Crystallochemical Characterization of Magnetic Spinels prepared from Aqueous Solution

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The crystallochemical characterization of magnetic spinels prepared from aqueous solution has been studied primarily by electron microscopy and ^{57}Fe Mössbauer spectroscopy. Two synthetic routes have been investigated: method 1; partial oxidation of Fe^{II} solutions in the presence of NO_3^- at 100 °C, and method 2; reaction of hydrated Fe^{III} oxide (ferrihydrite) with Fe^{II} ions at room temperature, pH = 7, 8 and 9. Both routes gave small (10–60 nm) irregular magnetite (Fe_3O_4) particles that were readily oxidised to maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The reaction proceeded *via* a green-rust intermediate and anions such as inorganic phosphate (P_i) and SO_4^{2-} reduced the rate of transformation. Spinel formation at room temperature was severely inhibited by P_i levels of 1 mol %, whereas 20–30 mol % P_i was required for retardation of crystallization at 100 °C. Intermediate levels (5–10 mol %) resulted in morphological enhancement of the octahedral crystal habit. A similar effect was observed in the presence of SO_4^{2-} and at neutral pH in method 2.

The current interest in advanced materials is primarily directed towards the synthesis of novel solids. However, a further important aspect of this initiative is the crystallochemical tailoring of known substances with the aim of achieving functional specificity in solid-state applications. In this respect, we are involved in the elucidation of processes which modulate the crystallochemical properties of known magnetic materials. Ultimately, our objective is to synthesise structurally well defined magnetic spinels with homogeneous particle sizes and unique crystal morphologies as these properties are important in determining the catalytic and magnetic use of these materials.

Magnetite (Fe_3O_4) has a cubic inverse spinel structure (space group, $Fd3m$, $a = 8.396$ Å) with half of the Fe^{III} ions in tetrahedral sites and both Fe^{II} and Fe^{III} cations randomly distributed in octahedral sites at temperatures above 119 K. The structure is related to the fully oxidised compound, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) which can be considered as an iron-deficient spinel of variable structure ranging from disordered cubic symmetry ($a = 8.34$ Å) to a tetragonal unit cell with ordered vacancies (space group, $P4_12_1$, $a = 8.34$ Å, $c = 25.02$ Å). Conventional synthesis of magnetite, either by partial reduction of hematite ($\alpha\text{-Fe}_2\text{O}_3$) or oxidation of Fe metal, is undertaken at high temperature (often 800 °C). Since these reactions occur under severe environmental conditions, the potential for crystallographic design of the products is limited. A more promising synthetic route for controlled crystallization is from the aqueous phase.¹

Here we report the characterization of magnetic spinels prepared by two independent methods based first on the partial oxidation of Fe^{II} in the presence of NO_3^- at 100 °C² and

secondly, on the reaction of hydrated Fe^{III} oxide (ferrihydrite) with Fe^{II} ions at room temperature.³ Other routes from aqueous media at elevated temperature⁴⁻⁶ and room temperature^{5, 7-10} have been reported. Our objectives have been to investigate: (i) the influence of low molecular weight additives such as inorganic phosphate (P_i) on spinel formation, and (ii) the potential for spinel growth at room temperature and neutral pH. Preliminary studies of the former have been reported.¹¹ The latter route offers the possibility of using a wide range of hydrophilic organic molecules (amino acids, peptides, proteins) or coordinating ligands that can be chemically tailored to induce a high degree of crystallochemical specificity in the products. In this respect, we note that biological magnetites are synthesized at ambient temperature and close to neutral pH with uniform particle sizes and novel species-specific morphologies.^{12, 13}

Experimental

Preparation of Magnetic Spinel

Method 1. Partial Oxidation of Aqueous Fe^{II} by NO_3^- at 100 °C

Magnetite was prepared under N_2 at 100 °C by the slow addition (*ca.* $0.5 \text{ cm}^3 \text{ min}^{-1}$) of a solution containing 0.1 mol KOH and 0.008 mol KNO_3 dissolved in 30 cm^3 of deoxygenated distilled water to 70 cm^3 of a boiling deoxygenated solution containing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ($0.514 \text{ mol dm}^{-3}$) at *ca.* pH 2.5. A green gelatinous precipitate was immediately formed which turned dark blue and then black on continued addition of the alkaline mixture. The suspension was boiled for a further 30 min and allowed to cool. The resulting black precipitate was washed several times with distilled water followed by two washings with acetone and left to dry at room temperature. Samples were removed at ten minute intervals during the course of the reaction, centrifuged, and the supernatant analysed for total dissolved Fe (by atomic absorption spectroscopy) and the pH measured. The $\text{Fe}^{\text{III}}:\text{Fe}^{\text{II}}$ ratio in the final product was calculated as follows. Fe^{II} concentration was determined by dissolving a known weight of the spinel in conc. HCl acid under N_2 and titrating against deoxygenated $\text{K}_2\text{Cr}_2\text{O}_7$, total Fe was determined by atomic absorption spectroscopy, and Fe^{III} was calculated from the difference between total Fe and Fe^{II} concentrations.

The above synthesis was repeated with the following modifications; (a) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in place of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and (b) 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.

Method 2. Room-temperature Transformation of Hydrated Fe^{III} Oxide (Ferrihydrite) in the Presence of Fe^{II} Ions

Ferrihydrite was prepared by the addition of deoxygenated NaOH to 100 cm^3 of a $19.6 \text{ mmol dm}^{-3}$ deoxygenated solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The resulting brown suspension was purged with N_2 overnight. 100 cm^3 of a deoxygenated solution of $19.6 \text{ mmol dm}^{-3}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the stirred suspension under N_2 and the pH adjusted to a value of 7.0, 8.0 or 9.0 depending on the experiment. The reaction was accompanied by an immediate darkening of the ferrihydrite suspension and a continual decrease in pH which was buffered by the addition of deoxygenated NaOH such that the pH was kept within 0.2 units of the starting value. All experiments were run at room temperature under a stream of N_2 gas until no further change in pH was noted (3–26 h depending on the starting pH). The resulting black precipitate was collected by centrifugation, washed with deoxygenated distilled water followed by deoxygenated acetate buffer (pH 4.1, 0.5 mol dm^{-3}) to remove any residual Fe^{II} ions. Further washings with deoxygenated water and finally deoxygenated acetone were undertaken and the precipitate left to dry at room temperature under N_2 .

The above procedure was modified at a reaction pH of 8.0 to include the presence of 1 and 5 mol % deoxygenated $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$ added to the ferrihydrite suspension prior to Fe^{II} addition.

Characterization of Products

Electron Microscopy

Samples for transmission electron microscopy were prepared by placing a droplet of the reaction suspension onto carbon-coated, nitrocellulose-covered copper electron microscope grids followed by blotting on filter paper and air drying. Changes in the crystallochemical properties of the precipitates formed during the phase transformation of hydrated ferric oxide (method 2 above) were determined by removing small aliquots of the suspension at different time intervals and mounting the material on electron microscope grids as above. Electron diffraction patterns were recorded on populations of particles and single crystals imaged in the selected area mode of the electron microscope. Compositional data on individual crystals as well as aggregates of particles were obtained using energy dispersive X-ray analysis (e.d.X) facilities coupled to the electron microscope. For conventional work a Jeol 100CX analytical transmission electron microscope operating at 100 keV was used. Lattice imaging studies were undertaken on individual crystallites using a Jeol 2000FX transmission electron microscope operated at 200 keV and capable of a point-to-point resolution of 0.28 nm.

X-Ray Diffraction, Infrared and ^{57}Fe Mössbauer Spectroscopy and Magnetic Measurements

Samples of the dried powders were examined by X-ray diffraction using a Debye–Scherrer camera and $\text{FeK}\alpha$ radiation. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer. ^{57}Fe Mössbauer spectra were recorded at variable temperature using a constant acceleration spectrometer with a ^{57}Co (Rh) source. Temperatures between 1.5 and 300 K were maintained and measured with a calibrated Si diode and a Lakeshore Cryotronics temperature controller. Spectra were analysed by a least-squares fitting program. Magnetic measurements were made with an S.H.E. Squid magnetometer.

Results

Method 1

(a) In the Absence of Phosphate

Fig. 1(a) shows the changes in pH and total dissolved Fe concentration accompanying the partial oxidation of a FeCl_2 solution in the presence of NO_3^- at 100 °C. Addition of the $\text{OH}^-/\text{NO}_3^-$ solution resulted in an initial rapid rise in pH with the dissolved Fe concentration remaining almost constant. After 10 min, the pH increase was reduced on continual addition of the alkali mixture although the Fe concentration decreased rapidly. Complete removal of soluble Fe after 50 min was accompanied by a rapid rise in pH and a black precipitate which showed a positive magnetic response to a small bar magnet. Chemical determination of the $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratio in the product gave a value of 1:3 and X-ray diffraction data identified the material as a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ spinels (table 1). These results were consistent with the Mössbauer spectrum of the sample recorded at 298 K [fig. 2(a)] which showed two overlapping subspectra corresponding to spinel-type tetrahedral Fe^{III} and octahedral Fe^{III} and Fe^{II} sites (table 2). The intensity of the averaged ($\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$) subspectrum was significantly reduced from that observed for stoichiometric magnetite¹⁴ indicating substantial oxidation of Fe^{II} ions in the octahedral sites. Magnetic moment measurements were also significantly smaller than

Fig. 1. Changes in soluble Fe concentration (mmol dm^{-3}) (●), and pH (■), during the reaction of aqueous Fe^{II} with NO_3^- ; (a) FeCl_2 solution; (b) FeSO_4 solution; (c) FeCl_2 with 10 mol % P_1 , (d) FeCl_2 with 20 mol % P_1 .

those of stoichiometric magnetite (table 2). However, infrared spectra showed only two bands at 570 and 360 cm^{-1} [fig. 3(a)] characteristic of Fe_3O_4 ¹⁵ indicating that the bulk structure of the sample was primarily magnetite. This suggests that the maghemite phase was probably confined to an oxidised surface layer around the magnetite particles.

Electron microscopic examination of the sample showed irregularly shaped particles in the size range $20\text{--}60\text{ nm}$ [plate 1 (a)]. E.d.X. analysis detected Fe and K (trace) (table 3) and powder electron diffraction patterns were consistent with the X-ray diffraction data.

Magnetic spinels prepared from Fe^{II} sulphate solutions were shown to be Fe_3O_4 with some surface $\gamma\text{-Fe}_2\text{O}_3$ on the basis of X.r.d., infrared spectroscopy and chemical analysis ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}} = 2.9$) (Mössbauer data were not available). The pH and dissolved Fe^{II} profiles were similar to those for Fe^{II} chloride [fig. 1(b)]. Electron microscopy showed that the spinel crystals formed from Fe^{II} sulphate solution were generally larger, often up to 150 nm in length, and the particles exhibited a well defined cubo-octahedral morphology [plate 1(b)] in contrast to the irregular crystals formed from the oxidation of Fe^{II} chloride solution [plate 1(a)].

Plate 1. Transmission electron micrographs of spinel products from partial oxidation of Fe^{II} solutions. (a) FeCl_2 solution; (b) FeSO_4 solution; (c) FeCl_2 with 5 mol % P_1 ; (d) FeCl_2 with 30 mol % P_1 . Needle-like particles in (d) are $\alpha\text{-FeOOH}$. Scale bar in all micrographs is 100 nm.

Plate 2. Transmission electron micrographs of precipitates from reaction of ferrihydrite with aqueous Fe^{II} ; (a) unreacted ferrihydrite, pH 8, 30 min; (b) green rust, pH 8 (or 9), 30 min; (c) green rust and Fe_3O_4 , pH 8, 60 min and (d) magnetite (the needle-like crystal is $\alpha\text{-FeOOH}$), pH 8, 22 h. Scale bars: (a) and (b) 500 nm; (c) and (d) 100 nm.

Plate 3. Precipitates formed from the reaction of ferrihydrite with aqueous Fe^{II} at pH 7; (a) green rust, 2 h; (b) green rust and Fe₃O₄, 3 h; (c) Fe₃O₄ and needle-like α-FeOOH and (d) lattice image of a Fe₃O₄ single crystal showing {200} (4.2 Å) fringes and well defined cubo-octahedral crystal edges. Scale bars: (a) and (b) 500 nm; (c) 50 nm and (d) 10 nm.

Plate 4. Precipitates formed from the reaction of ferrihydrite with aqueous Fe^{II} at pH 8 in the presence of 5 mol % P_i ; (a) unreacted ferrihydrite and green rust, 4 h; (b) green rust and trace amounts of ferrihydrite, 50 h. Scale bars: (a) 500 nm and (b) 1 μm .

Table 1. Representative X-ray diffraction data (d -spacings/Å) for spinel products^a

d -spacing/Å		
γ -Fe ₂ O ₃ ^b	Fe ₃ O ₄ ^c	product
4.82	4.85	4.84
4.18	—	4.18
3.20	—	3.26
2.95	2.97	2.96
2.78	—	2.78
2.514	2.532	2.525
2.408	—	2.416
2.086	2.100	2.090
1.701	1.714	1.708
1.604	1.617	1.614
1.474	1.485	1.479
1.318	1.327	1.324
1.272	1.280	1.277
1.258	1.266	1.263
1.204	1.212	1.209
1.115	1.122	1.119
1.086	1.093	1.090
1.043	1.050	1.047

^a All samples gave similar diffraction spacings but the number of γ -Fe₂O₃ lines varied in different experiments depending on the extent of air oxidation of the materials.

^b X.r.d. File 15-1402, ^c X.r.d. File 19-629.

(b) In the Presence of Inorganic Phosphate

Addition of 5–30 mol % KH₂PO₄ (P_i) to Fe^{II} chloride solutions prior to OH⁻/NO₃⁻ addition resulted in structural and morphological changes in the spinel products. X.r.d. patterns, infrared spectra [fig. 3(b)], room temperature Mössbauer spectra [fig. 2(b) and (c); table 2] and magnetic measurements (table 2) of crystals grown in the presence of 5% and 10% P_i showed that the samples comprised surface oxidised Fe₃O₄ similar to that formed in the undoped system. The infrared spectra showed an additional band at 950 cm⁻¹ [figure 3(b)] corresponding to the P–O–Fe symmetric stretch.¹⁶ Particles examined by e.d.X analysis showed that some P_i was closely associated with the spinel crystals (table 3). The pH and dissolved Fe^{II} profiles [fig. 1(c)] were essentially unchanged from the non-phosphate containing systems. The crystals were 50–100 nm in size and had a well defined cubo-octahedral morphology [plate 1(c)]. These results are similar to those described above for spinel formation from Fe^{II} sulphate solutions and indicate the importance of anion charge in determining the crystallochemical nature of the magnetic products.

Increasing the P_i concentration to 20–30 mol % resulted in marked changes in the structural and magnetic properties of the oxidation product. Addition of NO₃⁻/OH⁻ first gave a dark blue-green product which turned dark brown towards the end of the reaction. The Fe concentration and pH profiles [fig. 1(d)] showed a more rapid uptake of Fe from solution and a continual rise in pH throughout the reaction. X.r.d. patterns of the samples gave weak broad lines with d -spacings corresponding to Fe₃O₄/ γ -Fe₂O₃ indicating that the spinels were of low structural order. The degradation of structural

Fig. 2. ^{57}Fe Mössbauer spectra of samples from partial oxidation of FeCl_2 solutions; (a) 0; (b) 5; (c) 10; (d) 20 and (e) 30 mol % P_i . Spectra were recorded at 298 K.

order was also apparent in the marked reduction in the saturation magnetic moment (table 2) and in the Mössbauer spectra [fig. 1(d) and (e)] which showed that, although magnetic ordering was still present at 298 K, the lines were extensively broadened. Furthermore, the 30 mol % P_i product showed evidence of a weak high-spin Fe^{III} quadrupole doublet in the central region of the spectrum. Since no diffraction lines were observed for non-spinel crystalline iron oxides, this spectral component possibly corresponds to an amorphous or poorly crystalline Fe^{III} oxide of small particle size, for example, ferrihydrite. Infrared spectra of the samples showed only weak Fe_3O_4 bands and a strong P_i band at 950 cm^{-1} [fig. 3(c)], consistent with the above results. Electron micrographs showed that whereas the particles formed in the presence of 20 mol % P_i were 40–120 nm octahedral crystals, those prepared in 30 mol % P_i comprised ill defined grains of much lower size (10–40 nm) [plate 1(d)]. E.d.X analysis showed P_i closely associated with all the particles (table 3). Some needle-like particles (100 nm in length) of goethite ($\alpha\text{-FeOOH}$) were also occasionally observed in both samples [plate 1(d)] although this material was not detected by X.r.d.

Table 2. ^{57}Fe Mössbauer parameters

sample	T/K	$\delta/\text{mm s}^{-1a}$	$\Delta/\text{mm s}^{-1b}$	HF/kOe ^c	MM/emu g ^{-1d}
method 1					
0 mol % P_i	298	0.34	—	490 72 %	76.5
—	—	0.58	—	450 28 %	—
5 mol % P_i	298	0.34	—	485 54 %	76.8
—	—	0.55	—	445 46 %	—
10 mol % P_i	298	0.33	—	485 56 %	74.2
—	—	0.55	—	422 44 %	—
20 mol % P_i	—	—	—	—	42.6
30 mol % P_i	—	—	—	—	42.6
method 2					
pH 9	298	0.39	—	502 —	—
pH 8	298	0.39	—	503 —	—
pH 7	298	0.38	—	503 —	—
—	—	0.42	—	450 —	—
pH 8,	200	0.42	0.81	— 82 %	—
1 mol % P_i	—	0.39	—	470 18 %	—
pH 8,	80	0.47	0.80	—	—
5 mol % P_i	8	0.47	—	482 —	—

^a δ , Isomer shift. ^b Δ , quadrupole splitting. ^c HF, magnetic hyperfine field. ^d MM, saturation magnetic moment per gram; for comparison, stoichiometric Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have values of 92.0 and 56.0 emu g⁻¹, respectively.

Fig. 3. Infrared spectra of samples from partial oxidation of FeCl_2 solutions; (a) 0; (b) 10 and (c) 30 mol % P_i . Peak X, $\nu(\text{FeO-P})$; peaks Y and Z, $\nu(\text{FeO-Fe})$.

Method 2

Reaction of ferrihydrite at room temperature in the presence of Fe^{II} at pH 9 gave a magnetic product after 3 h which was identified as a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ by X.r.d. and electron diffraction. Mössbauer spectra showed only a single hyperfine sextet [fig. 4(a), table 2] indicating that the major component was $\gamma\text{-Fe}_2\text{O}_3$. The corresponding

Table 3. E.d.X. analysis data (wt % element) for spinel samples prepared by method I

element	dopant level/atom % P _i ^a				
	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

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

Fig. 4. ⁵⁷Fe Mössbauer spectra of samples from the reaction of ferrihydrite and aqueous Fe^{II} at room temperature and at (a) pH 9; (b) pH 8; (c) pH 7. Spectra were recorded at 298 K.

reaction at pH 8 was slower and a magnetic product was isolated after 12 h. X.r.d. data from a freshly prepared sample gave reflections corresponding to Fe₃O₄ although the dried sample rapidly oxidised in air to γ -Fe₂O₃ as shown by the Mössbauer spectrum [fig. 5(b)].

Changes in the crystallochemical properties of the reaction intermediates and spinel products were followed by electron microscopy. At both pH values the reaction proceeded *via* a pseudo-hexagonal plate-like precursor [plate 2(b)] that gave single-crystal electron diffraction patterns corresponding to a poorly-crystalline green rust II¹⁷ [*d*-spacings; 2.66 (101) and 1.52 Å (112)]. Whereas green rust (mean size *ca.* 450 nm) was predominant in samples taken after 30 min at pH 9, corresponding samples from the pH 8

Fig. 5. E.d.X. spectra of green rust prepared at pH 8 from the reaction of ferrihydrite and aqueous Fe^{II} ; (a) 0 and (b) 5 mol % P_i . Cu peaks originate from the sample holder and Si is a contaminant (from silicone grease).

system contained much of the unreacted starting material [plate 2(a)]. Subsequent transformation of green rust to magnetite appeared to take place at the surface of the intermediate and was associated with a concomitant corrosion of the pseudo-hexagonal platelets [plate 2(c)]. The magnetic crystals were irregular in shape during the early stages of the transformation but an octahedral or cubo-octahedral morphology was apparent in the mature crystals [plate 2(d)]. Particle size distributions and mean diameters for spinel crystals at different stages of growth were similar indicating that ripening of the early crystals was not a predominant mechanism of formation. Furthermore, the mean diameter, range and standard deviation (32, 10–60 and 9.5 nm, respectively, at pH 9) of the spinel crystals were not significantly different in the two systems even though the reaction was substantially slower at pH 8. Similar values were also obtained from particles grown at pH 7 (see below). This suggests that the particle size of the magnetic products is independent of the rate of formation and is possibly constrained by other factors such as the local supersaturation levels and structural disorder in the growing crystals.

E.d.X. spectra showed the presence of S [from Fe^{II} sulphate] in both the ferrihydrite and green rust materials [fig. 5(a)]. No S was observed in the corresponding analysis of the spinel crystals.

The above reaction, when carried out at pH 7, resulted in a mixture of magnetic and

Fig. 6. ^{57}Fe Mössbauer spectra of samples from the reaction of ferrihydrite and aqueous Fe^{II} at room temperature, pH 8; (a) 1 mol % P_i 200 K; (b) 5 mol % P_i , 80 K and (c) 5 mol % P_i , 8 K.

non-magnetic oxides. Green rust was formed during the first 2 h of the reaction followed by slow transformation (26 h to completion) to $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ (goethite) (plate 3). Mössbauer spectra were consistent with the diffraction data and showed hyperfine split components corresponding to $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ [fig. 4(c), table 2]. Whereas the Fe_3O_4 particles formed in close proximity to the green rust platelets [plate 3(c)], the $\alpha\text{-FeOOH}$ needle-like crystals were spatially separated. The spinel crystals had a size range 10–60 nm and mean diameter of 33 nm, which were not significantly different from spinels formed at higher pH values. There appeared, however, to be an increased morphological resolution when compared to the higher pH products, with many crystals exhibiting a well defined cubo-octahedral habit [plate 3(c)]. High-

resolution electron micrographs showed lattice fringes running continuously and coherently across the total width of the individual spinel particles [plate 3(d)]. These results indicated that the spinel particles are well ordered single-domain crystallites.

Addition of 1–5 mol % P_i prior to Fe^{II} addition to ferrihydrite inhibited spinel formation. The rate of green rust formation was significantly reduced and although green rust was present after 4 h, unreacted ferrihydrite was present throughout the reaction (plate 4). The initial green rust particles were irregular and associated with an amorphous gel of ferrihydrite [plate 4(a)]. At 50 h, well developed pseudo-hexagonal plate-like crystals were observed [plate 4(b)]. No spinel phases were detected by X.r.d. or electron diffraction. E.d.X spectra of both the ferrihydrite and green rust particles showed the presence of P and S (from sulphate) in these solids (fig. 5).

Mössbauer spectra of the above samples showed no evidence of spinel phases. The spectra recorded at 200 K consisted of a high-spin Fe^{III} quadrupole doublet [fig. 6(a), table 2]. A minor component, corresponding to a hyperfine split sextet, was also observed in the sample prepared in the presence of 1 mol % P_i [fig. 6(a)]. A similar component was only observed at temperatures below 80 K in the sample prepared in the presence of 5 mol % P_i [fig. 6(b) and (c), table 2]. Lowering the temperature to 8 K resulted in the loss of the central doublet and the concomitant increase in the sextet component. The relatively low hyperfine field value (table 2) and the broad lines of the sextet suggest that the material is not γ - Fe_2O_3 of small particle size. On the basis of the electron microscopy results, the spectral data can be interpreted as arising from a mixture of disordered Fe^{III} oxides, possibly formed by air oxidation of green rust in combination with unreacted ferrihydrite. The temperature dependence of the spectra is therefore characteristic of magnetically ordered small particles (< 10 nm) exhibiting superparamagnetism.

General Comments

The results presented in this paper show that magnetic spinels can be formed from aqueous media and that the crystallochemical properties of these materials are readily influenced by changes in pH, temperature and anionic species present in the reaction. Although Fe_3O_4 is the initial product formed by partial oxidation of Fe^{II} at 100 °C and by the reaction of ferrihydrite with Fe^{II} at room temperature, the material formed in the latter system rapidly oxidises to γ - Fe_2O_3 during sample isolation and storage. Since the particle sizes were similar in both systems, the low temperature product is possibly more disordered. Both synthetic routes involved green rust intermediates which are hydrated mixed valence compounds,¹⁷ and the subsequent dehydration and transformation to Fe_3O_4 will be favoured at higher temperature. Furthermore, the high final pH of method 1 compared with the lower buffered pH values of method 2, favours the formation of oxo- rather than oxy-bridges in the product.

Although we have been successful in preparing spinels at ambient temperature and neutral pH, we have not attained the degree of specificity characteristic of the biologically controlled synthesis of stoichiometric magnetite, as found, for example, in magnetotactic bacteria.^{13,18} Future work will focus on achieving greater chemical control over spinel formation through the use of gel media and micellar compartments which may limit the rate of reaction and provide increased regulation of nucleation and crystal growth.

Since ferrihydrite has been shown to be a precursor to magnetite formation in bacteria,^{18,19} method 2 has potential as a model system for the biomineralization of iron oxides. We note, however, that no green rust intermediates have been observed in the bacterial systems. Interestingly, magnetite formation in the teeth of marine molluscs (chitons) also involves the transformation of ferrihydrite but green rust intermediates have been observed;²⁰ the subsequent reaction products include both Fe_3O_4 and α - $FeOOH$ and the system appears to be chemically similar to the inorganic preparation at

pH 7 reported in this paper. Furthermore, the chiton Fe_3O_4 , like the inorganic products described here, does not show the crystallochemical specificity of bacterial magnetite. Thus a future strategy will be to eliminate green rust intermediates from the ferrihydrite to spinel reaction pathway.

Previous workers^{3,8} have proposed that the reaction of Fe^{II} with Fe^{III} oxides results in Fe_3O_4 by a mechanism involving the formation of soluble mixed valence complexes. The rate limiting step appears to be the transformation of green rust and this reaction step is profoundly influenced by the pH, temperature and nature of anionic additives present in the reaction medium. Both P_i and SO_4^{2-} stabilize the intermediate presumably through surface adsorption, and reduce the rate of spinel formation. At high temperature (100 °C), relatively large concentrations of additive can be tolerated, whereas at room temperature concentrations as low as 1 mol % P_i result in complete inhibition of Fe_3O_4 crystallization. The consequent reduction in rate at intermediate additive concentrations results in morphological enhancement of the octahedral habit of spinel crystals grown from partial Fe^{II} oxidation at 100 °C. A similar effect is observed with SO_4^{2-} and with a reduction in the pH to 7 in method 2. Since the (111) octahedral faces of Fe_3O_4 are intrinsically stable, the increased resolution in morphology is unlikely to be due to specific surface interactions between these crystal faces and PO_4^{3-} and SO_4^{2-} anions, although P was detected in the Fe_3O_4 crystals analysed by e.d.X analysis. Bacterial magnetites, on the other hand, show a range of species-specific morphologies that have not yet been replicated in inorganic preparations, and this must be a priority of future work since such speciality materials may have important technological application.

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