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Distribution of Fe-bearing compounds in an Ultisol as determined with selective chemical dissolution and Mössbauer spectroscopy

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Abstract The distribution of Fe-bearing compounds in the silt and clay fractions from samples of a Chilean Ultisol developing on pyroclastic material was determined in this study. The mineralogical analysis was carried out mainly by Mössbauer spectroscopy at 298, 80 and 6 K, for samples before and after treatment with ammonium oxalate (OX). The 298 and 80 K-Mössbauer spectra reveal relatively complex mineral assemblages for all samples. An intense central doublet, due to (super)paramagnetic Fe^{3+} is observed. The incipient broad-line sextet may be due to coexisting magnetically ordered forms of iron oxides. Goethite, hematite and maghemite were identified from the Mössbauer spectral analysis of patterns obtained at 6 K, which were numerically fitted with model-independent hyperfine field distributions. Some low hyperfine fields are identified for both, the silt and clay samples, being more intense in the last one. These species are likely due to poorly crystalline iron oxyhydroxides, which are more easily removed with the OX treatment; maghemite tends to remain in the coarse fraction, whereas poorly crystalline forms do occur mainly in the clay fraction.

Keywords Volcanic soils · Iron oxides · Ammonium oxalate · Mössbauer spectroscopy

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1 Introduction

The iron oxides (a broad term, meaning here iron hydroxide, oxyhydroxide or oxide) particles, part of them having a variable structural electric charge, are major components in many acidic soils and greatly influence the ion dynamic in the solid-solution relationship. In general, the ion sorption rate in soils depends on the surface area, chemical composition, cation exchange capacity, and on the proportion of iron or aluminum oxides or oxyhydroxides present as the surface coating of clay and silt particles. In this sense, the way these minerals are inter-related or chemically spatially distributed, either being freely distributed throughout the soil mass or coating silt and clay grains, is determinant on their chemical role in the whole ion sorption-desorption mechanisms.

Soils derived from volcanic materials are abundant and widespread in southern Chile. They are mostly found from latitude 19° to 56° S, and account for around 70% of the Chilean cultivated areas. The Ultisols (classification according to the U.S. Soil Taxonomy [1, 2]) are one of the most important volcanic Chilean soils. They have relatively high amounts of iron oxides in different degrees of crystallinity, low amounts of organic matter, and mineralogy mainly dominated by kaolinite and halloysite.

Physical extraction methods and selective chemical dissolution are useful laboratory procedures in the sample preparation that improve the mineralogical analysis of soil materials [3]. The oxalic acid—ammonium oxalate treatment is conventionally used to extract poorly crystalline Fe oxides. In this work, the characterization and distribution of Fe-compounds in the silt (mean diameter of particles, φ=0.002–0.053 mm) and clay (φ<0.002 mm) fractions from soil volcanic Chilean samples were studied.

2 Materials and methods

2.1 Soil collection and fraction separations

Soil samples collected at a depth of 15–30 cm from an Ultisol profile (geographical coordinates of the sampling site 36°58′ S 72°09′ W) in Collipulli, southern Chile, were selected. The collected soil material was sieved in the field, so to obtain a fraction with mean particle diameter of 2 mm, and packed under roughly the corresponding field moisture atmosphere. The particle size fractionation was first carried out by dispersing an aliquot of the soil sample in distillate water. The soil samples were first dispersed in distillate water; the suspension was then sieved, to separate the sand fraction (φ=2–0.05 mm). The silt (φ=0.05–0.002 mm) and the clay fraction (φ<0.002 mm) were separated by sedimentation according the method described in [4].

2.2 Mineralogical analysis

The powder X-ray patterns were obtained with a Philips Norelco Instrument equipped with a Cu-Kα radiation source and Ni filter. The Mössbauer spectra were collected with the sample at room temperature (298 K), 80 and 6 K in a constant acceleration transmission set up with a ×30 mCi ^{57}Co/Rh source. The specific soil magnetization was measured with a portable soil magnetometer developed and built by Coey et al. [5], which allows direct digital readings of the magnetic moment of soil samples expressed in microjoule per tesla; the specific saturation magnetization (*SM*) in joule per tesla per kilogram was deduced from

Table 1 Chemical composition, OX-extraction and organic carbon (O.C.) of the soil, silt and clay Collipulli samples

Sample	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	SiO_2 (wt.%)	TiO_2 (wt.%)	Fe_{OX} (wt.%)	O.C. (wt.%)
Soil	23.2	15.6	40.6	2.3	2.0	2.4
Silt	23.1	14.0	46.6	2.3	1.2	1.2
Clay	30.2	11.6	37.7	1.2	0.8	1.2

Table 2 Granulometric fractioning and values of specific saturation magnetization (*SM*)

Sample	Proportion/ wt.%	Specific saturation magnetization, SM/J T^{-1} kg^{-1}
Soil		2.4
Sand	10.4	1.7
Silt	37.6	1.4
Clay	52.0	1.2

the sample mass. About 50 mg were used to obtain an averaged *SM* value from 20 readings per sample.

2.3 Chemical analyses and dissolutive methods

Total concentrations were determined by digesting 0.100 g of the dry sample with HF and aqua regia (10:1.5) in a Parr bomb at 110°C during 12 h. The resultant digestion mixture was treated with ultra pure grade (Merck) boric acid and diluted to 100 mL with water, and stored in a plastic bottle at 5°C, prior to the chemical analysis. Data in Table 1 are averaged values for two sample replicas.

Each clay and silt fractions of the Ultisol volcanic soil samples were chemically treated with oxalic acid-ammonium oxalate (OX) during 4 h at pH 3, in darkness, to extract the poorly crystallized iron oxides, according to procedures described in [6]. After this extraction and total dissolution procedures, the limpid supernatant was separated, by centrifuging at 10,000 rpm, and analyzed for Fe, Al and Si, with ICP-OES. The organic matter content was determined by the Walkley-Black method [7], using a Radiometer automatic titrator provided with a Pt-calomel combined electrode. The chemical composition of untreated and OX-treated samples and organic carbon contents are presented in Table 1. The pH of samples was measured in soil suspension prepared with double distilled water at a ratio of 1:2.5 *w*/*v*. The granulometric distribution was determined according to the pipette method, based in the sedimentation velocity Stoke's law.

3 Results and discussion

The chemical composition of samples from the whole soil and its silt and clay fractions indicates that this Ultisol does contain a high proportion of iron oxyhydroxides, and is

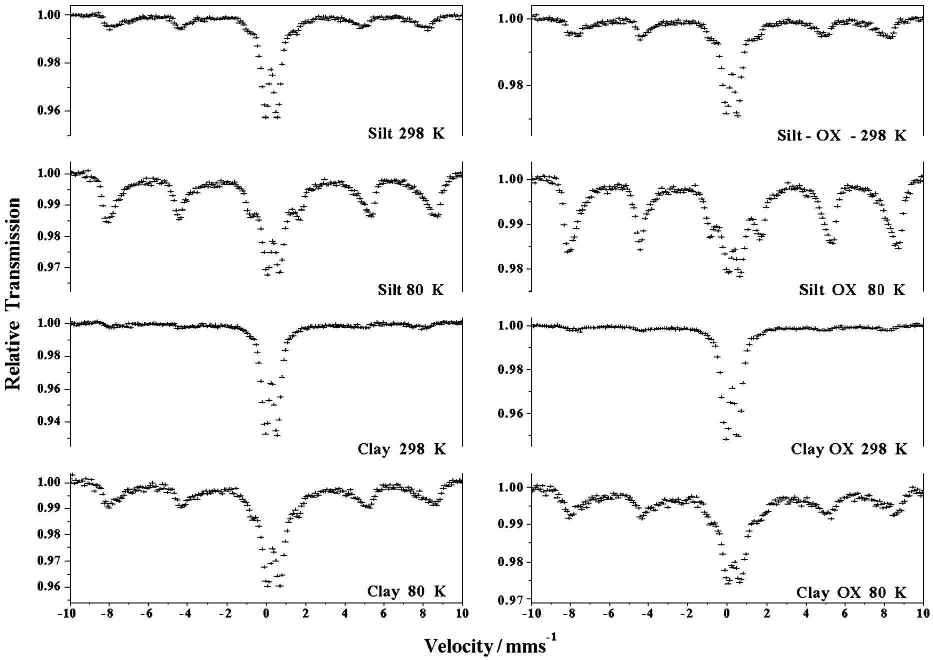

Fig. 1 298 and 80 K Mössbauer spectra for Collipulli silt and clay fractions, before and after of the OX treatment

relatively poor in organic matter (Table 1). This soil presents high clay content (Table 2). All these characteristics are similar to those found for other volcanic Chilean Ultisols [8]. This clay fraction was found to contain mainly kaolinite (>50 wt.%) along with α-cristobalite, halloysite, vermiculite at <1 wt.% [9]. The magnetic measurements (Table 2) indicated this is a magnetic soil.

For both, untreated and OX-treated silt and clay fractions, the 298 and 80 K-Mössbauer (Fig. 1) spectra reveal relatively complex mineral assemblages, with heterogeneous chemical compositions, rendering patterns mainly formed by an intense central doublet, due to paramagnetic Fe^{3+} in silicates and/or superparamagnetic iron oxides. The incipient broad-line sextet may be due to coexisting magnetically ordered forms of iron oxide. The sextet signals are more intense for the silt than for the clay sample. Goethite, hematite and maghemite were identified from the Mössbauer spectral analysis of patterns obtained at 6 K, for both particle size fractions, (Fig. 2). The relative area for maghemite in non-treated samples was found to be 46%, for the silt, and 13%, for the clay. These results are consistent with the measured values of specific saturation magnetization for silt and clay fractions (Table 2). Some low hyperfine fields are identified for both samples: (1) maximum probability at 44.7 T, accounting for about 16% of the relative spectral area (*RA*) of the silt, but more intense for the clay sample; (2) 44.2 T and 47.3 T, summing 31% *RA* (Table 3). These magnetically ordered species are likely due to poorly crystalline iron oxyhydroxides, which are more easily removed with the OX treatment (Fig. 2). In this volcanic soil, maghemite tends to remain in the coarse fraction, whereas poorly crystalline structures do occur mainly in the clay fraction (Table 4).

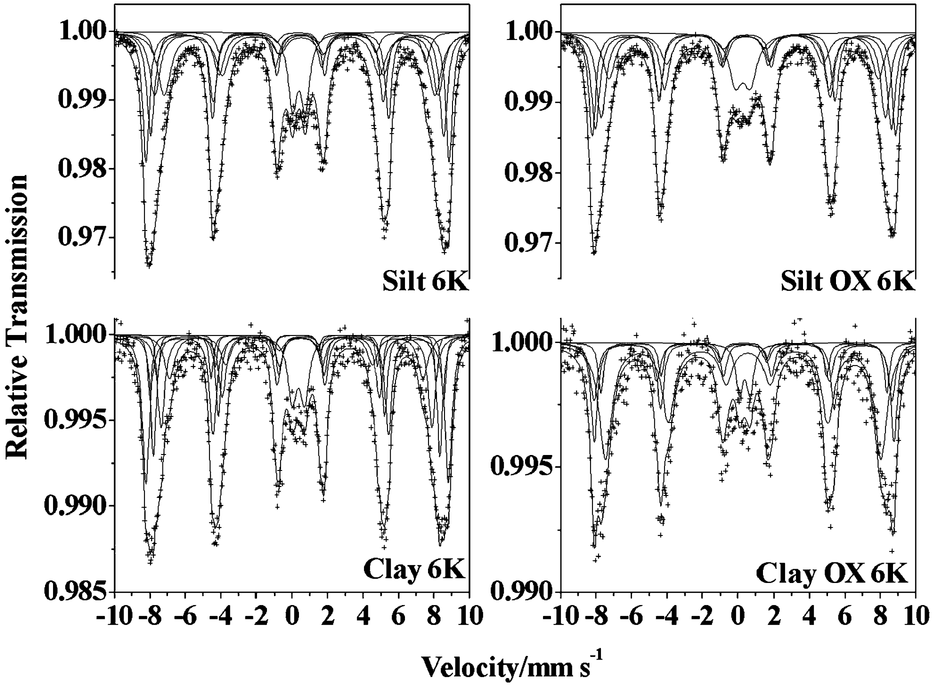

Fig. 2 6 K Mössbauer spectra for Collipulli silt and clay fractions, before and after of the OX treatment

Table 3 6 K Mössbauer parameters for the UT Collipulli and for the ammonium OX silt samples

Sample	Subspectrum	δ/mm s^{-1}	Δ,ε/mm s^{-1}	B_{hf}/T	*RA*/%
6K-UT	Fe(III)	0.32(1)	0.91(2)		11.8(2)
	Gt	0.57(1)	−0.35(1)	50.1(1)	11(3)
	Hm	0.54(1)	−0.21(1)	53.3(1)	16(3)
	[Mh]	0.45(1)	−0.08(2)	48.3(1)	21(5)
	{Mh}	0.43(1)	−0.04(1)	51.8(1)	25(3)
	Lower Field	0.53(2)	−0.19(4)	44.7(4)	16(3)
6K-OX	Fe(III)	0.39(1)	0.83(4)		13.7(2)
	Gt	0.50(1)	−0.20(3)	49.6(2)	24(8)
	Hm	0.52(1)	−0.17(1)	53.0(1)	22(6)
	[Mh]	0.45(2)	−0.07([a])	47.0(5)	17(5)
	{Mh}	0.44(1)	0.06(2)	51.7(2)	24(8)

[] and {} stand, respectively, for iron in tetrahedral and octahedral sites of maghemite. Numbers in parentheses refer to errors over the last significant digits as given by the least-squares procedure and may not represent the actual experimental uncertainties

UT Untreated, *OX* oxalate-treated δ isomer shift relative to αFe; ε quadrupole shift, B_{hf} hyperfine field, *RA* relative area of the subspectrum, *Fe(III)* subspectrum due to (super)paramagnetic Fe^{3+}, *Gt* goethite, *Hm* hematite, *Mh* maghemite, *Lower Field* any not-assigned subspectrum, for which the hyperfine field value is lower than to those of the previous magnetically ordered phases

[a] Fixed value during least-squares fitting convergence

Table 4 Mössbauer parameters for the UT Collipulli and for the ammonium OX clay samples

Sample	Subspectrum	δ/mm s^{-1}	Δ,ε/mm s^{-1}	B_{hf}/T	*RA*/%
6K-UT	Fe(III)	0.45(2)	0.70(2)		11.2(4)
	Gt	0.51(1)	−0.26(2)	50.0(1)	18(4)
	Hm	0.50(1)	−0.20(1)	52.8(1)	28(3)
	[Mh]	0.37(1)	−0.03(3)	48.7(3)	5(1)
	{Mh}	0.38(1)	−0.03(2)	51.3(1)	8(1)
	Lower Field	0.44(2)	−0.16(4)	44.2(3)	12(3)
	Lower Field	0.49(1)	−0.23(2)	47.3(1)	19(4)
6K-OX	Fe(III)	0.50(a)	0.60(a)		10.3(6)
	Gt	0.52(2)	−0.28(a)	48.1(2)	30(4)
	Hm	0.53(2)	−0.18(a)	52.3(1)	32(5)
	[Mh]	0.43(3)	0.0(a)	49(1)	11(2)
	{Mh}	0.38(1)	0.0(a)	52.0(2)	18(2)

[] and {} stand, respectively, for iron in tetrahedral and octahedral sites of maghemite. Numbers in parentheses refer to errors over the last significant digits as given by the least-squares procedure and may not represent the actual experimental uncertainties

UT Untreated, *OX* oxalate-treated, δ isomer shift relative to αFe, ε quadrupole shift, B_{hf} hyperfine field, *RA* relative area of the subspectrum, *Fe*(*III*) subspectrum due to (super)paramagnetic Fe^{3+}, *Gt* goethite, *Hm* hematite, *Mh* maghemite, *Lower Field* any not-assigned subspectrum, for which the hyperfine field value is lower than to those of the previous magnetically ordered phases

[a] Fixed value during least-squares fitting convergence

4 Conclusions

Goethite, hematite and maghemite were identified in the silt and clay fractions of this Collipulli volcanic Ultisol. Maghemite tends to remain in the coarse fraction, whereas poorly crystalline forms do occur mainly in the clay fraction. The selective chemical treatment revealed to be an essential step of sample preparation for the mineralogical analysis with physical methods.

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