



Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies

F. TROLARD,¹ J.-M. R. GÉNIN,² M. ABDELMOULA,² G. BOURRIÉ,^{1,3} B. HUMBERT,² and A. HERBILLON⁴

¹INRA-U.R. de Science du Sol et de Bioclimatologie, F 35042 Rennes Cedex, France

²Laboratoire de Chimie Physique pour l'Environnement, UMR 9992 CNRS-Université H. Poincaré, F 54600 Villers-lès-Nancy, France

³Géosciences Rennes, UPR 4661 CNRS-Université de Rennes, F 35042 Rennes Cedex, France

⁴Centre de Pédologie Biologique, UPR 6831 CNRS-Université Henri Poincaré, F 54501 Vandoeuvre-lès-Nancy, France

(Received May 10, 1996; accepted in revised form November 5, 1996)

Abstract—Mössbauer and Raman spectroscopies are used to identify for the first time a green rust as a mineral in a reductomorphic soil from samples extracted in the forest of Fougères (Brittany-France). The Mössbauer spectrum displays two characteristic ferrous and ferric quadrupole doublets, the abundance ratio Fe(II)/Fe(III) of which is close to 1. Comparison with synthetic mixed valence Fe(II)-Fe(III) hydroxides supports the conclusion that the most probable formula is $\text{Fe}_3(\text{OH})_8$, i.e., according to the pyroaurite-like crystal structure $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_4]^+ \cdot [\text{OH}]^-$. The microprobe Raman spectrum exhibits two bands at 518 and 427 cm^{-1} as for synthetic green rusts. When exposed to the air, the new mineral goes rapidly from bluish-green to ochrous. The formula is compatible with the values of ionic activity products Q for equilibria between aqueous iron species and minerals obtained from soil waters, which suggests that this new mineral is likely to control the mobility of Fe in the environment. Copyright © 1997 Elsevier Science Ltd

Green-blue colours showing in the deepest horizons of reductomorphic soils are frequently assumed to come from Fe(II)-Fe(III) hydroxides similar to synthetic green rusts compounds first prepared by Girard and Chaudron (1935), Feitknecht and Keller (1950), and since then by many others (cf. Schwertmann and Taylor, 1989). They are distinguished by their X-ray diffraction (XRD) pattern, green rust one (GR1), and green rust two (GR2) (Bernal et al., 1959), and Taylor (1973) proposed that they are part of the pyroaurite-sjögrenite group and consist of brucite-like layers carrying a positive charge alternating with layers constituted of anions and water molecules (Taylor, 1973; Génin et al., 1986; Olowe and Génin, 1991; Refait and Génin, 1993, 1994; Refait et al., 1994; Drissi et al., 1995; Génin et al., 1996). However, the anion determination is difficult. For this reason and because of the small presumed amount of green rusts in soils, XRD is not relevant for identification. In contrast, Mössbauer spectroscopy, sensitive only to iron atomic environments, is suited. Hansen et al. (1994) synthesized the sulphate green rust $\text{GR2}(\text{SO}_4^{2-})$ by repeating the protocol by Arden (1950), proposed an evaluation of the solubility product of this compound, and followed the reaction of NaNO_2 with $\text{GR2}(\text{SO}_4^{2-})$. They conclude that "if present in soils and sediments, green rusts may participate in abiotic reduction of nitrite" (Hansen et al., 1994) and could play a key role in the abiotic reduction of nitrate to ammonium (Hansen et al., 1996). However, as underlined by Hansen et al. (1994), "positive identification of the naturally occurring green compounds still awaits," and indeed reports of the natural occurrence of green rusts remain scarce, either related

to the rusting of man-made iron materials in anoxic condition (Stampfl, 1969; Bigham and Tuovinen, 1985; Olowe et al., 1990; Génin et al., 1993) or to precipitation in sludge (Bender Koch and Mørup, 1991). In depicting the speciation of Fe in soils from the geochemical study of soil solutions in situ (Ponnamperuma et al., 1967; Maître, 1991; Bourrié and Maître, 1994), a hypothetical Fe(II)-Fe(III) mineral written as $\text{Fe}_3(\text{OH})_8$ was suggested.

The purpose of this paper is to bring evidence for the existence of green rust as a natural mineral in soils for the first time. Mössbauer and Raman spectroscopies are used to identify this mineral and to compare it with different types of synthesized green rusts.

Reductomorphic soils often display a green-blue colour that changes rapidly to ochre on exposure to the air (Nguyen Kha and Duchaufour, 1969; Avery, 1973; Duchaufour et al., 1976). The green-blue colour of soils is frequently ascribed to the presence of green rusts (Taylor, 1981). A profile consisting of a granitic saprolite underlying genetic horizons of a soil testifying waterlogging is selected in the forest of Fougères (Ille and Vilaine). The horizon sampled is the reductive Gr horizon, according to the Référentiel Pédologique (Baize and Girard, 1995) at 25 cm depth. Once exposed to the air, the colour changes rapidly from a homogeneous bluish-grey colour (5BG6/1 of Munsell's chart) to greenish-grey (5GY6/1) after about 10 min, then to pale olive (5Y6/4) after one hour, and finally turns grey with light olive scattered spots (2.5Y5/6) after one day exposure. A large fresh soil sample is kept in anoxic conditions in a container

Table 1.

Majors (percent)											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Loss of ignition					
70.7	13.8	3.89	0.02	1.19	0.21	8.2					
Traces (ppm)											
V	Ni	Cr	Ba	Ga	Ca	Zn	Th	Pb	U	Nb	Zr
142	29	112	605	17	19	65	10	21	3.3	15.9	>347
Y	Sr	Rb	Co								
37	69	128	17								

with the aqueous solution collected in the sampling pit. Any unwitting oxidation is avoided (no change of colour is observed) and the Mössbauer experiment is done at 78 K on materials, about 100 mg, taken out of the core of the oversized sample. Bulk analysis (Table 1) shows that the total Fe amount is about 4% (Fe₂O₃). The hyperfine parameters of a Mössbauer spectrum (Fig. 1) are gathered in Table 2. Computer fitting is done using Lorentzian-shape line peaks with adjustable widths and Mössbauer *f* factor is the same for all Fe sites. Peak intensities are freely fitted. All green rusts spectra present two types of quadrupole doublets (cf.

Fig. 1; Génin et al., 1986, 1996; Drissi et al., 1995). One type, with an isomer-shift (IS) and quadrupole splitting (QS) of about 0.45 mm s⁻¹ and 0.50 mm s⁻¹, respectively, corresponds to Fe³⁺ ions, whereas the other type with IS and QS of about 1.25 mm s⁻¹ and 2.85 mm s⁻¹ corresponds to Fe²⁺ ions. Since the spectrum of the natural sample has a much smaller absorption percent, about 2%, compared to that of synthetic samples, up to 15%, it is difficult to put more quadrupole doublets; minor other components cannot be excluded, due to spurious Fe environments such as iron silicates etc.

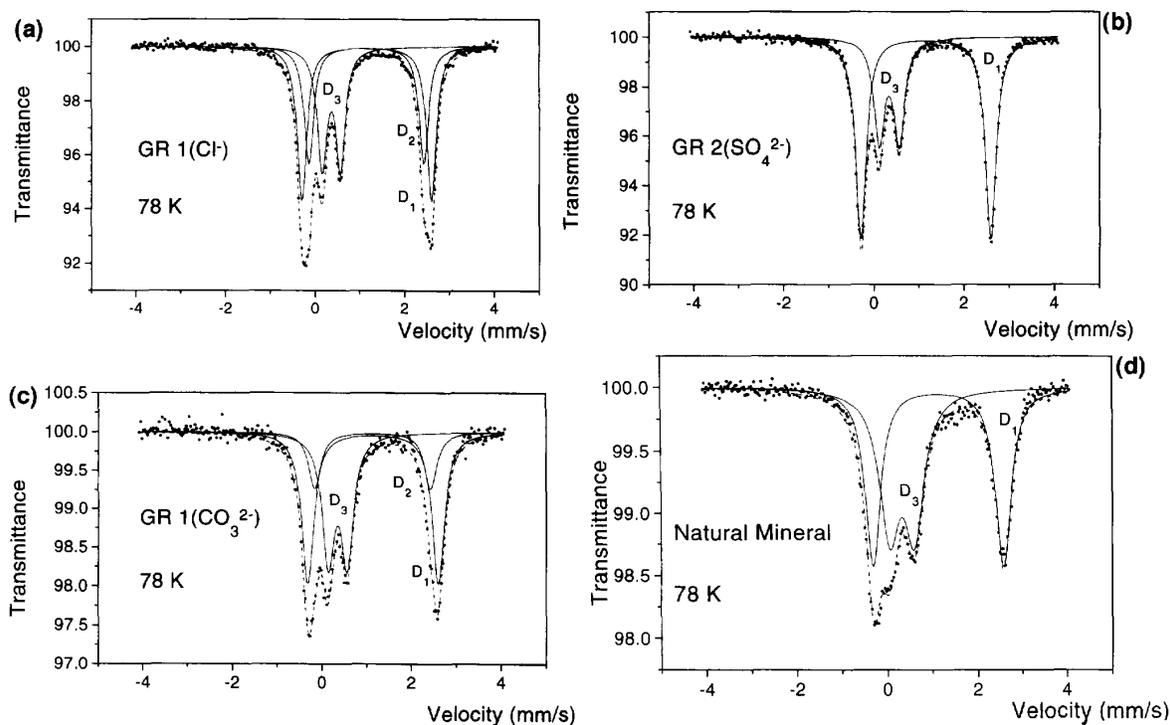


Fig. 1. Mössbauer spectra measured at 78 K of synthetic green rusts and of the studied mineral sample. (a) GR1(Cl⁻). (b) GR2(SO₄²⁻). (c) GR1(CO₃²⁻). (d) Natural sample.

Table 2.

	IS mm s ⁻¹	QS mm s ⁻¹	W mm s ⁻¹	RA (%)	Ref.
GR1(Cl⁻)					1
D ₁	1.26	2.88	0.34	46	
D ₂	1.25	2.60	0.34	26	
D ₃	0.47	0.41	0.34	28	
GR2(SO₄⁻)					2
D ₁	1.27	2.86	0.29	66	
D ₃	0.48	0.45	0.29	34	
GR1(CO₃⁻)					3
D ₁	1.27	2.92	0.28	49	
D ₂	1.28	2.69	0.28	17	
D ₃	0.47	0.43	0.28	34	
Mineral					This study
D ₁	1.25	2.87	0.40	50.7	
D ₃	0.45	0.54	0.51	49.3	

ref. (1) Génin *et al.* (1986); (2) Génin *et al.* (1996); (3) Drissi *et al.* (1995)

In order to confirm the identification of the green rust by Mössbauer spectroscopy, a Raman characterization is performed. A special cell used for Raman experiments allows us to keep the sample in a nitrogen or argon atmosphere in the absence of oxygen. The sample is set under an Ar flow in a glove box and the cell is tightly closed by a glass window through which a laser beam is focused and the Raman backscattering collected. The cell is mounted in the focal plane of an

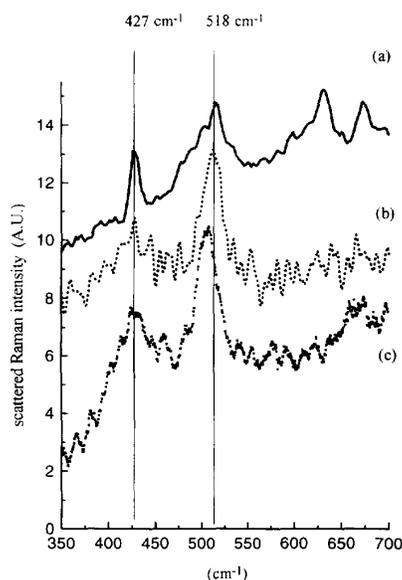


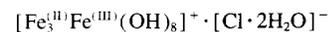
Fig. 2. Microprobe Raman spectra of synthetic green rusts and of the studied mineral sample. (a) Natural sample. (b) GR1(CO₃⁻). (c) GR1(Cl⁻). The mineral sample is made of small particles of about 5 μm. The laser beam at 514.53 nm wavelength is focused on an area of about 2 μm of diameter with a power lower than 1 mW.

Olympus B.H. microscope in a Jobin-Yvon/Instrument S.A. T 64000 Raman microprobe equipped with Charged Coupled Device detector and a motorized X-Y stage. A large working distance objective length of 50 × magnification is used; thus a true magnification at the viewing screen of about 1500 × and a viewing image of about 2 μm are achieved. A 514.53 nm exciting radiation is used with a power lower than 1 mW to prevent sample degradation. The spectra resolution is of about 6 cm⁻¹ and the precision on the wavenumber is 1 cm⁻¹. Three spectra obtained by the Raman microprobe are displayed in Fig. 2. The spectrum of the mineral green rust (Fig. 2.a) shows the same characteristic bands at 518 and 427 cm⁻¹ (cf. Boucherit *et al.*, 1992) as the synthetic green rusts (Fig. 2b,c).

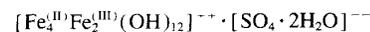
Therefore, the identification of a green rust mineral is established in a natural environment by two methods and the Fe(II)/Fe(III) abundance ratio is equal to one (50.7/49.3), favouring a definite stoichiometry.

Under laboratory conditions, the oxidation of Fe(OH)₂ precipitates in the presence of chloride, sulphate, and carbonate ions leads to the obtention of pure green rusts, GR1(Cl⁻) (Génin *et al.*, 1986; Refait and Génin, 1993, 1994), GR2(SO₄⁻) (Olowe *et al.*, 1991; Génin *et al.*, 1996), and GR1(CO₃⁻) (Drissi *et al.*, 1995) for acidic media and GR1(OH⁻) (Refait *et al.*, 1994) for basic media. E_h-pH diagrams were established (Refait and Génin, 1993; Drissi *et al.*, 1995; Génin *et al.*, 1996) with standard chemical potentials and Mössbauer spectra (Génin *et al.*, 1986, 1996; Drissi *et al.*, 1995). Various chemical formulae at stoichiometry are:

GR1(Cl⁻) (Refait and Génin, 1993)



GR2(SO₄⁻) (Génin *et al.*, 1996)



GR1(CO₃⁻) (Drissi *et al.*, 1995)

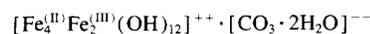


Table 3.

Temperature. (°C)	9.2	8.9	8.7	9.2	8.9	8.9	8.9
pH	5.15	5.15	5.35	5.50	5.70	5.70	5.55
pe	9.75	9.80	9.79	9.67	10.16	10.34	10.59
Fe(II) (10 ⁻⁶ M)	2.07	1.11	0.92	0.102	0.104	0.087	0.088
log [Fe ²⁺]	-5.77	-6.14	-6.12	-7.07	-7.06	-7.13	-7.15
log [SO ₄ ⁻]	-3.87	-3.88	-3.99	-4.05	-4.23	-4.17	-4.14
log [CO ₃ ⁻]	-10.13	-8.38	-9.63	-9.16	-8.76	-8.69	-9.50
log Q[GR1(CO ₃ ⁻)]	36.56	36.18	37.47	33.76	37.58	37.60	35.38
log Q[GR2(SO ₄ ⁻)]	42.81	40.69	43.11	38.87	42.11	42.11	40.75
log Q[Fe ₂ (OH) ₅]	23.96	23.27	24.32	23.03	24.53	24.58	24.04

and the general formula of green rusts is $[\text{Fe}_{1-x}^{(II)}\text{Fe}_x^{(III)}(\text{OH})_2]^{x+} \cdot [x/n \text{A}^{-n} \cdot m/n \text{H}_2\text{O}]^{-x}$ in a normalized form, where A^{-n} are the inserted anions. Thus, in this study, we are looking for $[\text{Fe}_{0.5}^{(II)}\text{Fe}_{0.5}^{(III)}(\text{OH})_2]^{+0.5} \cdot [0.5/n \text{A}^{-n} \cdot m/n \text{H}_2\text{O}]^{-0.5}$. No quoted synthetic green rust fulfills the requirement, and we suggest a Fe(II)-Fe(III) GR1(OH⁻) which forms in the presence of an excess of OH⁻ ions (Refait et al., 1994), the formula of which is not yet definitively established. Ponnampetuma et al. (1967) proposed $\text{Fe}_3(\text{OH})_8$. However, since experimentally $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ is equal to 1, $\text{Fe}_2(\text{OH})_5$ is preferred, a formula already forwarded by Arden (1950). Written along the pyroaurite-like structure, it becomes $[\text{Fe}^{(II)}\text{Fe}^{(III)}(\text{OH})_4]^+ \cdot [\text{OH}]^-$, the way other green rusts are formulated (Refait and Génin, 1993; Drissi et al., 1995; Génin et al., 1996). The analysis of aqueous solutions of the surrounding environment in the field is consistent with this formula. The Ionic Activity Products Q between ion species and minerals are computed according to the quoted green rusts (Table 3; Maître, 1991; Bourrié and Maître, 1994) and are not in favour of GR1(Cl⁻), GR2(SO₄⁻) and GR1(CO₃⁻). However, one cannot exclude either nonstoichiometric green rusts or a plausible stoichiometric GR1(OH⁻). The solution relative to GR1(OH⁻) corresponds to the equilibrium: $\text{Fe}_2(\text{OH})_5 + 1/2 \text{e}^- + 5/2 \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 5/2 \text{H}_2\text{O}$, giving $\log Q = \{2 \log [\text{Fe}^{2+}] + 5 \text{pH} + \text{pe}\}$, where $[\text{Fe}^{2+}]$ is the activity of Fe²⁺ ions, pe the electron potential, i.e., ($E_h/0.05916$), and E_h the electrode potential relative to the hydrogen standard electrode. A statistical Student's test gives a value $x = 0.5$ in the general formula of green rust with a confidence interval [0.378; 0.622] for a probability of 0.9.

A new mineral, occurring in the natural environment of gleyey soils due to reductomorphic conditions, is identified by Mössbauer and Raman spectroscopies from the forest of Fougères (Brittany-France) for the first time. Its tentative formula is written as $\text{Fe}_2(\text{OH})_5$ or $[\text{Fe}^{(II)}\text{Fe}^{(III)}(\text{OH})_4]^+ \cdot [\text{OH}]^-$. Therefore, green rusts are genuine minerals, i.e., compounds forming in natural environments. More work should be done to define their occurrence and crystal structure, especially to establish definitely which anions balance the positive charges due to the presence of Fe(III)

and these minerals are likely to control the mobility of Fe in the environment.

Acknowledgments—We would like to thank A. Regeard for her help in the analysis of soil solutions.

Editorial handling: G. Faure

REFERENCES

- Arden T. V. (1950) The solubility products of ferrous and ferrous hydroxides. *J. Chem. Soc.*, 882–885.
- Avery B. W. (1973) Soil classification in the Soil Survey of England and Wales. *J. Soil Sci.* **24**, 324–337.
- Baize D. and Girard M. C. (ed.) (1995) *Référentiel Pédologique*. INRA.
- Bender Koch C. and Mørup S. (1991) Identification of green rust in an ochre sludge. *Clay Minerals* **26**, 577–582.
- Bernal J. D., Dasgupta D. T., and Mackay A. L. (1959) The oxides and hydroxides of iron and their structural inter-relationships. *Clay Mineral. Bull.* **4**, 15–30.
- Bigham J. K. and Tuovinen O. H. (1985) Mineralogical, morphological, and microbiological characteristics of tubercles in cast iron water mains as related to their chemical activity. In *Planetary Ecology* (ed. Caldwell et al.), 239–250. Van Nostrand Reinhold.
- Boucherit N., Hugot-Le Goff A., and Joiret S. (1992) In situ Raman identification of stainless steels pitting corrosion films. *Material Sci. Forum* **111–112**, 580–588.
- Bourrié G. and Maître V. (1994) Iron control in solution from hydromorphic soils under temperate climate by equilibrium with a mixed Fe(II)-Fe(III) mineral, ferrous-ferric hydroxide. *Proc. 15th World Congr. Soil Sci. Acapulco* **3b-II**, 143–144.
- Drissi H., Refait Ph., Abdelmoula M., and Génin J.-M. R. (1995) The preparation and thermodynamic properties of Fe(II)-Fe(III) hydroxycarbonate (green rust one); Pourbaix diagram of iron in carbonate-containing aqueous media. *Corros. Sci.* **37**, 2025–2041.
- Duchauffour P., Faivre P., and Gury M. (1976) *Atlas Ecologique des Sols du Monde*. Masson.
- Feitknecht W. and Keller G. (1950) Über die Dunkelgrünen Hydroxyverbindungen des Eisens. *Z. Anorg. Allg. Chem.* **262**, 61–68.
- Génin J.-M. R., Rézel D., Bauer P., Olowe A. A., and Béral A. (1986) Mössbauer spectroscopy characterization and electrochemical study of the kinetics of oxidation of iron in chlorinated aqueous media structure and equilibrium diagram of green rust one. *Electrochem. Meth. Corros. Res. Mat. Sci. Forum* **8**, 477–490.
- Génin J.-M. R., Olowe A. A., Resiak B., Rollet-Benbouzid N. D., Confente M., and Prieur D. (1993) Identification of sulphated green rust 2 compound produced as a result of microbially induced corrosion of steel sheet piles in harbour. In *Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects*; *Eur. Fed. Corr. Inst. Mater.* **10**, 162–166.
- Génin J.-M. R., Olowe A. A., Refait Ph., and Simon L. (1996) On the stoichiometry and Pourbaix diagram of Fe(II)-Fe(III) hydroxy-sulphate or sulphate-containing green rust 2; an electrochemical and Mössbauer spectroscopy study. *Corros. Sci.* **38**, 1751–1762.
- Girard A. and Chaudron G. (1935) Sur la constitution de la rouille. *C. R. Acad. Sci.* **200**, 127–129.
- Hansen H. C. B., Borggaard O. K., and Sørensen J. (1994) Evaluation of the free energy of formation of Fe(II)-Fe(III) hydroxide-sulphate (green rust) and its reduction of nitrite. *Geochim. Cosmochim. Acta* **58**, 2599–2608.
- Hansen H. C. B., Koch C. B., Nancke-Krogh H., Borggaard O. K., and Sørensen J. (1996) Abiotic nitrate reduction to ammonium: key role of green rust. *Environ. Sci. Tech.* **30**, 2053–2056.
- Maître V. (1991) Géochimie des eaux libres extraites de sols de sols hydromorphes sur granite dans le Massif Armoricain. Mobilité du fer et dynamique saisonnière Doctorat Thesis, University Pierre and Marie Curie.

- Nguyen Kha and Duhaufour P. (1969) Note sur l'état du fer dans les sols hydromorphes. *Science du Sol*, 97–110.
- Olowe A. A. and Génin J.-M. R. (1991) Mechanism of oxidation of ferrous hydroxide in sulfated aqueous media: importance of the initial ratio of the reactants. *Corros. Sci.* **32**, 965–984.
- Olowe A. A., Génin J.-M. R., and Guézennec J. (1990) Mössbauer effect study of microbially induced corrosion of steel by sulphate reducing bacteria in marine sediments: Role of green rust 2. In *Microbially Influenced Corrosion and Deterioration* (ed. N. J. Dowling et al.); Vol. 5, pp. 65–72. University of Tennessee & N.A.C.E., Knoxville TN.
- Ponnamperuma F. N., Tianco E. M., and Loy T. (1967) Redox equilibria in flooded soils: I. The iron hydroxide systems. *Soil Sci.* **103**, 90–100.
- Refait Ph. and Génin J.-M. R. (1993) The oxidation of ferrous hydroxide in chloride-containing aqueous media and Pourbaix diagrams of green rust one. *Corros. Sci.* **34**, 797–819.
- Refait Ph. and Génin J.-M. R. (1994) The transformation of chloride-containing green rust one into sulphated green rust two by oxidation in mixed Cl^- and SO_4^{2-} aqueous media. *Corros. Sci.* **36**, 55–65.
- Refait Ph., Drissi H., Marie Y., and Génin J.-M. R. (1994) The substitution of Fe^{+2} ions by Ni^{2+} ions in green rust one compounds. *Hyp. Intl.* **90**, 389–394.
- Schwertmann U. and Taylor R. M. (1989) Iron oxides. In *Minerals in Soil Environments* (ed. J. B. Dixon and S. B. Weed); *SSSA Book Series 1*, 378–438. Soil Sci. Soc. Amer.
- Stampfl P. P. (1969) Ein basisches Eisen-II-III-karbonat. *Corros. Sci.* **9**, 185–187.
- Taylor H. F. W. (1973) Crystal structures of some double hydroxide minerals. *Mineral. Mag.* **39**, 377–389.
- Taylor R. M. (1981) Colour in soils and sediments. A review. In *International Clay Conference 1981* (ed. Van Olphen and Veniale); *Device Sediment.* **35**, 749–761. Elsevier.