

REPLY TO THE LETTER TO THE EDITOR BY CHRISTIANSEN, DIDERIKSEN, SKOVBJERG, NEDEL, AND STIPP: “ON FOUGERITE”

F. TROLARD AND G. BOURRIÉ*

INRA, UR 1119, Géochimie des Sols et des Eaux, Aix-en-Provence, France

Christiansen *et al.* (2011) questioned the validity of the description of fougérite as the natural mineral of the group of green rusts (GRs), homologated by the International Mineralogical Association (IMA) on the basis of numerous papers published from 1996 to present by Trolard and coworkers. Christiansen *et al.* (2011) proposed that “the material identified by Trolard *et al.* (2007), and named fougérite, 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.”

Christiansen *et al.* (2011) noted that the methods used by Trolard and colleagues included X-ray diffraction, Mössbauer spectroscopy, Raman spectroscopy, selective extraction, and scanning electron microscopy (SEM). All of the listed techniques are then questioned. Before entering into detail, however, the authors make an error of logic: in every branch of science, the fact that any single technique is questionable does not mean that a combination of those techniques cannot be used to lead to a clear conclusion. The conditions of formation of a rock are better constrained by the identification of a paragenesis than of a single mineral. The same is true in phytosociology, *etc.* The question is not, therefore, “Is fougérite the only Fe phase?” but rather, “Is a natural mineral with the structure type of GR present?” Several lines of evidence, given below, support the existence of just such a mineral type. Remarkably, Christiansen *et al.* (2011) do not question this evidence.

(1) The color change from green-blue to yellow on exposure to the air within minutes has long been considered, in soil classification systems and soil taxonomies, as evidence for the presence of GRs (*e.g.* WRB, 2006, p. 45; Driessen *et al.*, 2001, p. 314). Lewis (1997) observed experimentally the lability of GRs when in contact with air and their decomposition by dilution due to their great solubility and their oxidation to lepidocrocite.

(2) The formation of lepidocrocite or goethite occurs as an oxidation product of the solid phase, in agreement with all experimental evidence, including from Schwertmann and coworkers (*e.g.* Schwertmann and

Fechter, 1994). Christiansen *et al.* (2009) argued that “the solid oxidizes after only a few minutes of exposure to air.” This criterion is met in Fougères and is in favor of the presence of a green rust mineral. Christiansen *et al.* (2011) do not question this observation. Why should it be relevant for this latter study and not for that of Trolard *et al.*?

(3) Soil-solution composition, as interpreted by checking the equilibria with Fe minerals based on chemical thermodynamics and on our model of ternary solid solution, favors Fe control by mixed Fe(II)–Fe(III) phases and not by Fe(III) oxides *sensu lato*.

(4) *In situ* Mössbauer spectra of the Fougères soil (measured with the miniaturized MIMOS spectrometer, which produced a spectrum every 48 h at the implanted depth and without further disturbance of or air entry into the soil) at first revealed no fougérite, but after two weeks a spectrum consistent with fougérite was clearly observed (Feder *et al.*, 2005). This implies fougérite was not present initially, but formed within two weeks after implanting the spectrometer.

Observations 1 through 4 cannot be explained by oxidation of silicate-bound Fe. An Fe phase must be present which oxidizes readily to lepidocrocite, can be dissolved without previous reduction by dithionite, and closely resembles synthetic GR. This phase is the one we have named fougérite.

The statement “Trolard *et al.* (2007) . . . interpreted the results from the perspective of a GR mineral alone” is erroneous. The focus of our study was on redox processes in soils under alternating aerobic and anaerobic conditions, which implies Fe biogeochemical activity, and GRs are a key factor in this Fe cycle. Trolard *et al.* (2007) demonstrated the presence of GR as a natural mineral, while GRs were previously only known as synthetic compounds. This does not imply that 100% of the Fe is present as fougérite. The presence of other Fe (oxyhydr)oxides and clay minerals is discussed widely in the work of Trolard *et al.* (2007).

While it is perfectly acceptable to question an interpretation of observations and to propose alternative interpretations, any new interpretation offered must account for all the observations. Christiansen *et al.* (2011), however, deliberately ignored evidence that contradict their ideas, but they neither propose an alternative model accounting for all observations nor do they put forward any new data.

* E-mail address of corresponding author:

bourrie@aix.inra.fr

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DETAILED REMARKS

(1) In Table 1 of Christiansen *et al.* (2011) the minimum pH measured by Feder *et al.* (2005) should be shown as 6.28 and not 6.37.

(2) The deduction, based on comparing the Fe content in the soil with that in the bedrock, that “>80% of the original Fe remains in the soil” is incorrect. Weathering is well known to not be isovolumetric, so percentages cannot be compared unless they are referred to a conservative element, *e.g.* Ti or Th. During weathering, the Fe should be expected to become concentrated by the preferential weathering of other elements (Na, K, Ca, Mg, Si). The crude calculation of Christiansen *et al.* (2011) leads to the opposite conclusion, *i.e.* that Fe was mobilized in Fougères, which is easily explained in an environment where reduction is active. Christiansen *et al.* (2011) seemed to ignore most of the work done on weathering and soil formation, as one must not compare crude mass percentages, but take into account collapse of the structure during weathering. In this environment, Fe is in fact mobilized rather than concentrated, because of the reducing environment, thus overcoming the selective mobilization of other elements. Smectites, chlorites, and biotites are not stable in this environment. Kaolinite is present, but does not contain Fe. As evidenced by selective extractions, silicate-Fe is negligible (see below).

(3) For the XRD patterns, the attribution of the peaks at $\sim 8 \text{ \AA}$ to fougérite is based on the crystallographic properties of synthetic GRs, which indicate where one must look for the main peak of fougérite. This value is in perfect agreement with the value given by Lewis (1997) at 7.95 \AA . Due to the small abundance of fougérite and the proximity of the peak of kaolinite, one cannot easily detect the peak of fougérite in the raw XRD trace, but it appears after decomposition using the *DECOMPXR* program by Lanson and Besson (1992). Of course, the width of the fit must not be considered as an index of crystallinity of the mineral. Here, Christiansen *et al.* (2011) made another error of logic, asserting, “We cannot see where the particular ‘clear’ peak is present in the raw pattern.” When looking at the raw pattern, a small peak is visible as indicated by the arrow. Of course, it is more visible when a better data treatment is used. We argue that when the sensitivity of a data-treatment technique (raw diagrams) is insufficient, one can extract more information with a better data-treatment technique, such as by applying *DECOMPXR* to the analysis of a raw XRD pattern. After doing this, the presence of the fougérite peak is clear (figure 1 and figures 10–14 from Trolard and Bourrié, 2008). The arrow shows the presence of a small peak, which is more apparent after treatment with *DECOMPXR*.

(4) Clay minerals obviously exist in soils, and this is the case in both Fougères (mainly Al-vermiculite and mica) and Quintin. Not all of the observations can be

explained by considering that all Fe is present in phyllosilicates, however. The amount of Fe present in silicate was demonstrated by Feder *et al.* (2005) to be relatively minor. In that study, Fe phases extractible by dithionite-citrate-bicarbonate (DCB) from oximorphic silty (15–50 cm) and reductomorphic silty (50–80 cm) horizons (figure 2 in Feder *et al.*, 2005) comprised 86 to 95% of the total Fe, while Fe phases extractible by citrate-bicarbonate (CB) amounted to 60 to 70% of total Fe. The maximum content of silicate Fe was thus 10% of total Fe (4%), *i.e.* 0.4%. As an average in bulk samples, Fe (oxyhydr)oxides amount to 90% of total Fe, and $\frac{2}{3}$ of the Fe in those phases is labile, such as in fougérite (Trolard, 1996). The peak at $\sim 8 \text{ \AA}$ cannot be a harmonic of the peaks at 14 \AA or 10 \AA . After CB extraction, the Mössbauer peaks disappear (Feder, unpublished results).

(5) Christiansen *et al.* (2011) state “No study has been found to document the rate of CB-induced dissolution of GR compared to other soil minerals.” They, however, cite Trolard *et al.* (1996), who stated, “Kinetic extractions obtained on the natural sample show that the amounts of iron extractable with CB under nitrogen atmosphere are equal to the DCB ones after a few hours and represent 98% of total Fe (table I; fig. 1 [in Trolard *et al.*, 1996]). The Fe-CB fraction is drastically reduced – up to 60% – when the sample is oxidized. Kinetic extractions made on synthetic minerals show that CB does not dissolve goethite, only slightly dissolves a poorly crystallized lepidocrocite (less than 8% after 528 hours of treatment) (Soulier, 1995), whereas it dissolves green rust entirely in a few hours (fig. 2 [in Trolard *et al.*, 1996]). In these hydromorphic soils, these results indicate that iron is almost entirely included in minerals unstable to the air, soluble in the CB without reduction, and thus showing the same reactivity as the synthetic green rusts.”

(6) With regard to Mössbauer spectroscopy, Christiansen *et al.* (2011) state, “Feder (2005) contended that the relationship between isomer shift and quadrupole splitting for the soil is different from that for silicate minerals, but that the analysis temperature affects both of these hyperfine parameters. The soil samples were analyzed at different temperatures from the silicate minerals that were used for comparison, however, so the observed or apparent differences in Fe mineralogy could be attributed instead to the analysis-temperature difference.” This is excluded as all data were at the same (room) temperature (Feder, 2001, and detailed references therein).

(7) For XANES and EXAFS, Christiansen *et al.* (2011) admitted that the spectra “agree reasonably well” with those of synthetic GR, but state that they could equally well resemble those of Fe silicates. However, all the studies quoted were performed on pure clay minerals from ores (montmorillonite, nontronite) or monocrystals of biotite and chlorite. O’Day (2004) pointed out “the importance of a high quality, experimentally consistent

reference library, and the need for calibration of fluorescence spectra.” She concluded that extrapolation of data acquired on clays from ore deposits to sediments is difficult; this is also the case for soil clays.

(8) In the case of Raman spectroscopy, the Trolard *et al.* (2008) spectra were obtained by micro-Raman spectrometry, using an Olympus microscope (Trolard *et al.*, 1996, 1997). The size of the particles investigated was ~5 µm [micrometers], while the size of fougérite particles was ~0.5 µm [micrometers], so the spectrum is not a spectrum of fougérite alone. Christiansen *et al.* (2011) stated “Raman spectroscopy cannot exclude the possibility that Fe phyllosilicates are present.” Trolard *et al.* (1996) stated, “minor components such as iron silicates cannot be entirely ruled out.” Where is the contradiction?

(9) For the SEM image (Trolard, 2006), one can say correctly that the analysis was not given but was, however, presented to the IMA. As for micro-Raman spectrometry, the analysis includes neighboring kaolinite or mica particles, but Fe is clearly present at a high level.

To conclude, Christiansen *et al.* (2011) seem to have misunderstood the meaning of the work by Trolard and co-workers. Finding pure fougérite without other Fe-bearing phases is very unlikely. GRs have long been recognized (Taylor, 1981; Lewis, 1997; Christiansen *et al.*, 2009) as being labile, so they cannot be separated from other minerals. Many minerals have been described in parageneses, which are not as easy to describe as synthetic compounds. Obtaining a pure phase to homologate a mineral is unnecessary. In soils, many phases are complex mixtures and solid solutions. This is the case for fougérite, even though it is a well crystallized mineral and its symmetry group and cell parameters are well defined.

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