

Received 31 December 1979; accepted 15 April 1980.

- Mandolesi, N., Morigi, C. & Sironi, G. *Astr. Astrophys.* **67**, L5 (1978).
- van den Bergh, S. *Astr. J.* **84**, 71 (1979).
- Julien, P. F. & Helmen, H. F. *Nature* **272**, 699 (1978).
- Lamb, R. & Worrall, D. *Astrophys. J. Lett.* **231**, L121 (1979).
- Haymes, C., Meegan, C. A. & Fishman, G. J. *Astro. Astrophys.* **79**, 88 (1979).
- Helmen, H. F. & Weeks, T. C. *Astrophys. J.* **228**, 531 (1979).
- Thompson, D. J., Fichtel, C. E., Hartman, R. C., Kniffen, D. A. & Lamb, R. C. *Astrophys. J.* **213**, 252 (1977).
- Masnou, J. L. *et al.* *12th ESLAB Symp.*, ESA-SP-124, 33 (1978).
- Cheng, A. & Ruderman, M. Preprint Rutgers Univ. (1979).
- Swanenburg, B. N. *Europhys. Study Conf. γ -ray Astronomy after COS B*, Erice (1979).
- Pinkau, K. *Nature* **277**, 17 (1979).
- Abdulvahap, M. & Morrison, P. *Astrophys. J. Lett.* **221**, L33 (1978).
- Montmerle, T. *Astrophys. J.* **231**, 95 (1979).
- Pauliny-Toth, I. I. K., Wade, C. M. & Heeschen, D. S. *Astrophys. J. Suppl.* **13**, 65, (1966).
- Dickel, J. R., Yang, K. S., McVittie, G. C. & Swenson, G. W. *Astrophys. J.* **72**, 757 (1967).
- Hoglund, B. *Astrophys. J. Suppl.* **15**, 61 (1967).
- Gower, J., Scott, P. F. & Wills, D. *Mon. Not. R. astr. Soc.* **71**, 49, (1967).
- Biggami, G. F., Gavazzi, G. & Harten, R. H. *Astr. Astrophys.* **54**, 951 (1977).
- Manchester, R. N., Taylor, J. H. *Pulsars*, 59 (W. H. Freeman, San Francisco, 1978).

Does feroxyhyte occur on the surface of Mars?

Roger G. Burns

Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

The red colour of Mars has long been attributed to the occurrence of ferric oxides on its surface and in atmospheric dust storms. Such a belief has been accentuated by results of Viking Lander experiments on the surface of Mars, which suggested the presence of maghaemite, γ -Fe₂O₃ (refs 1, 2). This dark brown, ferromagnetic iron (III) oxide phase not only conforms with the colour and magnetic properties of dust on the martian surface, but suggests that maghaemite acted as a catalyst in some of the biological experiments performed *in situ* on Mars³. Many of the physical properties and chemical reactions attributed to maghaemite, however, are also displayed by δ -FeOOH, an oxide hydroxide polymorph of ferric iron^{4,5}. On Earth, δ -FeOOH occurs as the mineral feroxyhyte in gleyed soils and in submarine manganese nodule deposits⁶. Some of the properties and paragenetic relationships of feroxyhyte are described here and it is suggested that δ -FeOOH is a prime candidate for the red-brown ferromagnetic phase coating the surface of Mars.

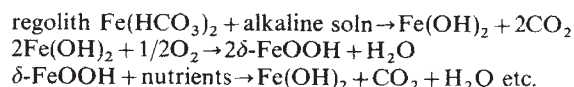
Synthetic δ -FeOOH is formed as a deep-brown precipitate during the oxidation of Fe(OH)₂ in partially deoxygenated, slightly alkaline solutions^{7,8}. It is generally poorly crystalline and may contain up to 3 wt % excess H₂O (ref. 7). Significantly, δ -FeOOH differs from other FeOOH polymorphs by being ferromagnetic ($T_c \approx 450$ K), and therefore resembles γ -Fe₂O₃. Depending on its particle size, the saturation magnetization of δ -FeOOH is 30–50% the value of γ -Fe₂O₃ at ambient martian temperatures (200 K)^{7,9}, so that δ -FeOOH, too, will adhere to magnets such as those attached to the Viking Lander spacecraft¹. The IR spectrum of δ -FeOOH contains three maxima in the range 2.95–3.4 μ m (refs 7, 10); similar spectral features are observed in remote-sensed spectra of Mars¹¹. The catalytic efficiency of δ -FeOOH in the decomposition of H₂O₂, for example, is 10-fold higher than α -FeOOH (goethite) and α -Fe₂O₃ (haematite)¹², and is comparable to γ -Fe₂O₃ (maghaemite) which was postulated to interfere with the biological experiments on the Viking Landers³.

In the marine environment on Earth, the formation of feroxyhyte is believed to involve redox reactions in buried sediments^{6,13}. The Fe(HCO₃)₂ generated there migrates in

pore waters to the surface of the sediments. At the sediment-seawater interface, where the temperature and pH are typically 275 K and 8.1, respectively, Fe(OH)₂ is formed initially, but is oxidized by the oxygenated seawater to feroxyhyte. This poorly crystalline δ -FeOOH phase coats debris and authigenic silicates such as zeolites, and forms a substrate for the deposition of manganese (IV) oxides in ferromanganese crust and nodule deposits¹⁴. The δ -FeOOH phase is also susceptible to secondary redox reactions inside manganese nodules, where it catalyses the decomposition of enclosed biogenic debris and organically chelated Ni(II) and Cu(II) species¹⁵, leading to the enrichment of these transition metals in manganese nodules on the sea floor beneath equatorial high biological productivity zones.

Such processes in the terrestrial marine environment enables us to postulate on the reactions on Mars which might lead to the formation of feroxyhyte in the martian regolith. Ferrous ions, derived from disintegration of basalt by chemical weathering, mechanical abrasion (ablation and freeze-thaw) and photochemical¹⁶ processes, form stable Fe(HCO₃)₂ in the chloride-sulphate-rich, CO₂-saturated, O₂-depleted brines in the permafrost on Mars. When the Fe(HCO₃)₂ is slowly oxidized, poorly crystalline feroxyhyte is produced which forms a thin red-brown veneer on the fractured rock surfaces. The fine-grained feroxyhyte particles are easily transported during dust storms and become major components in the bright areas of the martian surface. The large specific surface of the feroxyhyte particles also makes them effective substrates for the reversible chemisorption of water vapour from the martian atmosphere.

The synthesis and chemical properties of δ -FeOOH might also explain some of the results obtained during the Viking biological experiments on Mars^{3,17}. Metal peroxides or superoxides on the martian surface when moistened would liberate oxygen and produce alkaline solutions, thereby initiating the following reactions:



The biological experiments on Mars thus promoted the conversion of Fe(HCO₃)₂ in the regolith to feroxyhyte, the catalytic properties of which led to the breakdown of nutrients supplied during the Viking Lander experiments.

Feroxyhyte, therefore, has suitable colour, magnetic, chemisorption, spectral, redox and paragenetic properties to make it a constituent of the surface of Mars.

This research was supported by the NSF grant OCE 78-27495; and by NASA grant NSG 7604.

Received 20 February; accepted 14 April 1980.

- Hargraves, R. B., Collinson, D. W., Arvidson, R. E. & Spitzer, C. R. *J. geophys. Res.* **82**, 4547 (1977).
- Toulmin, P. III *et al.* *J. geophys. Res.* **82**, 4625 (1977).
- Oyama, V. I. & Berdahl, B. J. *J. geophys. Res.* **82**, 4669 (1977).
- Burns, R. G. & Burns, V. M. in *Marine Manganese Deposits* (ed. Glasby, G. P.) 212 (Elsevier, Amsterdam, 1977).
- Murray, J. W. in *Marine Minerals* Ch. 2 (ed. Burns, R. G.) 47 (Mineralogy Society of America Monograph 6, 1979).
- Chukhrov, F. V., Zvyagin, B. B., Yermilova, L. P. & Gorshkov, A. I. *Miner. Deposita* **11**, 24 (1976).
- Okamoto, S. *J. Am. ceram. Soc.* **51**, 594 (1968).
- Atkinson, R. J. *Aust. J. Chem.* **29**, 2149 (1976).
- Coey, J. M. D. & Khalafalla, D. *Phys. Stat. Sol. A* **11**, 229 (1972).
- Feitknecht, W., Haeni, H. & Dvorak, V. in *Proc. 6th int. Symp. Reactivity of Solids*, 237 (1969).
- Houck, J. R., Pollack, J. B., Sagan, C., Schaack, D. & Decker, J. A. Jr *Icarus* **18**, 470 (1973).
- Sara, J. *Chem. Listy*, **63**, 112 (1969).
- Burns, R. G. & Burns, V. M. in *The Sea* Vol. 7 (ed. Emiliani, C.) (Wiley, New York, in the press).
- Burns, R. G. & Burns, V. M. *Nature* **255**, 130 (1975).
- Burns, V. M. & Burns, R. G. *Earth planet. Sci. Lett.* **39**, 341 (1978).
- Huguenin, R. L., Prinn, R. G. & Maderazzo, M. *Icarus* **32**, 270 (1977).
- Klein, H. P. *Icarus* **34**, 666 (1978).