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## GEOCHEMICAL STUDIES ON PODZOLIZATION

### PART II. SILICON IN PODZOLIZATION

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#### INTRODUCTION

Compared with the bulk of writing devoted to the role of iron and aluminium in podzolization, the interest in the role of silicon in this process is much smaller. This is due partly to the belief, fairly common until comparatively recently, that silica released in the process of mineral decomposition is immobile in acid reaction. In pedological literature, especially in Soviet publications, the idea has been expressed that the decomposition of aluminosilicates is associated with the liberation of so-called "silica powder".

Some authors, e.g. Polinov, Reifenberg, Mohr, Kubiena, Karpatchevski [cit. 8], as well as Musierowicz [9] have assumed that under certain conditions silica also becomes mobile, and its basic migratory form is colloidal solution. More recent investigations [2, 5, 6, 8], however, have revealed that in soil solution of pH below 9 silica commonly occurs in the form of undissociated orthosilicic acid —  $\text{H}_4\text{SiO}_4$ . This acid is released in the process of silicate mineral weathering. Its concentration in soil solutions is generally below saturation condition, which prevents the formation of colloidal solutions. Schnitzer and Desjardins [13] and Biełousowa [1] suggest the possibility of silicoorganic combinations passing into the solution.

McKeague and Cline [7] and Jones and Handreck [4] have found that soil particles have the capacity of sorbing silicic acid from the solution, the highest activity being shown by freshly precipitated Fe and Al hydroxides. Sorption of silicic acid by sesquioxides is regarded as specific sorption [3, 10]. According to McKeague and

Cline [8], biological sorption also plays an important part in retaining silica in soil.

Considering the growing interest in silicon among pedologists, studies have been undertaken on the role of this element in podzolization. The studies have been based on a detailed examination of the profile distribution of total Si and of amorphous pedogenic silica in podzols derived from sands. The results obtained have been interpreted on the basis of literature data on geochemical properties of silicon.

#### MATERIAL AND METHODS

The study has been carried out on seven profiles of ferro-humic podzols, whose morphology and basic properties have been discussed in an earlier publication [11].

The ash silica content in raw humus has been determined by the gravimetric method after mineralizing the organic matter in conc.  $\text{H}_2\text{SO}_4$  with an addition of 30%  $\text{H}_2\text{O}_2$ . Before the samples were mineralized, the humus had been separated from the mineral grains in heavy liquids ( $d=2 \text{ g/cm}^3$ ). The precipitate remaining after mineralization was filtered off, ignited, screened at  $\phi=0.05 \text{ mm}$  and weighed. A microscope examination of the precipitate showed that the method allowed a fairly good separation of ash silica from quartz and other minerals.

The total Si content in the mineral portion of the profile ( $\text{Si}_t$ ) was determined by the gravimetric method after melting the samples with  $\text{Na}_2\text{CO}_3$ . Pedogenic silica was extracted in alkaline extract after Foster ( $\text{SiO}_{2a}$ ). The quantitative determination of Si in the extract was done by the colorimetric molybdenic blue method, using tartaric acid for masking phosphorus.

#### RESULTS AND DISCUSSION

Silica in raw humus. As shown by analyses (Table 1), silica is the dominant ash constituent in podzol raw humus. In the plant litter fall accumulated in subhorizon  $A_0L_0$  the  $\text{SiO}_2$  content is already high (0.64%) and constitutes an average 34% of the ashes. It is slightly exceeded only by the CaO content [11]. As mineralization and humification proceed, the silica content in the humus rapidly increases. In the most highly humified material of subhorizon  $A_0H''$   $\text{SiO}_2$  averages 7.7%, which constitutes 80% of ashes. It is then the accumulation of silica that is mainly responsible for the gradual increase in ash content of organic matter in the successive  $A_0$  subhorizons, and to a much lesser extent this is due to sesquioxide accumulation [11].

The high  $\text{SiO}_2$  content in raw humus is the result of the high content of this compound in the plant litter fall and, on the other hand, of the

T a b l e 1

Average content of silica and other ash constituents in the particular raw humus subhorizons of 6 profiles /in % of organic matter mass without mineral grains/

Subhorizon	% SiO <sub>2</sub> a	% /Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> + CaO + MgO + + K <sub>2</sub> O ... P <sub>2</sub> O <sub>5</sub> / b	a + b	$\frac{a}{a+b} \cdot 100\%$
AoLo	0,64	1,25	1,89	34
AoL	1,60	1,88	3,48	46
AoF	3,81	1,93	5,74	66
AoH'	4,81	1,72	6,53	74
AoH''	7,69	2,07	9,76	79

comparatively low migratory capacity of SiO<sub>2</sub> and the low uptake rate by plants.

In spite of its limited mobility, silica gradually passes into the soil solutions. According to Biełousowa [1], the silica content in the solutions flowing from under horizon A<sub>0</sub> exceeds that of any other mineral components.

Silica in mineral profile. The results of the analyses (Table 2) contradict the thesis of the immobility of silicon in podzols. The belief of some authors that, unlike the sesquioxides, the immobile silica becomes accumulated in the eluvial horizon is possibly due to misinterpretation of the results of total analysis. Such results (Table 2) in fact demonstrate a marked increase in SiO<sub>2</sub> content in the eluvial horizon. The total analysis, however, does not reflect the profile distribution of pedogenic silica; it only points out the change in proportion between SiO<sub>2</sub> and the other mineral components. The change results from the displacement of the majority of silicate decomposition products, while quartz remains comparatively inert. Quartz grains in the eluvial horizon are devoid of ferruginous envelopes and often dull, so that they assume a whitish colour. It is not unlikely that owing to their colour they have often been regarded as secondary silica ("silica powder"), which has been believed to be an immobile product of mineral decomposition.

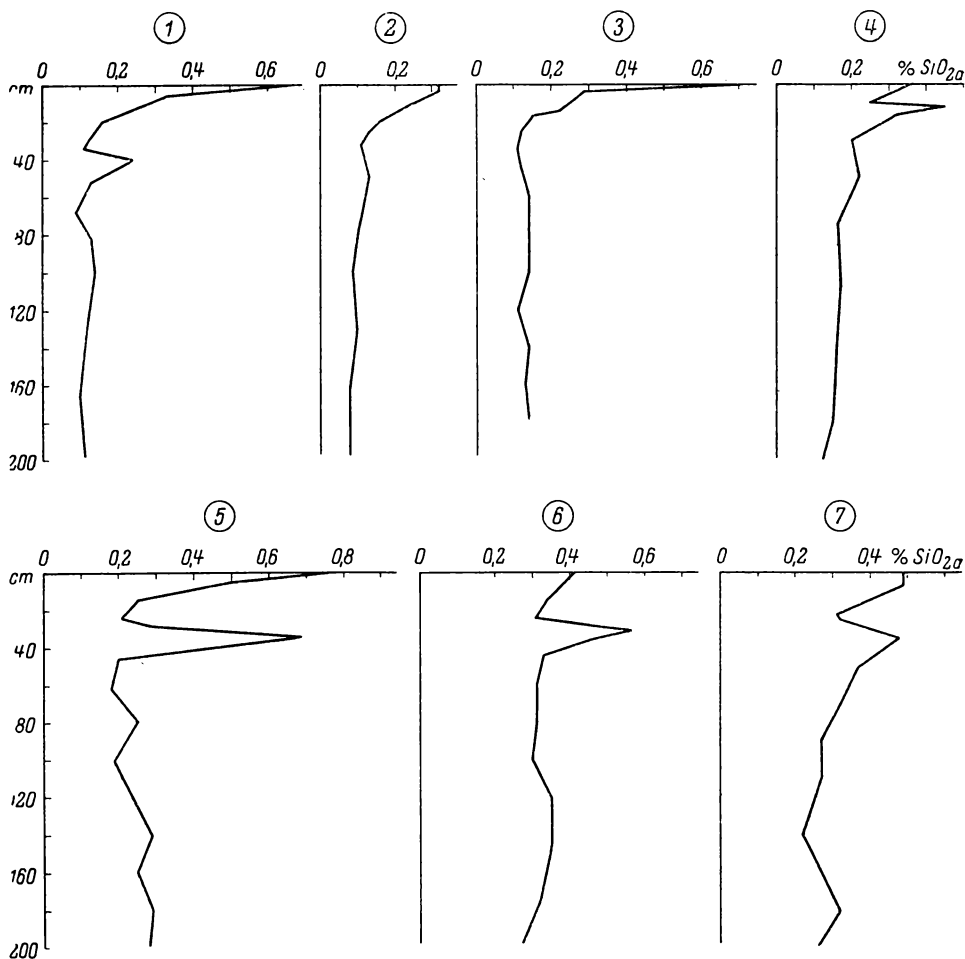
The pedogenic silica (SiO<sub>2a</sub>) content in the podzol profiles studied shows characteristic differentiation (Fig. 1). The highest concentration of this constituent occurs at the border between raw humus and the eluvial horizon, then the SiO<sub>2a</sub> content decreases rapidly to a certain minimum in the lower portion of the eluvial horizon. Beneath, there is generally a strongly marked illuvial accumulation of pedogenic silica, its maximum occurring in subhorizon Bhs.

Total SiO<sub>2</sub> and NaOH-extractable SiO<sub>2</sub> content in podzols under study

Pro-file No.	Horizon	Depth cm	SiO <sub>2t</sub> %	SiO <sub>2a</sub> %	Pro-file No.	Horizon	Depth cm	SiO <sub>2t</sub> %	SiO <sub>2a</sub> %
1	Ao/Ae	1-0-1	87,26	0,67	4	Bhs <sub>2</sub>	13-20	90,82	0,32
	Ae	12-28	96,67	0,16		Bs	20-40	92,98	0,20
	Bh	33-35	90,25	0,11		C	120-140	94,76	0,16
	Bhs	35-45	93,34	0,24	5	Ao/Ae	0,5-0-1	90,45	0,76
	Bs	60-75	95,18	0,09		Ae	10-20	98,23	0,25
	C	110-145	96,18	0,12		Bh	28,5-30	89,37	0,29
2	Ao/Ae	1-0-0,5	83,51	0,32		Bhs	30-38	92,78	0,69
	Ae	16-23,5	95,73	0,16		Bs	38-55	96,63	0,20
	Bh	23,5-26	92,19	0,13	C	110-130	97,19	0,25	
	Bhs	26-38	93,12	0,11	6	Ae	20-28	98,15	0,31
	Bs	60-85	94,78	0,11		Bh	28-29	89,28	0,45
	C	115-145	96,03	0,10		Bhs <sub>1</sub>	29-32	91,26	0,57
3	Ao/Ae	0,5-0-0,5	85,62	0,71		Bhs <sub>2</sub>	32-38	93,11	0,46
	Ae	4-12	95,50	0,26		Bs	38-50	95,45	0,33
	Bh	16-18	91,21	0,15	C	110-130	96,82	0,35	
	Bhs	18-28	93,08	0,12	7	Ao/Ae	0,2-0-0,5	89,49	0,49
	Bs	40-50	95,09	0,12		Ae	0,5-14	97,37	0,49
	C	110-130	93,41	0,11		Bh	28-29,5	91,77	0,32
4	Ao/Ae	0,3-0-0,5	88,77	0,36		Bhs	29,5-40	94,03	0,48
	Ae	0,5-10	95,03	0,31		Bs <sub>1</sub>	40-60	95,46	0,37
	Bh	10-11,5	84,55	0,25	Bs <sub>2</sub>	60-80	95,89	0,32	
	Bhs <sub>1</sub>	11,5-13	87,46	0,45	C	100-120	97,46	0,27	

The high silica content in the upper part of the eluvial horizon constitutes a prolongation of its biological accumulation in horizon A<sub>0</sub>. It has been found that there is a definite correlation between the SiO<sub>2a</sub> content and the organic carbon content in this portion of the profile. It seems possible that silico-organic combinations washed down from raw humus are precipitated there together with the washed in humus. The presence of such combinations in natural soil leachate from podzols has been found by Schnitzer and Desjardins [13] and Biełowska [1]. The nature of the silico-organic combinations has not been sufficiently studied yet. It is not unlikely that they may be low mobility combinations formed as a result of surface sorption.

Apart from a narrow zone just beneath the surface, no pedogenic silica accumulation is observed in the eluvial horizon. On the contrary,



Diagrams of profile distribution of pedogenic silica in podzols under study

it is there that the eluvial  $\text{SiO}_{2a}$  content minimum is found. This indicates that the silica released in decomposition of silicates in horizon  $A_e$  [11] is taken down the profile. Tamm [14] has already reported large amount of silica being washed down of the eluvial horizon of podzols. More recent works [2, 5, 6, 8] suggest that this constituent migrates with soil solutions chiefly in the form of orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ).

In the illuvial horizon there is another increase in  $\text{SiO}_{2a}$  content. The question arises what causes the immobilization of silica in that horizon. Earlier results [11] have revealed that in the illuvial horizon of the podzols studied there is a considerable accumulation of amorphous sesquioxides. It is also known from other reports [4, 7] that it is

precisely these soil components that are very active in sorbing silicic acid. The illuvial horizon constitutes then a kind of geochemical barrier picking silicic acid out of the percolating solutions. Since the maximum of illuvial  $\text{SiO}_{2a}$  accumulation always occurs in horizon *Bhs*, generally coinciding with the maximum of free aluminium oxides, it seems that  $\text{Al}_2\text{O}_3$  plays a greater part in binding silica than does  $\text{Fe}_2\text{O}_3$ .

It is not quite clear why in two of the profiles (No. 2 and 3) no illuvial  $\text{SiO}_{2a}$  accumulation has been found. One of the possible reasons may be that the illuvial horizons of these profiles, compared with those of the others, are poorer in free aluminium (Prof. 3) and less well cemented (Prof. 4), and do not therefore constitute an effective barrier for the solutions containing silicic acid.

As a result of the illuvial  $\text{SiO}_{2a}$  accumulation being rather small compared with that of  $\text{R}_2\text{O}_3$ , the majority of pedogenic silica migrates beyond the soil profile. Were it not for the loss of silica by this way, the fact that it is taken in large amounts by plants and continuously released both from raw humus and in the process of silicate decomposition would have to result in a much greater accumulation in the illuvial horizon. The belief that soil profiles in which there is a preponderance of the descending movement of soil solutions are subject to progressing desilification is shared by other authors [1, 8, 12].

### CONCLUSIONS

1. The results of the analysis of the profile distribution of pedogenic silica in podzols point out its active participation in podzolization.
2. A considerable biological accumulation of silica takes place in raw humus. The percentage of  $\text{SiO}_2$  in the ash content of organic remains accumulated in horizon  $A_0$  increases with the progress of humification.
3. The silica released in the eluvial horizon passes into the soil solution and migrates down the profile.
4. Part of the silica is retained in the illuvial horizon as a result of sorption by amorphous sesquioxides. A greater part in silica binding is probably played by free Al than by free Fe.
5. The bulk of soluble silica migrates beyond the podzol profile.

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И. ПОКОЙСКА

## ГЕОХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ ПОДЗОЛООБРАЗОВАТЕЛЬНОГО ПРОЦЕССА

### ЧАСТЬ 2-Я. КРЕМНИЙ В ПРОЦЕССЕ ПОДЗОЛИВАНИЯ

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### Резюме

В связи с возрастающей в почвоведении заинтересованностью геохимией кремния были предприняты исследования по участию этого элемента в процессе подзолообразования. Исследования базировали на детальном анализе профильного распределения валового содержания кремния ( $Si_t$ ) и аморфного кремнезема, определяемого в щелочной вытяжке по Фостеру ( $SiO_{2a}$ ) в подзолах образованных из песков.

Анализы показали (табл. 1), что кремний является доминирующим зольным элементом в сыром перегное подзолов. Доля  $SiO_2$  в золе органических остатков повышается по мере их разложения и в подгоризонте  $A_0H$  доходит до 80%. Из горизонта биологической аккумуляции кремний переходит постепенно в почвенные растворы. Согласно Белоусовой [1] в растворах стекающих из-под горизонта  $A_0$  содержание  $SiO_2$  превышает содержание остальных минеральных элементов.

Определения валового кремния в минеральной части профиля подзолов (табл. 2) выявили, что самое высокое содержание  $\text{SiO}_{2t}$  находится в элювиальных горизонтах. Этот факт не составляет доказательства аккумуляции аморфного кремнезема, как иногда бывает интерпретировано, но является следствием удаления большинства продуктов разложения силикатов при относительно инертном поведении кварца.

Профильное распределение аморфного кремнезема ( $\text{SiO}_{2a}$ ) показывают данные анализа по Фостеру (рис. 1). Самая высокая концентрация этого компонента обнаруживается в верхней части элювиального горизонта и представляет собой продление биологической аккумуляции  $\text{SiO}_2$  в горизонте  $A_0$ . Вне весьма тонкой подповерхностной полосы в горизонте  $A_e$  выступает элювиальный минимум содержания  $\text{SiO}_{2a}$ . Из изложенного следует, что кремнезем освобождаемый во время разложения силикатов отводится в глубину профиля. По новейшим исследованиям [2, 5, 6, 8] названный компонент мигрирует с почвенными растворами преимущественно в виде ортокремневой кислоты ( $\text{H}_4\text{SiO}_4$ ). Почвенные растворы наталкиваются в иллювиальном горизонте на зону аккумуляции полуторных окислов, принадлежащих к составным частям почвы особенно активным в сорбировании кремневой кислоты [4, 7]. Явление специфичного поглощения  $\text{H}_4\text{SiO}_4$  полуторными окислами это несомненно главная причина аккумуляции кремнезема в горизонте В большинства анализированных профилей. Поскольку иллювиальная аккумуляция  $\text{SiO}_{2a}$  по сравнению с аккумуляцией железа и алюминия очень невелика, то само собой разумеется, что большая часть аморфного кремнезема мигрирует вне пределов почвенного профиля. Если-бы не утечка кремнезема на этом пути, то постоянное его освождение из сырого перегноя и во время разложения силикатов должно было-бы приводить к значительно большей его аккумуляции в иллювиальном горизонте.



## U. POKOJSKA

## GEOCHEMICZNE BADANIA NAD PROCESEM BIELICOWANIA

## CZĘŚĆ II. KRZEM W PROCESIE BIELICOWANIA

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## Streszczenie

Nawiązując do wzrastającego w gleboznawstwie zainteresowania geochemią krzemu podjęto badania nad udziałem tego pierwiastka w procesie bielicowania. Badania te oparto na szczegółowej analizie profilowego rozmieszczenia krzemu ogółem ( $Si_t$ ) oraz amorficznej krzemionki oznaczonej w wyciągu alkalicznym według Fostera ( $SiO_{2a}$ ) w bielicach wytworzonych z piasków.

Analizy wykazały (tab. 1), że krzemionka jest dominującym składnikiem popielnym w próchnicy nadkładowej bielic. Udział  $SiO_2$  w popielności szczątków organicznych wzrasta w miarę ich postępującego rozkładu i w podpoziomiu  $A_0H''$  osiąga aż 80%. Z poziomu biologicznej akumulacji krzemionka przechodzi stopniowo do roztworów glebowych. Według Bieleusowej [1] w roztworach spływających spod poziomu  $A_0$  zawartość  $SiO_2$  przewyższa zawartość pozostałych składników mineralnych.

Oznaczenia krzemu ogółem wykonane w mineralnej części profili bielic (tab. 2) wykazały, że najwyższa zawartość  $SiO_{2t}$  występuje w poziomach eluwalnych. Nie świadczy to o akumulacji amorficznej krzemionki w tych poziomach, jak to bywa niekiedy interpretowane, lecz jest skutkiem usunięcia większości produktów rozkładu krzemianów przy względnie inercyjnym zachowaniu się kwarcu.

Profilowe rozmieszczenie krzemionki amorficznej ( $SiO_{2a}$ ) przedstawiają wyniki analizy według Fostera (rys. 1). Najwyższa koncentracja tego składnika występuje w górnej części poziomu eluwalnego, co stanowi przedłużenie biologicznej akumulacji  $SiO_2$  w poziomie  $A_0$ . Poza wąską strefą przypowierzchniową w poziomie  $A_e$  występuje eluwalne minimum zawartości  $SiO_{2a}$ . Wynika stąd, że krzemionka uwalniana podczas rozkładu krzemianów jest odprowadzana w głąb profilu. Z nowszych badań [2, 5, 6, 8] wynika, że składnik ten migruje z roztworami glebowymi głównie w postaci kwasu ortokrzemowego ( $H_4SiO_4$ ). Roztwory glebowe natrafiają w poziomie iluwalnym na strefę akumulacji półtoratlenków, które należą do składników glebowych szczególnie aktywnych w sorbowaniu kwasu krzemowego [4, 7]. Zjawisko sorpcji specyficznej  $H_4SiO_4$  przez  $R_2O_3$  jest niewątpliwie główną przyczyną akumulacji krzemionki w poziomie  $B$  większości analizowanych profili. Ponieważ iluwalna akumulacja  $SiO_{2a}$  jest w porównaniu z akumulacją żelaza i glinu niewielka, wynika stąd, że większa część amorficznej krzemionki wymywana jest poza profil glebowy. Gdyby nie straty krzemionki na tej drodze, jej pobieranie w dużych ilościach przez rośliny i stałe uwalnianie z próchnicy nadkładowej oraz podczas rozkładu krzemianów musiałyby doprowadzić do znacznie większej akumulacji w poziomie iluwalnym.

