

Solving Crystal Structures and Constructing Size-dependent Phase Maps for Nano-minerals

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Understanding interface structures, nano-precipitates, vacancies, impurities, and adsorbed heavy metals on mineral surfaces are important to elucidate formation mechanism and reactions of minerals in the earth environments. Modern technology allows us to detect, characterize, and understand the nature of nano-minerals. In the case of macroscopic minerals, X-ray diffraction is useful tool to study their structure from the Bragg peak positions and intensities. However, this is not realistic for nano-minerals, which show broad and continuous intensity distribution that is not amenable to a crystallographic structure solution. Especially, it is challenging to determine their structures when structures include the short-range ordering, defects, and local domain. Aberration-corrected Z-contrast imaging can provide chemical images with sub-Å resolution. Z-contrast images are HAADF images with atomic resolution. Multiple diffraction effects that appear in high-resolution transmission electron microscopic (HRTEM) images can be eliminated or minimized in Z-contrast images, because Z-contrast imaging uses non-coherent elastically scattered electrons at high scattering angle. We can obtain positions of atoms directly over a large range of thickness, with Z-contrast to help distinguish columns of different atoms and their occupancies along the beam direction. Interface structures and crystal structures of nano-minerals and nano-precipitates can be solved by combining the Z-contrast imaging and *ab-initio* calculation using density functional theory (DFT) methods. Vacancies, impurities, adsorbed heavy atoms can be also revealed directly. Vacancy ordering in Fe-bearing olivine and Fe-sulfides, adsorbed heavy metals (e.g., As, Au, U) on Fe-oxyhydroxide minerals are resolved clearly. Z-contrast imaging provides direct and local information about the nano-minerals. Z-contrast images of the Fe-oxyhydroxides show ordered FeOOH proto-goethite nano-domains intergrown with nanophase goethite. With determined structure topology, the structural details can be tuned by using pair distribution function (PDF) method using total X-ray and/or neutron scattering. Size dependent phase maps for FeOOH, Fe₂O₃, TiO₂, and nano gold systems based on experimental and theoretical calculation methods will be also be presented.