

Self-Sterilizing Properties of Martian Soil: Possible Nature & Implications

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ABSTRACT

As a result of the Viking missions in 1970s, the presence of a strong oxidant in Martian soil was suggested. Here we present a testable, by near-term missions, hypothesis that iron(VI) contributes to that oxidizing pool. Ferrate(VI) salts were studied for their spectral and oxidative properties and biological activities. Ferrate(VI) has distinctive spectroscopic features making it available for detection by remote sensing reflectance spectra and contact measurements *via* Mössbauer spectroscopy. The relevant miniaturized instrumentation has been developed or is underway, while XANES spectroscopy is shown to be a method of choice for the returned samples. Ferrate(VI) is capable of splitting water to yield oxygen, and oxidizing organic carbon to CO₂. Organic oxidation was strongly abated after pre-heating ferrate, similar to the observations with Mars soil samples. Using UV spectra and PCR studies, it was shown that ferrate(VI) destroys genetic material in the form of nucleotides or nucleic acids, as well as amino acids in proteins. This imposes severe limitations on the location of life as we know it on Mars, due to self-sterilizing properties of its soil.

INTRODUCTION

The "biological" experiments on the Viking landers [1,2] revealed unexpected chemical activity in the surface material, which in some ways resembled biology but was eventually assigned to a rather complex chemistry. These experiments showed that humidifying Martian soil resulted in oxygen formation, while addition of a bacterial nutrient solution (¹⁴C-formate, glycine, lactate, alanine, and glycolate) resulted in ¹⁴CO₂ evolution, together with some formation of oxygen. Release of CO₂ was inhibited almost completely after "sterilizing" the Martian soil sample at 160°C for 3

hours, while O₂ formation remained largely unaffected. These observations were interpreted as an indication of the presence of a strong oxidant on the Martian surface, or, most probably, several different types of oxidants [3–5]. No site on Earth has been found with such an oxidant present, strong enough to decompose water. This is not unexpected, when one takes into account the abundance of reductants that make unlikely the accumulation of such a strong oxidant anywhere on the surface of the Earth.

It is important to understand the nature of Martian oxidants and their likely distribution pattern. Are they located only on the surface, or what is their vertical profile in Martian soil? Are they distributed uniformly, and can areas entirely free of oxidant be located? The answers to these questions may significantly limit the areas to search for life, or its remnants, on Mars, and therefore are paramount for choosing landing sites, and for the entire program of Mars exploration.

Candidates proposed so far on the role of Martian oxidant include iron oxides (possibly γ -Fe₂O₃), hydrogen peroxide, and superoxide radical ions, which can form due to the UV irradiation of Martian surface [6-11]. Quinn and Zent [12] showed that titanium dioxide adsorbs hydrogen peroxide on its surface, and the resulting system can mimic Viking experiments in laboratory conditions fairly well. TiO₂, combined with other oxides in rocks, is very likely to be present in Martian soil [13], with an estimated abundance of 0.6% by mass. However, out of the other elements with well established set of variable oxidation states, iron is the most attractive candidate, due to its abundance in Martian soil (third most abundant element, after oxygen and silicon, about 18 % by mass on Fe₂O₃ basis).

Common oxidation states of iron are (+2) and (+3). However, at certain conditions, higher oxidation states can be formed, including Fe(IV), Fe(V), and Fe(VI). These are quite unstable under most usual conditions on Earth, where water is abundant, but they can form and persist in dry systems. Besides, Fe(VI) known as tetrahedral FeO_4^{2-} anion, although a very strong oxidant, is a well-characterized chemical species, with its standard electrochemical potentials $E^\circ = +2.2$ V in acidic, $+0.78$ V in alkaline solutions [14]. It is rather stable in strong alkaline solutions in the absence of efficient reductants. Ferrates(VI) salts with various cations, such as K^+ , Na^+ , Ba^{2+} , Li^+ , Rb^+ , Cs^+ , Ag^+ , and a few tetraalkyl/aryl ammonium cations, have been described [15-18]. Currently, there is a burst of interest to ferrate (VI) as a promising oxidizing reagent for organic synthesis [16, 19] and material for rechargeable alkaline batteries of increased capacity [20].

In order to assess the possible contribution of ferrate(VI) to the oxidizing pool in the Martian soil, we address the following questions:

1. Is there an opportunity to form ferrate (VI) on Mars, according to what is known about its surface composition and environmental conditions?
2. Would such a compound be stable enough to persist and accumulate under those conditions?
3. Would it display the essential reactivity that was found in the samples of Martian soil in the Viking experiments, i.e. produce oxygen gas while moisturized, and
4. Would it produce carbon dioxide when in contact with the organic materials that constituted nutrient solution in those experiments?
5. Would these chemical activities be impaired at heating in a way similar to the inactivation seen in Viking's experiments?
6. With Mars exploration program in mind, what are the possible approaches to identification of ferrate(VI), and in particular what are the spectral features of this species that would permit its characterization by both contact measurements and remote sensing?

HIGHER FERRATES: CHEMISTRY, BIOLOGICAL ACTIVITY, AND SPECTRAL FEATURES

ROUTES TO FERRATE(VI)

The regular way to ferrate(VI) is through the wet oxidation of Fe(III) with hypochlorite [15, 16]: we used this approach in our experiments. However, formation of ferrate(VI) was reported in dry, elevated-temperature reactions of iron-containing materials with some alkaline peroxides and superoxides [21, 22]. On the other hand, there is a strong belief that active oxygen species such as peroxides, superoxides, singlet oxygen, hydroxyl radicals, and ozone are formed under UV irradiation in Martian atmosphere, and affect its soil [6-11]. Overall, Martian atmosphere is highly oxidized, dominated by carbon dioxide and with presence of

some dioxygen and ozone. In these circumstances, ferrate(VI) can serve as a form of stabilization and storage of active oxygen, but only if its decomposition is slow enough to permit the accumulation of the product in question.

FERRATE(VI) STABILITY AND PRESERVATION

In aqueous solutions, ferrate(VI) is rather stable in alkali only, at $\text{pH} > 10$, and even then it is readily reduced by most organic materials. In a $\text{pH}-E^\circ$ diagram, where E° is reduction potential, the stability region can be approximately presented as in Fig. 1. Beyond that region, ferrate(VI) is reduced according to the following equilibria:

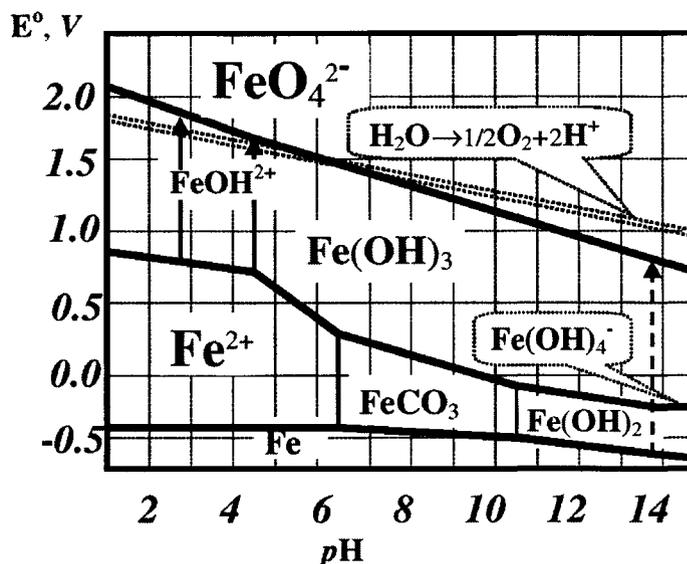
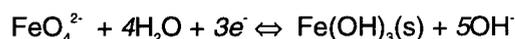
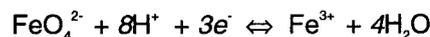


Fig. 1. E° -pH stability diagram for iron compounds in aquatic systems.

At a lower pH, not only organic materials, but also water is oxidized. So, thermodynamically one would need a highly alkaline environment for ferrate(VI) to be stored. This requirement is not so limiting for Mars soil, as it seems at first glance. Indeed, there are strong reasons to assume that in the absence of biogenic calcium carbonate deposits which now serve as a powerful buffer on the Earth surface, both pre-Cambrian Earth, and Mars at some stage of its geological history, were covered with a "soda ocean" of its $\text{pH} > 9$ [23, 24].

Different scenarios, with rather acidic evolution pathways have been suggested for Mars [25]. However, in the absence of conclusive pH measurements, the only experimental evidence now available, from the same Viking program, as Oyama pointed out [1], favors an alkaline environment: indeed, the solutions produced by mixing samples of Martian soil with water displayed a short-term

absorption of carbon dioxide, as any basic solution would do. From simulation experiments, Quinn and Orenberg [26] also concluded that Martian soil material is most likely at least mildly alkaline.

Ferrates of alkaline metals are unstable in the presence of moisture. However the Martian surface is dry and cold. Thus, even alkaline ferrates could be stabilized there. Besides, other ferrates, such as barium ferrate(VI), are much less water soluble and consequently fairly stable in humid milieu. It is essential that ferrate(VI) anions are not sensitive to light [27].

Thus, overall, there is enough reason to suggest that the formation of ferrate (VI) and its preservation in soil are consistent with the present knowledge of chemical composition and environmental conditions at the Martian surface.

CHEMICAL PROPERTIES OF FERRATE(VI)

In the Viking Gas Exchange Experiments, it was found that samples of Martian soil released oxygen gas upon introduction of water vapor into the sample cell [1,2]. Oxygen was also released from a sample of soil that had been pre-heated at 145°C, although the amount of gas was substantially reduced. When treated with a "nutrient" solution, i.e. an aqueous mixture of organic acids and amino acids, carbon dioxide was first rapidly released, then the rate of its production decreased after a small fraction of all organic carbon had been oxidized. Carbon dioxide release was completely prevented by preheating the soil samples at 160°C, and a consumption was observed instead. In light of these results, thermal decomposition of ferrate(VI) is relevant to the problem in hand.

Thermal Decomposition

Potassium ferrate(VI) as a dry powder is stable at room temperature. However, on heating it decomposes, releasing oxygen gas. Decomposition slowly proceeds, starting about 50°C, and is complete by 300°C. Its rate strongly depends on the traces of water: dry samples are less sensitive to heating. Thermal decomposition is a complex, multi-stage process, as can be seen from thermogram and DSC observations (Fig. 2). One may speculate that transient lower oxidation states of iron, such as Fe(+5) and Fe(+4), are first produced, before the final product, Fe₂O₃, forms. These intermediate forms still display high oxidative power. A catalytic effect of Fe(III) on ferrate decomposition is anticipated and may significantly complicate the results of DSC and thermogravimetry analysis. These results are essential to the understanding of Viking's data since they show that "sterilization" might result in a set of various iron products in a poorly predictable manner, depending on the other components of the soil and possibly on the rate of heating as well.

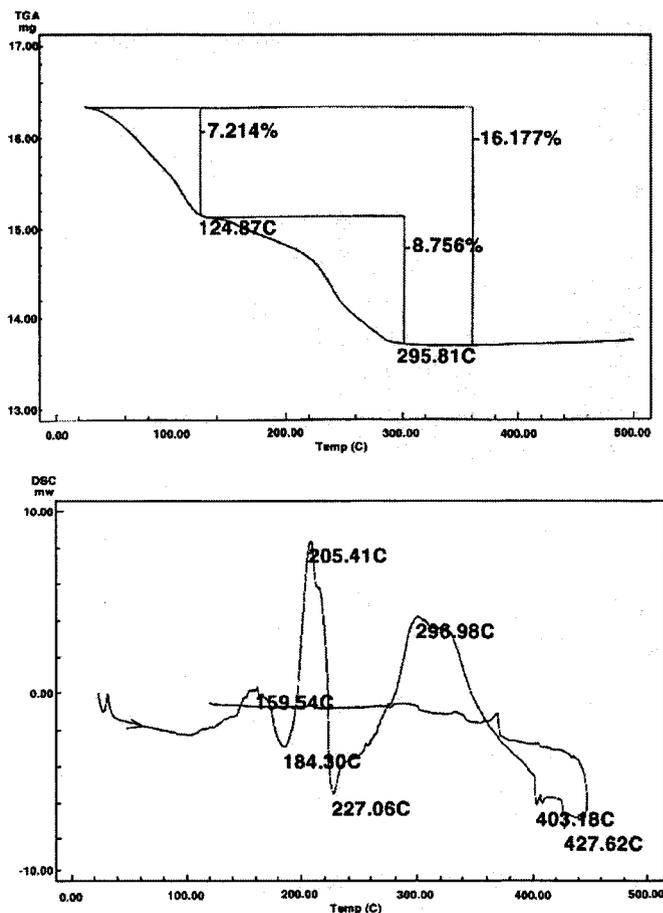


Fig. 2. Thermal decomposition of K₂FeO₄: Thermogravimetry (TGA), and differential scanning calorimetry (DSC). Heating rate: 5°C/min.

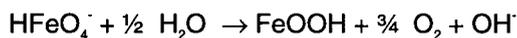
Oxygen Release in the Reaction with Water

Dry ferrate is not immediately reactive with aprotic solvents such as ether, chloroform, or benzene, which permits their application for removal of traces of water from ferrate preparations. Neither is ferrate(VI) soluble in any of those solvents.

Upon addition of water to potassium ferrate (VI), the mixture bubbles indicating an intense gas evolution. In Viking's experiments, no attempt was made to explore the interaction of soil samples with pure liquid water. Oxygen evolution was recorded, however, when water vapor from the nutrient solution accessed the solid soil. The nature of the reaction was not explored further, and it remained unclear if it were a stoichiometric oxidation of water, or decomposition of the solid material, catalyzed or initiated by water.

The reaction of water with potassium ferrate, however, is a true water oxidation: GC-MS analysis of the gas product after reaction of potassium ferrate with liquid H₂¹⁸O revealed that the gas product formed in the head space of the reactor vessel is ¹⁸O₂, indicating no significant oxygen exchange between ferrate and water. Water oxidation is enhanced by

acids, and the true active oxidizing species is HFeO_4^- anion, not FeO_4^{2-} dianion *per se* [24]. The reaction may be presented as:



Barium ferrate(VI), $\text{BaFeO}_4 \cdot \text{H}_2\text{O}$, formed by ion-exchange precipitation from the sodium ferrate(VI) solution with barium nitrate, was not reactive under comparable conditions, along with its low solubility.

We explored the kinetics of dioxygen accumulation in two ways. First, as in the Viking experiments, oxygen formation was measured in the setting wherein solid potassium ferrate(VI) contacted with water vapor only, while liquid water and ferrate were placed in separate open containers in one and the same chamber of the gas-meter instrument (Micro-Oxymax respirometer, with paramagnetic sensor for oxygen). Typical results on the kinetics of dioxygen accumulation under these conditions are in the Fig. 3A. The reaction develops slowly and steadily, and the kinetics obviously reflects the transfer of vapor to ferrate(VI).

In another set of experiments, potassium ferrate(VI), in the amount of ca. 50 mg, was placed in the respirometer chamber; then 0.2 mL of water was injected providing direct contact of the solid material with liquid water. In this setting, oxygen was released immediately (Fig. 3B). The reaction was not significantly impaired by pre-heating the solid potassium ferrate at 145°C, or even at 170°C for 2 hrs. In that sense, the observations were close, at least at a qualitative level, to the Viking results, which also indicated that oxygen formation was rather resistant to pre-heating of the soil sample. When water was replaced by a liquid "nutrient solution", a short burst of oxygen was typically first observed, although in a lesser amount than with pure water, but then oxygen consumption was recorded (Fig. 3C). More thorough heating, at 185°C for 4 hrs, resulted in ferrate(VI) decomposition (color of the solid drastically changed from dark purple to greenish), and produced solid material incapable of releasing oxygen (Fig. 3A, Graph 3 and Fig. 3C, Graph 3). Needless to say, a mixture of iron(III) oxide with alkali did not produce any oxygen, and only fluctuations within instrument stability limits of approx. $\pm 50 \mu\text{L}$ of gas volume could be seen.

Carbon Dioxide Release/Consumption in the Reaction with Nutrient Solutions

According to their respective redox potentials, ferrate(VI) is a stronger oxidant than permanganate and chromate. The extremely strong oxidizing power of ferrate(VI) was well documented in its reactions with a number of various compounds: it converts chromium(III) to chromate, oxidizes ammonia, cyanide, hydrogen sulfide and other sulfur compounds [29-34], and was proposed as a valuable oxidizing reagent for organic synthesis [16, 35] and wastewater treatment [36].

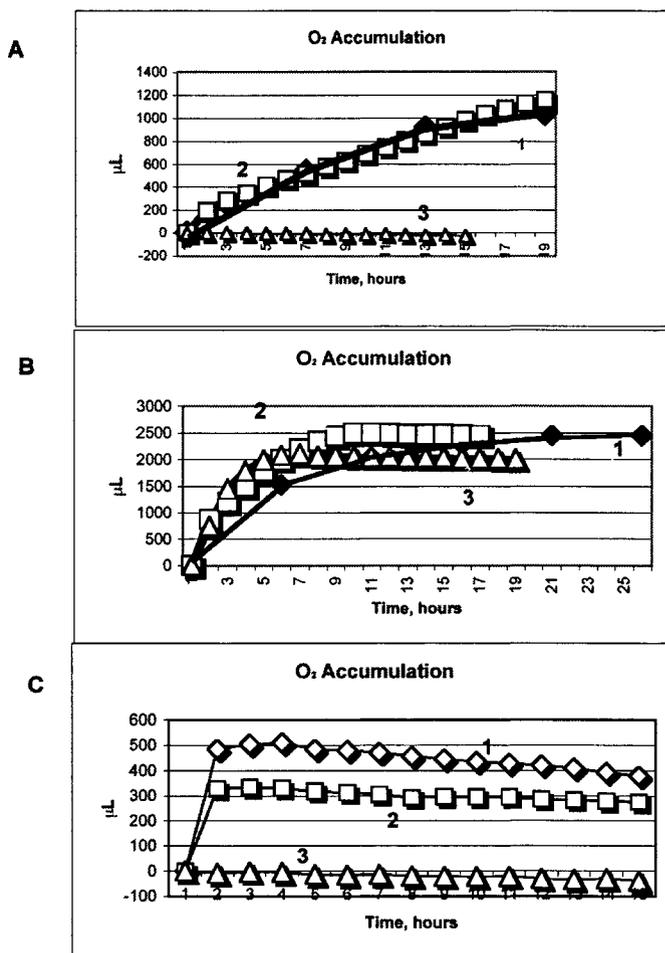


Fig. 3. Accumulation of oxygen at the reaction of potassium ferrate (50 mg) with water. **A:** Reaction with water vapor. **1:** Non-heated sample; **2:** Sample pre-heated at 170°C for 2 hrs; **3:** Sample pre-heated at 185°C for 4 hrs. **B:** Reaction with liquid water, 2 mL, injected through a septum. **1:** Non-heated sample; **2:** Solid pre-heated at 145°C for 2 hrs; **3:** Solid pre-heated at 170°C for 2 hrs. **C:** Reaction with 2 mL of nutrient solution (0.024 M in lactate, formate, alanine, glycine, glycolate, pH6). **1:** No pre-heating; **2:** Solid pre-heated at 145°C for 2 hrs; **3:** Solid pre-heated at 185°C for 4 hrs.

In our hands, addition of aqueous solutions of formate to powdered potassium ferrate(VI) resulted in the release of carbon dioxide in the head space of the reactor vessel (Fig. 4, Graph 1). Formate was chosen for these preliminary experiments because carbon dioxide is the only possible product of its oxidation. Therefore, even visual observations of the change in color (from purple to yellow-brown) serves an unambiguous indication of carbon dioxide formation. In further experiments, CO_2 was determined using IR sensor of the Micro-Oxymax respirometer. When a complete nutrient solution was added to solid ferrate(VI), release of carbon dioxide was recorded as well Fig. 4, Graphs 2,3,8). However, it was completely inhibited and actually reversed to a steady CO_2 consumption after pre-heating at 145°C or 170°C (Fig. 4, Graphs 4-7).

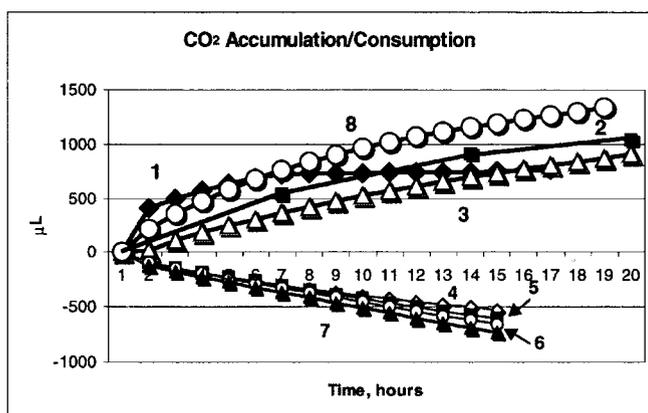


Fig. 4. Carbon dioxide release/consumption at the reaction of potassium ferrate (50 mg) with 0.2 mL 2.4 M formic acid, [Graph 1]; or pH 8 [Graphs 3, 4, 6]. 1–3: no or 2 mL nutrient solutions, pH 6; [Graphs 2, 5, 7], pre-heating; 4, 5: pre-heated at 145°C 2 hrs, at 170°C; 6, 7: pre-heated 3 hrs. Graph 8: mixture of 50 mg potassium ferrate with 150 mg silicon dioxide, nutrient solution pH 8.

At the same time, some dioxygen was formed in all experiments with diluted nutrient solutions, apparently due to a concomitant reaction with water, which is certainly a far more abundant reagent. It should be kept in mind that some background carbon dioxide consumption is anticipated in each case due to the alkaline nature of the solid reagent. The balance between oxidation and neutralization reactions may give various net concentrations of carbon dioxide in head space, and in the absence of oxidation (as after thermal treatment of ferrate(VI)), steady consumption of CO₂ is actually observed. The product of ultimate thermal decomposition of potassium ferrate displays essentially the same behavior in terms of CO₂ consumption, as a mixture of iron(III) oxide and KOH.

The above observations are in line with the results of the Viking Labeled Release Experiments. However a word of caution may be worthwhile concerning these similarities. We do not actually know what the other components of Martian soil are, or the way iron(VI), if present, is chemically bound to other oxides, and how such a combination would affect the reactions of ferrate. For instance, we do know already that a combination with barium oxide (barium ferrate(VI)) is far less reactive than alkaline ferrates. Besides, our lab experiments were designed in such a way as to make measurements convenient and distinctively visible. To this end, e.g., concentrations of “nutrient solutions” were taken hundred times those in standard microbiological media. As a result, all kinetics were completed within several hours. No attempt has been made to stretch out observations for months, as was the case in the real Viking’s missions. Experiments with more diluted solutions and different ratios of solid ferrate/ solution volume, which gave inconclusive results and approached the instability limits of the instrument, were not taken into account, and further effort would be necessary for a closer simulation of the original

Viking’s settings. Nevertheless, the overall set of results, i.e. evolution of oxygen on water vapor-ferrate contact and its relative lack of sensitivity to pre-heating, as well as carbon dioxide release and absorption, together with pre-heating effects, are in line with Viking’s observations.

BIOLOGICAL ACTIVITY OF FERRATE(VI)

Antiseptic properties of ferrate(VI) have been previously reported, and sodium ferrate has been suggested as a replacement for chlorine and ozone in waste-water treatment [35]. Experiments conducted on Viking landers failed to detect any organic material on the Martian surface. It has been concluded therefore that oxidants in Martian soil were responsible for the destruction of organic organics. Having that in mind, we decided to study in some more detail the interaction between ferrate(VI) and a few most important biogenic compounds. We applied two approaches in order to elucidate the efficiency and mechanism of the biological effects of ferrate(VI): the alterations of the UV absorption spectra of solutions containing aromatic amino acids, nitrogen bases, and nucleotides were measured in the presence of potassium ferrate(VI), and polymerase chain reaction (PCR) was conducted in the nucleic acid solutions before and after application of ferrate(VI).

Absorption spectra

It was found that contact with ferrate(VI) invariably eliminated characteristic 280 nm absorption peak of tryptophane and phenylalanine. Likewise, the peak at 260 nm in the solutions of the four nucleotides, A, T, G and C, was drastically decreased in the presence of ferrate(VI).

PCR Data

Ferrate(VI) reacts not only with isolated nucleotides, but with the entire cDNA molecules isolated from *Shewanella putrificiense* bacteria. We found also that plasmids containing inserted genes of 16sRNA from different sources could not be used as templates for polymerase chain reaction (PCR) after contacting ferrate(VI). In that sense, sterilization with ferrate(VI) is essentially different from other agents: usually, enzymes catalyzing template synthesis of DNA are damaged, while the genetic material itself remains unaltered and can be used again for synthesis once enzyme inhibitor is removed or destroyed. Genetic material in the form of bacterial DNA, was totally destroyed by ferrate(VI), so that no further polymerization of complementary chain were possible. Although the genetic material itself remains unaltered and can be used again for template synthesis once the enzyme inhibitor is removed or destroyed. With ferrate(VI), the situation is different: although ferrate(VI) is easily destroyed and removed from the solution as iron(III) oxide, no further DNA synthesis occurred until the solution was infected by outer sources. For that reason, it seems reasonable to believe that ferrate(VI) has some potential as a deeply sterilizing agent, including decontamination of air and water in spacecrafts or space stations. It is noteworthy

that no hazardous or harmful wastes are produced with ferrate, iron(III) oxide being the only byproduct.

SPECTRAL CHARACTERIZATION OF FERRATE(VI)

Ferrate(VI) displays multiple spectral features making it a convenient material for spectral detection and quantitative determination. We discuss here a few specific methods which are suitable for remote sensing, contact measurements *in situ*, and analysis of returned sample.

Absorption and reflectance spectra

A deep purple color which appears in highly alkaline iron-containing solutions when treated with strong oxidants was found centuries ago. This characteristic color is due to the tetrahedral ferrate(VI) anion, FeO_4^{2-} , with its absorption peak at 505-510 nm, and molar extinction of 1100-1300 $\text{M}^{-1}\text{cm}^{-1}$ at these wavelengths. This spectrum makes ferrate(VI) very distinct from other forms of dissolved iron, and makes absorption spectrum an appropriate tool for ferrate(VI) identification and quantitation when samples are available for dissolution.

With Mars exploration in view, a more practical alternative is the use of reflectance spectra that can be recorded by remote sensing from orbit. The broad-range reflectance spectrum of crystalline potassium ferrate is presented in Fig. 5, together with other forms of iron. The band at 1600 nm is a characteristic one, and it can be used as a marker to search for the presence of Fe(VI) on the Martian surface.

According to Viking's results, the content of oxidant in Martian soil is rather low, most likely in the ppm range. If this reactive material is the only one with ferrate(VI) spectral features, it certainly wouldn't be visible in reflectance spectra. However, we now know that combinations of ferrate(VI) anion with various metals may considerably differ in both their water solubility and reactivity. Most of ferrate(VI), if it is present at all, may be in the form of some non-reactive compounds, of which barium ferrate is an example. Though chemically rather resistant, they still give the characteristic peak at ca. 1600 nm, making the detection of ferrate(VI) likely by means of remote sensing reflectance spectroscopy.

Mössbauer Spectra

Mössbauer spectroscopy is the most powerful and straightforward approach to the identification of various oxidation states of iron. It is important in the context of these studies since a compact Mössbauer instrument has been developed for the future Mars missions and will be a part of the Athena payload [36]. The Mössbauer spectrum of a sample containing potassium ferrate(VI) and other iron species is shown in Fig. 6, together with a diagram of the ranges of isomer shifts in iron compounds with various valences and spin states, as referenced to iron metal at 300K. It is produced by a superposition of two main spec-

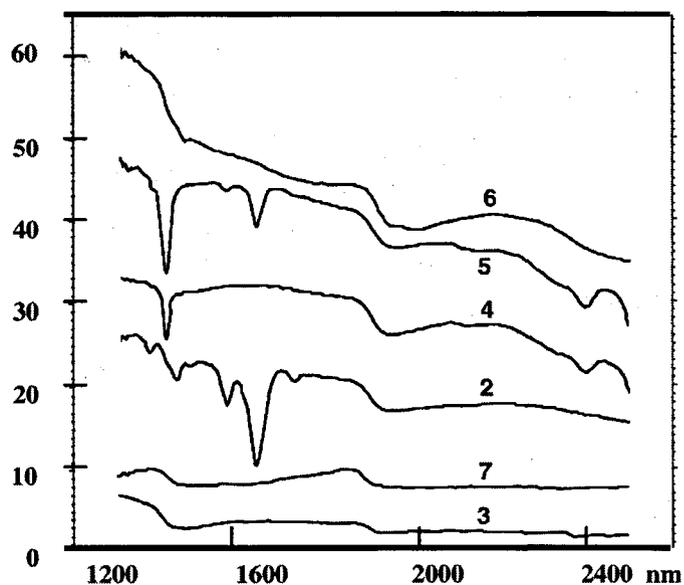
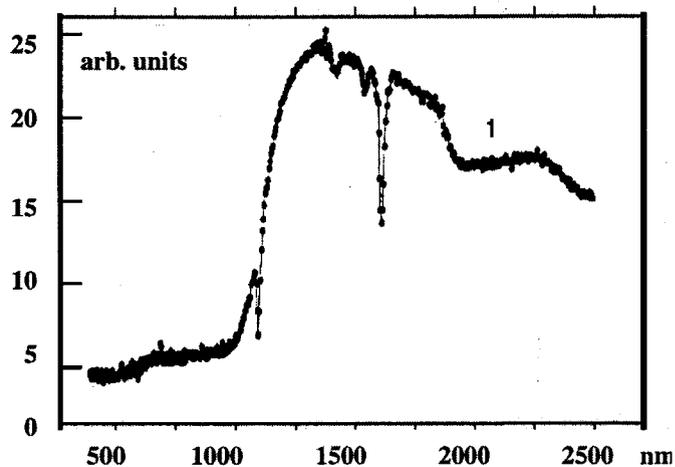


Fig. 5. Reflectance spectra of iron compounds. 1: Broad range spectrum of solid potassium ferrate; 2-7: spectra in the range 1200-2400 nm. 2: Solid K_2FeO_4 . 3: Fresh moisturized precipitate of Goethite, FeOOH . 4: $\text{CaO-Fe}_2\text{O}_3$ mixture, 10:1 by mass. 5: $\text{CaO-Fe}_2\text{O}_3\text{-K}_2\text{FeO}_4$ mixture, 20:2:1 by mass. 6: Solid FeSO_4 . 7: Solid $\text{Fe}_2(\text{SO}_4)_3$.

tral components. One component consists of a singlet line with a negative isomer shift of -0.91 mm/s, and the other is a quadrupole-split doublet with an isomer shift of $+0.32$ mm/s and quadrupole splitting of 0.57 mm/s. The relative abundance of these two components can be estimated from the relative area of the two sub-spectra. The singlet component has a negative isomer shift, which is opposite in sign to the isomer shifts for Fe(II) and Fe(III) phases and is identified as the Fe(VI) phase. The doublet component has an isomer shift and quadrupole splitting consistent with an

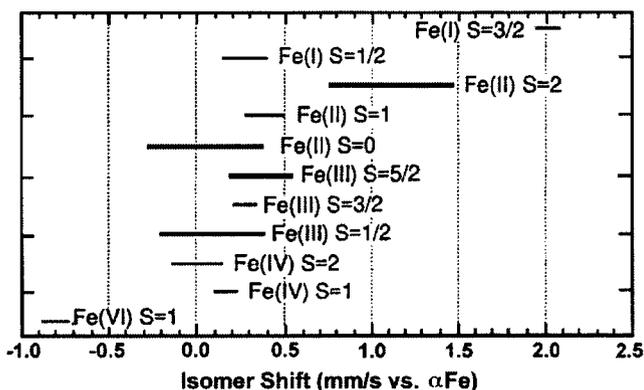
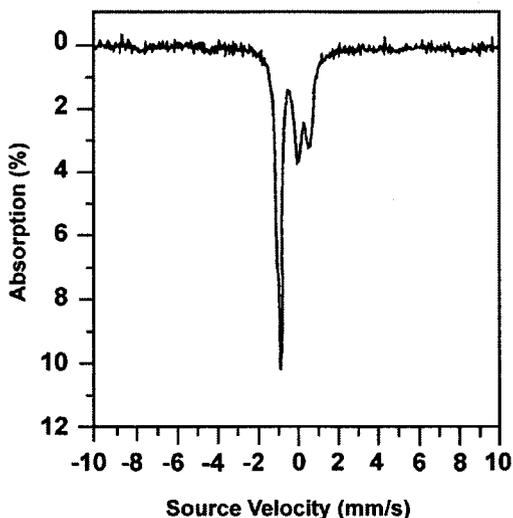


Fig. 6. Mössbauer spectrum of K_2FeO_4 , with an admixture of Fe_2O_3 , and the diagram of isomer shifts of iron in various oxidation states.

Fe(III)-bearing phase which is paramagnetic at room temperature.

X-Ray Spectra

X-Ray absorption near edge spectra (XANES) were obtained using the Material Research Collaborative Access Team Sector at the Advanced Photon Source, Argonne National Laboratory. This technique relies on heavy, large-scale facilities, and is not usable in any space mission in the foreseeable future. However, it has great potential for the analysis of returned samples, due to its sensitivity to the structural environment of iron atoms, and thus to its oxidation state as well. The focus, in this technique, is on the spectral region very close (within about 30eV) to the ionization threshold of the compound in question. A XANES spectrum of ferrate(VI) sample is shown in Fig. 7. Comparison of XANES spectra of a sample with XANES spectra of a known standard allows identification of the oxidation state and local geometry around iron. For iron, X-ray absorption edge energy is ~ 7112 eV, and a characteristic pre-edge feature is observed from both

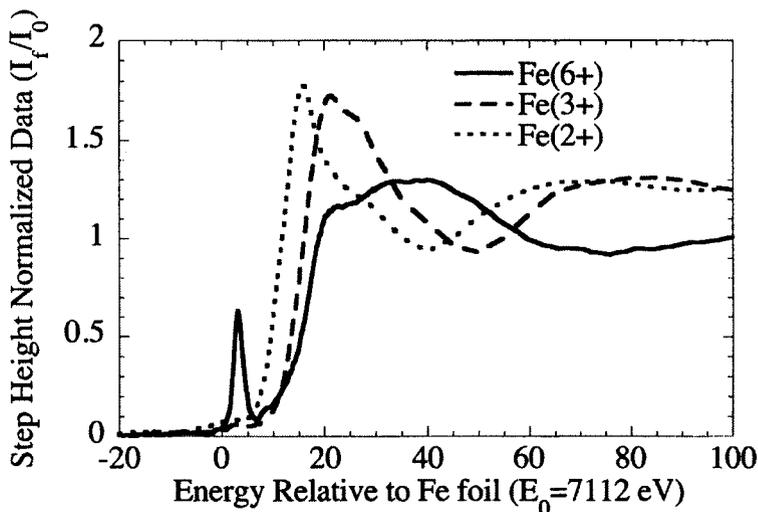


Fig. 7. XANES of solutions of iron compounds: Fe(VI) as K_2FeO_4 , Fe(III) as $Fe(NO_3)_3$, Fe(II) as $FeCl_2$.

solutions and solid samples containing tetrahedrally coordinated Fe(VI) in ferrate dianion. Additionally, more subtle changes in X-ray absorption edge energy have been shown to enable the identification of Fe(II) and Fe(III) valence states.

CONCLUSION

To summarize, the data presented are consistent with the hypothesis of ferrate(VI) and possibly other higher oxidation state iron contributing to the oxidizing pool in the Martian soil, and provide spectral and chemical approaches to make this hypothesis testable in forthcoming Mars missions.

ACKNOWLEDGMENTS

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REFERENCES

- Oyama, V.I., Berdahl, B.J. The Viking gas exchange experiment results from Chryse and Utopia surface samples. *J. Geophys. Res.* 82, 4669-4675 (1977)
- Levin, G.V., Straat, P.A. Recent results for the Viking labeled release experiment on Mars. *J. Geophys. Res.* 82, 4663-4667 (1977)

3. McKay, C.P., Grunthaner, F.J., Lane, A.L., Herring, M., Bartman, R.K., Ksendzov, A., Manning, C.M., Lamb, J.L., Williams, R.M., Ricco, A.J., Butler, M.A., Murray, B.C., Quinn, R.C., Zent, A.P., Klein, H.P., Levin, G.V. The Mars Oxidant experiment (MO_x) for Mars '96. *Planet. Space Sci.* 46, 769–777 (1998).
4. Klen, H.P. The Viking biological experiments on Mars. *Icarus* 34, 666–674 (1978)
5. Zent, A.P., McKay, C.P. The chemical reactivity of the Martian soil and implications for future missions. *Icarus* 108, 146–157 (1994).
6. Bullock, M.A., Stoker, C.R., McKay, C.P., Zent, A.P. A coupled soil-atmosphere model of H₂O₂ on Mars. *Icarus* 107, 142–154 (1994).
7. Hunten, D. Possible oxidant sources in the atmosphere and surface of Mars. *J. Mol. Evol.* 14, 57–64 (1979).
8. Huguenin, R.L., Miller, K.J., Harwood, W.S. Frost-weathering on Mars: experimental evidence for peroxide formation. *J. Mol. Evol.* 14, 103–132 (1979).
9. Levin G.V., Straat, P.A. A search for a non-biological explanation of the Viking labeled release life detection experiment. *Icarus* 45, 494–516 (1981).
10. McDonald, G.D., Vanssay, E. de, Buckley, J.R. Oxidation of organic macromolecules by hydrogen peroxide: implications for stability of biomarkers on Mars. *Icarus* 132, 170–175 (1998).
11. Yen, A.S. Ultraviolet radiation-induced alteration of Martian surface materials. Presented at the *Fifth International Conference on Mars*, Pasadena, California, #6076 (1999).
12. Quinn, R.C., and A.P. Zent 1999. Peroxide-modified titanium dioxide: a chemical analog of putative Martian oxidants. *Origins of Life* 29, 59–72.
13. Banin, A., Clark, B.C., Winke, H. Surface Chemistry and Mineralogy. In *Mars* (H.H. Kiefer, B.M. Jakosky, C.W. Snyder, and M.S. Matthews, Eds.), pp. 594–626. Univ. of Arizona Press, Tucson (1992).
14. Woods, R.H. Heat, free energy, and entropy of ferrate(VI) ion. *J. Am. Chem. Soc.* 80, 2038–2041 (1958).
15. Thompson, G.V., Ockerman, L.T., Schreyer, J.M. Preparation and purification of potassium ferrate(VI). *Ibid.* 73, 1379–1381 (1951).
16. Delaude L., Laszlo, P. A novel oxidizing reagent based on potassium ferrate(VI). *J. Org. Chem.* 61, 6360–6370 (1996).
17. Malchus, M., Jansen, M. Combination of ion exchange and freeze drying as a synthetic route to new oxoferrate(VI) M₂FeO₄ with M = Li, Na, N(CH₃)₄, N(CH₃)₃Bzl, N(CH₃)₃Ph. *Z. Anorg. Chem.* 624, 1846–1854 (1998).
18. Kulikov, L.A., Yurchenko, A.Y., Perfiliev, Y.D. Preparation of cesium ferrate(VI) from metallic iron. *Vestnik Moskovskogo Universiteta, ser. Chemistry*, 40, 137–138 (1999, Russ).
19. Johnson, M.D., Read, J.F. Kinetics and mechanism of the ferrate oxidation of thiosulfate and other sulfur-containing species. *Inorg. Chem.* 35, 6795–6799 (1996).
20. Licht, S., Wang, B., Ghosh, S. Energetic iron(VI) chemistry: the super-ion battery. *Science* 285, 1039–1042 (1999).
21. Kopelev, N.S., Perfiliev, Y.D., Kiselev Y.M. Mössbauer study of sodium ferrates(IV) and sodium ferrates(VI). *J. Radioanalyt. Nucl. Chem. Ar.* 162, 239–251 (1992).
22. Dedushenko, S.K., Kholodovskaya, L.N., Perfiliev, Y.D., Kiselev, Y.M., Saprykin, A.A., Kamozin, P.N., Lemesheva, D.G. On the possible existence of unusual oxidation state of iron in the Na-Fe-O system. *J. Alloys & Compounds* 262, 78–80 (1997).
23. Kempe, S., Degens, E.T. An early soda ocean? *Chem. Geol.* 53, 95–108 (1985).
24. Goff, H., Murmann, R.K. Studies of the mechanism of isotopic oxygen exchange and reduction of ferrate(VI) ion. *J. Amer. Chem. Soc.* 93, 6058–6065 (1977).
25. Mills, A.A., Sims, M.R. pH of the Martian surface. *Planet. Space Sci.* 43, 695–696 (1995).
26. Burns, R.G., Fisher, D.S. Rates of oxidative weathering on the surface of Mars. *J. Geophys. Res.–Planets* 98: (E2) 3365–3372 (1993).
27. Quinn, R.C., Orenberg, J. Simulations of the Viking gas exchange experiment using palagoinite and Fe-Orich montmorillonite as terrestrial analogs: Implications for the surface composition of Mars. *Geochim. et Geophys. Acta* 57, 4611–4618 (1993)
28. Wagner, W.F., Gump, J.R., Hurt, E.N. Factors affecting the stability of aqueous potassium ferrate(VI) solutions. *Anal. Chem.* 24, 1497–1498 (1952).
29. Schreyer, J.M., Thompson, G.W., Ockerman, L.T. Oxidation of chromium(III) with potassium ferrate(VI). *Anal. Chem.* 22, 1426–1427 (1951)
30. Sharma, V.K., Bloom, J.T., Joshi, V.N. Oxidation of ammonia with ferrate(VI). *J. Env. Sci. & Health A33*, 635–650 (1998).
31. Johnson, M.D., Read, J.F. Kinetics and mechanism of the ferrate oxidation of thiosulfate and other sulfur-containing species. *Inorg. Chem.* 35, 6795–6799 (1996).
32. Sharma, V.K., Smith, J.O., Millero, F.J. Ferrate(VI) oxidation of hydrogen sulfide. *Envir. Sci. Technol.* 31, 2486–2491 (1997).
33. Read, J.F., Mehlman, S.A., Watson, K.J. The kinetics and mechanism of the oxidation of 1,4-thioxane by potassium ferrate. *Inorg. Chim. Acta*, 267, 159–163. (1998).
34. Read, J.F., Wyand, A.E.H. The kinetics and mechanism of the oxidation of seleno-D, L-methionine by potassium ferrate. *Trans. Met. Chem.* 23, 755–762 (1998).
35. Carr, J.D., Keller, P.B., Tabatabai, A., Spichal, D., Erickson, J., McLaughlin, C.W. Properties of ferrate(VI) in aqueous solution: an alternative oxidant in wastewater treatment. In *Water Chlorination*, 5, 1285–1298 (1985).
36. Klingelhöfer, G., et al. The Miniaturized Spectrometer MIMOS II: The 2001 and 2003 US Mars Missions and Terrestrial Applications in Materials Science and Industry, In: *Mössbauer Spectroscopy in Materials Science*, (M. Miglierini and D. Petridis, eds). Kluwer Academic Publishers. (1999).