

A solid solution model for Fe^{II}-Fe^{III}-Mg Green Rust « fougérite »: structural and geochemical constraints

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Abstract

Fe(II)-Fe(III) green rust identified in soil as a natural mineral, for which the name "fougérite" has been proposed, is responsible for the blue - green colour of gley horizons, and exerts the main control on Fe dynamics (Trolard et al., 1997; Bourrié et al., 1999). An EXAFS study of the structure of the mineral, using preparation techniques that avoid any contact with oxygen from the atmosphere (Refait et al., 2001), confirms that the mineral belongs to the group of Green Rusts, in which brucite-like layers alternate with interlayers of anions and water molecules. According to the rhomboedral $R\bar{3}m$ crystal structure, the Fe - Fe distance corresponds to the parameter a of the conventional hexagonal lattice, *i.e.* 0.31-0.32 nm. The second peak of the pseudo radial distribution fonction (PRDF) P_2 peak is found at that distance, and the series of peaks is in accordance to the hexagonal array of successive neighbouring cations at $a\sqrt{3}$, $2a$, $a\sqrt{7}$, $3a$... However, the intensity of the P_2 peak is much less intense in the mineral than in synthetic green rusts. The comparison with synthetic pyroaurites shows that this is due to a partial substitution of Fe^{II} by Mg^{II} in the brucite-like layer, which leads to the general formula of the mineral : $[Fe_{(1-x)}^{II}Mg_y^{II}Fe_x^{III}(OH)_{2+2y}]^{+x} \cdot [x OH^- \cdot (1-x+y) H_2O]^{-x}$, where one water molecule is supposed intercalated over each Mg- occupied site as for Fe. From this finding, the regular solid solution model proposed previously (Génin *et al.*, 2001) must be modified, with provision for Mg incorporation in the mineral. Ionic Activity Products must then be written for each of the three end-members: Mg(OH)₂, Fe(OH)₂ and Fe(OH)₃, the pure end-members keeping the crystal structure of the green rust. Soil solutions from hydromorphic soils are used to check the model and to constrain the ranges of variation of the mole ratios $x = Fe^{III}/Fe_{total}$ and $y = Mg/Fe_{total}$.

Introduction

Green-blue colour in soils has been used as a diagnosis criterion in the definition of gley and soil classification since the early beginning of soil science, and ascribed immediately to the presence of Fe(II) oxide, called "protoxide", by Vysotskii (1905,[1999]). In the process of corrosion of steel, the role of a mixed Fe(II)-Fe(III) hydroxide called "hydrated magnetite" has been evidenced by Girard and Chaudron (1935). Bernal et al. (1959) have shown that these compounds were hydroxysalts rather than hydroxides or oxides and they designated them under the generic name of « green

rusts » (hereafter abbreviated as GRs). Stampfl (1969) identified the carbonate form as a corrosion product of urban water pipes and observed that GRs belonged to a large group of isostructural M(II)-M(III) hydroxides, the group of pyroaurite-sjögrenite, with Ca(II)-Al(III), Mg(II)-Fe(III) compounds among others. These compounds are highly reactive and labile, and when in contact with oxygen from the atmosphere, they readily oxidize into lepidocrocite or goethite, so that they cannot be determined by classical methods of preparation of soil samples, i.e. after air-drying. Moreover, their small abundance precludes their determination by XRD. The study of these compounds has thus remained confined to the laboratory and to synthetic products mostly in the field of corrosion science (Génin and coworkers). The discovery of these compounds in natural environments, specifically acid to neutral gley soils (Trolard et al., 1996 ; 1997) has confirmed the hypothesis formulated by Vysotskii (1905) about the existence of Fe(II) oxide in gley soils, and demonstrated for the first time the existence of GR as a natural mineral, for which the name « fougerite » and the global formula $\text{Fe(II)}_{1-x}\text{Fe(III)}_x(\text{OH})_{2+x}$ has been proposed.

This was obtained by combining Mössbauer and Raman spectroscopies and selective kinetic extraction technique. The mole ratio x is directly given by Mössbauer spectroscopy and the results obtained show that it is not constant and ranges from $x = 1/3$ to $2/3$ (Abdelmoula et al., 1998; Génin et al., 1998b). The analysis of soil solution and computation of Ionic Activity Products (*IAP*) show that (i) solutions are undersaturated with respect to chloride-, carbonate- and sulfate- GRs, the solubility products of which were previously known from laboratory studies of these synthetic products; (ii) conversely *IAPs* for GR-OH are quasi constant when the master variables (pH, p_e and $\log[\text{Fe}^{2+}]$) vary, and close to the value earlier proposed for $\text{Fe}_3(\text{OH})_8$ by Ponnamperna et al. (1967). Moreover, the « best » values of x estimated from the computation of *IAPs* are identical to the values obtained directly in the same locations by Mössbauer spectroscopy (Génin et al., 1998b; Bourrié et al., 1999). Tentative values were proposed for the standard enthalpies of formation of the three types of GR-OH evidenced in the field, namely for $x = 1/3$, $1/2$ and $2/3$ considered as discrete values (Bourrié et al., 1999). A solid solution model was later fitted to these data and to the experimental value for $\text{Fe}(\text{OH})_2$ from the literature (Génin et al., 2001), which proved to be regular and not ideal. Then an EXAFS study was undertaken on the mineral and synthetic GRs and pyroaurites, which (i) confirmed that the mineral belongs to the GRs group, but (ii) led to the conclusion that the natural mineral contains Mg(II) in addition to Fe(II) and Fe(III), which cannot be seen by Mössbauer spectroscopy (Refait et al., 2001), and was not taken into account in the solid solution model. The aim of this paper is thus to discuss the structural and geochemical constraints that must satisfy a solid solution model for Mg(II)-Fe(II)-Fe(III) GR.

Structure of the mineral and structural constraints for a solid solution model

Green Rusts consist of brucite-like layers of $\text{Fe}(\text{OH})_2$ in which part of Fe(II) is oxidized into Fe(III), the excess of charge being compensated by interlayered anions ; the interlayers are hydrated. Two types of structure exist depending on the nature of interlayered anions.

- With spherical or planar anions such as chloride and carbonate, GR1 compounds are obtained in which the stacking sequence is *AcBiBaCjCbAkA...* (Génin et al., 1998a)

where *A-C* designate OH⁻ planes, *a-c* metal cations layers and *i-k* intercalated layers, and the structure is rhomboedral. More specifically, the XRD study of GR1(Cl) (Refait et al., 1998a) shows that the structure resembles that of pyroaurite [Mg(II)₆Fe(III)₂(OH)₁₂]²⁺ [CO₃²⁻ • 4H₂O] and iowaite, a Mg(II)-Fe(III) pyroaurite-like mineral incorporating Cl⁻ anions. The rhomboedral structure is due to the stacking sequence of layers *AB BC CA*. Fe(II) and Fe(III) cations are distributed randomly among the octahedral positions. Water molecules in the interlayer are situated close to the 3-fold axis which connects two OH⁻ ions of adjacent hydroxide layers. The fit of the intensities of peaks improved with H₂O molecules slightly closer to the OH-OH 3 fold axis, at 0.032 nm vs. 0.080 nm for Cl⁻, which is consistent with the larger ionic radii of Cl⁻ (0.181 nm) as compared to OH⁻ (0.135 nm) (Shannon, 1976). The refined structure for GR1 (Cl) is thus rhomboedral, the symmetry group is $R\bar{3}m$ and the parameters of the conventional hexagonal lattice are $a = 0.31901$ nm and $c = 2.3856$ nm, where the interlayer to interlayer distance is $c/3$. In the GR1(Cl) studied, the mole ratio $x = 1/4$, so the structural formula obtained is [Fe(II)₃Fe(III)₃(OH)₈]⁺[Cl⁻•2H₂O], with two water molecules and one anion per mole formula. The mole ratio x is not constant however in GR1(Cl), and values were observed in the range from 1/4 to 1/3 until now (Refait et al., 1998a).

- With tetrahedral anions, such as sulphate and selenate, GR2 compounds form, in which the stacking sequence is the original sequence of Fe(OH)₂, *i.e.* *AcBiA...* (Génin et al., 1998a). GR2s crystallize in the trigonal system, and the c parameter is much smaller, since it corresponds to a single interlayer to interlayer distance. However, due to the larger size of the anions, two layers of water molecules can be intercalated.

The exact nature of the compensating anion in the Green Rust mineral « fougerite » cannot be directly determined as its abundance is small (total Fe₂O₃ content in soil is *ca.* 4 % only), the mineral is labile and cannot be separated from the other minerals and Mössbauer spectroscopy is only sensitive to Fe. From the composition of soil solutions analyzed in the localities where GRs were identified, it was concluded that the most likely anion is simply OH⁻ (Trolard et al., 1996 ; 1997 ; Génin et al., 1998b ; Bourrié et al., 1999), which leads to a general formula [Fe(II)_{1-x}Fe(III)_x(OH)₂]^{+x}[x OH⁻], with x ranging from 1/3 to 2/3. The GR “fougerite” would then be similar to meixnerite, a natural Mg₆Al₂(OH)₁₈ • 4H₂O, a nearly CO₂-free mineral that transforms rapidly to hydrotalcite, the carbonate form, in the presence of CO₂ (Koritnig and Susse, 1975). Synthetic [Mg(II)_{1-x}Al(III)_x(OH)₂]^{+x}[x OH⁻ • (0.81- x) H₂O] with $0.23 \leq x \leq 0.33$ could be obtained in CO₂ free conditions (Mascolo and Marino, 1980).

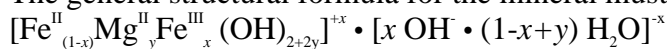
The structure was thus assumed to be analogous to GR1(Cl) , since OH⁻ is spherical as Cl⁻ ; but the latter anion has a larger size than the former, and in GR1(Cl), one water molecule is missing between two neighbouring anions. Instead, in GR1(OH), the interlayer space can be completely filled with water molecules and OH⁻ ions, that are of the same size, in a compact pavement, which leads to the complete general formula [Fe(II)_{1-x}Fe(III)_x(OH)₂]^{+x}[x OH⁻ (1- x) H₂O], or globally Fe(OH)_{2+x}. The variation of x when the mineral is oxidized or reduced does not imply the diffusion of an interlayered anion to or from the external solution, but merely the deprotonation of a water molecule or the protonation of a OH⁻ anion, which is extremely fast. This can explain the large range of variation observed for the mineral as compared to synthetic GRs. The structure for GR1(OH) was thus proposed to be analogous to GR1(Cl), with a

symmetry group $\bar{R}3m$ and lattice parameters $a \cdot 0.32$ nm and $c \cdot 2.25$ nm, *i.e.* the same value for a , but a smaller value for c , due to the smaller size of OH⁻ (Génin et al., 2001). The structure of the mineral was studied by X-ray absorption spectroscopy (XAS), both by recording the Extended X-ray absorption fine structure signal (EXAFS) and the X-ray absorption near edge structure signal (XANES) at the Fe K -edge, along with transmission Mössbauer spectroscopy (TMS). The same techniques were applied to synthetic GR1(Cl), GR1(CO₃), and to a synthetic pyroaurite with approximate formula [Mg(II)₅Fe(III)(OH)₁₄]²⁺[CO₃²⁻• n H₂O]. Two samples of hydroxycarbonates obtained by mixing Fe²⁺, Fe³⁺ and Mg²⁺ salts and coprecipitating hydroxides by addition of NaOH in presence of Na₂CO₃ were also prepared and analyzed by TMS. The x mole ratios were measured by Mössbauer spectroscopy, and powder X-ray diffractograms were performed on the synthetic samples. The global formulae of the compounds obtained were Fe(II)₂Mg(II)₂Fe(III)₂(OH)₁₂CO₃ and Fe(II)₄Mg(II)₂Fe(III)₂(OH)₁₆CO₃.

The main results obtained are the following (Refait et al., 2001):

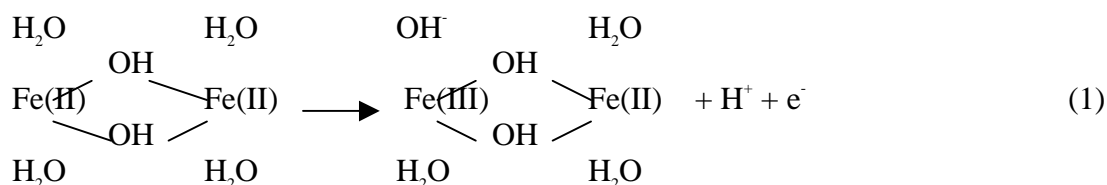
- (i) both Fe²⁺ and Fe³⁺ valence states occur in close neighbourhood, as evidenced from the XANES part of spectrum, which is sensitive to the oxidation state of Fe and to its local symmetry, that are very similar for GR1(CO₃) and the mineral; thus there are no separate clusters of Fe²⁺ and Fe³⁺;
- (ii) the mineral is confirmed as belonging to the group of GR1, as TMS spectra of the mineral and of the synthetic GR1s display the same sets of quadrupole doublets;
- (iii) the lattice parameter a , is obtained at about 0.31-0.32 nm, as earlier predicted, from the second P₂ peak, *i.e.* the Fe-Fe distance, of the Pseudo-radial distribution function (PDRF) ;
- (iv) no information can be obtained on the exact nature of the anion and the value of c parameter cannot be estimated as the signal is not sensitive to the interlayer occupancy, which is too far from the absorbing atoms and/or is composed of atoms with small atomic numbers Z ;
- (v) the positions of farther – and smaller - peaks of the PRDF correspond to the hexagonal array of cations, second, third etc. neighbours of Fe, in the sequence $a \cdot 3$, $2a$, $a \cdot 7$, $3a$ (Roussel et al., 2000).
- (vi) Mg substitutes for Fe in the mineral ; the evidence for this is that the intensities of peaks of the mineral do not match the intensities of GR1s either Cl or CO₃, which are very close to each other. The intensities of the Fe-Fe peaks P₂ for the synthetic GR1(Cl) and GR1(CO₃) are much larger than for the mineral. An even larger decrease of the intensity of P₂ peak is observed with synthetic pyroaurite, the PRDF of the mineral being thus intermediate between PRDF of GR1s and PRDF of synthetic pyroaurite ;
- (vii) the *local ratio* Mg/Fe is about 2 ± 1 ; this was estimated by fitting the contributions of Mg and Fe to the back-Fourier transform of the PRDF curve : in the case of synthetic GR1s, no Mg is present and backscattering atoms are Fe atoms, whereas in synthetic pyroaurite, each Fe atom is surrounded by Mg atoms, so that Mg atoms are the only backscattering atoms. The signal of the mineral could thus be fitted as a linear combination of the signals of synthetic pyroaurite and GR1s, with $a = 0.3125$ nm, specifically Fe-Fe = 0.312 ± 0.0005 nm, and Fe-Mg = 0.313 ± 0.0005 nm.

The general structural formula for the mineral must then be modified as :



From structural considerations, the lower possible value for x is zero, which would correspond to a solid solution between Fe(OH)₂ and Mg(OH)₂. The effective ionic radii

of Fe^{2+} and Mg^{2+} are very close to each other, respectively 0.078 nm and 0.072 nm, so that extensive substitution is possible and indeed most natural Fe(II) oxides, hydroxides and silicates admit continuous series between pure Fe(II) and Mg(II) end-members. The upper limit for GR1(OH) was proposed as $x = 2/3$ (Génin et al., 2001). According to Vucelic et al. (1997), there exists a local ordering so that Fe^{3+} cations never neighbour each other. As each cation is surrounded by 6 cations, this means that this rule can be generalized now as : every Fe^{3+} must be surrounded by 6 bivalent cations, either Fe^{2+} or Mg^{2+} . The basic question is thus : what is the exact structural cause of this limitation ? For GR1(OH), the excess positive charge is compensated in the interlayer by deprotonation of the water molecule, so that the elementary reaction of oxidation can be written as :



A further oxidation leading to two neighbouring Fe(III) would result then in two neighbouring OH in the interlayer. This is *a priori* structurally possible, but rather than deprotonating the remote interlayer water molecule, the repulsive field exerted by the two Fe(III) atoms would result in the deprotonation of the OH of the layer itself by an « oxolation » process (Jolivet, 1994) and to Fe(III)-O-Fe(III) bonds. The Green Rust structure is then no longer stable and it transforms into magnetite with spinel inverse structure, or oxyhydroxides such as lepidocrocite (Olowe and Génin, 1991).

Substitution of Fe(II) by Mg(II) in the structure stabilizes the Green Rust structure and the x mole ratio is allowed to increase to a limit given by the inequality :

$$\frac{\text{Fe(II)} + \text{Mg(II)}}{\text{Fe(III)}} \geq 2 \text{ or equivalently, } (1-x+y)/x \geq 2, \text{ i.e. } x \leq (1+y)/3 \quad (2)$$

• For $y = 0$, this corresponds to $x \leq 1/3$, i.e. to the global formula $\text{Fe}_3(\text{OH})_7$. This implies that the values obtained earlier for $x = 1/2$ ($\text{Fe}_2(\text{OH})_5$) and $x = 2/3$ ($\text{Fe}_3(\text{OH})_8$) must be ascribed in fact to Mg(II) – Fe(II) – Fe(III) GRs. It is worthwhile to note that the GRs heretofore synthesized without Mg have x ratios smaller than 1/3 (Table 1), except in one case, GR1(Cl), with a slightly larger value ($x = 0.36$), which either is not significantly different from $x = 1/3$ or would indicate that with some anions it is possible to accommodate a small increase of Fe(III). Moreover, in the case of selenate-GR2, the precipitate starts with $x = 1/3.25$, then x increases to a maximum value $x = 1/3$, over which it oxidizes into iron(III) oxyhydroxides FeOOH . It can thus be concluded that the inequality $x \leq 1/3$ is satisfied when $y = 0$, from all the experimental results obtained so far. Any further oxidation leads to formation of iron oxyhydroxides, lepidocrocite, goethite, or akaganeite, or to the formation of magnetite – maghemite minerals. Similar conclusions applied also to compounds based on other trivalent cations than Fe. It is for example the case for synthetic meixnerite, $[\text{Mg(II)}_x \text{Al(III)}_x (\text{OH})_2]^{+x} [x \text{ OH}^- \cdot (0.81-x) \text{ H}_2\text{O}]$, which were found to have $0.23 \leq x \leq 0.33$ (Mascolo and Marino, 1980).

Table 1 : Structural formulas and Gibbs free energies of formation at 298.15 K, 1 bar of synthetic Green Rusts, $x = \text{Fe(III)}/\text{Fe}_{\text{total}}$ mole ratio.

Structural formula	Group	x	Ref.	$\mu^{\circ}\text{exp.}$ kJ mol ⁻¹	$\mu^{\circ}\text{calc.}^c$ kJ mol ⁻¹
$[\text{Fe(II)}_3\text{Fe(III)(OH)}_8]^+[\text{Cl}^- \cdot 2\text{H}_2\text{O}]^-$	GR1	1/4	1	-2145 ± 7^a	-2132
$[\text{Fe(II)}_6\text{Fe(III)}_2(\text{OH})_{16}]^{2+}[\text{SO}_3^{2-} \cdot 4\text{H}_2\text{O}]^{2-}$	GR1	1/4	2	-	-5162
$[\text{Fe(II)}_6\text{Fe(III)}_2(\text{OH})_{16}]^{2+}[\text{C}_2\text{O}_4^{2-} \cdot 3\text{H}_2\text{O}]^{2-}$	GR1	1/4	3	-5383 ± 3^b	-5365
$[\text{Fe(II)}_{5.5}\text{Fe(III)}_2(\text{OH})_{15}]^{2+}[\text{SeO}_4^{2-} \cdot 8\text{H}_2\text{O}]^{2-}$	GR2	1/3.25	4	-	-5007
$[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+}[\text{SeO}_4^{2-} \cdot 8\text{H}_2\text{O}]^{2-}$	GR2	1/3	4	-	-4006
$[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+}[\text{SO}_4^{2-} \cdot 8\text{H}_2\text{O}]^{2-}$	GR2	1/3	5	-3790 ± 10^a	-3807
$[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+}[\text{CO}_3^{2-} \cdot n\text{H}_2\text{O}]^{2-}$	GR1	1/3	6, 7	-3590 ± 5^a	-3872

1. Refait et al., 1998a ; 2. Génin et al., 1996a ; 3. Refait et al., 1998b ; 4. Refait et al., 2000 ; 5. Refait et al., 1999 ; 6. Hansen, 1989 ; 7. Drissi et al., 1995 ; a. Bourrié et al., 1999 ; b. ref. 3 ; c. this paper (*cf. infra*).

• For $y = 0$, *i.e.* when other divalent metals substitute for Fe(II), further oxidation is possible as soon as the inequality (2) is fulfilled. Such a compound was synthesized, with $x = 1/2$ and $y = 1/2$, by co-precipitation of Mg^{2+} , Fe^{2+} and Fe^{3+} salts, at stoichiometry : $[\text{Mg(II)}_2\text{Fe(II)}_2\text{Fe(III)}_2(\text{OH})_{12}]^+[\text{CO}_3^{2-} \cdot n\text{H}_2\text{O}]^-$ (Refait et al., 2001).

For $y = 1/2$, the limit is $x = 1/2$, which corresponds to the former formula $\text{Fe}_2(\text{OH})_5$ and for $y = 1$, the limit is $x = 2/3$, which corresponds to the former formula $\text{Fe}_3(\text{OH})_8$. These compounds, whose Fe(II)/Fe_{total} ratios were observed in hydromorphic soils, can thus only be stable if they incorporate other divalent cations than Fe(II), for which Mg(II), due to its abundance in the environment is the more likely candidate.

The proposed complete formulas for the mineral are given in Table 2, under the assumption that the total number of water molecules and OH⁻ ions is constant and equal to the total number of cations in the mole formula, with one monolayer of water in GR1 type compounds. Larger Mg substitutions are possible, as this consists simply in diluting Fe atoms, and from $y = 2$, the complete oxidation of iron is possible, which leads to a compound isomorphous to pyroaurite, with OH⁻ as a compensating anion instead of carbonate. The inequality (2) can be graphically drawn in a triangular diagram in the system $\text{Mg}(\text{OH})_2 - \text{Fe}(\text{OH})_2 - \text{Fe}(\text{OH})_3$ (Figure 1).

Table 2 : Proposed structural formulas for the GR1(OH) mineral, with $x = \text{Fe(III)}/\text{Fe}_{\text{total}}$ mole ratio, and $y = \text{Mg}/\text{Fe}_{\text{total}}$ mole ratio (Refait et al., 2001), and for the isomorphous OH⁻ analogue of pyroaurite.

Structural formula (for minimum value of y)	x	y^a
$[\text{Fe(II)}_2\text{Fe(III)(OH)}_6]^+[\text{OH}^- \cdot 2\text{H}_2\text{O}]^-$	1/3	0
$[\text{Mg(II)Fe(II)Fe(III)(OH)}_6]^+[\text{OH}^- \cdot 2\text{H}_2\text{O}]^-$	1/2	1/2
$[\text{Mg(II)}_3\text{Fe(II)Fe(III)}_2(\text{OH})_{12}]^{2+}[\text{2OH}^- \cdot 4\text{H}_2\text{O}]^{2-}$	2/3	1
$[\text{Mg(II)}_2\text{Fe(III)(OH)}_6]^+[\text{OH}^- \cdot 2\text{H}_2\text{O}]^-$	1	2

a. minimum value for y (see text)

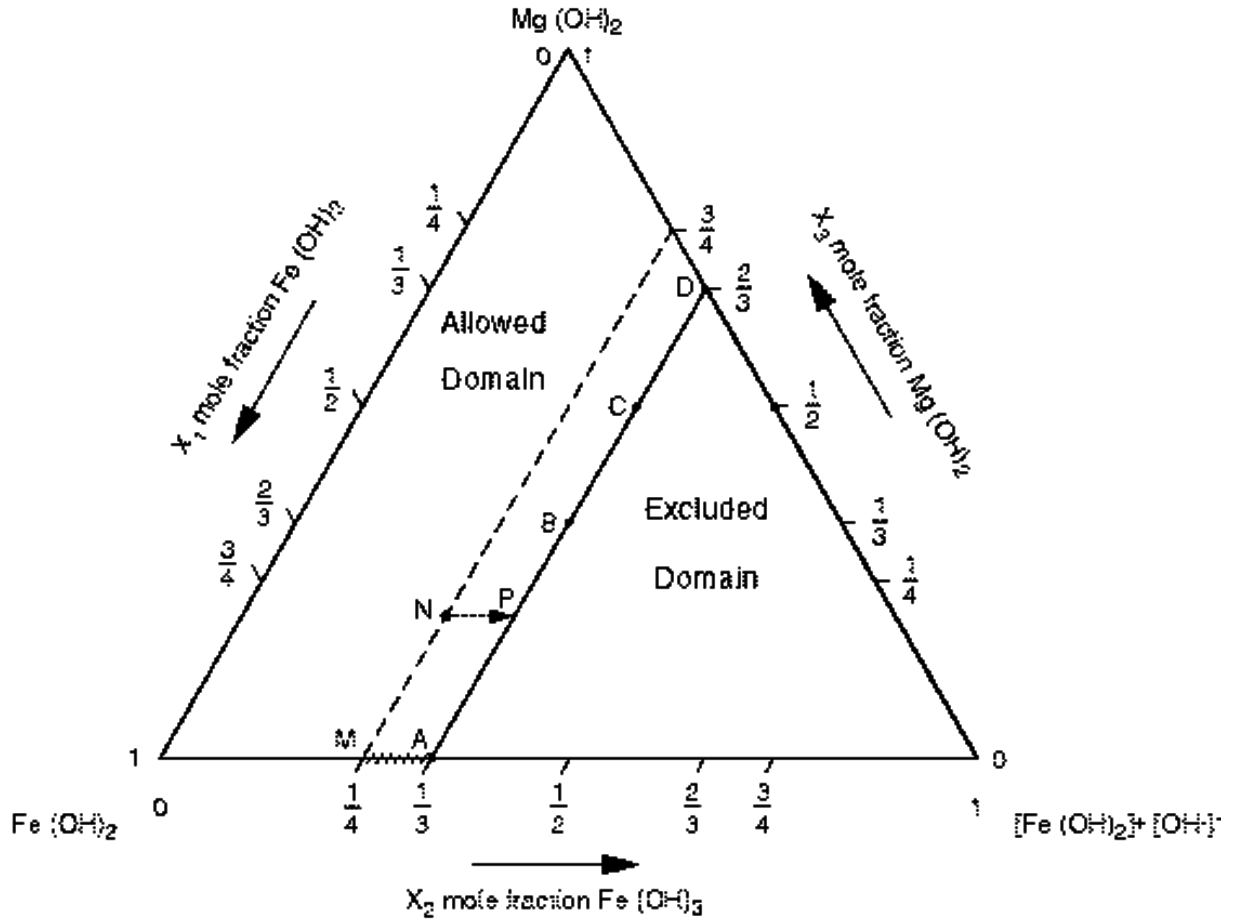


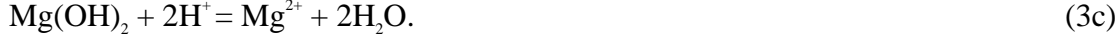
Figure 1 : Diagram for the ternary system $\text{Mg}(\text{OH})_2 - \text{Fe}(\text{II})(\text{OH})_2 - \text{Fe}(\text{OH})_3$.
Solid line : limit between the excluded domain and the domain allowed for GR structure to be stable;
dashed line : limit of the incipient precipitation of GR ; M-A (hatched) : interval of composition of synthetic GRs ; A. $\text{Fe}_3(\text{OH})_7$; B. previously « $\text{Fe}_2(\text{OH})_5$ » $\equiv [\text{MgFe}(\text{II})\text{Fe}(\text{III})(\text{OH})_6]^+[\text{OH} \cdot 2\text{H}_2\text{O}]^-$;
C. previously « $\text{Fe}_3(\text{OH})_8$ » $\equiv [\text{Mg}_3\text{Fe}(\text{II})\text{Fe}(\text{III})_2(\text{OH})_{12}]^{2+}[\text{2OH} \cdot 4\text{H}_2\text{O}]^{2-}$; D. limit with complete oxidation of Fe $[\text{Mg}_2\text{Fe}(\text{III})(\text{OH})_6]^+[\text{OH} \cdot 2\text{H}_2\text{O}]^-$; N-P : path of oxidation of natural GR (see text).

The Fe(III) mole fraction must be less than 1/3, which separates the excluded domain from the domain where Green Rusts are structurally possible to form. Among excluded forms are not only $\text{Fe}(\text{OH})_3$, but all mixed purely iron hydroxides $\text{Fe}(\text{II})_{1-x}\text{Fe}(\text{III})_x(\text{OH})_{2+x}$ with $x \cdot 1/3$, including the previously considered compounds $\text{Fe}_2(\text{OH})_5$ and $\text{Fe}_3(\text{OH})_8$ (ferrosic hydroxide of Arden, 1950). This is consistent with the formula $\text{Fe}(\text{OH})_2 \cdot 2\text{FeOOH}$ for « hydrated magnetite » used by Olowe and Génin (1991), Refait and Génin (1993), which implies an oxidation of Fe(III)-Fe(III) bridges.

Geochemical constraints

The solid solution model earlier proposed (Génin et al., 2001) must be revised according to the presence of Mg in the mineral. This adds a degree of freedom to the system. The solid solution is now ternary, and the end-members are the hypothetical minerals with a GR1 structure of the same composition as $\text{Fe}(\text{OH})_2$, $[\text{Fe}(\text{OH})_2]^+[\text{OH}]^-$ and $\text{Mg}(\text{OH})_2$, but not necessarily with the same thermodynamic properties as their

isomers of different structure. The equilibrium between soil solution and the solid solution must then be checked by writing a separate equilibrium equation for each pole :



In the following, indices 1, 2 and 3 will refer respectively to Fe(II), Fe(III) and Mg(II) pure end-members. Ionic Activity Products for each pole are defined by :

$$\log IAP_1 = \log(\text{Fe}^{2+}) + 2 \log a_w + 2 \text{pH} \quad (4a)$$

$$\log IAP_2 = \log(\text{Fe}^{2+}) + 3 \log a_w + 3 \text{pH} + \text{pe} \quad (4b)$$

$$\log IAP_3 = \log(\text{Mg}^{2+}) + 2 \log a_w + 2 \text{pH}, \quad (4c)$$

where quantities in parentheses are the activities of chemical species considered, a_w is the activity of water, pe is related to the redox potential measured with respect to the normal hydrogen electrode E_h , by $\text{pe} = (FE_h)/(\ln 10) RT$, T is the absolute temperature with $F = 96485.309 \text{ C.mol}^{-1}$, $R = 8.31440 \text{ J.mol}^{-1}\text{K}^{-1}$.

At equilibrium, one has :

$$\log IAP_1 = \log K_1 + \log a_1 \quad (5a)$$

$$\log IAP_2 = \log K_2 + \log a_2 \quad (5b)$$

$$\log IAP_3 = \log K_3 + \log a_3, \quad (5c)$$

where a_i is the activity of pole i in the solid solution, which is different from the unity, as the mineral is not a pure mineral in standard state.

The activity coefficient λ_i of pole i in the solid solution is defined by :

$$\lambda_i = a_i / X_i, \quad (6)$$

where X_i is the mole fraction of pole i in the solid solution, and the chemical potential of each pole in the solid solution is given by :

$$\mu_i = \mu_i^\circ + RT \ln X_i + RT \ln \lambda_i, \quad (7)$$

The condition of equilibrium can thus be checked by computing first for each pole :

$$\log X_i = \log IAP_i - \log K_i - \log \lambda_i, \quad (8)$$

and secondly by summing the X_i . The condition obtained is then :

$\sum_i X_i < 1$ the soil solution is undersaturated with respect to the solid solution ;

$\sum_i X_i = 1$ the soil solution is at equilibrium with the solid solution ;

$\sum_i X_i > 1$ the soil solution is oversaturated with respect to the solid solution.

This generalizes the condition $IAP < K$, $IAP = K$, $IAP > K$ for a pure solid (Bourri , 1983).

The values of $\log IAP_i$ can be obtained from the composition of soil solution and the computation of activities (Bourri  et al., 1999). One must know the values of K_i for pure end-members, which here it is not possible to directly measure as the purely ferric pole is virtual, and know a law relating λ_i to the composition of the solid solution, *i.e.* to the X_i . For an ideal solid solution $\lambda_i = 1$. For a regular ternary solid solution, the equations are (Prigogine & Defay, 1946, t.II p. 80) :

$$RT \ln \lambda_1 = A_{12}X_2^2 + A_{13}X_3^2 + X_2X_3(A_{12} - A_{23} + A_{13}) \quad (9a)$$

$$RT \ln \lambda_2 = A_{23}X_3^2 + A_{12}X_1^2 + X_1X_3(A_{12} + A_{23} - A_{13}) \quad (9b)$$

$$RT \ln \lambda_3 = A_{13}X_1^2 + A_{23}X_2^2 + X_1X_2(-A_{12} + A_{23} + A_{13}) \quad (9c)$$

This implies that three parameters must be experimentally measured and fitted to a model of ternary regular solid solution. For Green Rusts, we can make the assumption that the Fe(II) – Mg(II) substitution is ideal. This implies that $\lambda_1 = \lambda_3 \forall X_2$, and that if $X_2 = 0$, one obtains the ideal solid solution Mg(II)-Fe(II), hence :

$RT \ln \lambda_1 = A_{13} X_3^2 = 0$, hence $A_{13} = 0$. The same assumption implies that the effects of pole 1 and pole 3 on the activity coefficient of pole 2 are the same, *i.e.* $A_{12} = A_{23}$.

One eventually obtains :

$$RT \ln \lambda_1 = A_{12} X_2^2 \quad (10a)$$

$$RT \ln \lambda_2 = A_{12} (X_1 + X_3)^2 \quad (10b)$$

$$RT \ln \lambda_3 = A_{12} X_2^2 \quad (10c)$$

There remains only one adjustable parameter, $A_{12} = A_{32}$ and poles 1 and 3 play the same role, and this can be equivalently written as :

$$RT \ln \lambda_1 = A_{12} X_2^2 \quad (11a)$$

$$RT \ln \lambda_2 = A_{12} (1 - X_2)^2 \quad (11b)$$

$$RT \ln \lambda_3 = A_{12} X_2^2 \quad (11c)$$

The ideal and excess Gibbs free energy of mixing are respectively given by :

$$\Delta G_{\text{ideal}}/RT = X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3 \quad (12)$$

$$\Delta G_{\text{excess}}/RT = X_1 \ln \lambda_1 + X_2 \ln \lambda_2 + X_3 \ln \lambda_3, \quad (13)$$

and by substituting the equations (10), one obtains :

$$\Delta G_{\text{excess}} = A_{12} X_2 (1 - X_2), \quad (14)$$

$$\mu^\circ = X_1 \mu_1^\circ + X_2 \mu_2^\circ + X_3 \mu_3^\circ + RT [X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3] + A_{12} X_2 (1 - X_2), \quad (15)$$

which was the expression used to fit the regular solid solution model previously (Génin et al., 2001). The parameter A_{12} is identical to the parameter A_0 obtained previously, though the value earlier proposed must be revised as Mg was not considered. In principle, the system can be solved by successive iterations for each aqueous solution to check equilibrium, if K_i are known. In fact, as the solubilities of $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$ are very large, solutions are largely undersaturated with respect to these end-members, which results in numerical unstabilities. Moreover, the end-members have brucite-like structure, with no intercalation of a monomolecular layer of water, and as soon as some Fe(II) is oxidized, the layers separate, hydrate and compensating anions enter the interlayer, which explains why the solid solution is largely non-ideal (Génin et al., 2001). It is thus necessary to better constrain the range of variation of the mole fractions. On the basis of structural considerations, we have seen that the mole fraction of Fe(III) must be less than 1/3, *i.e.* $X_2 \leq 1/3$, as Fe(III) must not be direct neighbours. Now, if X_2 is too small, distance Fe(III)-Fe(III) is too large and the mineral will not form as the solubilities of $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are very large. Experimentally, starting from $\text{Fe}(\text{OH})_2$, and letting it oxidize gently in contact with air, synthetic GRs form in coexistence with $\text{Fe}(\text{OH})_2$ from $x = 1/4$.

With Ni(II) the compound obtained with the initial ratio $\text{Fe(II)/Ni(II)} = 1/3$ - *i.e.* $X_3 = 3/4$, by assimilating Ni(II) to Mg(II) in figure 1 – is a GR1 isomorphous to GR1Cl, with $x = 1$, and $X_2 = 1/4$ (Refait and Génin, 1993). The unique product obtained corresponds to $X_2 = 1/4$ (the point of intersection of the dashed line with the side $\text{Mg}(\text{OH})_2 - \text{Fe}(\text{OH})_3$ in the diagram). For larger initial ratios Fe(II)/Ni(II) , 1/2 and 1, the initial products obtained bear $X_2 = 1/4$ too.

In pyroaurite, $\text{Mg(II)}_6\text{Fe(III)}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, $X_2 = 1/4$; in GR1 (CO_3^{2-}), $\text{Fe(II)}_x\text{Fe(III)}_2(\text{OH})_{2x+4} \cdot n\text{H}_2\text{O}$, x ranges from four to six, ($X_2 = 1/4$ to $1/3$) according to Murad and Taylor (1984), while $x = 4$ following Drissi et al. (1994) ($X_2 = 1/3$). Similarly, when Al(III) substitutes for Fe(III), the product obtained by Taylor and MacKenzie (1980) is $\text{Fe(II)}_6 [\text{Al(III)}, \text{Fe(III)}]_2(\text{OH})_{15.9}\text{Cl}_{1.85}$, with X_2 (mole ratio of

trivalent ions) = 1/4, while in desautelsite, synthesized by Hansen and Taylor (1991), $\text{Mg(II)}_{8-x}\text{Mn(III)}_x(\text{OH})_{16}(\text{CO}_3^2-)_{x/2}$, with $2 < x < 2.67$, *i.e.* $1/4 < X_2 < 1/3$.

It can thus be concluded that the formation of GRs or more generally of pyroaurite-type compounds begins at the mole ratio $X_2 \equiv \text{M(III)}/[\text{M(III)} + \text{M(II)}] \geq 1/4$. The value $X_2 = 1/4$ corresponds structurally for GR1(OH) to a distance Fe(III) – Fe(III) minimum, $d = a\sqrt{3}$, where a is the parameter of the hexagonal lattice. We will then consider that the lower limit for the mole ratio X_2 is geochemically constrained to 1/4, and that the upper limit is structurally constrained to 1/3. The domain of composition of either synthetic or natural GRs is thus comprised between $X_2 = 1/4$ (dashed line in figure 1) and $X_2 = 1/3$ (solid line in figure 1).

We can now assume that the molar Gibbs free energy of formation of GRs is minimum in the range $X_2 = [1/4, 1/3]$, which is rather narrow. This is true even for pure Fe(II)-Fe(III) system. When expressed as a function of mole fractions, one has :

$$\mu^\circ \equiv G/n = X_1\mu_1 + X_2\mu_2, \quad (16)$$

and by derivating with respect to X_2 , one obtains (Prigogine & Defay, 1946, t.II, p. 12) :

$$\bullet \mu^\circ / \bullet X_2 = \mu_2 - \mu_1 = 0, \quad (17)$$

which can be solved for A_{12} , and gives eventually :

$$A_{12} = [\mu_1^\circ - \mu_2^\circ - RT \ln (X_{2, \min.}/1-X_{2, \min.})]/(1 - 2X_{2, \min.}), \quad (18)$$

or

$$A_{12}/RT = [(\mu_1^\circ - \mu_2^\circ)/RT - \ln (X_{2, \min.}/1-X_{2, \min.})]/(1 - 2X_{2, \min.}). \quad (19)$$

By taking as an average $X_{2, \min.} = 7/24 \pm 1/24$, a linear relation is obtained between A_{12} and the Gibbs free energies of formation of the ferrous and ferric end-members. As a first approximation, $(\mu_1^\circ - \mu_2^\circ)/RT$ can be considered as constant, so that from eq. (19), A_{12} can be computed at any temperature.

The pure end members are Fe(OH)_2 for which $\mu_1^\circ = -489.8 \text{ kJ mol}^{-1}$ at 298.15 K, 1 bar from Bourrié et al. (1999) and $\text{Fe(OH)}_3 \equiv [\text{Fe(OH)}_2]^+[\text{OH}]^-$. As Fe(OH)_3 is virtual, it is not measurable. This value must however be more positive than the values for lepidocrocite, goethite with 1 water molecule added, and haematite, with 2 water molecules added, which are the stable or metastable phases. Taking $-470.7 \text{ kJ mol}^{-1}$, for lepidocrocite (Hashimoto & Misawa, 1973), $-480.3 \text{ kJ mol}^{-1}$ for goethite (Détournay et al., 1975), $-755.45 \text{ kJ mol}^{-1}$ for haematite (Bratsch, 1989) and $-237.18 \text{ kJ mol}^{-1}$ for liquid water (Wagman et al., 1982), one obtains a minimum value and $\mu_2^\circ > -708 \text{ kJ mol}^{-1}$. The value previously proposed was $\mu_2^\circ = -641 \text{ kJ mol}^{-1}$ (Génin et al., 2001), but Mg was not considered in the mineral. Instead, for green rusts to form, A_{12} must be negative, which implies $\mu_2^\circ > -490 \text{ kJ mol}^{-1}$, by letting $X_2 = X_{2, \min.} = 7/24$ in eq. 19. The value of μ_2° is not thus constrained enough to give a reliable value of A_{12} from eq. 15. The previously published value $\mu_2^\circ = -641 \text{ kJ mol}^{-1}$ (Génin et al., 2001) leads to $X_{2, \min.} = 2/3$, which is inconsistent with the structural constraints, and must be discarded. A value for μ° must then be obtained in the range of variation of X_2 where green rusts exist, but as the natural mineral fougérite is labile and cannot be separated, and until now was not synthesized, this value must be estimated from the values measured on synthetic green rusts.

Estimation of the Gibbs free energy of formation of GR1-OH on the basis of the model of partial charges and electronegativities of Allred-Rochow of anions

The experimental values of the Gibbs free energies of formation of synthetic green rusts are reported in Table 1 at 298.15 K, 1 bar. As basically, the framework is the same, we can look for a relationship between this thermodynamic property and a suitable parameter. The changes are essentially the nature of the interlayered anion, the number of moles of water, which depends on the type of GR, and at a lesser degree, the mole ratio X_2 . Those factors are closely correlated, and the nature of the anion is the main factor. As the interactions between the layer and the anion are of electrostatic nature, we chose the electronegativity of the anion as parameter, more specifically the Allred and Rochow electronegativity scale, as it is based on the energetics of interaction between a molecule and the electron and is a function of the global charge Z of the molecule, following the model of partial charges developed by Jolivet (1994). Given the electronegativities χ_i^* of the elements, the electronegativity of a molecule is :

$$\chi = \frac{\sum_i \sqrt{\chi_i^*} + 1.36Z}{\sum_i \frac{1}{\sqrt{\chi_i^*}}} . \quad (20)$$

With $\chi_i^* = 2.50$ for C and Se, 3.50 for O, 2.83 for Cl, 2.48 for S (Jolivet, 1994) the values obtained for the anions are $\chi = 0.54$ for Cl^- , 1.86 for SO_4^{2-} , 2.0 for CO_3^{2-} and SO_3^{2-} , 2.29 for SeO_4^{2-} and 2.33 for oxalate $\text{C}_2\text{O}_4^{2-}$. The Gibbs free energies of formation of synthetic green rusts, normalized to 1 Fe atom, are plotted versus the electronegativities of the interlayer anions in Figure 2. The value of the Gibbs free energy of formation of $\text{Fe}(\text{OH})_2$ is plotted at $\chi = 0$, as the interlayer is empty. All points except $\text{GR1}(\text{CO}_3^{2-})$ and including $\text{Fe}(\text{OH})_2$ and $\text{GR2}(\text{SO}_4^{2-})$ are perfectly aligned, along a straight line following the empirical law :

$$\mu^\circ/n = -76.887 \chi - 491.5206, \quad r^2 = 0.9986 \quad (21)$$

where n is the number of Fe atoms per mole formula, and μ° is in kJ mol^{-1} .

The differences between calculated and experimental values are within 0.6 % except for $\text{GR1}(\text{CO}_3^{2-})$, which will be discussed just below. It is remarkable that (i) the value for $\text{Fe}(\text{OH})_2$ plotted at $\chi = 0$ is aligned with GRs, (ii) that $\text{GR2}(\text{SO}_4^{2-})$ is aligned with GR1s. This confirms that the main factor is the nature of the anion. The stacking differences between the two types of GRs and the number of molecules of water do not reflect in the dispersion. Considering the number of molecules of water and computing the electronegativities of $\text{Cl} \cdot 2\text{H}_2\text{O}$ etc. resulted in a large scattering of points in the diagram. The normalized Gibbs free energies of formation of GRs are entirely explained by the electronegativity of the anion.

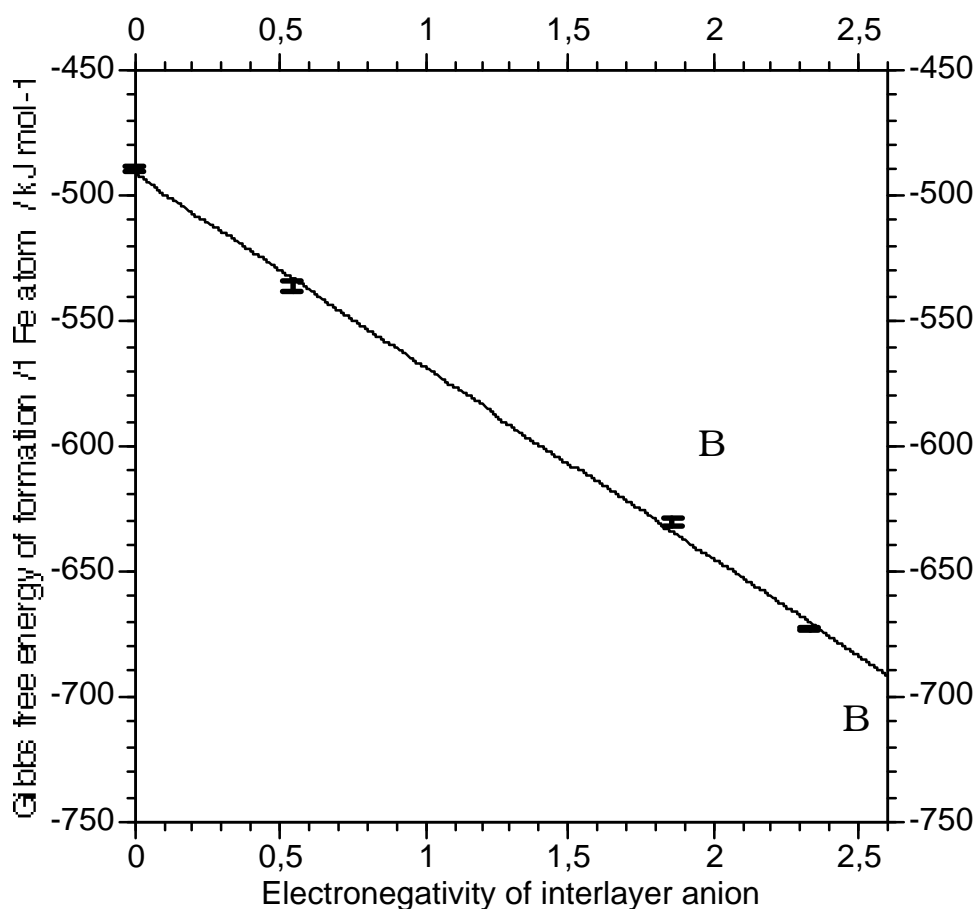


Figure 2 : Relation between Gibbs free energy of formation of synthetic Green Rusts (see Table 1), normalized to 1 atom Fe/mole formula and the Allred and Rochow electronegativity of the interlayer anion, computed following the model of partial charges (Jollivet, 1994) (see text, eq. 20).

Solid line : linear regression, through all points except $\text{GR1}(\text{CO}_3^{2-})$; black squares : Gibbs free energy of formation of $\text{GR1}(\text{CO}_3^{2-})$ (Table 1) at $\chi = 2$, and recalculated from experimental data (Table 3) as $\text{GR1}(\text{HCO}_3^-)$ (reaction 21), at $\chi = 2,49$; the dashed line connects those two extreme values for carbonate Green Rust 1.

For $\text{GR1}(\text{CO}_3^{2-})$, the discrepancy is 8 % and is largely out of range of the experimental uncertainty, i.e. $\pm 11 \text{ kJ mol}^{-1}$. This value is derived from measurements of Eh and pH at equilibrium between $\text{Fe}(\text{OH})_2$ and the Green Rust from Drissi et al., 1994 (Table 3).

Table 3 : Experimental data used to reevaluate the Gibbs free energy of formation of $\text{GR1}(\text{CO}_3^{2-})$, from Drissi et al. (1994)

R = OH/Fe (a)	Eh /V (a)	pH (a)	aCO_3^{2-} (a)	$\log \text{aCO}_3^{2-}$	$\log \text{aHCO}_3^-$ (b)	$\log K$ (c)	$\Delta_P G^\circ$ (d) /kJ mol ⁻¹	μ° (e) /kJ mol ⁻¹	$\mu^\circ/6$ /kJ mol ⁻¹
0.545	-0.598	10.82	0.027	-1.569	-2.059	24.33	-138.896	-4251.24	-708.54
0.600	-0.597	10.20	0.015	-1.824	-1.694	23.57	-134.539	-4246.88	-707.81

	0.615	-0.596	10.19	0.015	-1.824	-1.684	23.52	-134.232	-4246.57	-707.76
Average	-0.597	10.40	0.019	-1.739	-1.812	23.807	-135.89	-4248.23	-708.04	
SD	0.001	0.36	0.007	0.147	0.214	0.457	2.61	2.61	0.43	

a. Drissi et al. (1994) ; b. computed as $\log a\text{HCO}_3^- = \log a\text{CO}_3^{2-} - \text{pH} + 10.33$;

c. $\log K = -2[\text{FE}_h / (\ln 10) RT - 2 \log a\text{HCO}_3^-]$; d. $\Delta_P G^\circ = -(\ln 10)RT \log K$;

The value obtained for GR1(2HCO_3^-) when normalized to 1 atom Fe and plotted at $\chi(\text{HCO}_3^-) = 2.49$ is below the general regression line. Carbonate Green Rust is thus indeed a mixed $\text{CO}_3^{2-}\text{HCO}_3^-$ GR. The intersection between the solid line and dashed line in Figure 2 leads to an average value $\chi = 2.32 = 0.65 \chi(\text{HCO}_3^-) + 0.35 \chi(\text{CO}_3^{2-})$.

We can thus conclude that the best formula for carbonate GR1 is :

$2/3 \{[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+} [2\text{HCO}_3^-]^{2-}\} \bullet 1/3 \{[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+} [\text{CO}_3^{2-}]^{2-}\}$, or equivalently $[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+} [4/3 \text{HCO}_3^- \bullet 1/3 \text{CO}_3^{2-}]^{2-}$. Thus, we have :

$[\text{HCO}_3^-]/[\text{CO}_3^{2-}] = 4$ in the interlayer, which corresponds to $\text{pH} = 9.73$, i.e. 0.5 to 1.1 lower than the pH in the external solution, and can be ascribed to the classical surface acidity of the interlayer. There is no steric hindrance, as there are 6 Fe atoms, so there is space for 6 H_2O molecules, i.e. 6 O. In the formula proposed, there are 5 O, so there exists the possibility to have 1 water molecule in addition in the cell. From the value $\chi = 2.32$, and eq. 21, we obtain $\mu^\circ = -4018 \text{ kJ mol}^{-1}$ for GR1 ($4/3 \text{HCO}_3^- \bullet 1/3 \text{CO}_3^{2-}$) at 298.15 K, 1 bar.

From eq. 21, with $\chi(\text{SO}_3^{2-}) = 2$ and $\chi(\text{SeO}_4^{2-}) = 2.29$, we obtain the Gibbs free energies of formation of the other synthetic Green Rusts : GR1(SO_3^{2-}), GR2(SeO_4^{2-}), which are reported in Table 1.

From eq. 21, with $\chi(\text{OH}) = 1.60$, we eventually obtain $\mu^\circ = -614.5 \text{ kJ mol}^{-1}$ for GR1(OH), with 1 atom Fe per mole formula, from which we can solve entirely the regular solid solution model.

From eq. 17, we have at the minimum, $\mu_1 = \mu_2$ and from eq. 16, we obtain :

$$\mu^\circ = \mu_1 = \mu_2 = -614.5 \text{ kJ mol}^{-1} \quad (22)$$

which from eq. 7 and 11a, or 11b gives successively :

$$\mu_1 = \mu_1^\circ + RT \ln X_1 - A_{12} X_2^2, \quad (23)$$

$$\mu_2 = \mu_2^\circ + RT \ln X_2 - A_{12} (1 - X_2)^2. \quad (24)$$

With $X_1 = 17/24$, $X_2 = 7/24$ and $\mu_1^\circ = -489.8 \text{ kJ mol}^{-1}$, we obtain $A_{12} = -1455.8 \text{ kJ mol}^{-1}$, and from eq. 24, we obtain $\mu_2^\circ = +119. \text{ kJ mol}^{-1}$. As expected, A_{12} is negative, which implies that GRs will not demix at any temperature (Prigogine & Defay, 1946). The positive value for μ_2° implies that a GR structure for $\text{Fe}(\text{OH})_3$ is absolutely impossible. Electrostatic repulsions would be so large that this compound would be unstable with respect to the elements in their standard state, metallic Fe, $\text{O}_{2, \text{gas}}$ and $\text{H}_{2, \text{gas}}$!

The value $\mu^\circ = -614.5 \text{ kJ mol}^{-1}$ for GR1(OH) near the minimum at the limit $X_3 = 0$ (no Mg in the mineral) is in the range of the values previously proposed for $\text{Fe}_3(\text{OH})_7$, i.e. $-1799.7 \text{ kJ mol}^{-1}$, or $-600 \text{ kJ mol}^{-1}/1 \text{ atom Fe}$, and for « $\text{Fe}_2(\text{OH})_5$ », i.e. $-1244.1 \text{ kJ mol}^{-1}$, or $-622 \text{ kJ mol}^{-1}/1 \text{ atom Fe}$, but it must be preferred, as it is based on carefully controlled experiments on synthetic GRs, thermodynamics of solid solutions and the model of partial charges.

Our solid solution model for Green Rusts is now completed with the value for the pure $\text{Mg}(\text{OH})_2$ end-member, for which we take the value for brucite, $\mu_3^\circ = -833.67 \text{ kJ mol}^{-1}$, from $E^\circ = -2.690 \text{ V}$ for $\text{Mg}(\text{OH})_{2(c)}/\text{Mg}_{(c)}, \text{OH}^-$ (Bratsch, 1989).

Check of soil solution – Green Rust equilibrium

Soil solution was studied in the site where green rust was discovered (Trolard et al., 1996 ; 1997), in a gley soil developed on granite at Fougères (Brittany, France) and simultaneously three types of data were measured (Feder, 2001): (i) Mössbauer spectra were acquired in the field at different depths and times; (ii) Eh, pH were monitored in the groundwater at 70 cm depth every hour, in a gley horizon ; (iii) the soil solution was sampled every week or twice a month for complete analysis.

The results are presented elsewhere in this volume (Feder et al., 2002).

Mössbauer spectra show clear evidence for the presence of green rusts, and the mole ratio $x = \text{Fe(III)}/\text{Fe}_{\text{total}}$ in the mineral decreases monotonically with depth, from 0.64 to 0.34, as the milieu becomes more and more reductive. At a given depth, when repeated measurements are made at different times, significant variations of x are observed, though the amplitude is smaller than the entire variation in the profile. No values were observed outside the range $x = [1/3, 2/3]$.

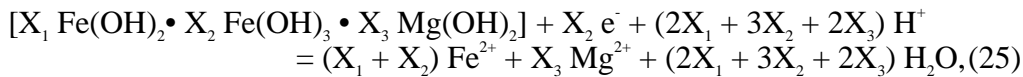
At the depth where the composition of soil solution was monitored, x ranges from 0.59 to 0.61. By definition, $x = X_2/(X_1 + X_2)$, hence with $x = 0.6$, $X_1 = 2X_2/3$.

With $X_2 = 1/4$, we obtain : $X_1 = 1/6$, and $X_3 = 7/12$, while with $X_2 = 1/3$, we obtain : $X_1 = 2/9$, which gives $X_3 = 4/9$. By combining the data from Mössbauer spectroscopy in the field and the structural and geochemical constraints for green rust composition, we can thus solve the system and obtain the three mole fractions of the components.

The range of composition of the green rust mineral *at that depth* is thus between $[\text{Mg}_{7/12}^{\text{II}}\text{Fe}_{1/6}^{\text{II}}\text{Fe}_{1/4}^{\text{III}}(\text{OH})_2]^{0.25+} [1/4 \text{ OH} \cdot 3/4 \text{ H}_2\text{O}]^{0.25-}$ designated as Fougérite 1 (F1) and :

$[\text{Mg}_{4/9}^{\text{II}}\text{Fe}_{2/9}^{\text{II}}\text{Fe}_{1/3}^{\text{III}}(\text{OH})_2]^{0.33+} [1/3 \text{ OH} \cdot 2/3 \text{ H}_2\text{O}]^{0.33-}$, designated as Fougérite 2 (F2).

The range of variation of mole fractions is narrow : $\Delta X_1 = 1/18$; $\Delta X_2 = 1/12$; $\Delta X_3 = 5/36$. In the narrow range where green rusts are stable $X_2 \cdot X_{2, \text{min.}} = 7/24$, and according to our assumption, μ° is minimum and can be considered as constant, so that as a first approximation, green rust can be approximated as a solid of fixed composition and the equilibrium reaction simply written in the classical way, for which it is convenient to use mole fractions :



and to which mass action law can be directly applied as :

$$(X_1 + X_2) \log (\text{Fe}^{2+}) + X_3 \log (\text{Mg}^{2+}) + X_2 \text{ pe} + (2X_1 + 3X_2 + 2X_3) \text{ pH} = \log K, (26)$$

where $\log K$ is given by :

$$\log K = [(X_1 + X_2) \Delta G_f^\circ(\text{Fe}_{\text{aq.}}^{2+}) + X_3 \Delta G_f^\circ(\text{Mg}_{\text{aq.}}^{2+}) \\ + (2X_1 + 3X_2 + 2X_3) \Delta G_f^\circ(\text{H}_2\text{O}) - \mu^\circ] / (\ln 10) RT., (27)$$

in which μ° is the chemical potential of the solid, and can be computed from our model, using eq. 15. The computations are made at 298.15 K.

The results obtained are $\mu^\circ(\text{F1}) = - 813.5 \text{ kJ mol}^{-1}$ and $\mu^\circ(\text{F2}) = - 761.6 \text{ kJ mol}^{-1}$, from which one obtains, for Fougérite 1 :

$$\log(\text{Fe}^{2+}) + 7/5 \log(\text{Mg}^{2+}) + 27/5 \log a_w + 3/5 \text{ pe} + 27/5 \text{ pH} = \log K_{\text{F1}} = 25.7, (28)$$

and for Fougérite 2 :

$$\log(\text{Fe}^{2+}) + 4/5 \log(\text{Mg}^{2+}) + 21/5 \log a_w + 3/5 \text{pe} + 21/5 \text{pH} = \log K_{\text{F}_2} = 20,2. \quad (29)$$

Activities were computed for a set of 68 soil solutions sampled in Fougères from February 1999 to June 2000 (Feder, 2001) :

$\log IAP_{\text{F}_1}$ values range from 22.8 to 32.2 (av. = 28.13, σ = 2.61) ;

$\log IAP_{\text{F}_2}$ values range from 17.6 to 24.8 (av. = 21.77, σ = 2.).

It can thus be concluded that $\log IAP$ for the natural mineral are close to the values obtained from our model. The uncertainty on the values of $\log K$ obtained for the mineral must be about $\pm 4 \text{ kJ mol}^{-1}$ for 1 atom Fe in the mineral, which gives ± 0.7 logarithmic units. Net supersaturations are observed for Fougérite 1, if one considers that $\log IAP > \log K + 2 \sigma$ indicates a supersaturation. Only slight supersaturations are observed for Fougérite 2.

Conclusions and implications concerning the genesis of green rusts and Mg and Fe geochemistry

A regular solid solution model has been developed for Green Rusts, in the ternary $\text{Mg}(\text{OH})_2 - \text{Fe}(\text{OH})_2 - \text{Fe}(\text{OH})_3$ system. This model degenerates to a binary system if the ideality of Fe(II) – Mg(II) substitution is assumed, so that it relies on four parameters, the chemical potentials μ° of the three end-members and the parameter of non ideality A_{12} . The values of μ° for $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are known, but μ° for $\text{Fe}(\text{OH})_3$ and A_{12} are unknown.

In accordance with the corpus of available data on the structure and composition of Green Rusts and similar compounds, the maximum value of the mole ratio $X_2 = \text{M(III)}/\text{M(II)}$ 1/3, which ensures that trivalent ions cannot be direct neighbours.

Due to the large solubility of both $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, trivalent ions cannot be too remote from each other, and Green Rusts only form from $X_2 = 1/4$. This constrains the mole ratio X_2 in the narrow range [1/4 – 1/3]. The proportions of Fe(II) and Mg(II) however can vary freely.

A linear relation has been obtained between the Gibbs free energies of formation of those compounds, μ° , normalized to 1 atom Fe, and the electronegativity χ of the interlayer anion, $\mu^\circ/n = -76.887 \chi - 491.5206$ ($r^2 = 0.9986$, $n = 4$).

The electronegativity of the interlayer anion entirely explains the variation of μ° ; the two types of GRs and $\text{Fe}(\text{OH})_2$ follow the same law. There is no evidence for either a screening effect of the interlayered water molecules, or an effect of the stacking mode of layers.

The discrepancy between the predicted value for $\text{GR1}(\text{CO}_3^{2-})$ and the observed value has been explained by the presence of both HCO_3^- and CO_3^{2-} in the interlayer, with a new formula $[\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}]^{2+} [4/3 \text{HCO}_3^- \cdot 1/3 \text{CO}_3^{2-}]^{2-}$, and $\mu^\circ = 4018 \text{ kJ mol}^{-1}$ at 298.15 K, 1 bar.

The Gibbs free energies of formation of other synthetic, sulfite- and selenate Green Rusts are predicted from the relation obtained.

Similarly, the Gibbs free energy of the limiting case of the natural mineral (without Mg) of formula $\text{Fe(II)}_{1-x}\text{Fe(III)}_x(\text{OH})_{2+x}$ is obtained as $\mu^\circ = -614.5 \text{ kJ mol}^{-1}$ with $1/4 < x < 1/3$. The two unknown parameters of the model are then solved : $A_{12} = -1455.8 \text{ kJ mol}^{-1}$ and

$\mu_2^\circ = +119 \text{ kJ mol}^{-1}$ for $\text{Fe}(\text{OH})_3$. This latter positive value is due to the large repulsion of trivalent ions, and explains the impossibility for $\text{Fe}(\text{OH})_3$ to adopt a brucite-type structure.

From this model, the chemical potential of any ternary solid solution can be computed. This is applied to field data from Fougères, where the natural mineral « fougérite » has been discovered. From Mössbauer in situ measurements, and the assumptions of our model, the three mole fractions can be obtained. The chemical potentials of two types of « fougérite » are computed and equilibria between soil solutions and these minerals checked. The solutions appear close to the equilibrium, but sometimes supersaturation is observed.

The implications as concerns Fe and Mg geochemistry are the following : due to its extremely small solubility, Fe(III) is absent from the solution, and when the oxides are reduced, Fe^{2+} is released in solution, in milieus where Mg^{2+} is present too. When oxidation occurs, Fe^{3+} precipitates with Fe^{2+} and Mg^{2+} to give rise to Green Rust « fougérite ». The initial Fe/Mg in the mineral is fixed by the composition of the solution. Then, « fougérite » is progressively oxidized at constant Mg mole ratio, (path from N to P, Figure 1). When the Fe(III) mole ratio reaches its maximum $X_2 = 1/3$, « fougérite » dissolves and lepidocrocite or goethite form.

The new consequence is that Mg geochemistry is involved: Green Rusts have been considered mainly with respect to their capacity to absorb anions in a first step and the to release them back to solutions. The same occurs here with Mg.

References

- Abdelmoula, M., Trolard, F., Bourrié, G. & Génin, J.-M.R. 1998. – Evidence for the Fe(II)-Fe(III) green rust Fougérite mineral occurrence in a hydromorphic soil and its transformation with depth. *Hyperfine Interactions*, **112**, 235-238.
- Bernal, J.D., Dasgupta, D.R. & Mackay, A.L. 1959. – The oxides and hydroxides of iron and their structural interrelationships. *Clay Minerals Bulletin*, **24**, 882-885.
- Bourrié, G. 1983. – Rôle des composés amorphes dans le contrôle de la composition chimique des solutions du sol. *Science du Sol*, **3-4**, 195-204.
- Bourrié, G., Trolard, F., Génin, J.-M.R., Jaffrezic, A., Maître, V. & Abdelmoula, M. 1999. – Iron control by equilibria between hydroxy-Green Rusts and solutions in hydromorphic soils. *Geochimica et Cosmochimica Acta*, **63**, 3417-3427.
- Bratsch, S.G. 1989. – Standard electrode potentials and temperature coefficients in water at 298.15 K. *Journal of Physical and Chemical Reference Data*, **18**, 1-21.
- Détournay, J., De Miranda, L., Dérié, R. & Ghodsi, M. 1975. – The region of stability of green rust II in the electrochemical E-pH equilibrium diagram of iron in sulphate medium. *Corrosion Science*, **15**, 295-306.
- Drissi, S.H., Refait, Ph. & Génin, J.-M.R. 1994. – The oxidation of $\text{Fe}(\text{OH})_2$ in the presence of carbonate ions : structure of carbonate green rust one. *Hyperfine Interactions*, **90**, 395-400.
- Drissi, S.H., Refait, Ph., Abdelmoula, M. & Génin, J.-M.R. 1995. – Preparation and thermodynamic properties of Fe(II)-Fe(III) hydroxide-carbonate (green rust one), Pourbaix diagram of iron in carbonate-containing aqueous media. *Corrosion Science*, **37**, 2025-2041.
- Feder, F. 2001. – *Dynamique des processus d'oxydo-réduction dans les sols hydromorphes – monitoring in situ de la solution du sol et des phases solides ferri-fères.*

Thèse, Université d'Aix-Marseille III, 200 p.

Feder, F., Klingelhöfer, G., Trolard, F. & Bourrié, G. 2002. – In situ Mössbauer spectroscopy and soil solution monitoring to follow spatial and temporal iron dynamics. *17th World Congress of Soil Science, Bangkok, Symposium 8*, this volume.

Génin, J.-M.R., Abdelmoula, M., Refait, Ph. & Simon, L. 1998a. Comparison of the Green Rust Two lamellar double hydroxide class with the Green Rust One pyroaurite class : Fe(II)-Fe(III) sulphate and selenate hydroxides. *Hyperfine Interactions, (C)*, **3**, 313-316.

Génin, J.-M.R., Bourrié, G., Trolard, F., Abdelmoula, M., Jaffrezic, A., Refait, Ph., Maître, V., Humbert, B. & Herbillon, A. 1998b. – Thermodynamic equilibria in aqueous suspensions of synthetic and natural Fe(II)-Fe(III) Green Rusts : occurrences of the mineral in hydromorphic soils. *Environmental Science & Technology*, **32**, 1058-1068.

Génin, J.-M.R., Olowe, A.A., Refait, Ph. & Simon, L. 1996a. – 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. *Corrosion Science*, **38**, 1751-1762.

Génin, J.-M.R., Refait, Ph., Bourrié, G., Abdelmoula, M. & Trolard, F. 2001 – Structure and stability of the Fe(II)-Fe(III) green rust « fougerite » mineral and its potential for reducing pollutant in soil solutions. *Applied Geochemistry*, **16**, 559-570.

Génin, J.-M.R., Simon, L. & Refait, Ph. 1996b. – Existence of sulphite-containing green rust one. *Conference Proceedings « ICAME 95 »*, (I.Ortalli, ed.), **50**, 51-54, SIF, Bologna.

Girard, A. & Chaudron, G. 1935. – Sur la constitution de la rouille. *Comptes-Rendus de l'Académie des Sciences, Paris*, **200**, 127-129.

Hansen, H.C.B. 1989. – Composition, stabilisation and light absorption of Fe(II)-Fe(III) hydroxycarbonate (green rust). *Clay Minerals*, **24**, 663-669.

Hansen, H.C.B. & Taylor, R.M. 1991. – Formation of synthetic analogues of double metal-hydroxy carbonate minerals under controlled pH conditions : II. The synthesis of desautelsite. *Clay minerals*, **26**, 507-525.

Hashimoto, K. & Misawa, T. 1973. – The solubility of γ -FeOOH in perchloric acid at 15°C. *Corrosion Science*, **13**, 229-231.

Jolivet, J.P. 1994. – *De la solution à l'oxyde – Condensation des cations en solution aqueuse – Chimie de surface des oxydes*. InterEditions / CNRS Editions, Paris, 387p.

Kelsall, G.H. & Williams, R.A. 1991. – Electrochemical behaviour of ferrosilicides (Fe_xSi) in neutral and alkaline aqueous electrolytes. *Journal of the Electrochemical Society*, **138**, 931-940.

Koritnig, S. & Susse, P. 1975. – Meixnerit, $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4\text{H}_2\text{O}$, ein neues Magnesium-Aluminium-Hydroxid-Mineral. *Tschermaks Mineralogische Petrologische Mitteilungen* **22**, 79-87.

Mascolo, G. & Marino, O. 1980. – A new synthesis and characterization of magnesium-aluminium hydroxides. *Mineralogical magazine*, **43**, 619-621.

Murad, E. & Taylor, R.M. 1984. – The Mössbauer spectra of hydroxycarbonate green rusts. *Clay Minerals*, **19**, 77-83.

Olowe, A.A. & Génin, J.-M.R. 1991. – The mechanism of oxidation of Fe(II) hydroxide in sulphated aqueous media : importance of the initial ratio of the reactants. *Corrosion Science*, **32**, 965-984.

- Ponnamperuma, F.N., Tianco, E.M. & Loy, T. 1967. – Redox equilibria in flooded soils : I. The iron hydroxide system. *Soil Science*, **103**, 374-382.
- Prigogine, I. & Defay, R. 1946. *Thermodynamique chimique conformément aux méthodes de Gibbs et De Donder*. Dunod, Paris, tome I, 348 p., tome II, 430 p.
- Refait, Ph., Abdelmoula, M & Génin, J.-M.R. 1998a. – Mechanisms of formation and structure of green rust one in aqueous corrosion of iron in the presence of chloride ions. *Corrosion Science*, **40**, 1547-1560.
- Refait, Ph., Abdelmoula, M ; Trolard, F., Génin, J.-M.R., Ehrhardt, J.J. & Bourrié, G. 2001. - Mössbauer and XAS study of a green rust mineral ; the partial substitution of Fe^{2+} by Mg^{2+} . *American Mineralogist*, **86**, 731-739.
- Refait, Ph., Bon, C., Simon, L., Bourrié, G., Trolard, F., Bessière, J. & Génin, J.-M.R. 1999. – Chemical composition and Gibbs standard free energy of formation of Fe(II)-Fe(III) hydroxysulphate green rust and Fe(II) hydroxide. *Clay Minerals*, **34**, 499-510.
- Refait, Ph., Charton, A. & Génin, J.-M.R. 1998b. – Identification, composition, thermodynamic and structural properties of a pyroaurite-like iron(II)-iron(III) hydroxy-oxalate Green Rust. *European Journal of Solid State Inorganic Chemistry*, **35**, 655-666.
- Refait, Ph. & Génin, J.-M.R. 1993. – The oxidation of Ni(II)-Fe(II) hydroxides in chloride-containing aqueous media. *Corrosion Science*, **34**, 2059-2070.
- Refait, Ph., Simon, L., Louis, C. & Génin, J.-M.R. 2000. – Reduction of SeO_4^{2-} anions and anoxic formation of iron(II)-iron(III) hydroxy-selenate green rust. *Environmental Science & Technology*, **34**, 819-825.
- Roussel, H., Briois, V., Elkaim, E., de Roy, A. & Besse, J.P. 2000. – Cationic order and structure of [Zn-Cr-Cl] and [Cu-Cr-Cl] layered double hydroxides : a XRD and EXAFS study. *Journal of Physical Chemistry*, **B25**, 5915-5953.
- Shannon, R.D. 1976. – Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751-767.
- Stampfl, P.P. 1969. – Ein basisches Eisen-II-III-Karbonat in Rost. *Corrosion Science*, **9**, 185-187.
- Taylor, R.M. 1981. – Color in soils and sediments. A review. In : « *International Clay Conference 1981* » (H.Van Olphen ed.), *Developments in Sedimentology*, **35**, p. 749-761, Elsevier, Amsterdam.
- Taylor, R.M. & MacKenzie, R.M. 1980. – The influence of aluminum on iron oxides. VI. The formation of Fe(II)-Al(III) hydroxy-chlorides, -sulfates, and -carbonates as new members of the pyroaurite group and their significance in soils. *Clays and Clay Minerals*, **28**, 179-187.
- Trolard, F., Abdelmoula, M., Bourrié, G., Humbert, B. & Génin, J.-M.R. 1996. – Mise en évidence d'un constituant de type « rouilles vertes » dans les sols hydromorphes – Proposition de l'existence d'un nouveau minéral : la « fougérite ». *Comptes-Rendus de l'Académie des Sciences, Paris*, **323, IIa**, 1015-1022.
- Trolard, F., Génin, J.-M.R., Abdelmoula, M., Bourrié, G., Humbert, B. & Herbillon, A. 1997. – Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies. *Geochimica et Cosmochimica Acta*, **61**, 1107-1111.
- Vucelic, M., Jones, W. & Moggridge, G.D. 1997. – Cation ordering in synthetic layered double hydroxides. *Clays and Clay Minerals*, **45**, 803-813.
- Vysotskii, G.N. 1905. – Gley. *Pochvovedeniye*, **4**, 291-327. (original paper in russian).
-----1999. Gley. An abridged publication of Vysotskii 1905 on the 257th

Anniversary of the Russian Academy of Sciences. *Eurasian Soil Science*, **32**, 1063-1068.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, L., Bailey, S.M., Churney, K.L. & Nuttall, R.L. 1982. – The NBS Tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. *Journal of Physical and Chemical Reference Data, Supplement n°2*, 11.

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