**Introduction:** The origin of iron bearing phases in the Martian regolith is classically interpreted as the heritage of titanomagnetite present in the primary magmatic rocks as well as neoformed Fe\(^{3+}\) phases (maghemite and hematite). However, on one hand, recent mass balance studies estimate that up to 10-30\% in mass of the regolith matter could be of meteoritic origin [1,2], as meteorite and IDP usually contains 10-20\% of iron rich phases (sulfides and metal) compared to 1-2\% in Martian rocks. Sulfides may also be more common in primary Martian rocks than on Earth [3]. On the other hand, weathering may play a key role in the neoformed oxide production. Nevertheless, the fundamentally different nature of Earth and Mars atmospheres (replacement of O\(_2\) by CO\(_2\) and presence of peroxides [4,5]) may induce strong variations in terms of oxidation processes. Therefore several possible primary iron minerals have been experimentally weathered, including pure metallic iron, magnetite, as well as hexagonal and monoclinic pyrrhotites, in various atmospheres [6].

**Protocol:** 10 g of finely powdered phases were put in a dessicator previously filled with 1 L either of pure water or of water containing 33\% of hydrogen peroxide H\(_2\)O\(_2\). The desiccators were then equilibrated with gaseous CO\(_2\) at the initial pressure of 0.8 bar and the temperature was controlled to remain in the range 15-20°C. Such conditions were used to increase kinetics of weathering processes, but also to model a possible primary Martian atmosphere enriched in H\(_2\)O and CO\(_2\). Two types of desiccators have been used for each atmosphere: the first was opened at various weathering steps, and the second type remained closed during the whole experiment (about 500 days) in order to control the influence of the contact of the powders with the Terrestrial atmosphere. The three experimentally weathered phases mentioned above have been characterized at different weathering steps, based on chemical analysis, X-ray diffraction, SEM, TEM and magnetic measurements.

**Results:** Magnetite has been observed to remain extremely stable in both atmospheres, and does not evidence any change during the whole experiment. Thus this phase is likely to be inherited from primary rocks in the Martian regolith through weathering processes.

Iron remains stable in the peroxide atmosphere but shows strong changes in water atmosphere, with formation of siderite further destabilized into goethite. A stabilization of iron particles has been observed and results from protective goethite varnishes on the surface of the particles. A similar process on Mars may allow the presence of iron particles in the regolith, contributing to the magnetic properties of the soil. Furthermore, such iron + goethite particles are in good accordance with the composite aspect often invoked by authors to describe the nature of the magnetic fraction attracted by the magnets onboard the landers [7]. Finally the contribution of meteoritic iron may explain the higher Ni content in the regolith than in the fresh part of rocks, as observed by MER Spirit [8].

Pyrrhotites present similar neoformed mineralogies in both atmospheres, i.e. elemental sulfur (ribbon shaped on the TEM figure (A) below), sulfates, and iron (oxy)hydroxides.

Goethite (goe) is the main iron product (see TEM figure (B) below), often associated to ferrihydrite precursor (fhd in the figure).

Lepidocrocite, which has been observed in control samples, results probably from slightly lower oxidant conditions than in the desiccators used for sampling, which products have been in contact with the oxygen of the Terrestrial atmosphere. Sulfates assemblages are
rather complex but consist mainly of Fe$^{2+}$ sulfates in water atmosphere and Fe$^{3+}$ sulfates (jarosite (jar) and copiapite (cop), see BEM figure (C) below) in peroxide atmosphere, reflecting a higher degree of oxidation due to hydrogen peroxide.

The similarity of the neoformed sulfates with those observed on Mars (jarosite [9]) highlight the importance of primary sulfides, either present in primary rocks or resulting from accumulation of sulfide-rich meteoritic material.

**Martian weathering processes:** The main conclusion resulting from this study is that goethite is almost the only neoformed iron (oxy)hydroxide under Martian conditions. Due to our experimental conditions, closer to a possible primitive atmosphere than to today’s ones, goethite represents a better indicator for conditions prevailing on early Mars, and particularly the presence of water. Moreover the water activity has a strong influence on the crystallinity of the neoformed goethite, ranging in our experiments from nanophase, poorly crystalline goethite to well formed crystals when water content in the powders increases. The figure below represents the evolution with time of goethite crystallinity, measured with main peak area ($d_{101}$ distance) normalized to maximal intensity of the peak, on X-ray diffraction pattern. Such evolution has implications on Mössbauer spectra interpretations, as indicating a progressive ordering of goethite.

The recent observation of goethite on Clovis rock by MER Spirit [10] is an important validation for our model. Therefore the presence of hematite may not reflect weathering in the primitive conditions. Hematite and especially the berries observed by MER Opportunity may rather be a transformation product of a goethite precursor [11], by heating (burial metamorphism [12]), by surface dehydroxylation process, or by evolution of surface conditions (dissolution followed by reprecipitation), in a similar way as previously observed in various Earth soil profiles. Similar processes may also transform lepidocrocite precursor to maghemite and hematite [13].

Finally these experiments, conducted in the nearly absence of gaseous oxygen, highlight the possibility of other weathering process than those usually invoking oxygen O$_2$ as the main oxidant. In our model, O$_2$ is replaced by H$^+$. The global process, and particularly the oxidation of Fe$^{2+}$ to Fe$^{3+}$, occurs through the following simplified reaction:

$$\text{Fe}^{2+} + \text{H}^+ = \text{Fe}^{3+} + \frac{1}{2}\text{H}_2$$

This reaction is favored because of two combined effects: (1) the volcanism which bring quantities of gas such as CO$_2$ and SO$_2$ allowing strongly acidic solutions (excess of reactant), and (2) the thermal escape of H$_2$ from Mars (defect of product). This process describes the global oxidation of the Martian surface without invoking absent species as O$_2$, and provides an efficient mechanism for trapping of water in the regolith through dissociation of water with H$^+$ used as oxidant, and OH$^-$ used to form iron (oxy)hydroxides.

**Conclusions:**

1. Although goethite is the only neoformed phase, strong changes in color occur in the resulting product, obviously depending on the proportions of primary and secondary phases, but also on goethite crystallinity.

2. In spite of their apparent metastability, various phases, like metallic iron, may describe properties of the Martian regolith. The possibility of metastable phases is supported by our model of out-of-equilibrium oxidation pathway, allowing kinetic effects to stabilize various phases.

**References:**