X-ray diffraction studies of vivianite, metavivianite, and baricite

T. SAMESHIMA, G. S. HENDERSON, P. M. BLACK, AND K. A. RODGERS

Department of Geology, University of Auckland, Private Bag, Auckland, New Zealand

ABSTRACT. Vivianite specimens from various world localities yield X-ray powder patterns of two types: one corresponds with that shown by synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$ and is not readily distinguished from that of baricite; the second shows reflections of monoclinic vivianite and triclinic metavivianite along with reflections of a bobierrite-type phase. The triclinic phase occurs as two twin-related lattices with twin plane 110 being the structural equivalent of 010 in the monoclinic phase. The relationship of the bobierrite-type lattice to the other two has not been established. The ternary pattern is produced by some coarse-grained vivianites on natural oxidation. Finer grained vivianites oxidise to an X-ray amorphous state without passing through a triclinic intermediate.

KEYWORDS: X-ray diffraction, vivianite, metavivianite, baricite.

RECENT X-ray diffraction studies of vivianite and some related iron phosphate minerals suggest that the status of some species needs reappraisal. For example, the results of Poullen (1979), Dormann and Poullen (1980), and Dormann et al. (1982) indicate that metavivianite is not a triclinic polymorph of vivianite but an intermediate oxidation product of the ferrous phosphate and contains both Fe^{2+} and Fe^{3+}. 'Il en résulte que la métavivianite est un minéral toujours associé à la vivianite' (Dormann and Poullen, 1980, p. 633). Further, powder diffraction examination of twenty-two vivianite specimens from New Zealand localities by Henderson et al. (1984) showed that the patterns of a number of samples, but not all, contained both monoclinic vivianite and triclinic metavivianite lines, although the presence of the triclinic pattern appeared to correlate more with mineral habit and mode of occurrence than with degree of oxidation of the specimen (cf. Dormann and Poullen, 1980).

Twenty-one additional specimens of vivianite from well-documented localities throughout the world have been examined by X-ray powder diffraction, using both Co-$K\alpha$ and Fe-$K\alpha$ radiation and 114.6 mm Debye–Scherrer cameras. Some samples were further examined by diffractometry employing Cu-$K\alpha$ with a graphite monochromator. All the resulting patterns were compared with those obtained from synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$, type baricite, and type metavivianite. Where necessary, silicon was used as an internal standard. A few very weak reflections that could be assigned to hydrated halloysite and/or illite were noted in some samples of earthy (cryptocrystalline) habit and the occasional nodular specimen.

Results

Examples of the diffraction data which were obtained are given in Tables I and II, along with some published data.

Synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$ was prepared according to several of the recipes given in Mellor (1935). X-ray reflections obtained for all samples correspond well with those given on ASTM Powder Diffraction Data cards 3-0070 and 30-0662. An annotation to 3-0070 suggests the sample was synthetic while 30-0662 is data for synthetic material. The results given in Table I, col. 5, are those obtained from the precipitate formed by mixing solutions of ferrous sulphate and sodium hydrogen phosphate.

Earthy (cryptocrystalline) vivianite. As found by Henderson et al. (1984) the majority of earthy specimens and some more coarsely crystalline samples gave results which correspond well with ASTM card 30-0662, published data of Kleber et al. (1965) and Dobra and Duder (1976), as well as with calculated d-values obtained using the lattice constants given on ASTM card 30-0662 (= US National Bureau of Standards Monograph 25, section 16, p. 38). It should, perhaps, be noted here that these constants differ from those given by Palache et al. (1951) cf. Barth (1937), and those given by Fejdi et al. (1980).

Typical results are given in Table I, cols. 6–9. Additional samples showing a typical vivianite pattern include nodular vivianite, Suhana Himeshima Island, Japan and crystalline vivianite,

TABLE 1. X-ray powder data for vivianite, baríčite, metavivianite and vivianite-metavivianite admixtures; d(Å) 8.8-2.1.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
110	7.92	7.93	13	7.89	7.89	7.89	7.89	7.89	7.90	8.68, 7.99	8.85, 8.02, 6.97*	8.68, 8.00, 6.96	8.60, 7.86, 6.71	8.59, 7.84, 6.71	8.62, 7.86, 6.96	8.62, 7.89, 6.97, 6.90	30	8.55	8.60	010
020	6.72	6.73	100	6.71	6.72	6.71	6.71	6.71	6.71	6.79	6.79	6.75		6.71	6.71	6.71	100	6.71	6.72	1̄10
200	4.895	4.900	12	4.90	4.91	4.90	4.91	4.90	4.87	4.91	4.93	4.90	4.90	4.92	4.90	4.90	30	4.90	4.89	110
1̄01	4.559	4.588	5	4.60	4.55	4.51	4.51	4.60	4.51	4.52	4.58	4.47	4.60	4.60		4.58				
011	4.346	4.341	2	4.40	4.34	4.40	4.40	4.40	4.33	4.33	4.38	4.38	4.38	4.40	4.38	4.40	10	4.27	4.27	0̄71
130	4.076	4.081	12	4.10	4.08	4.08	4.06	4.10	4.07	4.08	4.40	4.06	4.07	4.07	4.27	4.10				
1̄01	3.847	3.849	7	3.88	3.85	3.86	3.84	3.88	3.832	3.84	3.866	3.86	3.85	3.85	4.07	3.84	30	3.84	3.84	011, 2̄10
1̄21	3.774	3.768	<1				3.64								3.85				3.71	171
211	3.647																		3.64	101
040	3.362	3.361	1	3.65	3.64	3.36		3.64	3.610	3.64	3.555	3.65	3.65	3.65	3.67	3.37				
121	3.339	3.343	2	3.35	3.36			3.35	3.341	3.34	3.311		3.39		3.36					
031	3.208	3.210	16	3.22	3.20	3.19	3.19	3.22	3.196	3.20	3.217	3.21	3.22	3.20	3.23	3.20				
3̄01	2.987	2.985	10	2.99	2.98	2.99	2.96	2.99	2.956	2.97	2.993	3.07	3.10	2.97	3.08	3.00	20	3.07	3.08	111
211	2.960	2.960	8					2.90				2.98	3.00		2.99			3.01	3.01	110
2̄40	2.771	2.770	4	2.79	2.72	2.72	2.70	2.83	2.699	2.71	2.797	2.77	2.94	2.77	2.80	2.78		2.95	2.95	021
3̄21	2.730	2.728	9	2.73			2.68	2.73			2.737	2.72	2.80	2.70	2.73	2.72		2.90	2.91	121
1̄41	2.706	2.706	9								2.713		2.72				30	2.79	2.80	211
330	2.638	2.637	6	2.65	2.64	2.65			2.626	2.64	2.644		2.60		2.65	2.65		2.67	2.67	201
150	2.594	2.593	6				2.59						2.55	2.59			10	2.60	2.60	131
1̄41	2.532	2.530	4	2.54	2.54	2.55	2.53	2.54	2.526	2.52		2.53	2.47	2.53	2.54	2.55		2.50	2.49	320
2̄31	2.513	2.514	3									2.46	2.44				20	2.48	2.48	121
400	2.448	2.448	1	2.44	2.44	2.44	2.42	2.44	2.418	2.31	2.430	2.44		2.44	2.44	2.45		2.46	2.45	300
3̄01	2.421	2.421	6					2.36				2.37	2.37		2.34					
051	2.321	2.321	7	2.33	2.33	2.33		2.33	2.311			2.33	2.34	2.32	2.29	2.32				
0̄02	2.296	2.296	1	2.29	2.30															
2̄02	2.280	2.279	1				2.30		2.275										2.29	002
3̄41	2.233	2.233	5	2.25	2.25	2.24	2.22	2.25	2.217	2.23	2.233	2.25	2.25	2.23	2.25	2.24	5	2.27	2.27	321
2̄51	2.193	2.194	5	2.20	2.20	2.20	2.17	2.20	2.179	2.19	2.196	2.19	2.20	2.18	2.20	2.20				
4̄31,112	2.108	2.108	1	2.12				2.15			2.081		2.09		2.12		2	2.15	2.15	040

TABLE 1. continued:

1. hkl values for vivianite taken in large part from ASTM powder diffraction card 30-0662.
2. d_calc for vivianite (Å).
3. d_obs for vivianite; ASTM powder diffraction card 30-0662 (Å).
4. Relative intensity values of reflections given in col. 3.
5. Synthetic, freshly prepared $Fe_3(PO_4)_2 \cdot 8H_2O$ d(Å).
6. Earthy, cryptocrystalline vivianite, Waiotu, New Zealand. AU:2473.
7. Acicular crystalline vivianite nodule, Holocene Swamp, Auckland N.Z. AU:2469.
8. Coarsely crystalline vivianite, Ashio Mine, Japan BM (NH):1927,171.
9. Crystalline vivianite, Leadville, Colorado, U.S.A. BM(NH):1907,115.
10. Baríčite d_obs (Sturman and Mandarino, 1976).
11. Vivianite crystal, Haren, Noord Brabant, Netherlands (Zwann and Kortenburg van der Sluys, 1971) Probable vivianite-metavivianite admixture.
12. Vivianite, Ashio Mine, Japan (Minato et al. 1956). Probable vivianite-metavivianite admixture.
13. Vivianite crystals, Ashio Mine, Japan. AU:2773. Probable vivianite-metavivianite admixture.
14. Vivianite nodule, Monmouth, New Jersey, U.S.A. U.S. National Museum 96424. Probable vivianite-metavivianite admixture.
15. Large vivianite single crystal, N'gaundere, Cameroons. BM(NH):1962,413.
16. Vivianite, Richmond, Virginia (A.Roebling Collection) U.S. National Museum R16855. Probable vivianite-metavivianite admixture.
17. Acicular crystalline vivianite nodule, Hunua, N.Z. AU:2514. Probable vivianite-metavivianite admixture.
18. Relative intensity values of reflections given in cal 19.
19. d_obs for metavivianite, this study.
20. d_calc for metavivianite, modified after Ritz et al (1974).
21. hkl values for metavivianite, modified after Ritz et al (1974).

Spodumene Mine, Kings Mountain, North Carolina, along with numerous New Zealand specimens as given in Henderson et al. (1984).

Coarsely crystalline 'vivianite'. Many X-ray diffraction photographs of specimens, such as large crystal fragments and groups of crystals, particularly those of granular and acicular habits, show, along with their monoclinic vivianite pattern, the presence of a number of reflections which correspond well with prominent reflections of metavivianite as enumerated by Ritz et al. (1974). Examples are given in Table I, cols. 13–17 and Table II, cols. 2 and 3.

Further specimens that show both vivianite and metavivianite patterns include nodular vivianite from: Tarusaka Machi, Japan; Fujie Beach, Japan; Katada, Kobe, Japan; Tomigaoka, Nara, Japan; Oshibedani, Hyogo, Japan; Washington DC; and crystalline vivianite from: Carroll, Virginia; Wannon River, Victoria, Australia; Wheal Jane, Truro, Cornwall; and various New Zealand samples as given in Henderson et al. (1984).

Similar patterns showing both sets of reflections have been recorded without comment by Minato et al. (1956) and Zwann and Kortenburg van der Sluys (1971) from Haren, Noord Brabant Province, Netherlands (Table I, cols. 11 and 12). Presumably, it was this type of binary pattern that Poullen (1979, p. 51) obtained within his grouping 'Vivianites naturelles oxydées artificiellement'.

In the present examples, there are generally distinct metavivianite reflections close to 8.6 and 2.8 Å. Depending on exposure times, further lines may be noted at (d Å) 4.27, 3.01, 2.25, and 1.63. Vivianite reflections at d (Å) 6.73 (020), 4.90 (200), 4.34 (011), 3.85 (101), 2.96 (211), 2.64 (330), 2.53 (141), 2.42 (301), 1.89, 1.79, 1.66, and 1.60 are coincident with, or close to metavivianite lines at $(d$ Å) 6.72 (1$\bar{1}$0), 4.89 (110), 4.27 (0$\bar{1}$1), 3.84 (011, 2$\bar{1}$0), 2.95 (021), 2.67 (201), 2.50 (3$\bar{2}$0), 2.46 (300), 1.86, 1.82, 1.75, 1.665, and 1.60.

A prominent reflection at 6.90–6.97 Å frequently occurs in those patterns showing metavivianite lines and appears to show sympathetic variation in intensity with that occurring at 8.6 Å. The same reflection was recorded by Minato et al. (1956) in their Ashio Mine sample (Table I, col. 12). Such a reflection does not occur in the pattern of type metavivianite nor can it be indexed using the lattice constants of Ritz et al. (1974). However, 6.96 Å is the strongest reflection of bobierrite as given by Frazier et al. (1963) which is that data given on ASTM Diffraction Data File card 16-0330. Of other strong reflections of bobierrite, those at (d Å) 3.02 ($\bar{1}$71), 2.94 (350), 2.57 ($\bar{1}$91), and 2.41 ($\bar{2}$91, 2, $\bar{1}$0, 0) are coincident with or close to vivianite or metavivianite reflections; 8.04 Å (120) was not specifically identified and may be obscured by the very strong 110 vivianite reflection.

Samples of vivianite from Hunua, New Zealand (AU: 2408), Puy-de-Dome, France (Smithsonian Institute, Bosch Collection, B14026), and Clearwater, Idaho (Smithsonian Institute, 87220) were re-examined by X-ray diffractometry using Cu-$K\alpha$ with a graphite monochromator. Results are given in Table II.

The Hunua cryptocrystalline sample, col. 1, is monomineralic vivianite. No additional reflections exist in its pattern.

The Clearwater and Puy-de-Dome samples are altered vivianites showing additional metavivianite reflections as well as the strong diffraction line at 6.9 Å. In addition the Puy-de-Dome specimen also shows peaks at (d Å) 3.98, 3.46, and 2.815 which,

TABLE II. *X-ray powder diffraction data for 'vivianite' samples derived using a graphite monochromator; d (Å) 8.8–2.4*

1	1a	2	2a	3	3a
		8.77	4	8.8	1
7.93	37	8.01	2	7.91	5
		6.96	100	6.92	30
6.71	100	6.76	89	6.70	100
		4.955	3		
4.906	40	4.905	3	4.901	5
4.535	7	4.493	2	4.570	1
4.353	2	4.366	1	4.353	1
4.073	10	4.095	3	4.077	7
		3.980	2		
3.857	14	3.800	2	3.850	3
3.636	5	3.650	1	3.650	1
		3.460	2	3.356	<1
3.202	26	3.214	7	3.209	7
2.978	40	2.985	2	2.988	4
				2.967	3
		2.815	1		
2.768	4	2.775	3	2.771	2
2.718	19	2.714	4	2.725	4
2.700	17			2.711	5
2.639	10			2.640	2
2.592	2	2.600	3	2.594	3
2.524	11	2.536	2		
2.431	13	2.430	5	2.424	3

1. Earthy (cryptocrystalline) vivianite; Hunua, New Zealand. AU: 2408.
2. Crystalline vivianite; Menat, Puy-de-dome, France. US National Museum (Karl Bosch Collection): B14026.
3. Crystalline vivianite; Dent, Clearwater Co., Idaho, US National Museum: 87220.

1a, 2a, 3a. Relative intensities of reflections given in 1, 2, 3, respectively.

along with that at 6.96 Å, are common to bobier-rite. In the Clearwater pattern the 010 metavivian-ite reflection is only just visible above background but is pronounced in the Puy-de-Dome pattern.

The relationship of the triclinic lattice to the monoclinic vivianite lattice in some of the present samples was confirmed by precession photography of several crystal fragments, the precession axes used being that perpendicular to the b^*c^* plane in one instance and to a^*c^* in the other. Reflections from three lattices were obtained, one being the vivianite monoclinic lattice and the others being twinned related triclinic lattices in which the twin plane 110 of the triclinic phase is the structural equivalent of the 010 monoclinic phase. Identical results were obtained by Poullen (1979) for artifically oxidized vivianites (cf. Wolfe, 1940; Ritz *et al.*, 1974).

Metavivianite. Powder diffraction data for type metavivianite as determined in this study are given in Table I, cols. 18–21. Some differences exist between these data and those recorded by Ritz *et al.* (1974). For example, not all lines recorded by those authors were observed, e.g. 3.71 and 3.64 Å, while minor differences were noted in the position of some lines and these have been re-indexed using the unit cell parameters derived by Ritz *et al.* from single-crystal studies. It should be noted that a misprint in the original paper results in 010 being assigned to both 8.60 and 3.64; 010 belongs to 8.60 while 3.64 calculates as 101.

Since its description, metavivianite has been regarded by most workers as isostructural with symplesite and a dimorph of vivianite. In the original description of the mineral, Ritz *et al.* calculated all the iron found in their microprobe analysis as Fe^{2+}. Poullen (1979) and Dormann *et al.* (1982) contend that this triclinic species contains considerable essential Fe^{3+} and, while being iso-structural with symplesite, can no longer be regarded as a dimorph of vivianite. (The implica-tion would appear to be that symplesite is not dimorphous with parasymplesite and contains Fe^{3+} in its formula.)

Baricite. Powder diffraction data, as recorded by Sturman and Mandarino (1976), are given in Table I, col. 10. Identical data were obtained in the present study from type material from the Yukon. As can be seen, the powder patterns of baricite and vivianite cannot be readily distinguished.

Discussion

The results of Dormann and Poullen (1980) and Dormann *et al.* (1982) point to a need to reassess metavivianite as a mineral species and to compare the Yukon material used by these authors with type metavivianite from Big Chief. In the present discus-sion, the term 'triclinic phase' will be used for that mineral showing the diffraction pattern of meta-vivianite.

This triclinic phase may form on alteration (oxidation) of vivianite but not necessarily so; it is not 'un minéral toujours associé à la vivianite' (Dormann and Poullen, 1980, p. 663). Not only is type metavivianite found in a vivianite-free assem-blage (Ritz *et al.*, 1974) but certain fine-grained and some more coarsely crystalline vivianite specimens do not appear to yield a triclinic phase on oxida-tion.

Further, it appears that the extent of oxidation of natural specimens does not necessarily imply that the triclinic phase will be present (cf. Dormann and Poullen, 1980; Dormann *et al.*, 1982). For example, in the present study, a fragment of a large crystal from N'gaudere, Cameroon, which yielded the typical ternary pattern (Table I, col. 15) showed a ferrous/ferric ratio of 16.64 from Mössbauer studies. In contrast, an earthy (cryptocrystalline) specimen from Hunua, New Zealand, with an iron ratio of 2.05, gave a vivianite pattern only.

The presence of a second, bobierrite-like phase associated with the triclinic phase does not appear to be a new discovery. Apart from the X-ray record of Minato *et al.* (1956), Ritz *et al.* (1974) recorded the presence of an additional unindexed line in their metavivianite pattern, and which they ascribed to an impurity, at 3.47 Å ($= 0.5 \times 6.94$). Frazier *et al.* (1963) assign a bobierrite reflection at 3.48 Å to 131, 060. More recently, Vochten *et al.* (1979) have noted that the strongest diffraction line in X-ray diffrac-tion patterns of vivianites with Fe^{2+}/Fe^{3+} ratios of 3 occurred at 7.01 Å. They suggested that it is 'probably due to the presence of another oxydation [*sic*] product of vivianite' (p, 215).

These last-named authors assert on the same page, an introductory section to their X-ray studies, that 'the change of the structure of the vivianite upon oxydation [*sic*] is so small that it cannot be detected by X-ray investigation'. They cite Tien and Waugh (1969) in support of this contention but it would appear they may have misinterpreted this paper. They do record a further reflection to that at 7.01 Å, at 2.78 Å ($I = 10$). While such a reflection is common to both vivianite and the triclinic phase patterns, as well as being close to 350 of bobierrite, it is relatively intense in the triclinic phase only.

A comparison of the present results with those of the various studies mentioned above, suggests that natural vivianite may alter on natural oxidation to yield a triclinic phase comparable to that presently described as metavivianite plus an associated bobierrite-type structure. Artificial alteration of vivianite or a high degree of natural oxidation appears to yield the triclinic phase alone, which

contains both ferric and hydroxyl ions. However, crystalline vivianite may oxidize to an X-ray amorphous state without passing through a triclinic intermediate (cf. Dormann and Poullen, 1980). This appears to be the path followed by most cryptocrystalline specimens. However, in view of the different results obtained by Dormann and Poullen and the present study for comparable specimens from N'gaundere, and the differing results shown in Table I, cols. 8 and 12 from Ashio Mine, it is evident that not all specimens from the same locality yield similar results.

Further, there is insufficient evidence at the moment to show conclusively that the triclinic phase is generated solely by the reduction of symmetry which occurs on partial oxidation of ferrous iron preferentially in Fe_t sites and that a physical inversion is not also involved.

It is hoped that publication of the above, preliminary data, may assist other researchers in appraising fruitful lines of study; perhaps in the redefinition or validation of metavivianite as a mineral species or the investigation of Poullen's (1979) assertion that no triclinic phases exist in the vivianite structural series.

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