Changes in the mineralogy of a cultivated marsh soil caused by simulated weathering

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SUMMARY

Differential heats and isotherms for K–Ca exchange and CEC values show that simulated weathering by grinding and NaTPB treatment of the coarse clay fraction of a rice-growing marsh soil exposed vermiculitic layers to reaction with ions in solution, and also created more montmorillonitic layers and uncharged clay. Calcium selectivity was also increased, especially at K saturations > 50%. Changes in the CEC values of the fine clay, fine silt and coarse silt by such treatment, compared with that in the coarse clay fraction, were used to predict changes in the layer charges of their component phyllosilicates.

INTRODUCTION

Some 4000 a ago the River Guadalquivir in Andalusia, Spain, discharged into a saline lake which was isolated from the Atlantic Ocean by a littoral cord of dunes. The saline lake bottom was formed by a very thick layer of Lower Miocene–Upper Pliocene impermeable blue marls (Viguier, 1977). The runoff of the Guadalquivir valley filled the lake with different, mostly non-swelling clays (Moreno *et al.*, 1978), and 2000 km² of marshes developed through which the river cut its estuary. The marshes became drier and a calco-sodic gley, or takinic solonchak, type of soil developed on the fluvio-marine sediments. About 40 000 ha of this soil have been reclaimed (Moreno *et al.*, 1981) and are used to grow very high yields of rice only (medium yield 6 t ha⁻¹) with very specialized agricultural techniques. The rice is sown and treated with pesticides from the air, but the soil is fertilized, the rice harvested and the wet straw ploughed deeply into the soil using very heavy machinery. The heavy machinery and the use of ammonium compounds as fertilizers can enhance the loss of soil potassium and facilitate the development of swelling clays with consequent damage to the physical properties of the soil.

In previous work (Navarro *et al.*, 1984), we found that these soils, when ground, increased their labile K content and showed changes in their X-ray powder diagrams. The effects of treatments designed to simulate weathering, the use of heavy machinery and the effects of K uptake by the rice crop on the nature of the clay in this soil have been investigated by a microcalorimetric 'finger print' method (Talibudeen & Goulding, 1983a, b; Talibudeen, 1984).

MATERIALS AND METHODS

A range of particle size fractions was separated from the soil. These were ground and their potassium extracted with sodium tetraphenylboron (NaTPB) to simulate and accelerate weathering and K uptake. NaTPB was added in excess to the soil fractions and the mixtures ground for 60 min in a ball mill at 60 r.p.m. The KTPB thus produced and the unreacted NATPB were washed out with 0.1 M CaCl₂ at pH 7 until the clay was Ca saturated and the X-ray diffraction (XRD) peak of NaTPB had disappeared. The soil fraction was then rinsed with alcohol and acetone, and air-dried.

The cation exchange capacities (CEC) of the untreated and treated samples was determined by M NH₄NO₃ and 0.1 M MgCl₂ extraction, and Ca and K analyses of the solution and solid phases. The coarse clay (0.2–2.0 µm) were examined at 20°C by the Gaines and Thomas thermodynamic

treatment of K–Ca exchange isotherms and by the microcalorimetry of K–Ca exchange (Talibudeen & Goulding, 1983a,b; Talibudeen, 1984). Briefly, the Ca saturated samples were brought to equilibrium with KCl+CaCl₂ solutions of contrasting composition and the solution and clay phases analysed for K and Ca contents, and for exchangeable K and Ca, respectively, to give K–Ca exchange isotherms. In parallel experiments, the Ca-saturated samples were treated with increasing amounts of KCl solution, and the heats evolved measured in a LKB microcalorimeter.

RESULTS AND DISCUSSION

X-ray diffraction

XRD analysis examines the mineralogical composition of the matrix of a sample. The K–Ca exchange properties investigated in this work deal with the redistribution of layer charge in 2:1 phyllosilicates on grinding and NaTPB treatment, which may not necessarily correspond with XRD data. A semi-quantitative XRD analysis of the 0.2–2.0 µm fraction before and after treatment showed that the ratios of illite:smectite:kaolinite changed from 1:0.06:0.33 to 1:0.21:0.20, suggesting that illitic mica 'degraded' to smectite, and kaolinite to amorphous oxides. It was most likely that some of the original smectite also degraded like the kaolinite, which was supported by the fact that the CEC of the <0.2 µm fraction (containing only smectite and amorphous oxides) decreased on treatment—see below and Table 3.

The percentage increase in CEC of the coarse clay fraction (0.2–2.0 µm) brought about by treatment was about the same at any point on the K–Ca isotherm, whether determined by M NH₄NO₃ extraction (69%), or by exchangeable Ca in the Ca-saturated clay extracted with 0.1 M MgCl₂ (61%). This was caused by the treatment opening up negatively charged layers in the clay to make contact with ions in solution.

Thermodynamic measurements

Preference for K, as expressed by the standard free energy (ΔG_0) (Table 1), was decreased after treatment. This implied that prolonged treatment might eventually convert this clay into one that had an overall preference for Ca over K. The standard enthalpy (ΔH_0) values were obtained by extrapolating the integral enthalpy v K saturation curve to 100% K saturation, and showed that K binding strength was greatly increased by treatment but not sufficiently to increase K preference. The more negative standard entropy value (expressed in $T\Delta S$ units) after treatment showed that the disorder in the arrangement of charged layers and the counter ions was greatly increased. This decreased K preference more than the increase caused by the increased binding strength. The contribution of the hydration of interlayer K and Ca ions to the enthalpic and entropic components of the free energy of K–Ca exchange has already been discussed in detail (Deist & Talibudeen, 1967; Goulding & Talibudeen, 1980, 1984; Talibudeen & Goulding, 1983a).

From 0 to 25% K saturation, the values of the selectivity coefficient, $\ln K_c$ (where K_c is the equilibrium quotient for the reaction $\text{Ca-soil} + 2\text{K}^+ \rightleftharpoons 2\text{K-soil} + \text{Ca}^{2+}$; Deist & Talibudeen, 1967), were greater, showing higher K selectivity for the treated clay than for the untreated sample; this reversed to lower K selectivity at K saturations $\geq 55\%$ (Table 1). The curve of $\ln K_c$ against K% saturation showed a minor inflexion at about 25% K saturation, indicating a change in layer charge in the untreated clay involved in the K–Ca exchange, whereas $\ln K_c$ decreased smoothly with K saturation in the treated sample; this suggested a change in the distribution of layer charge induced by treatment.

Adsorbed ion activity coefficients

The adsorbed ion activity coefficients, or f values, express the 'freeness' of the ion adsorbed on the clay surface (relative to that at 100% saturation with that ion) to leave the surface and react with ions in the equilibrating solution. Although at zero K saturation f_K values were the same for both samples, the untreated clay showed a maximum near 35% K saturation (Table 1), indicating a greater lability of K ions than that at 100% saturation. This did not occur with the treated clay, suggesting that the treatment changed the nature of some of the charged layers. The f_K values for

Table 1. Ca-K exchange isotherms of the coarse clay fraction (0.2–2.0 μm) from the surface soil of the Guadalquivir marshes, before and after grinding and NaTPB treatment

Parameter		Untreated clay	Treated clay	
Standard free energy $\Delta G_0/\text{kJ eq}^{-1}$		-1.70	-0.90	
Standard enthalpy $\Delta H_0/\text{kJ eq}^{-1}$		-8.1	-12.0	
Standard entropy $T\Delta S_0/\text{kJ eq}^{-1}$		-6.4	-11.1	
Cation exchange capacity*/ $\mu\text{eq g}^{-1}$		376	634	
Selectivity coefficient, $\ln K_c$				
K saturation/%	0	5.33	6.28	
	10	2.35	3.84	
	25	0.94	1.80	
	55	0.02	-0.18	
	100	-0.43	-1.45	
Adsorbed ion activity coefficients		f_K	f_{Ca}	f_K f_{Ca}
K saturation/%	0	0.17	1.00	0.18 1.00
	35	1.42	0.42	0.54 0.28
	90	1.05	0.17	1.03 0.01
	100	1.00	0.16	1.00 0.007

*The CEC values determined by extracting Ca from the Ca-saturated clay with 0.1 M MgCl_2 were 505 and 810 $\mu\text{eq g}^{-1}$.

Table 2. Results of microcalorimetry of Ca-K exchange of the coarse clay fraction (0.2–2.0 μm) from Guadalquivir marshes, before and after grinding and NaTPB treatment

Determination		Untreated clay	Treated clay
<i>Differential heat of exchange</i>			
$\frac{d(\Delta H)}{dx_K}/\text{kJ eq}^{-1}$			
K saturation/%	0–22	– 15.0	– 14.8
	23–52	– 7.7	for 0–45%
	53–57	– 7.1	
<i>Mineralogical composition* % w/w</i>			
Vermiculitic mica		3.4	11.6
Montmorillonite		22.6	26.8
Uncharged minerals, by difference		74.0	61.6

*Calculated from the differential heats 'spectrum', assigning layer charges of 2460 and 1300 $\mu\text{eq g}^{-1}$ to vermiculitic mica and montmorillonite, respectively (Talibudeen & Goulding, 1983a, b).

both samples decreased smoothly from the standard state value of 1.0 at zero K saturation to much lower values at 100% K saturation, but this decrease was much more for the treated sample; indicating its greater Ca selectivity as K saturation increased.

Differential heat measurements

These measurements of $d\Delta H/dx_K$, where x_K is the fractional K saturation, are given in Table 2; they were quite independent of the exchange isotherm studies, and the mineralogical compositions were derived from them. It was reassuring that they confirmed the conclusions from the analysis of the results of the K-Ca exchange isotherms. The differential heat attributed to vermiculitic mica (Talibudeen & Goulding, 1983a, b) indicated that the untreated sample contained 3.4% of this mineral, which increased to 11.6% on treatment, creating and exposing charged layers to make contact with ions in solution, and contributing most to the increase in CEC (Table 1). The remaining negative charge in the untreated clay was attributed to 'pure' montmorillonite layers, at least up to 57% K saturation, based on differential heats of 7.7 and 7.1 kJ eq⁻¹. As this is the phyllosilicate with the smallest layer charge, the remaining 43% of the CEC can be attributed to it also. After allowing for the weight percentages of vermiculitic mica and montmorillonite, the remaining 74% of mass had to be ascribed to uncharged 'pure' 1:1 phyllosilicates (Talibudeen & Goulding, 1983a, b), uncharged 2:1 phyllosilicates and oxides. Thus, the artificial weathering treatment increased the vermiculitic and montmorillonitic layers (with about half the layer charge of the vermiculitic layers) exposed to contact with the solution phase. The montmorillonitic layers were presumably increased by the degradation of the vermiculitic layers.

Table 3. Changes in the CEC of particle size fractions of the soil caused by the grinding and NaTPB treatment

Particle size (μm)	Percentage of original soil	Cation exchange capacity	
		Untreated ($\mu\text{eq g}^{-1}$ of fraction)	Treated ($\mu\text{eq g}^{-1}$ of fraction)
<0.2	22.1	755	645
0.2-2.0	43.2	505	805
2.0-5.0	31.1	370	810
5.0-20.0	2.9	240	293

Such detailed examination could not be extended to the other soil fractions, but the increase in CEC (Table 3) of the 2-5 μm fraction (220%) and the 5-20 μm fraction (22%) after grinding and NaTPB treatments suggested that the conclusions reached from the detailed work on the 0.2-2.0 μm fraction (CEC increase 60%) must apply to these coarser fractions. The CEC of the fine clay (<0.2 μm) fraction decreased by 15% after treatment, indicating that the untreated sample's charged layers consisted entirely of pure montmorillonite layers—compare the analysis of <0.2 μm Wyoming bentonite in Talibudeen & Goulding (1983a). These layers must have degraded to uncharged amorphous layers by the grinding and NaTPB treatment—hence the loss in CEC.

If such treatment simulated weathering by natural processes and cultivation, then these results suggest that (a) the finest clay fraction weathers least, creating more amorphous oxides and kaolinites in the process, (b) the coarse clay and fine silt fractions weather most: since the latter contain the largest amounts of micas and interstratified 2:1 phyllosilicates, the weathering treatments exposed more charged layers to the solution phase, and (c) the coarse silt fraction behaves similarly, though to a much lesser extent, since its micaceous minerals consist of larger and more crystalline particles than those in the smaller particle size fractions.

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