

ANALOG STUDIES OF NANOPHASE IRON OXIDES IN MARS SOIL

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The surface of Mars is covered with fine weathered soil material which has been studied rather intensively over the last 15 years. The mineralogical constituents of the soil have not been analyzed directly yet, and much controversy has been surrounding the issue, with numerous candidates proposed (1). Much attention was given to the iron minerals in the soil, due to their pronounced absorption features in the VIS and NIR, making them easily detectable by telescopic observations (2,3).

The typical reflectance spectrum of the bright regions of Mars in the visible/short wavelength NIR bears the strong fingerprints of oxidized iron (4,5,6). It has been reproduced more or less faithfully in laboratory measurements of a number of different iron-containing systems. These include "amorphous" iron oxides (7,8), palagonite (2,9,10), nanophase hematite deposited in silica or alumina matrix (11,12), and iron-enriched smectites (13,14). It appears that iron in the weathered component of Mars soil is mostly characterized by having clusters of poorly crystallized oxide or oxyhydroxide ferric iron, or crystalline minerals in extremely small particle size. Recent telescopic observations detected typical hematite features at 860 nm, and possibly other crystallized iron oxides (6,15). However, these features are very weak and estimates of the content of hematite and/or other crystalline phases are in the range of 1-5% of the soil (6,16). Thus the reflectance data still suggest that the bulk of the iron oxide-oxyhydroxide in the Mars soil is amorphous or short-range ordered and is characterized by extremely small particle sizes ("nanophases" (np)).

The two most thoroughly studied mineral analogs to the iron nanophases in Mars soil are np-hematite studied by Morris et al. (6,11,12) and iron-enriched clays studied by Banin et al. (13,14,17-19). Which one of these is the "true" Mars soil analog, if any?

Analog synthesis: The production of np-hematite (11,12) follows a common procedure for hematite synthesis i.e. prolonged high temperature (550°C) calcination of ferric iron solutions pre-deposited inside silica or alumina matrix. Samples with varying iron contents were obtained by different numbers of cycles of ferric nitrate solution impregnation followed by drying and calcination. The procedure is clearly conducive to the formation of hematite, and hematite only, since this mineral is the most thermally stable iron oxide form. It does not represent a prevailing nature alteration environment where hematite is likely to form, at least not as a monomineralic product. It can be seen, however, as a method to produce np-iron oxides using the narrow cavities of the silica gel as a "mechanical mold" which confines the growth of the precipitated iron oxide crystals. The end-product is thus a valid mineral analog to Mars iron oxide nanophases but its formation scenario is highly artificial (Morris and Lauer (12) point that out). The iron phases are either x-ray amorphous or show only broad hematite features. However Mossbauer measurements have suggested that even the x-ray amorphous samples are hematitic (11).

The iron nanophase oxides-oxyhydroxides in the Mars soil analog clays are deposited on the surface of the clay in a laboratory process (14,20,21) which generally simulates, but considerably enhances, the natural reaction sequences of hydrolysis-precipitation-oxidation occurring during the oxidative weathering of ferrous-iron containing primary silicate rocks on Earth. The process involves slow titration of acidic clay with a solution of Fe(II) salt while the pH is controlled by the presence of OH-ion exchange resin. The later stages of the process, during which most of the iron is deposited, occur within a narrow range of pH, in a slightly acidic to slightly basic environment (pH 6.6-7.4), and at practically constant redox ($pe + pH = 11.5-12.0$). The double hydroxy salt of iron, ferrosic oxide (Fe(II)Fe(III)₂(OH)₈), appears to form at this stage (19). This is typical for many natural environments on Earth in which ferrous iron in solution is oxidized and forms insoluble "green-rust" (a double hydroxy-iron phase) which then, upon further oxidation, may transform to either goethite, lepidocrocite, maghemite or ferrihydrite. Such processes may have taken place on Mars during acidic-oxidative weathering of rocks (22). Crystal growth of iron oxides in the iron-enriched clays is limited by the thermodynamic and electrostatic conditions in the precipitation system and not mechanically. Furthermore, precipitation is done from solution at low ferrous iron concentration, involving in situ oxidation at acidic to near-neutral pH - all representing potentially realistic weathering environments on Earth or on Mars. The iron phases are virtually x-ray amorphous, but selected area electron diffraction have detected some crystallization and identified lepidocrocite (γ -FeOOH) as the mineral present (19). The mineral appears to crystallize only after a relatively high load of iron was added to the clay (3-4 times the cation exchange capacity; 8-10% Fe₂O₃ added). It forms extremely small particles and quantitatively remains a minor phase.

Spectral properties: The reflectance spectra of both Mars-soil iron-analogs strongly resemble the reflectance curves of the bright regions on Mars in the visible range (11,13). Both the Mars and the analog's

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spectra do not show any well defined absorption features of the crystalline iron oxides in the visible range but are characterized by monotonous and significant decrease in reflectance from the NIR towards the UV. This spectral behavior has been generally attributed to nanophase iron oxides, and was recently specifically attributed to superparamagnetic nanophase hematite (6,11). This assignment does not appear to be unique and singular since we find that amorphous iron oxides and nanophase lepidocrocite also show the same reflectance spectrum in the VIS and agree quite well with the Martian spectra. Similarity to Mars spectrum has been shown to improve by mixing and adding various minor phases (either actually or by computation). However, at the present stage of the refinement of the spectral telescopic data for Mars, it is doubtful to what extent such "fine-tuning" is warranted.

Viking Biology Simulations: The chemical reactivity of Mars soil, as recorded in the Viking biology experiments, has been simulated successfully with the iron enriched clays. The analogs decomposed ^{14}C formate, the most labile organic component in the media used in the Labeled Release experiment, at a rate and to the extent measured on Mars (14,17) and simulated the sorption ("peak 1") and synthesis ("peak 2") activities of the Mars soil measured during the Pyrolytic Release experiments (23). These unique chemical reactivities are attributed to the combined catalytic effects of the iron oxide-oxyhydroxide and silicate phase surfaces (14,17). Information is lacking for np-hematite, but simulation studies with palagonites (18) and with pure hematite (17) have shown that they do not induce the LR reaction.

Magnetic properties: We have recently found that heating of the iron-enriched clays, in which lepidocrocite has been identified, renders them magnetic (24). The saturation magnetization (J_s) of an iron enriched clay (containing 9.68% total iron as Fe_2O_3) increased from $15.6 \times 10^{-8} \text{ m}^3/\text{kg}$ ($1.61 \times 10^{-6} \text{ m}^3/\text{kg}$ Fe_2O_3) for the unheated sample to 2.8×10^{-6} ($2.89 \times 10^{-5} \text{ m}^3/\text{kg}$ Fe_2O_3) for the heated (300°C , 12h) sample, bringing it to the range of magnetic susceptibilities estimated for the Mars soil, if total iron was the same (25,26). The heat treatment converted the antiferromagnetic lepidocrocite to the strongly ferrimagnetic maghemite - a well known conversion.

The J_s values for np-hematite are about 10 times higher than those of hematite (11). To account for the observations in the magnetic experiment on Mars, all the iron in the soil has to be present as np-hematite (11). Because J_s of maghemite is about three orders of magnitude higher than that of hematite (and ca. two orders of magnitude higher than np-hematite), it is sufficient that a small fraction of the np-iron oxides in the soil are converted to maghemite (via lepidocrocite) to develop saturation magnetization similar to the Mars soil.

Summary: np-hematite produced in confining matrixes and np-iron oxyhydroxide + np-lepidocrocite on clay surfaces, are two mineral analogs to the nanophase iron oxides/oxyhydroxides in Mars soil, which have been studied extensively in recent years. Both analogs show convincing overall spectral and magnetic similarities to the Mars soil. The np-iron oxide on clay surfaces also simulates the chemical reactivity of the soil. The evidence they supply is quite compellingly leading to the conclusion that much of the iron oxides in the weathered Mars soil and in the dust, are in the nanophase. However, the formation scenarios and detailed mineralogy of the two analogs are grossly different from one another. In order to select either one of them as the "true" analog, or reject both, better and more detailed spectral data for Mars and additional simulation studies on Earth are required.

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