

EXPERIMENTAL DISSOLUTION OF GIBBSITE BY FULVIC ACIDS.

Consequences for the pedogenesis of the soils in Plateau de Millevaches (France)

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The soils of the Plateau de Millevaches generally contain a large amount of gibbsite (up to 20 % of the clay-sized fraction). This mineral, which crystallized during the weathering of granitic parent material, is usually regarded to be present in soils as an unweatherable relict (DEJOU et al., 1977 ; JACKSON, 1968). However, in most of the studied soils the amount of gibbsite decreases from the C horizon to the surface horizon (Table 3). This may be caused by a relative decrease of the amount gibbsite which would be "diluted" in the other clay minerals which are formed during pedogenesis (DEJOU et al., 1970). An alternative explanation was given by WILKE and SCHWERTMANN (1977) who established the instability of gibbsite in podzolic soils. ROBERT and VENEAU (1978) also demonstrate the instability of gibbsite when it is in contact with simple, complexing organic acids.

In the soils of the Plateau de Millevaches, the acidity of the parent material (granite) and a cool and wet climate lead to an accumulation of acid organic matter with complexing properties. This study was performed to test the behaviour of gibbsite in this environment.

Fulvic acids (FA) were extracted from a "sol brun ocreux humifère" (Umbric Dystrochrept) of the Plateau de Millevaches. They were purified and dialyzed against HCl-HF and H₂O, and after that they were dispersed in water and passed through a 0.45 µm "Millipore" filter. The solutions of FA which were used contain either 30 or 150 meq of carbon by liter. The pH of the solutions was 4. Experiments were conducted in plastic bottles with permanent rotative agitation lasting from one day to three weeks. At the same time, gibbsite was dissolved with an HCl solution at pH 4 in the same experimental conditions ; this served as a "reference". At the end of the experiment solutions were passed through 0.01 µm millipore filter and freeze dried. The powders which were collected were characterized by infrared (IR) spectrometry and differential thermal analysis (DTA). The remnants of undissolved gibbsite were examined with the scanning electron microscope (SEM).

Table 4 gives the amount and ratio of aluminum which was solubilized a the end of the three weeks of experiment. The dissolution was fast during the first two days it decreased during the following days and finally stopped after one week of attack. It must be stressed that the dissolution by organic acids was considerably more efficient than the dissolution by HCl.

After three weeks in contact with gibbsite, the FA solution (30 mg C/l) contained 123 meq Al/100 g FA, so these Fa were not saturated (about 400 meq would be needed to saturate the carboxylic acidity). However, the IR spectra of the powder obtained showed clearly the absorption band of carboxylate (COO⁻), and DTA in O₂ of the same powder confirmed the formation of a soluble FA-aluminum complex (exothermic peak at 410°C) (DUPUIS et al., 1977).

This experiment demonstrates the instability of gibbsite in contact with FA. The solutions of FA which was used had a pH and a concentration in carbon similar to those of natural solutions percolating through podzolic soils : 6 to 62 mg C/l for a podzol in the Vosges (GUILLET et al., 1979), 35 to 50 mg C/l for a brown podzolic soil in the Ardennes (NYS et al., 1979). The amount of aluminium which was extracted by the FA solution was similar to that obtained by ROBERT and VENEAU (1978) with simple complexing organic acids. Therefore, in the case of gibbsite, FA not only act in the transport process of aluminum (VICENTE and ROBERT, 1981), but they are also effective agents of alteration.

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With FA solutions of similar concentration than those we used, VICENTE and ROBERT (1981) obtained a very slight alteration of triohedral micas. So, in acid and complexing conditions, gibbsite appears to be more weatherable than phyllosilicates. In the soils of Plateau de Millevaches a significant solubilization of gibbsite may be suspected; it is confirmed by the mineralogical composition of the clay fraction of these soils : gibbsite disappears in the A₁ horizons. Dissolution of gibbsite by FA leads to the formation of complexes, therefore, in the soils of the Plateau de Millevaches, saturation of the complexing capacity of FA and the correlative immobilization of FA by aluminum coming from the dissolution of gibbsite may be suspected. FA-aluminum complexes are very resistant to microbiological degradation and accumulate in soils. This would be an explanation of the humiferous character of the soils of the Plateau de Millevaches.

Table III : Content of gibbsite in the granulometric fractions of the horizons of S.B.O. profile (in brackets : ratio of total gibbsite of the soil for the fraction indicated).

Horizons Fractions	A ₁		(B)		C	
	En % de la fraction	En % de terre < 2 mm	En % de la fraction	En % de terre < 2 mm	En % de la fraction	En % de terre < 2 mm
0 - 2 μ	Pas de gibbsite		6,3	0,5 (32)	6,9	0,5 (43)
2 - 20 μ	Pas de gibbsite		1,0	0,3 (18)	0,6	0,2 (17)
20 - 50 μ	Pas de gibbsite		1,3	0,8 (50)	0,5	0,05
50 - 200 μ					0,8	0,1
200 - 2000 μ					0,8	0,3
Total				1,6		1,15

Table IV : Attack of gibbsite (0.45 μ - 2 μ) with a fulvic acid solution at 30 mg C/l.

Durée de l'attaque	pH d'équilibre	Al en solution mg/l	Al en solution % Al initial	Carbone en solution mg/l	Attaque témoin HCl pH = 4,0	
					Al en sol. mg/l	Al en sol. % Al initial
1 jour	4,05	0,31	1,70	29,6		
2 jours	3,85	0,47	2,60	41,1		
4 jours	3,85	0,62	3,44	19,2		
7 jours	3,95	1,02	5,66	27,3		
2 semaines	4,40	0,94	5,22	30,6		
3 semaines	4,60	0,94	5,22	25,6	0,31	1,70