

## Composite ferric oxyhydroxide-containing phases formed in neutral aqueous solutions of tryptophan and indole-3-acetic acid

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(Received May 8, 2000)

Mössbauer, FTIR and XRD analyses showed that in aqueous medium in air in the presence of L-tryptophan (Trp) or indole-3-acetic acid (IAA) the ambient-temperature ageing of the precipitates formed from ferrous sulphate at pH~7 gave composite phases with varying proportions of  $\gamma$ -FeOOH (a dominating crystalline phase),  $\alpha$ -FeOOH (both fine-grained, showing superparamagnetic behaviour at 298 K, and relatively better crystallized) and amorphous ferric hydroxide. The experimental data suggested a competition for adsorption sites at the oxyhydroxide surface in the suspension during phase transformations, as well as the transformation of  $\gamma$ -FeOOH (and/or amorphous ferric hydroxide) to  $\alpha$ -FeOOH via the dissolution-reprecipitation mechanism. The formation of certain ferric oxyhydroxide phases in the presence of Trp and IAA – released e.g., in the course of bacterial and plant metabolism – can contribute to the regulation of soil mineral composition.

### Introduction

Iron, one of the most essential microelements for virtually all living cells, is usually abundant in the environment, particularly in soils and natural aquifers. However, its bioavailability is relatively low, which is connected with a dramatically decreased solubility of ferric species under physiological pH values owing to their complete hydrolysis.<sup>1,2</sup> This has resulted in the development of special biologically regulated mechanisms of Fe<sup>III</sup> solubilization, e.g., involving specific natural low-molecular-weight chelating agents (siderophores) which transport iron(III) to the cell surface in the form of a complex,<sup>2,3</sup> with further Fe<sup>III</sup> release from the latter in the course of its reductive assimilation.<sup>4</sup>

Chemical (i.e., abiotic) reduction of Fe<sup>III</sup> involving natural reducing agents may also be possible under certain conditions, giving more soluble and, therefore, more bioavailable Fe<sup>II</sup> species.<sup>5–8</sup> In addition, the activity of dissimilatory iron(III)-reducing microorganisms, which obtain energy by coupling Fe<sup>III</sup> reduction to oxidation of organics (including biodegradation of xenobiotics),<sup>9–11</sup> contributes to the overall pool of ferrous iron in soils and in ground waters. The resulting Fe<sup>II</sup>, in its turn, undergoes further re-oxidation either as a result of a specific microbial activity or, abiotically, under aerobic conditions.<sup>12–14</sup>

The aforementioned processes lead to the formation of iron(III) oxyhydroxide species, of which poorly crystallized (amorphous) materials are more readily involved both in biologically regulated reduction<sup>13–15</sup>

and, owing to their lower thermodynamic stability and higher solubility, most probably in chemical reduction as well. This results in gradual accumulation of crystalline forms of ferric oxyhydroxides in sediments and in soils. However, the presence of certain substances in the medium may retard or even totally inhibit transformation of amorphous ferric species (precursors) to their crystalline analogues, or facilitate the formation of a certain crystalline phase (or phases) in preference to others.<sup>13,16,17</sup> Thus, a number of organic substances<sup>18–27</sup> (in particular, organic bases and aminoacids containing N-donor atoms)<sup>18–25</sup> are well known to influence the formation of certain ferric oxide and/or oxyhydroxide crystalline phases in aqueous solution at the steps of both precipitation (hydrolysis of Fe<sup>3+</sup> ions) and transformation of amorphous ferric hydroxide (ferrihydrite).

In our previous work, redox transformations of iron in aqueous solution in the presence of naturally occurring bioligands (indole-3-acetic acid, a phytohormone of the auxin series, and its metabolically related precursors L-tryptophan and anthranilic acid) have been studied<sup>6–8,28,29</sup> using Mössbauer spectroscopy (in addition to other techniques) as a sensitive and powerful tool giving quantitative information on the valent states, structure and composition of the reaction products both in the solid state and in frozen solutions. It has been found that, whereas in slightly acidic media (pH $\leq$ 5) iron(III) can be gradually reduced by these bioligands, which may have some ecological significance,<sup>6–8</sup> at circumneutral pH this process is retarded, and the precipitated products appear to contain hydrolysed ferric species.

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In the present work, the phase composition and structure of solid products, formed during ageing under aerobic conditions in neutral iron(II)-containing aqueous solutions of L-tryptophan (Trp) and indole-3-acetic acid (IAA), were studied using Mössbauer spectroscopy complemented with Fourier transform infrared (FTIR) spectroscopic and X-ray diffraction (XRD) analyses.

## Experimental

### *Preparation of samples*

Samples were synthesized by dropwisely adding freshly prepared and filtered 0.1M aqueous solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (chemical purity) to an appropriate volume of solutions of potassium salts of L-tryptophan (Trp; Sigma) or indole-3-acetic acid (IAA; Eastman Kodak, U.S.A.) obtained by dissolving Trp or IAA in distilled water adding 0.1M KOH solution and adjusting its pH to 7.0 (final Fe-to-ligand molar ratio is 1:3). The precipitates formed therein were left ageing in the mother liquor at ambient temperature for 3 (Trp) or 4 days (IAA) during which visual transformation of the colour of precipitates completed (colours turned to yellowish-orange with a brownish tint). After ageing, the precipitates were separated by single-step decantation and filtration, thoroughly washed with distilled water or acetone (chemical purity) on the filter and dried in air for at least a day at ambient temperature. In appropriate cases, where acetone was used for washing the filtered samples, the latter were completely dried in a few minutes.

### *Mössbauer spectroscopic measurements and data treatment*

Mössbauer spectra of the dry solid samples placed in a "cold finger" cryostat filled with liquid nitrogen (at ca. 80 K) were collected in the transmission geometry using a RANGER MS-700 constant-acceleration Mössbauer spectrometer (Ranger Electronics, USA) with a NaI/Tl scintillation detector, combined with a computer-operated NUCLEUS PC card multichannel analyser; a  $^{57}\text{Co}[\text{Cr}]$  source used (ca. 1 MBq activity) was calibrated relative to  $\alpha\text{-Fe}$  at ambient temperature. Room temperature measurements of Mössbauer spectra of the samples were performed similarly (in the same cryostat after complete evaporation of liquid nitrogen, retaining the mounting geometry of the solid sample relative to the gamma-ray beam path, after the sample temperature had reached that in the laboratory). Standard computer-based statistical analysis included fitting the experimental data obtained to a sum of Lorentzian-shaped component lines with a least squares fit using the MOSSWINN program,<sup>30</sup> which enabled calculation of the values of

isomer shift (IS; all data are given relative to  $\alpha\text{-Fe}$ ), quadrupole splitting (QS), linewidth (i.e., full width at half maximum, FWHM), hyperfine magnetic splitting (HFMS), as well as partial resonant absorption areas of superimposed components composing the overall spectrum, which represent relative contents of the corresponding iron forms if a common recoilless fraction is assumed for all forms.

### *Fourier transform infrared spectra acquisition*

Solid air-dried samples (see above) were carefully pressed into pellets with spectroscopically pure KBr (Merck). Spectra were collected with a total of up to 60 scans at a resolution of  $4\text{ cm}^{-1}$  in the transmission mode (mid-infrared region) using a Perkin-Elmer Fourier transform infrared (FTIR) spectrometer (Model 2000; U.K.) coupled with a personal computer loaded with an IR Data Manager Program supplied by the manufacturer.

### *X-ray powder diffraction measurements*

X-ray powder diffraction (XRD) patterns were obtained using an automatic Philips diffractometer, model MPD 1880 (Cu  $K\alpha$  radiation; graphite monochromator; proportional counter). Crystalline phases ( $\gamma\text{-FeOOH}$  and  $\alpha\text{-FeOOH}$ ) were identified using the powder diffraction data filed at the International Center for Diffraction Data (ICDD), USA.<sup>31</sup>

Unless otherwise stated, all experimental procedures and measurements were conducted at  $295 \pm 3\text{ K}$ .

## Results and discussion

In soil and other natural environments, the presence of L-tryptophan (Trp, as well as of other vitally essential amino acids) may primarily be due to degradation of proteins from living matter or dead cells of microorganisms; it may also be present among exudates of plant roots.<sup>32</sup> Trp is utilized by many soil microorganisms in the course of biosynthesis and excretion of indole-3-acetic acid (IAA),<sup>33,34</sup> the most abundant naturally occurring phytohormone (auxin) which regulates plant growth, this route being an essential part of associative plant-microbe interactions.<sup>32-36</sup>

However, it has been shown that the presence of iron(III) under certain conditions may lead to oxidative degradation of IAA with simultaneous reduction of iron(III).<sup>7,8</sup> As was mentioned above, some other naturally occurring substances (anthranilic acid, Trp, cysteine) are capable of reducing ferric iron.<sup>6,7,19,20,28,29</sup> On the other hand, they may affect the process of crystallization of ferric oxyhydroxides formed during aerobic oxidation of iron(II) in aqueous media.

In this work, we used Mössbauer spectroscopy to monitor the phase composition of the solids precipitated from neutral aqueous solutions of ferrous sulphate containing Trp and IAA. Phase analysis was also complemented by XRD, while FTIR spectroscopy contributed to the structural information.

Since long-term ageing of ferric hydroxide in aqueous solution and subsequent gradual drying in air are known to result in the formation of a number of more or less crystalline products, we also used washing the samples with acetone to immediately dry the solid product. Also, as IAA may form a complex with Fe<sup>III</sup> poorly soluble in water but well soluble in nonaqueous oxygen-containing solvents, including acetone (A. A. KAMNEV, unpublished data), similar to the ferric complex with anthranilic acid,<sup>37</sup> this treatment would remove both the acetone-soluble complex and the admixture of the initial organic acid. Thus, the following three samples were studied:

*Sample 1:* formed in Trp solution; washed with acetone.

*Sample 2:* formed in Trp solution; washed with water.

*Sample 3:* formed in IAA solution; washed with acetone.

Figure 1 shows that rapid drying of the precipitate, formed in Trp solution, with acetone results in a product (sample 1) which gives quadrupole-split spectra both at ambient and at liquid nitrogen temperatures. This behavior is typical for both amorphous ferric hydroxide (ferrihydrite) and crystalline  $\gamma$ -FeOOH (lepidocrocite).<sup>38</sup> The Mössbauer parameters for these products (IS and QS) differ only slightly;<sup>39</sup> the somewhat broadened lines (FWHM~0.5 mm/s; Table 1) indicate that, most likely, both products are coexisting. XRD phase analyses confirmed the latter conclusion (amorphous phase was found to be dominating), showing also traces of  $\alpha$ -FeOOH (goethite; data not shown).

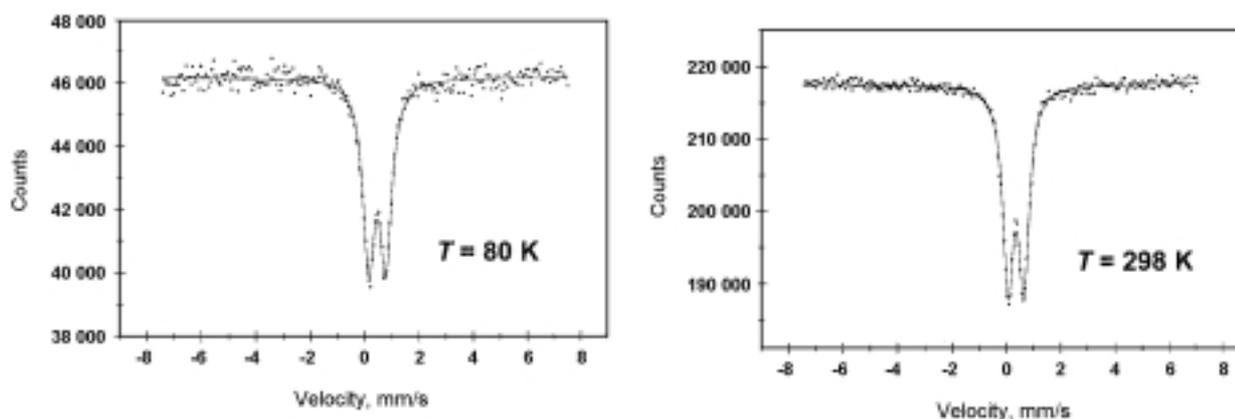


Fig. 1. Mössbauer spectra of the dry precipitate formed and aged at room temperature for 3 days under aerobic conditions in neutral aqueous FeSO<sub>4</sub> solution of L-tryptophan (filtered and washed with acetone) measured at 298 and 80 K

Table 1. Mössbauer parameters (measured at  $T = 298$  and  $80$  K) for the products formed and aged at room temperature in air in neutral aqueous FeSO<sub>4</sub> solutions of L-tryptophan filtered and washed with acetone (sample 1) and water (sample 2) and of indole-3-acetic acid filtered and washed with acetone (sample 3); see also Figs 1–3 (samples 1–3, respectively) and Fig. 4

Sample	T, K	Spectral component	IS, <sup>a</sup> mm/s	QS, <sup>b</sup> mm/s	FWHM, <sup>c</sup> mm/s	HFMS, <sup>d</sup> kOe	S <sub>r</sub> <sup>e</sup> , %
1	298	Doublet	0.36 ± 0.01	0.59 ± 0.01	0.46 ± 0.02	–	100
1	80	Doublet	0.47 ± 0.01	0.63 ± 0.02	0.51 ± 0.03	–	100
2	298	Doublet	0.37 ± 0.01	0.55 ± 0.01	0.43 ± 0.02	–	42.5
		Sextet	0.36 ± 0.04	0.27 ± 0.07	1.64 ± 0.28	309 ± 5	57.5
2	80	Doublet	0.47 ± 0.02	0.57 ± 0.02	0.44 ± 0.04	–	38.2
		Sextet	0.49 ± 0.02	0.22 ± 0.04	0.60 ± 0.09	485 ± 2	61.8
3	298	Doublet	0.36 ± 0.01	0.56 ± 0.01	0.36 ± 0.01	–	100
		Sextet	0.51 ± 0.12	–	0.93 ± 0.54	472 ± 10	18.7

<sup>a</sup> Isomer shift (relative to  $\alpha$ -Fe).

<sup>b</sup> Quadrupole splitting.

<sup>c</sup> Full line width at half maximum (for sextets, the values for external lines 1 and 6 are given).

<sup>d</sup> Hyperfine magnetic splitting.

<sup>e</sup> Partial resonant absorption areas of spectral components.

Note that well-crystallized goethite is characterized by magnetically split Mössbauer spectra both at room and liquid nitrogen temperature;<sup>38–40</sup> however, poorly crystallized goethite may exhibit superparamagnetic behavior at room temperature.<sup>17,39,41</sup> If present in trace amounts, goethite may not be distinctly observed in the Mössbauer spectrum even at 80 K, the more so that its lines are magnetically split in a sextet, thus being distributed over a larger velocity scale.

It is noteworthy that the same sample washed thoroughly with water with a prolonged subsequent drying (sample 2, see above) gives a superposition of a quadrupole doublet and a magnetically split sextet with broadened lines already at room temperature (see Fig. 2). At 80 K, the sextet becomes better shaped, and its lines become narrower (Fig. 2 and Table 1). The values of HFMS for the sextet at 298 and 80 K in general correspond to those for poorly crystallized natural goethite<sup>38,41</sup> (Table 1).

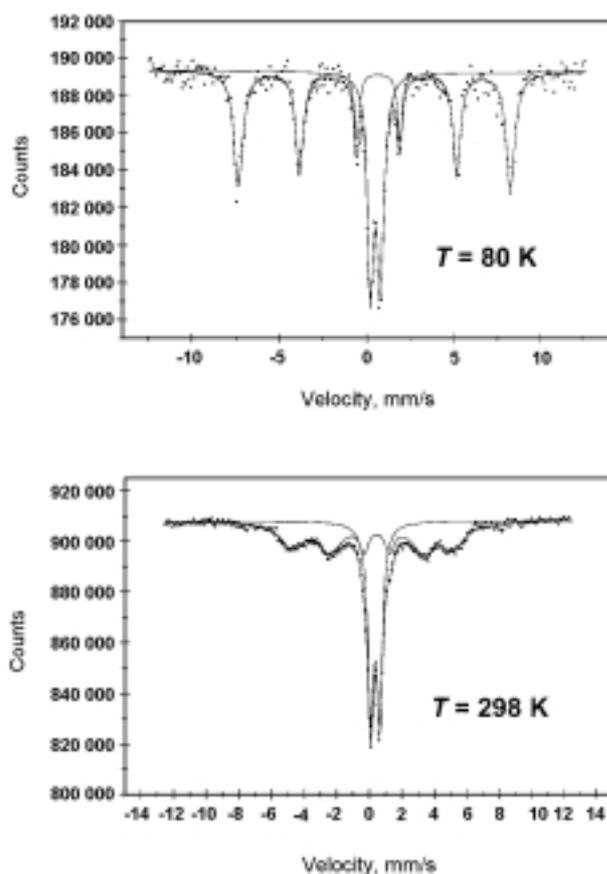


Fig. 2. Mössbauer spectra of the same sample as in Fig. 1 (washed with water with subsequent drying in air) measured at 298 and 80 K

The magnetically split spectral component in sample 2 (the sextet in Fig. 2) increases from 57.5% (at 298 K) to 61.5% (at 80 K) only, showing that the other part is most probably amorphous ferric hydroxide + lepidocrocite ( $\gamma$ -FeOOH). However, XRD measurements, though qualitatively confirming the presence of both  $\gamma$ -FeOOH and  $\alpha$ -FeOOH (in the ratio ca. 4:1, respectively; data not shown), still pointed to the presence of a dominating amorphous phase. This quantitative discrepancy between the Mössbauer data (ca. 60% of the magnetically ordered phase, viz.,  $\alpha$ -FeOOH) and the XRD data is most likely due to a poor crystallinity of the major part of the  $\alpha$ -FeOOH phase which may largely be represented by XRD as amorphous.<sup>42</sup> Another possible explanation consists in the fact that for fine-grained ferric hydroxide particles (amorphous phase) the recoilless fraction representing the probability of the Mössbauer effect may be essentially decreased,<sup>43,44</sup> thus giving a relatively smaller proportion in the overall spectrum area (see Table 1).

It should be emphasized that, as compared to sample 1 (rapidly dried after washing with acetone), sample 2 (which had been washed with water (and, therefore, undergone a longer drying) contained essential quantities of  $\alpha$ -FeOOH, though evidently rather poorly crystalline (giving minimal HFMS values).<sup>38,41</sup> This may well be connected with the removal of sulphate ions during washing with water in contrast to acetone (see below), as the adsorption of sulphate is known to suppress the ordering of ferrihydrite, thus hindering the formation of crystalline goethite (and of hematite as well).<sup>13,16</sup>

Sample 3 (formed and aged in IAA solution and rapidly dried with acetone) gave at 298 K a single doublet with the parameters well close to those for samples 1 and 2 (see Fig. 3 and Table 1) with a somewhat lower linewidth. At 80 K, however, in contrast to sample 1 (also rapidly dried with acetone), it reveals a weak sextet with rather broad lines and the parameters characteristic for poorly crystalline  $\alpha$ -FeOOH. In this case XRD data also confirmed the presence of a dominating amorphous phase and a  $\gamma$ -FeOOH/ $\alpha$ -FeOOH ratio of ca. 4:1 (see above). Thus, partial formation of fine-grained goethite (superparamagnetic at room temperature) is already more pronounced during ageing of the precipitate in IAA solution in the presence of sulphate, which, in the case of Trp, largely inhibits its crystallization. In this case, a competition between the organic ligands and the sulphate ions for the adsorption sites at the iron(III) hydroxide surface may evidently be suggested.

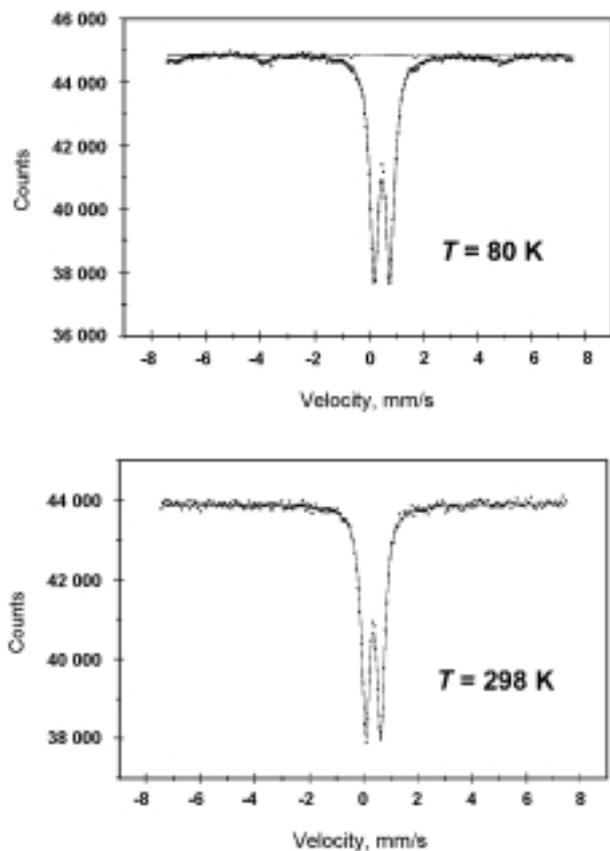


Fig. 3. Mössbauer spectra of the dry precipitate formed and aged at room temperature for 4 days under aerobic conditions in neutral aqueous  $\text{FeSO}_4$  solution of indole-3-acetic acid (filtered and washed with acetone) measured at 298 and 80 K

FTIR spectroscopic data for samples 1–3 (Fig. 4) seem to corroborate the above discussed Mössbauer spectroscopic results on the formation of ferric oxyhydroxides. In sample 1, the characteristic absorption bands of  $\gamma\text{-FeOOH}$  (at ca. 1023 and 747  $\text{cm}^{-1}$ )<sup>22–25,45</sup> are seen, whereas in sample 2 they are accompanied by characteristic absorption of  $\alpha\text{-FeOOH}$ <sup>22–25,45,46</sup> at 890 and 796  $\text{cm}^{-1}$  which in sample 3 is essentially weaker. Note that the region below 600  $\text{cm}^{-1}$  includes a number of bands typical for oxygen and hydroxo groups coordinated to  $\text{Fe}^{\text{III}}$  in different polyhedra,<sup>46</sup> including well resolved bands featuring the symmetric stretching modes  $\nu_s(\text{Fe-OH})$  at ca. 360  $\text{cm}^{-1}$  and  $\nu_s(\text{Fe-O})$  at ca. 270–280  $\text{cm}^{-1}$  (typical both for  $\gamma\text{-FeOOH}$  and  $\alpha\text{-FeOOH}$ ).<sup>46,47</sup>

It is noteworthy that the strong  $\nu_3$  and  $\nu_4$  bands of the  $\text{SO}_4^{2-}$  anion (at ca. 1130 and 620  $\text{cm}^{-1}$ , respectively)<sup>48</sup> are present in samples 1 and 3 (washed with acetone), but not in sample 2 (washed with water; see Fig. 4), which confirms the above mentioned considerations on the effect of sulphate. The latter was readily removed by washing with water (but not with acetone), thus being evidently weakly adsorbed on ferric oxyhydroxide particles rather than incorporated into the structure. On

the other hand, in sample 2 the absorption related to the functional groups of Trp are well pronounced (see a series of bands in the range of 1700–1300  $\text{cm}^{-1}$ , as well as a strong  $\gamma(\text{C-H})$  band of the benzene ring in Trp and related aromatic structures<sup>6,49</sup> at ca. 740–750  $\text{cm}^{-1}$  which overlaps with that of  $\gamma\text{-FeOOH}$ , somewhat increasing its relative intensity as compared to the ratio of the two  $\gamma\text{-FeOOH}$  bands in samples 1 and 3), while they are much weaker in sample 1 (acetone-dried).

Similarly, only traces of organic components may be detected in sample 3 (Fig. 4).

The results presented here are in agreement with the general knowledge on the processes of precipitation of ferric oxyhydroxides from ferrous sulphate solutions. It is known that in the absence of organic complexing ligands oxidation of iron(II) ions can lead to the formation of green complexes or green rust, as a function of pH. Green rust or non-stoichiometric mixtures of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  hydroxides can precipitate at pH 7 to 8, while  $\gamma\text{-FeOOH}$  and  $\text{Fe}_3\text{O}_4$  ( $\gamma\text{-Fe}_2\text{O}_3$ ) can be formed in the course of further oxidation of iron(II) ions.  $\text{Fe}_3\text{O}_4$  ( $\gamma\text{-Fe}_2\text{O}_3$ ) transforms into  $\gamma\text{-FeOOH}$  in a similar way as observed during corrosion of steel. Rapid oxidation of green rust favours the formation of  $\gamma\text{-FeOOH}$ , whereas slow oxidation favours the formation of  $\alpha\text{-FeOOH}$ . In the presence of organic ligands, the formation of  $\text{Fe}_3\text{O}_4$  ( $\gamma\text{-Fe}_2\text{O}_3$ ) can be totally suppressed, as is observed in the present work. Organic complexing ligands inhibit crystallization of iron hydroxides and oxides, and this effect is also confirmed in the present investigation, as the formation of significant fractions of amorphous and/or poorly ordered crystalline phases was found.

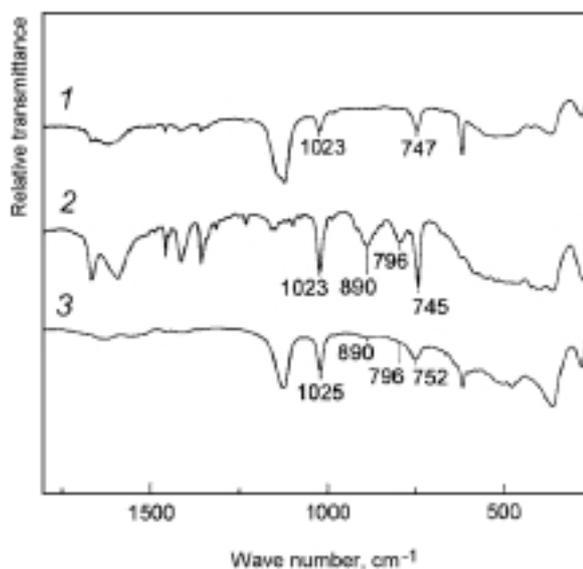


Fig. 4. Fourier transform infrared spectra of the products formed and aged at room temperature under aerobic conditions in neutral aqueous  $\text{FeSO}_4$  solution of L-tryptophan filtered and washed with acetone (1) and water (2) and of indole-3-acetic acid filtered and washed with acetone (3)

$\gamma$ -FeOOH obtained was not stable and (probably along with the amorphous ferric hydroxide) could be transformed into  $\alpha$ -FeOOH via the dissolution/reprecipitation mechanism. This phase transformation can easily occur at low temperatures.

### Conclusions

Mössbauer and FTIR spectroscopic studies and XRD analyses showed that in aqueous medium under aerobic conditions in the presence of L-tryptophan (Trp) or indole-3-acetic acid (IAA) the ambient-temperature ageing of the precipitates formed from ferrous sulphate at pH~7 gave composite phases with varying proportions of lepidocrocite ( $\gamma$ -FeOOH, a dominating crystalline phase), goethite ( $\alpha$ -FeOOH, both relatively better crystallized, giving a typical hyperfine magnetic splitting (HFMS) in Mössbauer spectra at both 298 and 80 K, and poorly crystallized, showing a superparamagnetic behavior at 298 K)<sup>38-42,50</sup> and amorphous ferric hydroxide. Removal of sulphate by washing with water led to an increased proportion of fine-crystallite goethite in the resulting dry phase, whereas washing the precipitate with acetone (with subsequent rapid drying), essentially decreasing the organic impurity, did not remove the sulphate impurity and led to a lowered  $\alpha$ -FeOOH content in the dry product. The data obtained suggest a competition for adsorption sites at the oxyhydroxide surface in the suspension during phase transformations.  $\gamma$ -FeOOH formed at early stages of the precipitation process (probably along with the amorphous ferric hydroxide) could be transformed into  $\alpha$ -FeOOH via the dissolution-reprecipitation mechanism.

The formation of certain oxyhydroxide phases in the presence of the substances studied (L-tryptophan and indole-3-acetic acid), released, e.g., in the course of bacterial and plant metabolism,<sup>32-34</sup> can contribute to the regulation of soil mineral composition.<sup>51</sup> The importance of bacterial activity in iron biomineralization has recently been confirmed by comparing biogenic (formed in the presence of certain bacteria) and abiotically obtained multi-phase ferric oxyhydroxides using Mössbauer spectroscopy.<sup>52,53</sup>

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The authors are grateful to Dr. Gy. VANKÓ (Budapest, Hungary) for help in experimental work and fruitful discussions, to A. B. KAMNEVA (Saratov, Russia) and Dr. V. ABLAMUNITS (Rehovot, Israel) for encouragement and technical assistance. This work was supported in part by the EC (INTAS Project No. 96-1015) and by Hungarian OTKA Fund (Project No. T 029537), as well as under the Agreement on Scientific Cooperation between the Russian and Hungarian Academies of Sciences for 1996-1998 (Protocol, Suppl. 2, Item 29) and for 1999-2001 (Protocol, Supplement, Item 37). A.A.K. also gratefully acknowledges the support of his stay and research at the

Department of Nuclear Chemistry, Eötvös Loránd University (Budapest) under the UNESCO short-term fellowship programme in biotechnology (1998).

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