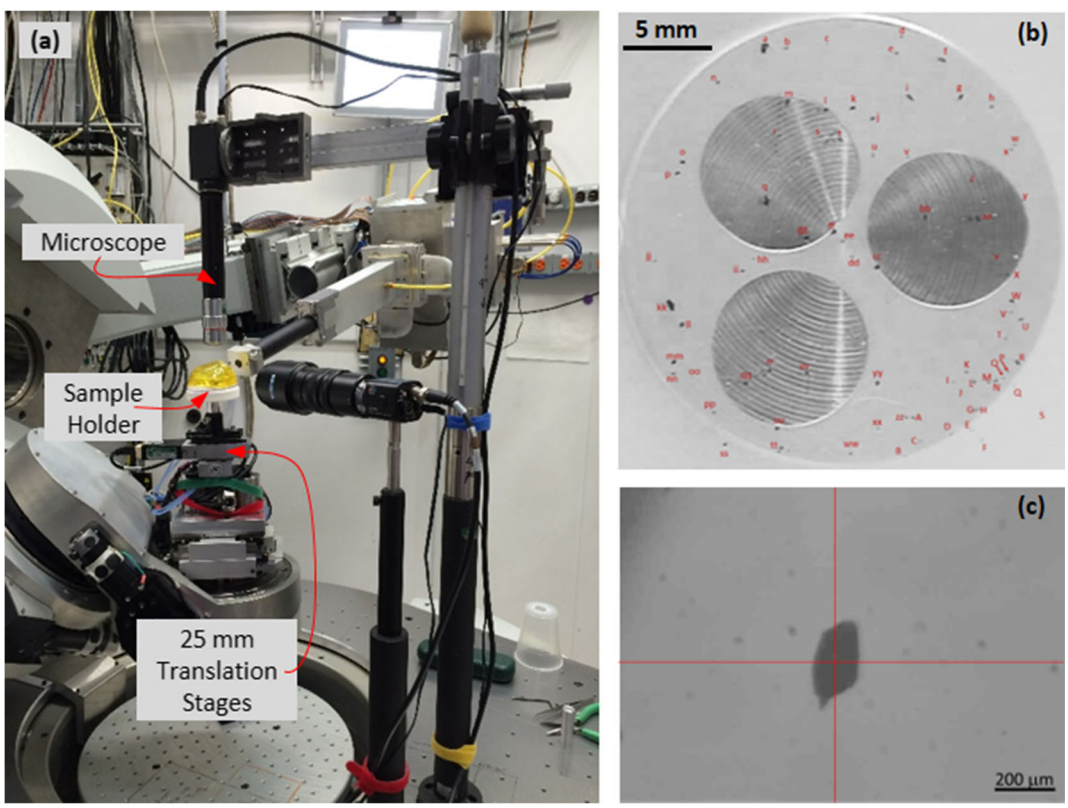


Fig. 3. Crystal screening setup on the diffractometer at beamline 13-BM-C. **a** Samples in Kapton-covered holder are mounted on 25 mm translation stages and viewed with microscope. **b** Chalcophanite crystals are distributed on quartz wafer for efficient screening. **c** Microscope crosshair is used to center crystals on diffractometer rotation axis

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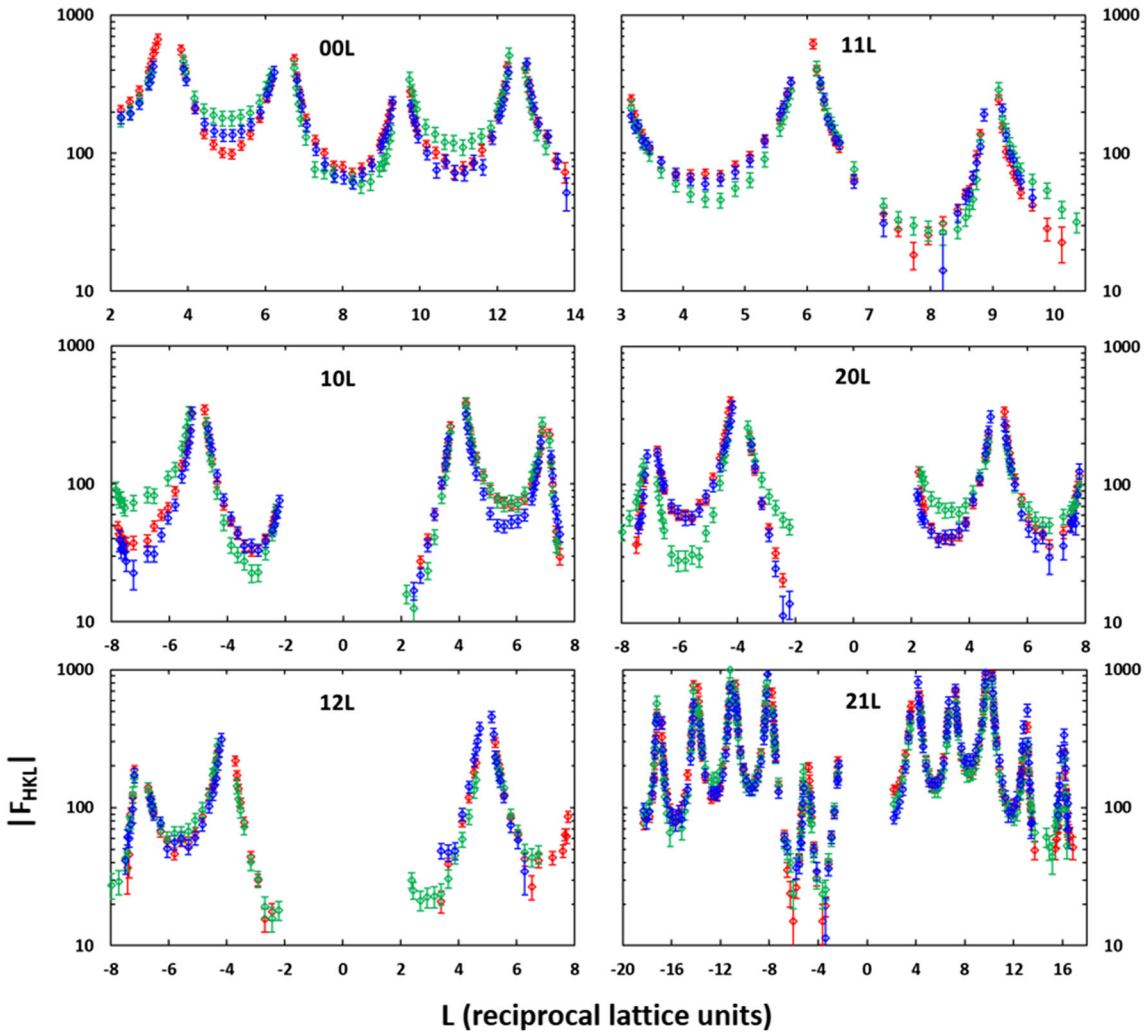


Fig. 4. CTR data collected from a chalcophanite surface in a clean state (red), after dosing with 100 mM CsCl solution (green), and after rinsing with DI water (blue). The 10L, 20L, and 11L rods experienced reversible modifications. Modifications to the 00L (specular) rod were partially reversed upon rinsing.

Ex situ Adsorption

In addition to measurement of the untreated growth surface, the feasibility of adsorption experiments was also tested. Crystals were exposed to a 100 mM solution of CsCl (Alfa Aesar, Haverhill, Massachusetts, USA), wicked dry, and measured in the same humid He environment as the untreated growth surfaces. Modifications were observed on both specular and off-specular rods (Fig. 4) that were reproducible across multiple crystals. For changes to appear on the off-specular rods, adsorption must occur in a manner that is laterally registered with respect to the bulk. Upon rinsing with DI water, the off-specular CTRs returned to their original, untreated profiles (Fig. 4), while the specular CTR recovered partially. These results indicated that the laterally registered Cs sorption was reversible. They also suggested that the Cs atoms did not replace surface Zn atoms. Had they done so, the off-specular CTRs would not have returned to their original profiles after rinsing. Additional crystals were exposed to solutions of $ZnCl_2$ and $Zn(NO_3)_2$ (Alfa Aesar, Haverhill, Massachusetts, USA), again resulting in modifications to both specular and off-specular CTRs (Fig. S2), including regions of reciprocal space other than those affected by CsCl. This suggests structurally different adsorbate conformations for the Cs^+ and Zn^{2+}. In the case of the Zn-bearing solutions, powder diffraction rings were observed indicating the precipitation of powders on the mineral surface and highlighting the need for environmental cells that retain liquid solution in contact with microcrystal surfaces for in situ measurements.

Mounting Crystals for in situ Measurements

Static adhesion to diamond and quartz substrates is an excellent method for mounting microcrystals for measurement in a gas-filled environment, but cannot be used when exposure to aqueous solutions is required, as is the case for many geochemical investigations. While large crystals can be held in place by the same thin Kapton membranes that are used to

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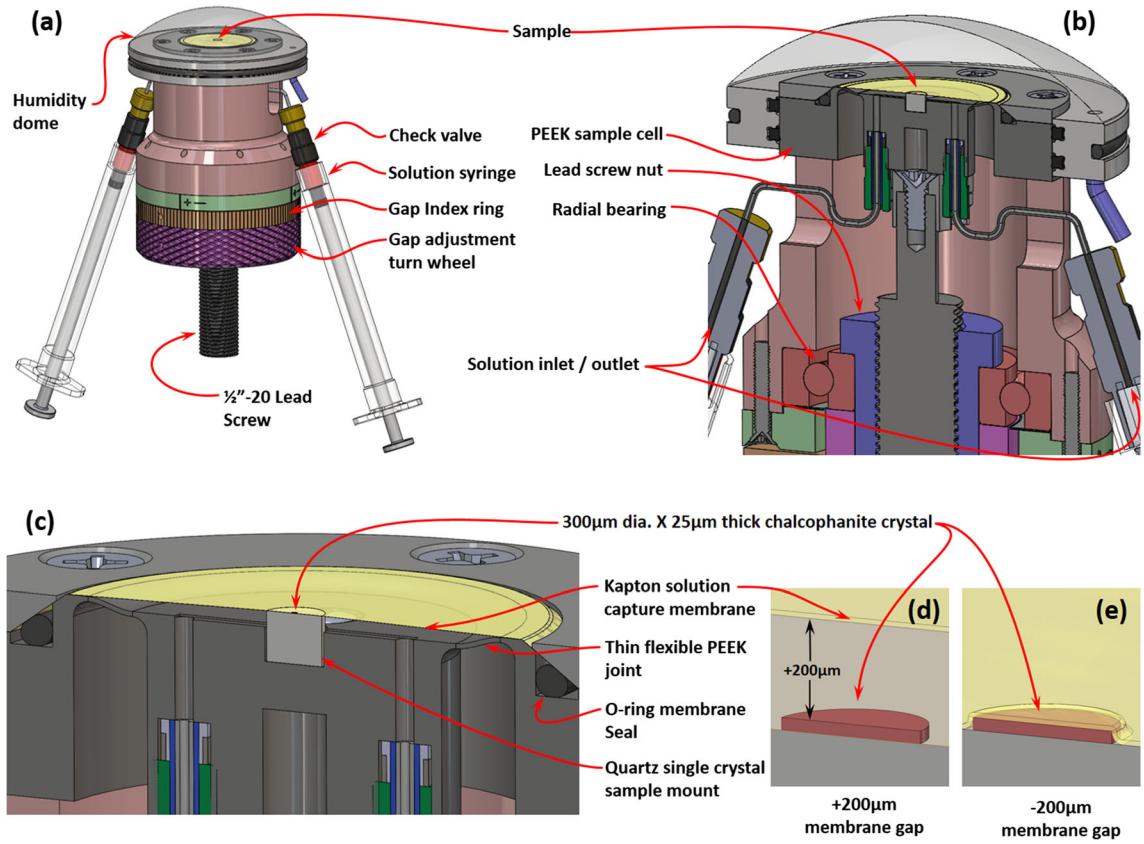


Fig. 5. Liquid cell. **a** Full cell with solution connections, humidity dome, lead screw, and gap-adjustment turn wheel. **b** PEEK sample cell, lead screw nut, and radial bearing. **c** Quartz single crystal sample mount, microcrystal sample, thin flexible PEEK joint, and Kapton solution capture membrane. **d** Sample cell set to a positive membrane gap so that reactions can occur under a thick layer of bulk solution. **e** Sample cell set to a negative gap that traps a solution layer a few microns thick and lowers the rim of the cell below the sample surface to allow X-ray access at low incident and scattering angles

hold liquids on their surfaces (Fenter, 2002; Stubbs et al., 2019), this strategy falls short for microcrystals, especially when the back surface of the crystal is rough or stepped. Early attempts using this method revealed that pulling a membrane tightly against chalcophanite microcrystals results in significant strain or fracture, and indicated the need for a robust, but more gentle means of affixing a crystal that is independent of the film that holds the liquid in place. This motivated a search for an adhesive that can be used to mount these inherently difficult to handle microcrystals. Thermoplastic resins such as Crystalbond™ are used frequently in CTR measurements of larger crystals, but their use is not feasible when the crystal

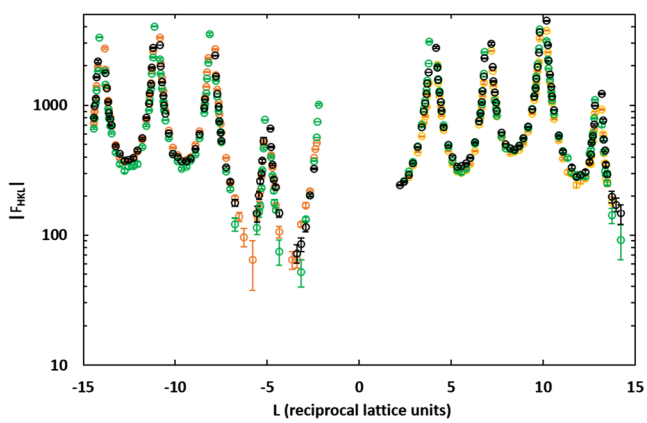


Fig. 6. 21L and symmetry equivalent CTRs show excellent agreement. Data are from a crystal mounted on a quartz substrate using UV-cured adhesive and measured under water in the new, in situ cell

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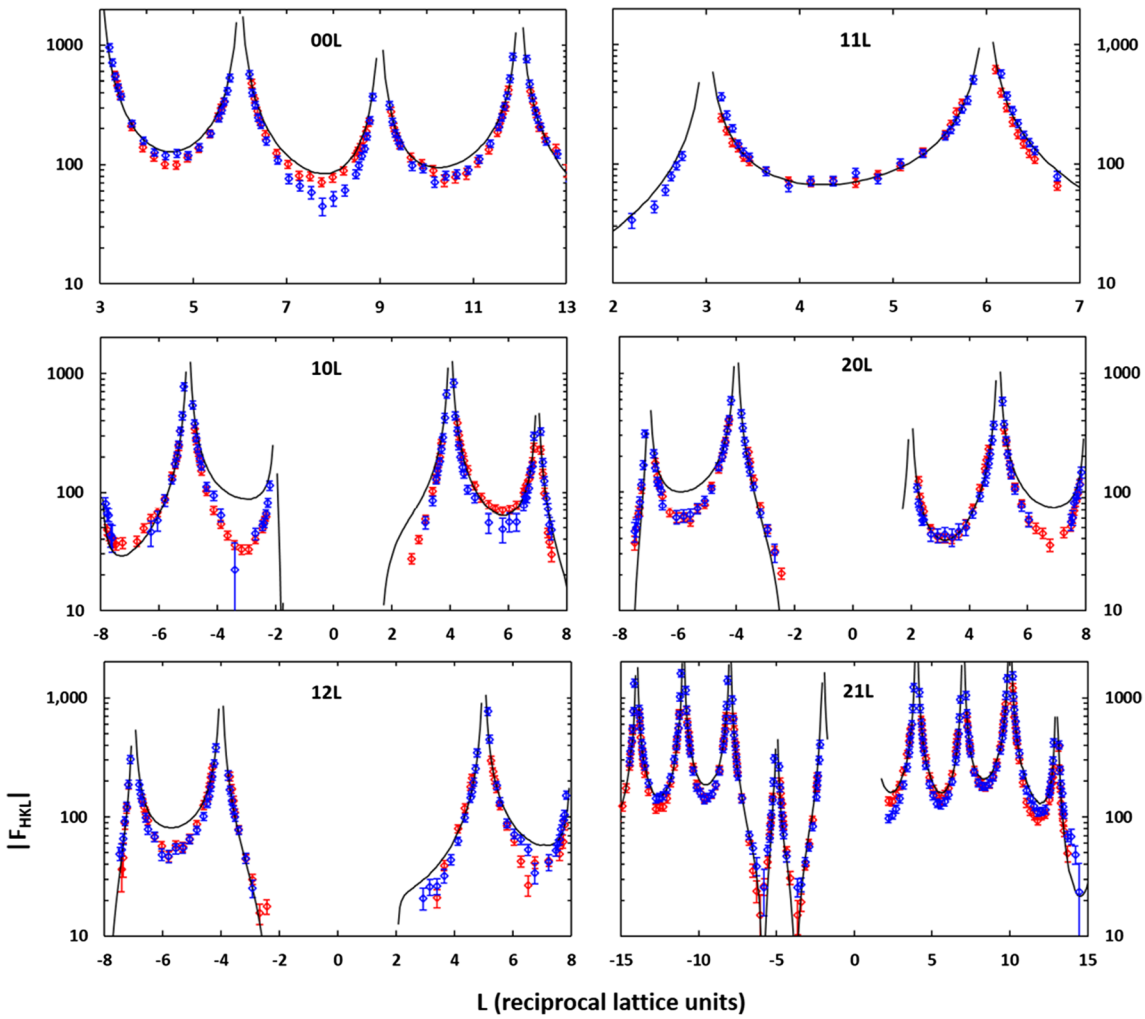


Fig. 7. Data collected from a chalcophanite crystal affixed to quartz with UV adhesive under deionized water (blue) are qualitatively similar to those collected from a different crystal attached by static attraction to diamond under humid helium (red). Black curves are calculated CTRs from a model that includes a layer of Zn and water at the surface, as shown in Fig. 1d, with no roughness or relaxation of atoms from bulk positions and occupancies

must be manipulated with a needle and positioned under a microscope.

A process has been optimized for depositing 100–300 μm crystals onto similarly sized droplets of UV-cured adhesive, and curing with UV light from behind**.** Several UV adhesives from multiple vendors were evaluated, and the most successful was Norland Optical Adhesives (Cranbury, New Jersey, USA) NOA86. A UV cure box (FormCure, Formlabs, Somerville, Massachusetts, USA) has been modified to replace the standard 405 nm wavelength LEDs with 365 nm wavelength LEDs, and the adhesive is cured overnight at a temperature of 60°C. It is then allowed to sit in fluorescent room light for several days while polymerization continues. Chalcophanite CTRs measured after UV curing by this method are very similar to those measured before, indicating that the crystal is undamaged and the ordered part of the surface is unchanged. Other minerals, however, could possibly experience damage and the method should be validated when applied to new systems.

Quartz single crystals are highly transparent to 365 nm UV light, aiding with adhesive curing, and are chemically inert, making them excellent substrates for aqueous surface chemistry experiments. Quartz wafers oriented to the (5-1-1) surface are commercially available as 'no background' holders for powder diffraction experiments (MTI Corp., Richmond, California, USA). In this orientation, the first Bragg reflection in the specular direction is at L ~22.7 for chalcophanite, mitigating interferences between quartz Bragg peaks and the chalcophanite specular CTR. Sometimes interferences are observed between low-angle quartz reflectivity and the lowest-L region of the specular CTR. This is usually alleviated by a mismount or tilt of the microcrystal (due to steps or

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protuberances on the back side) with respect to the quartz surface of several tenths of a degree, which makes separation of the two signals straightforward, and the quartz reflectivity is simply excluded during data integration. For off-specular CTRs, it would take an extraordinary coincidence in alignment to produce overlap of a Bragg peak or CTR from the quartz with a CTR from the microcrystal, although occasionally thermal diffuse scatter from nearby quartz Bragg peaks interferes over small regions of reciprocal space. These regions are excluded from the data sets. Far from quartz Bragg peaks, diffuse scatter arising from the quartz single crystal is weak and broad when compared to CTRs, and is easily subtracted as background.

In situ Sample Environment

Quartz wafers 2.5 mm thick are core drilled into cylinders with 3 mm diameters, which are clamped rigidly inside a PEEK sample cell (Fig. 5). This cell includes two ports for solution injection and extraction, which are capped with Luer Lock check valve fittings (Idex Health and Science, Oak Harbor, Washington, USA) such that solution exchanges can be made with syringes that are disconnected prior to measurement (Fig. 5a). The central post into which the quartz cylinder is clamped is supported rigidly on a ½ inch - 20 lead screw, which is itself mounted rigidly on the diffractometer. Solution is held in place by a Kapton membrane that is attached to an outer ring which surrounds the inner post (Fig. 5c, d, e). The two sections of the cell (post and membrane support) are machined from a single piece of PEEK, and are connected by a thin, flexible PEEK joint (Fig. 5c). The Kapton membrane is raised and lowered with respect to the sample surface by means of a nut that rides on the central lead screw, flexing the thin PEEK joint. This mechanism is hand-actuated using the gap adjustment turn wheel (Fig. 5a). Prior to solution injection, the membrane is raised to produce a gap between Kapton and sample (Fig. 5d), such that reactions can occur under several hundred microns of bulk solution. Prior to measurement, solution is extracted by closing one check valve and gently withdrawing liquid through the other while lowering the membrane ring to a height below the sample surface (negative gap), trapping a layer of solution a few microns thick (as verified by the appearance of visible-light interference fringes, i.e. Newton's rings) (Fig. 5e). To mitigate diffusion and evaporation of water through the Kapton membrane, humidified helium is flowed through a domed Mylar membrane cover (Fig. 5a). This cell design is conceptually similar to a previous cell (Trainor et al., 2006), but offers a simplified, easy to manufacture and customizable cell that can be modified to match sample size. The manually driven nut mechanism replaces an earlier motorized stage, making it possible to produce multiple cells quickly and inexpensively. The new cell's PEEK flexure joint between the sample support post and membrane eliminates, from the earlier design, a sliding O-ring seal that was often a source of solution leaks and excess sliding friction.

Stability During in situ Measurements

The UV adhesive mounts are dimensionally stable in the X-ray beam under dry and humid gas, and also stable for many hours in liquid water in the absence of X-rays. The microcrystal alignment drifts gradually over time in the presence of both X-rays and water, however, indicating that the adhesive is sensitive to the products of X-ray-induced water radiolysis. A software solution was developed that realigns the crystal using two Bragg peaks on each CTR immediately prior to its measurement, enabling automatic correction for slowly drifting alignments during data collection. Symmetry-equivalent CTRs show excellent agreement (Fig. 6), indicating that the software alignment correction is effective, and the practice of allowing the beam to overfill the sample surface and spill over the edges results in uniform illumination, even during the azimuthal rotation required for off-specular measurements. Data collected from chalcophanite crystals under deionized water are qualitatively similar to those measured under humid helium (Fig. 7), indicating that the beam damage to the adhesive does not result in ordered modification of the surface, although the deposition of disordered contaminants cannot be ruled out. CTRs calculated from a model with Zn and water molecules at the surface, as shown in Fig. 1d (with no roughness or relaxation of atoms from bulk positions) reproduce measured intensities near Bragg peaks and over much of the CTRs between them (Fig. 7). Discrepancies between the model and data result from differences between the real interfacial structure and this simplified, idealized model. Quantitative fitting of an atomic scale model is ongoing and will be the subject of a separate publication. Measurements designed to probe in situ adsorption and cation exchange are also under way, using solutions containing Cs^{+}, Zn^{2+}, and other cations.

DISCUSSION AND OUTLOOK

The ability to measure CTRs from crystals with lateral dimensions as small as 100 μm, especially in the presence of liquid water, expands significantly the range of candidate synthetic and natural mineral surfaces that can be studied, and represents a major advance in the technique. The next stages of development will target even smaller crystals, which pose challenges with respect to sample handling, adhesive deposition, and signal-to-background ratios as the number of surface atoms decreases.

A second set of considerations arises around the thickness of the crystals being measured, and whether the measurement will probe both the front and back surfaces. CTR measurements are usually made at X-ray energies from 10 to 20 keV, and off-specular data are typically collected at an X-ray incidence angle, α, between 2 and 6°. At 15 keV and $\alpha = 4°$, a chalcophanite crystal would need to be >23 μm thick in order to prevent 99% of incident X-rays from reaching the back surface – a criterion more than sufficient to prevent scattering from the back surface from contributing to the measurement.

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Because X-ray absorption depends on density and atomic number in addition to incident energy and path length, the importance of these effects varies widely for different materials. At 15 keV and $\alpha = 4°$, uraninite (UO_2) would require a thickness of ~2 μm whereas quartz would require >200 μm to satisfy the 99% absorption criterion. That criterion overestimates the contribution from the back surface, as X-rays that diffract from a back surface with sufficiently low roughness to present a strong CTR would need to travel back through the thickness of the crystal to be measured. Along this path these X-rays would be subject to diffuse scattering by the bulk microcrystal, further diminishing the CTR signal. Furthermore, some of the X-rays that reach the back surface will exit the microcrystal and be absorbed or scattered by the quartz substrate, and thus be unavailable for return to the front. The contribution from the back surface can be evaluated by reducing α, thus increasing the X-ray path length through the crystal, or by lowering X-ray energy and utilizing the inverse energy cubed dependence of absorption. Specular CTR measurements vary the incidence angle over a wide range, and therefore require extra care in their interpretation when thin crystals with high quality back surfaces are involved. Here again, measurements collected at multiple energies would be highly effective for evaluating the strength of such contributions.

Even with the newly expanded capabilities described here, some crystals remain too small for CTR, and other methods must be employed. Promising among these are those that leverage X-ray coherence, such as Bragg Coherent Diffraction Imaging (BCDI) (Robinson et al., 2001; Pfeifer et al., 2006; Williams et al., 2006). This technique has been used to investigate morphology, defects, strain, and structural responses to aqueous chemistry in mineral nanoparticles including calcite (Clark et al., 2015; Ihli et al., 2016, 2019; Liu et al., 2018) and magnetite (Yuan et al., 2019b). Upgrades are planned or underway for a number of synchrotron facilities, including the APS, that will increase X-ray coherence by roughly two orders of magnitude. Such advances will render the coherent techniques both more powerful and more routinely available to synchrotron users, including members of the Earth Science community.

CONCLUSIONS

Capabilities for screening, mounting, and measuring crystal truncation rods from mineral crystals with lateral dimensions of <300 μm have been developed at the University of Chicago GSECARS beamlines located at the Advanced Photon Source. More than 100 crystals at a time can be screened for bulk and surface quality. The best of these are mounted using UV adhesive onto quartz substrates and clamped in novel environmental cells, enabling exposure to aqueous solutions for in-situ mineral-water interfacial structural measurements. These new capabilities promise to expand dramatically the list of minerals accessible to investigation using CTR.

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Declarations

Conflict of Interest

The authors declare that they have no conflict of interest.

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