

THERMAL AND X-RAY STUDIES ON EARTHY VIVIANITE IN GRANEROS SHALE (UPPER CRETACEOUS), KANSAS

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ABSTRACT

Samples of earthy vivianite were treated thermally at different temperatures. The intensity of the peaks on their X-ray diffractometer patterns decreases with increasing temperature up to 300°C. Vivianite becomes amorphous after heating to 300°C. A poorly crystalline material is developed between 500°C and 625°C. Above 650°C, a mixture of iron (III) ortho phosphate (FePO_4) and an unknown compound is formed. A reversible polymorphous transformation takes place between 675°C and 750°C. Infrared studies indicate that vivianite may contain hydroxyl ions, and favor to the structural formula of $\text{Fe}_{3-x}^{2+}\text{Fe}_x^{3+}(\text{PO}_4)_2 \cdot [(8-x)\text{H}_2\text{O} \cdot x(\text{OH})]$ for vivianite rather than the conventional formula of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

INTRODUCTION

The occurrence of earthy vivianite in Graneros Shale (Upper Cretaceous), central Kansas, was reported by Tien, Waugh and Dilts (1969). In that study, powdered samples were treated thermally in order to obtain a weight-loss curve. It was noted that the thermal products of vivianite were of different colors and had distinctive X-ray patterns. This paper reports the results of a continuation of the previous investigation, but concentrates on the thermal and X-ray portions of the study.

HEAT TREATMENT AND COLOR CHANGES

Powdered samples of vivianite were air dried under laboratory conditions (21°C, 50% relative humidity), and the weight checked periodically until no further loss was noticed within 24 hours. A 0.5-gram sample was then heated in the furnace. The colors were recorded after the samples were first heated to predetermined temperatures and then air-cooled to room temperature. The observed color change of heated vivianite varies greatly from grayish blue to different shades of brown (Table 1). The same color also can be obtained at lower temperature with longer duration of heating.

MICROSCOPIC EXAMINATION

The crystallites of vivianite show pleochroism which gradually disappears in the heat-treated samples. No pleochroism was observed on samples heated above 300°C. Because the particles and crystallites of the thermal products are so small, most of the optical properties could not be determined. Samples heated between 300°C and 500°C are amorphous. Above 500°C, the numbers of anisotropic particles or crystallites increase with increasing temperatures. Between 675°C and 900°C, the material is essentially anisotropic. Ultra fine, reddish brown spots on the surface of the relatively large aggregates of the crystallites have been observed in reflected light. This suggests that the thermal products formed between 675°C and 900°C is a mixture.

TABLE 1. COLORS OF HEATED VIVIANITE

Temperature °C	Color Munsell System*	Weight-loss %
175	gy. blu. gn. 5B5/2	1.8
200	gy. gn. 5G5/2	2.4
250	dusky yel. gn. 5GY3/2	6.4
275	gy. olive 10Y4/2	11.3
305	mod. yel. brn. 10YR5/4	17.4
360	yel. brn. 10YR5/8	21.1
400	lt. brn. 5YR5/6	22.1
450	lt. brn. 5YR5/6	23.3
475	mod. brn. 5YR4/4	23.5
500	mod. brn. 5YR4/4	23.6
535	mod. brn. 5YR4/4	23.6
575	dk. red. brn. 10R3/4	22.9
590	dk. red. brn. 10R3/4	22.9
615	dk. red. brn. 10R3/4	22.9
650	red. brn. 10R4/4	23.5
675	mod. red. brn. 10R4/6	24.0
700	pale red. brn. 10R5/4	24.0
750	pale red. brn. 10R5/4	24.0
800	pale red. brn. 10R5/4	24.0
850	pale red. brn. 10R5/4	24.0
900	pale red. brn. 10R5/4	24.0

* Rock-color Chart (1948), Natl. Res. Council, Washington, D.C.

X-RAY EXAMINATION

The thermal products of vivianite at different temperatures were examined using X-ray diffraction methods. Samples were gently disaggregated to pass 61-micron sieve and packed in aluminum holders. Diffractometer patterns were obtained with a Norelco X-ray unit using copper radiation and curved lithium crystal focusing monochromator. The center of the peak at half-high was used for measurement of the reflections. All samples were X-rayed under the same mechanical conditions.

X-ray diffractometer patterns of samples heated below 300°C show only vivianite reflections. The intensities of the peaks, however, decrease as the temperature increases. Samples heated between 300°C and 475°C show very diffuse X-ray diffraction patterns. A poorly crystalline material is developed at temperatures between 500°C and 625°C. Above 625°C, a new phase is gradually formed. The representative X-ray diffractometer patterns are shown in Figure 1. From Figure 1 it is clear that the X-ray diffraction patterns of samples heated above 650°C are similar. The intensities of the peaks, however, increase with increasing temperatures or length of heating periods at particular temperatures. X-ray diffraction data of these thermal products indicate that they are mixtures of iron (III) ortho phosphate (FePO_4) and an unknown compound as shown in Table 2.

DIFFERENTIAL THERMAL ANALYSES

The differential thermal curve of vivianite from Kansas shows two exothermal peaks at

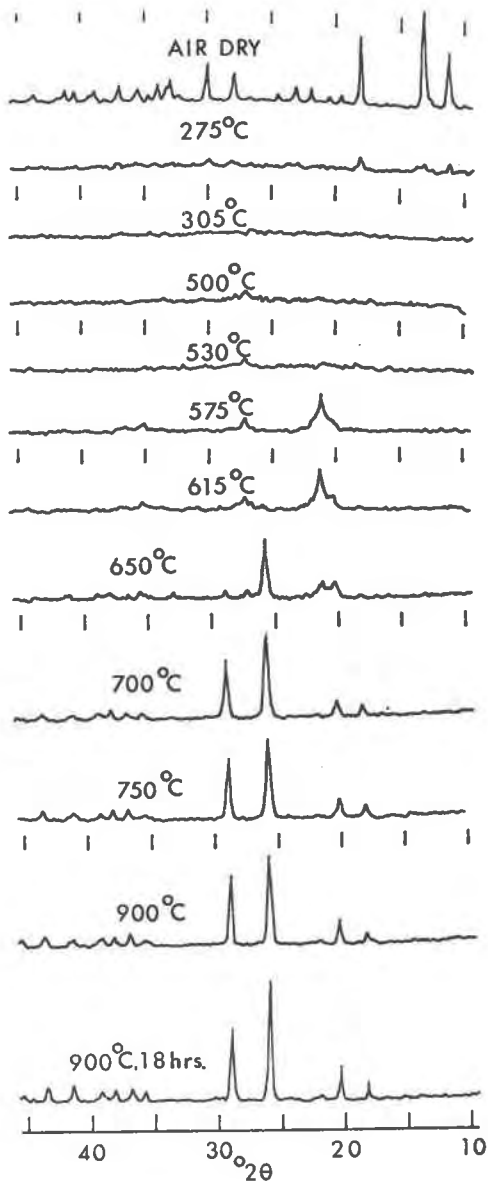


FIG. 1. X-ray diffractometer traces of vivianite and its thermal products

650°C and 755°C. The latter was interpreted as an indication of a phase change (Tien, Waugh and Dilts, 1969). X-ray diffraction data, however, indicate no difference for the samples heated between 650°C and 900°C. In order to clarify this ambiguity, two differential thermal and cooling curves were made (Fig. 2). The cooling curve of the first run shows

TABLE 2. X-RAY POWDER DATA FOR VIVIANITE HEATED TO 900°C

1		2		3		1		2		3	
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
		11.9	1			2.300	8	2.30	7	2.30	15
		8.4	1			2.183	12	2.18	8	2.18	15
		6.46	1			2.087	12	2.10	4		
4.900	17					2.003	10	2.00	3		
4.378	25	4.39	23	4.392	25	1.988	3				
4.077	5							1.94	3		
4.046	3	3.98	4			1.877	10	1.88	17	1.88	15
		3.72	1			1.855	5				
3.455	100	3.47	100	3.45	100			1.82	5		
		3.33	11					1.78	4		
3.104	58					1.7269	5				
		3.02	40			1.7187	3	1.72	9	1.698	15
		2.82	1			1.6664	2	1.67	4		
		2.69	3			1.6274	12	1.62	5		
2.523	8	2.54	11	2.53	15	1.5826	7	1.59	17	1.585	15
2.457	8					1.5486	5	1.54	5		
2.440	12	2.44	1			1.5055	5	1.51	8		
2.367	12	2.37	9	2.37	15			1.48	4		
2.321	5					1.4445	7	1.45	3		
2.308	8					1.4225	8	1.42	17	1.421	15

1. Vivianite heated to 900°C for 18 hrs.

2. FePO₄, ASTM X-ray Powder Data File, 3-0379.

3. FePO₄ (quartz-like phase), ASTM X-ray Powder Data File, 17-837.

one exothermic peak at 715°C (Fig. 2B). The same sample was reheated and the thermal curve (Fig. 2C) shows an endothermic peak at 715°C and an exothermic peak at the same temperature on the recooling curve (Fig. 2D). This phenomena definitely indicates a reversible polymorphous transformation takes place between 675°C and 750°C as observed by Kleber, Wilde and Frenzel (1965).

INFRARED ABSORPTION SPECTRA

Infrared spectra were obtained on a Perkin-Elmer 521 grating spectrophotometer using a disc that consists of a mixture of 1.2 mg of sample and 250 mg of KBr. The spectra of vivianite and its thermal products were compared with the available spectra (Adler, 1964; Corbridge and Lowe, 1954; Omori, 1961, 1964; Omori and Seki, 1960) for phosphates and other possible minerals or compounds that may form as the thermal products of vivianite.

Absorption peaks of the infrared spectrum of vivianite at 3450, 3150, 1620, 790, and 550 cm⁻¹ (Fig. 3A) either gradually decrease in intensity or disappear upon heating (Fig. 3B-E). The peaks in the region higher than 1100 cm⁻¹ are related to the presence of hydroxyls, water of crystallization, and adsorbed water in the samples. The broad peak in the region between 900 and 1100 cm⁻¹ is associated with PO₄³⁻. The peaks in the low frequency region are probably related to the development of the unknown compound referred to earlier.

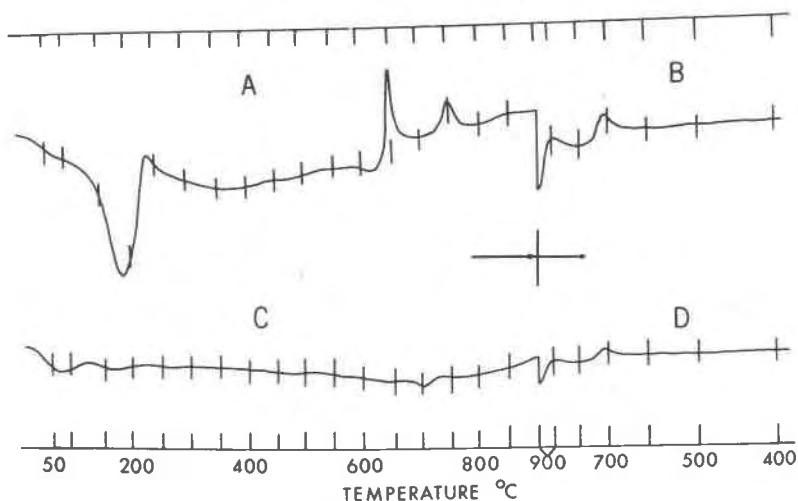


FIG. 2. Differential thermal and cooling curves of vivianite. A, differential thermal curve; B, cooling curve; C, differential curve for heated material; D, recooling curve.

DISCUSSION AND CONCLUSIONS

The empirical formula for vivianite is considered conventionally to be $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Barth, 1937; Palache, Berman and Frondel, 1951; Vanders and Kerr, 1967) with two moles per unit cell (Takane and Omori, 1936; Mori and Ito, 1950). The mineral, however, usually contains more or less ferric iron (Palache, Berman and Frondel, 1951, p. 744) due to oxidation effects (Watson, 1918). "Fresh" vivianite which is white or colorless with a composition of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is not stable after exposure to air. Different names, therefore, have been given for oxidized vivianite, e.g. kerchenites (α -, β -, and γ -kerchenite) and bosporite (Teodorovich, 1961) depending on the ratio of ferrous to ferric irons. According to the description of Teodorovich (1961) for kerchenite, the blue or green material derived from white or colorless vivianite is no longer to be called vivianite but one of the varieties of kerchenite, though the crystal structures of vivianite and kerchenites are similar. Gamidov and Mamedov (1960) have found that the structure of vivianite changes upon oxidation. Because the change is so small, it can not be detected by X rays. They proposed a formula of $\text{Fe}_{6-x}^{2+} \cdot \text{Fe}_x^{3+}(\text{PO}_4)_4[(16-x)\text{H}_2\text{O} \cdot x(\text{OH})]$, for vivianite and the oxidized varieties, for H_2O may be transformed into (OH) H during the oxidation of ferrous iron. Infrared spectra of air dried vivianite and vivianite heated to 275°C have an absorption peak at 3450 cm^{-1} in which position wavellite $[\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}]$ and turquoise $[\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}]$ show similar but more pronounced peaks (Anderson, Stringham and Whelan, 1962, Fig. 3, p. 1307). Both wavellite

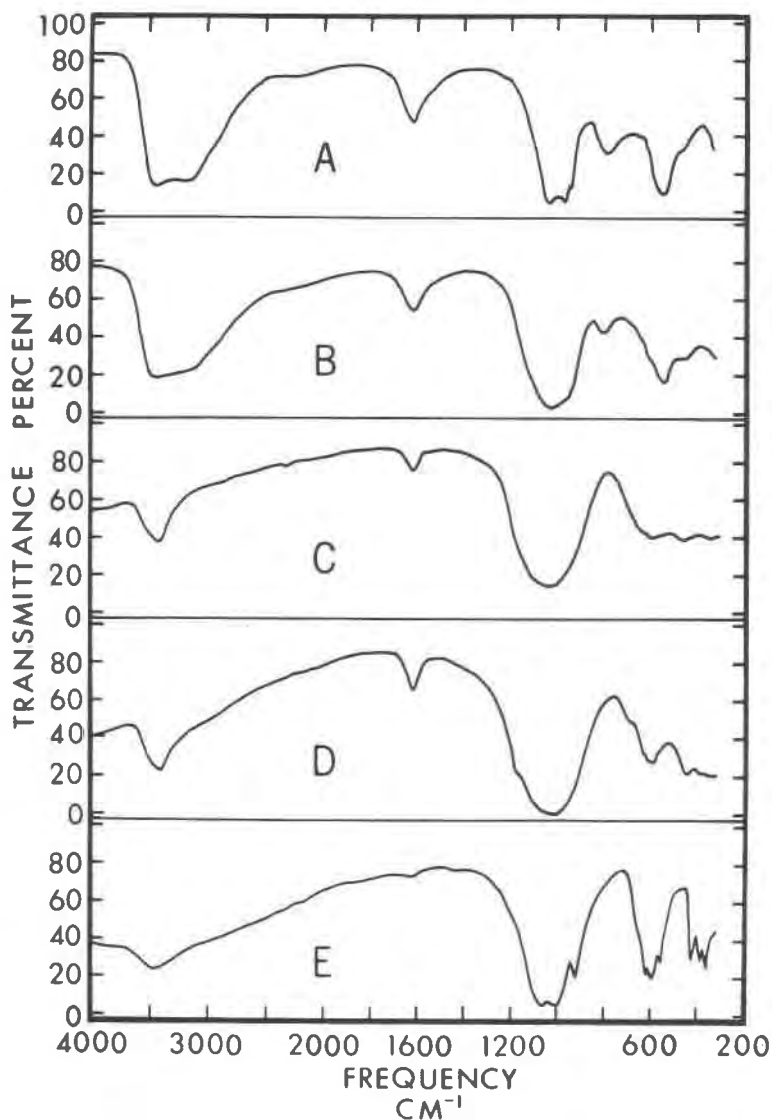


FIG. 3. Infrared spectra of vivianite and its thermal products. A, air-dry vivianite; B, vivianite heated to 275°C; C, heated to 500°C; D, heated to 590°C; E, heated to 800°C.

and turquoise are known to have hydroxyl ions in their crystal structures. The similarity of the infrared spectra of vivianite, vivianite heated to 275°C, wavellite, and turquoise suggest that vivianite may contain different amounts of hydroxyl ions in its crystal structure during different

stages of oxidation. The authors favor the structural formula proposed by Gamidov and Mamedov (1960). This formula may be simplified as $\text{Fe}_{3-x}^{2+}\text{Fe}_x^{3+} \cdot (\text{PO}_4)_2 \cdot [(8-x)\text{H}_2\text{O} \cdot x(\text{OH})]$.

Vivianite from Kansas has a chemical composition very close to that of empirical formula (Tien, Waugh and Dilts, 1969). This experimental study indicates that the structure of vivianite is broken down completely at 305°C with a corresponding total weight loss of more than 17 percent, which is equal to the loss of 5H₂O. Between 675°C and 900°C, vivianite loses weight to a maximum of almost 24 percent, which equals the loss of 8H₂O plus the gain of 1.5 (O) from the transformation of Fe²⁺ to Fe³⁺. It would be logical to assume that the thermal products of vivianite present between 675°C and 900°C have an overall chemical composition of 3 Fe₂O₃ · 2P₂O₅. Most of the X-ray diffraction peaks for vivianite heated between 675°C and 900°C match those of FePO₄. Accordingly, these thermal products possibly are a mixture of either 4 FePO₄ and Fe₂O₃, or 2 FePO₄ and 2 Fe₂O₃ · P₂O₅. X-ray diffraction powder data, however, indicate no Fe₂O₃ present. Whether the extra reflections are related to 2 Fe₂O₃ · P₂O₅ is not known.

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