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A STRUCTURAL CLASSIFICATION OF Fe-Mn ORTHOPHOSPHATE HYDRATES

PAUL B. MOORE, *Department of Geophysical Sciences, University of Chicago, Chicago, Illinois.*

ABSTRACT

The Fe-Mn orthophosphate hydrate structures are based on linkages of octahedra and tetrahedra. Since the tetrahedra composed of PO_4^{3-} groups are insular (not linked to other tetrahedra), a classification analogous to the silicates is fruitless. However, linkages of octahedra can be easily related to general formulae which specify the ligands participating in octahedral bonding, with the metal ions as octahedral centers. The ratio of the metal ions to the octahedrally coordinating oxygens (associated with OH^- H_2O and PO_4^{3-} ligands) is the key to the classification since octahedral groups and linkages can be specified.

Various types of octahedral isomerisms are discussed and the known crystal structures of Fe-Mn orthophosphate hydrates are reviewed.

INTRODUCTION

Classification of anisodesmic oxysalts, particularly of mineral species, on the basis of some linking unit and structure cell stoichiometry sheds much light on the bewildering forest of erstwhile disconnected families of compounds. Schemata offered for the mesodesmic silicates, relating chemical stoichiometry and framework structure, with the SiO_4^{4-} tetrahedron as linking unit, were developed by Machatschki (1928) and Bragg (1930), and later expanded by Belov (1963) and Zoltai (1960) to include other groups such as BeO_4 and AlO_4 tetrahedra. Classification of borate structures on the basis of complex polyanions erected from linkages of BO_4^{5-} tetrahedra and BO_3^{3-} equilateral triangles by Christ (1960) and Tennyson (1963) has met with considerable success, and in some instances, led to the prediction of unknown structures. Fluoroaluminate classification was investigated by Pabst (1950), the octahedron being used as linking unit.

The Fe-Mn orthophosphate hydrates comprise a sizable body of mineral species. A previous attempt at classification of orthophosphates, orthoarsenates, and orthovanadates was based on chemical stoichiometry (Palache *et al.*, 1951). It lacks a direct relationship to crystal structure and is incapable of elucidating the role of water.

The classification offered here is limited to Fe-Mn orthophosphate hydrates. Fe-Mn orthoarsenate (and orthovanadate) hydrates could also be included but as yet very few crystal structures of these oxysalts have been revealed.

The structural unit chosen is the regular octahedron, since, for the phosphate minerals, the PO_4-tetrahedra are insular (that is, not linked to other tetrahedra) and a classification based on linked tetrahedra—

analogous to the silicates—would be impossible. hermore, the metal-centered octahedra are of more interest from 1 andpoint of crystal field theory.

Octahedral coordination about Fe^{2+}, Mn^{2+}, 'e^{3+} ions can be explained by hybridization of bonding orbitals of S4P^3 (or 4S4P^{3}4D^2) type; that is, bonds whose directions point to apices of a regular octahedron. The ligands supplying the necessa ired electrons to fill these empty hybridized orbitals can be either OH^-, or the tetradentate PO_4^{3-} group. The known crystal structı f Fe-Mn orthophosphate hydrates support the assumption that t ɜtals reside in octahedral centers.

THE SCHEME

Before suggesting a general formula which is y related to crystal structures based on octahedral linkages, thr ɜumptions must be made:

1) the metals are octahedrally coordinated, with oxyg ns at the vertices of the octahedra,
2) the PO_4^{3-} group is tetradentate, each oxygen associa h at least one octahedral center, and,
3) the remaining OH^- and H_2O ligand stoichiometry is .

Assumptions 1 and 2 are borne out by the exis ɹnown crystal structures. Assumption 3 perhaps needs some clarifi . Only the OH^- and H_2O groups which behave as octahedrally coor ing ligands are considered. It is assumed that non-octahedrally bc water, for example, "zeolitic water," can be determined separately.

For metals of charge 2+, the general formula

$$X_n^{2+}(OH)^-_{2n-3z}(PO_4)_z^{3-}(H_2O)_r \qquad 3z$$

where,

X = metal
OH^-, H_2O, PO_4^{3-} = ligands
n = number of octahedra
z = number of tetrahedra
r = octahedrally coordinating wat cules

A further symbol, P, is used, which is simply ɜum of octahedrally coordinating oxygens,

$$P = r + 2n + z$$

Likewise, for metals of charge 3+,

$$X_n^{3+}(OH)^-_{3(n-z)}(PO_4)_z^{3-}(H_2O)_r \qquad z$$

$$P = r + 3n + z$$

and, for mixed charge 2+ and 3+,

$$X_{n1}{}^{2+}X_{n2}{}^{3+}(OH)^{-}{}_{2n1+3(n2-z)}(PO_4)_z{}^{3-}(H_2O)_r \qquad 2n_1 + 3n_2 \geqq 3z$$

$$n = n_1 + n_2$$

$$P = r + 2n_1 + 3n_2 + z.$$

Octahedral Linkages of Finite Extent (*Isolated Groups*). It is a simple matter to relate the above general formulae, based solely on charge balance and the three assumptions, to octahedral linkages of finite extent. The nature of the octahedral linkage is dependent on the *formula* nP or, analogously, the *ratio* n/P.

The term "n" can be the number of octahedra (isolated and/or "clustered") in an asymmetric unit of structure. Though the ratios n/P for $nP = XO_6$ ($n = 1$) and $nP = X_3O_{18}$ ($n = 3$) are the same—in this case, structures based on insular octahedra—X_3O_{18} implies further that there are three insular octahedra in an asymmetric unit of structure (*i.e.*, octahedra which cannot be made congruent by space group symmetry operations). Such information is very important in nuclear magnetic resonance and Mössbauer resonance investigations, studies which the Fe-Mn orthophosphates will no doubt enjoy in the future.

Table 1 is a format for finite linkages of octahedra, listing n, the number of octahedra in an asymmetric unit of structure; the formula nP; the linking type and a simple code. Only permissible formulae for $n \leqq 4$ are listed, since higher n-values would, in all probability, be manifest in structures of considerable complexity. Using the information in Table 1 and working out the appropriate formula, there results Table 2, a list of permissible chemical formulae for metals of charge +2. Similar formulae can be generated for metals of charge +3 and for metals of mixed charges.

Octahedral Linkages of Infinite Extent. No simple table of permissible structures can be given here, for the number of permissible patterns of structure is infinite. However, some simple motifs can be offered and the more complex groups derived from fusion or addition of these simple linkages when possible. For chains, vertex $(XO_5)_n$, edge $(XO_4)_n$, and face $(XO_3)_n$ linkages are permissible; for sheets, vertex $(XO_4)_n$ and edge $(XO_3)_n$ linkages (face linkages leave re-entrants); and for 3-dimensional frameworks, vertex $(XO_3)_n$ linkages (face and edge linkages leave re-entrants).

Table 3 is an outline of the known crystal structures of Fe-Mn orthophosphate hydrates. In rather complex fused groups, as in scorzalite, several alternative choices of linkages are possible.

The advantages of this scheme over the previous one is (1) the role of water is emphasized and (2) the characterization of octahedral linkages

TABLE 1. A FORMAT FOR FINITE OCTAHED NKAGES

	v=vertex	e=edge f=	
n	nP	link-type	code
1	XO_6	insular	a
2	X_2O_{12}		a+a
	X_2O_{11}	v-v	b
	X_2O_{10}	e-e	c
	X_2O_9	f-f	d
3	X_3O_{18}		a+a+a
	X_3O_{17}		a+b
	X_3O_{16}		a+c
	X_3O_{15}		a+d
	X_3O_{16}	v-v-v	e
	X_3O_{15}	v- 3-ring	e′
	X_3O_{14}	f-f-v	f
	X_3O_{14}	e-e-e	g
	X_3O_{12}	f-f-f	h
	X_3O_{13}	e-e(f)-f	i
4	X_4O_{24}		a+a+a+a
	X_4O_{23}		a+a+b
	X_4O_{22}		a+a+c
			b+b
			a+e
	X_4O_{21}		a+a+d
			b+c
			a+e′
		v-v-v-v	j
	X_4O_{20}		b+d
			c+c
			a+f
			a+g
		v-e-e-v	k
		v- 4-ring	l
	X_4O_{10}		c+d
			a+i
		v-v(e)-e-e	m
	X_4O_{18}		d+d
			a+h
		e-e-e-e	n
	X_4O_{17}	f-f-f(v)-v	o
	X_4O_{16}	f-f-f(e)-e	p
	X_4O_{15}	f-f-f-f	q

leads to permissible structural isomerisms including ligand stereoisomerisms about the octahedra. In reference to silicate classification, the scheme suffers one disadvantage: whereas only vertex-sharing of tetrahedral groups need be considered in silicate structures (excluding possible rare exceptions), in this classification, edge-sharing and face-sharing of octahedra as well must be considered. Furthermore, the exact "ligand water" cell stoichiometry must be known. This makes predictions of unknown structures difficult and ambiguous.

ISOMERISM

The problem may be posed this way: given a chemical formula, what are possible crystal structures that will satisfy that formula? Four types of isomerism play a potentially important role in Fe-Mn orthophosphate hydrate crystallography: 1) polymerization isomerism, 2) stereoisomerism, 3) polynuclear isomerism, and 4) hydrate isomerism.

Polymerization isomerism. Tables 1, 3 show that for a general formula nP there can exist more than one link-type. For example, laueite (Table 3) and vivianite (Table 1), both with $nP = X_3O_{16}$ are polymerization isomers. A further finite link-type exists (Table 1), consisting of a vertex-joined triplet of octahedra.

TABLE 2. FORMULAE FOR ISOLATED GROUPS FOR n<4, CHARGE 2+

nP	z	Formula
XO_6	0	—
X_2O_{12}	1	$X_2(OH)(PO_4)(H_2O)_7$
X_2O_{11}	1	$X_2(OH)(PO_4)(H_2O)_6$
X_2O_{10}	1	$X_2(OH)(PO_4)(H_2O)_5$
X_2O_{09}	1	$X_2(OH)(PO_4)(H_2O)_4$
X_3O_{18}	1	$X_3(OH)_3(PO_4)(H_2O)_{11}$
	2	$X_3(PO_4)_2(H_2O)_{10}$
X_3O_{17}	1	$X_3(OH)_3(PO_4)(H_2O)_{10}$
	2	$X_3(PO_4)_2(H_2O)_9$
X_3O_{16}	1	$X_3(OH)_3(PO_4)(H_2O)_9$
	2	$X_3(PO_4)_2(H_2O)_8$
X_3O_{15}	1	$X_3(OH)_3(PO_4)(H_2O)_8$
	2	$X_3(PO_4)_2(H_2O)_7$
X_3O_{14}	1	$X_3(OH)_3(PO_4)(H_2O)_7$
	2	$X_3(PO_4)_2(H_2O)_6$
X_3O_{13}	1	$X_3(OH)_3(PO_4)(H_2O)_6$
	2	$X_3(PO_4)_2(H_2O)_5$
X_3O_{12}	1	$X_3(OH)_3(PO_4)(H_2O)_5$
	2	$X_3(PO_4)_2(H_2O)_4$

TABLE 3. CLASSIFICATION OF Fe-Mn ORTHOPHOSPHATE HYDRATE STRUCTURES

	nP	Code	Mineral	Formula	Reference
Finite linkages	XO_6	a	strengite, metastrengite[1]	$Fe(PO_4)(H_2O)_2$	Hiriyana, 1949; Moore, 1965
	X_3O_{16}	a+c	vivianite, symplesite[2]	$Fe_3(PO_4)_2(H_2O)_8$	Mori, 1950
Infinite linkages					
a. simple chains	$(XO_5)_3$	edge-linked chain	ludlamite	$Fe_3(PO_4)_2(H_2O)_4$	Ito, 1951
b. mixed linkages	$XO_6+(XO_5)_2$	a+vertex-linked chain	laucite, strunzite,[2] stewartite[2]	$MnFe_2^{3+}(OH)_2(PO_4)_2(H_2O)_6 \cdot 2H_2O$	Moore, 1965
c. complex fusions	(XO_4) chain fused to (XO_5) chains giving (X_2O_7)		cosphorite	$MnAl(PO_4)(OH)_2(H_2O)$	Hanson, 1960

[1] A partially known structure.

[2] Formal crystal structure analysis lacking.

Stereoisomerism. Whereas polymerization isomerism is concerned with the types of octahedral linkages, stereoisomerism is concerned with the arrangement of ligands about the octahedra. In octahedral complexes, stereoisomerism may occur when two or more ligand species are arranged about the coordination center such that congruency is destroyed by at least one rearrangement of the ligands. Since an octahedron possesses six apices, five ligands of one species and one ligand of another species, briefly written (5+1), or the trivial case of six like-ligands (6+0) are incapable of stereoisomerism.

Our concern is with at most three ligand species. In all, oxygen atoms associated with these ligands also reside on the apex positions of octahedra. The (x+y) and (x+y+z) various stereoisomerisms are illustrated in figure 1.

If the proposed structures of strunzite and stewartite are correct (Moore, 1965), then laueite, strunzite and stewartite would be stereoisomeric structures.

Another type of stereoisomerism can be conceived, even when there is no interchange of ligands about the octahedron. This could be considered as a tilting or twisting of the ligands. A good example is the strengite-metastrengite pair. Both are cis-$(X)(O_p)_4(O_b)_2$ structures and the near-completed crystal structure determination of metastrengite suggests that its only major difference from strengite rests on the "tilt" of the PO_4^{-3} tetrahedra about an asymmetric octahedron of structure.

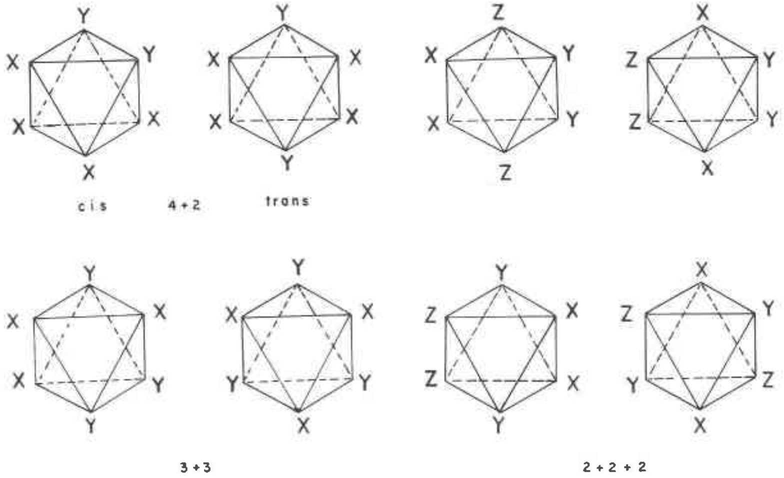


FIG. 1. Illustration of stereoisomerisms involving two and three different vertex species about an octahedron.

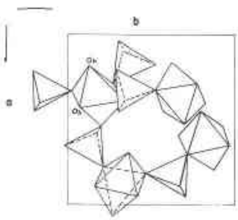
Polynuclear Isomerism. Since two metal specie and Mn, are being considered, polynuclear isomerism is possible. T nilarities in bonding orbital hybridization of Fe^{2+} and Fe^{3+} ions an Mn^{2+} ion, and the similarities in crystal radii suggest possibilities o iorphic replacement as evidenced in the triphylite-lithiophilite series childrenite-eosphorite series, and the reddingite-phosphoferrite s However, notable exceptions are known: vivianite and ludlamite contain more than 2% MnO and it appears that in some structur e Fe:Mn ratios are fixed (or bounded). For laueite and its polymor his is nearly 2:1. In such an instance, polynuclear isomerism is po ; that is, the interchange of Fe and Mn in non-equivalent octahe centers results in an interchange of environment about each of the metals. As yet, no examples of polynuclear isomeric pairs among p iates can be offered.

Hydrate Isomerism. Hydrate isomerism implie it water may play different roles in structures; for example, it cou have as a ligand or participate in filling space in a cavity in a stru Both examples are present in laueite, $MnFe^{3+}_2(OH)_2(PO_4)_2(H_2O)$ O, $nP=X_3O_{16}$. If a hypothetical $MnFe^{3+}_2(OH)_2(PO_4)_2(H_2O)_8$, $nP=$ $_8$ (a structure composed of insular octahedra) exists, considerabl erences in physical properties and morphology between it and lau would be expected, though in both cases the total water content be the same. This emphasizes the importance of specifying all the r for a coordination complex. It is now evident that the familiar "·n in texts contributes little to the understanding of these compounds. possible, the ligand waters should be specified in parentheses.

OCTAHEDRAL LINKAGES IN KNOWN CTURES

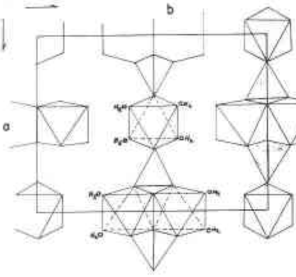
The Fig. 2 series are projections of the know uctures. Polyhedral diagrams are used to show linkages of octahedra tetrahedra, and are the most accessible visually in picturing phosp structures. In these diagrams, only the basic features have been show ease the "visualization" of the formula for the octahedral skeleto itten at the base of each diagram. The symbolism used here has l explained in Moore (1965), O_h being oxygen affixed to H_2O and/or (gands and O_p being PO_4^{3-} oxygen. The differentiation of OH^- from is not easy (in most structures, the parameters are not good enoug meaningful interatomic distances) and no attempt is made here.

Scorzalite and eosphorite are not strictly Fe- orthophosphate hydrates but have been included since Al in the r tive species is octahedrally coordinated and behaves like Fe in the s ure. Furthermore, a



Strengite (4+2)

cis-$x(o_p)_4(o_h)_2$

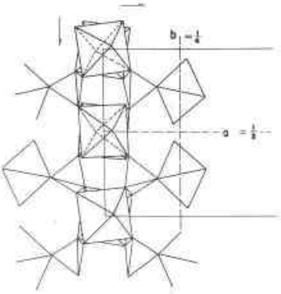


Vivianite

(2+4), (4+2) pair

isolated octahedron: trans-$x(o_p)_2(o_h)_4$

double group: $[x(o_h)_2(o_p)_2] < \begin{smallmatrix} o_p \\ o_p \end{smallmatrix} > [x(o_h)_2(o_p)_2]$



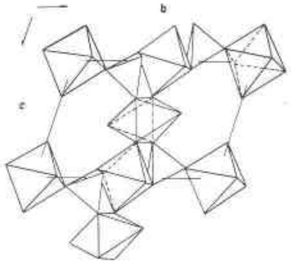
Strunzite (4+2), fused [(4+2) and (4+2)]$_1$

and fused [(2+4) and (2+4)]

Isolated octahedron : [trans-$(x)(o_p)_2(o_h)_4$]

chain 1 : ···$-o_h-[(x)(o_p)_4]-o_h-[(x)(o_p)_4]-$···

chain 2 : ···$-o_h-[$trans-$(x)(o_p)_2(o_h)_2]-o_h-[$tr.-$(x)(o_p)_2(o_h)_2]-$···

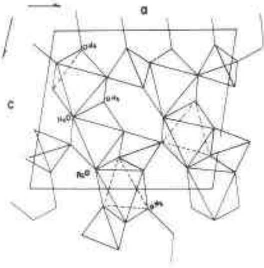


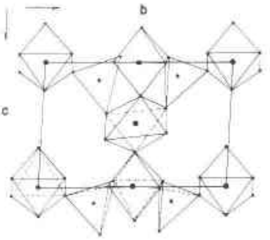
Laueite (4+2) and fused

[(4+2) and (2+4)]

isolated octahedron: [trans-$(x)(o_h)_4(o_p)_2$]

chain: ···$[(x)(o_p)_4]-o_h-[$trans-$(x)(o_h)_2(o_p)_2]-o_h-[(x)(o_p)_4]$···





Ludlamite fused [(3+3) and (2+4)]

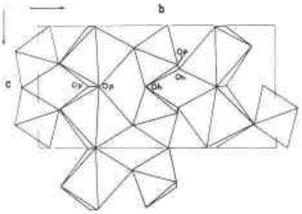
chain: ···$< \begin{smallmatrix} o_h \\ o_h \end{smallmatrix} > [(x)(o_p)_2] < \begin{smallmatrix} o_h \\ o_p \end{smallmatrix} > [(x)(o_p)_2] < \begin{smallmatrix} o_p \\ o_h \end{smallmatrix} > [(x)(o_p)_2] < \begin{smallmatrix} o_h \\ o_h \end{smallmatrix}$···

Stewartite (4+2) and fused

[(4+2) and (2+4)]

isolated octahedron: [cis-$(x)(o_h)_4(o_p)_2$]

chain: ···$[(x)(o_p)_4]-o_h-[$cis-$(x)(o_h)_2(o_p)_2]-o_h-[(x)(o_p)_4]$···

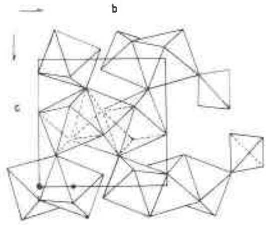


Eosphorite

fused (4+2), fused (2+4)

chain 1: ···$< \begin{smallmatrix} o_p \\ o_p \end{smallmatrix} > [x(o_h)_2^{*}] < \begin{smallmatrix} o_p \\ o_p \end{smallmatrix} > [x(o_h)_2^{*}] <$···

chain 2: ···$-o_h-[$trans-$x(o_h)_2^{*}(o_p)_2]-o_h-$···



Scorzalite

triple group (3+3, 2+4, 3+3)

$[x(o_p)(o_h)(o_h)^{*}] \begin{smallmatrix} o_h^{*} \\ o_p \\ o_p \end{smallmatrix} [x] \begin{smallmatrix} o_p \\ o_p \\ o_h^{*} \end{smallmatrix} [x(o_p)(o_h)(o_h)^{*}]$

TABLE 4. CELL DATA OF SOME Fe-Mn ORTHOPHOSP YDRATE STRUCTURES

	a	*b*	*c*	α		γ	S.G.	Z
strengite	10.07	9.83	8.67 Å	—		—	*Pcab*	8
vivianite	10.05	13.42	4.70		10		*C*2/*m*	2
ludlamite	10.50	4.65	9.18		10		*P*2_1/*a*	2
laueite	5.28	10.66	7.14	107°55′	11	71°07′	*P*$\bar{1}$	1
strunzite	9.80	18.06	7.34		11		*C*2/*c*	4
stewartite	2×5.23	10.77	7.25	90°35′	10	71°21′	*P*1	2×1
eosphorite	10.38	13.36	6.91	—		—	*Bba*2	8
scorzalite	7.15	7.32	7.14		11		*P*2_1/*n*	2

Data from Palache *et al.* (1951) and Peacor (1963).

Fe endmember (barbosalite) of scorzalite is kno lthough its structure has not been refined.

As these drawings are projections, in some ces (as in ludlamite and vivianite) tetrahedra appear to share edges octahedra. Actually, these tetrahedra link to symmetry equivalent edral groups normal to the plane of the drawing so that the effect trahedral bridging is lost.

Though the formulae may appear to be mor g on the cake,' they help when various other isomerisms are being s . Notice that around each metal center (X) there are six specified ox , some of which may be shared with other octahedral centers. They rtitioned by a dash. The tetrahedra are not specified in the formulae

Table 4 lists the cell data and space groups structures in Fig. 2.

CONCLUSIONS AND FURTHER D SION

The Fe-Mn orthophosphate hydrate structu far revealed consist of linkages of somewhat distorted octahedra trahedra. The PO_4^{3-} tetrahedron is tetradentate, each oxygen ass d with at least one octahedral center. The metal-centered octahe nk together to form isolated groups, vertex-linked chains, edge-lin hains, sheets, or incomplete three-dimensional arrays. All the wat most of the water is

FIG. 2. Projection representations of some Fe-Mn orth ate structures. Unit cell is outlined and only parts of the structure are shown. Su t stars indicate oxygens shared by other groups. Reference for atom parameters: str (Hiriyana, 1949), vivianite (Mori, 1950), ludlamite (Ito, 1951), laueite, strunz ewartite (Moore, 1965) eosphorite (Hanson, 1960), scorzalite (Lindberg, 1959). trunzite and stewartite structures are inferred and have not yet been confirmed by l structure analysis.

octahedrally bound;[1] when heated in an oxidizing environment, hydrogen is split off during oxidation of the metal, but the essential structure remains intact—apparently a true case for most Fe-orthophosphates. If all of the water is octahedrally bound, the loss of water results in destruction of the structure, as in vivianite. More detailed results of heating studies on Fe-Mn orthophosphate hydrates will appear in another paper.

Since at least 50 other Fe-Mn orthophosphate hydrates are known, novel linkages should be found in the course of further studies.

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[1] An exceptional situation is cacoxenite, $Fe_4(PO_4)_3(OH)_3(H_2O)_x \cdot (12-x)H_2O$. Apparently much of the water is of a zeolitic nature, and about half the water can be lost without severe damage to the structure.

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