



***Mössbauerite*; polytypes in Tatkul Lake (Russia) marls and evidence in a Murray River reservoir (Australia)**

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Abstract Mössbauer spectroscopy characterizes “Green rust related minerals” of the *fougèrite* group within the *hydrotalcite* supergroup (Mills et al. Mineral. Mag. **76**(5), 1289–1336, 2012) in locations on Earth quite different from the original studies done in a temperate climate such as Brittany- France, Western Europe. Two examples are described, the gley at the bottom of Tatkul Lake in South Urals (Russia), which is representative of permafrost conditions, and a gley at the bottom of Yanga Lake, a reservoir in the Murray River catchment (NSW-Australia), which is representative of warm and desert conditions. Complementary information is obtained from XRD patterns.

Keywords Green rust related minerals · *Mössbauerite* · *Fougèrite* · *Trébeurdenite* · Gleys · DLH

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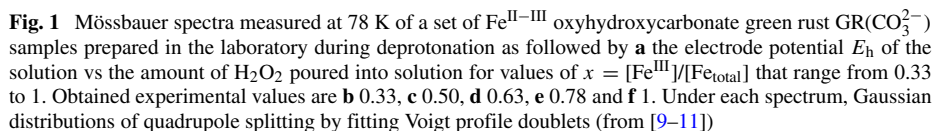
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1 Introduction

Green rusts are $\text{Fe}^{\text{II-III}}$ oxyhydroxysalts that have been extensively studied for understanding the corrosion behavior of iron based materials and steels [2–4]. Obtained by oxidizing metallic iron or $\text{Fe}(\text{OH})_2$, they are intermediate compounds comprising ferrous and ferric ions. Several types have been synthesized incorporating various anions, e.g. Cl^- and other halogens, SO_4^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$ or COOH^- [3–7]. They all belong to the double layered hydroxide (HDL) family where in the most stable one, i.e. with CO_3^{2-} , $[\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}]^{2+}$ layers alternate with $[\text{CO}_3 \cdot n\text{H}_2\text{O}]^{2-}$ interlayers within $R3^-m$ space group that leads to a ferric molar fraction $x = [\text{Fe}^{\text{III}} / \text{Fe}_{\text{total}}] = 1/3$ with $n \leq 3$ [2, 7]. Green rusts dissolve usually by oxidation whereas a ferric oxyhydroxide precipitates such as ferrihydrite [8]. However, another process of oxidation may happen as revealed by using a progressive amount of H_2O_2 [9–11]; this is illustrated by the Mössbauer spectra measured with increasing oxidation (Fig. 1, Table 1 [9–11]). The intensity of the initial ferrous quadrupole doublets D_1 and D_2 with large splitting Δ of about 3 mm s^{-1} diminishes whereas that of a new ferric doublet D_4 with small splitting Δ of about 0.5 mm s^{-1} increases ending into a fully ferric phase called “the ferric green rust” (later *mössbauerite* [12]) that is in fact orange; it leaves the ferric doublet D_3 unchanged with its initial intensity of 33%.

XRD and transmission electron microscopy showed that the in situ oxidation process kept the crystal structure practically unchanged with hexagonal platelets and it was thought for a while that by deprotonation of OH^- ions any value of x within the $[1/3, 1]$ range could be reached leading to a general formula $[\text{Fe}_{6(1-x)}^{\text{II}}\text{Fe}_{6x}^{\text{III}}\text{O}_{12}\text{H}_{2(7-3x)}]^{2+} \cdot [\text{CO}_3^{2-} \cdot n\text{H}_2\text{O}]^{2-}$ for the $\text{Fe}^{\text{II-III}}$ oxyhydroxycarbonate [9–11]. However, magnetic properties prove long range ordering of Fe^{3+} ions within the hexagonal Fe cation layers for $x = 1/3, 2/3$ and 1. For $x = 1/3$ and $2/3$, the compounds are ferrimagnetic with Néel temperature of 5 K and about 20 K, respectively, while “ferric green rust” is also ferrimagnetic, but with a Néel temperature around 80 K. Intermediate values of x correspond in fact to mixtures of these topotactically related magnetic domains [13, 14]. The structure of these compounds at the values of $x = 1/3, 2/3$ and 1 has been fully described: (i) for $x = 1/3$, all Fe^{3+} ions are surrounded by six Fe^{2+} ions, now called *fougèrite F*; (ii) for $x = 2/3$, all Fe^{2+} ions are surrounded by six Fe^{3+} ions; we shall call it *trébeurdenite T*; (iii) for $x = 1$, the fully ferric phase later called *mössbauerite M*. The brucite-like layer is represented with a CO_3^{2-} anion interlayer above it and also an interlayer alone (Fig. 2).

These outstanding features of $\text{Fe}^{\text{II-III}}$ oxyhydroxycarbonates have been detected by measuring the Mössbauer spectra of samples extracted from gleysols of bluish shade that are characteristic of hydromorphic soils [15]. However, a big difference exists between permanently waterlogged soils of a continental aquifer with an average value of x within the $[1/3, 2/3]$ range as firstly extracted in Fougères [16], from the gley of the schorre of maritime marshes with x in the $[2/3, 1]$ range as extracted in Trébeurden [17] (Fig. 3a & b). The presence of three minerals was proposed (i) “*fougèrite*” *F*: $\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ at $x = 1/3$; (ii) “*trébeurdenite*” *T*: $\text{Fe}_2^{\text{II}}\text{Fe}_4^{\text{III}}(\text{OH})_{10}\text{O}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ at $x = 2/3$ and (iii) “*mössbauerite*” *M*: $\text{Fe}_6^{\text{III}}(\text{OH})_8\text{O}_4\text{CO}_3 \cdot n\text{H}_2\text{O}$ at $x = 1$ and $n \leq 3$. Any average formula can be obtained by topotactic mixture of these minerals following the lever rules, *F* and *T* in the $[1/3, 2/3]$ range and *T* and *M* in the $[2/3, 1]$ range leading to formula $\text{Fe}_{6(1-x)}^{\text{II}}\text{Fe}_{6x}^{\text{III}}\text{O}_{12}\text{H}_{2(7-3x)}\text{CO}_3 \cdot n\text{H}_2\text{O}$ ($n \leq 3$ and water molecules are likely disordered). Thus, $\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ *fougèrite F* belongs to the same mineral family as *pyroaurite* or *hydrotalcite* but its unusual in situ deprotonation property comes from the fact that the divalent and trivalent cations are from the same element, iron. The continuous in situ



Up till now, most studies of these minerals were preceded in Western Europe, north of Brittany (France) close to the English Channel where gleys exist in granitic saprolites. Noteworthy, two studies were done for determining the local extension of these occurrences; one used a version of the miniaturized Mössbauer spectrometer MIMOS II by back reflection for studying initially the soil of planet Mars [19, 20]; the in situ variability of x with the depth in the aquifer of the forest of Fougères was monitored; the second study was devoted to the maritime marshes in the widespread Bay of Mont-Saint-Michel [12]. Here, we show that the existence of these minerals can be extended in many other locations on Earth under very different conditions: permafrost climate in Siberia, on the one hand, and warm and desert climate in the Australian bush, on the other hand.

2 Tatkul Lake (Urals-Russia); polytypes in *mössbauerite*

This occurrence is most constructive because it is representative of Siberia and North of Canada. The minerals have been extracted from the bottom sediments of the lakes Tatkul' and Bol'shoe Miassovo (Great Miassovo) located on the eastern slope of the South Urals (Russia), within the Ilmenogorsky complex of magmatic and metamorphic rocks. These are

Table 1 Hyperfine parameters of Mössbauer spectra of GRs measured at various temperatures as illustrated in Figs. 1, 3 and 4; δ (mm s⁻¹): isomer shift (α -iron as reference at ambient); Δ (mm s⁻¹): quadrupole splitting; *RA* (%): relative abundance

Mössbauer spectra parameters													
N°	<i>x</i>	Fe ²⁺							Fe ³⁺				
		<i>D</i> ₁			<i>D</i> ₂			<i>D</i> ₃			<i>D</i> ₄		
		δ	Δ	<i>RA</i>	δ	Δ	<i>RA</i>	δ	Δ	<i>RA</i>	δ	Δ	<i>RA</i>
Synthetic samples (Génin et al. [10, 11])													
1	0.33	1.25	2.92	50	1.25	2.63	17	0.48	0.47	33	–	–	–
2	0.50	1.21	2.98	38	1.21	2.72	12	0.49	0.40	33	0.49	0.70	17
3	0.63	1.24	2.80	28	1.24	3.05	9	0.48	0.49	32	0.48	0.90	31
4	0.78	1.21	2.89	22	–	–	–	0.47	0.45	35	0.47	0.95	43
5	1.00	–	–	–	–	–	–	0.47	0.60	33	0.47	0.88	67
Gleysoils of Fougères & Mont-Saint-Michel Bay													
6	0.50	1.27	2.86		1.25	2.48		0.46	0.48		0.46	0.97	
7	0.72	1.245	2.842	28	–	–	–	0.429	0.560	56	0.44	1.05	16
8	0.74	1.263	2.908	26	–	–	–	0.471	0.381	52	0.47	0.98	22
9	0.77	1.292	2.877	23	–	–	–	0.466	0.405	46	0.43	1.07	31
10	0.75	1.294	2.66	25	–	–	–	0.301	0.549	50	0.31	0.97	25
Tatkul Lake marls													
11	0.66	<i>1.153</i>	2.52	19	<i>1.05</i>	2.14	14	<i>0.33</i>	0.51	38	<i>0.29</i>	0.96	29
12	0.69	<i>1.211</i>	2.38	21	<i>1.04</i>	2.06	10	<i>0.32</i>	0.53	22	<i>0.27</i>	0.90	47
13	0.77	<i>1.280</i>	2.32	16	<i>1.03</i>	2.14	7	<i>0.30</i>	0.550	45	<i>0.31</i>	0.99	32

Spectra n°1–5 were run at 78 K; they are the references for the deprotonation of synthetic GR(CO₃²⁻) (*fougèrite*) vs the ferric ionic ratio *x* (from [9–11]). Spectra n°6–10 were run at 78 K; n° 6 is that of the gley extracted from Fougères [16] and n°7–10 were extracted from Mont-Saint-Michel Bay [12, 17]. Spectra n°11–13 in this study are from the marl of Tatkul Lake; they were measured at room temperature and for comparison with 78 K the isomer shift is different (temperature shift dependence); the values are in italics. The similarity between spectra n°4, 9 and 13 is remarkable (Fig. 1e, versus Fig. 4b & c)

shallow lacustrine lakes (water depth 1.75 m) close to the city of Miass that constitute a good example of permafrost climate conditions. The first Tatkul' column is at N 55° 11,640'; E 060° 17,200'.

The sampling was made in July 2012. Samples from this horizon were taken through 5 cm. Five samples characterizing intervals of 550–555, 555–560, 560–565, 565–570, 570–575 cm have been selected. These samples were packed to the grippers; a part of samples was kept in the refrigerator; another part was kept under room conditions. The fresh samples are wet, water-saturated; they have “cold” dark bluish-gray color (steel-colored, dove-colored) and are characterized by visual homogeneity (look as homogenous substances). They are dehydrated partly in time, regardless of the keeping conditions. They lose the cold bluish shade; more “warm” tones appear in their color and they become lighter, greenish-gray and more compact. The samples from the lowest intervals 565–570 cm and 570–575 cm have dehydrated most of all. The sample 570–575 cm is dry now looking as

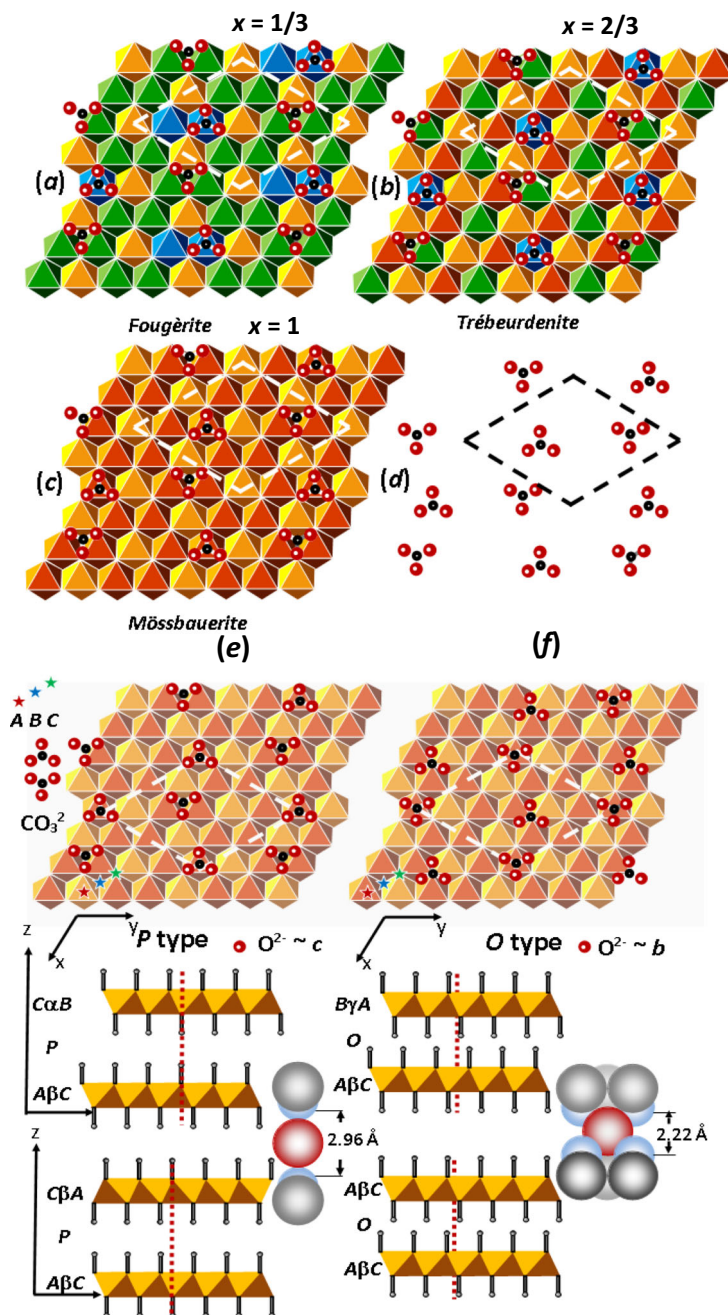


Fig. 2 2D long range order of Fe cations in layers of “Green rust related minerals” with one CO_3^{2-} interlayer above (disordered water molecules are omitted): **a** *Fougèrite* with $x = 1/3$; **b** *Trébeurdenite* with $x = 2/3$; **c** *Mössbauerite* with $x = 1$; Fe^{2+} ions are in green and blue (D_1 and D_2 doublets), Fe^{3+} ions are in yellow and orange (D_3 and D_4 doublets); **d** an interlayer alone with 2D order of CO_3^{2-} anions. **e** and **f** Stacking faults in *mössbauerite* illustrating the *P* and *O* types of stacking as observed in the polytypes of *mössbauerite* (see text)

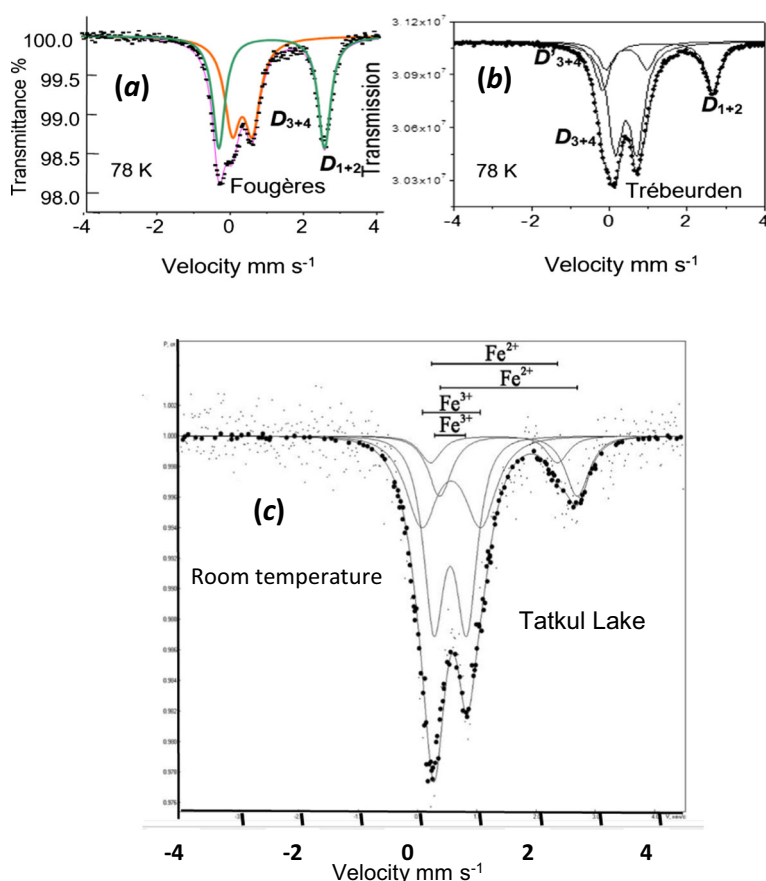


Fig. 3 Mössbauer spectra of gley samples: **a** The first Mössbauer spectrum of a mixture of *fougèrite* and *trébeurdenite* extracted from the forest of Fougères (Brittany-France) measured at 78 K in 1996 [16]. **b** The first Mössbauer spectrum of a mixture of *trébeurdenite* and *mössbauerite* extracted from a maritime marsh of Trébeurden (Brittany-France) measured at 78 K in 2010 [12, 17]. **c** Mössbauer spectrum of a mixture of *trébeurdenite* and *mössbauerite* extracted from the lacustrine marl of Tatkul Lake (South Urals-Russia) measured at room temperature (Table 1)

a compact light-gray lump substance with numerous inclusions of white mica and other minerals. The main minerals of samples 565–570 cm and 570–575 cm are carbonates (calcite, probably dolomite) and clayish ones (illite, kaolinite, montmorillonite, etc). Quartz and feldspar (acid plagioclase) are also present. Sediments of the all rest column (0–5.50 m) are much darker (black or dark-brown), friable and contain organic matter, the quantity of which increases from the bottom layers to the top ones.

Mössbauer spectroscopy characterizes the *fougèrite* group minerals in samples from lacustrine marls. A small amount of Fe (~5%) does not allow to detect Fe-containing minerals, which are in minority if using X-ray diffraction since line intensities as well as positions can hardly be seen in the background (Fig. 3a & b). Spectra of marls from Tatkul Lake (South Ural-Russia) were run at room temperature. The fitting is that used for a mixture of *trébeurdenite* and *mössbauerite* from maritime marshes of Mont-Saint-Michel bay [12] (Fig. 4c). They contain the same type of Fe^{II-III} minerals with varying x values in a small domain around 0.75 (Table 1). Then, most precise X ray diffraction patterns have revealed

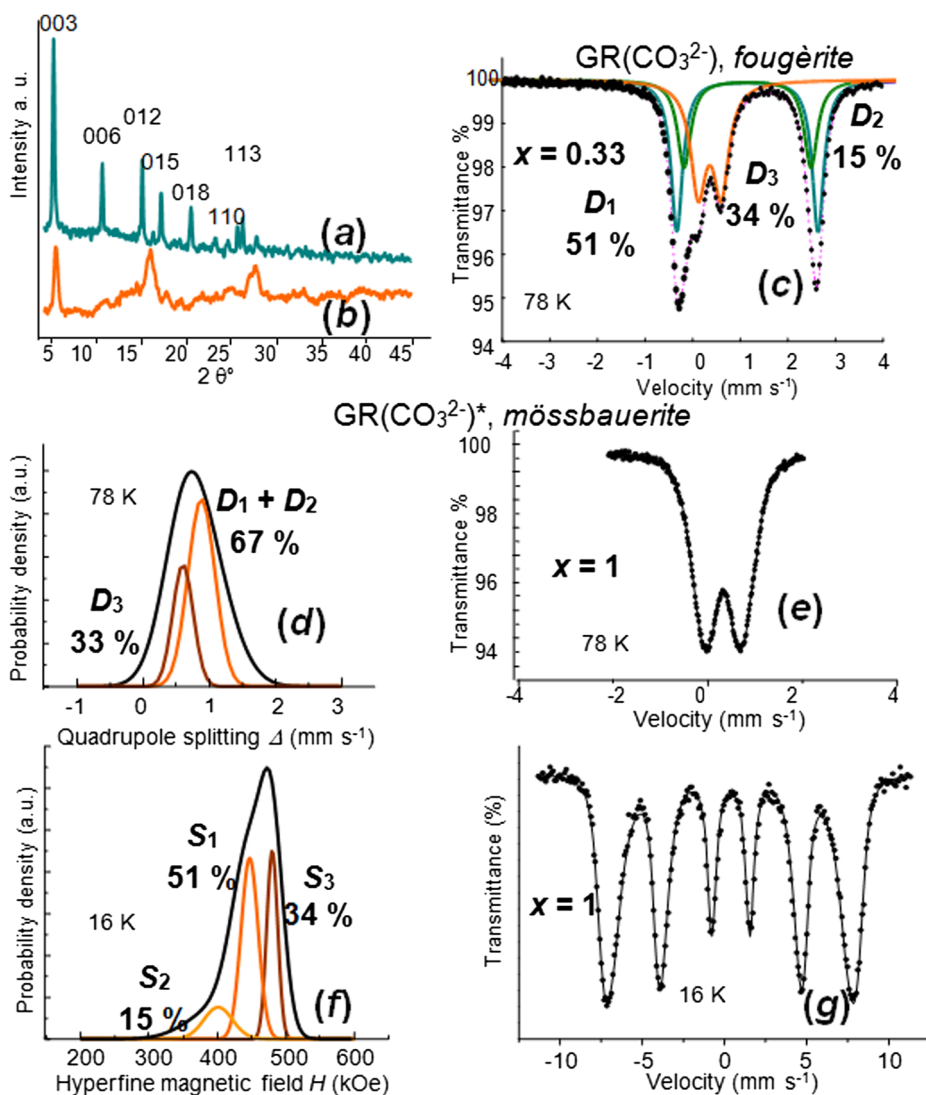


Fig. 4 Various spectra for characterizing pure synthetic samples homologous to “green rust related minerals” for $x = 1/3$ (fougèrite) and for $x = 1$ (mössbauerite) [9–11]. **a** and **b** Respective XRD patterns for $x = 1/3$ and $x = 1$. **c** Mössbauer spectrum for $x = 1/3$ (fougèrite) measured at 78 K with Lorentzian shape-lines. **d–g** Temperature dependence of spectra for $x = 1$ (mössbauerite): **d** Gaussian distribution of the quadrupole splitting for fitting the spectrum **e** measured at 78 K with Voigt profile. **f** Gaussian distribution of the Zeeman splitting for fitting the spectrum **g** measured at 16 K with Voigt profile in its magnetic state (from [13, 14])

the main minerals, kaolinite, quartz, feldspars, mica. Once the afferent lines deleted, small peaks that were not yet attributed to any known other mineral are hardly distinguished out of the background (Fig. 5a). Meanwhile, a study of XRD was performed using a 0.35 Å wavelength at the synchrotron facility of Zurich to obtain data at low angle scattering with a synthetic mössbauerite prepared by coprecipitation of Fe^{II} and Fe^{III} salts (Fig. 5b & c). Stacking sequences due to stacking faults within synthetic samples defining 3T and 2T

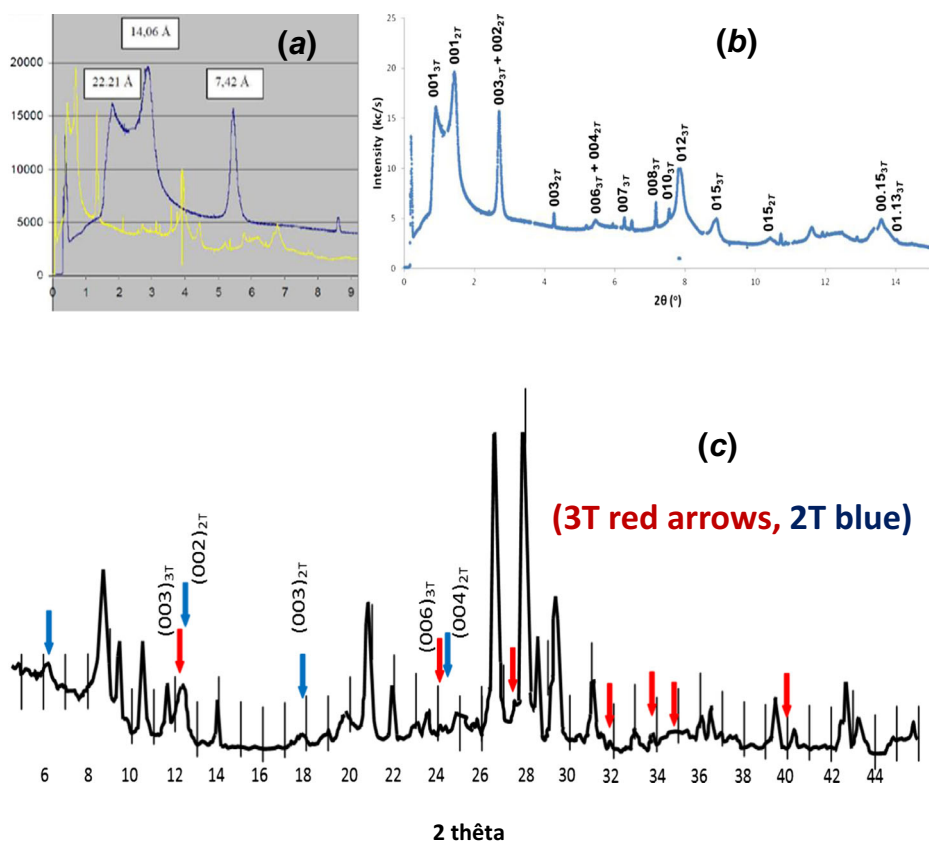


Fig. 5 **a** XRD pattern of the lacustrine marl extracted from the bottom of Tatkul Lake (South Urals-Russia) displaying small peaks out of the background, which were not attributed to any known minerals yet; they come from the 3T and 2T polytypes inside *mössbauerite* (see text). **b** Synchrotron powder XRD pattern of pure synthetic *mössbauerite* ($\lambda = 0.350156 \text{ \AA}$). Note that (001) peaks from 3T and 2T polytype structures are connected by strong diffuse intensity, implying nanoscale intergrowths. **c** Indexing of peaks [12]

polytypes are observed also in natural samples (Fig. 5a). They exist in *mössbauerite* since, all cations being ferric, anion interlayers are no longer fixed by the Fe^{III} cation positions as for *fougèrite* or *trébeurdenite*. The identity of peak positions shows that the mineral owns the same polytypes as in the synthetic sample; most intense peaks at 22.21, 14.06 and 7.42 Å that correspond to (001)_{3T}, (001)_{2T} and (003)_{3T} + (002)_{2T} allow us to confirm the values of the gaps of 2.96 and 2.22 Å for stacking of *P* and *O* types, respectively (Fig. 2e & f).

3 *Mössbauerite* alone in a sample of a lake within the Murray River catchment (NSW-Australia)

Murray River and its tributary Darling River in Australia is the third largest catchment on Earth ranking behind the Amazon and Nile Rivers. Dams and reservoirs have been

constructed to irrigate the bush now transformed into a fertile plain devoted to intensive agriculture; water sustainability is a major concern because of the lowering of the aquifer and its salinity. Before characterizing an actual sample of gley, let us recall some previous studies about the “carbonated green rust” $\text{GR}(\text{CO}_3^{2-})$, the synthetic *fougèrite* that is obtained by coprecipitation for $x = 1/3$ and of the fully ferric *mössbauerite* $\text{GR}(\text{CO}_3^{2-})^*$ at $x = 1$ that is obtained by in situ deprotonation [9–11]. XRD patterns are somehow similar, but if all lines of $\text{GR}(\text{CO}_3^{2-})$ are very intense, those of $\text{GR}(\text{CO}_3^{2-})^*$ become very weak and broadened due to the local lattice strains since some OH^- become O^{2-} at the apices of the octahedrons (Fig. 3a & b). The Mössbauer spectrum of *fougèrite* displays at 78 K in its paramagnetic state the three doublets D_1 , D_2 and D_3 in the 1/2: 1/6: 1/3 relative abundances where D_1 and D_2 correspond to ferrous ions whereas D_3 corresponds to ferric ions ($x = 1/3$) using a fitting with Lorentzian shape-lines (Fig. 3c). In contrast, the homologous spectrum of *mössbauerite* displays at 78 K a broadened asymmetrical ferric doublet, which is in fact made of two unresolved doublets that can be fitted by a Voigt profile analysis (Fig. 3d & e); this shows two components D_3 and D_4 in the 1/3: 2/3 abundance ratio. D_3 comes from the initial ferric ions that are balanced by the charges of the CO_3^{2-} anions, whereas D_4 comes from the ions that were initially ferrous and became ferric by in situ deprotonation. A spectrum of the same sample of *mössbauerite* was run at 16 K (Fig. 3f & g). It displays a Zeeman splitting in magnetic state; the Voigt profile analysis reveals the existence of three Gaussian distributions of hyperfine field, three sextets S_1 , S_2 and S_3 in the 0.51: 0.15: 0.34 ratio as obtained experimentally very close to 1/2: 1/6: 1/3: thus, the quadrupole doublet D_4 is in fact made of two unresolved doublets and should be noted D_{1+2} ; its magnetic splitting at 16 K obviously corresponds to the two sextets S_1 and S_2 (Fig. 3f & g); all this fully validates the structural model of in situ deprotonation (Fig. 2a–c).

We can now characterize pale ocher marl from Yanga Lake (NSW-Australia) by Mössbauer spectra measured at 78 K within various velocity intervals (Fig. 6a & b). An asymmetrical doublet with small splitting characteristic of ferric state appears in the $[-10, +10 \text{ mm s}^{-1}]$ range; no other component is observed and no other doublet with large splitting characteristic of a ferrous state (Fig. 6a). Then, in the $[-4, +4 \text{ mm s}^{-1}]$ range, two badly resolved doublets with small splitting resemble doublets D_3 and D_4 as observed in synthetic *mössbauerite* and any other ferric hydroxide is thus excluded (Fig. 6b & c). The overall aspect of Yanga Lake is ocherous far from the usual aspects of marls previously extracted (Fig. 6d).

Finally, *mössbauerite* can be characterized unambiguously with a measurement down to 4 K (Fig. 6e); small sextets appear after two months of counting at the same positions than those found in the synthetic reference (about 400 kOe [13, 14]). But, it differs: a major doublet in the center (82%) shows up; the sextets are hardly visible, needing a long counting time to appear. The reference spectrum of synthetic *mössbauerite* displays three sextets slightly below 78 K (Fig. 6f) [13, 14]. Therefore, the same phenomenon appears with the marl sample, but the size distribution of crystals is much smaller at a nanoscale that is responsible for superparamagnetic behavior. *Mössbauerite* alone is observed here in natural conditions for the first time. Finally, one notes that the shades of the gleys between that extracted from the bottom of Yanga Lake and that found on the beach of the maritime marsh of Trébeurden are quite different; in the first case, the shade is completely ocher whereas, in the second case, the shade is bluish (Fig. 6g); this is the difference between a sample comprising only fully ferric *mössbauerite* ($x = 1$) and a mixture of *trébeurdenite* and *mössbauerite* ($x \sim 0.75$).

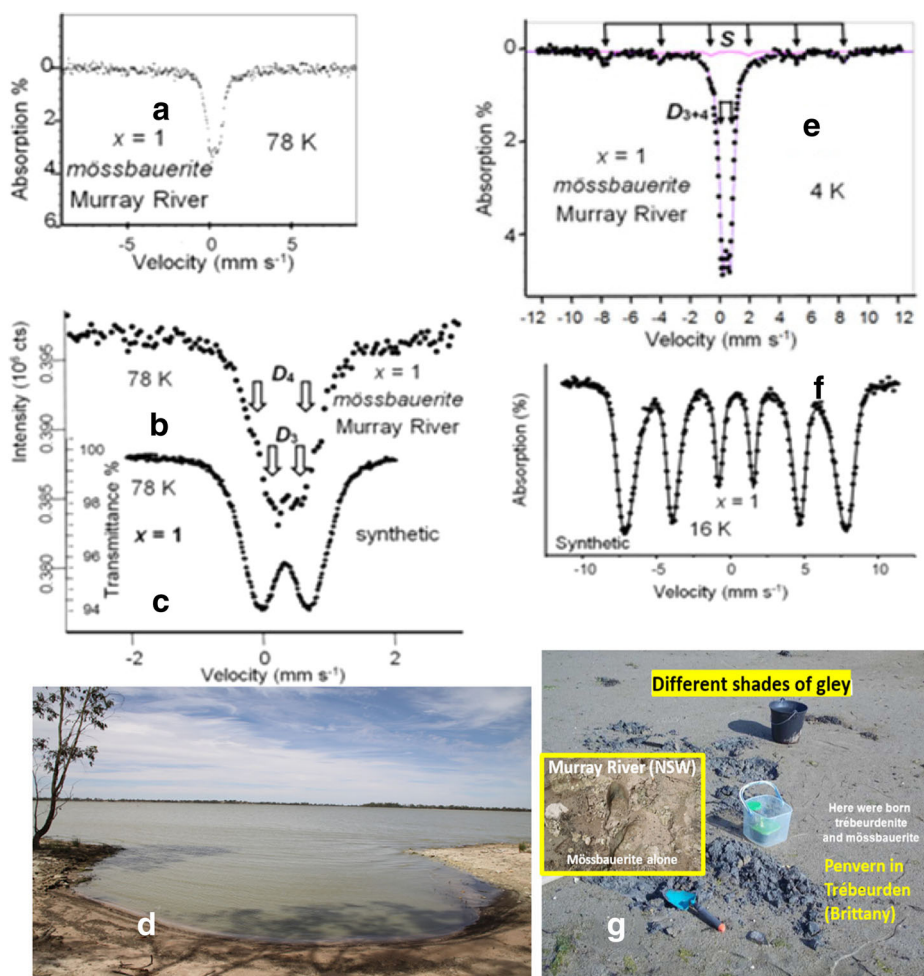


Fig. 6 Mössbauer spectra of a sample of *mössbauerite* alone in the gley of lacustrine marl from a reservoir (Yanga Lake) in the catchment of the Murray River (NSW-Australia). **a** Spectrum measured at 78 K in the $[-10, +10 \text{ mm s}^{-1}]$ range displaying only doublets with small quadrupole splitting characterizing ferric state in paramagnetic state. **b** Spectrum measured at 78 K in the $[-2, +2 \text{ mm s}^{-1}]$ range of the gley sample. **c** Spectrum measured at 78 K in the $[-2, +2 \text{ mm s}^{-1}]$ range of a synthetic sample at $x = 1$ (*mössbauerite*) for easy comparison. **d** The Yanga Lake and its other shade. **e** Spectrum measured at 4 K in the $[-12, +12 \text{ mm s}^{-1}]$ range of the gley sample that displays a strong central quadrupole doublet (ferric state) and a sextuplet with a large hyperfine field (about 400 kOe) (see text). **f** Spectrum measured at 16 K in the $[-12, +12 \text{ mm s}^{-1}]$ range of a 100% *mössbauerite* synthetic sample fitted by Voigt profile analysis displaying the convolution of three sextuplets with Gaussian distributions to be compared with that of the gley sample displayed in **e**. **g** Comparison between the shades of the gley of the beach of Penvern-Trébeurden and that of the reservoir (Yanga Lake) in the catchment of the Murray River

4 Conclusion

“Green rust related minerals”, *fougèrite*, *trébeurdenite* and *mössbauerite*, which were originally discovered in Brittany as responsible for the greenish color of gleys in hydromorphic soils and belong to the “*fougèrite* group” within the “*hydrotalcite* supergroup” according to

the nomenclature adopted by the International Mineralogical Association (IMA2012-025 & 049) [1] have been identified in other locations under very different climate conditions: permafrost in South Urals (Russia) and desert in the Australian bush where *mössbauerite* alone is detected. It becomes clear that the existence of these biominerals is widely spread all over the Earth wherever a gley appears due to bacterial activity in anoxic conditions [18]. Their role in the natural reduction of many oxidized pollutants such as nitrates is out of the scope of this article. Finally, we have tried to show that if Mössbauer spectroscopy is the adequate method to characterize the existence of these minerals and XRD can yield complementary information.

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