

Synchrotron-based X-ray scattering studies of mineral reactions in complex geochemical systems

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Mineral-solution reactions such as nucleation, particle growth, crystallisation and biomineralisation occur in a wide variety of low-temperature geochemical systems including soils, sediments and contaminated land environments (e.g. permeable reactive barriers). Studying these processes *in situ* can be challenging, as many of these reactions occur in suboxic or anoxic environments, on fast time-scales (seconds-minutes), or are mediated by microorganisms.

Synchrotron-based scattering techniques have been used to characterise the mechanisms and kinetics of mineralogical reactions occurring in a wide variety of geochemical environments. Using facilities on beamlines located at the Synchrotron Radiation Source, UK and European Synchrotron Radiation Facility, France, systems have been developed to allow time-resolved studies of mineral colloid reactions occurring within precisely controlled/monitored (pH, Eh) geochemical environments. Including both abiotic and biotic mineralisation processes.

An automated chemostat/fermentor system has been customised to allow precise control of pH and dissolved oxygen/Eh in a solution/colloid. This facility has been used to synthesize a variety of mineral phases (e.g. green rusts) under suboxic conditions using the controlled manipulation of solution geochemistry. During the mineral formation and crystallisation reactions the colloid is constantly circulated through the X-ray beam allowing time-resolved Small and Wide Angle X-ray Scattering (SAXS/WAXS) data to be collected. This has provided detailed information on particle growth (SAXS) and crystallisation/transformation (WAXS) mechanisms as the pH and Eh of the system was manipulated. Linking the scattering data to the electrochemical information provides a unique and complete picture of the solution and solid-state reaction chemistry.

SAXS studies of biogenic MnOOH nanoparticle formation have enabled particle size and shape to be determined as the biominerals formed on the surface of Mn oxidising microorganisms. Achieved by isolating the X-ray scattering pattern from the particles, and removing background scattering from the microbes and organic matter.

Clays exposed to H₂SO₄ between pH 1.0 and -3.0: A Si and Al XANES study

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Natural and constructed clay liners are routinely used to contain waste and wastewater. Although widely investigated in relation to acid mine drainage systems at pH > 1.0, we know little about the impact of sulfuric acid (H₂SO₄) on the geochemistry and mineralogy of clays at pH < 1.0 (including negative pH values).

Batch experiments were conducted on three clays with different mass ratios of smectite, illite, and kaolinite using four different H₂SO₄ concentrations (pH = 1.0, 0.0, -1.0, -3.0) over four exposure periods (14, 90, 180, and 365 d). The altered clay was recovered and the short-range order of Al and Si analyzed using Al and Si K-edge and L-edge X-ray absorption near edge spectroscopy (XANES).

Results demonstrated that the coordination of Al and degree of Si polymerization of the altered clays can be determined through comparisons with known phyllosilicate, Al, and Si standard spectra. Considerable alteration of the Al and Si crystal structure results from acidic dissolution of the clays. Additionally, results indicate that the Al-octahedral undergoes dissolution, with four-fold coordinated Al persists relative to six-fold coordinated Al under increasingly acidic conditions. Conversely, Si-tetrahedral layers were shown to undergo dissolution only under more acidic conditions and that the degree of Si-tetrahedral polymerization increased as a result. Finally, the formation of a secondary Al-SO₄-rich phase within all three altered clays was noted.

The current study demonstrates the utility of XANES to provide unique and valuable surface and bulk information on the coordination of Al and polymerization of Si in clays altered by acidic dissolution, information that cannot be attained using conventional mineralogical analyses.