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# LETTER TO THE EDITOR

# ON FOUGERITE

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**Abstract**—Fougerite (IMA 2003-057) was accepted by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA) in 2004 as a new mineral to represent the green rust (GR) family. The data on which it was approved, however, are inconsistent. X-ray diffraction patterns from the Fougères soils contain no peaks that could meaningfully be attributed to a GR phase. The sequential dissolution procedure used to identify GR in the soils was not rigorously tested for selectivity. If indeed it is selective, the results indicate the presence of 40−78% Fe in minerals other than GR. Other Fe-bearing phases were not included in the interpretation of the spectroscopy data that were presented. The data are consistent with the presence of Fe-bearing clays and other silicate minerals. In light of the ambiguous and conflicting data, we recommend that the case for fougerite as a mineral be re-evaluated by the IMA.

**Key Words**—Fougerite, Green Rust, IMA 2003-057, Mineral Ambiguity.

Based on data from soil samples and synthetic green rust (GR), fougerite ($(Fe^{2+},Mg)_6Fe_2^{3+}(OH)_{18}\cdot 4H_2O$; Trolard *et al.*, 2007) was accepted by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA 2003-057) (Burke and Ferraris, 2004) as the representative mineral for the GR family. Several studies have shown that Fe(II),Fe(III) layered double hydroxides are found in natural settings and many have shown that the composition and structure of synthetic material vary widely and are defined by the formation conditions. In nature, GR minerals play a significant role in Fe cycling and their activity in reducing anthropogenic contaminants has been documented clearly (lists in Hansen, 2001; Christiansen *et al.*, 2009a). Undoubtedly, the GR family of compounds deserves to be characterized and described rigorously and the application to the IMA for naming fougerite was a step in that direction. The purpose of this letter is to propose that the material identified by Trolard *et al.* (2007), and named fougerite, does not represent a single GR mineral because the evidence is insufficient to prove that the material is not a mixture of several Fe phases. A further aim of this letter is to clarify what can, and what cannot, be concluded about the soil from Fougères.

The samples used to establish the existence of fougerite were collected from three locations in Brittany, France: five soil profiles from Fougères, examined from 1996 to 2008 (Trolard *et al.*, 1996; Abdelmoula *et al.*, 1997; Trolard *et al.*, 1997; Génin *et al.*, 1998; Bourrie *et al.*, 1999; Refait *et al.*, 2001; Trolard, 2006; Trolard *et al.*, 2007) and single profiles from Quintin and Naizin (Génin *et al.*, 1998). Published data (Table 1) for the soil mineral assemblage, chemical composition, and the techniques used to study them revealed that the basement rock that has weathered to produce the soil is a cordierite granodiorite (Vire type; Jonin, 1973) and contains quartz (29%), alkaline feldspar (17%), plagioclase (36.5%), biotite (14%), cordierite (1.5%), and muscovite (1%). When the rock weathers, biotite, smectite, chlorite, kaolinite, and vermiculite are expected to form. Trolard *et al.* (1996; 1997) reported that the soil contains considerable Fe (expressed in oxide form as 3.89% $Fe_2O_3$ equivalent), which is not far from the total Fe content (4.6% $Fe_2O_3$) of the underlying bedrock (Jonin, 1973), suggesting that >80% of the original Fe remains in the soil.

Trolard *et al.* (2007) examined the soil with several techniques and interpreted the results from the perspective of a GR mineral alone. Results published by these same investigators over the years, however, provide clear evidence that other Fe phases are also present in these soils, particularly Fe phyllosilicates, which are common weathering products of cordierite granodiorite. In the following paragraphs, attention is drawn, in particular, to their published data from X-ray diffraction (XRD) (Trolard and Bourrie, 2008), Mössbauer spectroscopy (MS) (*e.g.* Trolard *et al.*, 1996; Abdelmoula *et al.*, 1997; Trolard *et al.*, 1997; Feder *et al.*, 2005), Raman spectroscopy (RS) (Trolard *et al.*, 1996; Trolard *et al.*, 1997), scanning electron microscopy (SEM) (Trolard, 2006), X-ray absorption spectroscopy (XAS) (Refait *et al.*, 2001), and selective extraction (*e.g.* Feder *et al.*, 2005; Trolard, 2006; Trolard and Bourrié, 2008).

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Table 1. Summary of the soil samples studied, including location, soil type, minerals identified, soil water pH, chemical composition in % (unless otherwise noted), and the methods used for characterization. Square bracketed numbers are the references to the data sources, as listed below.

| Location | Type | Minerals (abundance in %) | Soil water pH | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | Methods used |
|---|---|---|---|---|---|---|---|---|---|---|
| Fougères | Granodiorite bedrock (Vire type) [1] | Quartz (29), alkali-feldspar (7.3), plagioclase (36.5), biotite (14), cordierite (1.5), muscovite (1) – all from [1] | | 68.1 [1] | 15.1 [1] | 4.6 [1] | 0.05 [1] | 1.6 [1] | 1.6 [1] | not reported |
| | Granitic saprolite soil [2–7] | Quartz [3], plagioclase feldspars [3], K-feldspars [3], kaolinite [2, 3, 6, 8], smectite [6], hydroxyl-aluminous vermiculite [3, 6] (Al-beidelite) [8], illite [6, 8], interstratified minerals [3, 6] | 5.15–5.70 [9]<br>5.15–5.79 [9]<br>4.08–5.18 [3]<br>6.37–8.17 [3] | 70.7 [9, 10] | 13.8 [9, 10] | 3.89 [9–11]<br>51.4 g/kg [2] | 0.02 [9, 10] | 1.19 [9, 10] | 0.21 [9, 10] | XRD [2–7], MS [2–7, 9–12], Raman [8–10], XAS [5, 8], selective extraction [3, 4, 9, 10], SEM [13] |
| Naizin | Schistose saprolite [2, 4] | Kaolinite [2], illite [2], some chlorite [2], interstratified minerals [2] | 5.0–6.17 [2, 4] | | | 29.3 g/kg [2] | | | | XRD [2, 4], MS [4] |
| Quintin | Gleyed granitic saprolite [2] | Kaolinite [2], smectites [2], some micaceous illite [2], hydroxyl-aluminous vermiculite [2], interstratified minerals [2] | 5.45–6.9 [2, 4] | | | 60.0 g/kg [2] | | | | XRD [2, 4], MS [4] |

1. Jonin (1973)
2. Bourrié *et al.* (1999)
3. Feder *et al.* (2005)
4. Génin *et al.* (1998)
5. Refait *et al.* (2001)
6. Trolard and Bourrié (2008)
7. Trolard and Bourrié (2006)
8. Trolard *et al.* (2007)
9. Trolard *et al.* (1997)
10. Trolard *et al.* (1996)
11. Abdelmoula *et al.* (1997)
12. Feder *et al.* (2002)
13. Trolard (2006)

Table 2. Parameters for the two types of GR (Trolard *et al.*, 2007).

| | | |
|---|---|---|
| GR type 1 | $d_{003}$ = 7.5−8 Å | Space group $R\bar{3}m$ |
| GR type 2 | $d_{001}$ = 11.0−11.6 Å | Space group $P\bar{3}m_1$ |

X-ray diffraction (XRD) is the widely accepted standard method for identifying minerals and defining their structure. The basal peaks for the GR family of minerals are very characteristic (Table 2) but, in the description for fougerite, no XRD patterns of the soil were presented. Data from other techniques were used instead, justified by the claim that the characteristic GR peaks were masked by peaks from other minerals (Abdelmoula *et al.*, 1997; Génin *et al.*, 1998; Refait *et al.*, 2001; Trolard *et al.*, 2007). In XRD data from the same soils presented in 2008 (Trolard and Bourrié, 2008), however, major reflections at 3.3, 5, and 10 Å were observed from material sampled from all horizons. These spacings are consistent with kaolinite and illite and the peak at 14.1 Å is characteristic of smectite, a common Fe-bearing clay mineral (Jefferson *et al.*, 1975; Murad and Wagner, 1994; Kanket *et al.*, 2005). The presence of these clay minerals is completely consistent with weathering of the cordierite granodiorite. Furthermore, the XRD patterns for many of the phyllosilicates are similar (Moore and Reynolds, 1997). For example, muscovite, biotite, and chlorite have XRD peaks at similar *d* spacings. To prove that the 3.3 and 10 Å peaks were not from one specific phyllosilicate, these investigators should have shown the (060) reflection at ~1.5 Å (Moore and Reynolds, 1997). Unfortunately, data from this region are missing (figures 10−14 in Trolard and Bourrié, 2008).

To check for the presence of GR, the soil samples were treated with ethylene glycol and solutions of KCl and $MgCl_2$ and then heated to 350, 450, and 550ºC. Although XRD patterns for the untreated, original soil were not included, data from the dried, treated solids were presented. Trolard and Bourrié (2008) "clearly" observed a peak in the XRD patterns representing a GR phase. No peak was present, however, at 7.5−8 Å (Figure 1 here and figures 10−14 in Trolard and Bourrié,

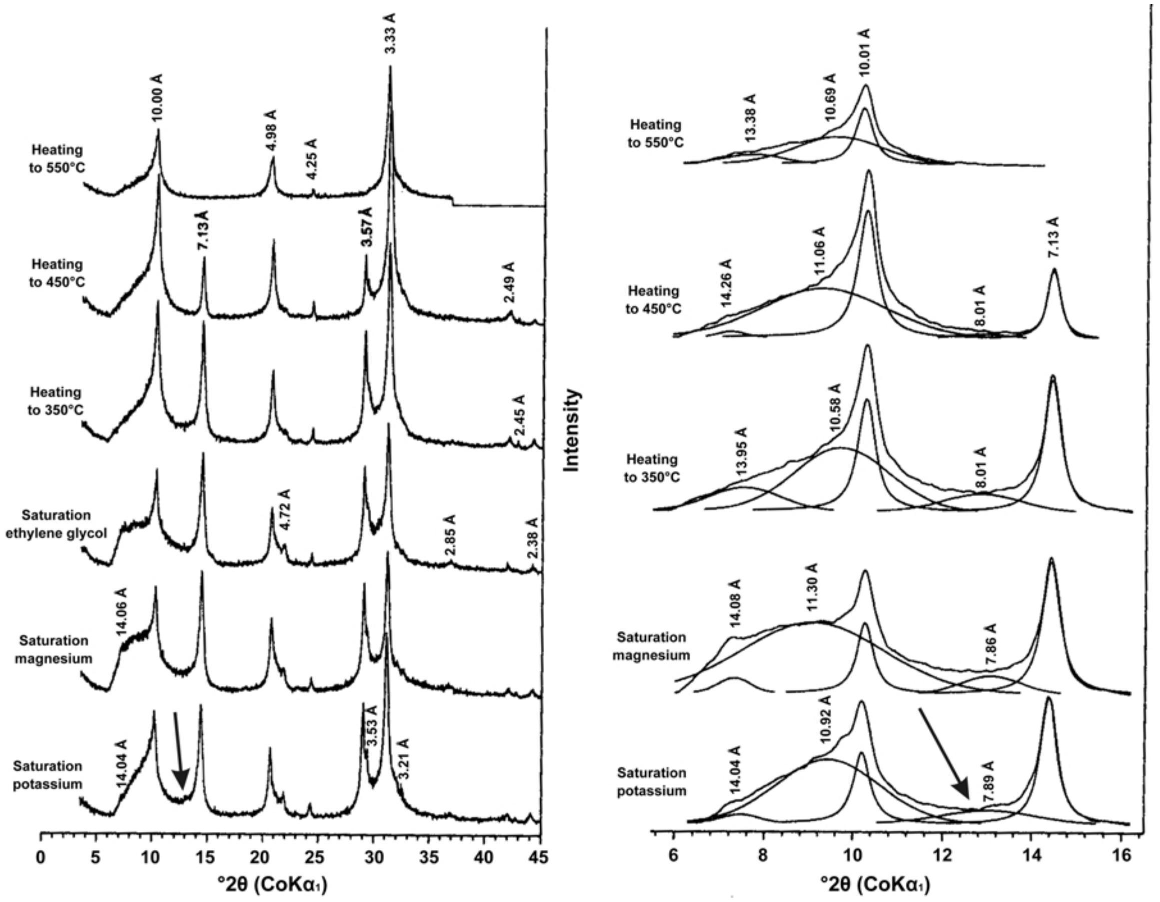

Figure 1. XRD patterns of the clay fraction for "Sample 4" from Fougères (reprinted from Trolard and Bourrié, 2008, with permission from Elsevier). This figure is claimed to show clearly peaks of fougerite (green rust) at ~13º2θ (black arrow), but no such peak is "clear" in the raw pattern.

2008). The Rietveld fitting presented, which should describe a GR peak, resulted in a peak width of 3 Å, which is unrealistic. In fact, in the region where these peaks ought to be, the diffraction intensity is at a minimum. It is a region between two major silicate peaks at 10 Å, which can represent illite, and 7 Å, for kaolinite. The data from the treatment experiments are, therefore, inconclusive.

Selective extraction, using citrate-bicarbonate (CB) as the active agent, was also used to check for a GR phase (Trolard *et al.*, 1996; Génin *et al.*, 1998; Feder *et al.*, 2005; Trolard 2006; Trolard *et al.*, 2007). The CB is assumed to extract only "complexed Fe", *i.e.* Fe from GR and from Fe-organic complexes (Trolard and Bourrié, 2008). Although selective extraction methods can provide information about the composition of a soil, their use as a stand-alone tool for mineral identification is questionable (Borggaard, 1988) because dissolution is much less selective than one might hope (*e.g.* Mitchell *et al.*, 1971; Borggaard, 1988; Acebal *et al.*, 2000, 2003). Based on the rate of Fe release, between 22% and 60% of the total Fe in the soils was attributed to dissolving GR (Trolard et al., 2007). No study has been found to document the rate of CB-induced dissolution of GR compared to other soil minerals, so this evidence does not demonstrate convincingly the presence of a GR phase. However, if CB truly is able to selectively dissolve fougerite, the observed rates of Fe release would mean that from 40% to 78% of the soil Fe is associated with other minerals, quite possibly silicates. Yet, in the interpretation of the XAS, RS, and MS data, no other Fe phases were considered. This is indefensible, considering that XRD reveals Fe-bearing phyllosilicates.

Mössbauer spectroscopy (MS) data were fitted with four absorption lines from Fe(II) and Fe(III), exclusively interpreted to represent Fe in a GR phase (Génin *et al.*, 1998; Feder *et al.*, 2005). Although MS parameters from synthetic GR are similar to those of the interpreted soil data (Table 3), Fe from a range of other bonding environments has absorption lines that are compatible with the soil spectra. Examples include Fe in biotite, smectite, vermiculite (Heller-Kallai and Rozenson, 1981; Diamant *et al.*, 1982; Cardile *et al.*, 1987), muscovite (Ferrow, 2002; Dainyak *et al.*, 2004), illite (Murad and Wagner, 1994; Murad, 1998; Dainyak *et al.*, 2004), and fine-grained Fe oxides (Cornell and Schwertmann, 2003), all of which are expected in a soil formed from weathered cordierite granodiorite. Feder *et al.* (2005) contended that the relationship between isomer shift (IS) and quadropole splitting (QS) for the soil is different from that for silicate minerals. However, the analysis temperature affects both of these hyperfine parameters. The soil samples were analysed at 283 K. References for the silicate MS data were not

Table 3. Mössbauer parameters of synthetic GR and soil samples at 77 K (unless otherwise noted).

| | IS (mm/s) | QS (mm/s) | Relative area (%) | Reference |
|---|---|---|---|---|
| $GR_{Cl}$ | | | | Refait *et al.* (1997) |
| $D_1$ | 1.26 | 2.80 | 46 | |
| $D_2$ | 1.27 | 2.55 | 26 | |
| $D_3$ | 0.48 | 0.38 | 28 | |
| $GR_{SO_4}$ | | | | Génin *et al.* (1996) |
| $D_1$ | 1.27 | 2.86 | 66 | |
| $D_3$ | 0.48 | 0.45 | 34 | |
| $GR_{NaSO_4}$ | | | | Christiansen *et al.* (2009b) |
| $D_1$ | 1.27 | 2.90 | 63 | |
| $D_3$ | 0.46 | 0.49 | 37 | |
| $GR_{CO_3}$ | | | | Drissi *et al.* (1995) |
| $D_1$ | 1.27 | 2.92 | 49 | |
| $D_2$ | 1.28 | 2.69 | 17 | |
| $D_3$ | 0.47 | 0.43 | 34 | |
| Soil (1) | | | | Trolard *et al.* (1997) |
| $D_1$ | 1.25 | 2.87 | 50.7 | |
| $D_3$ | 0.45 | 0.54 | 49.3 | |
| Soil (2) | | | | Refait *et al.* (2001) |
| $D_1$ | 1.27 | 2.86 | 59 | |
| $D_2$ | 1.25 | 2.48 | 7 | |
| $D_3$ | 0.46 | 0.48 | 20 | |
| $D_4$ | 0.46 | 0.97 | 14 | |
| Soil (3) 283K | | | | Feder *et al.* (2005) |
| $D_1$ | 1.00–1.08 | 2.6–2.74 | 28–62 | |
| $D_2$ | 0.6–1.0 | 2.2–2.7 | 0–30 | |
| $D_3$ | 0.21–0.30 | 0.65–0.80 | 35–67 | |

provided in Feder *et al*. (2005), so we cannot rule out the possibility that temperature is responsible for the differences. If the analyses were conducted at room temperature, we note that synthetic chloride-bearing green rust, which is assumed by Trolard *et al*. (2007) as structurally very similar to fougerite, has room-temperature MS parameters (Fe(II): IS: 1.22, QS: 2.34; IS: 1.11, QS: 2.02; Fe(III): IS: 0.35 QS: 0.58; Refait *et al*., 1998) that are well within the range for silicates and that differ significantly from those of the soil sample. The MS parameters for soil resemble those for some Fe-phyllosilicates more closely than they match those for the fougerite analog. Thus MS cannot be used to exclude the presence of Fe-phyllosilicates or to prove the presence of fougerite.

X-ray absorption spectroscopy (XAS) also provides information about the bonding environment. Refait *et al.* (2001) presented Fe-XAS data on Fougères soils. The near-edge portion of the spectra (XANES) agrees reasonably well with that from $CO_3$-bearing GR, but XANES spectra from Fe silicates could also strongly resemble those of GR (Brigatti *et al.*, 2000; O'Day *et al.*, 2004). For example, for the 7100 to 7160 eV region investigated by Refait *et al.* (2001, figure 2), the location of three of the four inflection points for $CO_3$-bearing GR and chlorite differ by <0.4 eV (O'Day *et al.*, 2004).

From extended X-ray absorption fine structure (EXAFS) spectra of the soil, the $k^3$-weighted Fourier transform (radial structure function; RSF) shows peaks at $R \approx 2$ Å (Fe–O) and 3.1–3.2 Å (Fe–Fe), as well as peaks for more distant Fe at ~5.5 Å, ~6.3 Å, ~8.3 Å, and ~9.2 Å (corrected for phase shift). In addition to the peaks that the authors reported, the RSF also shows three small but clear peaks at R values from ~3.7 to ~4.5 Å (Refait *et al.*, 2001, figure 3), which do not appear in the RSF of GR. Noted also is that the 3.1–3.2 Å peak attributed exclusively to the Fe–Fe distance is compatible with the signal from Fe and a next-nearest neighbor tetrahedrally coordinated Si or Al in phyllosilicates (Manceau *et al.*, 2000). Furthermore, the ~4.5 Å shoulder corresponds to the distance expected between Fe and a second neighbor Si or Al (*e.g.* Manceau *et al.*, 1988) and a similar, low-intensity peak has been observed for preferred and randomly oriented smectites (Manceau *et al.*, 2000; Vantelon *et al.*, 2003). Therefore, although the EXAFS spectra from the soil samples have features resembling GR and pyroaurite (another fougerite analog), the match with Fe-bearing phyllosilicates is actually more complete.

Raman spectroscopy (RS) in the range 350–700 $cm^{-1}$ on soil samples from Fougères shows peaks at ~427, 518 (very broad), 630, and 675 $cm^{-1}$. For synthetic GR, peaks at 427 and 518 $cm^{-1}$ have been identified, but peaks at 630 and 675 $cm^{-1}$ are absent. Published data from kaolinite, cordierite, illite, muscovite, and smectites show vibration bands that match all four peaks (Frost, 1995; Frost, 1997; Sontevska *et al.*, 2007). In addition, the peaks for the soil are narrower than those for synthetic GR, suggesting that the natural material is more ordered than synthetic material, a feature that is in conflict with the lack of well defined peaks in the XRD patterns. Raman spectroscopy cannot, therefore, exclude the possibility that Fe phyllosilicates are present; in fact, the evidence is to the contrary.

An SEM image from a soil sample (Trolard, 2006, figure 5) shows a well defined, hexagonal particle that is ~500 nm wide, but composition data proving the presence of Fe are absent. Such clear hexagonal morphology is also characteristic of kaolinite (Ekosse, 2000). If the GR phase were as abundant and well crystallized as this image would suggest, the XRD pattern should provide clear, sharp peaks for GR.

In conclusion, the data from XRD and selective extraction show clearly the presence of Fe-bearing minerals, including Fe silicates. In the analysis of the spectroscopic data, however, the possibility that Fe could exist in bonding environments other than GR has been overlooked, resulting in a less than complete description of the Fe-bearing minerals in the Fougères soils. The case presented for establishing the presence of the mineral, fougerite, is ambiguous.

This comment does not challenge the hypothesis that GR could be present in soils, as such, but contends that the nature and structural parameters of the GR minerals in the Fougères soil are poorly constrained. Therefore, the authors recommend that the IMA re-evaluate the merits of the case for fougerite.

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