

The Influence of Inorganic Phosphate on the Crystallization of Magnetite (Fe₃O₄) From Aqueous Solution

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The formation of magnetite (Fe₃O₄) from the oxidation of Fe^{II} solutions results in small (20–60 nm) irregular-shaped crystals; in the presence of 5–10% inorganic phosphate Pⁱ the crystal morphology is selectively enhanced whilst at 20–30% Pⁱ-doping crystallization is severely inhibited.

Magnetite (Fe₃O₄) is an important component of numerous catalytic and magnetic systems. Functional specificity in these applications often requires the controlled growth of crystals of well defined morphology and size; properties which are difficult to obtain under laboratory conditions. In contrast, biological systems can synthesize magnetite crystals at ambient temperature and neutral pH with precise crystallochemical characteristics.^{1,2} We are involved in the elucidation of processes which modulate crystal growth processes in magnetite and report here, for the first time to our knowledge, the influence of inorganic phosphate (PO₄³⁻, = Pⁱ) on laboratory preparations of Fe₃O₄ formed by the partial oxidation of Fe^{II} solutions in the presence of NO₃⁻.

Magnetite was prepared under N₂ at 100 °C by the slow addition (*ca.* 0.5 ml min⁻¹) of a solution containing 0.1 mol KOH and 0.008 mol KNO₃ dissolved in 30 cm³ of deoxygenated distilled water to 70 cm³ of a boiling deoxygenated solution containing FeCl₂ · 4H₂O (0.514 M). A green gelatinous solid was immediately precipitated which turned blue

and then black on continued addition of the OH⁻/NO₃⁻ solution. The pH and dissolved Fe concentration were determined at 10 min intervals. The pH remained essentially constant (*ca.* 6.0) as the dissolved Fe concentration fell rapidly

Table 1. E.d.x.a. data (weight % element) for magnetite samples.^a

Element	Dopant level (atom % P ⁱ)				
	0	5	10	20	30
Fe	67.53	70.29	66.33	70.26	67.73
O	25.15	26.85	25.33	26.17	25.22
P	—	0.95	2.08	1.14	2.06

^a Elements Al (sample holder), Si (silicone grease), and K (residual KOH/KNO₃) were also present in trace amounts giving a total weight % of 100 for each sample.

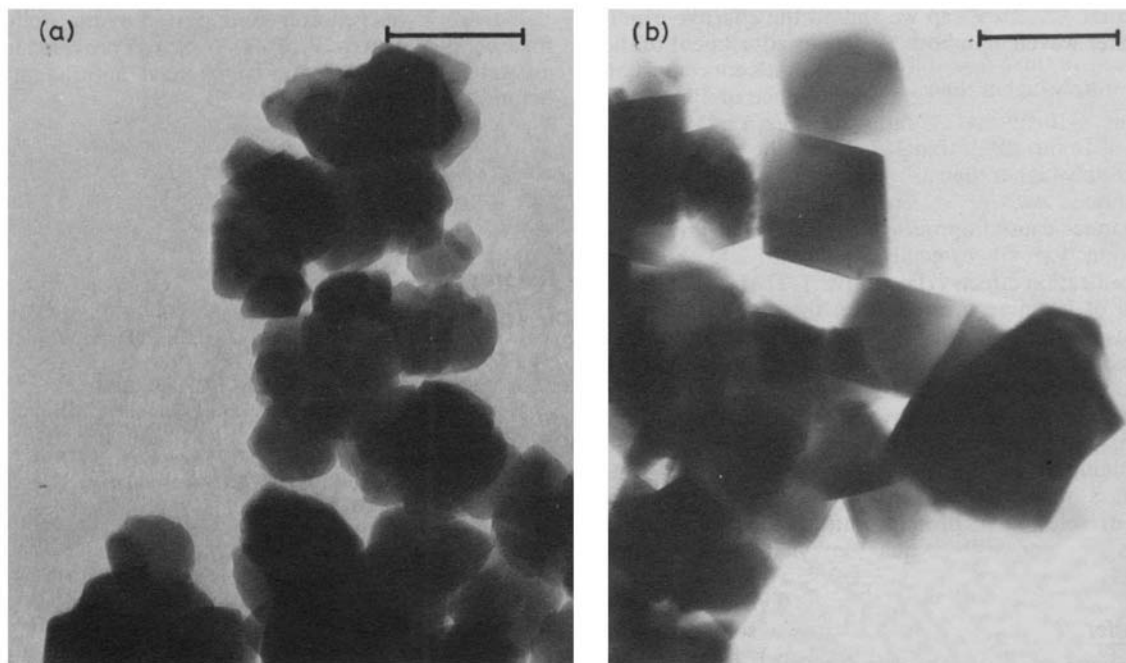


Figure 1. Electron micrographs of magnetite prepared in (a) the absence of P_i , bar = 120 nm, and (b) the presence of 5% P_i , bar = 105 nm.

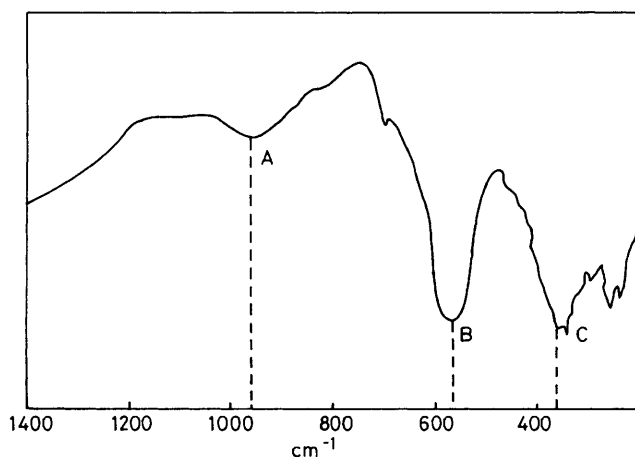


Figure 2. I.r. spectra of magnetite prepared in the presence of 10% P_i ; peak A, $\nu(\text{FeO-P})$; peaks B and C, $\nu(\text{FeO-Fe})$.

on continued addition of the $\text{OH}^-/\text{NO}_3^-$ solution. Complete removal of soluble Fe was accompanied by a rapid rise in pH to 13. At this stage (*ca.* 50 min) the precipitate was black and magnetic.

The resulting magnetite crystals were characterised by X-ray diffraction (x.r.d.), i.r., electron microscopy, energy-dispersive X-ray analysis (e.d.x.a.), and chemical (titrimetric) analysis. The synthesis was repeated in the presence of 5, 10, 15, 20, and 30 mol% KH_2PO_4 added to the Fe^{II} solution prior to $\text{OH}^-/\text{NO}_3^-$ addition.

Magnetite crystals grown in the absence of P_i were irregular in morphology (Figure 1a). Crystal sizes were in the range 20–60 nm. I.r. spectra showed two bands at 570 and 340 cm^{-1} . X.r.d. and chemical analysis indicated that the major

phase was stoichiometric magnetite with a trace amount of $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) formed probably by surface oxidation during analytical procedures. In contrast, crystals grown in the presence of 5 and 10 mol% P_i had well defined octahedral habits with smooth $\{111\}$ faces (Figure 1b). Crystal sizes were 50–100 nm. Electron and X-ray diffraction showed the products to be well ordered cubic Fe_3O_4 with no modification in unit cell size. I.r. spectra showed an additional band at 950 cm^{-1} (Figure 2) corresponding to the P–O–Fe symmetric stretch.³ E.d.x.a. results (Table 1) showed the presence of P_i within the samples.

At higher P_i concentrations (20 and 30%) magnetite crystallization was severely inhibited. The product was a brown gel which rapidly oxidised on isolation to $\alpha\text{-FeOOH}$ and ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$).

Fe_3O_4 formation proceeds *via* a green rust intermediate which undergoes further oxidation, dehydration, and structural modification prior to crystallization.⁴ The changes in morphology and ultimately, composition and structure, in the presence of P_i can be attributed to two possible mechanisms both of which reduce the crystal growth rate of Fe_3O_4 ; (a) stabilization of the green rust precursor and (b) stabilization of specific crystal faces of magnetite. Since there is significant lattice rearrangement during the transformation of green rust to magnetite a dissolution–renucleation mechanism is favoured.⁴ Binding of P_i to the precursor would reduce the transformation rate by surface stabilization. Similarly the close-packed $\{111\}$ faces of Fe_3O_4 have a high density of Fe-tetrahedral sites at which P_i can be readily adsorbed thereby inhibiting the growth rate along the $[111]$ direction and enhancing the well-defined octahedral habit. Our i.r. and e.d.x.a. results clearly show that P_i is present, presumably at the crystal surface of the P_i doped samples. Inhibition of Fe_3O_4 crystallation at high (20–30 mol%) P_i concentration indicates the increased kinetic stability of the green rust precursor with respect to undergoing phase transformation. Stabilization of the Fe^{II} oxidation state within the Fe_3O_4

structure is no longer possible and the gel rapidly oxidises to Fe^{III} hydrated oxides on contact with air.

Our results indicate that inorganic phosphate has a subtle influence on the crystallization of Fe₃O₄ from Fe^{II} solution. We note that bacterial Fe₃O₄ formation occurs within phosphate rich media in the presence of Fe^{II}, with NO₃⁻ as a possible electron acceptor.⁵ Control over phosphate levels may therefore be an important factor in establishing unique Fe₃O₄ morphologies in these biological systems.

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