Crystal-chemical transformations and iron reduction in clay minerals of two Brazilian mangrove soils

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RIO18 21st World Congress of Soil Science

Soil science: beyond food and fuel

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The formation of clay minerals in mangrove soils is an important key to understand pedogenic and biogeochemical processes. To investigate the chemical transformations and the role of Fe reduction in clays, two Brazilian mangroves were selected (Bragança, Pará State, BR - humid Amazonian coast; Acaraú, Ceará State, AC - semiarid northeastern coast). Samples of 2-0.2 µm and < 0.2 µm size fractions were studied using modeling of XRD patterns (program ClaySIM®), X-ray fluorescence spectroscopy (XRF) and Mössbauer spectroscopy.

Table 1 – Phase distribution and crystal-chemical parameters used for XRD modeling procedure (corresponding experimental and calculated XRD patterns are shown in Fig. 1)

Sample	% phase	Components	% layers	Fe kaol	Fe sm	Fe il	K il	Nmax	Nave
2-0.2 µm size fraction									
BR1_20-30	73	K-S	98-2	0.71	1.40			58	42
	1	K-S	90-10	0.71	1.40			10	3
	11	I-S	90-10		1.40	0.45	0.50	7	1
	15	Illite	100			0.45	0.50	25	15
AC1_0-5	11	K-S	98.5-1.5	0.54	1.40			40	25
	3	K-S	90-10	0.54	1.40			12	7
	18	Smectite	100		1.40			7	1
	1	Vermiculite	100		0.98			12	6
	60	Fe-illite	100			1.40	0.50	22	16
	8	Al-illite	100			0.20	0.80	30	20
< 0.2 µm size fraction									
BR1_20-30	28	K-S	99-1	0.00	1.10			35	25
	14	K-S	85-15	0.00	1.10			12	7
	50	K-S	10-90	0.00	1.10			7	1
	8	K-I	90-10	0.00		0.20	0.80	15	7
AC1_0-5	25	K-S	97-3	0.27	1.40			25	20
	17	K-S	80-20	0.00	1.40			10	7
	26	K-S	50-50	0.00	1.60			7	1
	26	I-S	15-85		1.40	1.50	0.80	7	1

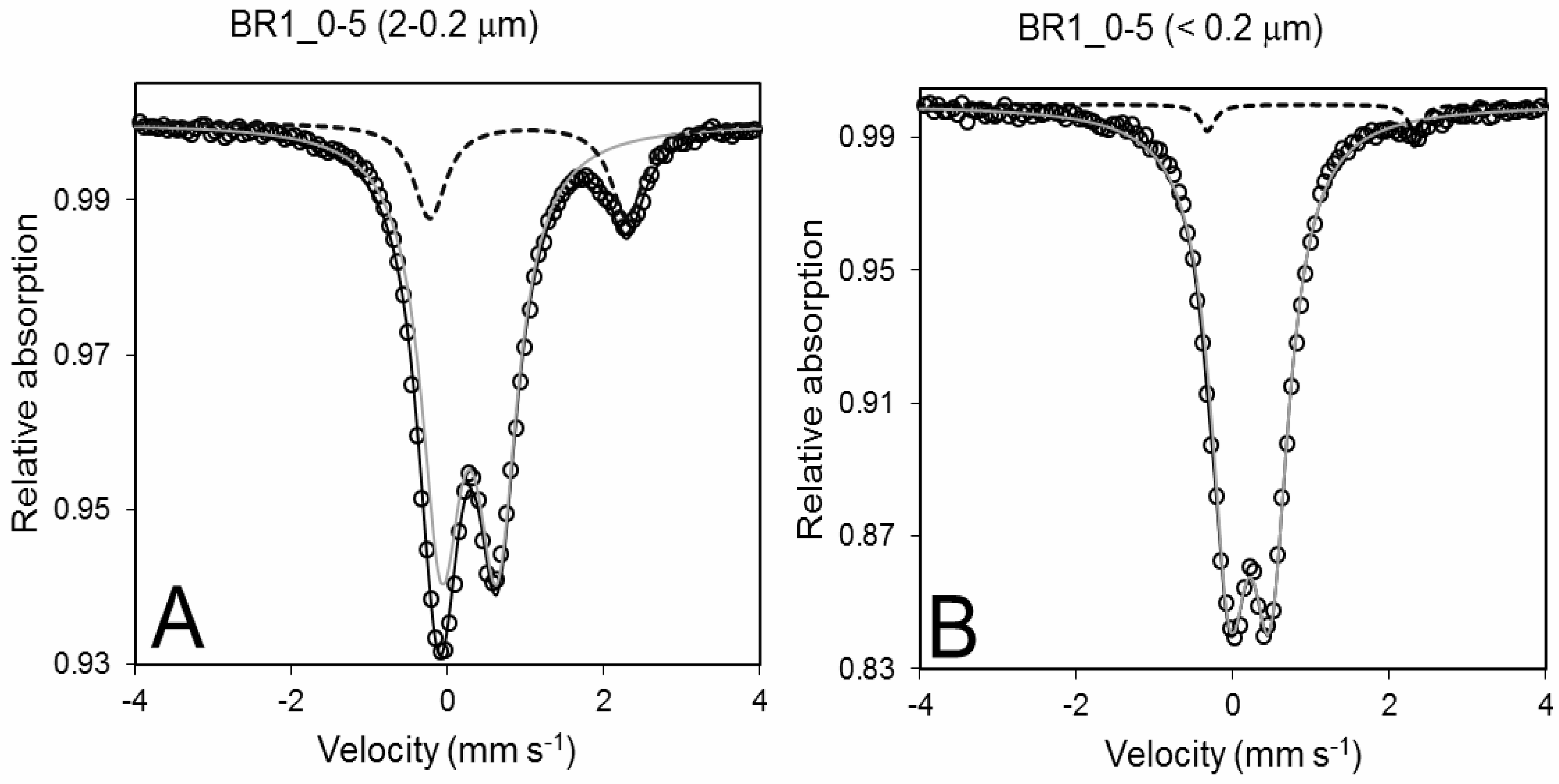

Fig. 2 – Examples of Mössbauer spectra of samples from BR mangrove soil. A- Sample from 2-0.2 µm size fraction. B – Sample from < 0.2 µm size fraction. Circles – experimental data; Black line – overall fit; Gray line – octahedral Fe^{3+} doublet; Dash line – octahedral Fe^{2+} doublet

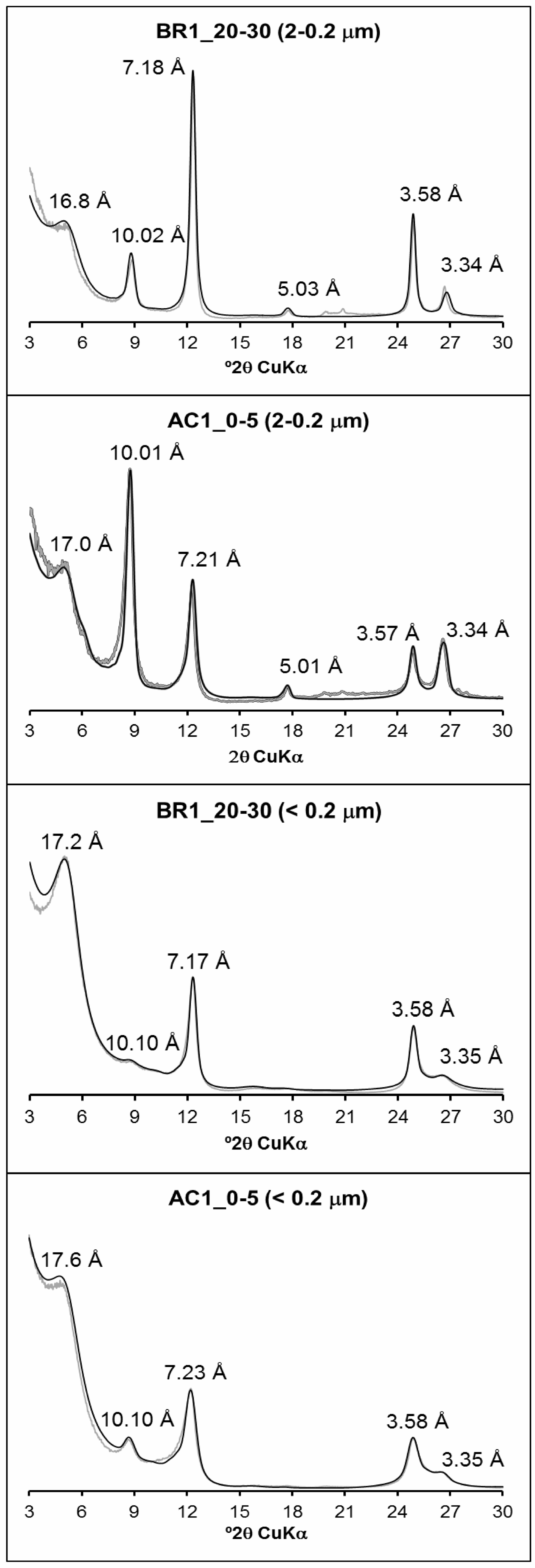

Fig. 1 – Examples of XRD patterns from the two mangroves. Black lines – experimental glycolated patterns. Gray line – fitted calculated patterns, using the program ClaySIM®

The deposited kaolinite is progressively transformed into smectite via K-S. This step includes the formation of a new tetrahedral sheet, gradual substitution of cations in tetrahedral (Al for Si) and octahedral sites (Fe+Mg for Al), and intercalation of cations, leading to the formation of Fe-rich smectite layers. The second step is the illitization of smectite layers, which includes further Fe incorporation and reduction. This is concluded because both total Fe and Fe^{2+}/TotFe proportion in the 2-0.2 µm size fraction correlated very well with Fe-illite contents from XRD. The AC samples have higher Fe-illite content because continental 2:1 clays are deposited in the mangrove and they are transformed more quickly into Fe-illite than kaolinite. We conclude that Fe sequestration and reduction during illitization are important biogeochemical processes operating in mangrove soils.

Published as: Andrade et al., 2018. Sequential mineral transformation from kaolinite to Fe-illite in two Brazilian mangrove soils. **Geoderma** 309, 84-99

FAPESP FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO

Grants n. 2011/13924-0 and 2013/17571-0