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NOTE

APPARENT DISSOLUTION DURING ULTRASONIC DISPERSION OF ALLOPHANIC SOILS AND SOIL FRACTIONS

Key words—Allophane, Dissolution, Soil, Ultrasonic dispersion, Zeta potential.

Several procedures have been proposed to obtain soil clay fractions for mineralogical and surface properties studies, without introducing chemical changes in the materials being examined. Among them, ultrasonic dispersion at room temperature without the addition of dispersing agents has been widely used. Hinds and Lowe (1980), however, reported that ultrasonic dispersion of soils in water causes significant dissolution of Al, Si, and Fe. Undoubtedly, such treatment also affects the surface composition and the properties of clay minerals, and thus ultrasonic dispersion should be avoided in many of the methods often employed in soil classification studies, such as the selective dissolution of Al and the preparation of samples for surface studies.

The main objective of the present work was to establish the extent of the dissolution of allophanic materials (from a volcanic-material-derived soil and its clay fraction subjected to organic matter and iron oxide removal) caused by ultrasonic dispersion. In addition, this work relates the dissolution effect with the dispersive efficiency and the degree of surface composition and subsequent surface charge modifications of the clay particle by means of zeta potential measurements (Gil-Llambias and Escudey-Castro, 1982).

EXPERIMENTAL

A sample of Osorno soil, a Chilean Andept described by Galindo (1974), was used. The soil was treated with 30% hydrogen peroxide until no dark residues remained to remove organic matter (Kunze, 1965). No change in the isoelectric point (IEP) was noted with further addition of hydrogen peroxide (Escudey *et al.*, 1986).

The clay size fraction was obtained by a sedimentation procedure based on Stoke's Law; an organic-matter free (OM-free) sample was suspended in one liter of doubly distilled water, the suspension pH was adjusted to 5 with 0.1 M HCl, and the sample was dispersed with a Biosonic IV ultrasonic vibrator for a period of 5 min. The <2-μm material was removed with a siphon from a depth of 20 cm after a period of 30 hr; the sample was labeled Osorno-OM-free. Half of this sample was treated with dithionite-citrate-bicarbonate (DCB) to remove iron oxides, as proposed by Mehra and Jackson (1960). This procedure was repeated seven times. The sample was then washed five times with doubly distilled water and treated with hydrogen peroxide to remove adsorbed citrate (Escudey *et al.*, 1986). This iron-oxide free (IO-free) sample was labeled Osorno-IO-free.

Osorno soil, Osorno-OM-free, and Osorno-IO-free samples were made homoionic with an 0.2 M KCl solution, using amounts of potassium approximately 50 times the cation-exchange capacity in a 24-hr, one-time treatment. The samples were then repeatedly washed with doubly distilled water until no Cl^- was detected in the supernatant.

Electrophoretic mobilities were measured with a zeta meter (ZM-77). Dilute dispersions (0.05 g/liter) were prepared in 10^{-3} M KCl. The pH was adjusted with 10^{-2} M HCl or KOH. The mobilities were averaged, and the zeta potential was calculated using the Helmholtz-Smoluchowski equation (Hunter, 1981). A computation program, in BASIC language, was employed to obtain the isoelectric point (IEP).

A 10-g portion of soil or a 1.3-g portion of the soil fraction suspended in 200 ml of doubly distilled water or 200 ml of 0.1 M KCl placed in a 400-ml Teflon beaker was used for the ultrasonic treatments. The pH was adjusted with 0.01 M HCl or KOH and the sample was ultrasonically dispersed using 200 W of energy at 20 KHz frequency for 30 min in a high-intensity continuous-flow chamber and a standard probe connected to a 25.0° ± 0.1°C water bath. A 10-ml portion of suspension was collected every 10 min and centrifuged. Sufficient solid KCl to obtain a 0.1 M solution was then added to the supernatants of the aqueous suspension, and the samples were centrifuged again. Supernatants from the 0.1 KCl suspensions were centrifuged for a second time. In all the experiments the samples were centrifuged at 20,000 g for 20 min (McKeague and Schuppli, 1982). Al, Si, and Fe in all supernatants were determined by atomic absorption spectroscopy (AA).

All the experiments were replicated twice, and de-

Table 1. Chemical analysis, organic carbon content, and isoelectric point (IEP) of samples.

Sample	Organic carbon (wt. %)	Al_2O_3 (wt. %)	SiO_2 (wt. %)	Fe_2O_3 (wt. %)	IEP
Osorno B	3.1	32.7	27.5	10.1	7.2
Osorno-OM-free	1.4	28.3	32.6	16.0	8.6
Osorno-IO-free	0.9	30.1	40.8	6.2	4.9

OM-free = Organic-matter-free; IO-free = iron oxide-free.

terminations were made at least twice; mean values are reported with a precision that ranges from 5 to 10%.

RESULTS AND DISCUSSION

Samples were largely composed of noncrystalline species, similar to allophane, and oxides and oxyhydroxides of iron and aluminum (Escudey *et al.*, 1986). The chemical composition and IEP of all samples are presented in Table 1.

Tables 2–4 show the "dissolution" (apparent dissolution) effect and IEP changes as a function of equilibrium pH, sonification time, ionic strength, and sample composition. In all samples Al, Si, and Fe (expressed as oxides) were determined in the supernatants of dispersions in water; the values increased as sonification time increased and depended on the experimental equilibrium pH, due to the presence of variable surface-charge minerals and organic matter.

The results were related to the experimental conditions needed to obtain a high dispersive efficiency. A zeta potential >20 mV, obtained away from the IEP, and a low ionic strength fixed by indifferent electrolytes (Escudey and Galindo, 1983) were required. Thus, the determination of large amounts of Al, Si, and Fe was coincident with experiments carried out 3 pH units away from the IEP in water suspensions. Under these conditions the samples presented a zeta potential of >30 mV, which increased as sonification time increased. Obviously, suspended particles were distributed in a specific size range, and fine particles had to be separated beforehand by ultrafiltration (Manley *et al.*, 1987) or centrifugation. For example, particles <500 Å in diameter need >20 min at 20,000 *g*, and particles <250 Å needed 6 hr at 80,000 *g* (McKeague and Schuppli, 1982). The determined amounts were reduced after the addition of KCl and centrifugation, because an increase of ionic strength compressed the electrical dou-

Table 2. Effect of pH, sonification time, and ionic strength on the dissolution of B horizon of Osorno soil.

					Supernatant + KCl[1]			
pH	Sonification time (min)	Al_2O_3 (mg/100 g)	SiO_2 (mg/100 g)	Fe_2O_3 (mg/100 g)	Al_2O_3 (mg/100 g)	SiO_2 (mg/100 g)	Fe_2O_3 (mg/100 g)	IEP
			Suspension in water					
3.5	0	25	43	2	13	33	nd	6.7
	10	177	139	27	21	53	nd	
	20	203	225	38	21	67	nd	
	30	228	263	65	25	67	nd	7.1
5.9	0	nd	34	nd	nd	19	nd	5.7
	10	nd	34	nd	nd	29	nd	
	20	nd	48	nd	nd	38	nd	
	30	nd	53	nd	nd	38	nd	6.2
8.0	0	4	24	2	nd	19	nd	5.2
	10	4	43	2	nd	19	nd	
	20	38	43	12	nd	19	nd	
	30	123	62	30	nd	19	nd	5.2
			Suspension in KCl 0.1 M					
					Centrifuged[2]			
3.5	0	38	34	nd	38	19	nd	6.7
	10	38	53	nd	38	29	nd	
	20	38	77	nd	38	48	nd	
	30	42	91	nd	42	57	nd	7.4
5.2	0	4	14	nd	nd	14	nd	6.9
	10	4	24	nd	nd	24	nd	
	20	4	34	nd	nd	24	nd	
	30	4	34	nd	nd	24	nd	7.4
8.2	0	nd	10	nd	nd	nd	nd	4.6
	10	nd	10	nd	nd	nd	nd	
	20	nd	10	nd	nd	nd	nd	
	30	nd	10	nd	nd	nd	nd	4.3

[1] Solid KCl was added to the supernatants until 0.1 M ionic strength was reached, followed by a new centrifugation.

[2] Supernatants in KCl 0.1 M were centrifuged again for 20 min at 20,000 g.

Table 3. Effect of pH, sonification time, and ionic strength on the dissolution of organic matter-free Osorno soil.

pH	Sonification time (min)	Al_2O_3 (mg/100 g)	SiO_2 (mg/100 g)	Fe_2O_3 (mg/100 g)	Supernatant + KCl[1] Al_2O_3 (mg/100 g)	Supernatant + KCl[1] SiO_2 (mg/100 g)	Supernatant + KCl[1] Fe_2O_3 (mg/100 g)	IEP[3]
				Suspension in water				
3.5	0	124	284	224	95	143	16	8.6
	30	2133	2872	1824	251	284	32	8.7
6.5	0	33	143	34	nd	71	16	9.0
	30	62	247	56	nd	143	22	9.2
8.0	0	nd	70	nd	nd	70	nd	8.8
	30	nd	177	nd	nd	141	nd	8.8
				Suspension in KCl 0.1 M				
					Centrifuged[2]			
3.5	0	124	320	nd	124	143	nd	9.2
	30	280	460	nd	280	389	nd	9.0
5.8	0	nd	107	nd	nd	107	nd	8.8
	30	nd	213	nd	nd	143	nd	9.1
8.0	0	nd	70	nd	nd	70	nd	8.4
	30	nd	107	nd	nd	107	nd	8.4

[1] Solid KCl was added to the supernatants until 0.1 M ionic strength was reached, followed by a new centrifugation.
[2] Supernatants in KCl 0.1 M were centrifuged again for 20 min at 20,000 g.
nd = Values are zero or less than instrument sensitivity.
[3] IEP = isoelectric point.

ble layer of suspended particles, decreased the zeta potential, and promoted flocculation and sedimentation of particles (Goldberg and Glaubig, 1987). For example, a sample of Osorno-OM-free having an IEP of 8.6 had the greatest "dissolution" value at pH 3.5 in water and the lowest at pH 8.0 in 0.1 M KCl. Ultrasonic dispersion, with the exception of the Osorno-IO-free sample at pH 3.5, did not significantly modify the IEP values, considering that IEPs were determined with an uncertainty of ±0.2 pH unit. Dissolved amounts came chiefly from organo-allophanic complexes, easily dissolved at acid pH (Osorno soil) or from the inorganic fraction (Osorno-OM-free and Osorno-IO-free). The lowest IEP was observed for the Osorno-IO-free material. At pH 3.5, this sample developed a negative surface charge, probably from Si–OH surface sites having an IEP of 2, experimentally determined on a precipitated SiO_2 from sodium silicate solution. This value is close to 2.5, IEP reported by Tadros and Lyklema (1968) for silica. Thus, dissolved Al (present chiefly as Al^{3+} at this pH) was adsorbed, shifting the IEP to a more basic pH, due to a typical cation adsorption (Stumm and Morgan, 1981). Moreover, sonification time had a rapid effect on shifting of IEP; in the first 10 min the value changed from 4.9 to 7.0. The IEP then rose gradually with sonification time to 7.2 at 20 min and 7.4 at 30 min. Furthermore, readsorption took place in the other samples, but the effect was not important, because the IEP of the dissolved ions and the surface sites were similar, therefore electrostatic repulsion predominated. Thus, ultrasonic treatment produced little or no change in the surface composition of the Osorno soil and the Osorno-OM-free sample.

Table 4. Effect of pH, sonification time, and ionic strength on the dissolution of iron oxide-free Osorno soil.

pH	Sonification time (min)	Al_2O_3 (mg/100 g)	SiO_2 (mg/100 g)	Supernatant + KCl[1] Al_2O_3 (mg/100 g)	Supernatant + KCl[1] SiO_2 (mg/100 g)	IEP[3]
			Suspension in water			
3.5	0	1	3	1	3	5.4
	30	26	33	1	5	7.4
8.6	0	57	69	nd	3	4.9
	30	58	85	nd	3	5.1
			Suspension in KCl 0.1 M			
				Centrifuged[2]		
3.5	0	nd	1	nd	1	5.5
	30	9	12	10	11	8.2
7.2	0	nd	2	nd	2	4.9
	30	nd	3	nd	2	5.1

[1] Solid KCl was added to the supernatants until 0.1 M ionic strength was reached, followed by a new centrifugation.
[2] Supernatants in KCl 0.1 M were centrifuged again for 20 min at 20,000 g.
nd = Values are zero or less than instrument sensitivity.
[3] IEP = isoelectric point.

Differences observed between original IEP (Table 1) and those reported for equilibrium pH for Osorno soil can be attributed to the hysteresis that has been observed in soils having a large quantity of organic matter, for which zeta potential vs. pH curves change as a function of initial pH of measurement.

The high "dissolution" of Al, Si, and Fe in water (with or without sonification) therefore appears to have been artificial; AA analyses were erroneously high because of the presence of very fine suspended particles, the result of efficient dispersion imposed by the experimental conditions. The dissolution depended more on the equilibrium pH of the suspension, rather than on the ultrasonic treatment. Ultrasonic dispersion had a lesser dissolution effect than has usually been considered, and it was not observed in those samples in which readsorption occurred.

The analyses of dissolved elements must therefore be made after centrifugation at high ionic strength to avoid the dispersion effect if ultrafiltration is not used.

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Departamento de Química MAURICIO ESCUDEY
Facultad de Ciencia MARÍA DE LA LUZ MORA
Universidad de Santiago de Chile PATRICIA DÍAZ
Casilla 5659, Correo 2 GERARDO GALINDO
Santiago, Chile

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