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Redox topotactic reactions in Fe^{II-III} (oxy)hydroxycarbonate new minerals related to fougèrite in gleysols: “trébeurdenite and mössbauerite”

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Abstract Fougèrite mineral responsible for the bluish-green shade of gleysols in aquifers was identified as Fe^{II-III} oxyhydroxycarbonate, $[Fe^{II}_{6(1-x)}Fe^{III}_{6x}O_{12}H_{2(7-3x)}]^{2+} \cdot [CO_3^{2-} \cdot 3H_2O]^{2-}$ where the average ferric molar fraction $x = [Fe^{III}/Fe_{total}]$ was restricted to the [1/3–2/3] range, up till now. In this paper, Mössbauer spectra of gleys extracted from the schorre of maritime marshes have values of x in the [2/3–1] range. Magnetic properties of homologous chemical compounds studied by Mössbauer

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spectroscopy are explained with long range order of Fe^{III} ions within Fe cation layers for $x = 1/3$, 2/3 and 1. Observed values are mixtures of topotactic domains that are in fact minerals with names proposed to IMA: fougèrite for $x = 1/3$, trébeurdenite for $x = 2/3$ and mössbauerite for $x = 1$.

Keywords Fe^{II-III} (oxy)hydroxycarbonate • Green rust • Mössbauer spectroscopy • Fougèrite • Trébeurdenite • Mössbauerite • Topotaxy

1 Introduction

Redox reactions in soils are of utmost importance for understanding their genesis but also the mechanisms of their remediation in view of sustainable development. For instance, we are involved in programs of denitrification in Brittany (France) where a proliferation of green algae is due to intensive agricultural practice and Fe^{II-III} green rusts which are able to reduce nitrates are forwarded [1, 2]. In parallel, the same type of compounds was found in natural "gleysols" [3, 4]. Thus, in this paper, we intend to compare gleysols found in continental aquifers with those in maritime marshes.

Gleys are ubiquitous, wherever water lies in soils; their shade goes from bluish-green to ocher through olive green. Mössbauer spectra allowed us to show that this phenomenon was due to the presence of iron containing compounds strongly resembling Fe^{II-III} hydroxycarbonate green rust, GR(CO_3^{2-}), that was studied for its intermediate role during the corrosion of iron-based materials [5–7]. GR(CO_3^{2-}) belongs to the layered double hydroxide family; it consists in stacking brucite-like $[Fe_4^{II}Fe_2^{III}(OH)_{12}]^{2+}$ layers that alternate with $[CO_3 \cdot 3\ H_2O]^{2-}$ interlayers within $R\bar{3}\,m$ space group [8–10]. GR(CO_3^{2-}) usually gets oxidised into ferrihydrite that evolves to goethite by aerial oxidation [11, 12]; this process is responsible for the corrosion of iron since GR(CO_3^{2-}) is dissolved by rejecting the anions into solution and Fe^{III} ions, that form, precipitate as a ferric solid. In contrast, it was demonstrated recently that it could also follow another route by *in situ* oxidation into a "ferric green rust" GR(CO_3^{2-})*, $[Fe_6^{III}O_4(OH)_8]^{2+} \cdot [CO_3 \cdot 3H_2O]^{2-}$, where some OH^- ions get deprotonated [12, 13]. For instance, any intermediate value of ferric molar fraction $x = [Fe^{III}/Fe_{total}]$ from 0.33 to 1 can be reached by oxidising a synthetic GR(CO_3^{2-}), if one uses an appropriate amount of H_2O_2 solution that leads to Fe^{II-III} (oxy)hydroxycarbonate, $[Fe^{II}_{6(1-x)}Fe^{III}_{6x}O_{12}H_{2(7-3x)}]^{2+} \cdot [CO_3^{2-} \cdot 3H_2O]^{2-}$, where $x \in [0.33,1]$ [13, 14].

The identification of a green rust in a "gleysol" was first accomplished in 1996 with samples extracted from the aquifer of the State owned forest of Fougères (Brittany-France) and the mineral was thus christened fougèrite (IMA2003–057) [3, 4]. Up till now, samples were taken out of permanently waterlogged gleys that lie in water tables and measurements accomplished by Mössbauer spectroscopy showed that the value of x was restricted to the [1/3–2/3] range [15, 16]. In this paper, samples that are extracted from gleys lying in maritime marshes display values of x in the [2/3–1] range and, consequently, the definition of fougèrite must be revisited whereas the existence of two new minerals related to GR(CO_3^{2-}) must be forwarded, the names of which, trébeurdenite and mössbauerite, are proposed.

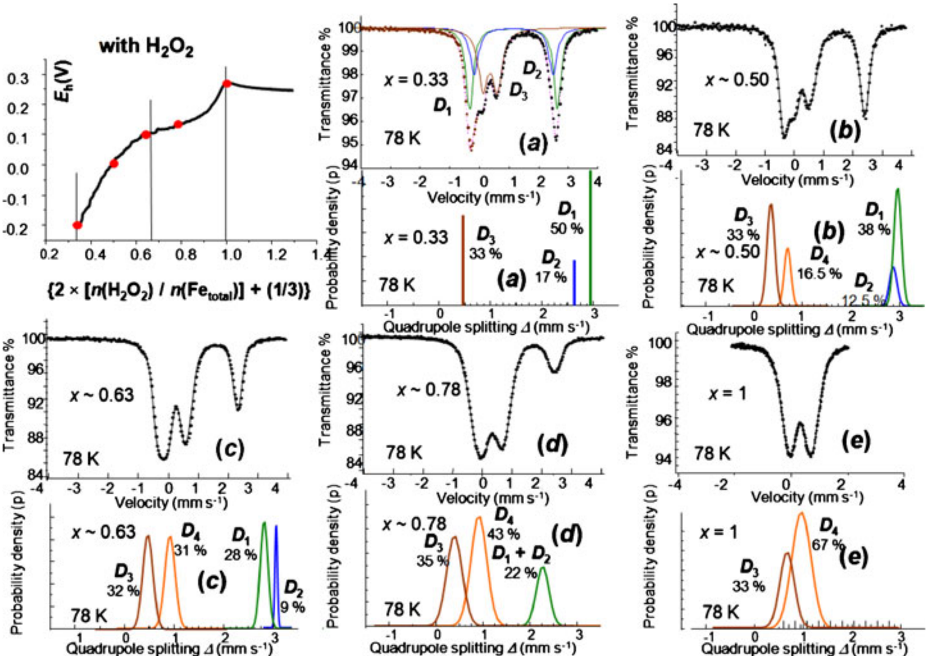


Fig. 1 Mössbauer spectra measured at 78 K of a set of Fe^{II-III}oxyhydroxycarbonate green rust samples during depronation as followed by the electrode potential E_h of the solution vs the amount of H_2O_2 poured into solution for values of $x = [Fe^{III}]/[Fe_{total}]$ ranging from 0.33 to 1. The experimental values that are obtained are 0.33, 0.50, 0.63, 0.78 and 1. Under each spectrum, Gaussian distributions of quadrupole splitting by fitting Voigt profile doublets (from [8, 12, 14])

2 Experimental

Almost all beaches of Northern Brittany and of the bay of Mont Saint Michel present levels of clayey sediments, sometimes developed on several meters. These fine sediments display a characteristic blue color, corresponding to ancient salt marshes in which halophyte roots are easily recognized. These marshes have developed behind foredunes or shingle bars and were filled with sediments of marine origin or coastal river input, mainly between 4000 and 3000 years BP at a time when the sea level was low. In Northern Brittany, the erosion of quaternary cliffs provides silky sediments into these old salt marshes, which locally take advantage of three factors for their settlement and conservation, namely fine sediment supplies, appropriate tidal range and level, and finally, sheltered location.

In the bay of Mont Saint Michel, a high proportion of carbonate fraction indicates an important or even prevailing supply of shelly bioclasts. Most of the present salt marshes have resulted in an active filling with sedimentary supply of about one million m^3 per year. The more or less carbonated sediments are saturated with water and rich biological substances (diatoms) and their colors vary most of the time from grey to black. Blue "marls" are only found in some few places where sediments are compacted; this would suggest that the gley we have sampled in these old fossil salt marshes at many scattered locations in the bay contains minerals in the course of

Table 1 Hyperfine parameters of GR(CO_3^{2-})* for $x = [Fe^{III}]/[Fe_{total}] \in [(1/3)\text{-}1]$ (from [14])

	Quadrupole doublets	δ(mm s^{-1})	$<\Delta>$(mm s^{-1})	$<\delta\Delta>$ (mm s^{-1})	RA (%)
$x = 0.33$					
Fe^{II}	D_1	1.25	2.92	0	50
	D_2	1.25	2.63	0	17
Fe^{III}	D_3	0.48	0.47	0	33
$x \sim 0.50$					
Fe^{II}	D_1	1.21	2.98	0.14	38
	D_2	1.21	2.72	0.16	12.5
Fe^{III}	D_3	0.49	0.40	0.15	33
	D_4	0.49	0.70	0.28	16.5
$x \sim 0.63$					
Fe^{II}	D_1	1.24	2.80	0.15	28
	D_2	1.24	3.05	0.05	9
Fe^{III}	D_3	0.48	0.49	0.20	32
	D_4	0.48	0.90	0.21	31
$x \sim 0.78$					
Fe^{II}	$D_1 + D_2$	1.21	2.89	0.31	22
Fe^{III}	D_3	0.47	0.45	0.32	35
	D_4	0.47	0.95	0.34	43
$x = 1$					
Fe^{III}	D_3	0.47	0.60	0.30	33
	D_4	0.47	0.88	0.41	67

Values of x experimentally obtained are approximately 0.50, 0.63 and 0.78 and precisely 0.33 and 1. Spectra are measured at 78 K (Fig. 2) and fitting uses a Voigt profile. δ : isomer shift in mm s^{-1} (reference is α-iron at ambient), $<\Delta>$: mean value of quadrupole splitting in mm s^{-1} and $<\delta\Delta>$: its standard deviation; RA(%): relative area

diagenesis. The samples were extracted from the beaches at low tide at a reasonable depth (less than one meter) and no particular precautions were taken for conservation once they are completely dry. Mössbauer spectra were done by transmission and computed with a classical least-square fit procedure using Lorentzian shape lines. Displayed spectra are examples of many others intended to study the diagenesis of maritime gleys and sediments out of the scope of this paper.

Since Mössbauer spectra of the natural samples must be compared to those of the corresponding synthetic compounds measured at 78 K, let us recall the procedure for preparing the synthetic samples [8, 12, 14]: (i) GR(CO_3^{2-}) was coprecipitated by mixing ferrous and ferric sulphates in a 2:1 $[Fe^{II}]/[Fe^{III}]$ ratio in the presence of HCO_3Na, (ii) hydrogen peroxide was introduced with a peristaltic pump into the GR(CO_3^{2-}) solution while the electrode potential E_h was followed versus the amount of H_2O_2 (Fig. 1). Four samples were measured at 78 K by transmission Mössbauer spectroscopy besides the initial GR(CO_3^{2-}) at values of $x = 0.50, 0.63, 0.78$, and 1 (Fig. 1, Table 1).

3 Results and discussion

Spectra were fitted by a deconvolution procedure with Voigt profile (Fig. 1) and results yielded values of isomer shift δ and quadrupole splitting Δ with the standard

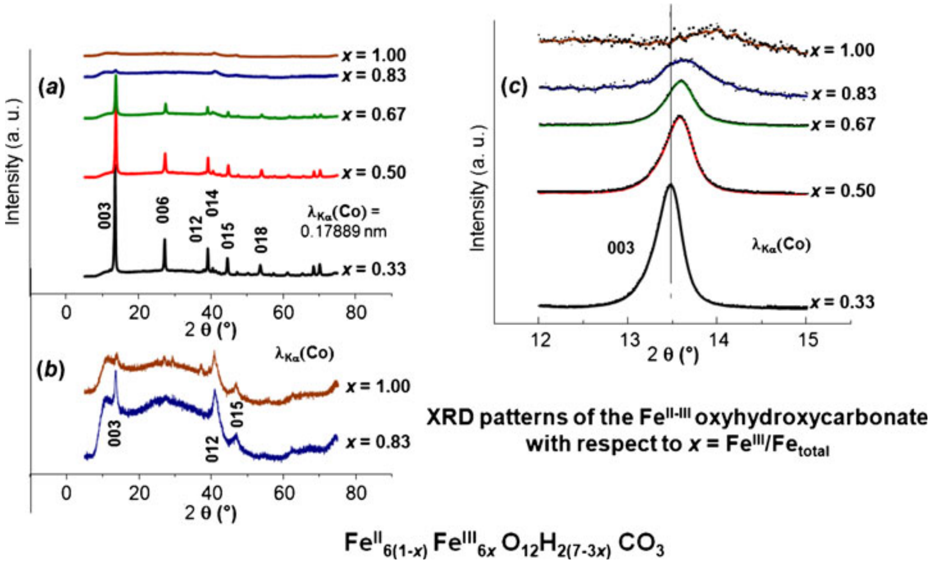


Fig. 2 X-ray diffraction patterns (XRD) of a set of hydroxycarbonate green rust samples during deprotonation for values of $x = [\mathrm{Fe^{III}}]/[\mathrm{Fe_{total}}]$ ranging from 0.33 to 1. (**a**) all patterns using the same scale for intensity, (**b**) details for $x = 0.83$ and 1, (**c**) the (003) lines demonstrating the contraction of the lattice with x and the resulting strain due to the progressive deprotonation (from [17])

Table 2 Interplanar distances d_{hkl} and cell parameters of $R\bar{3}\,m$ space group GR[$\mathrm{CO_3^{2-}}(x)$] computed from XRD data versus average ferric molar fraction $x = [\mathrm{Fe^{III}}]/[\mathrm{Fe_{total}}] \in [(1/3)\text{-}1]$ (from [17])

x	0.33	0.50	0.67	0.83	1
d_{003} (Å)	7.632	7.569	7.565	7.54	∼ 7.34
d_{012} (Å)	2.679	2.669	2.672	–	–
c (Å)	22.896	22.707	22.695		
a (Å)	3.182	3.168	3.173		

deviation of gaussian distributions (Table 1) [8, 14]. Four quadrupole doublets were displayed, where D_1 and D_2 with large splitting were attributed to Fe^{II} state and D_3 and D_4 with small splitting to Fe^{III} state. The ferrous D_1 and D_2 were always in a 3:1 abundance ratio as due to Fe^{II} in register to water molecules or to a carbonate ion in the neighbouring interlayer. D_3 had always an abundance of 33% corresponding to the Fe^{III} cations that balanced the carbonate anions as in GR($\mathrm{CO_3^{2-}}$) whereas D_4, which did not exist initially in GR($\mathrm{CO_3^{2-}}$) (Fig. 1a), appeared with the deprotonation of OH$^-$ ions at the vertices of the octahedrons that surrounded the Fe^{II} cations getting oxidised.

The structure keeps essentially that of GR($\mathrm{CO_3^{2-}}$) as testified by X-ray diffraction patterns (Fig. 2) [17] meaning that the long range order of anions is conserved within the interlayers and that Fe^{III} ions in layers are also ordered leading to diversified magnetic properties [18]. When x increases, OH$^-$ ions at the vertices of the octahedrons surrounding Fe cations get deprotonated, and consequently, the lattice contraction shifts the diffraction lines towards higher angles that results in a strain

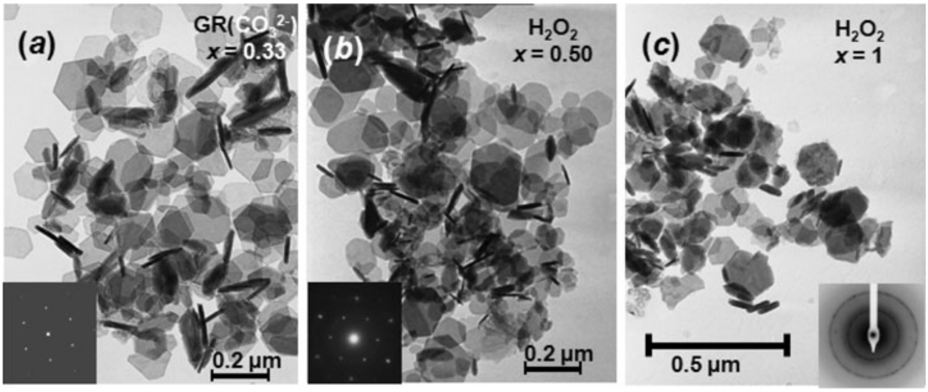


Fig. 3 Transmission electron micrographs of synthetic samples (**a**) GR(CO_3^{2-}) green rust with $x = 1/3$, (**b**) $x = 0.50$ and (**c**) GR(CO_3^{2-})* "ferric green rust" with $x = 1$. The shape of the crystals is identical since the reaction is topotactic (from [12])

since the octahedrons are no longer regular in shape (Fig. 2, Table 2) [17]; this fact is well illustrated by following the main (003) line while x increases and which becomes very hard to distinguish with ferric GR(CO_3^{2-})*. In contrast, no change occurs in the hexagonal shape of the crystals as observed by transmission electron microscopy (Fig. 3) [12].

Long range orders appear when x increases. At $x = 1/3$, for initial GR(CO_3^{2-}), each Fe^{III} ion is surrounded by 6 Fe^{II} ions; in contrast, at $x = 2/3$, each Fe^{II} ion is surrounded by 6 Fe^{III} ions and at $x = 1$, all cations are ferric (Fig. 5b–d). These ordered domains are topotaxically mixed and enable to reach any intermediate value of x as it is observed from Mössbauer spectra. Magnetic properties reflect the long range ordering of Fe^{III} cations for the definite values of x at 1/3, 2/3 and 1 [18]. The two sublattices of Fe^{II} and Fe^{III} ions in the hexagonal layer display an antiparallel coupling for $x = 1/3$ and 2/3 showing a ferrimagnetic behaviour with Néel temperatures of 5 K and about 20 K, respectively. In contrast, the "ferric green rust" at $x = 1$ is obviously ferromagnetic with a Curie temperature around 80 K with a broad range of transition.

Now, let us look at the Mössbauer spectra obtained with the samples extracted from the gleys (Fig. 4). Their fitting is classically done by using Lorentzian shape lines (Table 3). Firstly, the spectrum of the synthetic sample at $x = 0.50$ and that of the first sample extracted from the water table of the forest of Fougères can be compared (Fig. 4a & b); only two quadrupole doublets, one ferrous, in fact the superimposition of D_1 and D_2, and one ferric, the superimposition of D_3 and D_4 were considered [3, 4]. Then, the spectra of four samples extracted from the maritime marshes are displayed (Fig. 4c–f); the first one was extracted at Trébeurden and measured at room temperature (Fig. 4c) and the three others were extracted from the bay of Mont saint Michel and measured at 78 K (Fig. 4d–f). These spectra are fitted with three quadrupole doublets, one ferrous and two ferric, D_{1+2}, D_{3+4} and D'_{3+4}. When looking at the first one (Fig. 4c), we were very surprised since we were expecting to find a spectrum resembling all those previously extracted from the gley within water tables

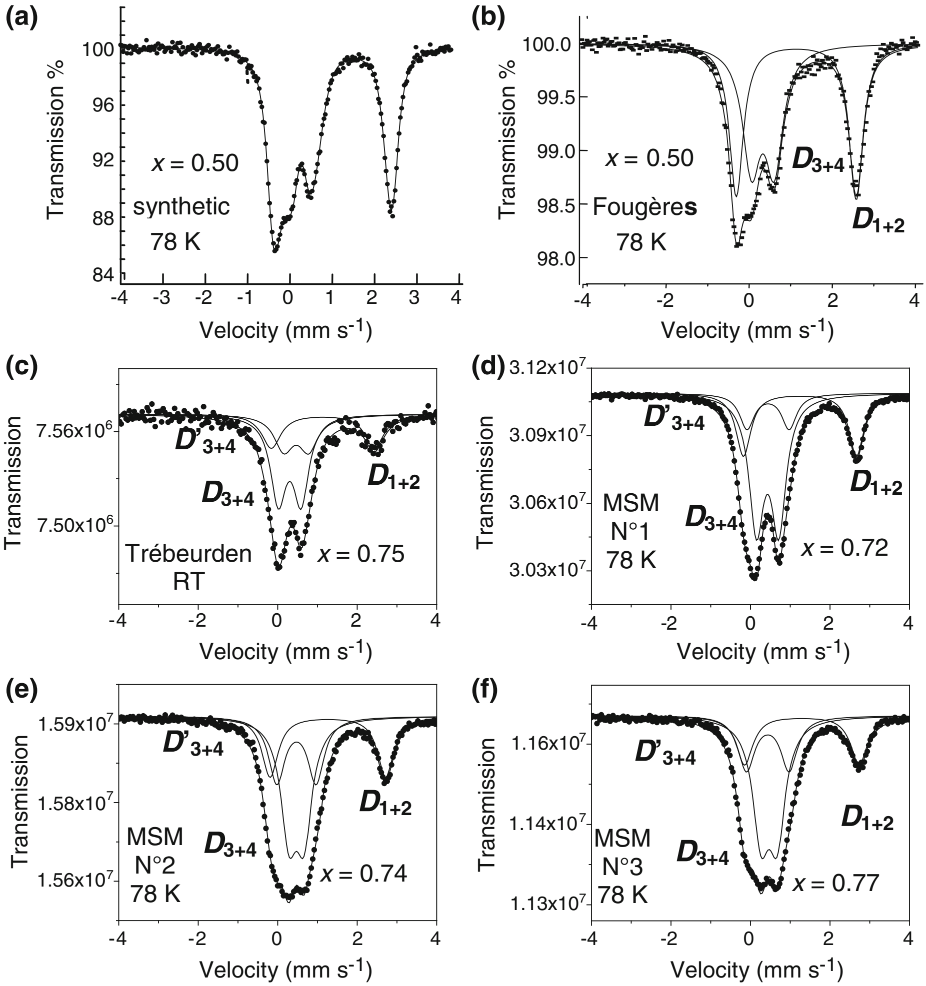


Fig. 4 Transmission Mössbauer spectra measured at 78 K of (**a**) a synthetic sample of GR(CO_3^{2-})* at $x = 0.50$ [8, 14], (**b**) the first sample of gley extracted from the aquifer of the forest of Fougères [4], (**c**) the first spectrum measured at room temperature of a gley sample extracted from the schorre of a maritime marsh in Trébeurden (Brittany), (**d**–**f**) spectra measured at 78 K of samples extracted from widely scattered locations in the bay of Mont Saint Michel (Normandy)

(Fig. 4b) where x belonged to the [1/3–2/3] range. Obviously, this assertion must be revisited since x belongs to the [2/3–1] range and we do know now that gleys from maritime marshes are different of those from continental aquifers. The first difference we can think of is that the schorre of marshes is most of the time dry and covered of water only at high tide (above tidal level 70); therefore the gley gets partially oxidized and a steady state is reached at an x value higher than for permanently waterlogged aquifers. All samples extracted from the bay of Mont Saint Michel do confirm this observation (Fig. 4d–f).

Table 3 Hyperfine parameters of quadrupole doublets in gley samples extracted from maritime marshes

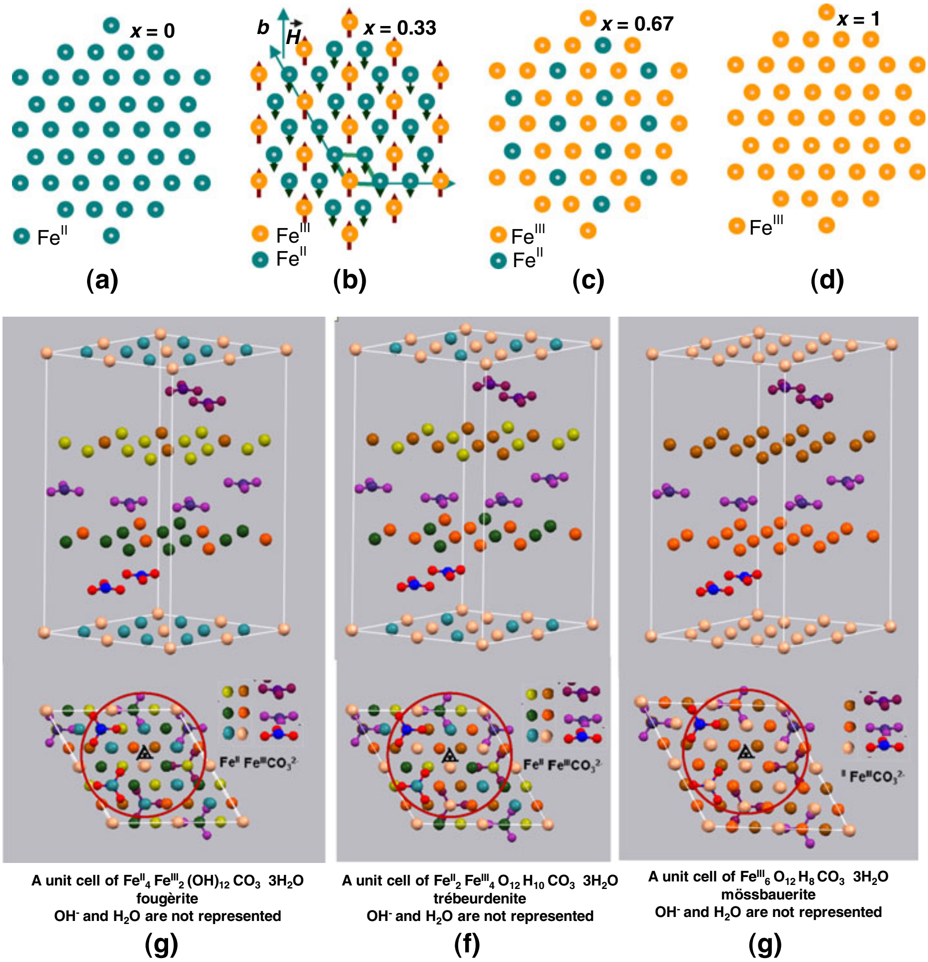
Quadrupole doublet		D_{1+2} $\mathrm{Fe^{II}}$(T)	D_{3+4} $\mathrm{Fe^{III}}$(T)	D'_{3+4} $\mathrm{Fe^{III}}$(M)
Trébeurden room temperature				
$x = 0.75$	δ(mms^{-1})	1.294 ± 0.000	0.301 ± 0.000	0.307 ± 0.000
	Δ(mm s^{-1})	2.66 ± 0.001	0.549 ± 0.000	0.972 ± 0.000
	RA (%)	25	50	25
	Γ(mm s^{-1})	0.56	0.45	0.49
Mont Saint Michel bay 78 K				
N°1	δ(mm s^{-1})	1.245	0.429	0.441
$x = 0.72$	Δ(mm s^{-1})	2.842	0.560	1.059
	RA(%)	28	56	16
	Γ(mm s^{-1})	0.45	0.49	0.50
N°2	δ(mm s^{-1})	1.263	0.471	0.470
$x = 0.74$	Δ(mm s^{-1})	2.908	0.381	0.986
	RA(%)	26	52	22
	Γ(mm s^{-1})	0.45	0.49	0.50
N°3	δ(mm s^{-1})	1.292	0.466	0.434
$x = 0.77$	Δ(mm s^{-1})	2.877	0.405	1.073
	RA (%)	23	46	31
	Γ(mm s^{-1})	0.45	0.49	0.50

Spectra are measured at room temperature or 78 K (Fig. 3) and fitting uses Lorentzian shape lines. δ: isomer shift in mm s^{-1} (reference is α-iron at ambient), Δ: quadrupole splitting in mm s^{-1}, *RA* (%): relative area and Γ: half width at half maximum in mm s^{-1}

In order to stress the long range orders that define the three distinct compounds corresponding to x values, 1/3, 2/3 and 1, and which are mixed, computer fittings used here with the samples extracted from the maritime marshes (Fig. 4c–f, Table 3) display doublets attributed to the ordered compound at $x = 2/3$, i.e. D_{1+2} and D_{3+4} in a 1:2 intensity ratio, and one other ferric doublet D'_{3+4} attributed to the ferric compound at $x = 1$. Note that the quadrupole splitting is much larger for D'_{3+4} (around 1 mm s^{-1}) than for D_{3+4} (around 0.5 mm s^{-1}) as it was also the case with synthetic samples.

Three minerals must correspond to the three compounds that are topotaxically mixed. We propose (i) to redefine and limit to $x = 1/3$ "fougèrite" $\boldsymbol{F}$, the $\mathrm{Fe^{II-III}}$ hydroxycarbonate green rust $\mathrm{GR(CO_3^{2-})}$, i.e. $\mathrm{Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O}$, (ii) to name "trébeurdenite" $\boldsymbol{T}$, the $\mathrm{Fe^{II-III}}$ oxyhydroxycarbonate, i.e. $\mathrm{Fe^{II}_2Fe^{III}_4(OH)_{10}O_2CO_3 \cdot 3H_2O}$ with $x = 2/3$, and finally (iii) to name "mössbauerite" $\boldsymbol{M}$, the "ferric green rust" $\mathrm{GR(CO_3^{2-})^*}$, i.e. $\mathrm{Fe^{III}_6(OH)_8O_4CO_3 \cdot 3H_2O}$ ferric oxyhydroxycarbonate, with $x = 1$. The three dimensional structure of these minerals is drawn (Fig. 5).

An average formula $\mathrm{Fe^{II}_{6(1-x)}Fe^{III}_{6x}O_{12}H_{2(7-3x)}CO_3 \cdot 3H_2O}$ can be obtained by mixing these minerals and, in fact, any sample in the range [1/3, 2/3] is a mixture of $\boldsymbol{F}$ and $\boldsymbol{T}$ and their proportions are obtained by the lever rule: $\left[(2-3x)\,\boldsymbol{F} + (3x-1)\,\boldsymbol{T}\right]$, whereas, in the range [2/3, 1], it is a mixture of $\boldsymbol{T}$ and $\boldsymbol{M}$ with proportions of $\left[3\,(1-x)\,\boldsymbol{T} + (3x-2)\,\boldsymbol{M}\right]$. Up till now, occurrences of gleys extracted from continental aquifers as in Fougères [3, 4, 15, 16] and Denmark [12], or from maritime marshes as in Trébeurden and Mont Saint Michel display values of $x \in [0.33, 0.67]$ or [0.67, 1], respectively.



A unit cell of $Fe^{II}_4 Fe^{III}_2 (OH)_{12} CO_3\ 3H_2O$
fougèrite
OH^- and H_2O are not represented
(g)

A unit cell of $Fe^{II}_2 Fe^{III}_4 O_{12} H_{10} CO_3\ 3H_2O$
trébeurdenite
OH^- and H_2O are not represented
(f)

A unit cell of $Fe^{III}_6 O_{12} H_8 CO_3\ 3H_2O$
mössbauerite
OH^- and H_2O are not represented
(g)

Fig. 5 Ordering of Fe^{III} ions within an hexagonal layer of Fe cations leading to various magnetic properties [18]: (**a**) $Fe^{II}_6(OH)_{10}(H_2O)_2\ CO_3 \cdot 3H_2O$; (**b**) $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O$; (**c**) $Fe^{II}_2Fe^{III}_4(OH)_{10}O_2CO_3 \cdot 3H_2O$ (**d**) $Fe^{III}_6(OH)_8O_4CO_3 \cdot 3H_2O$. Three dimensional views of (**e**) fougèrite ***F***, (**f**) trébeurdenite ***T***, and (**g**) mössbauerite ***M***

4 Conclusion

Several occurrences of "gleys" extracted from maritime marshes reveal that the iron containing minerals which are responsible for their bluish-green or grey shade are topotaxically related with an average ferric molar fraction $x = [Fe^{III}/Fe_{total}]$ belonging to the [2/3–1] range whereas "gleys" that were extracted from continental aquifers displayed, up till now, x values within the [1/3–2/3] range. By comparing the Mössbauer spectra with those of synthetic samples, one concludes that there exist three definite minerals we propose to call (i) "fougèrite", ***F***: $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O$ where $x = 1/3$, (ii) "trébeurdenite", ***T***: $Fe^{II}_2Fe^{III}_4(OH)_{10}O_2CO_3 \cdot 3H_2O$ where

$x = 2/3$ and (iii) "mössbauerite", ***M***: $Fe^{III}_6(OH)_8O_4CO_3 \cdot 3H_2O$ where $x = 1$. Any average formula, i.e. $Fe^{II}_{6(1-x)}Fe^{III}_{6x}\ O_{12}H_{2(7-3x)}\ CO_3 \cdot 3H_2O$ can be obtained by topotactic mixture of these minerals, ***F*** and ***T*** in the [1/3, 2/3] range (continental aquifers) and ***T*** and ***M*** in the [2/3, 1] range (maritime marshes). We shall use these findings for studying the diagenesis of littoral sediments into thalassasoils.

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