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Metavivianite and kerchenite: a review

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ABSTRACT. Metavivianite has been shown to be not dimorphous with vivianite. Assuming the homogeneity and uniformity of the original type samples, it is a triclinic hydrated ferri-ferrous hydroxy phosphate whose formula may be given as $Fe^{2+}_{3-x}Fe^{3+}_{x}(PO_4)_2(OH)_x(8-x)H_2O$ where $x > 1.4$. The precise oxidation limits between which the triclinic lattice is stable are not known but the structure persists close to total oxidation of all iron. The structure of metavivianite was established using a fragment of kerchenite whose formula as originally given is covered by the general metavivianite formula. Assuming the homogeneity of the original (1907) samples, kerchenite and metavivianite appear to be identical.

KEYWORDS: metavivianite, vivianite, kerchenite.

METAVIVIANITE is a triclinic iron phosphate hydrate. It was first described by Ritz *et al.* (1974) from the Big Chief pegmatite, South Dakota, occurring as green crystals intimately intergrown with kryzhanovskite in cavities in triphylite. These authors adjudged the mineral to be dimorphous with vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and isostructural with symplesite ($Fe_3(AsO_4)_2 \cdot 8H_2O$). These conclusions were reached on the basis of similarities in the X-ray diffraction patterns of metavivianite and symplesite and from direct electron microprobe comparison of the composition of metavivianite with an unlocalized vivianite: 'metavivianite and the vivianite are nearly identical in composition for all elements with $Z < 10$ [*sic*] and therefore by analogy with vivianite the formula of metavivianite is $(Fe,Mn)_3(PO_4)_2 \cdot 8H_2O$' (pp. 897–8). Regrettably, no separate analyses were reported for either Fe^{2+}/Fe^{3+} or water. Recent work has shown that the above conclusions are not correct and that metavivianite is neither a ferrous phosphate nor an octahydrate and so cannot be dimorphous with vivianite (e.g. Dormann *et al.*, 1982; Rodgers and Johnston, 1985).

Crystal chemistry. For some years X-ray diffraction data for vivianites have been reported which include prominent reflections of metavivianite (e.g. Poullen, 1979; Henderson *et al.*, 1984; Sameshima *et al.*, 1985) although such reflections may not have been recognized as coming from metavivianite (e.g. Minato *et al.*, 1956; Zwann and Kortenburg van der Sluys, 1971). Poullen interpreted his results as showing that oxidation of monoclinic vivianite resulted in a reduction of symmetry through production of a ferri-ferrous hydroxy phosphate hydrate of the type

$$Fe^{2+}_{3-x}Fe^{3+}_{x}(PO_4)_2(OH)_x(8-x)H_2O$$

assuming that compensation of the kind proposed by Moore (1971) applied (and cf. Gamidov and Mamedov, 1960). The X-ray diffraction signature of this alteration product was that given by Ritz *et al.* (1974) for metavivianite. Poullen (1979) noted, in passing, that a similar alteration may occur in parasymplesite with partial oxidation producing a mixed diffraction pattern containing prominent reflections of triclinic symplesite.

In a series of papers, Chevalier *et al.* (1980), Dormann and Poullen (1980), Fejdi *et al.* (1980), and Dormann *et al.* (1982) presented extensive structural and chemical data in support of Poullen's conclusions. Many of these data were derived from vivianite–metavivianite admixtures produced by both artificial and natural oxidation of vivianite and synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$. While this information is useful in defining the nature and limits of the structural and compositional relationship that exists between vivianite and the redefined metavivianite, it is data concerned with two metavivianite samples identified as being monomineralic that help characterize the ferri-ferrous nature of the mineral.

The first of these was a specimen identified by Dormann and Poullen (1980, p. 634) as metavivianite from the Yukon, Canada, and containing MnO 2.83%, MgO 2.98%, and CaO 0.72%. The Mössbauer spectrum of this sample was interpreted as indicating a percentage occupancy of iron sites in the lattice of $Fe^{2+}_{I} = 1\%$, $Fe^{3+}_{I} = 32\%$, $Fe^{2+}_{II} = 2\%$, $Fe^{3+}_{II} = 65\%$, ($Fe^{3+}_{IIa} = 49\%$, $Fe^{3+}_{IIb} = 16\%$), where sites I and II are similar to and derived from those specified by Mori and Ito (1950) for their model of the vivianite structure, and where Fe^{3+}_{IIa} and Fe^{3+}_{IIb} are identified as distinct types of Fe^{3+}_{II} sites within metavivianite (cf. Dormann *et al.*, 1982); the hyperfine spectral parameters of Fe^{3+}_{IIb} are close to those of Fe_I. While no formula was given by Dormann and Poullen (1980) their data were calculated by Rodgers and Johnston (1985) as $Fe^{2+}_{0.1}Fe^{3+}_{2.9}(PO_4)_2(OH)_{2.9}5.1\,H_2O$.

The second sample came from Kamysch-Burun (USSR) and was used by Dormann *et al.* (1982) to determine the precise nature of the metavivianite structure. 'Le cristal utilisé pour l'étude structurale est un fragment de clivage prélevé sur un échantillon . . . est conserve sous le nom de "kerchenite α" mais se compose en réalité de deux phases minérales, l'une monoclinique et l'autre triclinique' (p. 148). In their earlier study, Dormann and Poullen (1980) had been able to distinguish and separate vivianite and metavivianite in similar samples using a binocular microscope: 'Cette operation fut relativement aisée, les limites des domaines monocliniques et tricliniques étant toujours très nettement marquées' (p. 634). Presumably, the same technique was used to select the fragment of metavivianite in the 1982 study. The Mössbauer spectrum of this fragment showed 85% of the total iron was Fe^{3+} which must yield a formula (as above) $Fe^{2+}_{0.45}Fe^{3+}_{2.55}(PO_4)_2(OH)_{2.55}$ $5.4H_2O$ (but cf. Dormann *et al.* (1982, p. 154) although the formula given by them does not use a simple $Fe^{2+} \rightarrow Fe^{3+} + OH^-$ compensation as its basis of calculation and, further, there should be 3 Fe atoms with a valency of $+2.66$ and not 1 as they indicate).

Subsequently, Rodgers and Johnston (1985) reinvestigated type metavivianite from Big Chief by Mössbauer spectroscopy. They obtained a formula of $Fe^{2+}_{1.14}Fe^{3+}_{1.86}(PO_4)_2(OH)_{1.86}6.1H_2O$ in which 62% of the iron was Fe^{3+}, a considerably lower proportion than in either the Kamysch-Burun or Yukon specimens. Composition and structural parameters of the above samples are summarized in Table I.

Compositional range. Both Dormann and Poullen (1980) and Dormann *et al.* (1982) were primarily concerned with examining the oxidation sequence of vivianite. Structural changes occurring in the sequence monoclinic vivianite → triclinic metavivianite → X-ray amorphous iron phosphate enabled them to attempt to define the compositional limits within which the triclinic phase was the preferred stable entity. Unfortunately, the results obtained by artificially oxidized synthetic and natural vivianites and naturally oxidized natural vivianites are not in complete agreement. These difficulties have led to inconsistencies in interpreting oxidation data in earlier studies, e.g. Vochten *et al.* (1979), McCammon and Burns (1980), Henderson *et al.* (1984), (and cf. Sameshima *et al.*, 1985).

TABLE I. Chemical and structural data for metavivianite and kerchenite

	1	2	3	4	5
Fe^{2+}/Fe^{3+}	0.613	0.034	0.176	0.321	0.319
FeO	23.85			9.50	9.49
Fe_2O_3	13.55			32.89	32.965
NiO	0.13				
MnO	4.2	1.83		1.99	1.84
MgO		2.98		1.54	1.56
CaO	0.5	0.72		0.49	0.46
P_2O_5	28.4			28.19	28.21
H_2O				25.04	24.91
Total				99.64	99.435
aÅ	7.81		7.84		
bÅ	9.08		9.11		
cÅ	4.65		4.67		
α°	94.77		95.04		
β°	97.15		96.94		
γ°	107.37		107.72		

1. Type metavivianite, Big Chief, South Dakota. Ritz et al (1974), Rodgers and Johnston (1985).
2. Metavivianite, Yukon. Dormann and Poullen (1980).
3. Metavivianite, Kamysch-Burun. Dormann et al (1982).
4,5. Kerchenite, Kerch. Popoff (1907).

Dormann and Poullen (1980, p. 636) regarded the structure of vivianite as being maintained in the oxidation sequence until 40% of the total iron had been oxidized, corresponding to a formula

$$Fe^{2+}_{1.8}Fe^{3+}_{1.2}(PO_4)_2(OH)_{1.2}6.8H_2O.$$

They stress that in the triclinic lattice the Fe_I site is completely oxidized while 'Le taux d'oxydation du site II varie de 20% environ, valeur inférieure à celle des vivianites monocliniques les plus oxydées jusqu'à pratiquement 100% (métavivianite de Yukon). L'espèce triclinique admet donc des teneurs en Fe^{3+} allant de 50% à 100% du fer total, (p. 637). Further, Mössbauer spectral studies were unable to distinguish triclinic phase, Fe^{3+}-rich specimens from disordered X-ray amorphous material.

Dormann *et al.* (1982) appeared to have qualified the above on the basis of combined Mössbauer, structural and thermal studies. They summarized their findings for natural crystals as:

(i) limits of oxidation of monoclinic lattice

$$0 \leqslant Fe^{3+}_{II} < 50\%, \quad 0 \leqslant Fe^{3+}_{I} \leqslant 40\%,$$
$$0 \leqslant Fe^{3+}_{tot} \leqslant 47\%,$$

all iron being in the monoclinic phase only;

(ii) lower limits of oxidation for the triclinic lattice to be stable

$$Fe^{3+}_{II} \geqslant 20\text{–}25\%, \quad Fe^{3+}_{I} = 100\%,$$
$$Fe^{3+}_{tot} \geqslant 47\text{–}50\%,$$

all iron being in the triclinic phase only. The percentages are for each lattice site or for the total sites. The only observation these workers make concerning the upper limit of oxidation is that the disordered phase is not formed until all the iron has been oxidized.

Rodgers and Johnston (1985) found that 8 % of iron in Fe_I was unoxidized while, despite their assertion to the contrary, Dormann and Poullen (1980) reported that 3 % of iron in Fe_I was ferrous. Clearly then, the above limits represent ideals and further study of natural specimens which are close to these limits is necessary to establish the compositional field within which the triclinic lattice is stable. However, on the basis of the above discussion, the formula of metavivianite can be written, to a first approximation, as

$Fe^{2+}_{3-x}Fe^{3+}_{x}(PO_4)_2(OH)_x(8-x)H_2O$ where $x > 1.4$.

Kerchenite. The Kamysch-Burun locality from which the sample of Dormann *et al.* (1982) came, is one of several in the Kerch-Taman area of Crimea from which Popoff (1906, 1907, 1910*a*, *b*, and elsewhere) described the mineral kerchenite which he found as forming by oxidation of vivianite. In so far as the crystalline phosphates of Kerch were concerned, the 1906 publication was essentially a preliminary note; that of 1907 was far more comprehensive. In it he drew a distinction between the crystalline vivianites and his new kerchenite. The former occurred as colourless to pale blue crystals with a pale blue streak, a hardness of 2, and showed cleavage on {010} only. Kerchenite occurred as green to black crystal pseudomorphs after vivianite, had a hardness of 3½ and, in addition to cleavage parallel to {010} of vivianite, also showed a less perfect cleavage parallel to {100} of that mineral and a third parting perpendicular to the other two. Chemically, the mineral varied in its ferrous-ferric ratio. The two analyses given by Popoff (Table I, cols. 4, 5) had a high level of ferric iron and he gave a formula close to $FeO \cdot Fe_2O_3 \cdot P_2O_5 \cdot 7H_2O$. On the basis of the substance's comparative stability, its stoichiometry, the differences in physical properties and chemistry from those of vivianite, he argued that kerchenite was a distinct mineral species. The subsequent fate of the species in the mineralogical literature has been one of fluctuating fortunes.

Initial support for the mineral's validity appeared to come from further studies, e.g. Popoff (1910*a*, *b*) and Dvoichenko (1914) (cf. Hey, 1962). Mellor (1935) even provided representations of the structures of variously oxidized kerchenite varieties. However, as workers found themselves unable to recognize such kerchenite varieties among the oxidation products of vivianite from areas outside the Kerch and Taman peninsulas, using the criteria of Popoff, kerchenite came to be regarded as being a mixture of vivianite and rather indeterminate oxidation products. This attitude was strengthened when some researchers reported failure to obtain any new distinct X-ray signature from oxidized vivianite, e.g. Chuov and Rudnitzkaja (1966). Palache *et al.* (1951) placed the name under a 'Variety' heading within their section on vivianite and equated it with 'Oxidized Vivianite', noting that while cleavable pseudomorphs may be obtained these 'give very diffuse X-ray patterns' (p. 744). Hey (1962) indicated there was some doubt as to the mineral's validity, regarding the varieties as 'ill-defined' (p. 245), while Fleischer (1975) in his *Glossary* listed kerchenite as '= oxidation products of Vivianite' (p. 82). Moore (1976) discounted the term as not belonging to a true, crystalline mineral entity and decried the introduction of additional, trivial names for crystalline compounds of intermediate composition between end members.

Moore's comment highlights the fact that many of the difficulties which kerchenite appears to have given mineralogists stem not from Popoff's (1907) findings as summarized above, but from his associated interpretation of the relationship between vivianite and kerchenite. For him the two were part of a solid solution series: $Fe_3P_2O_8 \cdot 8H_2O \ldots nFe_3P_2O_8 \cdot mFePO_4 \cdot pH_2O \ldots FePO_4 \cdot pH_2O$. He was unaware of the requirements of modern crystal chemistry such as Goldschmidt's rules and that continuous electrostatic compensation could be achieved in solid solution series by simultaneous substitutions such as $Fe^{2+} + H_2O \rightarrow Fe^{3+} + OH^-$. He became preoccupied with stoichiometry and it was this that appears to have led him to become entangled in a tortuous argument whose main thrust was to show that in such a series as the above, a distinct species had formed whenever stoichiometry was satisfied. Since he had not identified OH^- radicles amongst the components of the series, stoichiometry could not be achieved continuously.

This unnecessarily complicated approach was compounded in 1910. However, the title and concluding paragraph of the 1907 study make it quite clear that as far as Popoff was concerned, in this 1907 study he was dealing with phosphates at Kerch that occurred in crystallized habits only, be these the original crystals or their pseudomorphs. He noted that the more usual habit for the phosphates was as friable, earthy, heterogeneous, brown materials. These were what he described in the 1910 publications and it was here that he specified the stoichiometric proportions for three subspecies of kerchenite with differing Fe^{2+}/Fe^{3+} ratios. The heterogeneous brown materials he regarded as mixtures of these subspecies in varying proportions. Subsequently, additional subspecies were recognized on the same basis, e.g. Dvoichenko (1914) (cf. Palache *et al.*, 1951; Hey, 1962).

A second difficulty in identifying kerchenite outside the type area appears to have arisen from no worker encountering green to black crystals derived from oxidation of vivianite. Most researchers appear to have been concerned with trying to interpret friable, earthy, heterogeneous, brown alteration products and, indeed, many museum specimens labelled as kerchenite or one of the subspecies, appear to be no more than mixtures such as alluded to by Popoff (1907) and described (1910*a*, *b*). It was from such a museum specimen that Dormann *et al.* (1982) selected their cleavage fragment of metavivianite for structural determination. The condition of many museum specimens, partly as a consequence of their instability in the conditions under which they are stored, has provided a lack of quality material for critical, comparative study and has helped endorse the notion that all kerchenites, *ipso facto*, are mixtures. The descriptions Popoff gave of the samples he examined in his 1907 paper gives little reason to assume that they were other than monomineralic, whatever may have been the nature of those described in later papers.

Discussion. Metavivianite was incorrectly described by Ritz *et al.* (1974). Their Big Chief specimen consisted of green crystals which ranged from transparent to opaque with the smaller grains being transparent. The fragment from this same locality examined by Rodgers and Johnston (1985) was khaki and near opaque. It was the same as X-rayed by Sameshima *et al.* (1985, Table I, col. 19) and yielded the same diffraction pattern as given by Ritz *et al.* (1974) without showing any other reflections. The Yukon and Kamysch-Burun specimens were described by Dormann and Poullen (1980) and Dormann *et al.* (1982) as brown and opaque. Their identity and homogeneity were confirmed by X-ray diffraction.

If it is assumed that all the data given by Ritz *et al.* (1974) apply equally to the small transparent crystals and to the opaque material, then it is clear that Poullen's contention that metavivianite is a triclinic, hydrated, ferri-ferrous hydroxy phosphate is upheld. The mineral has a variable Fe^{2+}/Fe^{3+} ratio and Mn can substitute for iron. Presumably, the variation in colour and transparency reflect this variability as do the slight variations in physical parameters (Table I).

However, this assumption may be incorrect and two minerals may have been confused in the original description. It may be that the green transparent crystals are one phase which oxidizes to yield a ferri-ferrous opaque brown product which is identical with that obtained by oxidation of vivianite. In the absence of ferrous/ferric analyses in the original description this possibility should not be overlooked. It would therefore seem prudent that the original specimens of metavivianite and, if necessary, the original locality be carefully reassessed and the identity and homogeneity of all the material be established along with the applicability of all the published data on metavivianite as defined above. Unfortunately, no further material was available for further study from either of the repositories of type metavivianite as given by Ritz *et al.* (1974, p. 896).

If more than one phase does exist at Big Chief then the question may arise as to which the name *metavivianite* properly belongs. The name as redefined by Poullen (1979) is now a misnomer in so far as Ritz *et al.* (1974) chose it to 'emphasise the dimorphous relationship to vivianite' (p. 896).

While Popoff's attempt to establish a continuous solid solution oxidation series between vivianite and ferric phosphate hydrate was also in error, he did describe kerchenite as forming by oxidation of vivianite. The samples he used in his original description appear to have been homogeneous from the physical description he gave, which included optical examination. The mineral had distinctive physical properties and its Fe^{2+}/Fe^{3+} ratio could vary over a wide range. While there appears to be no justification for setting up separate names for intermediate compositions between end members, the problem is to ascertain what are the correct end members of the oxidation solid solution series. It can be noted that all the various formulae of Popoff's stoichiometric intermediate compounds are included within the general formula of metavivianite as given above, once $H_2O \rightarrow OH^-$ compensation is allowed for. For example, his so-called α-kerchenite can be recalculated as $Fe^{2+}_{1.66}Fe^{3+}_{1.33}(PO_4)_2(OH)_{1.33}6.66H_2O$. Further, it must be emphasized that the oxidized product of vivianite does give a positive X-ray signature (e.g. Poullen, 1979; Dormann and Poullen, 1980; Dormann *et al.*, 1982; Henderson *et al.*, 1984; Sameshima *et al.*, 1985) despite statements to the contrary (e.g. Palache *et al.*, 1951; Chuov and Rudnitzkaja, 1966; Tien and Waugh, 1969; Vochten *et al.*, 1979). The signature is that given by Ritz *et al.* (1974) for metavivianite.

When Dormann *et al.* (1982) provided structural substantiation of Poullen's (1979) redefinition of metavivianite they did so using a cleavage fragment of kerchenite. It would appear that kerchenite and re-defined metavivianite are identical.

Consideration could be given to reinstating kerchenite as the name for triclinic ferri-ferrous hydroxy phosphate hydrate pending a re-examination of both the Big Chief and Kerch localities to establish unambiguously the identity of the two minerals and, in the case of Kerch, to confirm that the prefixed varieties of kerchenite are intermediate compositions within a solid solution series and not discrete mineral species. Such a re-examination could help in defining the limits within which the triclinic lattice is stable as well as the nature of the reportedly X-ray amorphous brown product that results from complete oxidation.

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