

**THE STABILITY OF OXYAMPHIBOLES: EXISTENCE OF FERRIC-BEARING MINERALS UNDER THE REDUCING CONDITIONS ON THE SURFACE OF VENUS**

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**Introduction:** An enigma of Venusian mineralogy is the suggestion that  $\text{Fe}^{3+}$ -bearing minerals exist under the reducing conditions of the Venusian atmosphere. Analysis of the spectrophotometric data from the Venera 13 and 14 missions, combined with the laboratory reflectance spectral measurements of oxidized basalts at elevated temperatures, led to the suggestion that metastable hematite might exist on Venus [1]. Heating experiments at  $475^\circ\text{C}$  when  $f_{\text{O}_2} \sim 10^{-24}$ , demonstrated that the hematite to magnetite conversion is rapid, indicating metastable hematite is not present on Venus [2]. In addition to hematite, several other ferric oxide and silicate minerals have been proposed to occur on Venus, including laihunite or ferrifayalite [3],  $\text{Fe}^{3+}$ -bearing tephroite, oxyamphiboles [4], and oxybiotites [4]. Heating experiments performed on these  $\text{Fe}^{3+}$ -bearing minerals under temperature- $f_{\text{O}_2}$  conditions existing on Venus suggest that only oxyamphiboles and oxybiotites may be stable on the surface of Venus.

**Experimental Procedure:** To simulate the appropriate redox conditions of the Venusian atmosphere, a Ni/NiO solid buffer was used. The Ni/NiO buffer, when heated to  $475^\circ\text{C}$  in an evacuated quartz cell, provides an  $f_{\text{O}_2}$  of approximately  $10^{-24}$  [5]. The Ni/NiO buffer and mineral samples were wrapped in separate silver foil sheets. After heating periods of 1-30 days, the samples were quenched and analyzed by Mössbauer spectroscopy.

**Results:** The laihunite (25%  $\text{Fe}^{3+}$ ) and the tephroite (16%  $\text{Fe}^{3+}$ ) samples were each shown to have all of their  $\text{Fe}^{3+}$  reduced to  $\text{Fe}^{2+}$  when heated with the Ni/NiO buffer at  $475^\circ\text{C}$  for 7 days and 14 days, respectively. Conversion of the  $\text{Fe}^{3+}$  in these olivines to  $\text{Fe}^{2+}$  is demonstrated by the Mössbauer spectra of laihunite, illustrated in figure 1.

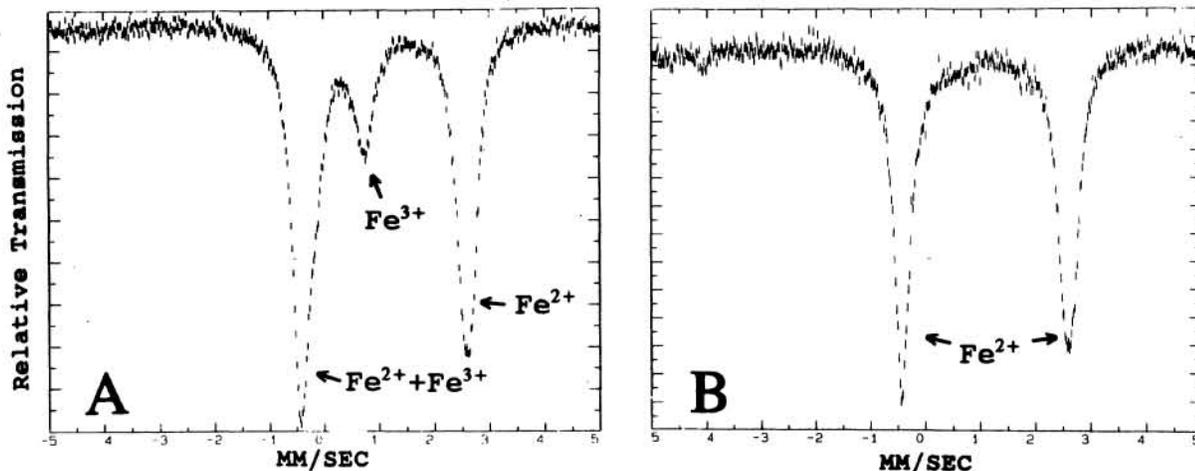


Figure 1: Laihunite before (A) and after (B) heating with Ni/NiO.

Heating experiments performed with a variety of amphiboles, including glaucophane, actinolite, hornblende, and kaersutite, indicated that  $\text{Fe}^{3+}$  ions initially present in the amphiboles are stable under Venusian surface conditions, where  $T \sim 475^\circ\text{C}$  and  $f_{\text{O}_2} < 10^{-21}$ . For example, the Mössbauer spectra illustrated in figure 2 of hornblende before and after heating for 28 days show that virtually none of the  $\text{Fe}^{3+}$  has been reduced (cf. laihunite in figure 1). In a related experiment, hornblende was first heated in air for 20 minutes at  $700^\circ\text{C}$  to oxidize most of the  $\text{Fe}^{2+}$  ions, after which the oxidized sample was heated at  $475^\circ\text{C}$  with the Ni/NiO buffer for 7 days. The Mössbauer spectra of these reaction products, illustrated in figure 3, show that  $\text{Fe}^{3+}$  ions remain in the oxidized hornblende when heated under the reducing conditions of the Ni/NiO buffer.

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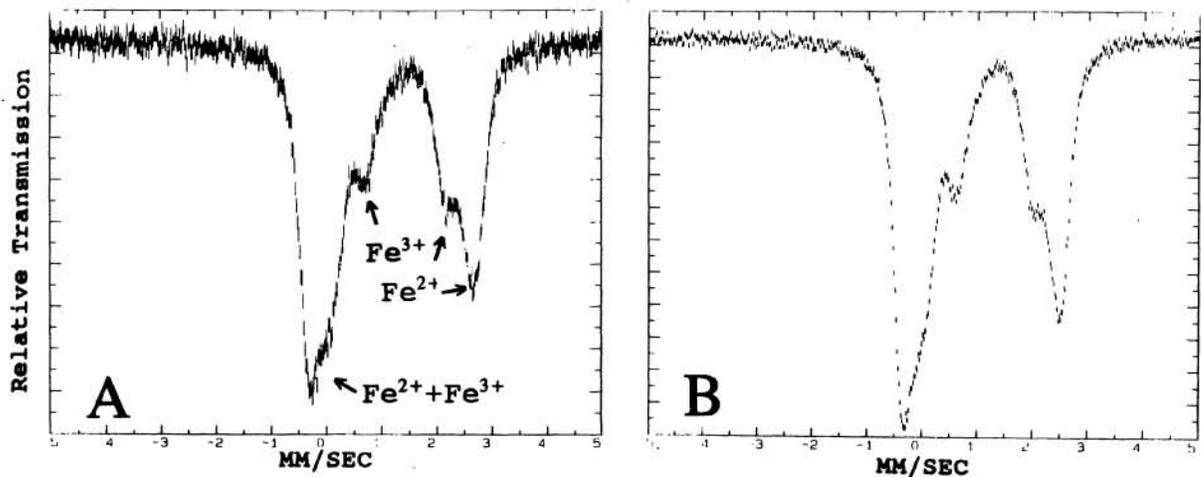


Figure 2: Hornblende before (A) and after (B) heating with Ni/NiO.

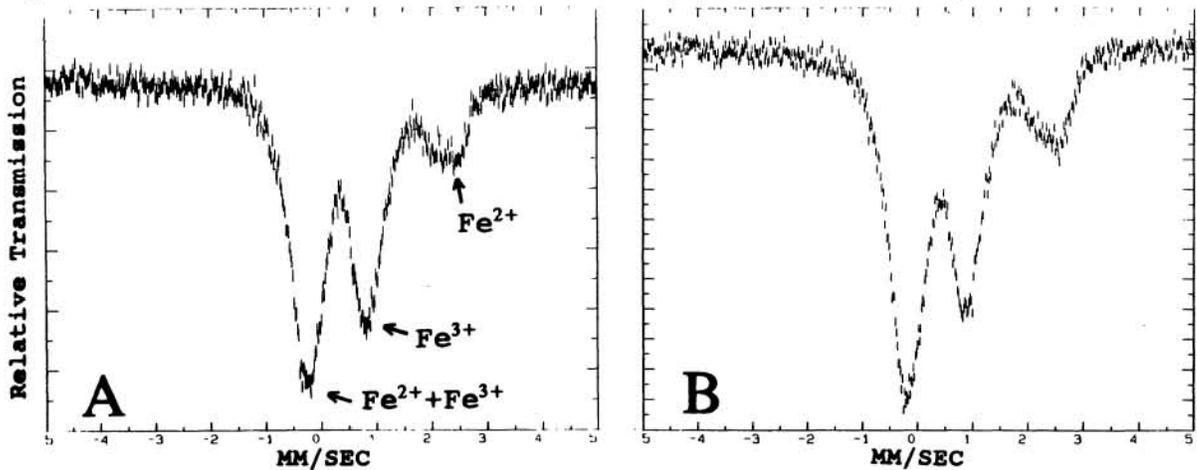


Figure 3: Oxidized hornblende before (A) and after (B) heating with Ni/NiO.

**Discussion:** The stability of  $\text{Fe}^{3+}$  in the oxyamphiboles may be explained by the intracrystalline redox reaction



The  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  ions remain in the crystal structure as a result of this dehydrogenation reaction. Thus, no oxygen is added to the amphibole. This contrasts with the laihunite and hematite in which reduction, when heated with the Ni/NiO buffer, proceeds by diffusion of oxygen atoms from their crystal structures. The amphiboles lack this "excess" oxygen and cannot be reduced with the Ni/NiO buffer. Preliminary studies show that oxybiotites, which also can be formed by the removal of hydrogen during intracrystalline redox reactions, are also stable when heated at 475°C with the Ni/NiO buffer. These results also conform with phase equilibrium diagrams for iron-bearing calcic amphiboles and oxybiotites [6], which indicate that they have stability fields within ranges of temperatures, oxygen fugacities and atmospheric pressures existing on the Venusian surface.

**References:** [1] C.M. Pieters et al., *Science*, 234, 1379 (1986); [2] D.W. Straub & R.G. Burns, *Lun. Planet. Sci.*, XXIII, 1375 (1992); [3] B. Fegley, Jr., A.H. Treiman & V.I. Sharpton, *Proc. Lunar Planet. Sci.*, 22, 3 (1992); [4] R.G. Burns & D.W. Straub, *Intern. Colloq. Venus, LPI Contrib. No. 789*, p.15 (1992); *EOS, Trans. Amer. Geophys. Un.*, 73, 332 (1992); [5] D.H. Lindsley, *Rev. Min.*, III, L-61 (1976); [6] H.P. Eugster & D.A. Wones, *J. Petrol.*, 3, 82 (1972); [7] Research supported by NASA grant NAGW-2220.