

Dissolution Kinetics of Silicon and Aluminium in a Mollic Fragiudalf of Central Italy, Derived from a Volcanoclastic Sediment

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Abstract

In the sedimentary basin of Rieti (Central Italy) a Mollic Fragiudalf was studied in order to verify, through the analysis of differential dissolution kinetics of Si and Al, whether the presence of these two elements could be involved in determining the fragic characters of its deep horizons. The results of the main physico-chemical analysis confirmed the fragic features of the deep horizons Bt3x and Ctgx which have been already observed in the field study. Differential dissolution of Si and Al was performed using 0.5 N NaOH at 25 °C, and the values of silica and alumina obtained after each of ten consecutive extractions were cumulated to trace the cumulative curves of dissolution. Slope changes of the curves, which indicate changes in dissolution rate, allowed us to recognize three mineralogical phases with different degree of solubility. The total quantity of SiO₂ and Al₂O₃ dissolved in all the extractions and relative to each of these three phases was estimated, by a graphic method, together with SiO₂/Al₂O₃ molar ratio. This one was indicative of the mineralogical composition and behaviour of each horizon. This study showed an accumulation of free silica which could be present in the form of phytoliths or diatoms as well as a fine precipitate of opal-A and silica-gel in the whole soil, mainly in the Ap and Ctgx horizons. Moreover neogenesis of clay was more evident in Bt3x horizon. The volcanic origin of the parent material, a trachytic ash fall, probably deposited in a lacustrine environment, could have favoured the availability of Si and the authigenic formation of halloysitic clay from the weathering of glass and feldspars. Our study therefore corroborates the findings of previous studies by Chadwick et al. (1987) and Karathanasis (1989) indicating the important role played by silica, probably as bonding agent, in contributing to produce characteristics of a fragipan.

Keywords: *Fragipan - Al and Si Forms - Volcanoclastic Sediment - Italy*

INTRODUCTION

The term *fragipan* is used in Soil Taxonomy to designate a diagnostic subsurface horizon with particular characteristics such as compaction, high bulk density, very low porosity, moderate or weak brittleness in the moist state, very hard consistence after drying. These features represent a serious limiting factor for agricultural and nonagricultural uses of soils

since they restrict rooting depth and water percolation. As a result of their extent and importance fragipans have been for several years the subject of a great number of papers which, nevertheless, have not yet completely clarified the mechanism of their formation. A few soil scientists think its peculiar features mainly derive from physical processes (see Bryant, 1989), others believe that fragipans are a result of chemical bonding between the different constituents of the soil. Karathanasis (1989) has recently strengthened the role of amorphous SiO_2 and Si-rich amorphous aluminosilicate as bonding materials in fragipan formation. The present study was therefore carried out in order to verify, through the analysis of the differential dissolution kinetics of Si and Al in a soil with fragipan (Mollic Fragiudalf), whether the presence of this two elements in their amorphous or crystalline forms, could have taken part in determining the fragic characters of deep soil horizons of the soil studied. We selected for this analysis a soil outcropping in the Rieti basin (Central Apennines; Carrara *et al.*, 1993).

MATERIALS AND METHODS

We excavated an Alfisol, whose deep horizons show characters of a fragipan in the form of extreme compaction and presence of a polygonal pattern bounded by bleached vertical streaks. The study site is located at 406 m a.s.l. (42°23' N, 12°52' E), on the left side of the Velino river, on a terraced surface mainly formed by a travertine. The parent material of the soil is a fine volcanoclastic deposit, probably reworked in a lacustrine environment. The soil was classified according to Soil Survey Staff (1992) as Mollic Fragiudalf. Five horizons, Ap, Bt1, Bt2, Bt3x and Ctgx were recognized and sampled. We also sampled a thick clayey infilling between prismatic peds in the deep part of the Bt horizon. Physico-chemical analysis (particle size distribution, bulk density, Cole, pH (H_2O), pH (KCl), pH (NaF), organic C, exchangeable basis, extractable acidity, CEC, Feo, Fed, total Fe) were carried out by standard methods. Clay mineral analysis was performed by XRD both on the powder and oriented Mg saturated clay; the following treatments were also carried out: glycerol solvation, heating at 110 °C and 500 °C. The following procedure was used to study the differential dissolution kinetics of Si and Al: 0.5 g of soil, of each horizon, were placed in a centrifuge tube and shaken for 5 minutes with 0.5 N NaOH at 25°C. This procedure was repeated ten times consecutively and after every shaking the extractant solution was separated off the ground by centrifugation, collected separately in a 200 ml flask and finally made to volume with deionized water after adding 37 ml of concentrated HCl. Si and Al in solution so extracted were determined by AAS and the obtained values, converted to oxides, were cumulated to trace the dissolution curves. The amount of allophane from the rapidly soluble phase was calculated according to hydrated halloysite formula ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$) using the content of Al_2O_3 extracted (allophane % = Al_2O_3 % x 2.88). Allophane-linked SiO_2 was estimated multiplying Al_2O_3 extracted by 1.176 and free SiO_2 was estimated from it, by difference from total SiO_2 .

RESULTS AND DISCUSSION

Physical and chemical properties

Table 1 shows the results of the physico-chemical analysis.

Oven dry bulk density increases from 1.11 Mg m⁻³ in Bt2 to 1.53 and 1.57 in Bt3x and Ctgx respectively. On the contrary Cole (coefficient of linear extensibility) decreases from 0.076 in Bt2 to 0.027 and 0.023 in the two deeper horizons. Clay content is higher than 53 % both in the Ap horizon and in the three Bt subhorizons with a maximum of 66 % in Bt1. The highest

Horizon	Ap	Bt1	Bt2	Bt3x	Ctgx	clayey infilling
Depth (cm)	0-35/40	35-40/65	65-120	120-190	190-220+	
Texture (%)						
sand	15.1	10.4	19.8	20.1	23.9	7.8
silt	31.5	23.9	23.5	22.5	38.5	15.2
clay	53.4	65.7	56.7	57.4	37.6	77.0
Oven dry bulk density (Mg.m ⁻³)	n.d.	n.d.	1.1	1.5	1.6	n.d.
Bulk dens. 20 % hum. (Mg.m ⁻³)	n.d.	n.d.	n.d.	1.9	1.9	n.d.
COLE	n.d.	n.d.	0.1	0.0	0.0	n.d.
pH (H ₂ O)	7.4	7.4	7.2	6.9	7.0	n.d.
pH (KCl)	6.0	6.3	6.1	5.9	5.8	n.d.
pH (NaF)	9.8	10.3	10.2	10.1	10.0	n.d.
C (%)	0.9	0.1	0.1	0.0	0.0	n.d.
Exchang. basis (cmol(+)/Kg ⁻¹)						
Ca	15.8	15.3	14.8	11.4	9.3	n.d.
Mg	1.1	0.8	0.6	0.4	0.6	n.d.
Na	1.2	1.1	1.2	1.4	1.2	n.d.
K	0.9	1.1	1.8	2.5	1.0	n.d.
Extr. ac.(BaCl ₂) (cmol(+)/Kg ⁻¹)	8.7	11.2	12.5	12.5	5.0	n.d.
CEC (NH ₄ -Ac.) (cmol(+)/Kg ⁻¹)	27.4	29.3	34.3	32.8	10.5	n.d.
Base saturation (NH ₄ -Ac.) (%)	69.0	63.0	54.0	48.0	115.0	n.d.
(Mg+Na)/Ca	0.1	0.1	0.1	0.2	0.2	n.d.
Fe _o (%)	2.0	2.1	2.3	2.5	0.8	0.8
Fe _d (%)	2.8	3.3	3.8	3.7	1.7	1.7
Fe _t (%)	6.6	7.7	8.3	8.0	4.0	4.2

Table 1 - Analysis of the Main Physico-chemical Properties of the Soil Studied

value of clay content (77 %) is found in the clayey infilling. Clay content decreases to 37 % in Ctgx horizon. Both pH_{H₂O} and pH_{KCl} decrease downward, the former from 7.4 to 6.9, the latter from 6.3 to 5.8. The pH_{NaF}, except in the Ap horizon, ranges from 10.0 to 10.3 in the whole profile. DpH (pH_{H₂O} - pH_{KCl}), a little higher than 1 in all the horizons, indicates clays with strong permanent charge (halloysite, illite) and consequently absence of Al-rich allophane. Organic C content is very low, 0.07 both in Bt1 and Bt2 and is absent in Bt3x and Ctgx horizons. CEC ranges from 34.3 in Bt2 to 10.5 in Ctgx, corresponding to $\approx 45 \pm 60$ cmol(+)/100 g of clay; this is probably related to the presence of a halloysite-illite mixture. Base saturation decreases from the epipedon to Bt3x horizon. In Ctgx a value of oversaturation shows that this trend is reversed. (Mg+Na)/Ca ratio, proposed by Hutcheson *et al.* (1959) as revealing index for fragipan horizons, increases from 0.12 in Bt1 and Bt2 to 0.16 and 0.19 in Bt3x and Ctgx respectively.

Clay mineral analysis

X-ray diffraction patterns of clay powder show the presence of halloysite (0.7 nm) (peaks relative to $d \approx 7.50 - 4.46 - 3.59 - 2.56$ Å) and quartz (peak relative to $d = 3.34$ Å).

The height of the halloysite peaks remains almost even in all the analyzed horizons but is higher in the clayey infilling sample; the height of quartz peak in Ctgx horizon is twice greater than that in Bt2 horizon. X-ray diffraction patterns show that halloysite (0.7 nm) is the main clay mineral and detect also a small quantity of illite (the peak relative to 1.0 nm remained in fact also after heating at 500 °C). Illite is relatively more present in the deep zone of the profile (Ctgx horizon) than in subsurface horizons (Bt1 and Bt2), while the minimum quantity is in the Bt3x horizon.

Dissolution kinetics of Si and Al

Figs. 1a and 1b show dissolution curves of Si and Al, traced by cumulating the values obtained after each extraction.

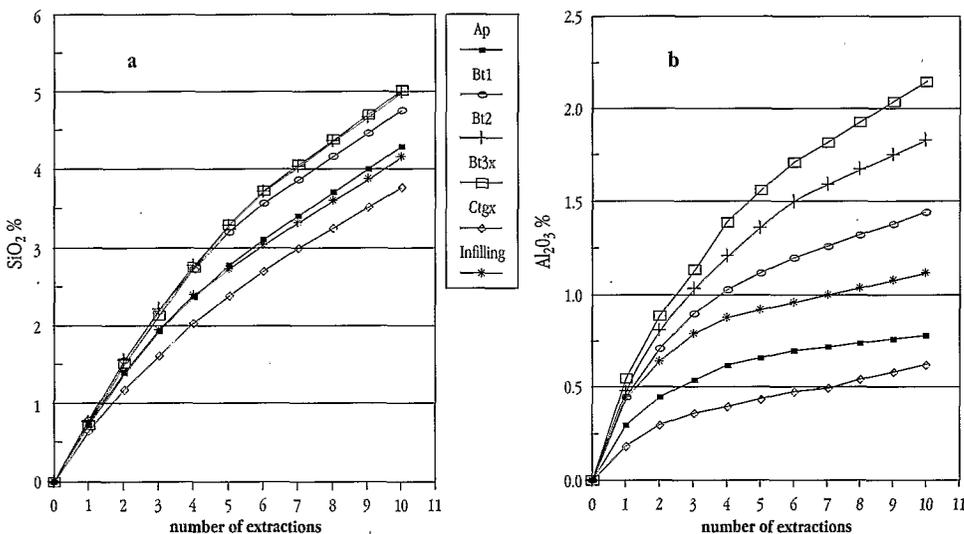


Fig. 1 - Dissolution Kinetics of Si (1a) and Al (1b)

The cumulative values of SiO₂ and Al₂O₃ are expressed in % on weight of the fine earth, after each extraction with 0.5 N NaOH at 25 °C.

Changes in the slope of the curves indicate changes in dissolution rate which correspond, in turn, to mineralogical phases with different degree of solubility. We recognized three phases: a rapidly soluble phase (**phase «a»** represented by the initial, steeper part of the curve) mainly corresponding, at concentration and temperature condition of the extractant, to mineral hydrated non crystalline products (silica gel and allophane); a little more stable phase with intermediate solubility (**phase «b»**) corresponding to a mixture of non crystalline components (e.g. opal-A < 0.1 μm in size and allophane); a more slowly and regularly soluble phase (**phase «c»**) represented by a mixture of more stable non-crystalline minerals (e.g. biological opal a few μm in size) and fine instable clay minerals of halloysitic and illitic type. Starting from the segment of the curve which presents a lower and even slope it was possible to obtain by a graphic method on the

axis of ordinate the quantity of product dissolved on the whole in all the extractions and relative to this phase. Subsequently we estimated the approximate quantity corresponding to the other phases by difference from total amount. Table 2 shows these values together with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio corresponding to the three phases. The values of molar ratio indicate the mineralogical composition and behaviour of each horizon. In Fig. 2 they are presented, extraction by extraction, with the likely trend of the corresponding curves. In a general way the proportion of SiO_2 increases towards a high limit. This shows that phase «c» is dominated by a more stable silica, non-crystalline, type opal-A, probably of biological origin, or derived from a mineral precipitate. This trend is more clear in the Ap horizon reaching a value (≈ 25) close to that of biological opal, diatoms or phytoliths type. Phase «a» of this horizon also indicates the presence of very soluble silica (gel) while phase «b» indicates very fine opal ($< 0.1 \mu\text{m}$) because the molar ratio was found to be higher than the expected values for clay minerals.

Horizons		Ap	Bt1	Bt2	Bt3x	Ctgx	Infilling
SiO_2 %	Total	4.29	4.77	4.98	5.04	3.82	4.10
	Phase a	0.58	0.62	0.62	0.62	0.62	0.60
	Phase b	0.77	1.03	1.14	1.14	0.40	0.76
	Phase c	2.94	3.12	3.22	3.28	2.80	2.74
Al_2O_3 %	Total	0.81	1.44	1.83	2.12	0.62	1.12
	Phase a	0.30	0.30	0.40	0.37	0.05	0.25
	Phase b	0.22	0.55	0.63	0.73	0.20	0.45
	Phase c	0.29	0.59	0.80	1.02	0.42	0.42
$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	Total	9.00	5.63	4.63	4.04	10.47	6.22
	Phase a	3.29	3.51	2.64	2.85	21.08	4.08
	Phase b	5.95	3.18	3.08	2.65	3.40	2.87
	Phase c	17.23	8.99	6.84	5.47	11.33	11.09

Table 2 - Selective Sequential Dissolution with NaOH 0.5 at 25 °C
 SiO_2 and Al_2CO_3 , on weight basis of the fine earth, and molar ratio $\text{SiO}_2/\text{Al}_2\text{CO}_3$

The curves relative to the Bt horizons firstly show an increasing trend from values of 2÷3 to 6÷9 and become stable on a line parallel to x axis. The relative increasing of SiO_2 in the upward segment of the curves, corresponding to «a» and «b» phases, indicates that the aluminosilicate component decreases and that there is a trend towards a stable mixture (phase «c») of opal-A and a slowly soluble clay mineral.

The opal proportion decreases from Bt1 to Bt3x. Phase «a» ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio from 2.2 to 3) seems to be formed by a mixture of allophane and silica gel. The curve corresponding to the infilling is similar to those of Bt horizons but is characterized by a twice greater proportion of silica (opal-A) in phase «c», while the Ctgx horizon curve shows a particular trend: the first segment is similar to the Ap horizon one, with a certain relative abundance of a silica gel and scarcity of allophane (phase «a»); then, at the 4th extraction, it reaches an easily soluble product, almost exclusively formed by silica

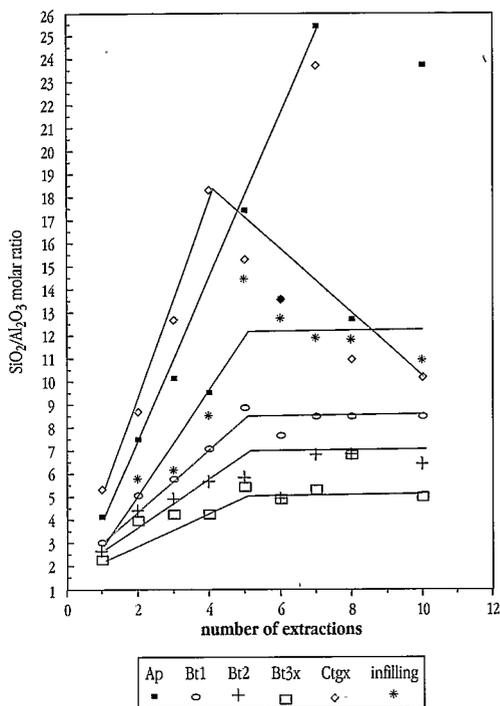


Fig. 2 - SiO₂/Al₂O₃ Molar Ratio after Each Extraction with 0.5 N NaOH at 25 °C and the Likely Trend of the Corresponding Curves

(opal A); finally it decreases towards values of 12÷10, corresponding to a dominant opal-A and a slowly soluble fine clay mineral. In Table 3, the estimate (in percentage of total soil) of free silica and allophane in phase «a+b», and of free silica and equivalent halloysite in phase «c» clearly show a greater amount of free silica and a smaller one of allophane in phase «a+b» of Ctgx horizon compared to the Bt horizons.

The horizon Ctgx, where the fragic characters are mostly expressed, shows a lower content of equivalent halloysite in the phase «c» and a free SiO₂/total (Al₂O₃+ SiO₂) ratio higher than those corresponding to Bt horizons.

Horizons	Ap	Bt1	Bt2	Bt3x	Ctgx	Infilling
Phase a+b						
Al ₂ O ₃ %	0.52	0.85	1.03	1.10	0.25	0.70
SiO ₂ %	1.35	1.65	1.76	1.76	1.02	1.36
Allophane % ⁽¹⁾	1.50	2.45	2.97	3.17	0.72	2.02
SiO ₂ of allophane % ⁽¹⁾	0.61	1.00	1.21	1.29	0.29	0.82
free SiO ₂ % ⁽²⁾	0.74	0.65	0.55	0.47	0.73	0.54
Phase c						
Al ₂ O ₃ %	0.29	0.59	0.80	1.02	0.42	0.42
SiO ₂ %	2.94	3.12	3.22	3.28	2.80	2.74
Hydrated equivalent halloysite % ⁽³⁾	0.84	1.70	2.31	2.94	1.21	1.21
free SiO ₂ (basic formula Ht) % ⁽³⁾	2.60	2.43	2.28	2.08	2.31	2.25
free SiO ₂ / total (Al ₂ O ₃ + SiO ₂) %	80	65	57	48	72	71

(1) Hydrated halloysite as basic formula (2SiO₂.Al₂O₃.4H₂O); basic estimate: allophane = Al₂O₃ x 2.88

SiO₂ of allophane = Al₂O₃ x 1.176.

(2) free SiO₂ = total SiO₂ - SiO₂ of the allophane

(3) Same calculation constants as in note (1) from the amount of Al₂O₃ present in phase «c».

Table 3 - Estimation of Free Silica, Allophane and Equivalent Halloysite, on Weight Bass of the Fine Earth, in Phases «a + b» and «c»

CONCLUSIONS

The results of the physico-chemical analysis and the observations in the field study confirmed the fragic features of the deep horizons Bt3x and Ctgx of the profile studied. We found in fact extreme compaction and very hard consistence in the dry state, high bulk density, the presence of a polygonal pattern bounded by bleached vertical streaks, the absence of organic C and a relatively high Mg+Na/Ca ratio. The study of differential dissolution kinetics of Si and Al showed an accumulation of free silica which could be present in the form of gel and fine precipitate of opal-A as well as more stable biological forms (phytoliths, diatoms) in the whole soil, mainly in the Ap and Ctgx horizons. Moreover, from the data presented, neogenesis of clay was more evident in Bt3x horizon. The volcanic origin of the parent material, a trachytic fine ash fall, probably deposited in a lacustrine environment, has favoured the availability of Si and the authigenic formation of halloysitic clay from the weathering of glass and feldspars. The soil-forming processes occurred under hardwood forest vegetation in a warm temperate climate characterized by a dry season. Our study therefore corroborates the findings of previous studies by Chadwick *et al.* (1987) and Karathanasis (1989) indicating the important role played by silica, probably as bonding agent, in contributing to produce the characteristics of a fragipan. However we don't exclude that the original tuffaceous lacustrine deposit could have been involved in a process of physical ripening by compaction and desiccation of a waterlogged material during an initial phase of pedogenesis.

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