

Use of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) to prevent iron chlorosis in calcareous soils

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Received 30 May 1991; accepted in revised form 22 September 1991

Key words: Iron phosphate, Fe amendment, Fe deficiency, chlorophyll content, *Cicer arietinum* L., chickpea

Abstract

For various reasons, iron phosphate might be effective in correcting Fe chlorosis in calcareous soils. To test this hypothesis, several pot experiments were conducted using an Fe chlorosis-sensitive chickpea (*Cicer arietinum* L.) cultivar cropped in soils to which partially oxidized vivianites ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and Fe(III) phosphates with different characteristics had been added. Vivianites mixed with the soil at a rate of 1 g kg^{-1} were as effective in preventing chlorosis as Fe chelate (FeEDDHA). However, the effectiveness of Fe(III) phosphates was less, suggesting that the presence of Fe(II) in the phosphates used was a key factor in their Fe-supplying value to plants. The effectiveness of vivianites, however, seemed to be largely independent of their Fe(II) content.

The future of vivianite as a Fe amendment will depend not only on economic considerations (production and application costs) but also on its long-term capacity to release plant-available Fe in soil environments.

Introduction

The mineral vivianite is a monoclinic octahydrated ferrous phosphate of formula $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. It is formed predominantly in reducing environments, appearing in the form of concretions and associated with organic matter in waterlogged clays, peaty soils and sediments. It also appears as a weathering product in hydrothermal and pegmatitic deposits and as a secondary mineral in iron-bearing ore veins.

Ferrous phosphate with the same crystalline properties as vivianite (subsequently also referred to as vivianite) can be prepared in the laboratory by neutralization of a solution of H_3PO_4 and FeSO_4 . Freshly precipitated vivianite has a light bluish gray colour which changes to indigo-blue by a slight auto-oxidation of ferrous

iron after a short exposure to air. Blue colours are observed in natural vivianites since they are also partly oxidized. Strong oxidation of vivianite leads to progressive destruction of its crystalline structure, resulting in an X-ray amorphous compound [28]. Simultaneously, its colour changes to olive yellow and finally to a bright yellowish brown. The mechanisms and factors of oxidation have been extensively studied [7, 28].

Vivianite (peat vivianite) has been used occasionally as a phosphorus fertilizer [1, 6, 9, 11, 16, 18, 20, 21]. To the authors' knowledge neither natural nor synthetic vivianites have ever been used to correct iron deficiency. However, *a priori* several reasons justify this possible use: (a) Vivianite (>32% Fe) has a higher Fe content than most Fe sources used as Fe fertilizers and a high content of ferrous iron (up to

25%, after the unavoidable oxidation mentioned above).

- (b) Although vivianite is only slightly soluble at normal soil pH values, its dissolution in soils is likely to be favoured by quick removal of the released phosphate through plant uptake, adsorption by mineral surfaces and precipitation by soil cations.
- (c) Dissolution of vivianite, followed by oxidation of ferrous iron, probably leads to precipitation of poorly crystalline ferric hydroxide phases (ferrihydrite), since the phosphate ion is known to impede crystallization of Fe oxides [25]. Owing to its high specific surface area, ferrihydrite has been shown to be a good source of Fe for plants [27].
- (d) Absorption of Fe by plants is favoured if Fe in solution is in the ferrous form. Consequently, the ferrous iron released by vivianite that remains unoxidized in the relatively reducing rhizosphere environment can be readily absorbed by plants.
- (e) Synthesis of vivianite is simple; the products needed are cheap and commonly used in the fertilizer industry. Therefore, this product could be economically competitive.

The present study shows that vivianite is effective in alleviating Fe chlorosis in calcareous soils. The effectiveness of vivianites with different properties is reported and compared with that of various ferric phosphates.

Material and methods

Synthesis of vivianites and Fe(III) phosphates

Vivianites V1, V2 and V3 were obtained by slow neutralization of a solution of FeSO_4 (1 M for V1 and V2 and 0.05 M for V3) in H_3PO_4 (0.7 M for V1 and V2 and 0.035 M for V3) with KOH (5 M for V1 and V2 and 0.05 M for V3) to pH 8 for V1 and pH 6 for V2 and V3. Samples V4 and V5 were prepared as for V1 but in the presence of MgSO_4 (the $\text{Mg}/(\text{Fe} + \text{Mg})$ molar fractions were 0.1 and 0.2, respectively). The same procedure was followed for V6 and V7, where Mn, instead of Mg, was used (the $\text{Mn}/(\text{Mn} + \text{Fe})$ molar fractions were 0.1 and 0.2, respectively) and for V8, where Zn was used ($\text{Zn}/(\text{Zn} + \text{Fe})$

molar fraction = 0.1). Amorphous ferric phosphate (E1) was obtained by increasing to 3 the pH of a solution 0.2 M in Fe_3Cl and 0.3 M in H_3PO_4 . Strengite (E2) was obtained by digesting E1 at 100°C for 5 days [2, 13].

After precipitation and/or crystallization the precipitates were washed (by successive centrifugations and decantations) with deionized water until salt-free. Suspensions were then freeze-dried and the dry products stored in polyethylene bottles. Finally, sample V9 was obtained by heating vivianite V2 at 100°C for 2 h.

Mineralogical and chemical analyses of iron phosphates

The crystalline properties of the synthesized products were examined by X-ray powder diffraction with a Philips PW 1130 instrument with CoK_α radiation. Crystal size and shape were observed with a Zeiss petrographic photomicroscope. Specific surface area was determined by the BET method using N_2 as adsorbate with a Quantasorb Jr. surface area analyzer.

Total Fe was determined by dissolving samples in 6 M HCl and ferrous Fe by oxidation with 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ in acid medium and back-titration of the excess of dichromate with 0.1 M FeSO_4 . Oxalate-extractable Fe was determined with 0.2 M NH_4 -oxalate at pH 8 and DTPA-extractable Fe according to Lindsay and Norvell [15] using 25 mg of product per 50 ml of extracting solution for both methods.

The Fe, Mg, Mn and Zn dissolved by the different extractants were determined by atomic absorption spectroscopy. Phosphorus was determined by the method of Murphy and Riley [17].

Soils

The four soils used in this study were collected in Andalusia, southern Spain, where calcareous soils are widespread and Fe chlorosis frequent in peach, citrus, sunflower and other crops. Sampling was carried out on calcareous horizons exposed by erosion and under cultivation. Samples (0–30 cm) were air-dried, passed through a 2-mm sieve and analysed for texture, pH, total CaCO_3 equivalent (CCE), active CaCO_3 equivalent

Table 1. Properties of the soils

Soil	Horizon	Soil classification ^a	Textural class ^a	pH ^b	Extractable P ^c	CaCO ₃ ^d		Fe forms		
						CCE	ACCE	Fe _o	Fe _d	Fe _{DTPA}
					mg kg ⁻¹	g kg ⁻¹			mg kg ⁻¹	
1	Btk	Calcic Haploxeralf	Sandy clay loam	8.5	9.5	415	130	0.45	5.3	2.2
2	Bk	Calcixerollic Xerochrept	Sandy loam	8.2	33.5	625	240	0.38	2.4	3.9
3	BCK	Calcixerollic Xerochrept	Clay	8.4	16.5	780	275	0.38	0.4	1.6
4	BCK	Calcic Haploxeralf	Sandy loam	8.6	15.5	545	170	0.43	4.8	2.6

^a Soil Survey Staff [26]. Classification of non-eroded contiguous soils.

^b in H₂O (1:2.5).

^c Olsen et al. [19].

^d CCE = calcium carbonate equivalent; ACCE = active calcium carbonate equivalent.

^e Fe_o = acid NH₄-oxalate extractable Fe; Fe_d = citrate-bicarbonate-dithionite extractable Fe; Fe_{DTPA} = DTPA-extractable Fe.

lent (ACCE), citrate-bicarbonate-dithionite (CBD) extractable Fe (Fe_d) and DTPA-extractable Fe (Fe_{DTPA}) as described by del Campillo and Torrent [5]. Acid NH₄ oxalate extractable Fe was analysed according to Schwertmann [24]. Soil properties are shown in Table 1.

Growth chamber experiments

Chickpea (*Cicer arietinum* L.) cultivar ICC 11224, which is very susceptible to Fe chlorosis, was chosen for all experiments. Three growth experiments were carried out. In experiment 1, vivianite V2 was mixed with 220 g of soil at rates of 0.4, 0.7 and 1.4 g kg⁻¹ soil for soils 1, 2 and 3. In this experiment the soils were not fertilized with phosphate except for the Vivianite + P treatment (Table 3). In experiment 2, rates of 0.5 and 1 g of vivianites V1, V4, V5, V6, V7 V8 were mixed with 220 g soil 4 (Table 4). In experiment 3, rates of 0.6 and 1 g of various iron phosphates (V1, V3, V9, E1 and E2) were mixed with 220 g of soil 4 (Table 5). In all experiments, a control (without Fe phosphate) and a Fe chelate (without Fe phosphate) treatment were included. Iron chelate as FeEDDHA (Sequestrene 138 Fe G 100, Ciba-Geigy) having 6% of Fe was applied at a rate of 11 mg kg⁻¹ soil. All pots were fertilized with a nutrient solution so that 597 mg Ca(NO₃)₂·4H₂O, 301 mg KNO₃, 295 mg MgSO₄, 100 mg KH₂PO₄, 2 μg KCl, 910 μg H₃BO₃, 201 μg MnSO₄·5H₂O, 343 μg ZnSO₄·7H₂O, 77 μg CuSO₄·5H₂O and

396 μg Na₂MoO₄·2H₂O per kg of soil were applied during the growth period.

Chickpea seeds were germinated on moistened paper towels for 3 days. Two seedlings were transplanted to 4.5 cm-diameter, 11 cm-high PVC cylinders; after 4 days only one plant was left. The plants were grown in a growth chamber with a light/dark photoperiod of 16/8 h, using fluorescent tubes yielding a photosynthetically active radiation of 450 μmol m⁻² s⁻¹. Day/night temperatures were 25/20°C. The pots were irrigated every day with deionized water, keeping moisture content 1–2% lower than field capacity.

A randomized block design was used with each of the three replicates corresponding to a block. Pots were rerandomized every day to minimize the influence of location in the growth chamber. Plants were harvested 20 days after planting. The topmost fully expanded (> = 2 cm) leaves were cut for chlorophyll extraction. Chlorophyll was extracted by immersing the leaf in 5 ml of methanol for 7 hours in the dark. Absorbance readings for chlorophyll were taken at 663 and 645 nm with a Perkin-Elmer Lambda 3 UV-VIS Spectrophotometer. Total chlorophyll concentration was calculated in μg cm⁻² of leaf area using the equation cited by Cianzio et al. [3]. The surface area of the leaf was measured with a LI-COR portable area meter.

The ANOVA of each experiment was carried out according to a randomized complete block design. Means were separated by Duncan's Multiple Range Test (P < 0.05).

Results

Properties of iron phosphates

The properties of the 11 synthetic iron phosphates are summarized in Table 2. Samples V1 to V8 showed the diffraction X-ray lines corresponding to vivianite (monoclinic phase). The distinctive 0.86 and 0.28 nm peaks of metavivianite (triclinic phase) were not detected in any of the samples. Metavivianite is frequently reported as an intermediate product of vivianite oxidation [8, 23].

The vivianite synthesized from diluted solutions (V3) was the one with the largest crystal size, its crystals being prismatic in habit and reaching up to 11 μm . This large size probably explains its resistance to oxidation during washing, resulting in the highest Fe(II) content of all samples (Table 2). This vivianite was also the most stable against oxidation by heating or H_2O_2 treatment (Table 2).

The aim of adding Mg, Mn or Zn in some preparations was to obtain Mg-, Mn- or Zn-substituted vivianites. According to Rodgers [22] and Dormann and Poullen [8] the presence of Mg or Zn in the structure of vivianite makes it more resistant to oxidation. Under our synthesis conditions, however, complete substitution did

not seem to occur, since the microscope showed irregular-shaped (probably amorphous) masses together with typical vivianite crystals. No effect of Mg, Mn or Zn was observed in the resistance of vivianite to oxidation. In addition, the Fe(II) content of these samples was generally lower than in the other vivianites.

The product resulting from the heating (and consequent oxidation) of vivianite V2 (V9) did not show any diffraction lines. This amorphous Fe(III) phosphate had, however, the prismatic habit and the crystal size of the parent vivianite. Total Fe content of V9 was the highest of all samples, due to water loss caused by heating. Sample E1 was also X-ray amorphous. Sample E2 showed the typical diffraction lines of strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, orthorhombic).

The amounts of Fe dissolved by DTPA and alkaline NH_4 -oxalate were taken as indices of the solubility of the products. No relationship was found, however, between these indices and the crystallochemical properties shown in Table 2.

Effectiveness of vivianite in preventing Fe chlorosis

Table 3 shows the results of experiment 1. Chlorosis symptoms (yellowing) due to Fe deficiency

Table 2. Selected properties of the synthetic iron phosphates

Sample	Chemical composition					Fe solubility ^a		Fe(II) after oxidation ^b		Specific surface area	Crystal length range
	Fe(III)	Fe(II)	P	H ₂ O	Mg, Zn, Mn	Fe _{DTPA}	Fe _o	70°C	H ₂ O ₂		
	g kg ⁻¹									m ² g ⁻¹	μm
V1	166	191	122	25.0	0	7	163	99	8	8	1.5–4.5
V2	334	72	122	23.9	0	8	78	15	11	6	1.0–8.0
V3	134	223	126	24.9	0	7	65	162	57	16	1.0–11.0
V4	227	106	121	25.7	13 (Mg)	7	173	25	2	–	0.5–3.5
V5	220	93	123	26.9	31 (Mg)	19	150	50	3	22	0.5–3.5
V6	270	63	114	24.6	40 (Mn)	11	146	6	3	–	0.2–1.5
V7	257	40	113	24.7	78 (Mn)	12	163	5	3	–	0.2–1.5
V8	228	79	114	24.4	36 (Zn)	14	180	15	2	–	0.5–2.5
V9	398	0	138	16.0	0	6	37	0	0	12	0.2–3.5
E1	269	0	148	30.3	0	30	180	0	0	26	0.2–1.5
E2	270	0	140	30.1	0	3	7	0	0	25	0.2–1.5

^a Fe_{DTPA} = DTPA-extractable Fe; Fe_o = Alkaline NH_4 -oxalate extractable Fe.

^b Dry oxidation treatment at 70°C for 5 hours; treatment with 15% H_2O_2 for 2 h.

^{a,b} Values refer to the initial weight of vivianite.

Table 3. Chlorophyll content of chickpea leaves in experiment 1 (vivianite V2 applied to soils 1, 2 and 3)

Treatment	Rate	Soil		
		1	2	3
	g kg ⁻¹ soil	--- μg cm ⁻² leaf area ---		
Control	0.0	4.3c ^a	13.0b	7.3bc
Vivianite	0.4	25.7	21.7	20.0
Vivianite	0.7	32.0	27.3	36.7
Vivianite	1.4	41.3a	33.0a	32.3a
Vivianite + P	1.4	34.0a	32.3a	33.7a
FeEDDHA	0.011	38.3a	35.3a	40.7a

^a Means followed by the same letters are not significantly different at the 5% level (Duncan's Multiple Range Test)

were clear for plants in the control (no V2 added) treatment of the three soils and in some low-rate vivianite treatments. For the control treatment there were significant differences in the chlorophyll content of plants grown in the different soils, probably due to differences in soil properties.

Vivianite V2 was effective in alleviating Fe stress even at the lowest rate (0.4 g kg⁻¹ soil). Increasing amounts of vivianite resulted in increased leaf chlorophyll content. At the

1.4 g kg⁻¹ rate the chlorophyll content was not significantly different from that corresponding to the chelate treatment. For this rate, there were no significant differences between the three soils. This experiment also showed that, even for the high-P soil 2 and with supplementary P addition, the phosphate of the vivianite did not seem to affect Fe uptake by plants. A detrimental effect of phosphate on Fe nutrition has been reported at high P levels [12], but, in calcareous soils, most of the solution phosphate is likely to be adsorbed on, and precipitated by calcium carbonate [10].

Effectiveness of vivianites prepared in the presence of Mg, Mn and Zn

Experiment 2 (Table 4), showed that, except for one of the Mg-vivianites (V4), all vivianites prepared in the presence of foreign cations had, at the 1 g kg⁻¹ rate an effectiveness not significantly different from that of the Fe chelate. In practice, therefore, vivianite can be used as a source of other plant nutrients without losing its effectiveness as an Fe amendment.

Table 4. Chlorophyll content of chickpea leaves in experiment 2 (pure and Mg-, Mn- and Zn-vivianites in soil 4)

Treatment	Rate	Vivianites ^a					
		V1	V4	V5	V6	V7	V8
	g kg ⁻¹ soil	--- μg cm ⁻² leaf area ---					
Control	0.0	10.7					
Vivianite	0.6	32.0	26.0	27.0	27.0	31.3	39.7
Vivianite	1.0	34.3ab ^b	27.3b	39.6ab	34.3ab	34.7ab	39.7ab
FeEDDHA	0.011	42.0a					

^a V1 = vivianite; V4, V5 = vivianites with Mg; V6, V7 = vivianites with Mn; V8 = vivianite with Zn.

^b Means followed by the same letters are not significantly different at the 5% level (Duncan's Multiple Range Test).

Table 5. Chlorophyll content of chickpea leaves in experiment 3 (different Fe phosphates applied to soil 4)

Treatment	Rate	Iron phosphates ^a				
		V1	V3	V9	E1	E2
	g kg ⁻¹ soil	--- μg cm ⁻² leaf area ---				
Control	0.0	10.8				
Iron phosphate	0.5	35.3	31.6	20.5	25.0	17.8
Iron phosphate	1.0	41.0ab ^b	40.7ab	31.5bc	25.5bc	22.5c
Fe-EDDHA	0.011	48.0a				

^a V1, V3 = vivianites; V9 = heated vivianite; E1 = amorphous Fe(III) phosphate; E2 = strengite.

^b Means followed by the same letters are not significantly different at the 5% level (Duncan's Multiple Range Test).

Effectiveness of vivianites versus other iron phosphates

Table 5 summarizes the results of experiment 3 (different iron phosphates applied to soil 4). All iron phosphates tested were able to alleviate Fe deficiency to a greater or lesser extent, chlorophyll content in the leaves increasing as the rate of Fe phosphate increased. The most effective Fe phosphates were vivianites V1 and V3, which were effective even at the lowest rate (0.6 g kg^{-1}). The chlorophyll content for the treatments with either V1 or V3 at the 1 g kg^{-1} rate was not significantly different from that corresponding to the chelate treatment. For the 1 g kg^{-1} rate, the Fe(III) phosphates (E1 and E2) and the heated vivianite (V9) were not as effective in preventing Fe chlorosis as vivianites V1 and V3.

Discussion

The experiments reported here show that vivianite is effective in preventing Fe chlorosis at relatively low ($\leq 1 \text{ g kg}^{-1}$ soil) addition levels. The lower effectiveness of the Fe(III) phosphates with respect to vivianite suggests that the pres-

ence of Fe in ferrous form is a key factor in the Fe chlorosis-alleviating effect of Fe phosphates. This hypothesis is supported by the fact that, when all experiments were considered together, it was found that the leaf chlorophyll content was better correlated with the Fe(II) ($r = 0.66^{**}$) (Fig. 1) than with the total Fe applied ($r = 0.47$). It was also found that chlorophyll content was unrelated to alkaline NH_4 -oxalate- or DTPA-extractable Fe of the applied products ($r = 0.2^{ns}$ and -0.02^{ns} , respectively). This is congruent with the former hypothesis, since oxalate and DTPA have the ability to effectively complex both Fe(II) and Fe(III) [4, 14], not allowing, therefore, a discrimination between the two Fe forms.

Although the presence of Fe(II) in the structure of Fe phosphates strongly influences their effectiveness, the present data suggest that low-Fe(II) (V2, V4, V5, V6, V7 and V8) are as effective as high-Fe(II) (V1, V3) vivianites. It seems, therefore, that relatively small amounts of Fe(II) are sufficient to lend vivianite susceptibility to oxidation, leading to faster structure disruption and release of plant-available Fe. The obvious practical consequence is that "effective" vivianites can be prepared without taking excessive care to prevent a partial oxidation of Fe(II).

While the present results encourage the use of vivianite as a Fe amendment to be mixed with the soil before planting, its usefulness will depend not only on economic factors, such as price and cost of application, but also on its ability to release plant-available Fe compounds in the soil environment for several growing seasons. Some experiments (not reported here) indicate that vivianite is still effective even after a 3-month incubation at 28°C in a calcareous soil at field capacity.

Acknowledgements

This work was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT), Spain, under Project PA86-0337. Ms. M.C. del Campillo acknowledges the financial help of the Ministerio de Educación y Ciencia, Spain (1987 Postgraduate Grant of the Plan Nacional).

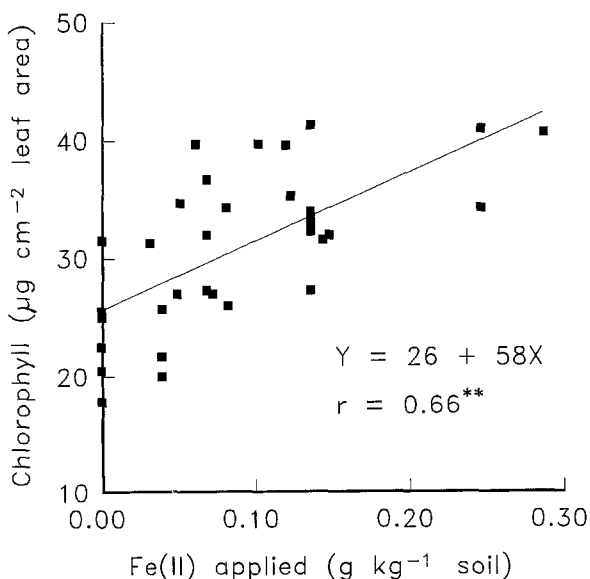


Fig. 1. Relationship between leaf chlorophyll content of chickpea and Fe(II) added to soil in the form of different Fe phosphates.

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