Chemical reducing pedoenvironment in a peatland influenced by hematitic phyllite lithology in the southern Espinhaço chain, Brazil

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Abstract A peatland in Pinheiro, Diamantina City, Minas Gerais State - Brazil, was sampled at different depths of two profiles with diverse vegetation coverings (grassland field and bush) in order to collect materials that might reflect changes in the chemical states of iron over the peat formation coming from original minerals such as hematitic phyllite surrounding the boggy pedon. Samples collected were chemically, structurally and magnetically characterized. The results show that both series of peats are composed of organic matter and minerals such as quartz, kaolinite, gibbsite, rutile and muscovite. Deeper layers present only quartz. Mössbauer spectroscopy shows that iron is present in both electron states, Fe^{2+} and Fe^{3+}, under both vegetations, each valence appearing in the spectra in the form of a discrete doublet. No hyperfine magnetic splitting was observed in any spectrum at room temperature. The Mössbauer subspectral area of Fe^{2+} tended to increase from the upper to deeper layers. Magnetic measurements reveal that the magnetic response of the surface samples is the highest, displaying a sharp decrease below 15 cm and that the magnetic signal is a superposition of (super)paramagnetic and ferrimagnetic contributions. Samples from the grassland field also show a diamagnetic component for the deeper layers.

Keywords Peatland · Iron oxidation states · Soil organic matter · Hematitic phyllite

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1 Introduction

Peatlands are ecosystems resulting from successive accumulation of plant remains at sites where local conditions of excess of moisture, low pH, lack of oxygen, and low temperatures do not favor the decomposing activity by microorganisms. They consist of a heterogeneous substrate with varying physical properties, depending on the botanical characteristics of the original vegetation to render the decomposed organic matter and also on the decomposition rate. These systems present exceptionally high capacity to accumulate and long-standing stock freshwater, providing a continuous supply of groundwater to the local basin. Their contents of inorganic elements, especially those percolating from the surrounding rocks, may affect its water storage capacity. Additionally, peatlands sequester and fix carbon from the atmosphere, thus playing an important environmental role. For all these reasons, they represent natural evidence of paleoenvironmental changes to the climate and vegetation of this region.

Peatlands are common in the southern part of the Espinhaço mountain chain [1, 2], in Brazil. The reducing chemical potential in such a pedosystem is generally thought to progressively increase from the top down to the bottom of the profile. Aiming to trace the changes of chemical states of the iron released from the surrounding rocks, predominantly a hematitic phyllite, samples were collected from two profiles of a peatland in the Espinhaço geodomain. These samples were characterized by techniques of complementary nature, in an attempt to add to the available chemical and physical dataset to describe and improve further our understanding about these important ecosystems.

The main objective of the present study was to provide an essential picture about the iron chemical states and their changes from the rock source throughout this pedon profile that is exceptionally rich in organic matter of the peatland forming in a surrounding hematitic phyllite lithology.

2 Experimental details

A peatland in the Pinheiro District (sampling site, 18° 03′ 48 ″S 43° 39′ 41″ W; altitude, 1,242 m), Minas Gerais State, Brazil, was sampled in two profiles (under field and bush vegetations) at different depths (15–90 cm). In the laboratory, the samples were first dried in air but not subjected to any further physical or chemical treatment.

The samples collected were characterized with energy dispersive X-ray fluorescence (EDX), elemental analysis, scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), magnetization techniques and, more extensively, ^{57}Fe Mössbauer spectroscopy (MS).

The sample chemical composition was determined with a Shimadzu energy dispersive X-ray fluorescence spectrometer, EDX Series, and with an CHNS/O elemental analyser (Leco – Truspec Micro).

SEM analysis was made using a Shimadzu Superscan SS-550 microscope, after a very thin gold layer was deposited on the samples through thermal evaporation.

Characterization by XRPD was done using a conventional diffractometer, in Bragg-Brentano reflection geometry, with Cu Kα radiation (λ = 1.5418 Å). Data were obtained between 10° and 80° (2θ), in steps of 0.02° and 6 sec per step.

The MS was performed using the 14.4 keV transition of the ^{57}Fe isotope gamma rays emitted by a ^{57}Co(Rh) source, with the spectra acquired at room temperature. The Mössbauer spectra collected were analyzed using a non-linear least-square routine, with
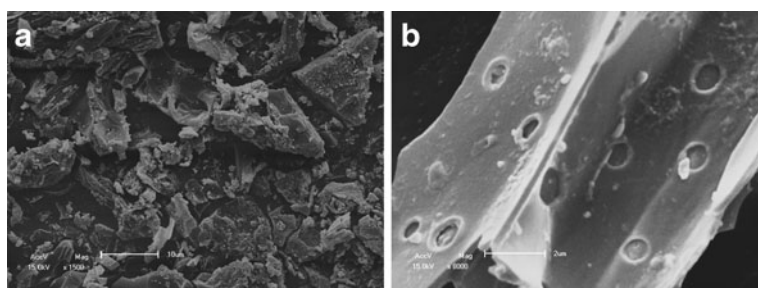
Fig. 1 Selected scanning electron micrographs taken on samples collected at Pinheiro Peatland under grassland field / 0–15 cm (**a**) and bush / 0–15 cm (**b**)

Table 1 Main chemical composition for the peat samples

| Sample Depth (cm)	Si	Fe	Al	Ti	S	K	H	C	N	O
Bush	Mass%									
0–15	16.94	9.56	6.42	2.74	0.79	0.57	4.08	28.45	1.59	28.60
15–30	16.99	1.83	9.84	3.16	1.03	0.59	4.42	35.01	1.09	25.36
30–45	14.03	1.21	12.33	3.79	0.79	0.60	4.27	36.02	1.04	25.73
45–60	34.63	2.59	17.13	11.13	1.54	3.01	1.99	15.34	0.48	11.92
60–75	36.31	2.50	19.86	10.74	1.45	3.40	1.72	12.95	0.43	10.37
75–90	21.27	4.59	26.23	4.29	1.33	4.64	1.36	10.11	0.36	25.20
Grassland Field	Mass%									
0–15	13.21	5.40	4.96	0.44	0.94	0.60	5.71	35.94	1.78	30.76
15–30	15.61	0.46	16.49	1.36	0.99	2.04	4.47	30.86	1.50	26.20
30–45	29.86	1.55	13.50	7.24	1.28	2.49	4.38	30.80	1.34	7.43
45–60	12.93	1.96	18.85	2.24	0.73	2.46	4.28	30.15	1.21	24.57
60–75	13.57	1.94	19.41	2.40	0.60	2.66	3.84	28.19	0.98	25.52
75–90	14.49	2.10	19.54	3.32	0.79	2.90	3.82	28.44	1.05	23.33

Values are normalized for the complete (not all detected elements are actually displayed) set as 100 mass% per sample

Lorentzian line shapes. The isomer shift (δ) data are given relative to α-Fe, throughout this paper.

The magnetic measurements – i.e., magnetization *vs.* applied field curves – were performed at ~295 K, with a LakeShore 7404 vibrating sample magnetometer, applying fields as large as 1.8 T.

3 Results and discussion

Figure 1 shows some micrographs of samples collected at the top (0–15 cm) of the profiles under (a) grassland field and (b) bush vegetations. They reveal an aspect characteristic of mineralized organic matter that compose the peatland surface.
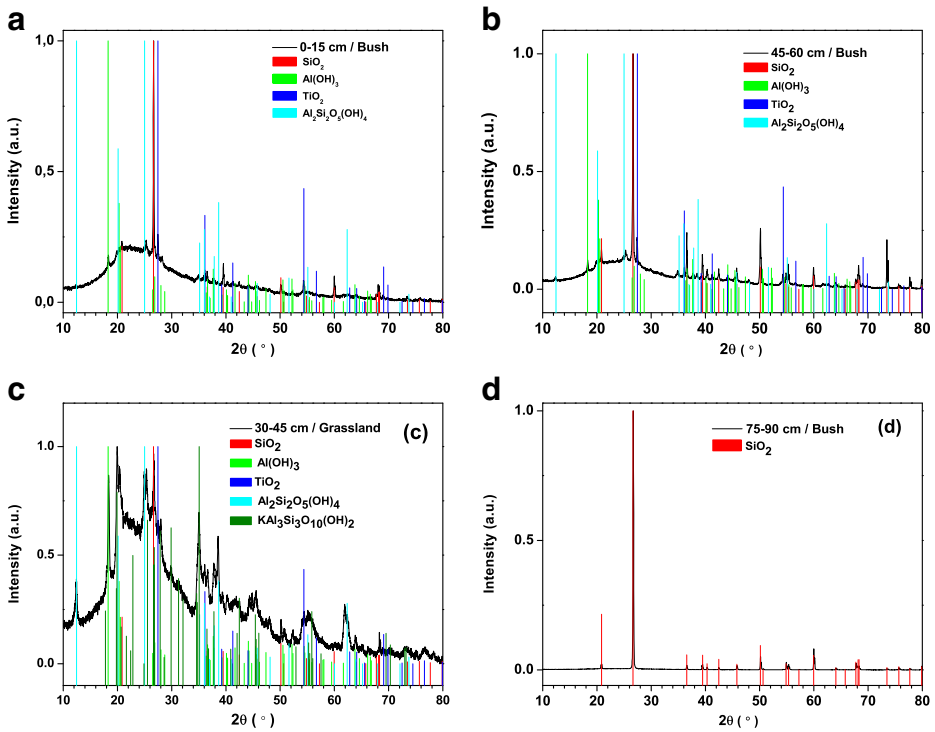
Fig. 2 X-ray diffractograms for some bush and grassland samples: 0–15 cm / bush (**a**), 45–60 cm / bush (**b**) and 30–45 cm / grassland (**c**) and 75–90 cm / bush (**d**)

Table 1 shows the chemical analysis obtained by X-ray fluorescence and elemental analysis for all samples. It can be seen that along with carbon, hydrogen and oxygen, mainly from organic matter, silicon, aluminum, titanium and iron are also found in significant amounts, but contents vary with the sample depth in the profile. Sulfur and potassium are, in average, minor constituents. In general, there is not a clear difference between samples collected from grassland field and bush profiles. Conversely, they present some similarities such as, e.g., maximum concentrations for titanium and silicon are at intermediary depths, whereas the aluminum fraction increases with the distance from the surface, for both sites. In addition, the uppermost sampled layer shows the highest iron concentration for the grassland field or bush sites.

Figure 2 shows X-ray patterns for some selected samples from grassland field and bush profiles. Diffractograms are presented with colored bars that represent the positions of diffraction peaks according to the JCPDS database files [3]. The sample collected closer to the surface shows a pattern (Fig. 2a) with a poorly crystalline fraction and minor proportions of crystalline phases. The other diffractograms (Fig. 2b, c and d) reveal that the quartz (SiO_2) the mineral phase occurs in all samples but kaolinite ($Al_2Si_2O_5(OH)_4$), rutile (TiO_2) and gibbsite ($Al(OH)_3$) are also significantly detected in deeper layers. A similar trend is observed from the analysis of all diffractograms for samples from the two profiles, although peaks of muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) were only recognized for the
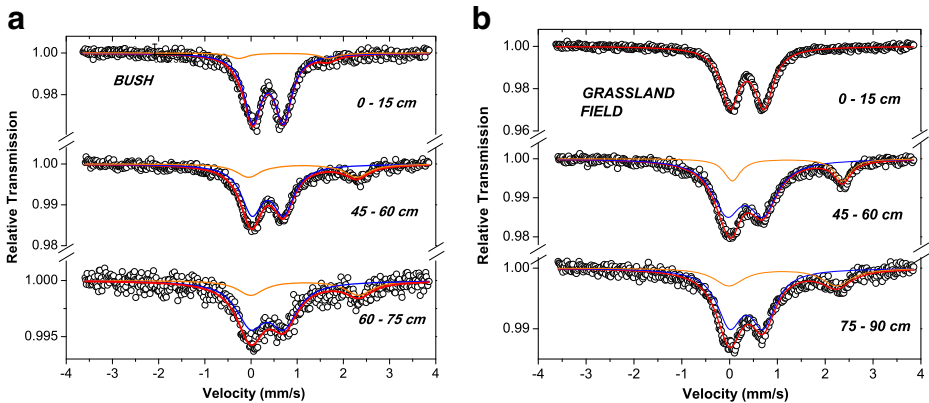
Fig. 3 Mössbauer spectra for samples collected at 0–15 cm, 45–60 cm and 60–75 under bush (**a**) and at 0–15 cm, 45–60 cm and 75–90 cm under grassland field (**b**). — Doublet 1 ; — Doublet 2

samples collected from the grassland profile. This phase accounts for the potassium presence and, surprisingly, was not found for the bush samples.

Quartz is the only phase detected for samples collected at the deepest layers (Fig. 2d). Thus, iron is thought to appear as nanosized basic oxide or isomorphically replacing aluminum in clays.

Figure 3 shows Mössbauer patterns for samples from both profiles. Table 2 presents the hyperfine parameters; corresponding subspectral areas are also shown in a histogram in Fig. 4.

Spectra were fitted with two doublets (except for the sample collected at 0–15 cm from the grassland field profile); no hyperfine magnetic splitting was observed with broader full-scale Doppler velocity in any spectrum taken at room temperature (figures not shown).

One of the two doublets can be assigned to Fe^{3+} and the other is typical of high spin Fe^{2+}. The isomer shift and quadrupole splittings values for the grassland field and bush samples are actually very similar. Also, no significant dependence of the hyperfine parameters on the sampling depth is observed for either of both profile series. However, the area of Fe^{2+} tended to increase from the upper to deeper layers. Regarding the fate of the iron, the presence of ferrous iron reveals a different depiction from other samples from a geomorphologically similar peatland, also in the southern Espinhaço mountain chain [4]. In that case there was no evidence of ferrous species, even at deeper profiles. In the present case, Fe^{3+} responds for the whole Mössbauer spectrum for the 0–15 cm sample from the grassland field profile (Fig. 4a) and 90 % of the bush profile (Fig. 4b). There may have at least two main reasons for the difference between the two sites: (i) the primary ferric species being accumulated on the top of these profiles are chemically more susceptible to conversion in the reducing environment of the deeper part of this peatland or (ii) the reducing potential in this case is much higher than in that of the peatland of São João da Chapada.

Figure 5 shows magnetization as a function of applied magnetic field curves. As far as the magnetic behaviors are concerned, (super)paramagnetic and ferrimagnetic minority phases are observed for the upper profile layers, especially for the topmost layers, which shows a

**Table 2** Hyperfine parameters and subspectral areas for the peatland samples

Sample		Subspectrum	Γ (mm)	δ (mm/s)	Δ (mm/s)	Area (%)
Bush	0–15 cm	Doublet 1	0.44	0.37	0.66	91.9
		Doublet 2	0.46	0.71	1.94	8.1
	15–30 cm	Doublet 1	0.54	0.36	0.67	78.9
		Doublet 2	0.70	1.12	2.36	21.1
	30–45 cm	Doublet 1	0.60	0.33	0.71	78.2
		Doublet 2	0.46	1.20	2.25	21.8
	45–60 cm	Doublet 1	0.55	0.36	0.68	75.1
		Doublet 2	0.64	1.12	2.34	24.9
	60–75 cm	Doublet 1	0.74	0.35	0.72	74.8
		Doublet 2	0.70	1.16	2.34	25.2
	75–90 cm	Doublet 1	0.85	0.38	0.75	75.5
		Doublet 2	0.70	1.15	2.27	24.5
Grass land field	0–15 cm	Doublet 1	0.47	0.37	0.71	100
		–	–	–	–	–
	15–30 cm	Doublet 1	0.71	0.37	0.67	80.5
		Doublet 2	0.35	1.03	2.45	19.5
	30–45 cm	Doublet 1	0.68	0.33	0.76	76.6
		Doublet 2	0.49	1.21	2.30	23.4
	45–60 cm	Doublet 1	0.72	0.32	0.76	79.4
		Doublet 2	0.42	1.21	2.30	20.6
	60–75 cm	Doublet 1	0.66	0.33	0.75	79.6
		Doublet 2	0.45	1.21	2.28	20.4
	75–90 cm	Doublet 1	0.64	0.35	0.70	71.8
		Doublet 2	0.75	1.11	2.25	28.2

Γ = *Linewidth*; δ = *Isomer shift*; Δ = *Quadrupole splitting*

relatively high magnetization. This must be somehow related to the iron containing phases at the surface, although MS did not reveal any magnetically ordered phase. It was also seen that none of the magnetization curves of Fig. 5 reaches saturation, even at the higher applied field (1.8 T / results not shown), which is additional evidence of superparamagnetic particles presence. A diamagnetic contribution is more evident for the two deepest layers (60–75 cm and 75–90 cm) in the bush profile, in agreement with the quartz rich composition, as identified by XRD. For samples under the grassland field vegetation, magnetization at the higher applied fields decreases with the depth and a diamagnetic component, if any, is not that clear.

4 Conclusions

The uppermost layers in the profiles of Pinheiro peatland sampled in this study are composed of organic matter in an apparent process of mineralization, along with silicon, iron
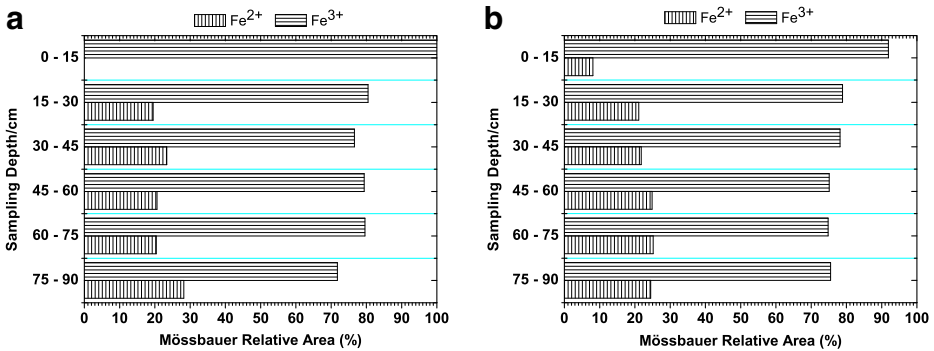
Fig. 4 Breakdown of Mössbauer relative areas for samples collected at different depths from profiles under grassland field (**a**) and bush (**b**) vegetations
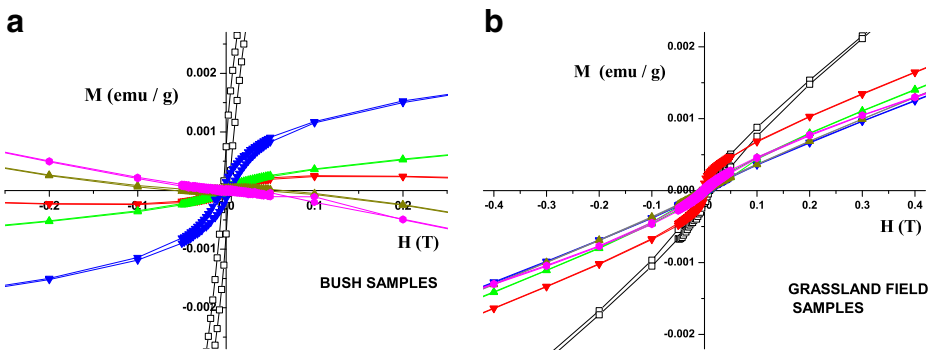
Fig. 5 Magnetization curves as a function of applied magnetic field for samples collected from profiles under bush (**a**) and grassland field (**b**) vegetations. □ = 0-15 cm; | = 15-30 cm; ∫ = 30-45 cm; | = 45-60 cm ∫ = 60-75 cm; ∫ = 75-90 cm

or aluminum oxides or hydroxides. The upper samples tend to be slightly richer in carbon, hydrogen and oxygen than in deeper layers and this may be sufficient evidence of higher contents of organic matter in these surface layers compared to the mineral fraction. Quartz, gibbsite, rutile and kaolinite do occur in significant amounts in both the peatland sites, but these occurrences vary significantly according to the profile depth.

Iron is present in both oxidation states, i.e., Fe^{2+} and Fe^{3+}, and the ferric iron of the surface is readily reduced to ferrous forms down the two profiles studied. The iron containing phase(s) are paramagnetic.

The magnetic measurements show a clear magnetic response, particularly for the samples from the upper layer for both profiles, and are characteristic for the occurrence of superparamagnetic phases plus a minor ferrimagnetic contribution. A dominant diamagnetic signal also appears for deeper samples in the bush profile.

The inconsistency found between the Mössbauer and magnetic results is now being more systematically investigated to better understand the complex system represented by this peatland.

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