Direct Observation of Heavy Metals and Impurities in Minerals Using Z-contrast Imaging

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Understanding interface structures, nano-precipitates, vacancies, impurities, and adsorbed atoms on mineral surfaces are important to elucidate formation mechanism and reactions of minerals in the earth environments. 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 [1-2]. Z-contrast images of the Fe-oxyhydroxides show ordered FeOOH proto-goethite nano-domains intergrown with nanophase goethite. The FeOOH nanophase is a precursor to the goethite. DFT calculations indicate that goethite is more stable than proto-goethite. Our results suggest that ordering between Fe and vacancies in octahedral sites result in the transformation from feroxyhyte to goethite through a proto-goethite intermediate phase. Combining Z-contrast images and TEM-EDS reveals that arsenate (AsO_4^{3-}) tetrahedra are preferentially adsorbed on the proto-goethite (001) surface (Fig.1). Vacancy ordering in Fe-bearing forsterite olivine was observed. The phenomenon may explain observed highly anisotropic diffusion in some Fe-bearing olivine minerals and more ordered structure analyzed at high-temperature in air. In a Si-bearing magnetite, Si replaces Fe^{3+} in tetrahedral sites of the magnetite structure and vacancies are introduced in the octahedral Fe^{2+} sites (Fig. 2). Nano-precipitates of Si-magnetite with composition of $(\square_{0.5} Fe^{2+}_{0.5})^{VI}(Fe^{3+})^{VI}Si^{IV}O_4$ or $\gamma-Fe_{1.5}SiO_4$ occur in the magnetite [4].

References:

[1] Lee, S., Shen, Z., and Xu, H. American Mineralogist, **101** (2016), p. 1986.
[2] Xu, H., Shen, Z., and Konishi, H. Mineralogical Magazine **79** (2015), p. 377.
[3] Xu, H., Shen, Z., and Konishi, H. American Mineralogist, **99** (2014), p. 2196.
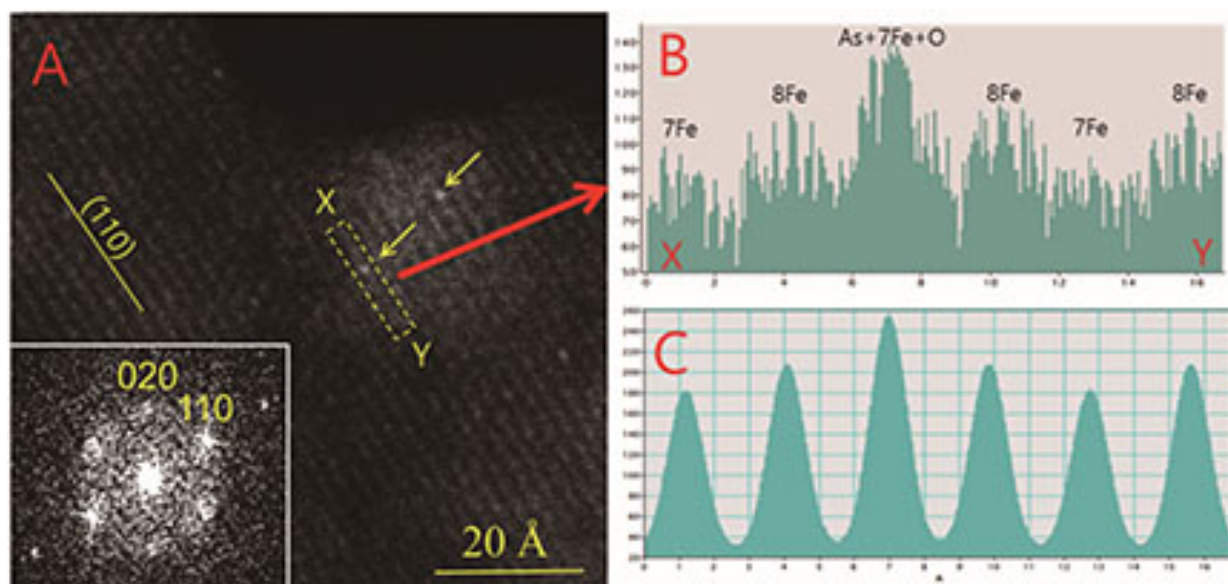[4] Author thanks supports from NASA Astrobiology Institute, National Science Foundation, and US Department of Energy.

Figure 1. (A) a [001]-zone-axis Z-contrast image of proto-goethite, bright spots are positions of Fe atom columns. Very bright spots are adsorbed arsenic (As) atoms on the surface right above Fe; (B) the intensity profile of an outlined area from X to Y; (C) the intensity profile of simulated Z-contrast image showing the peak with As atom above an Fe atom column (Lee at el., 2016).
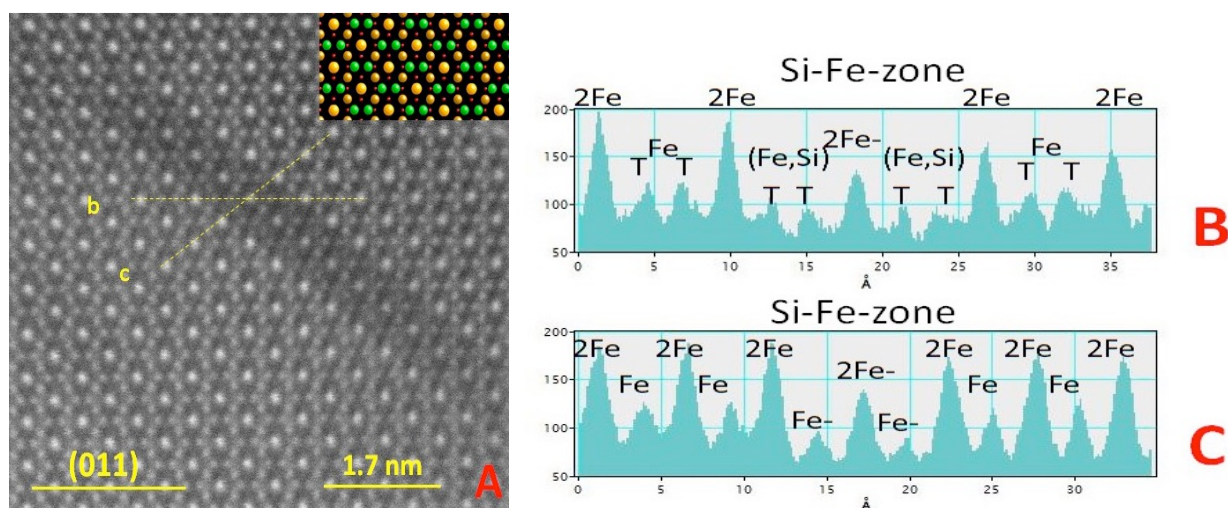

Figure 2. Z-contrast image showing a thin nano-precipitate with thickness of $2d_{111}$. The precipitates are of the Si-magnetite phase, although both the host and precipitates have the same structure. Intensity line profiles can indicate occupancies of Si in tetrahedral sites (T) and vacancies in octahedral sites (labeled by 2Fe-, and Fe- (Xu et al., 2014).