

FE(VI) AS A POSSIBLE OXIDANT ON THE MARTIAN SURFACE. A.I.Tsapin¹, M.G.Goldfeld², G.D. McDonald¹, and K.H. Nealon¹, ¹Jet Propulsion Laboratory, MS 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109, USA, tsapin@jpl.nasa.gov, ²California Institute of Technology, 1200 E. California Blvd. Pasadena, CA 91125

Surface Oxidants on Mars: The essential findings of the three biological experiments (Gas Exchange, Labeled Released, and Pyrolytic Release) aboard the Viking Mars landers were the discovery of the presence of one or more strong oxidants on the Martian surface. The Gas Exchange experiments showed that wetting Martian soil leads to the evolution of oxygen, while in the Labeled Release experiment addition of a nutrient solution containing ¹⁴C-labeled formate, glycine, lactate, alanine, and glycolic acid induced CO₂ evolution [1].

A general consensus was reached that all data taken together pointed to the presence on Martian surface of a strong oxidant, or most probably several different types of oxidants. Several candidates have been proposed as oxidants, including superoxides, hydrogen peroxide, and iron oxides (possibly gamma-Fe₂O₃).

Fe(VI) As a Mars Oxidant: In this study we propose Fe(VI) as a possible oxidant on the Martian surface. Fe(VI) can be synthesized in the laboratory under strong alkaline conditions from Fe(III), in the presence of strong oxidants. As the climate of ancient Mars became colder and drier with time, open bodies of water would have entered a regime in which evaporation exceeded input from precipitation or runoff. This would have resulted in increases in salinity and perhaps pH [2-4]. The high UV flux on the Martian surface can generate free radicals with very high redox potential, which could interact with Fe(II) and Fe(III) present on the Martian surface to generate Fe(VI).

Fe(VI) is a very unstable compound under normal conditions on Earth. Fe(VI) compounds such as potassium ferrate (K₂FeO₄) can be stored only under very dry conditions. Any contact with organic compounds leads to reduction of Fe(VI) to Fe(II). Most likely due to this instability of Fe(VI) under normal conditions, there are few references in the chemical literature to studies or properties of Fe(VI). However, an attempt to use ferrate (VI) as a biocide to prevent formation of biofilms was recently reported[5].

Laboratory Studies: Crystalline potassium ferrate (VI) was prepared by iron(III) nitrate dodecahydrate oxidation with potassium hypochlorite in concentrated potassium hydroxide solution. The ferrate was purified by repeated crystallization out of saturated potassium hydroxide. The product identity was

established by visible absorption spectra, with molar extinction of 1300 M⁻¹cm⁻¹ at a peak absorption wavelength of 507 nm.

Reflectance spectra of crystalline potassium ferrate are shown in Fig.1. The band at 1.6 μm can be used as a marker to search for the presence of Fe(VI) on Martian surface, either in situ or from orbit. Absorption at 507 nm also can be used for Fe(VI) detection in experiments in situ.

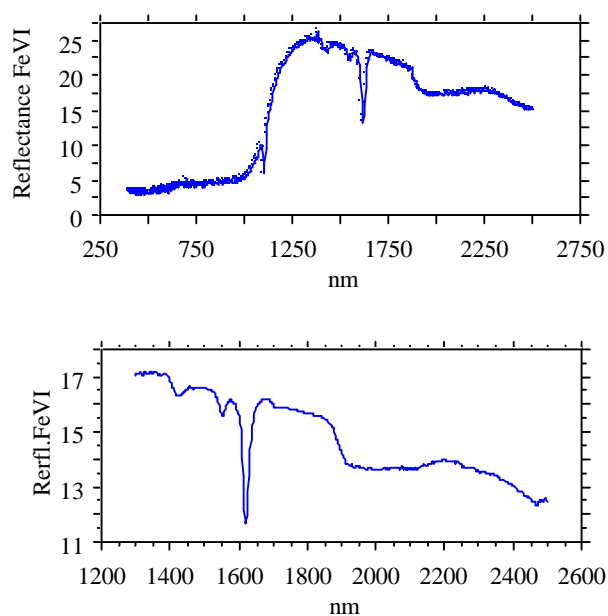


Fig. 1. Reflectance spectra of crystalline potassium ferrate. Top - visible and IR regions; bottom – IR region enlarged.

We have also carried out preliminary experiments in which ¹⁸O-labeled water was added to potassium ferrate and the headspace monitored by GC-MS. Analysis of gas products after reaction of potassium ferrate with H₂¹⁸O revealed that ¹⁸O₂ was produced. These experiments clearly indicate that Fe(VI) can oxidize water with resultant oxygen evolution, consistent with the results of the Viking Gas Exchange experiments.

Addition of aqueous solutions of formate or lactate to potassium ferrate resulted in the evolution of both oxygen and CO₂. These results are again consistent with the Viking experiments. Studies of the kinetics of these reactions as well as interactions of Fe(VI)

with other organic compounds are currently underway.

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