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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM) OF NANOPHASE FERRIC OXIDES: D. C. Golden<sup>1</sup>, R. V. Morris<sup>2</sup>, D. W. Ming<sup>2</sup> and H. V. Lauer, Jr<sup>3</sup>; <sup>1</sup>Dual Inc. <sup>2</sup>NASA-JSC, <sup>3</sup>Lockheed ESC, Houston, TX 77058

**INTRODUCTION.** Iron oxide minerals are the prime candidates for Fe(III) signatures in remotely sensed Martian surface spectra. Magnetic, Mossbauer, and reflectance spectroscopy has been carried out in the laboratory in order to understand the mineralogical nature of Martian analog ferric oxide minerals of submicron or nanometer size range [1,2]. Out of the iron oxide minerals studied, nanometer sized ferric oxides are promising candidates for possible Martian spectral analogs [1]. "Nanophase ferric oxide (np-Ox)" is a generic term for ferric oxide/oxyhydroxide particles having nanoscale (<10 nm) particle dimensions [1,3,4]. Ferrihydrite, superparamagnetic particles of hematite, maghemite and goethite, and nanometer sized particles of inherently paramagnetic lepidocrocite are all examples of nanophase ferric oxides. np-Ox particles in general do not give X-ray diffraction (XRD) patterns with well defined peaks and would often be classified as X-ray amorphous. Therefore, different np-Oxs preparations should be characterized using a more sensitive technique e.g., high resolution transmission electron microscopy (HRTEM). The purpose of this study is to report the particle size, morphology and crystalline order, of five np-Ox samples by HRTEM imaging and electron diffraction (ED).

**MATERIALS AND METHODS.** Five samples of np-Ox were analyzed: TNA13/210 and S6FN28 have been characterized by Mossbauer and reflectance data as np-Hm [2,6]. TNA13/260 based on the same data has larger oxide particles than TNA13/210. Sample TNA13/210 was prepared by oxidation in air of trinuclear acetato hydroxy iron(III) nitrate (TNA) at 210 °C, TNA13/260 was prepared in a similar fashion except that the oxidation was carried out at 260 °C. 6LSFEH 20 was prepared by dialyzing a dilute ferrous sulfate solution incubated at 70 °C for 5 hr against distilled water. 6LSFEH was prepared by heating the 6LSFEH 20 to 400 °C. For HRTEM analysis sub milligram quantities of the samples were embedded in embed 812 epoxy resin and cut into 50 to 70 nm thin sections using a Microstar diamond knife mounted on a Porter Blum ultramicrotome. Thin sections were transferred on to carbon coated holey plastic substrates mounted on Cu grids. The sections were C-coated and observed under the JEOL 2000 FX transmission electron microscope operated at 200 keV.

**RESULTS AND DISCUSSION.** Sample TNA13/210 had a distinct ring ED pattern, with some spots due to discrete nanocrystals. The presence of rings at 3.67 and 2.72 Å (Table 1) confirmed the presence of hematite. However the very intense rings at 2.53 and 1.54 Å suggests the possible presence of an additional ferrihydrite like phase or smaller nanophase hematite particles. This observation was confirmed by the HRTEM images where a few nanocrystals of ~10 nm hematite crystals and a bulk of much smaller rounded particles with no discernible lattice structure (<5 nm) were observed. Presence of 2.72 and 3.67 Å lines in the ED pattern confirm the presence of hematite. TNA13/260 sample was similar to the above except that a stronger ED spot pattern suggesting more crystalline hematite than TNA13/210 was observed. HRTEM revealed the sample TNA13/210 to contain rounded hematite crystals of ~10 nm, although smaller areas consisting of much finer crystals were found. S6FN28 electron diffraction was masked by a diffuse broad central spot due to silica gel, however, the HRTEM images indicated the presence of very fine ferric oxide (~1 to 4 nm) particles dispersed in the silica gel matrix. No lattice fringes were observed. 6LSFEH had a few particles with lattice fringes corresponding to hematite (2.7 Å), whereas 6LSFEH20, the precursor to the above sample had only a two-line ED pattern (2.52 and 1.46 Å) typical of ferrihydrite. Out of the five np-Ox samples studied, TNA13/260 had predominantly hematite, TNA13/210 and 6LSFEH

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had hematite, and the rest were near amorphous ferric oxides exhibiting two or more ED lines in common with ferrihydrite (Table 1). By extrapolation, HRTEM-ED amorphous particles in all samples except 6LSFEH20 can be considered nanophase hematite which we were unable to confirm using our technique.

Because these np-Ox particles do not have defined ferric crystal field transitions, the reflectivity spectrum is unlike those for powders of crystalline ferric oxides. Also the lattice defects which cause the imbalance in two antiferromagnetic lattices give rise to a net magnetization [6]. The electron diffraction data indicates that the np-Ox particles studied here are large enough to be considered as particles, and the five samples provide a range of crystallinity near the amorphous end (Figure 1). The information on crystal structure obtained by HRTEM and ED in conjunction with earlier published spectral data [1,2,6] may help to constrain the Martian iron mineralogy with greater precision.

References: [1] Morris et al. (1989) *JGR* 94:2760-2778. [2] Morris et al. (1985) *JGR* 90:3126-3144 [3] Golden et al. (1993) *JGR* 98:3401-3411 [4] Bell et al (1993) *JGR* 98:3373-3385. [5] Towe, K. M. (1990), Origin, Evolution, and Modern Aspects of Biomineralization in Plants and Animals. Plenum Press. New York. [6] Morris et al. (1991) *LPSC XXII* pp. 927-928.

Table 1. Electron diffraction spacings in Angstroms for reference hematite (Hem), reference ferrihydrite (Fh) [5] and for the five np-Ox samples

Hem <sup>1</sup>	Fh <sup>1</sup>	TNA13/210	TNA13/260	S6FN28	6LSFEH	6LSFEH20
←-----Angstroms----->						
3.67(012)		3.67	3.67			
2.69(104)		2.72				
2.51(110)	2.54(110)	2.48	2.53	2.48	2.52	2.52
2.20(113)	2.24(200)	2.20	2.19			
	1.98(113)			2.01		
1.84(024)					1.80	
1.69(116)	1.72(114)		1.68			
1.64					1.63	
1.60(018,122)						
1.48(214)	1.51(115)					
	1.47(106)	1.48	1.47	1.49	1.6	1.46

<sup>1</sup>Values in paranthesis are the Miller indices assuming a hexagonal lattice structure.

Figure 1. Particle sizes of the np-Ox samples as observed by high resolution transmission electron microscopy.

