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Thermal Behaviour and Physico-chemical Characterization of Synthetic and Natural Iron Hydroxyphosphates

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The thermal behaviour of five hydroxyphosphates, lipscombite [$Fe_3(PO_4)_2(OH)_2$], barbosalite [$Fe_3(PO_4)_2(OH)_2$], giniite [$Fe_5(PO_4)_4(OH)_2 \cdot 2H_2O$], rockbridgeite $Fe_5(PO_4)_3(OH)_5$] and $Fe_4(PO_4)_3(OH)_3$, has been studied. Thermogravimetric analysis revealed the hydroxyphosphates to have distinct behaviours: some underwent dehydroxylation between 623 and 893 K like other phosphates [lipscombite, barbosalite, $Fe_4(PO_4)_3(OH)_3$], while rockbridgeite and giniite differed. Rockbridgeite, which appeared to contain only iron(III) ions, underwent a first partial dehydroxylation at only 438 K, while giniite totally dehydroxyated only at between 623 and 823 K. Comparison of the results obtained by thermogravimetric analysis with those obtained by other techniques, including chemical analysis, X-ray diffraction and Mössbauer spectroscopy, allowed us to propose the existence of a new solid solution for the giniite compound and to confirm that previously observed for rockbridgeite. The solid solution of the former corresponds to a variation in composition due to dehydroxylation–hydration: $Fe^{III}_{4+x}Fe^{II}_{1-x}(PO_4)_4(OH)_{2-x}(2+x)H_2O$ with $0 < x < 1$. The latter corresponds to a variation in the composition due to dehydroxylation–oxidation: $Fe^{III}_{4+x}Fe^{II}_{1-x}(PO_4)_3(OH)_{5-x}O_x$ with $0 < x < 1$. In both cases, Mössbauer spectroscopy indicates that Fe^{2+} or Mn^{2+} substituents may be localized on the different crystallographic sites of the structures.

A recent study[1] has shown that several hydroxyphosphates are potential oxidative dehydrogenation catalysts. For catalytic reactions conducted between 573 and 723 K, it appeared of interest to study the thermal behaviour of these compounds in this temperature range. This paper reports the thermal and thermogravimetric analyses conducted in argon of four synthetic and one natural hydroxyphosphate: the two polymorphic forms of $Fe_3(PO_4)_2(OH)_2$, (i) lipscombite, (ii) barbosalite, (iii) $Fe_4(PO_4)_3(OH)_3$, (iv) $Fe_5(PO_4)_4(OH)_2 \cdot 2H_2O$ called giniite and (v) $Fe_5(PO_4)_3(OH)_5$, a natural sample called rockbridgeite. Although several published studies have dealt with these hydroxyphosphates, which are well known mineral compounds, none of them have reported in detail their thermal behaviour in a neutral atmosphere.

Experimental

Sample Preparation

$Fe_4(PO_4)_3(OH)_3$, lipscombite and barbosalite samples were prepared as described previously.[2,3] They were obtained by hydrothermal synthesis using vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] and an amorphous iron(III) phosphate gel as precursors. The hydrothermal syntheses were conducted at 473 K for 5 h. The samples obtained were filtered, washed with water and dried at 373 K overnight. The giniite sample has been prepared by hydrothermal synthesis using a mixture of 5 g of synthetic vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ along with 5 g of phosphoric acid and 1 ml of distilled water per g of solid. The hydrothermal treatment was conducted at 383 K for 120 h. The solid obtained was washed with water and air-dried at 373 K. To our knowledge, this is a novel method for giniite synthesis. The rockbridgeite was kindly supplied by the Museum National d'Histoire Naturelle (Paris, France). The chemical analysis of this mineral showed that it contained a relatively large amount of manganese (Table 1).

Sample Characterization

The chemical composition of the solids was determined by atomic absorption. X-Ray diffraction analysis was performed on the samples using a Siemens D500 diffractometer and Cu-Kα radiation. Differential thermal analyses (DTA) and thermogravimetric (TG) analyses were performed simultaneously using a SETARAM TGA–DTA 92 thermobalance coupled to a Balzers 420 QMC mass spectrometer. 30–60 mg of the samples were placed in a platinum crucible suspended from one arm of the balance. The analyses were conducted at atmospheric pressure under a deoxygenated and dehydrated argon flow (1 l h^{-1}) with a heating rate of 5 K min^{-1} and a temperature limit of 1023 K. Mass spectrometry was used to verify the nature of the eventual gaseous reaction products, namely O_2, H_2, H_2O, CO and CO_2; the precision of the thermogravimetric analyses was *ca.* 2%.

Mössbauer spectra were recorded at room temperature, using a 2 GBq ^{57}Co–Rh source and a conventional constant acceleration spectrometer, operated in triangular mode. The samples were diluted in Al_2O_3 in order to avoid a too high Mössbauer absorption, and pressed into pellets. The isomer shifts (δ) were given with respect to α-Fe and were calculated, as the quadrupole splittings (Δ) and the linewidth (W), with a precision of *ca.* 0.02 mm s^{-1}.

Results

Physico-chemical Characterization

The main characteristics of the solids studied are presented in Table 2. The P : Fe ratios were calculated from chemical analyses and the values of Fe^{3+} : (Fe^{3+} + Fe^{2+}) were determined from Mössbauer spectroscopy. The values obtained

Table 1 Chemical analysis of the natural rockbridgeite sample

element	wt.%
Fe	30.2
P	13.0
Mn	5.5
Al	0.2
Ca	0.1
Mg	0.06

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Table 2 Main characteristics of the hydroxyphosphates studied; theoretical values are given in parentheses

compound		P : Fe	Fe^{3+} : (Fe^{3+} + Fe^{2+})[a]
$Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$	barbosalite	0.69 (0.66)	0.66 (0.66)
$Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$	lipscombite	0.69 (0.66)	0.65 (0.66)
$Fe_4^{III}(PO_4)_3(OH)_3$		0.76 (0.75)	1.00 (1.00)
$Fe_4^{III}Fe^{II}(PO_4)_4(OH)_2 \cdot 2H_2O$	giniite	0.80 (0.80)	0.65 (0.80)
$Fe_4^{III}Fe^{II}(PO_4)_3(OH)_5$	rockbridgeite	0.64 (0.60)[b]	0.87 (0.80)[b]

[a] Determined by Mössbauer spectroscopy. [b] In the case of rockbridgeite P : (Fe + Mn) and Fe^{3+} : (Fe^{3+} + Mn^{2+} + Fe^{2+}) are given.

for the P : Fe ratios were in good agreement with the theoretical ratios. The calculated values for the Fe^{3+} : (Fe^{3+} + Fe^{2+}) ratios corresponded to the theoretical ones except for the giniite and rockbridgeite samples which both indicated an excess of iron(III) cations. The X-ray diffraction spectra all revealed pure phases.[1]

Thermogravimetric Analyses

$Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$, *Barbosalite and Lipscombite*

The weight loss of the samples occurred at 715, 802 and 823 K for lipscombite and at 743, 793 and 868 K for barbosalite [Fig. 1(*a*) and (*b*)] (Table 3). The mass spectrometric analyses performed simultaneously allowed the mass losses to be attributed to the dehydration of the solids. The mass losses of the lipscombite and barbosalite are 0.97 and 1.05 mol, respectively, per mol of solid. These values are very close to the theroetical values, corresponding to a total content of water, of 1.00. In both cases the dehydration process began at *ca.* 623 K, the first weight losses were the most important and corresponded approximately to half of the water contained in the compounds. The other half corresponded to the two final smaller water departures and seemed to be equal. Results from DTA analyses have not been presented in all cases. They confirmed the weight losses characterized by poorly defined endothermic peaks. After heating to 923 K, the X-ray diffraction patterns of the samples were totally modified, showing a complete transformation of the solids after dehydration.

$Fe_4^{III}(PO_4)_3(OH)_3$

The thermogravimetric analysis of this compound showed three weight losses at 802, 818 and 849 K [Fig. 1(*c*)] (Table 3). These weight losses, which were attributed to water departures, corresponded to 1.54 mol of water per mol of solid. This value was again very close to the theoretical value of 1.50. The first two water departures, which were very close in temperature, corresponded in total to *ca.* 1 mol of water.

Giniite, $Fe_4^{III}Fe^{II}(PO_4)_4(OH)_2 \cdot 2H_2O$

Thermogravimetric analysis of this compound showed three water departures at 473, 658 and 773 K [Fig. 2(*a*)]. The first weight loss, which was the most important, corresponded to

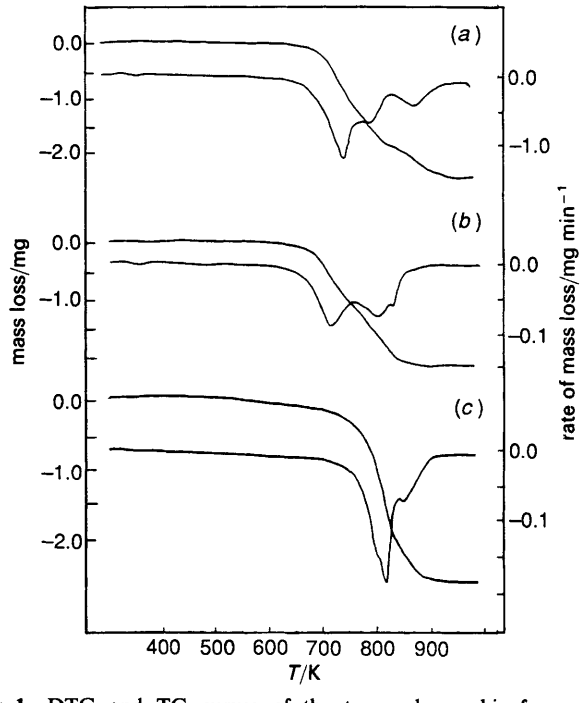

Fig. 1 DTG and TG curves of the two polymorphic forms of $Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$, namely (*a*) barbosalite and (*b*) lipscombite and (*c*) $Fe_4(PO_4)_3(OH)_3$

Table 3 Details of the DTA and TG analyses of the hydroxyphosphates

compound		temperature/K	loss of water /mol of H_2O mol^{-1}	total loss of water[a] /mol of H_2O mol^{-1}
$Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$	barbosalite	743	0.54	1.05 (*1.00*)
		793	0.24	
		868	0.27	
$Fe_2^{III}Fe^{II}(PO_4)_2(OH)_2$	lipscombite	715	0.48	0.97 (*1.00*)
		802	0.24	
		843	0.24	
$Fe_4^{III}(PO_4)_3(OH)_3$		802		1.54 (*1.50*)
		818	1.05	
		849	0.49	
$Fe_4^{III}Fe^{II}(PO_4)_4(OH)_2 \cdot 2H_2O$	giniite	573	2.60	3.20 (*3.00*)
		633		
		763	0.60	
$Fe_4^{III}Fe^{II}(PO_4)_3(OH)_5$	rockbridgeite	434	0.20	2.40 (*2.50*)
		658	2.20	
		823		

[a] Theoretical values are given in italic.

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2.6 mol of water per mol of giniite and should correspond to the hydration water (Table 3). The two other water departures, which took place between 623 and 827 K, should correspond to the departure of the hydroxy groups. These weight losses correspond to 0.6 mol of water per mol of giniite. This value was lower than that expected from the stoichiometry, whilst that corresponding to the first loss was higher.

Rockbridgeite $Fe_4^{III}Fe^{II}(PO_4)_3(OH)_5$

The thermogravimetric analysis of the rockbridgeite sample showed three water departures [Fig. 2(*b*)]. The first occurred at 434 K and the other two at much higher temperatures, 658 and 823 K (Table 3). Of these last two, the first was sharper and more significant than the second. The first departure corresponded to 0.20 mol of water per mol of rockbridgeite and the others to 2.20 mol of water per mol of rockbridgeite, which gave a total of 2.40 per mol of rockbridgeite.

Mössbauer Spectroscopic Study

The Mössbauer spectroscopic analyses of the barbosalite, lipscombite and $Fe_4(PO_4)_3(OH)_3$ samples, have been published.[2,4] The results obtained were in good agreement with both the results of the thermogravimetric and chemical analyses.

The Mössbauer spectrum of the giniite sample, which is presented in Fig. 3, shows four doublets (Table 4). These doublets, two of which correspond to iron(III) cations and the other two to iron(II) cations, could not be directly attributed since the detailed crystallographic structure of the compound is not known. However, it was observed that the $Fe^{3+}:(Fe^{2+}+Fe^{3+})$ ratio was equal to 0.65 instead of 0.80 as deduced from the stoichiometry.

Characterization of the sample of rockbridgeite by Mössbauer spectroscopy showed that the sample contained only iron(III) cations (Table 4). The spectrum presented in Fig. 4, shows three doublets. These doublets could correspond to the three crystallographic sites known[5] to exist in the structure of rockbridgeite $\{[Fe_2^{III}][Fe_2^{III}][Fe^{II}](PO_4)_3(OH)_5\}$. The unit framework of the structure of rockbridgeite consists of a cluster of three face sharing octahedra Fe(2)–Fe(1)–Fe(2). These clusters and other FeO_6 octahedra [Fe(3)] are connected to each other by corner sharing (Fig. 5). The crystallographic sites [Fe(1), Fe(2), Fe(3)] have a relative ratio equal to 20 : 40 : 40. From bibliographic data and by considering the relative areas of the doublets, the doublet with the quadrupolar splitting equal to 0.66 mm s^{-1} could be attributed to Fe^{3+} in the cluster [Fe(2) sites] and that with the smaller quadrupolar splitting (0.38 mm s^{-1}) to Fe^{3+} in the Fe(3) sites. The last doublet with the larger quadrupolar splitting (0.99 mm s^{-1}) should correspond to the Fe(1) sites. The occupation of these last sites by Fe^{3+} instead of Fe^{2+} cations

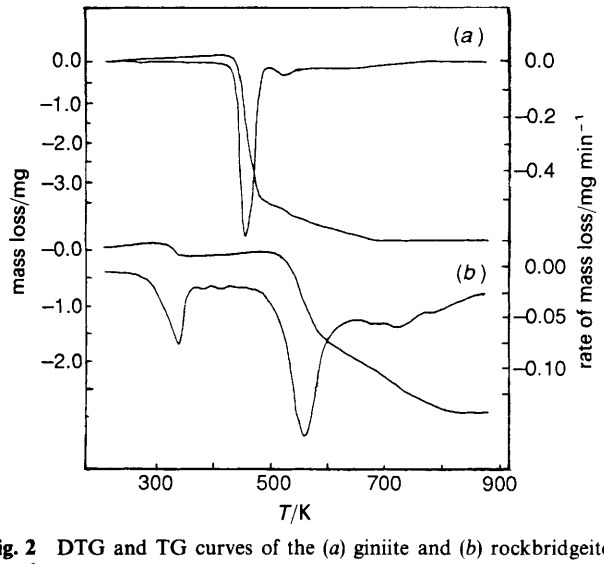

Fig. 2 DTG and TG curves of the (*a*) giniite and (*b*) rockbridgeite sample

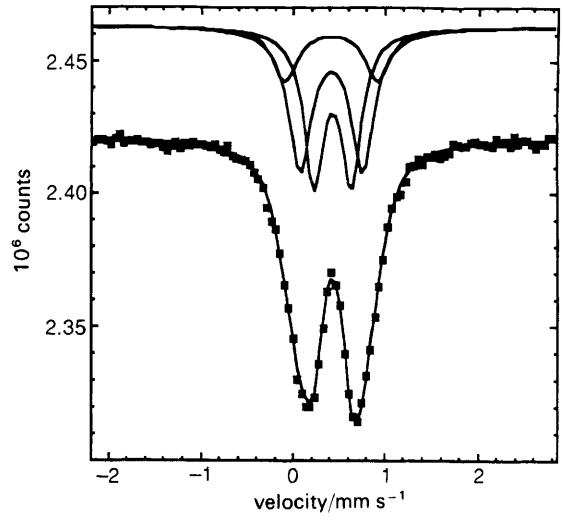

Fig. 3 Experimental Mössbauer spectrum of the giniite sample, recorded at 295 K. Solid lines are derived from least-squares fits.

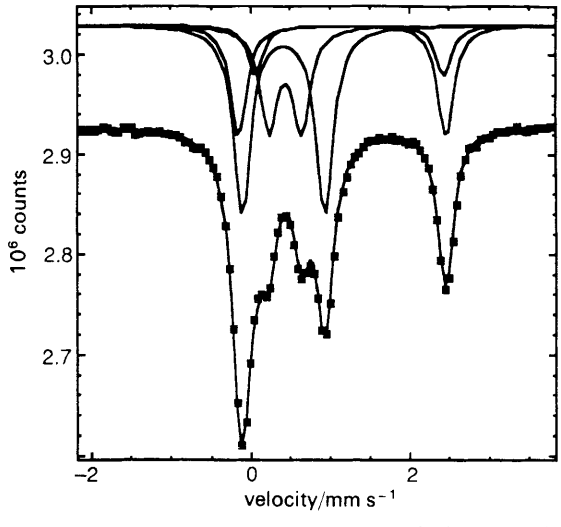

Fig. 4 Experimental Mössbauer spectrum of the rockbridgeite sample, recorded at 295 K. Solid lines are derived from least-squares fits.

Table 4 Mössbauer parameters computed from the spectrum of the synthetic giniite and natural rockbridgeite sample, recorded at 295 K

compound	site	Mössbauer parameters/mm s^{-1} δ	W	Δ	relative intensities (%)
giniite	$Fe^{3+}(1)$	0.42	0.26	1.05	42
	$Fe^{3+}(2)$	0.44	0.26	0.41	24
	$Fe^{2+}(2)$	1.24	0.24	2.37	11
	$Fe^{2+}(3)$	1.15	0.25	2.61	23
rockbridgeite	$Fe^{3+}(1)$	0.42	0.34	0.99	45
	$Fe^{3+}(2)$	0.43	0.29	0.66	33
	$Fe^{3+}(3)$	0.44	0.24	0.38	22

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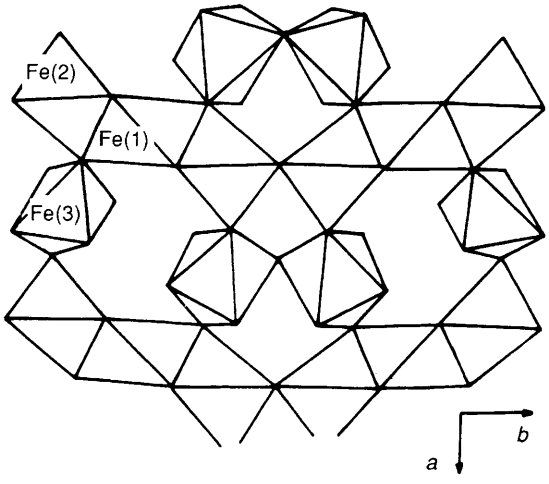

Fig. 5 Fe—O polyhedra connection in the rockbridgeite structure[5]

should give rise to some local distortions responsible for the large quadrupolar splitting observed. This seemed acceptable, but note that a discrepancy between the relative intensities of the observed doublets (22 : 45 : 33) and the theoretical ratio exists.

Discussion

Lipscombite, barbosalite and $Fe_4(PO_4)_3(OH)_3$ compounds which adopt relatively similar structures, were shown to undergo dehydroxylation in the same temperature range. Two main weight-loss stages could be distinguished. The first corresponded to a sharp DTG peak and the second to a broad and complex DTG peak due to at least two distinct losses of water molecules. If the temperature range of dehydroxylation of the three basic phosphates cited above (Table 3) is compared with the temperature range of departure of constitutional water of acid phosphates (Table 5), it can be seen that these temperature ranges are approximately the same. Nathan *et al.*[6] showed that natural lipscombite lost its constitutional water between 603 and 843 K and Gleith[7] reported the stabilization of the lipscombite structure up to 823 K. These results which seem incompatible may be explained by our results. We confirmed the results obtained by Nathan *et al.*[6] on natural lipscombite as we observed that the weight loss occurs before 843 K. We observed two very distinct weight losses for the synthetic lipscombite, the first one at *ca.* 715 K and the second between 802 and 843 K. An X-ray diffraction study performed on a sample heated to 773 K (*i.e.* a temperature intermediate between the two water departures) and quenched at this temperature, allowed us to show that the first water departure, which corresponds to the departure of half of the water, did not affect greatly the structure of the lipscombite.[8] This stabilization of the structure independently reported by Gleith[7] may presumably be explained by the formation of OH vacancies up to 803 K: $Fe_3(PO_4)_2(OH)_2 \rightarrow Fe_3(PO_4)_2O_x(OH)_{2-2x} + xH_2O$ (where $x \leqslant 0.5$).

There are differences between our results and those of Nathan *et al.*[6] for natural samples. First, the natural samples appear to lose water at a lower temperature since the dehydration begins at 603 K, and four poorly defined peaks at 628, 683, 783 and 833 K are also observed. Secondly, we did not observe the oxidation of the iron(II) ion in lipscombite in an inert atmosphere. This oxidation observed at *ca.* 473 K, as in air, is proposed to take place without the addition of oxygen, but by removing the H ions from the OH groups, thus forming H_2.

The Mössbauer data obtained for the giniite sample showed that the solid is in a more reduced form than would be expected from the stoichiometry.[9] However, the chemical analysis of the sample showed the expected P : Fe ratio and DTG analysis showed two water departures which should correspond to the hydration and hydroxylation water. The first water departure corresponded to 2.6 mol of water per mol of giniite, whereas the second corresponds to 0.6 mol per mol of giniite. This last result, together with the result from Mössbauer spectroscopy, allowed us to propose that the synthesized sample giniite corresponds to a reduced sample with the formula $Fe^{III}_{3.3}Fe^{II}_{1.7}(PO_4)_4(OH)_{1.3} \cdot 2.6H_2O$. Therefore, it is postulated that the giniite can correspond to a solid solution in which reduction of the iron is possible and is accompanied by the substitution of hydroxy groups by water molecules: $Fe^{III}_{4+x}Fe^{II}_{1-x}(PO_4)_4(OH)_{2-x} \cdot 2 + xH_2O$. This oxido–reduction process is the fifth process known to occur to iron hydroxyphosphates: type 1 corresponds to a variation in composition with formation of iron vacancies; this is the case for lipscombite, as has been postulated by Gleith:[7]

$$Fe^{III}_2Fe^{II}(PO_4)_2(OH)_2 \rightarrow Fe^{III}_{2+2x}Fe^{II}_{1-2x}(PO_4)_2(OH)_2; \quad \text{where } 0 \leqslant x \leqslant 1$$

Type 2 corresponds to a variation in composition due to dehydroxylation and oxidation. This is the case for rockbridgeite:[10]

$$Fe^{III}_4Fe^{II}(PO_4)_2(OH)_2 \rightarrow Fe^{III}_{4+x}Fe^{II}_{1-x}(PO_4)_2(OH)_{2-x}O_x; \quad \text{where } 0 \leqslant x \leqslant 1$$

Type 3 is a combination of types 1 and 2; it has been shown to take place for $Fe^{III}_4(PO_4)_3(OH)_3$:[4]

$$Fe^{III}_4(PO_4)_3(OH)_3 \rightarrow Fe^{III}_{4-3x}Fe^{II}_{3x}(PO_4)_3(OH)_{3-3x}O_{3x}; \quad \text{where } 0 \leqslant x \leqslant 1$$

$$\beta Fe^{III}Fe^{II}(PO_4)O; \quad \text{when } x = 1$$

Type 4 corresponds to an auto-oxidation by decomposition of crystal water. This process has been shown, by Hanzel *et al.*,[11] to proceed for vivianite upon heating under vacuum:

$$Fe^{II}_3(PO_4)_2 \cdot 8H_2O \rightarrow Fe^{II}_{3-x}Fe^{III}_x(PO_4)_2(OH)_x \cdot (8-x)H_2O + H_2$$

Type 5 corresponds to a variation in composition due to dehydration and oxidation. It has also been shown to occur for vivianite upon heating in the presence of oxygen:[12,13]

$$Fe^{II}_3(PO_4)_2 \cdot 8H_2O + 1/2O_2 \rightarrow Fe^{II}_{3-x}Fe^{III}_x(PO_4)_2(OH)_x \cdot (8-x)H_2O + H_2O$$

The existence of the giniite solid solution is related to this last process. A solid solution has previously been reported

Table 5 Temperatures of water departure for several acidic and condensed phopshates

compound	temperature of water departure/K	
$FePO_4 \cdot 2H_2O$	423–473	
$Fe(H_2PO_4)_3$	423–473	
$FeH_2P_2O_7$	823–923	
$FeH_2P_3O_{10} \cdot 2H_2O$	373–423	673–823[a]
$FeH_2P_3O_{10}$		673–773
$FeH_2P_3O_{10} \cdot 5H_2O$	373–473	673–773[a]
$Fe_3(PO_3OH)_4 \cdot 4H_2O$	473–503	673–723[a]
$Fe_3(PO_4)_2(OH)_{0.87} \cdot 7.13H_2O$	373–473	

[a] First temperature ranges correspond to the dehydration process.

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which contained only pure iron(III) giniite.[14] The latter was believed to vary in content of iron cations and hydroxy groups as well as hydration water molecules from $Fe^{III}_{4.52}(PO_4)_4(OH)_{1.56} \cdot 2.75H_2O$ to $Fe^{III}_{5.00}(PO_4)_4(OH)_{3.00}O_x \cdot 4.60H_2O$. It is, however, improbable that a solid solution with such a variation in composition could really exist.

Note that the temperature corresponding to the departure of the hydration water molecules is exceptionally high for giniite compared with other phosphates. As shown in Table 5, the temperature of dehydration of either condensed, acidic or basic phosphates is generally between 373 and 473 K. In contrast, the departure of the hydroxy groups begins at rather low temperatures compared with other hydroxyphosphates. This phenomenon may be linked to the fact that after the departure of the hydration water molecules the structure of giniite is weakened by the empty channels and collapses immediately, resulting in its dehydroxylation. Our results indicate that the structure of the giniite presents three crystallographic sites in a 40 : 40 : 20 ratio which resembles rockbridgeite. The two most numerous sites [Fe(1) and Fe(2)] would be occupied by Fe^{III} and the less common one Fe(3), by Fe^{II}. With this hypothesis, the results obtained by Mössbauer spectroscopy could be interpreted as a partial oxidation of one of the two more numerous sites [Fe(2)]. The doublet characterized by $\delta = 0.42$ mm s^{-1} and $\Delta = 1.05$ mm s^{-1} would correspond to Fe^{III} occupying site Fe(1), that with $\delta = 1.15$ mm s^{-1} and $\Delta = 2.61$ mm s^{-1} to Fe^{II} occupying site Fe(3) and those with $\delta = 0.44$ mm s^{-1} and $\Delta = 0.41$ mm s^{-1}, and $\delta = 1.24$ mm s^{-1} and $\Delta = 2.37$ mm s^{-1} would correspond, respectively, to Fe^{III} and Fe^{II} occupying site Fe(2). The formula of giniite obtained from DTG and chemical analyses could then be rewritten as:

$$[Fe^{III}_2][Fe^{III}_{1.3}Fe^{II}_{0.7}]\ [Fe^{II}](PO_4)_4(OH)_{1.3} \cdot 2.6H_2O.$$

Such a formula leads to a ratio between the four doublets equal to 40 : 26 : 14 : 20, which is not far from what is observed 42 : 24 : 11 : 23 (Table 4).

The Mössbauer analysis of the rockbridgeite sample showed that it contained only iron(III) cations. This is possible since it has been shown that the rockbridgeite corresponds to a solid solution in which the oxidation level of the solid could change with the variation in the hydroxy group content: $Fe^{III}_{4+x}Fe^{II}_{1-x}(PO_4)_3(OH)_{5-x}O_x$ with $0 < x < 1$.[10] However, the observed water loss, equal to 2.4 mol per mol of rockbridgeite, is much higher than that of 2.0, weighted for a totally oxidized sample. At this point the presence of a large amount of Mn^{2+}, shown by chemical analysis (Table 1), has to be considered. Mn^{2+} is known to substitute for Fe^{2+} in the natural hydroxyphosphates. The stoichiometry of our compound has been determined from chemical analysis results (Table 1) as $Fe^{III}_{4.2}Mn^{II}_{0.8}(PO_4)_3(OH)_{4.8}O_{0.2}$. In this case the sample would then have a water content corresponding to 2.4 mol of water per mol of solid which is in better agreement with our TGA experimental results. Normally the Mn^{2+} ions should substitute the Fe^{2+} ions in the structure and thus occupy the less numerous sites. This was not shown in the Mössbauer spectroscopy results. The three sites observed for the iron(III) cations give a relative ratio which did not agree with the substitution of Fe^{2+} by Mn^{2+} which would lead to a 48 : 48 : 4 ratio. The discrepancy between the relative intensities of the observed doublets (45 : 33 : 22) and the relative ratio of the crystallographic sites (40 : 40 : 20) can only be explained if the Mn^{2+} ions occupy the Fe(3) sites of the structure normally occupied by Fe^{3+} ions. In such a case, the ratio calculated from Mössbauer spectroscopy and chemical analysis would be 39 : 42 : 19, which is approximately the theoretical ratio. The Fe^{2+} site Fe(1) would then be occupied by Fe^{3+} cations and the Fe^{3+} site Fe(3) by Mn^{2+} cations: $[Fe^{III}_2][Fe^{III}_{1.2}Mn^{II}_{0.8}][Fe^{III}](PO_4)_3(OH)_{4.8}O_{0.2}$. This interpretation does not fully agree with the results of the crystal structure refinement which points to the occupation of the Fe(3) site only by trivalent cations.[5] However, note that a possible substitution of the iron cations in this site by Mn^{2+}, Ca^{2+} or Fe^{2+} cations has already been proposed.[15] Finally one may suggest that the first water depature, which occurs at a lower temperature and corresponds to 0.20 mol of water per mol of rockbridgeite, could correspond to the formation of water from hydroxy groups and neighbouring oxygen ions already present in the structure.

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