Identification criteria for fougerite and nature of the interlayered anion

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Abstract

Fougerite, responsible for the blue-green colour of gleysols can be identified simply in the field by its colour that changes to ochre when in contact with oxygen from the atmosphere, by selective dissolution techniques, by Mössbauer, Raman and EXAFS spectroscopies. The nature of the interlayer anion cannot be determined by these techniques. XRD identification allows this determination, but is difficult because the main peak of fougerite is very close to the peak of kaolinite. A closer examination of XRD diagrams and decomposition by DECOMPXR software (Figure 1) makes it possible to identify fougerite and to complete the identification criteria for fougerite (Table 1). In addition, the nature of the interlayer anion can be discussed. In fougerite from Fougères, the eponyme site of the mineral, OH^- appears as the most likely anion, but in other soil environments, other anions can be present in the interlayer. The generic name of fougerite designates the triple Fe(II)-Fe(III)-Mg hydroxy-salt, analogous to pyroaurite (Table 2). The originality of fougerite is that instead of the other layered double hydroxides (LDH) such as Ca – Al(III) or Ni(II) – Al(III) LDH, Fe(II) and Fe(III) can exchange electrons in the layer between each other. Though it is generally a nano-mineral, it is however not poorly ordered, but well crystallized (trigonal system).

Key Words

Fougerite, Fe, gleysols, oxides, hydromorphy

Introduction

Fougerite (IMA 2003-057) is the natural green rust mineral responsible for the bluish to greenish colours expressing *reductomorphic properties* (Driessen *et al.* 2001, Annex 2, p.314). As early as in the original definition of gley by Vyssotskii (1905; 1999), the colour of gley was considered as indicating the presence of Fe "protoxide", *i.e.* of ferrous oxide (*s.l.)*. This colour has been ascribed to "green rust" by Taylor (1981). Green rusts are intermediate compounds in the corrosion of steel first evidenced by Girard and Chaudron (1935). The first evidence for green rust as a natural mineral was provided by Trolard *et al.* (1996, 1997), in a gleysol developed on granite in Fougères (Brittany, France), from which the name fougerite was proposed. The mineral has been homologated by the International Mineralogical Association in 2004 (Trolard *et al.* 2007). Green rusts belong to a larger group of compound, layered double hydroxysalts (LDH) consisting of brucitic layers in which octahedral sites are occupied either by bivalent cations or by trivalent cations. As all sites are occupied, this generates an excess positive charge, compensated in the interlayer by anions. Water molecules are present too in the interlayer. Green rusts can be easily synthesized in the laboratory (Murad 1990), form by oxidation of Fe(II) in solution (Lewis 1997), by partial oxidation of $Fe(OH)_2$ (Génin *et al.* 1994) or by bacterial oxidation of Fe(III) oxides (Fredrickson *et al.* 1998). The generic formula of green rusts is $[Fe(II)_{1-x} Fe(III)_x (OH)_2][x/n A^{-n}, mH_2O]$, where x is in the range [1/4 – 1/3]. The interlayer anion is largely variable: bromide, carbonate, chloride, iodide, oxalate, selenate, sulphite, sulphate… With bromide, carbonate, chloride, iodide, oxalate and sulphite, that are small sized, spherical or planar anions, there is only one layer of water molecules in the interlayer, and the symmetry group is trigonal (GR1 structure) (Refait *et al.* 1998), while with selenate and sulphate, that are tetrahedral, there are two layers of water molecule, and the layer stacking is different (GR2 structure) (Simon *et al.* 2003). Fougerite was first characterized by selective dissolution techniques, Mössbauer and Raman spectroscopies, then by EXAFS, which confirmed the structure, but proved that in addition to Fe, Mg was present in the natural mineral (Refait *et al.* 2001). Due to the small abundance of fougerite in gleysol, (about 2-4 %), XRD are generally considered as ineffective to identify it. Moreover, the main peak of synthetic green rust such as GR1(Cl) is at 7.97 Å, very close to the main peak of kaolinite at 7.13 Å. However, XRD is much more widely accessible than Raman and Mössbauer spectroscopies. These latter techniques do not give access to the *c* parameter, which depends on the nature of the interlayer anion. This nature is not necessarily constant anayway, as anion exchange is possible, but for fougerite *from Fougères*, the nature of the interlayer anion is controversial. It was simply proposed that it is OH^- (Trolard *et al.* 1996, 1997; Génin *et al.* 1998), but on the sole basis of experimental data obtained on carbonate synthetic green rust Ruby *et al.* (2006) claim that fougerite is "the mineral counterpart" of this synthetic compound, without any direct data on the natural mineral. XRD data previously acquired on the mineral were thus examined more closely to verify if fougerite can be identified with this simpler technique, and if the nature of the interlayer mineral can be determined.

Methods

Five samples were taken in the gleysol from Fougères, of which two (silty and saprolite) showed a reductomorphic colour pattern and three (two silty and one saprolite) an oximorphic colour pattern; clay fraction was separated by sedimentation under inert atmosphere in a glove box, then saturated with Mg, K and ethylene-glycol or heated to 350, 450 and 550 °C. Diffractograms were acquired with a Siemens D-500 (40 kV, 20 mA) diffractometer, equipped with a graphite monochromator, using Co-$K_{\alpha 1}$ from 3° to 45° (2θ), by 0.02° steps, 10 s counting time per step, in scan mode (Feder 2001). The DECOMPXR software (Lanson and Besson 1992) was used in the range 3-15 ° (2θ) to decompose the peaks.

Results

The raw and decomposed diagram of a sample (saprolite) with a reductomorphic colour pattern (Figure 1) show that without decomposition, kaolinite peak masks nearly completely the fougerite peak. Only a slight shoulder can be seen in the raw diagram. The decomposition shows clearly a peak at 7.89 Å, distinct from the peak of kaolinite at 7.13 Å. Similar peaks are observed on two other samples, at 7.94 and 7.92 Å. This peak disappears on heating and shifts to either smaller or larger values with Mg saturation.

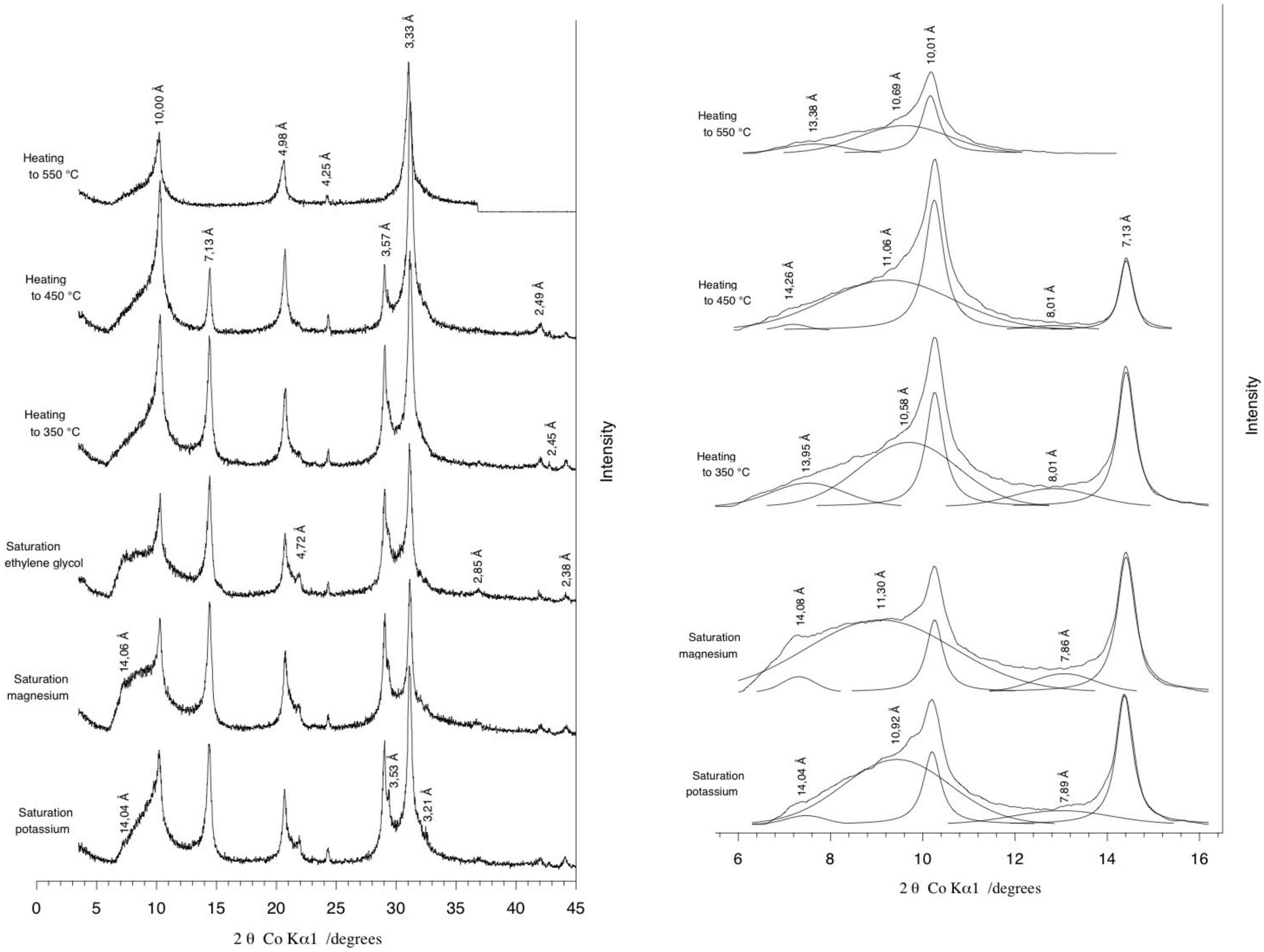

Figure 1. Raw (left) and decomposed (right) XRD diagram of the clay fraction in a reductomorphic saprolite in Fougères, where fougerite was originally described (from Feder 2001; Trolard and Bourrié 2008).

Discussion

Identification of fougerite by XRD

Mg saturation can modify the mineral through absorption of Mg in the layer, modifying its charge. Instead K is too large to enter the octahedral layer. We retain thus the peak positions with K saturation, and we propose to ascribe them to fougerite. XRD, used with decomposition of the diagrams and close examination of the region where the main peak of fougerite occurs, *i.e.* near 8 Å, is thus a means to identify the presence of fougerite. This completes the identification criteria of fougerite (Table 1).

Table 1. Identification criteria proposed for fougerite

Method	Criteria
Colour of soil	Bluish or greenish (Munsell 2.5 Y, 5 Y, 5 G, 5 B) turning to ochreous or reddish brown within a few hours of exposure to the air
Selective dissolution	Extractible by citrate-bicarbonate without the necessity of reduction by dithionite
XRD	Main peak depending on the structure and the nature of the interlayered anion: GR1: $d_{003} = 7.5 – 8.7$ Å; 7.5 Å for carbonate-fougerite; 7.92 Å for hydroxy-fougerite; 7.97 Å for chloride-fougerite, 8.6 – 8.7 Å for sulphate-fougerite with only one plane interlayer; GR2: $d_{001} = 11.0 – 11.6$ Å for sulphate-fougerite with two planes interlayer.
Mössbauer spectroscopy	GR1: two ferrous and two ferric doublets, at 77 – 78 K: D_1: $\delta \approx 1.27$ mm/s ; $\Delta E_Q \approx 2.86$ mm/s. D_2: $\delta \approx 1.25$ mm/s ; $\Delta E_Q \approx 2.48$ mm/s D_3: $\delta \approx 0.46$ mm/s ; $\Delta E_Q \approx 0.48$ mm/s D_4: $\delta \approx 0.46$ mm/s ; $\Delta E_Q \approx 0.97$ mm/s GR2: only two doublets, one ferrous and one ferric D_1: $\delta \approx 1.27$ mm/s ; $\Delta E_Q \approx 2.83$ mm/s D_3: $\delta \approx 0.47$ mm/s ; $\Delta E_Q \approx 0.45$ mm/s
Raman spectroscopy	Bands at 427 cm^{-1} and 518 cm^{-1}
Structural formula	$[(Fe^{2+}, Mg^{2+})_{1-x} Fe^{3+}_x (OH)_2][x/n\ A^{-n}, mH_2O]$, $1/4 < x < 1/3$, cell multiplicity Z = 3; for *Fougères* – fougerite, $A^{-n} = OH^-$
System	Trigonal, space group $R\bar{3}m$
Unit cell	a = 0.3125(5) nm, c ≈ 2.25(5) nm, V = 0.1903 nm^3

Nature of the interlayered anion in fougerite from Fougères

The main peak of GR1(Cl) is at 7.97 Å, and $d_{003} = c/3$, hence the parameter *c* is obtained as: $c = 3\ d_{003} = 2.375 \pm 0.0075$ nm. This is close to, but smaller than the value obtained for GR1(Cl), c = 2.3856 nm. For carbonate-GR1, the range admitted for c is [2.25 – 2.28 nm] (Abdelmoula *et al.* 1996). The confidence interval for our measurements is [2.36 – 2.39 nm] (Student test, $n = 3$, $\nu = 2$, $\alpha = 0.05$, $t = 2.92$, $\sigma = 0.0075$ nm), which is completely out of the range above. We can thus rule out carbonate as the interlayer anion in fougerite from Fougères. This is in agreement with previous assumptions and with soil and water acidity: gleysol in Fougères is surrounded by alocrisols. Solutions are acid, with pH ≈ 4.5 – 7, and carbonate concentration is about 10^{-10} M (Bourrié *et al.* 1999). The larger *c* parameter for OH^- as compared to carbonate-GR1 can be ascribed to a less compact arrangement due to hydrogen bonding (Trolard and Bourrié 2008). As smectites can accommodate different cations in the interlayer, fougerite, green rusts and other LDHs can accommodate different anions. Indeed, natural minerals have been described with the same structure, in which OH^-, Cl^-, CO_3^{2-} are the interlayered anions (Table 2).

Table 2. Structural formula of natural minerals of the fougerite group and interlayer anions

Mineral	Structural formula	Anion
Fougerite	$[(Fe^{2+}, Mg^{2+})_{1-x} Fe^{3+}_x (OH)_2][x/n\ A^{-n}, mH_2O]$, $1/4 < x < 1/3$	OH^- in Fougères
Meixnerite	$[Mg_6Al_2(OH)_{16}][(OH)_2, 4H_2O]$	OH^-
Woodallite	$[Mg_6Cr_2(OH)_{16}][Cl_2, 4H_2O]$	Cl^-
Iowaite	$[Mg_4Fe^{III}(OH)_{10}][Cl_2, H_2O]$	Cl^-
Takovite	$[Ni_6Al_2(OH)_{16}][(OH, CO_3)\ 4H_2O]$	OH^-, CO_3^{2-}
Hydrotalcite	$[Mg_6Al_2(OH)_{16}][CO_3, 4H_2O]$	CO_3^{2-}
Pyroaurite	$[Mg_6Fe^{III}_2(OH)_{16}][CO_3, 4H_2O]$	CO_3^{2-}

Conclusion

As we speak of Ca-montmorillonite and of *Wyoming* montmorillonite, we can speak of hydroxy-fougerite and of *Fougères* fougerite. We can expect finding other types of fougerite, in hydromorphic soils with neutral or alkaline pH, carbonate-fougerite may form, while in marshes, mangroves we can expect sulphate- and chloride-fougerite to form. Identification criteria proposed here should help their determination.

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