

TEM/STEM Characterization of Soil

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Soil is a complex heterophase material containing clay platelets, humus, and metal oxides, such as those of iron and titanium [1]. Ultimately, it is the nanostructure of these colloids that determines their interaction with plant material, their electrochemistry, and their chemical and physical reactivity. Because of their extremely small size they represent a very large reactive surface area.

In this work we report nanocharacterization of a soil from southeastern Australia, technically classified as an *oxisol* order, but also called *ferrosol*. Specimens for TEM examination were prepared by embedding soil particles in epoxy resin, ultramicrotoming at room temperature, and then depositing the 50- to 100-nm-thick sections on lacey-carbon-covered copper grids. A LaB6 TEM was used for the initial examination of the soil sections, and some typical bright-field images are shown in Fig. 1. On the left we see a stack of clay plates in approximate cross section, and on the right is an aggregate of Fe₂O₃ particles, characteristic of this red-colored soil. Figure 2 shows an HRTEM image acquired with a Tecnai F20 FEGTEM exhibiting the characteristic spacing of hematite in the small particles, consistent with selected-area diffraction.

The structure of the clay phase of the soil is that of kaolinite, a 1:1-type aluminosilicate clay. In this clay there are sheets composed of tetrahedrally coordinated silicon covalently attached to octahedrally coordinated aluminum. In the idealized structure, the outer layer of the coordinated aluminum atoms is hydroxylated, which can react with and bind specific anions. These hydroxyl groups are electron beam sensitive, resulting in dose-limited imaging and spectroscopy. A critical dose of $\sim 10^6$ to 10^7 e⁻/nm² determined by electron diffraction spot fading was consistent with studies of other clays [2,3].

For spatially resolved elemental analysis we used EELS spectrum imaging on the NION UltraSTEM at 60 kV with subpixel scanning and 40 pA beam current. Preliminary dose calculations suggested these operational conditions would minimize radiation sensitivity at 3 nm/pixel resolution. We were particularly interested in observing any association between the iron and clay phases. Figure 3 shows a HAADF image and indicates the area used for elemental analysis. Because of poor signal/background ratios of Si and Al, we used O as a surrogate for the kaolinite phase. In the center of the area marked as *spectrum image* there appears to be a kaolinite particle in approximate cross section and perhaps an iron phase on top. These conjectures are supported by the elemental mapping on the right of the figure.

References

- [1] N. C. Brady and R. R. Weil, *The Nature and Properties of Soils*, 14th ed., Pearson Education, New Jersey (2008).
- [2] B. X. Gu et al., *J. Nucl. Mat.* **297**, 345-354 (2001).
- [3] L. F. Drummy et al., *J. Phys. Chem.* **109**, 17868-17878 (2005).

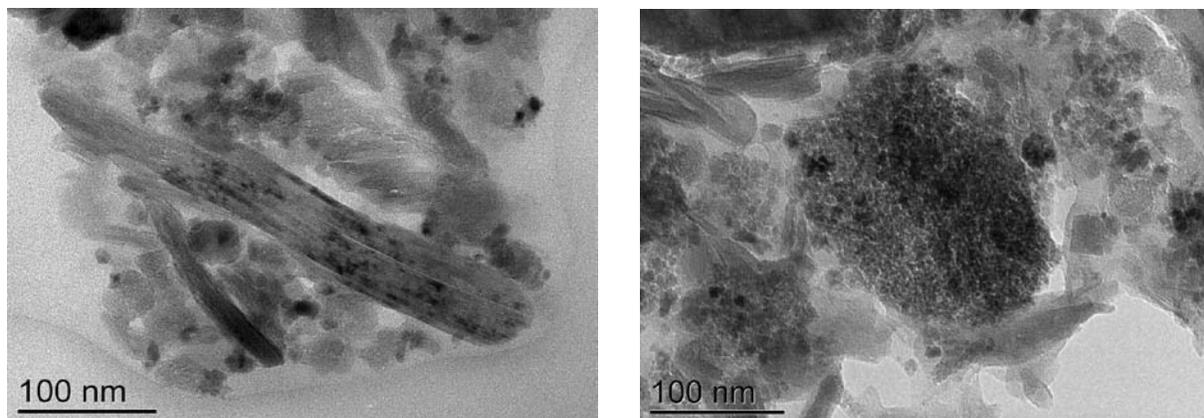


FIG. 1. Bright-field TEM images of Australian soil, showing a clay sheet stack, left, and Fe₂O₃ agglomerate, right.

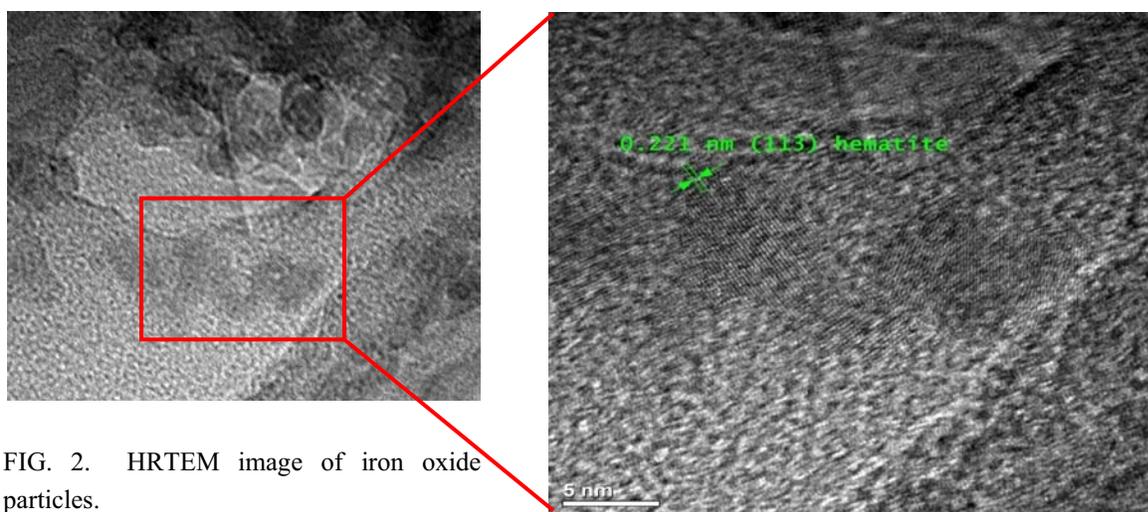


FIG. 2. HRTEM image of iron oxide particles.

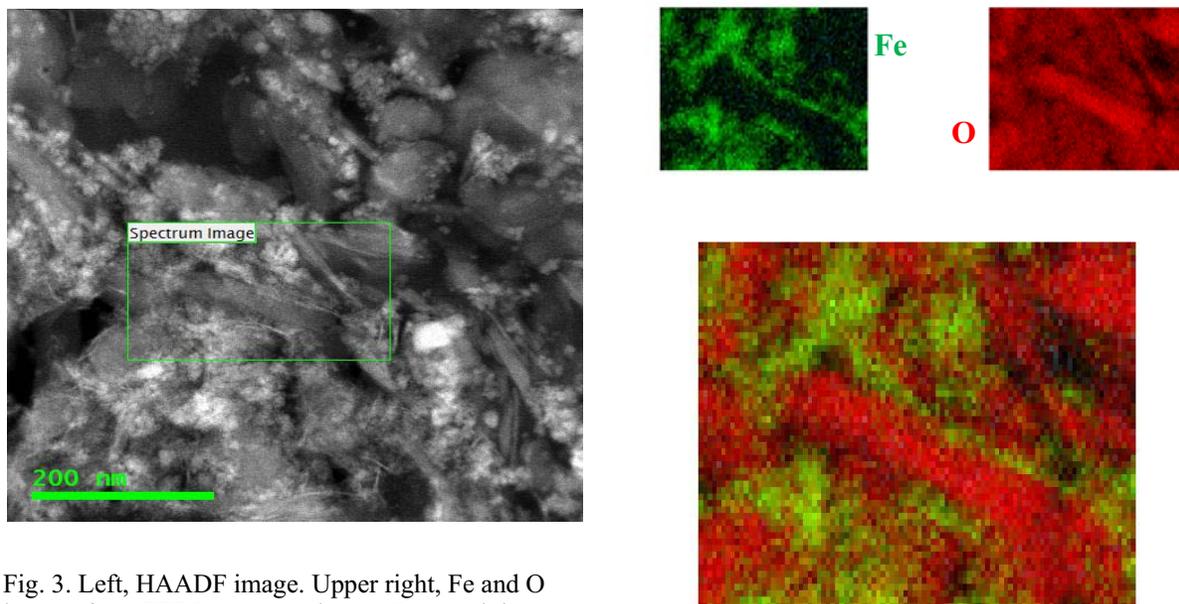


Fig. 3. Left, HAADF image. Upper right, Fe and O images from EELS spectrum image. Lower right, composite image.