

## Structural characterization of iron oxides and hydroxides in the clay fraction of soil from the Inca civilization Moray terraces

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### Abstract

We introduce the structural characterization of iron oxides and hydroxides in clay fraction obtained from soil collected in the Inca Moray terraces of Peru. This characterization is important since these terraces are considered as a major advance in the Inca civilization agricultural technology. We have utilized the following techniques: a selective dissolution by dithionite-citrate-bicarbonate (DCB) and sodium hydroxide (NaOH). Also, it was used analytical X-ray diffractometry (XRD) techniques and transmission Mössbauer spectroscopy (TMS). XRD of untreated samples showed that all the terraces samples contain quartz and calcite. After treatment with NaOH and DCB, peaks from quartz kept defined; XRD analysis shows a well-crystallized Fe<sup>3+</sup> oxide in all analyzed samples, along with a mixture of quartz, stratified illite-montmorillonite-sanidine clay mineral and muscovite. The main peak of gypsum, observed by XRD in untreated samples, dissolved almost completely. In the TMS analysis it is observed efficiency of NaOH to concentrate iron; concerning the DCB treated samples, the area ratio of Mössbauer absorption indicates an increase of Fe<sup>3+</sup> sites. Besides, DCB treatment, sequentially applied four times, dissolved the poorly crystallized hematite.

**Keywords:** Sedimentation method, Selective dissolution techniques, Dithionite-citrate-bicarbonate, X-ray diffractometry, Iron oxides and hydroxides, Transmission Mössbauer spectroscopy.

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### Introduction

This research constitutes a follow up of CerónLoayza *et al.*<sup>(1)</sup>; we aim to understand the importance of clay fraction from soils in Moray; this is of great significance, inasmuch as this archeological site – located at 38 km northeast of Cusco city, Peru, and comprised by 12 concentric terraces – contributed to the betterment of the agriculture during the Inca civilization times. The samples were obtained by sedimentation and analyzed with selective dissolution treatments DCB and NaOH (Lelis *et al.*<sup>(2)</sup> showed these methods are very effective in removing hematite, goethite, and other paramagnetic mineral phases). The importance of organic matter (OM) for lands is well known; its presence enhances the soil physical properties, such as a reduction of the apparent density and a better segregation of soil aggregates. However, in present work we have observed a low amount of OM and a high content of silt and fine sand (see Table 1); this fact produced a structureless mass during the drying (Acebal *et al.*<sup>(3)</sup>); this condition may be related to the presence of iron oxides and oxyhydroxides, since these compounds act as soil

conservation agents; especially, they are found whether deposited as coating of primary and secondary minerals or infiltrated in clay aggregates. These iron oxides and oxyhydroxides, as well as the aluminum oxides and oxyhydroxides, serve as a cap for the soils having them. CerónLoayza *et al.*<sup>(1)</sup> reported results of samples having particles less than 2 mm. In this work we study clay fractions smaller than 2 μm. As indicated by Acebal *et al.*<sup>(3)</sup>, in the main, iron oxides concentrate in clay fraction; and selective dissolution techniques as well as X-ray diffractometry and transmission Mössbauer spectroscopy, are common to identify iron oxides and oxyhydroxides in soils. Following to Acebal *et al.*<sup>(3)</sup>, these iron compounds may represent the smallest particle fraction, and the crystallinity of these phases can be very poor; these two features require a conscientious study.

Finally, concerning the samples studied herein, we want to lay emphasis on the following: CerónLoayza *et al.*<sup>(1)</sup> reported already EDXRF results; likewise, they detailed the values about of the acidity or alkalinity for the respective samples. In addition, we must indicate that we have changed the symbol

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name for each sample investigated in <sup>(1)</sup>; it was done to avoid confusion with other parameters appearing in this new work.

### Materials and methods

We used 12 samples extracted from the terrace surface (0-20 cm), air-dried them, ground them in an agate mortar, and passed them in stainless steel sieves of 2 mm to get a fraction whose size was less than 2 mm; then, the silt and clay fraction were obtained with the sedimentation technique (Soil Laboratory Manual, UNMSM<sup>(4)</sup>). As a consequence the final size of the silt became less than 45µm; and the one of the clay fraction, less than 2 µm. From the silt and clay fraction obtained, the most representative were treated with two selective-dissolution methods: (1) citrate-dithionite-bicarbonate (DCB), and (2) sodium hydroxide (NaOH).

As regards the usage of DCB, it can be used for iron oxides removal. It is known that the dissolution of free iron oxides favors the dispersion of silicates, which is important for an effective separation into different particle-size fractions. As it is indicated by Varadachari *et al.*<sup>(5)</sup>, spectroscopic studies of soil clays will become perplexing if iron oxides are present in them. Evidently, apart from

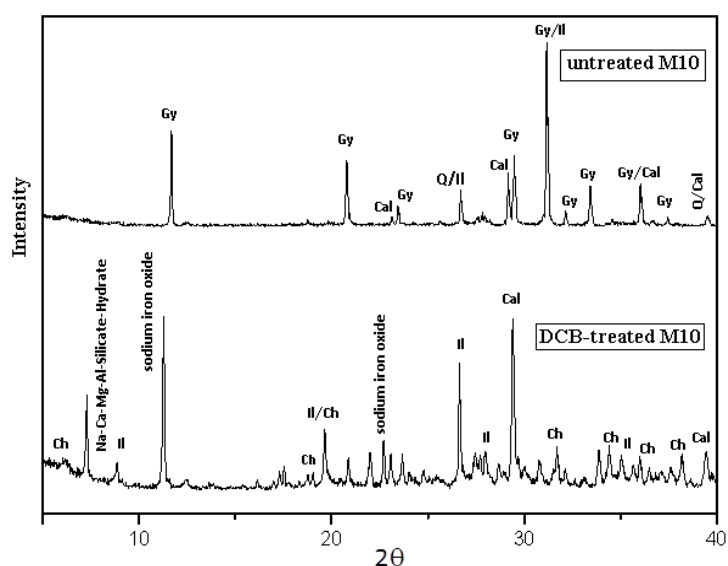
the DCB method already mentioned, we point out that acid-ammonium oxalate (AAO) is another commonly used one too, see van Oorschot & Dekkers.<sup>(6)</sup> This method uses a mix of oxalic acid and ammonium oxalate. Both DCB and AAO utilize organic anions which can be adsorbed on the clay surfaces; and this fact produces an alteration in the charge properties at the clay surfaces. Furthermore, in respect of DCB, we used the method proposed by Mehra & Jackson<sup>(7)</sup> – for a controversial discussion about this method see the criticism done by Varadachari *et al.*<sup>(5)</sup> We employed 1 gram of clay sample (CerónLoayza<sup>(8)</sup>), 1 gram of solid sodium dithionite, 40 ml of 0.3 M sodium citrate, and 5 ml of 1 M NaHCO<sub>3</sub>; this process was held four consecutive times. We used NaOH to concentrate iron oxides, to remove, and to dissolve phyllosilicates (CerónLoayza&MejíaSantillán<sup>(9)</sup>; Pizarro *et al.*<sup>(10)</sup>). All the samples were analyzed by analytical techniques available at our university laboratories, such as XRD and TMS. Moreover, NaOH is used to concentrate iron oxides. Singh & Gilkes<sup>(11)</sup> pointed out that many times iron oxides are poorly crystalline in soils, besides of presenting at low concentrations inside them. Therefore, for the characterization of iron oxides by using some techniques, an iron oxide concentrate may be required.

**Table 1.** Values of the OM percentages and soil texture of the Moray terraces

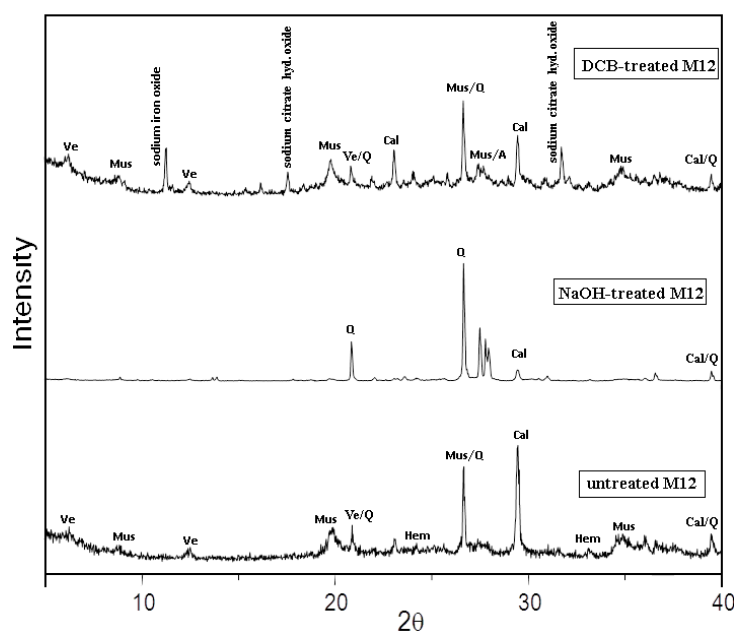
Samples	OM %	Sand %	Clays %	Silt %	Texture type
M1	5.5	40.6	25.8	33.6	Loam
M2	4.1	58.6	5.76	35.6	Sandy loam
M3	5.0	57.6	6.36	36.0	Sandy loam
M4	5.0	48.6	3.36	48.0	Sandy loam
M5	6.1	46.2	17.4	36.4	Loam
M6	5.0	40.6	11.4	48.0	Loam
M7	3.5	68.6	8.36	23.0	Sandy loam
M8	6.1	67.6	6.36	26.0	Sandy loam
M9	5.0	44.6	7.00	48.4	Sandy loam
M10	1.8	43.6	11.4	45.0	Sandy loam
M11	2.7	39.6	25.8	34.6	Loam
M12	7.0	20.6	11.8	67.6	Silt loam

In order to obtain more detailed information about the presence of compounds containing iron, TMS was used, Stevens.<sup>(12)</sup> The Mössbauer spectra of the whole samples were taken at room temperature (RT) in the Laboratory of Soil Analysis and Archaeometry at San Marcos University. Concerning the utilized spectrometer it is a conventional one, which performed using a sinusoidal velocity modulation signal together with a multichannel analyzer, 1024; a <sup>57</sup>Co source in an Rh matrix was used and the spectra were fitted by using the NORMOS program, created by R. A. Brand (Brand<sup>(13)</sup>), in its version for crystalline sites (Site NORMOS).

For the structural analysis of the minerals present in the samples, the XRD technique, Moore<sup>(14)</sup>, was utilized by using a BRUKER diffractometer, model D8-Focus; the X-ray generator has an X-ray tube, whose made-in-copper anode renders CuK $\alpha$  radiation (1.5406 Å); the tube output voltage is 40 kV and the tube output current is 40 mA. A NaI(Tl) scintillation detector was utilized for detection of X-rays. Also, it was utilized a vertical goniometer having a radius of 150 mm, the scanning angle interval was 4° <math>2\theta</math> <math>45^\circ</math> for both the untreated and treated samples; in both cases the



**Figure 1.** X-ray diffraction patterns of the untreated and DCB-treated sample M10. Abbreviation is as follows: gypsum (Gy), calcite (Cal), quartz(Q), Chlorite(Ch), and illite(II).



**Figure 2.** X-ray diffraction patterns of DCB- and NaOH- treated sample M12, as well as untreated. Abbreviation Ve stands for vermiculite; Mus, muscovite; Q, quartz; A, albite; and Hem, hematite.

### Regarding quantification of the iron content

To quantify the iron content we use a usual formula which can be found in Danon<sup>(15)</sup>; see CerónLoayza&MejíaSantillán<sup>(9)</sup> too. The one is as follows:

$$\text{Concentracion (\%)} = 0.149 \left( \frac{\text{mg/cm}^2}{\text{mm/s}} \right) \frac{A_{\text{spec.}} (\text{mm/s})}{0.01 (\text{mm/s})} \times \frac{A_{\text{sh}} (\text{cm}^2)}{m_s (\text{mg})} \times \frac{100}{f_A G} \dots\dots\dots (1)$$

where  $A_{\text{spec.}}$  is the spectral area;  $A_{\text{sh}}$ , the sample-holder area;  $m_s$ , the sample mass;  $f_A$ , Lamb–Mössbauer factor; and  $G$  stands for the fraction of the 14.4-keV  $\gamma$  radiation that processes the detector holding the sample.

### Discussion and results

On the one hand, XRD analysis of untreated samples showed that all samples in terraces contain quartz and calcite. Also, one or more phases may correspond to phyllosilicates such as vermiculite, montmorillonite, muscovite, and illite. After treatment with NaOH and DCB, we observed that the peaks from quartz are kept well evident; a well-defined high-intensity peak appeared, which corresponds to sodium iron oxide. Then, now we analyze the most relevant results; for example, in Figure 1, for sample M10, we realize the previously observed peaks of gypsum disappeared entirely after DCB treatment, but two peaks of sodium iron oxide arise in the diffractogram. Likewise, Figure 2 reveals that sample M12 also presents one peak of sodium iron oxide after a DCB treatment. Furthermore, in the same sample, the treatment with NaOH showed efficacy to eliminate peaks related to silicates as vermiculite, muscovite and dolomite. In relation to hematite, it is difficult to observe the intensity of the peaks due to overlapping. DCB dissolves crystalline iron oxides, but in some samples, as M2, they were not fully dissolved.

On the other hand, concerning the TMS analysis, Table 2 lists the hyperfine parameters for all clay fractions untreated, and treated with NaOH and DCB, separately. In this same register, it is listed the hyperfine parameters of the Mössbauer spectra corresponding to figures 3 and 4 for samples M10 and M12, respectively. For the preparation of Table 2, paramagnetic sites with similar values of fit-variables ISO and QUA have been grouped in order to identify a possible connection with mineral structures. Also, therein ISO stands for isomer shift relative to  $\alpha$ -Fe;  $2\epsilon$ , quadrupole shift;  $B_{\text{hf}}$ , hyperfine magnetic field;  $A$ , spectral area; and QUA, quadrupole splitting. The TMS from all untreated samples (Table 2) shows the presence of the two magnetic

sixtets S1 and S2 both assigned to the  $\text{Fe}^{3+}$  oxide (hematite). Likewise, we detected several paramagnetic doublets : D1 and D2, which are assigned to sites occupied by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , respectively, in vermiculite. We assigned them after grouping the hyperfine parameters and compared their values with known parameters for clay minerals observed by XRD. Doublets D3 and D4 are assigned to sites occupied by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , respectively, in montmorillonite, whose presence is observed superimposed on illite, assigned as D6. In other treated samples, illite increases the intensity of its peak, as observed by XRD in sample M10. Also, D5 is assigned to muscovite, which is also found by XRD in sample M12.

In addition, after calculating the iron content with Eq. (1), we found out that the total iron percentages for untreated and DCB-treated sample M2 are 5.0% and 4.6%, respectively. The contribution only from magnetic sextets S1 awarded to  $\text{Fe}^{3+}$  sites, is 1.7% (untreated) and 1.3% (DCB). Likewise, the total iron percentages in untreated and DCB-treated sample M10 are 2.1% and 1.97%, respectively; besides, only the contribution from  $\text{Fe}^{3+}$  magnetic sites are 0.96% (untreated) and 0.75% (DCB). On this last point, we want to emphasize that 0.96% is the sum of the two  $\text{Fe}^{3+}$ -site (hematite), that is, S1 and S2 (see Table 2); however, after the DCB treatment site S2 was dissolved, so 0.75% stands for the contribution from S1 only. With regard to untreated sample M12, the total iron percentage is 5.3%, while in treated M12 is 4.2% (NaOH) and 3.8% (DCB), respectively. In detail, for untreated sample M12, we calculated the two sextets S1 and S2 have 1.2% and 0.31%, respectively, of their sites occupied with  $\text{Fe}^{3+}$ ; whereas S1 and S2 of the NaOH-treated sample M12 have, respectively, 1.3% and 0.4%  $\text{Fe}^{3+}$ ; additionally, S1 and S2 of the DCB-treated samples M12 have 0.7% and 0.4%  $\text{Fe}^{3+}$ , respectively.

**Table 2.** Mössbauer hyperfine parameters of the untreated-and-treated clay fractions from Moray, Cusco

Sites	Paramet	Samples									
		Untreat. M2	DCB-Treated M2	Untreat. M7	DCB-Treated M7	NaOH-Treated M7	Untreated M10	DCB-Treated M10	Untreated M12	DCB-Treated M12	NaOH-Treated M12
Hem (S1)	ISO (mm/s)	0.27	0.30	0.27	0.30	0.29	0.28	0.31	0.28	0.30	0.31
	2ε (mm/s)	-0.22	-0.23	-0.22	-0.22	-0.23	-0.21	-0.23	-0.22	-0.23	-0.23
	Bhf (T)	52.34	51.35	51.40	51.34	51.40	51.55	51.88	51.82	51.27	51.88
	A (%)	34	27	33	27	41	35	39	22	19	31
Hem(S2)	ISO (mm/s)			0.28	0.28	0.29	0.23		0.27	0.27	0.22
	2ε (mm/s)			-0.20	-0.20	-0.21	-0.18		-0.15	-0.22	-0.31
	Bhf (T)			49.49	49.45	49.49	50.00		48.77	49.34	48.77
	A (%)			11	21	11	10		6	10	9
Fe <sup>2+</sup> D1 (Ve)	ISO (mm/s)	1.03	1.00						1.05	1.08	1.08
	QUA (mm/s)	2.77	2.70						2.66	2.65	2.63
	A (%)	7	4						15	14	15
Fe <sup>3+</sup> D2 (Ve)	ISO (mm/s)	0.20	0.30						0.28	0.30	0.31
	QUA (mm/s)	0.68	0.63						0.71	0.52	0.51
	A (%)	52	63						42	22	19
Fe <sup>2+</sup> D3 (Mon)	ISO (mm/s)	1.25	1.35	1.20	1.24	1.06	1.19				
	QUA (mm/s)	2.32	2.49	2.24	2.28	2.66	2.30				
	A (%)	6	4	9	11	12	11				
Fe <sup>3+</sup> D4 (Mon)	ISO (mm/s)			0.20	0.24	0.28	0.14	0.31			
	QUA (mm/s)			0.75	0.87	0.62	0.75	0.96			
	A (%)			46	38	26	4	25			
Fe <sup>3+</sup> D5 (Mus)	ISO (mm/s)				0.26	0.50	0.24	0.30	0.28	0.31	0.31
	QUA (mm/s)				0.51	0.82	0.68	0.51	0.46	0.77	0.96
	A (%)				3	11	39	24	15	36	26
D6 (II)	ISO (mm/s)							1.08			
	QUA (mm/s)							2.63			
	A (%)							12			
Fe <sup>2+</sup> D7	ISO (mm/s)		0.95	0.85							
	QUA (mm/s)		0.85	1.71							
	A (%)		2	1.40							

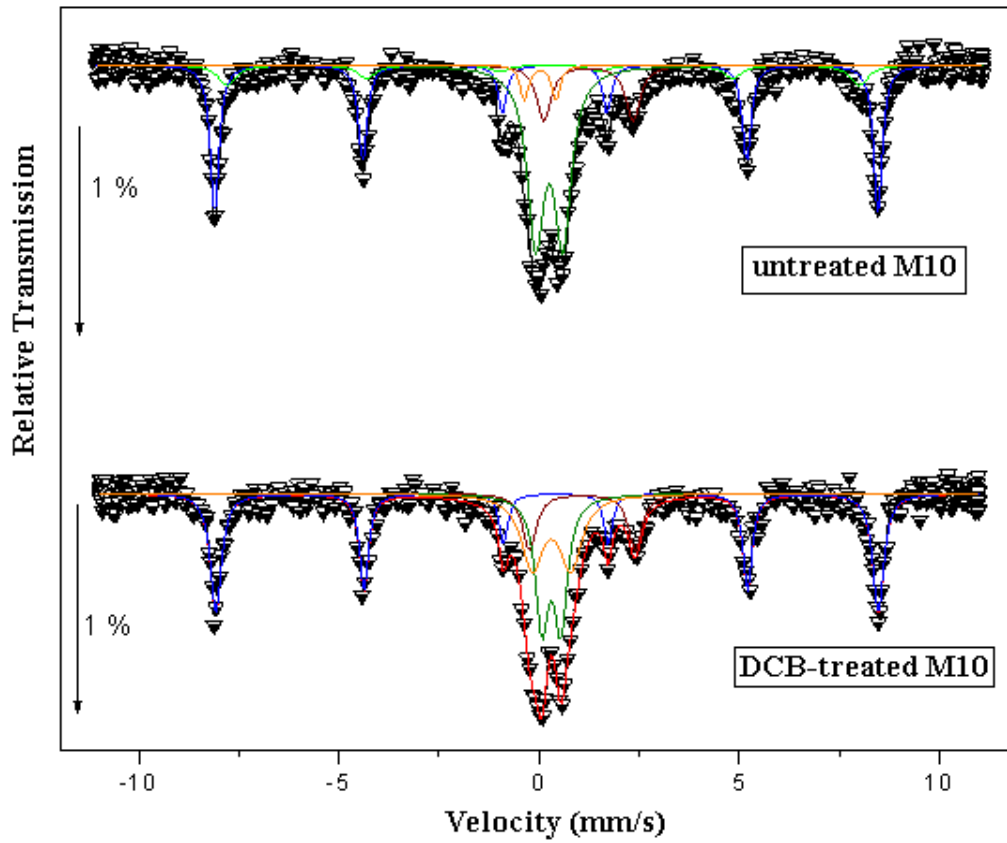


Figure 3. Mössbauer spectrum of the untreated and DCB-treated sample M10, respectively.

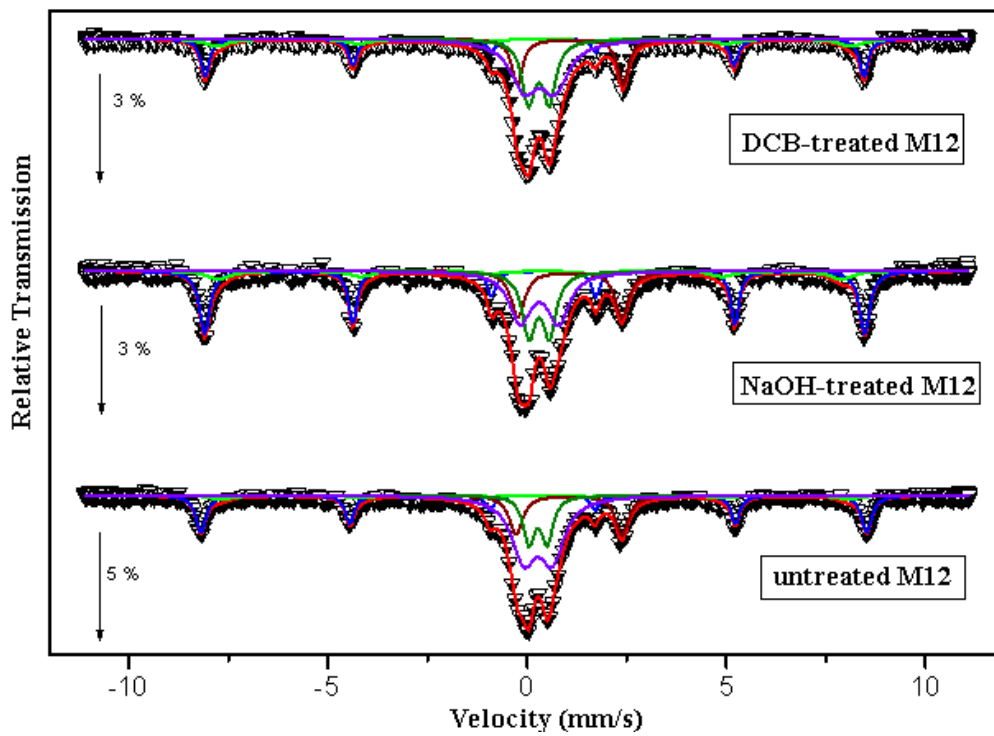


Figure 4. Mössbauer spectra of sample M12: treated with DCB and NaOH, respectively, as well as untreated.

## Conclusions

The XRD analysis of the untreated samples shows that all Moray terraces contain quartz and calcite. Also one or more phases may correspond to the phyllosilicates such as vermiculite, muscovite, and illite. After treating the samples with either NaOH or DCB, we observe that new well-defined high-intensity peaks appear, which corresponds to sodium iron oxide. Probably, this might have happened because in the preparation process the reagents contain sodium in their composition. The treatment with NaOH shows efficacy to dissolve phyllosilicates; besides, after this treatment peaks of quartz kept defined. The DCB treatment dissolved crystalline iron oxides, but in some samples, as M2, it is not fully dissolved. Also, specifically in sample M10, peaks of gypsum entirely disappeared after this last treatment. Regarding  $\text{Fe}^{3+}$  oxide hematite, it is difficult to observe the intensity of peaks due to overlapping.

For the treated samples, after utilize both TMS results and computing of iron percentages, we realize that the iron percentage with a NaOH treatment increased slightly in sextet S1 (it was maintained in sextet S2). Therefore, from the total iron percentage existing in untreated and NaOH-treated samples, we can affirm that a large amount of iron sites localized in the phyllosilicates was removed. This last fact is corroborated by the second XRD diffractogram showed already. For all samples treated with NaOH, we observe the effectiveness of this method to concentrate iron oxides and increasing  $\text{Fe}^{3+}$  sites. Concerning the samples treated with DCB, the area ratio of Mössbauer absorption (A) indicates an increase of  $\text{Fe}^{3+}$  sites. From Table 2, for sample M10, when we compared the untreated samples with the DCB-treated, we noticed that DCB resulted effective since sextet S1 was reduced whereas sextet S2 was totally dissolved.

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