

**DETECTION OF NANOPHASE LEPIDOCROCITE ( $\gamma$ -FeOOH) IN IRON-SMECTITE MARS SOIL ANALOG MATERIALS (MarSAM)** A. Banin<sup>1,2</sup>, D.F. Blake<sup>2</sup> and T. Ben-Shlomo<sup>1</sup> (<sup>1</sup>The Hebrew University, Rehovot, Israel; and <sup>2</sup>NASA Ames Research Center, Moffett Field, CA 94303)

Smectite clays were suggested as important components of the Mars soil on the basis of various spectral, chemical and geological evidence (1-3). Specifically, iron enriched smectite clays were shown to simulate many of the findings of the Viking Labeled Release experiments on Mars (2,4), and to have spectral reflectance in the VIS strongly resembling the bright regions on Mars (5). The mineralogical nature of the iron phases of these Mars analog clay systems has not been fully characterized yet. The iron phases were found to be virtually amorphous using X-ray powder diffractometry (6), possess extremely small particle size, and have high specific surface area and high reactivity in the catalytic decomposition of certain organics (2).

We have now employed selected area electron diffraction (SAED) and micro analytical methods to characterize the nano-size iron phases in MarSAM iron-enriched smectite clays. We have found that the major crystalline phase is lepidocrocite ( $\gamma$ -FeOOH). The presence of less-crystalline phases such as the double-hydroxy salts of Fe(II)-Fe(III) ("green rust"), ferrihydrite ( $\text{Fe}_5\text{O}_7(\text{OH}) \cdot 4\text{H}_2\text{O}$ ) and completely "amorphous" iron oxides and oxyhydroxides cannot be ruled out.

Precipitation Environment: Ferrosic-oxide ( $\text{Fe}_3(\text{OH})_8$ ) seems to have been formed in the fresh suspensions in samples 7 to 16 (Fig.1). At lower iron additions the suspensions are undersaturated with respect to this mineral due to adsorption of iron as an exchangeable ion. Aging caused slow transformation into more stable crystalline iron oxides, involving perhaps completion of iron oxidation; After 24 months, iron solubility was apparently controlled by a solid slightly more soluble than lepidocrocite and maghemite and less soluble than  $\text{Fe}(\text{OH})_3$  and soil Fe. At the lower iron additions (suspensions 1-5) undersaturation is observed again and adsorption still controls iron solubility.

Microscopic Observations: Transmission electron microscopy showed no discrete particles of iron oxide-oxyhydroxides forming until added iron reached 3-4%  $\text{Fe}_2\text{O}_3$  but the clay particles became somewhat more electron dense indicating fine coating with the added iron. Small, electron-dense, discrete and isodiametrical particles appeared at added iron contents above 8-9%  $\text{Fe}_2\text{O}_3$ . The iron oxide-oxyhydroxide particles are in a size range of <10 nm, smaller than typically found in solution-synthesis studies of iron oxides (7). They appear to preferentially bind at the edges of the clay particles.

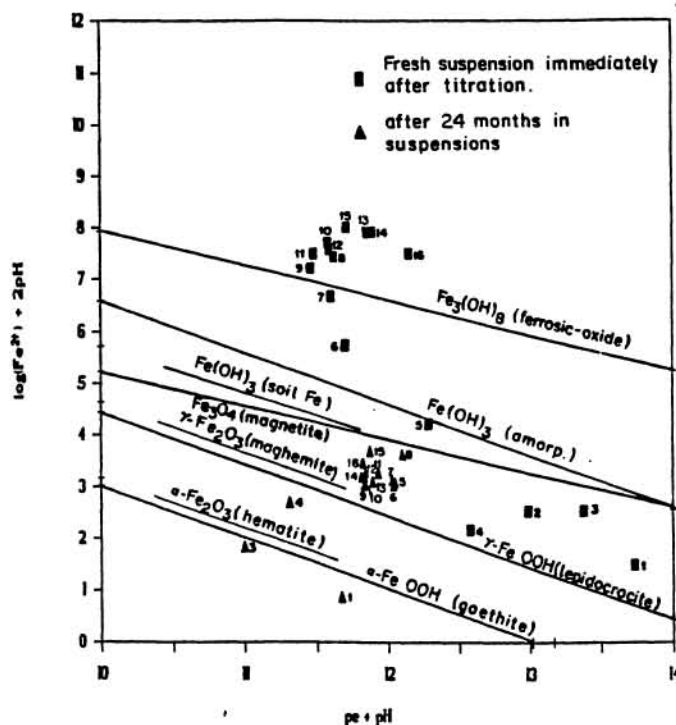
Mineral Identification: Previously we reported that powder X-ray diffractograms of the MarSAM were all similar to that of the SWy-1 clay, and none of the characteristic features of well crystallized iron oxides were detected (6). SAED patterns taken on limited areas have revealed lepidocrocite as the sole crystalline iron oxide-oxyhydroxide mineral present. Identification was based on lines at d-spacings of 3.26, 2.34, 1.92, 1.83, and 1.51Å, corresponding to the (120), (111), (051) and (200), (220), and (231) planes of lepidocrocite, respectively (ASTM card 8-98). The small domain size explains why identification by routine powder X-ray diffraction was not successful. The basal spacing for the clay could not be seen in the DP's, since the clay was preferentially oriented parallel to the support film and perpendicular to the beam. The (020) reflection of lepidocrocite (which is the most intense line of the mineral) was not seen also. This suggests that the lepidocrocite is oriented parallel to (0k0) on the clay surface. This orientation may be the result of either mechanical orientation or a topotactic crystal growth. The preferential attachment to the clay's edges suggests that the iron-oxyhydroxide nuclei were negatively charged and attached to the

positively-charged edge sites. The suspension pH during the formation of these iron-oxides was in the range of 5.5-7.0, which is below the zero point of charge (ZPC) of lepidocrocite.

**Relevance to Mars:** Lepidocrocite ( $\gamma$ -FeOOH) has been suggested as the major iron mineral in Mars soil mainly on the basis of speculations on the weathering scenarios of rocks at a fluctuating water table on Mars(8). Another geological scenario, supported by laboratory experiments, suggested oxidative weathering of iron sulfide minerals by acidic ground water leading to the formation of goethite( $\alpha$ -FeOOH) and jarosite( $(M)Fe_3(SO_4)_2(OH)_6$ ) (9,10). Nanophase hematite( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has also been suggested as the major iron-oxide mineral in the weathered surface materials on Mars (11-12). This was based on similarities between laboratory measurements of the spectral reflectance of certain mixtures of nanophase hematite with other matrix minerals, and the spectral reflectance of Mars measured from Earth.

The present report shows that iron enriched smectites, mineral systems that have shown spectral and chemical similarity to Mars soil, contain nanophase lepidocrocite and not nanophase hematite. We conclude that spectral reflectance may not be efficient and discriminative-enough method for the identification of nanophase iron oxide minerals that seem to prevail on Mars surface. Furthermore, it is demonstrated again that nanophase minerals may be unambiguously defined by selected area electron diffraction but not by X-ray diffraction. This should be taken into consideration in planning and instrument identification for future missions to Mars.

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**Fig. 1.** Solubility relationships of iron oxide and oxyhydroxide minerals and of iron-enriched Mars soil analogs. Smectite clays were treated with increasing amounts of FeCl<sub>2</sub> solutions (1-16). Measurements of pH, Eh, and Fe<sup>2+</sup> in solution were taken immediately, and after 24 months of storage at 5°C. (pe=Eh(mV)/59).