

The oxidation mechanism of vivianite as studied by Mössbauer spectroscopy

CATHERINE A. MCCAMMON¹ AND ROGER G. BURNS

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

Abstract

The crystal structure of vivianite contains Fe^{2+} ions in isolated Fe_A^{2+} octahedra and in paired Fe_B^{2+} octahedra. Mössbauer spectral measurements of vivianites mechanically ground in air demonstrate that $\text{Fe}_B^{2+}/\text{Fe}_A^{2+}$ increases with rising Fe^{3+} concentration, suggesting that there is a greater probability of oxidizing remaining Fe_A^{2+} ions than the second Fe_B^{2+} ion of an existing $\text{Fe}_B^{2+}-\text{Fe}_B^{3+}$ pair. A model is proposed whereby the electronic configuration of $\text{Fe}_B^{2+}-\text{Fe}_B^{3+}$ stabilizes the pair relative to $\text{Fe}_B^{2+}-\text{Fe}_B^{2+}$. Our experimental data indicate that between 35% and 50% of the $\text{Fe}_B^{2+}-\text{Fe}_B^{3+}$ pairs are stable with regard to oxidation. The mechanism of oxidation of Fe^{2+} ions in vivianite involves H_2O ligands which are converted to OH^- ions. As a result, the vivianite structure collapses due to the elimination of hydrogen bonds, facilitating further oxidation. Extensively oxidized vivianites not only disintegrate into friable powders but also become deep blue due to $\text{Fe}_B^{2+} \rightarrow \text{Fe}_B^{3+}$ charge transfer transitions.

Introduction

Vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, is well known for its vulnerability to atmospheric oxidation (Watson, 1918; Moore, 1971), during which the color changes from virtually colorless to a dark blue (α)-pale green (β , γ) pleochroism. Although vivianite has been the focus of numerous crystal-chemical and spectral studies (e.g., Faye *et al.*, 1968; Moore, 1971; Mao, 1976; Mattievich and Danon, 1977), the mechanism of oxidation of Fe^{2+} ions in the vivianite structure has not been determined.

The crystal structure of vivianite (Mori and Ito, 1950) contains iron in two distinct octahedral sites. In the isolated Fe_A octahedra, Fe^{2+} ions are coordinated to four H_2O ligands in the rhombic plane and to two *trans*-oxygens of $[\text{PO}_4]^{3-}$ tetrahedra. In the Fe_B octahedra, two H_2O ligands are coordinated to Fe^{2+} in a *cis* arrangement, and four oxygens of $[\text{PO}_4]^{3-}$ tetrahedra supply the remaining ligands of the octahedron (Fig. 1). Two Fe_B octahedra share a common O-O edge across which the Fe^{2+} ions are separated by only 2.96 Å along the *b* axis. Hydrogen bonding between the H_2O ligands holds together sheets consisting of linked Fe_A octahedra, PO_4 tetrahedra, and

double Fe_B octahedra. This weak bonding accounts for the perfect (010) cleavage of vivianite.

The occurrence of paired Fe_B octahedra and the short Fe_B-Fe_B interatomic distance provide a simple explanation for the blue-green pleochroism caused by the polarization dependence of the intense absorption band centered at about $15,000 \text{ cm}^{-1}$ ($E \parallel b$ (α) axis); the color originates from $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer between adjacent ferrous and ferric ions in edge-shared Fe_B octahedra (Faye *et al.*, 1968; Loeffler *et al.*, 1975). Vivianite is regarded as a type example of homonuclear intervalence transitions (Hush, 1967; Robin and Day, 1967; Burns *et al.*, 1980). Implicit in these assignments, however, is the assumption that some of the Fe^{2+} ions in Fe_B sites have been oxidized to Fe^{3+} . The question of whether Fe_A^{2+} ions are also oxidized has not been answered.

Using the Mössbauer effect, we have studied the oxidation of vivianite resulting from mechanical grinding in air. The results obtained from the Mössbauer spectral measurements suggest a mechanism for the oxidation of Fe^{2+} ions in vivianite.

Experimental procedures

Eight vivianite specimens donated from mineral collections at Harvard, the Massachusetts Institute of Technology, and the Geological Survey of Canada

¹ Present address: Research School of Earth Sciences, Australian National University, Canberra, ACT 2600, Australia.

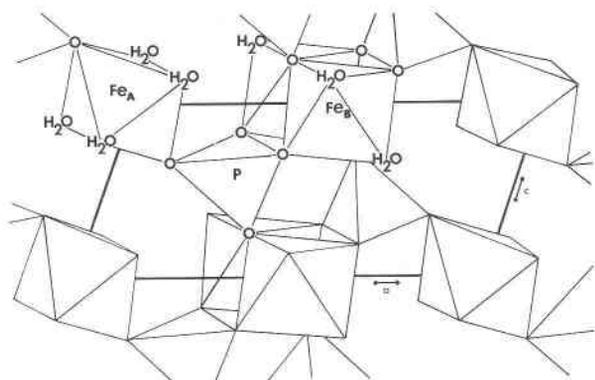


Fig. 1. The structure of vivianite viewed along the b axis (after Mori and Ito, 1950). Note that hydrogen bonds between *cis* H_2O ligands of Fe_B octahedra and H_2O ligands of Fe_A octahedra in adjacent a - c planes account for the perfect (010) cleavage of vivianite.

were subjected to X-ray diffraction, electron microprobe, optical absorption, and Mössbauer spectral measurements (McCammon, 1978). Two specimens showing minimal initial oxidation were selected for further studies described below: (a) #100794, from Ruth, Nevada (Dana Collection, Harvard University); (b) #14198, from Llallagua, Bolivia (Geological Survey of Canada, Ottawa). X-ray diffraction analysis confirmed the identity and homogeneity of

the vivianites, and electron microprobe analyses revealed that less than 0.5 wt.% of impurities such as Mg, Mn, and SiO_2 were present.

For the initial Mössbauer measurements, the samples were first gently pulverized in an inert atmosphere, and then bulked with sucrose under acetone to aid in the randomization of the crystallites. The effective thickness of all samples was kept below 10 mg Fe/cm² to prevent line broadening. The Mössbauer spectra were recorded on a constant acceleration Austin Science Associates spectrometer using a 50 mCi Co^{57} source diffused into a Pd matrix. Calibration is reported relative to the spectrum of metallic Fe foil.

Samples of the two vivianites chosen for further measurements were oxidized by mechanical grinding in air for different periods ranging from a few minutes to several hours. Two different experimental procedures were used. Five separate samples of vivianite #14198 were ground for successively longer periods of time and the Mössbauer spectrum recorded for each sample. Conversely, one sample of vivianite #100794 was ground in air for a few minutes, mounted and run in the Mössbauer spectrometer. It was then reground for a longer period of time and another Mössbauer spectrum was recorded. This cycle was repeated five times.

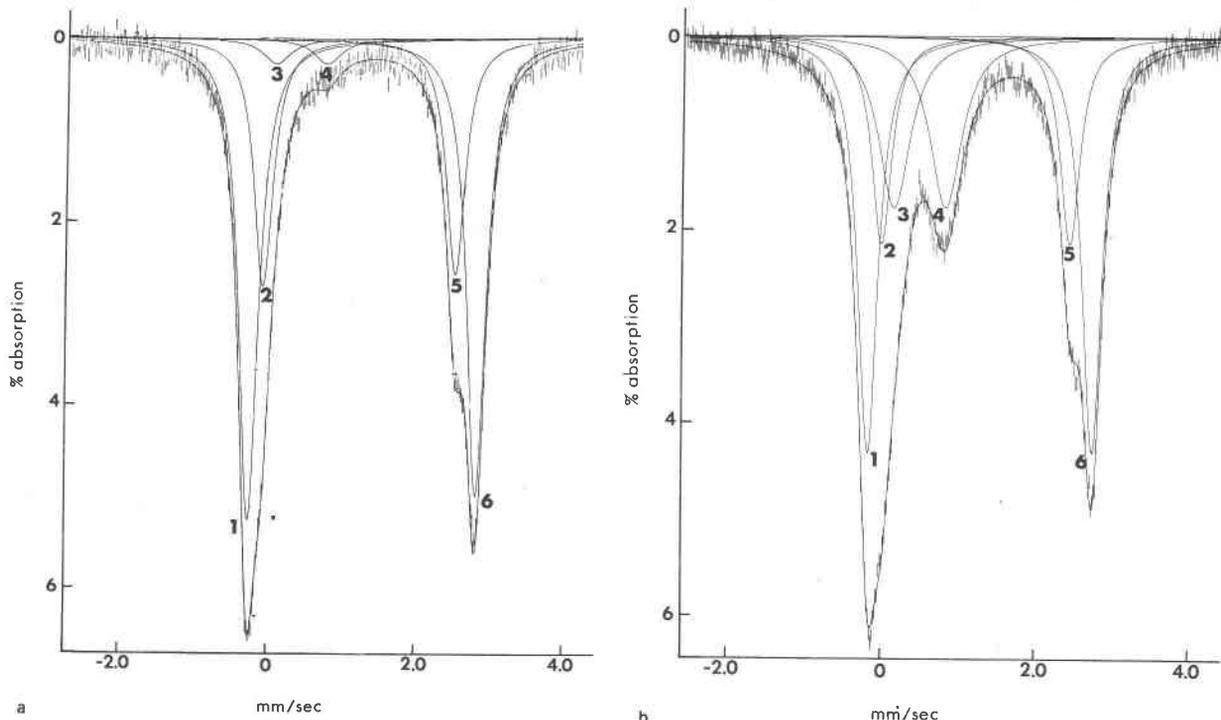


Fig. 2. Mössbauer spectra of vivianite #14198 (a) before and (b) after oxidation by mechanical grinding in air. Peaks 1 and 6: Fe_B^{2+} ; Peaks 2 and 5: Fe_A^{2+} ; Peaks 3 and 4: Fe^{3+} .

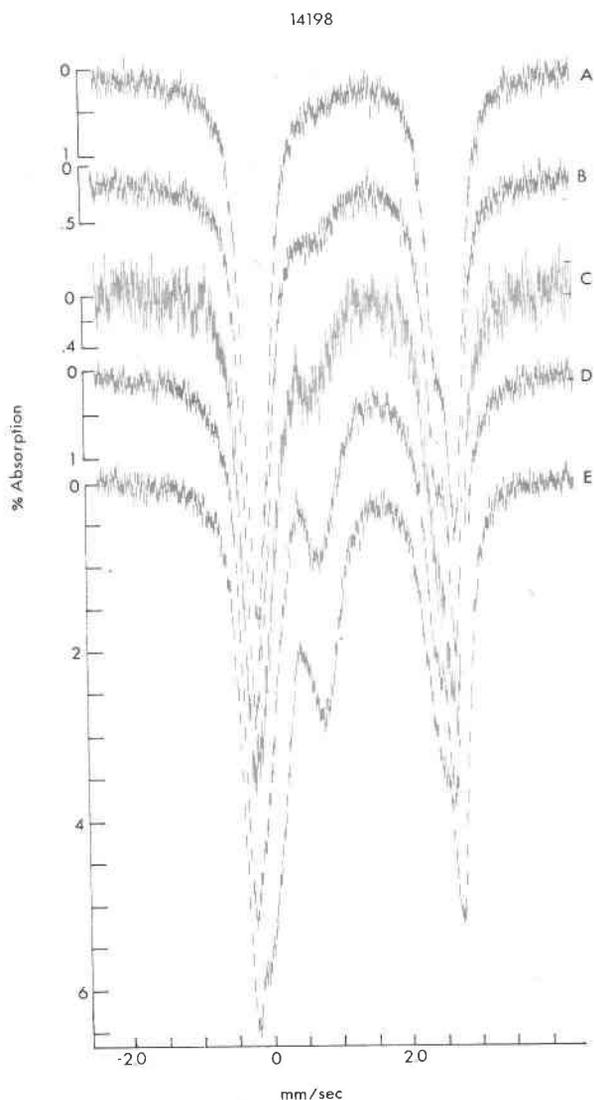


Fig. 3. Mössbauer spectrum profiles of vivianite #14198 mechanically ground in air for periods ranging from a few minutes (spectrum A) to several hours (spectrum E). Note the emergence and increased intensity of the peak at 0.75 mm/sec attributed to Fe^{3+} ions.

The Mössbauer spectra were fit to Lorentzian peaks using a non-linear least-squares computer method (Stone *et al.*, 1971). The presence of two distinct Fe sites in vivianite motivated our fitting the spectra to two Fe^{2+} doublets and one Fe^{3+} doublet, since ferric Mössbauer parameters are relatively insensitive to ligand environment. The widths and intensities were constrained to be equal for the component peaks of each quadrupole doublet in oxidized samples, and all Fe^{2+} peaks were constrained to have equal widths. Relative concentrations of Fe^{2+} and Fe^{3+} ions were estimated from computed peak areas

assuming equal recoil-free fractions for Fe_A^{2+} , Fe_B^{2+} , and Fe^{3+} .

The validity of the computed fits was judged on the basis of χ^2 values, consistency of peak parameters between samples, and convergence of the fitting process. Examples of fitted Mössbauer spectra of vivianite #14198 before and after oxidation by mechanical grinding are shown in Figure 2.

Results

The Mössbauer spectra of vivianites change appreciably as samples are mechanically ground in air for progressively longer periods. This is demonstrated by the sequence of spectrum profiles illustrated in Figure 3, which show the emergence and increased intensity of the peak at 0.75 mm/sec attributed to Fe^{3+} ions. Spectra fitted to three doublets, such as those shown in Figure 2, yielded the Mössbauer parameters summarized in Table 1. The isomer shift and quadrupole splitting parameters of the Fe^{2+} doublets are in excellent agreement with published data (Matiievich and Danon, 1977). The computed areas for doublets assigned to Fe_A^{2+} , Fe_B^{2+} , and Fe^{3+} were used to calculate $\text{Fe}_B^{2+}/\text{Fe}_A^{2+}$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. The $\text{Fe}_B^{2+}/\text{Fe}_A^{2+}$ ratio tends to increase with increasing values of $\text{Fe}^{3+}/\Sigma\text{Fe}$, which indicates a preferential depletion of the Fe_A^{2+} species over the Fe_B^{2+} species at

Table 1. Mössbauer parameters for oxidized samples of vivianite #14198^a

	Progressively Oxidized Samples					
	Unoxidized Sample ^b	A	B	C	D	E
	<u>Isomer Shift (mm./sec.)^c</u>					
Fe_B^{2+}	1.219(3)	1.219(3)	1.227(4)	1.193(3)	1.216(3)	1.199(5)
Fe_A^{2+}	1.173(3)	1.173(4)	1.183(6)	1.139(4)	1.159(4)	1.148(13)
Fe^{3+}	0.426(3)	0.430(15)	0.415(17)	0.414(5)	0.458(4)	0.422(13)
	<u>Quadrupole Splitting (mm./sec.)</u>					
Fe_B^{2+}	2.928(3)	2.909(2)	2.922(5)	2.907(3)	2.964(3)	2.885(11)
Fe_A^{2+}	2.470(4)	2.447(4)	2.453(10)	2.443(4)	2.408(4)	2.352(25)
Fe^{3+}	0.655(.4)	0.634(17)	0.592(19)	0.668(5)	0.648(3)	0.648(14)
	<u>Half Widths (mm./sec.)</u>					
Fe^{2+}	0.30(.2)	0.28(.2)	0.32(1)	0.31(.3)	0.33(.2)	0.44(1)
Fe^{3+}	0.43(.3) ^d	0.51(3)	0.47(4)	0.50(1)	0.47(1)	0.63(3)
	<u>Area Ratios</u>					
$\frac{\text{Fe}_B^{2+}}{\text{Fe}_A^{2+}}$	1.94(3)	1.91(3)	2.06(10)	2.00(4)	2.12(3)	2.29(22)
$\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}$.05(.3)	.11(.4)	.17(1)	.31(.3)	.34(.2)	.37(1)
χ^2	1.05	1.03	.92	1.19	1.80	1.04

a - Room temperature spectra

b - Spectrum fitted with asymmetric Fe^{2+} doublets (see Figure 2a)

c - Relative to metallic Fe foil

d - Fe^{3+} peak widths constrained to 0.43 mm./sec. due to divergence of the fitting procedure on its release

Table 2. Fe_B^{2+}/Fe_A^{2+} as a function of x for $Fe^{3+}/\Sigma Fe = 0.57$

x	Fe_B^{2+}/Fe_A^{2+}	x	Fe_B^{2+}/Fe_A^{2+}
0	2.00	0.6	2.92
0.1	2.10	0.7	3.19
0.2	2.22	0.8	3.52
0.3	2.36	0.9	3.95
0.4	2.51	1.0	4.49
0.5	2.70		

high values of $Fe^{3+}/\Sigma Fe$. Any model for oxidation must hence incorporate a mechanism which provides for unequal oxidation of Fe_A^{2+} and Fe_B^{2+} species in highly oxidized vivianites.

A model for oxidation

We have adopted a model for the oxidation of vivianite based on experimental evidence and known crystal-chemical principles. According to our model, when one Fe_B^{2+} ion has been oxidized to create an $Fe_B^{2+}-Fe_B^{3+}$ pair, the second Fe_B^{2+} is relatively immune to oxidation due to the electronic configuration of the $Fe^{2+}-Fe^{3+}$ pair. When Fe^{2+} adjoins Fe^{3+} in Fe_B sites in vivianite, intervalence transitions occur (Hush, 1967; Faye *et al.*, 1968). Such electronic transitions take place between molecular orbital energy levels of the paired octahedral $Fe_B^{2+}-Fe_B^{3+}$ cluster. We suggest that the $Fe_B^{2+}-Fe_B^{3+}$ group is stabilized relative to $Fe_B^{3+}-Fe_B^{3+}$. Although theoretical calculations of energy levels in such linked Fe_B-Fe_B octahedra are not yet available, second order effects such as the dynamic Jahn-Teller effect (Burns, 1970 p. 20-22, 46) may contribute to the electronic stability of the $Fe_B^{2+}-Fe_B^{3+}$ group. The stability of this configuration can be lowered, however, by local effects such as variation in the metal-metal distance; hence a small proportion of $Fe^{2+}-Fe^{3+}$ pairs become completely oxidized. At low concentrations of Fe^{3+} , Fe_B^{2+}/Fe_A^{2+} shows little deviation from 2:1, since the Fe^{2+} population is so large. As the Fe^{3+} concentration increases, however, Fe_A^{2+} is observed to be preferentially oxidized relative to Fe_B^{2+} as the number of immune Fe_B^{2+} ions becomes greater. This leads to a rapid increase in Fe_B^{2+}/Fe_A^{2+} with increasing oxidation.

Our model can be formulated in the following manner. Let a , b , and c represent the number of Fe_A^{2+} , Fe_B^{2+} , and Fe^{3+} ions, respectively. Then initially,

$$\begin{aligned} 2a_0 &= b_0 \\ c &= 0 \end{aligned}$$

If x corresponds to the proportion of Fe_B-Fe_B pairs in which only one member becomes oxidized, the oxidation relations can be expressed as:

$$da = -\frac{a}{a + b(x+1) - xb_0} dc$$

$$db = -\frac{b(x+1) - xb_0}{a + b(x+1) - xb_0} dc$$

The limits $x = 0$ and $x = 1$ correspond to no preferential oxidation and maximum preferential oxidation, respectively. Using the relation:

$$b = 3b_0 - a - c$$

the equations can be solved for a and b in terms of c for different values of x . In the special case of $x = 0$, one obtains solutions of

$$\begin{aligned} a &= a_0 - c/3 \\ b &= 2a_0 - 2c/3 \end{aligned}$$

Fe_B^{2+}/Fe_A^{2+} will therefore be a constant 2:1 over the entire range of oxidation.

To determine a and b for values of x other than 0, an equation of the form:

$$\begin{aligned} a^{x+1} + 1/2(x+1)a_0^x a - 1/2 a_0^x [(x+3)a_0 \\ - (x+1)c] = 0 \end{aligned}$$

must be solved. Tables of Fe_B^{2+}/Fe_A^{2+} and $Fe^{3+}/\Sigma Fe$ can then be generated as a function of x . The effect of x on Fe_B^{2+}/Fe_A^{2+} is shown in Table 2, where x is varied from 0 to 1 at a constant value of $Fe^{3+}/\Sigma Fe$.

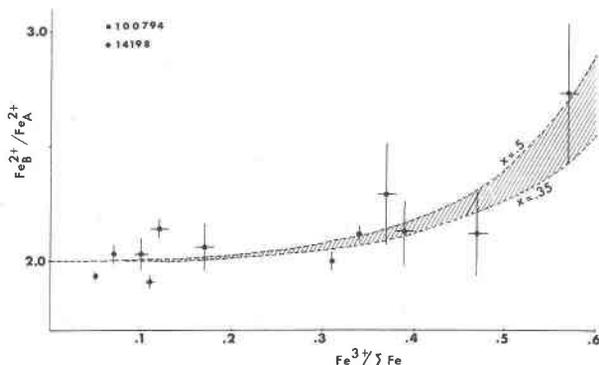
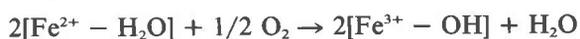


Fig. 4. Ratio data Fe_B^{2+}/Fe_A^{2+} vs. $Fe^{3+}/\Sigma Fe$ for vivianites #100794 and #14198 mechanically ground in air. The shaded region indicates the theoretical curves derived from our model for values of x between 0.35 and 0.5 (see Table 3).

The ratio data plotted in Figure 4 show that there is a progressive trend towards increasing Fe_B^{2+}/Fe_A^{2+} when both vivianite specimens are subjected to prolonged oxidation during mechanical grinding in air. To determine the values of x which correspond to our experimental data, we generated a family of curves from our model for different values of x , and judged by eye which one gave the best fit to our data. The large amount of scatter at low values of $Fe^{3+}/\Sigma Fe$ rendered any detailed statistical tests of the fits, such as χ^2 , meaningless. A reasonable fit to the data is given by values of x between 0.35 and 0.5 (Table 3), indicating that between 35% and 50% of the Fe_B-Fe_B pairs can only be partially oxidized. It is impossible to conclude from our experimental data, however, whether the proportion of partially oxidized Fe_B-Fe_B groups remains constant during oxidation, or whether a systematic increase or decrease occurs as oxidation progresses. This question can only be resolved by further experiments.

Discussion

Oxidation of Fe^{2+} to Fe^{3+} ions in both the Fe_A and Fe_B positions in vivianite involves H_2O ligands, which are simultaneously converted to OH^- ions according to the reaction (Mattievich and Danon, 1977):



This oxidation reaction, which takes place on the surfaces of the crystallites, is enhanced as fresh surfaces are exposed by mechanical grinding. However, oxidation is also facilitated by the rupture of hydrogen bonds each time a H_2O ligand is converted to OH^- . Moore (1971) described the vivianite structure as consisting of sheets of linked PO_4 tetrahedra, Fe_A single octahedra, and Fe_B double octahedra lying in (010) planes. Adjacent planes are held together by a network of hydrogen bonds between the two *cis* H_2O ligands of Fe_B octahedra in one plane and two H_2O ligands in the rhombic plane of the Fe_A octahedra in neighboring (010) planes. These four H_2O ligands involved in hydrogen bonding are located at the vertices of a nearly regular tetrahedron (Mori and Ito, 1950), giving structural rigidity to unoxidized vivianites. Therefore, when oxidation of Fe^{2+} to Fe^{3+} occurs, neighboring portions of the vivianite structure collapse as hydrogen bonds are eliminated by the conversion of H_2O to OH^- . As a result, oxidized vivianites characteristically show a flaky habit parallel to (010) (Moore, 1971), while extensively oxidized

Table 3. Fe_B^{2+}/Fe_A^{2+} as a function of $Fe^{3+}/\Sigma Fe$ for $x = 0.35$ and $x = 0.5$

$x = 0.35$		$x = 0.5$	
$\frac{Fe^{3+}}{\Sigma Fe}$	Fe_B^{2+}/Fe_A^{2+}	$\frac{Fe^{3+}}{\Sigma Fe}$	Fe_B^{2+}/Fe_A^{2+}
0.1	2.00	0.1	2.01
0.2	2.02	0.2	2.03
0.3	2.05	0.3	2.08
0.4	2.12	0.4	2.18
0.5	2.25	0.5	2.40
0.6	2.55	0.6	2.91

specimens disintegrate into friable dark blue powders indicative of $Fe_B^{2+} \rightarrow Fe_B^{3+}$ intervalence processes.

Despite the short Fe_B-Fe_B interatomic distance of 2.96 Å, vivianite displays no electron delocalization behavior (Burns *et al.*, 1980), the iron cations existing as trapped valence Fe_A^{2+} , Fe_B^{2+} , and Fe^{3+} species, as evidenced by the Mössbauer parameters. Thus, vivianite is a typical Class II mixed-valence compound (Robin and Day, 1967).

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