

## Chemical fate of iron in a peatland developing in the southern Espinhaço chain, Brazil

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**Abstract** A peatland (geographical coordinates of the sampling site, 18° 05' 43.6'' S, 43° 47' 6.4'' W; altitude 1,330 m asl) in São João da Chapada, municipality of Diamantina, state of Minas Gerais, was sampled at different depths of two profiles with different vegetation coverings (namely, field grassland and bush) in order to collect materials that might reflect changes of the chemical states of iron over the peat formation coming from original minerals like basic rock very likely influenced by hematitic phyllite surrounding the boggy pedon. Mössbauer spectroscopy spectra at room temperature and chemical composition analysis reveal that the iron contents for the peatlands under both vegetations decreases on going from the surface downwards. Also, a central doublet of (super)paramagnetic ferric chemical species, even for samples from deeper positions on the profile, where the reducing chemical potential of the pedoenvironment is thought to be higher, dominates the spectral patterns for all samples. In agreement with the Mössbauer results, magnetic measurements give evidence that the magnetic response of the surface samples is the highest, displaying a sharp decrease below 15 cm and a slight but steady increase with depth down along the profile.

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

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## 1 Introduction

Peatlands are pedosystems resulting from successive accumulation of plant remains at boggy pedoenvironments where local conditions of excessive moisture, low pH, lack of oxygen, and low temperatures do not favor the complete decomposition of organic matter by microorganisms. They are common in the southern part of the Espinhaço mountain chain, in Brazil and play an important environmental role for (i) being a system with exceptionally high capacity to stock fresh water to continuously supply groundwater flows to the local basin and (ii) sequestering and fixing carbon from the atmosphere. They are a heterogeneous substrate with varying physical and chemical properties, depending upon the botanical characteristics of the originally covering vegetation to render the decomposed organic matter, but also upon the intensity of decomposition and the content of inorganic elements, especially those percolating down the soil profile from the surrounding rocks. All these factors may also affect its water storage capacity.

Recent works reported elsewhere about these same pedoenvironments have been focusing on the relation between the amount of water retention with the organic matter and mineral constituents in peatland sites along the Espinhaço chain [1, 2]. A geological survey of Minas Gerais, Espinhaço Project [3] indicates that mafic rocks form the lithology of the area. However, the fate of the iron minerals percolating from basic rocks, mixed with phyllite, surrounding the boggy pedon and their pedogenetic pathways in these complex, highly organic pedosystems, are still to be better understood. In this work, samples were collected at selected depths (Table 1) throughout two profiles, under field grassland and bush vegetations, in the peatland site of São João de Chapada in the southern Espinhaço mountain chain, state of Minas Gerais, Brazil. This work was intended to trace chemical changes, essentially based on the oxidation states of iron, as can be detected mainly through Mössbauer spectroscopy and other complementary techniques, particularly elemental chemical analysis and magnetic measurements. These data might help understand the effects of dominant redox potential and its variation along the profile. This variation might actually reflect not only some conditioning local environment, as water table fluctuations and biological activities, but also chemical interactions involving iron with the organic compounds. This is also intended to form a basic dataset to be systematically compared with other pedons from peatland sites in related geomorphology but eventually influenced by different lithologies of the same mountain chain.

## 2 Experimental

The samples were collected in a peatland in São João da Chapada, municipality of Diamantina, state of Minas Gerais (18° 05' 43.6" S, 43° 47' 6.4" W; altitude, 1,330 m above sea level), in two soil profiles with different vegetation coverings, either under typical seasonably boggy field grassland or sparse patches of bushes (islands of shrub and tree species). Saadi [4] has described the site as a hydromorphic depression containing peatlands overlying riverine or colluvial sands and gravel, surrounded by quartzitic rock outcrops associated with hematite phyllites. Both sets were taken at depth intervals of 15 cm down to a depth of 105 cm for the grassland covering and down to 159 cm for the bush covered samples. The lower samples were found to be in contact with the underlying rock. Samples were collected with a 50 mm diameter PVC sampler [5].

In the laboratory, the samples were first dried in air but were not subjected to any further physical or chemical treatment. The chemical composition of samples was determined

**Table 1** Main chemical composition for the studied samples (not all detected elements are actually displayed)

Sample depth/cm	Si	Fe	Al	Ti	S	K	H	C	N	O
Mass%										
Bush										
0–15	15.15	12.94	10.00	1.45	0.74	0.17	4.17	27.87	1.52	25.66
15–30	16.84	2.76	17.36	2.98	0.99	0.12	4.62	29.44	1.30	23.30
30–45	19.94	1.71	23.67	4.48	0.84	0.07	3.83	23.84	0.87	20.41
45–60	26.85	1.72	27.08	5.80	0.91	0.15	2.80	17.19	0.47	16.80
60–75	35.32	2.12	30.12	7.48	1.11	0.56	1.90	10.17	0.33	10.66
75–90	35.11	2.17	27.97	7.52	1.37	0.15	2.22	12.35	0.37	10.46
90–105	40.14	2.15	30.23	7.76	1.12	0.36	1.63	7.63	0.25	8.44
105–120	40.53	2.24	29.03	7.93	1.45	0.16	1.72	8.04	0.26	8.22
120–135	42.89	1.80	28.16	6.35	1.17	0.53	1.71	8.29	0.26	8.10
135–138	36.04	2.41	38.83	7.12	1.00	0.55	1.67	4.43	0.16	7.16
138–159	34.42	2.96	37.95	7.96	0.98	0.24	2.15	4.84	0.19	7.91
Grassland										
Mass%										
0–15	21.38	10.33	11.34	1.73	0.80	0.18	3.95	23.30	1.81	23.79
15–30	15.28	2.73	17.56	3.98	1.09	0.12	4.59	28.23	1.48	24.70
30–45	27.06	3.21	29.23	5.14	1.17	0.14	3.00	16.86	0.72	13.22
45–60	31.67	2.63	23.15	5.57	1.49	0.17	2.64	16.88	0.82	14.49
60–75	35.71	2.64	28.59	7.20	1.19	0.34	2.05	9.76	0.41	11.83
75–90	32.76	2.85	32.37	7.48	1.14	0.46	1.88	7.99	0.32	12.45
90–105	40.77	3.08	29.24	5.13	1.31	0.47	1.66	8.20	0.47	9.15

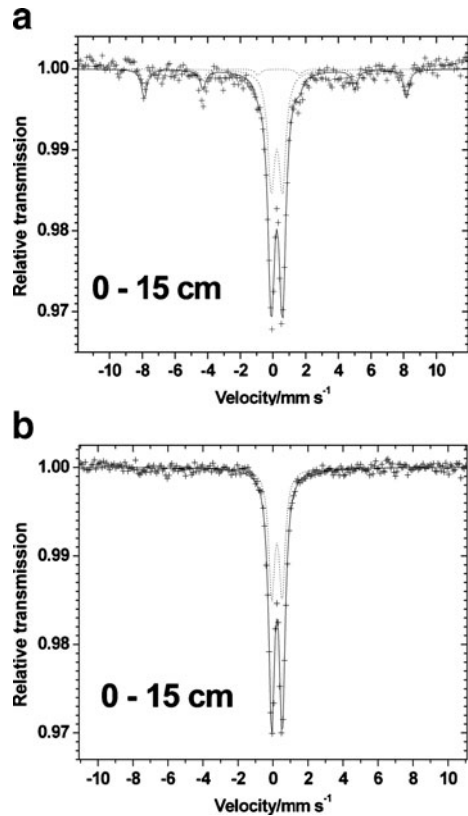
Values are normalized for the complete dataset as 100 mass% per sample

with a Shimadzu energy dispersive X-ray fluorescence spectrometer, EDX Series. The sampling depths along with the main chemical composition for these samples are shown in Table 1.  $^{57}\text{Fe}$  Mössbauer data were collected for samples at room temperature ( $\sim 298$  K) in a conventional constant acceleration spectrometer of 512 channels with a  $\sim 50$  mCi nominal activity  $^{57}\text{CoRh}$  source, in transmission geometry. The Mössbauer absorbers were made of these powders conveniently weighed so to correspond to the optimum thickness calculated after the method described in ref. [6]. Isomer shifts were calibrated against an  $\alpha\text{Fe}$  foil at room temperature. Mössbauer spectra were analyzed using static distributions of hyperfine parameters by applying the extended Voigt-based fitting method included in version 1.05 of a commercial fitting program [7]. The magnetic measurements were made at  $\sim 295$  K with a LakeShore 7,404 vibrating sample magnetometer and a LakeShore 7,130 AC susceptometer with a helium-closed-cycle cryogenic system from 16 to 325 K.

### 3 Results and discussion

As a first trial, 298 K-Mössbauer spectra for samples from the top of the two profiles, under grassland and bush vegetations, were taken with maximum Doppler velocity at approximately  $\pm 12$  mm  $\text{s}^{-1}$  in an attempt to detect any magnetic hyperfine structure. The pattern (Fig. 1(a)) for the grassland sample shows a typical structure of iron in hematite ( $\alpha\text{Fe}_2\text{O}_3$ ; very likely inherited from the surrounding rock) with an intense internal  $\text{Fe}^{3+}$  doublet. A

**Fig. 1** 298 K Mössbauer spectra for the samples collected from the top (0–15 cm deep) of the two peatland profiles (a) under field grassland and (b) bush vegetations. *Solid lines* indicate the calculated spectra resulting from the fitting method described in the text. The *dashed lines* represent the subspectral components. Fitted hyperfine parameters are displayed in Table 2

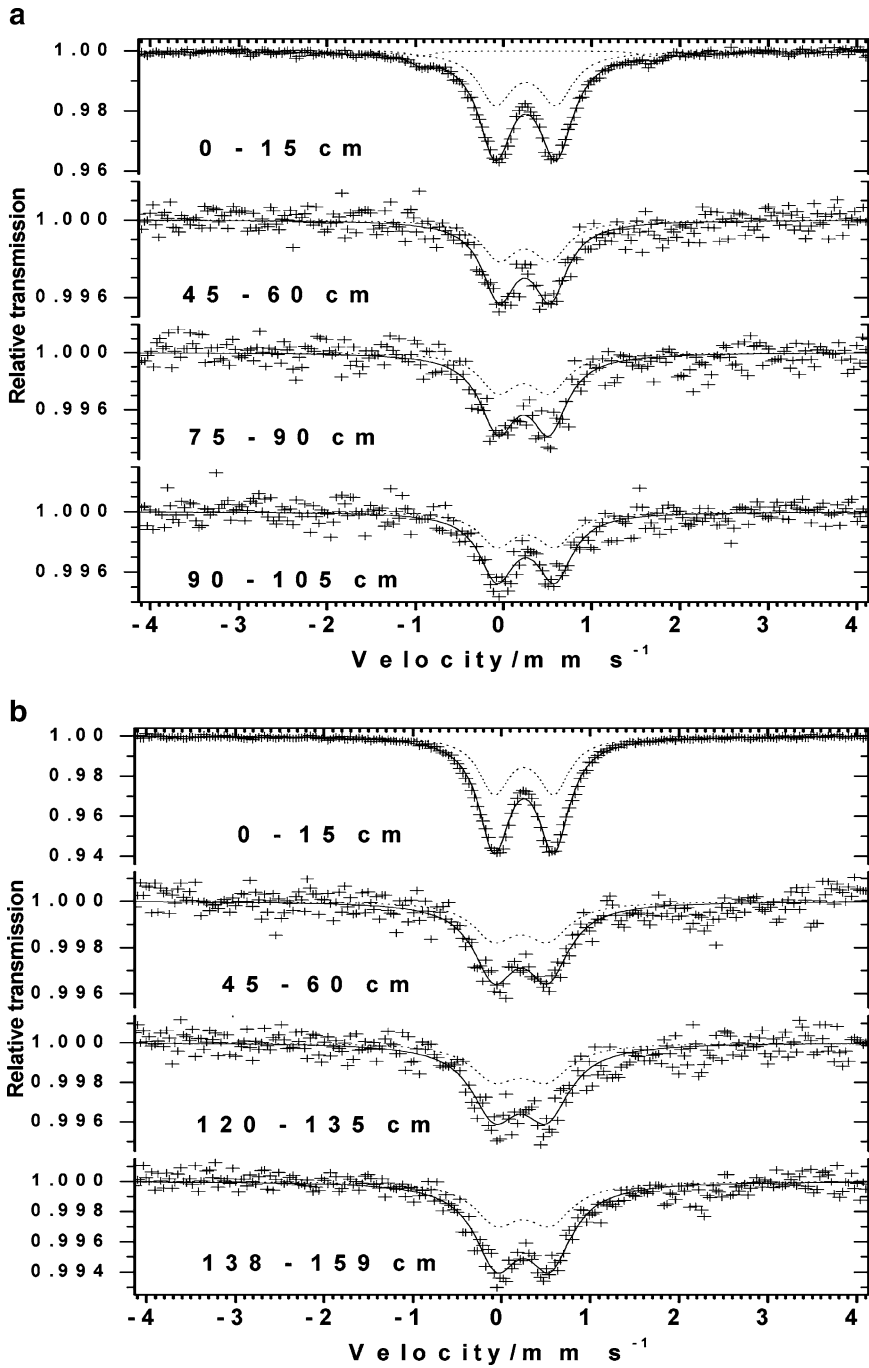


similar (super)paramagnetic doublet (Fig. 1(b)) is also observed for the sample from the top of the profile under bush vegetation, but no clear hyperfine magnetic structure appears in this case.

Mössbauer spectra (Fig. 2(a) and (b)) at room temperature, taken with narrower Doppler velocity ranges, allow assigning the hyperfine parameters for all samples collected along the two profiles, under grassland and bush vegetations. Doublets for all spectra are assignable to high spin  $\text{Fe}^{3+}$  (corresponding fitted parameters are shown in Tables 2 and 3) even for samples from deeper positions on the profile, where the chemical reducing chemical potential of the pedoenvironment is thought to be progressively higher.

Although the assignment of high spin  $\text{Fe}^{3+}$  overlaps slightly with the isomer shift values also characteristic of low-spin  $\text{Fe(II)}$  species, our isomer shift values tend to be slightly higher than the maximum values usually found for low-spin  $\text{Fe(II)}$  (e.g., Figure 1.14 of ref. [8]). There might be also a possibility that part of the  $\text{Fe(II)}$  ions were forming complexes with organic matter ligands or even forming a proportion of pyrite. However, at this stage of our studies, we have found no clear experimental evidence of any occurrence of  $\text{Fe(II)}$ -bearing chemical species in a low-spin electronic configuration; further research is needed to confirm unambiguously this hypothesis.

The signal-to-background ratio of the Mössbauer spectra at room temperature shows that the iron contents for the peatlands under both vegetation types decrease downwards from the surface. This qualitative indication is confirmed by the chemical composition of the samples displayed in Table 1.



**Fig. 2** 298 K Mössbauer spectra for the samples collected from peatland profiles (a) under field grassland and (b) bush vegetations. *Solid lines* indicate the calculated spectra resulting from the fitting method described in the text. The *dashed lines* represent the subspectral components. Corresponding fitted hyperfine parameters are displayed in Table 3

**Table 2** Hyperfine parameters as measured with  $^{57}\text{Fe}$  Mössbauer spectroscopy at room temperature ( $\sim 298$  K), with a wider Doppler velocity range, for samples collected from peatland profiles under field grassland and bush vegetations

Profile	Depth/cm	$^{57}\text{Fe}$ site	$\Gamma/\text{mm s}^{-1}$	$\delta/\text{mms}^{-1}$	$\varepsilon, \Delta/\text{mms}^{-1}$	$B_{hf}/\text{T}$	RA/%
Grassland	0–15	$\text{Fe}^{3+}$	0.51(7)	0.35(1)	0.68(5)		83
		Hm	0.41(5)	0.36(2)	-0.21(3)	49.7(1)	17
Bush	0–15	$\text{Fe}^{3+}$	0.40(4)	0.34(1)	0.60(3)		100

$\Gamma$  = resonance line-width;  $\delta$  = isomer shift relative to  $\alpha\text{-Fe}$ ;  $\Delta$  = quadrupole splitting,  $\varepsilon$  = quadrupole shift<sup>a</sup>;  $B_{hf}$  = hyperfine magnetic field and RA = relative subspectral area. Hm = hematite and  $\text{Fe}^{3+}$  = (super)paramagnetic high spin ferric species. Numbers in parentheses are uncertainties on the last significant digit of the numerical value, as output by the least-squares-fitting computer program. Corresponding patterns are shown in Fig. 1

<sup>a</sup>In this convention,  $\varepsilon = \frac{e^2 Q V_{zz}}{4} (3 \cos^2 \theta - 1)$ , where  $V_{zz}$  is the principal component of the electric field gradient;  $e^2 Q$  is the quadrupole moment and  $\theta$  is the angle between the direction of the magnetic hyperfine field and the principal axis of the electric field gradient

**Table 3** Hyperfine parameters as measured with  $^{57}\text{Fe}$  Mössbauer spectroscopy at room temperature ( $\sim 298$  K) for samples collected from peatland profiles under field grassland and bush vegetations

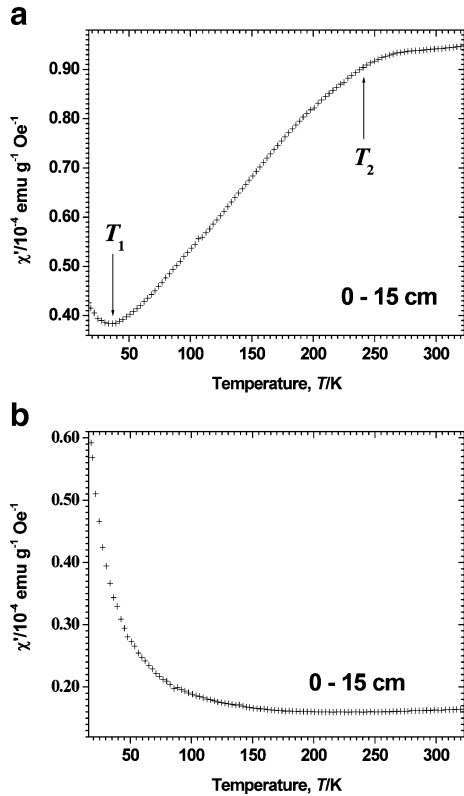
Profile	Depth/cm	$^{57}\text{Fe}$ site	$\Gamma/\text{mm s}^{-1}$	$\delta/\text{mms}^{-1}$	$\varepsilon, \Delta/\text{mms}^{-1}$	$B_{hf}/\text{T}$	RA/%
Grassland	0–15	$\text{Fe}^{3+}$	0.47(4)	0.37(1)	0.68(3)		79
		Hm	0.29(5)	0.38(2)	-0.21 <sup>a</sup>	50.7(5)	21
	45–60	$\text{Fe}^{3+}$	0.47(3)	0.32(1)	0.58(2)		100
	75–90	$\text{Fe}^{3+}$	0.50(4)	0.34(1)	0.58(2)		100
	90–105	$\text{Fe}^{3+}$	0.49(3)	0.37(1)	0.66(2)		100
Bush	0–15	$\text{Fe}^{3+}$	0.43(2)	0.37(1)	0.67(1)		100
	45–60	$\text{Fe}^{3+}$	0.58(4)	0.34(1)	0.60(2)		100
	120–135	$\text{Fe}^{3+}$	0.64(5)	0.33(1)	0.59(2)		100
	138–159	$\text{Fe}^{3+}$	0.61(3)	0.36(1)	0.60(1)		100

$\Gamma$  = resonance line-width;  $\delta$  = isomer shift relative to  $\alpha\text{-Fe}$ ;  $\Delta$  = quadrupole splitting,  $\varepsilon$  = quadrupole shift<sup>a</sup>;  $B_{hf}$  = hyperfine magnetic field and RA = relative subspectral area. Hm = hematite and  $\text{Fe}^{3+}$  = (super)paramagnetic high spin ferric species. Numbers in parentheses are uncertainties on the last significant digit of the numerical value, as output by the least-squares-fitting computer program. Corresponding patterns are shown in Fig. 2. Hm = hematite

<sup>a</sup>Fixed parameters during least squares fitting convergence

The magnetic responses of the surface samples for both profiles are remarkably different probably reflecting that the grassland sample is constituted by a mixture of organic and mineral matter, whereas the bush vegetation sample consists almost exclusively of organic matter. The curve of the AC magnetic susceptibility ( $\chi'$ ) against temperature for the top sample of the profile covered with grassland vegetation (Fig. 3(a)) resembles that of a dominant, but not pure, behavior of a magnetically ordered material. The Mössbauer spectra (patterns of Figs. 1(a) and 2(a)), reveal that this sample is made up of some hematite particles magnetically blocked at 298 K and, like other soil samples, probably paramagnetic iron-containing species along with a fraction of superparamagnetic hematite particles. From the corresponding AC curve  $\chi'(T)$ , the three segments separated by changes in its slope

**Fig. 3** Thermal dependence of the AC susceptibility ( $\chi'$ ) for the top samples collected from the top (0–15 cm deep) of the two peatland profiles (a) under field grassland and (b) bush vegetations



might be associated to the magnetic phase transitions in hematite. The first segment comprises temperatures below  $T_1$  in Fig. 3(a), for which the increase of  $\chi'$  may be interpreted to be due to the contribution of the paramagnetic phases since all relaxation related to hematite is already blocked in its antiferromagnetic state at these temperatures. A second segment might be roughly identified for temperatures above  $T_2$  in Fig. 3(a). The decrease in the slope usually observed for pure hematite is not so clearly observed here because of the existing complex mixture of magnetic phases. However,  $T_2$  is close to the value of the Morin temperature  $T_M \sim 260$  K for bulk hematite, above which hematite displays a weak ferromagnetic behavior. Between those two temperatures the magnetic response may be interpreted as being a mixture of mainly antiferromagnetic ordered species and a lower portion of paramagnetic iron oxides or hydroxides.

The corresponding sample from the top of the profile under bush vegetation shows a different magnetic behavior: the grassland sample is constituted of a mixture of organic and mineral species that contrasts with that under the bush vegetation sample, which contains more dominantly organic matter (Fig. 3(b)). Although it may not be regarded as a single paramagnetic material, its magnetic thermal response may be thought as that of a Curie-like law with multiple contributions. This result is again consistent with Mössbauer data, taking into account that no magnetically ordered phase has been detected and that the broad resonance line-width indicates a relatively complex assemblage of paramagnetic species containing iron in this sample.

## 4 Conclusions

These Mössbauer and magnetic results are inter-consistent within experimental uncertainties and support a model in which the iron originated in minerals from surrounding rocks somehow percolates down along the peatland profiles through very complex chemical pathways, interacting with the transforming organic matter and soil biota. The reducing potential of the pedoenvironment presumably increases on going from the top to the bottom of the profile. However, it seems that in this site it is not enough to reduce source ferric to ferrous forms, except for the deepest sample from the profile under bush vegetation. For this same profile, the magnetic properties of the samples differ significantly from those of the profile under grassland vegetation. These differences are currently being investigated in more detail in an attempt to model the general pathways governing the chemical changes involving iron in these pedosystems.

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