# 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 fougerite 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 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.''

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 fougerite 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

\* E-mail address of corresponding author: bourrie@aix.inra.fr DOI: 10.1346/CCMN.2011.0590103

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 Fougeres 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 Fougeres 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 fougerite, but after two weeks a spectrum consistent with fougerite was clearly observed (Feder et al., 2005). This implies fougerite 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 fougerite.

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 fougerite. 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.

#### 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 Å to fougerite is based on the crystallographic properties of synthetic GRs, which indicate where one must look for the main peak of fougerite. This value is in perfect agreement with the value given by Lewis (1997) at 7.95 Å. Due to the small abundance of fougerite and the proximity of the peak of kaolinite, one cannot easily detect the peak of fougerite 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 datatreatment technique (raw diagrams) is insufficient, one can extract more information with a better datatreatment technique, such as by applying DECOMPXR to the analysis of a raw XRD pattern. After doing this, the presence of the fougerite 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  $(15-50 \text{ cm})$  and reductomorphic silty  $(50-80 \text{ cm})$ 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 fougerite (Trolard, 1996). The peak at  $\sim$ 8 Å cannot be a harmonic of the peaks at  $14 \text{ Å}$  or  $10 \text{ Å}$ . 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 quadropole 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 analysistemperature 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  $\sim$ 5  $\mu$ m [micrometers], while the size of fougerite particles was  $\sim 0.5$  µm [micrometers], so the spectrum is not a spectrum of fougerite 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 fougerite 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 fougerite, even though it is a well crystallized mineral and its symmetry group and cell parameters are well defined.

#### REFERENCES

- Christiansen, B.C., Balic-Zunic, T., Petit, P.O., Frandsen, C., Mørup, S., Geckeis, H., Katerinopoulou, A. and Stipp, S.L.S. (2009) Composition and structure of an iron-bearing, layered double hydroxide  $(LDH)$  – green rust sodium sulphate. Geochimica et Cosmochimica Acta, 73, 3579-3592.
- Christiansen, B.C., Dideriksen, K., Skovbjerg, L.L., Nedel, S. and Stipp, S.L.S. (2011) Letter to the Editor: On fougerite. Clays and Clay Minerals,  $75, 3-9$ .
- Driessen, P., Deckers, J., Spaargaren, O., and Nachtergaele, F. (2001) Lecture notes on the soils of the world. World soil resources reports, 94, FAO, Rome, 334 pp.

Feder, F. (2001) Dynamique des processus d'oxydo-réduction

dans les sols hydromorphes - Monitoring in situ de la solution du sol et des phases ferrifères. Thèse, Université d'Aix-Marseille III, France, 200 pp.

- Feder, F., Trolard, F., Klingelhöfer, G., and Bourrié, G. (2005) In situ Mössbauer spectroscopy  $-$  Evidence for green rust (fougerite) in a gleysol and its mineralogical transformations with time and depth. Geochimica et Cosmochimica Acta,  $69, 4463 - 4483$ .
- Lanson, B., and Besson, G. (1992) Characterization of the end of smectite-to illite transformation: decomposition of X-ray patterns. Clays and Clay Minerals,  $40, 40-52$ .
- Lewis, D.G. (1997) Factors influencing the stability and properties of green rusts. Pp. 345-372 in: Soils and Environments (K. Auerswald, H. Stanjek, and J.M. Bigham, editors). Advances in GeoEcology, 30, Catena Verlag, Reiskirchen, Germany.
- O'Day, P. (2004) X-ray absorption spectroscopic study of Fe reference compounds for the analysis of natural sediments. Geochimica et Cosmochimica Acta, 89, 572-585.
- Schwertmann, U. and Fechter, H. (1994) The formation of green rust and its transformation to lepidocrocite. Clay Minerals, 29, 87-92.
- Soulier, A. (1995) Les formes solides du fer dans les sols hydromorphes - Approches géochimique, micromorphologique et minéralogique. Thèse, ENSA de Rennes, 275 pp.
- Taylor, R.M.  $(1981)$  Colours in soils and sediments  $-$  A review. Pp. 749-761 in: Proceedings of the International Clay Conference. Developments in Sedimentology, 35, (H. van Olphen and F. Veniale, editors). Elsevier, Amsterdam.
- Trolard, F. (2006) Fougerite: from field experiment to the homologation of the mineral. Comptes Rendus Geosciences, 338, 1158-1166.
- Trolard, F. and Bourrié, G. (2008) Geochemistry of green rusts and fougerite: a reevaluation of Fe cycle in soils. Advances in Agronomy, 99, 227-287.
- Trolard, F., Abdelmoula, M., Bourrié, G., Humbert, B., and 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, série IIa, 1015-1022.
- Trolard, F., Génin, J.M.-R., Abdelmoula, M., Bourrié, G., Humbert, B., and Herbillon, A. (1997) Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies. Geochimica et Comoschimica  $Acta, 61, 1107-1111.$
- Trolard, F., Bourrié, G., Abdelmoula, M., Refait, P., and Feder, F. (2007) Fougerite, a new mineral of the pyroaurite-iowaite group: description and crystal structure. Clays and Clay Minerals, 55, 323-334.
- WRB (2006) World reference base for soil resources  $2006 A$ framework for international classification, correlation and communication. World Soil Resources Reports 103, IUSS, ISRIC, FAO, Rome, 128 pp.

(Received 15 December 2010; revised 3 February 2011; Ms. 455a; A.E. J.W. Stucki)