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Liquid Cell and Environmental TEM: Frontier Techniques Applied to Geochemical Interface Reactions

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ABSTRACT

Liquid cell and environmental transmission electron microscopy (LC-TEM and eTEM, respectively) are two relatively new techniques that allow for the real time measurement and in situ study of reactions between solids and liquids (LC-TEM) and solids and gases (eTEM). Both techniques offer unprecedented opportunities for exploring, at the subnanometer-scale, the dynamics and mechanisms of interfacial processes that directly control the reactivities of minerals or glasses in contact with liquids and/or gases.

1. ENVIRONMENTAL TEM

The eTEM research we present here is based on experiments conducted at IRCELYON (Institut de Recherche sur la Catalyse et l'Environnement de Lyon, CNRS-UMR 5256, Univ. Claude Bernard Lyon 1, France). More specifically, we are studying nucleation and crystallization processes that occur in the Sr-sulfate-water system. Our experimental work has focused on documenting the transformation of a hydrated metastable precursor phase, Sr-sulfate-hemihydrate (SrSO₄·½H₂O) that has a hexagonal crystal structure, to the final and thermodynamically stable phase, celestine (SrSO₄), which crystallizes with an orthorhombic structure. Each experiment starts by mixing a solution of SrCl₂ and NaSO₄ (both at 100 mM concentration) with gentle stirring, and then immediately filtering the solution with a lab bench vacuum system. A small amount of the residual solid cake is then added to EtOH, followed by placement of a solution aliquot on to a TEM grid. After excess EtOH is wicked away the sample is dried under vacuum overnight. At this early stage of the protocol, the sample is largely composed of bundles of needle-like hydrate crystals.

The first eTEM experiments were performed at ambient temperatures (~20 °C), with $P_{\text{H}_2\text{O}} \leq 20$ mbar. We carried out preliminary imaging at electron fluxes and doses that were adjusted to minimize irradiation effects, based on tests carried out before the experiments. At a macroscopic (μm) scale, the transformation process from the metastable phase to the stable phase is characterized by rapid morphological changes and subsequent disappearance of the elongated needle-like crystals of the hydrate; concomitant to this is the growth of small polygonal crystals of celestine. The two most striking changes we noted were changes in the contrast and surface morphology of the hydrate needles. The smooth surfaces of the hydrate needles all underwent surface roughening over short periods of time (≤ 16 h). This roughening appears to be due to the nucleation and growth of what appear to be individual celestine crystals- these protuberances were quite noticeable on nearly all of the hydrate crystals. Detailed observations at the sub-nanometer-scale often show individual proto-celestine crystals touching the hydrate needles. In these cases, the lattice fringes of celestine are in direct contact with those of the hydrate. The exact nature of the atomic-scale interface between the two structures is still being elucidated. Overall, these high-resolution observations possibly point to a heterogeneous nucleation pathway based on an interfacial mechanism controlled by a spatially close and nearly synchronous coupling between dissolution of hydrate and reprecipitation of Celestine, most likely within a thin interfacial fluid phase in contact with the surface of the hydrate. While referred to by various names by different research groups, we refer to this mechanism as coupled interfacial dissolution-precipitation, or CIDR (e.g., see Hellmann et al., 2003, 2012, 2015, 2021a, b; Hellmann, 2021a, b; and references therein). In other cases, the relation between celestine and hydrate was less clear, as it appeared that isolated groups of celestine crystals may have nucleated directly from the solution. The exact pathway describing how these crystals formed directly, or indirectly via a precursor phase, from the solution is not yet clear. These preliminary results (Lauer et al., 2023) at 20°C are currently being augmented by new experimental data that were obtained at 3-5 °C. Lower temperatures allowed us to achieve very high relative humidities within the sample cell, which led to H₂O vapor condensing on the sample.

2. LIQUID CELL TEM

The second technique that will be presented is the application of LC-TEM to study mineral dissolution in a native solution in real time. One of the major challenges/problems in studying solid-liquid interfaces has been the necessity of using dry, post-reaction samples that are analyzed in instruments that require a high vacuum. Such conditions may have a deleterious effect on the state of the surface and secondary authigenic surface layers (SALs). An LC-TEM project is being carried out in collaboration with the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory, TN (USA). Using the mineral wollastonite (CaSiO₃), we have been conducting experiments that allow us to measure surface dynamic processes in real time, including dissolution, precipitation, step and terrace movement, as well as other surface morphological changes. It turns out that wollastonite is well adapted to this technique because it has an intermediate reactivity, much slower than carbonate minerals, and yet much higher than most silicate minerals. In addition, the wollastonite-liquid interface after alteration (post mortem) has already been extensively studied by classical 'dry' TEM techniques at atomic-scale resolution (Hellmann et al., 2012). The review of the results presented here is based both on published results (Leonard and Hellmann, 2017) and newer unpublished data.

We detail the pioneering technique of welding FIB lamella to the liquid cell holder frame- this enabled us to study relatively large areas on a μm -sized lamella obtained by liftout from a bulk wollastonite sample. In particular, we have thereby avoided using suspensions of nm-sized particles that have an artificially high reactivity. The use of a FIB section using LC TEM allowed us to study dynamic surface processes, such as terrace and step edge movement in situ and in real time at ambient temperatures (~20 °C) and at

List Authors in Header, surnames only, e.g. Smith and Tanaka, or Jones et al.

circum-neutral pH. The time evolution of the various morphological features of the lamella (including a central crack that formed on the lamella during assembly of the liquid cell) showed very unexpected results. It turns out that in most cases the edge and terrace-step retreat velocities were not linear with time, but rather showed three stages: an initial rapid increase (dry to wet transition in liquid cell), a period of stability, and then a quasi-constant rate. The steady-state rates of retreat, corresponding to $t > 200$ minutes (determined by a linear fit to the data), ranged from 1.0 to 1.6 nm/min for horizontal terrace/step features, and 1.8 to 2.2 nm/min for vertical features. Within the error of the measurements, the rates were consistent for the horizontal features (rates corresponding to crack expansion on the lamella). However, the initial terrace-step velocities ($t < 200$ min) associated with crack widening were very different, this pointing to velocity heterogeneity for the same crystallographic plane. Other observations from the same FIB ultrathin section show that it is even possible to observe both precipitation and dissolution reactions occurring simultaneously at adjacent areas of the same surface- this interesting phenomenon reveals the extent to which fluid-mineral interfaces can react in a non-uniform manner.

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