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POSSIBILITY OF FELDSPAR FORMATION IN BENTONITE SUSPENSIONS DURING STORAGE, DRYING AND/OR HEATING

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ABSTRACT

Study in microstructures of bentonite suspensions /XRD, SEM, TG-analysis/ indicates that feldspar grains may be formed, preferably from cluster structure, either at elevated temperature or due to storage and drying.

INTRODUCTION

Study in microstructures of commercial bentonite suspensions, used in Civil Engineering, indicated the possible phase transformation /XRD peaks and SEM/. Also evidence was found that bentonite suspensions may distribute into various microstructural phases /parallel particle arrangement, cluster-aggregate structure, floc-aggregate structure/, which favour formation of various new phases /paragonite-, feldspar- zeolite-like grains respectively, see [11] /. Feldspar formation is energetically possible even at room temperature at a high pH and at a suitable Na^+ ion and silica concentration [4], see also [6]. Authigenic feldspar in saline-lake deposits was reported by Hey [1]. In silica saturated marine environment with Na^+ ion prevailing, albite was detected in lowest zones of temperature 120 - 125 °C [2], whereas in montmorillonite heated at 1100 °C, Na-photoelectron binding energy and Auger electron kinetic energy both shift to those of Na-albite [7].

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THEORETICAL CONSIDERATIONS

In the clay-water system there exist long-range interactions between colloidal particles and other structural elements /clusters, aggregates/ at the mutual distance, 2$\underline{d}$: attraction, $V_A < 0$, and repulsion, $V_R > 0$, which energies are definite functions of $\underline{d}$ /DLVO-theory, 13 , Fig. 1/. Balance of internal forces and external pressure, p_E /expressed as density of energy, V_E/ must exist at equilibrium, which takes place at an extremum, preferably minimum of the total energy curve, $V_T = V_A + V_R + V_E$ vs. $\underline{d}$, in which case the resultant pressure: $p_T = - dV_T/d\underline{d} = 0$. This condition is fulfilled in the system by change in: /1/ distance between structural elements due to /a/ change in water content at consolidation or swelling, /b/ internal water redistribution, /c/ change in particle thickness, /2/ separation into various microstructural phases of local equilibrium, /3/ change in size of structural elements: attraction, $-V_A$, increases with size of interacting bodies [8].

Decrease in $\underline{d}$ during consolidation or drying results in a positive change of repulsion /$\Delta V_R > 0$/ and in a negative change of attraction /$\Delta V_A < 0$/, which may transform into thermal energy or energy of formation of new mineral phases or its other forms. This change is the higher, the more dense the final structure is, e.g. parallel particle arrangement.

It is postulated here that: /1/ activation energy of phase transformation, Δ E, is dependent on microstructure of the system, i.e. paragonite is formed preferably from parallel structure, feldspar from cluster structure, zeolite from floc structure, which was indeed observed in bentonite suspensions [9], [11], /2/ probability of phase transformation is a function of action, i.e. the supplied energy multiplied by time and indeed similar forms were observed in air dried and heated suspensions and in those stored for a prolonged time and air dried.

MATERIALS AND METHODS

Suspensions of commercially activated to Na-form Brebent /B/R/ and Berkbent /B/B/ bentonites were prepared at various concentrations and various stirring actions /energy x time/, [9], [10], [11]:

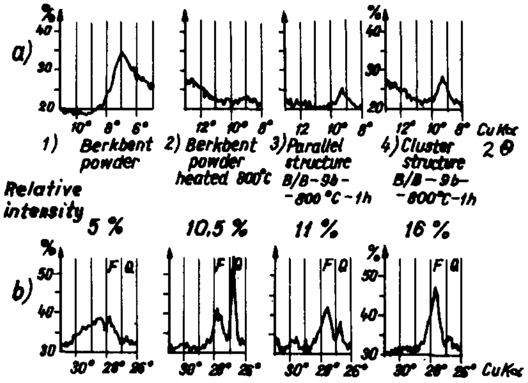


Fig. 2 XRD: /a/ smectite peak,
/b/ F -feldspar peak 3.2 A,
Q -quartz

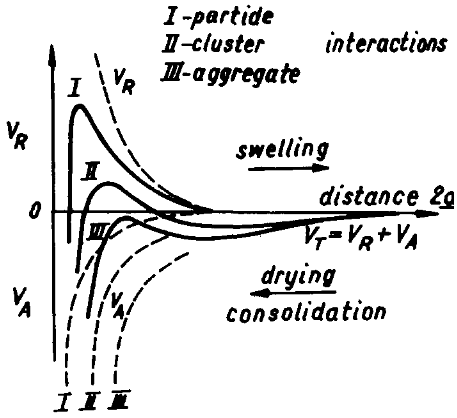


Fig. 1

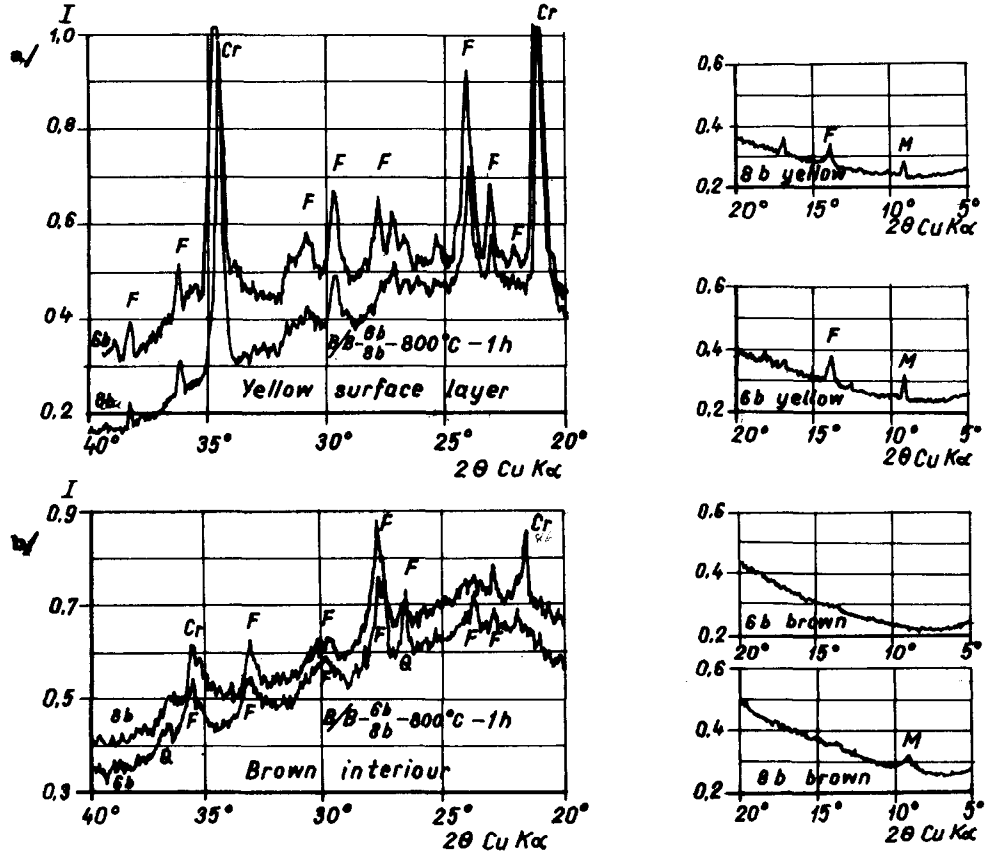


Fig. 3 XRD: F - feldspar,
Cr - cristobalite,
Q - quartz

Sample number:	B/R-	1	2	3	4		
	B/B-	5	6	7	8	9	10
Concentration:		4%	5%	6%	5%	ca.6% 5%	ca.7% 6% oven dry
Stirring energy:		2000 RPM		7000 RPM			5000 RPM
Stirring time:			5 min				15 min

Series:	0	a	b	d	e	f	g	
Storing time ca.	0	2	4	4	5	8	8	months

Unstored samples: B/B-A ca. 6%, 5000 RPM, 15 min
B/B-B ca. 6%, mixed by hand.

Samples were air dried either at 18°C /series 0/ or at 45°C, in glass containers, h=Ø=5cm, after storing times mentioned above. Some oven dried and some oriented samples were prepared. They were studied in various laboratories by XRD, SEM, water sorption test, DTA, DTG and TG analysis. Here only results pertaining to feldspar formation will be presented.

RESULTS AND DISCUSSION

Drying at 110°C of samples B/B-A and B/B-B resulted in dense packing of particles and formation of some hard grains difficult to grind. XRD peaks were observed either at 3.3 Å or at 3.75 Å or several peaks around 3.2 Å, which may belong to feldspar. Similar reflections besides peaks at 4.25 and 3.35 Å were shown by these thick well oriented samples /air dried on a glass slide/. All these peaks were not detected in powder B/B samples, [10].

Dried residuals of specimens series b and d /3-4g, 4 months storage/ were heated stepwise statically at 110°C, 220°C, 400°C and 800°C for 1h /series b/ or 18h /series d/, see [9] and weight losses were recorded as Δ G. Heated samples indicated external yellow crust and internal brown core containing yellow grains. SEM study revealed parallel structure on the sample surface and cluster structure in the sample interior /Fig. 5/. Except for the Na_2O-content, which was increased in the external yellow crust and decreased in the internal brown core, the content of remaining elements was almost identical in both sample parts [10]. Similar migration of Na to the surface of the heated powder sample of montmorillonite was observed by Seyama and Soma [7].

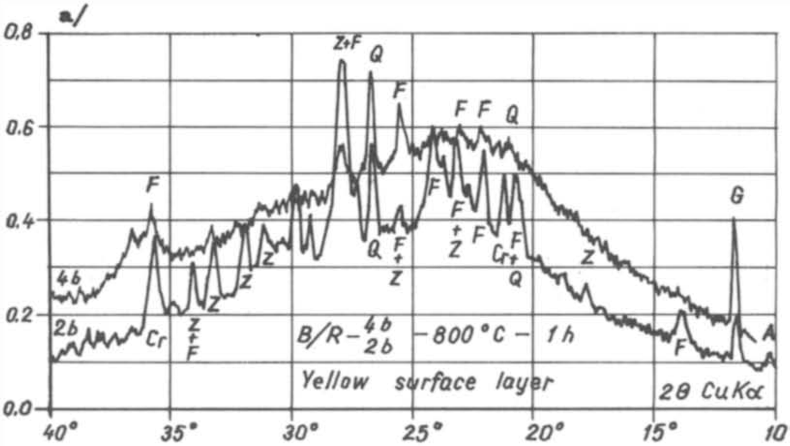
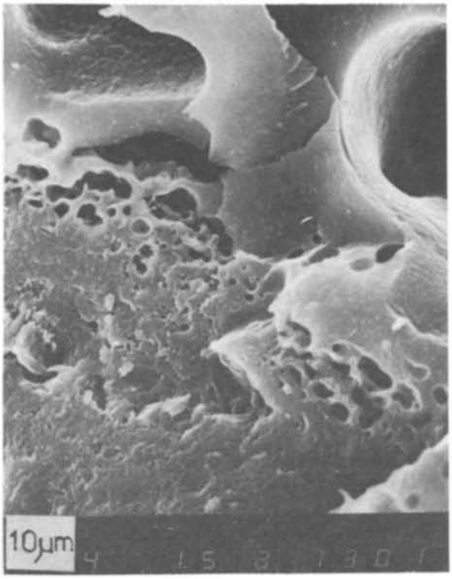
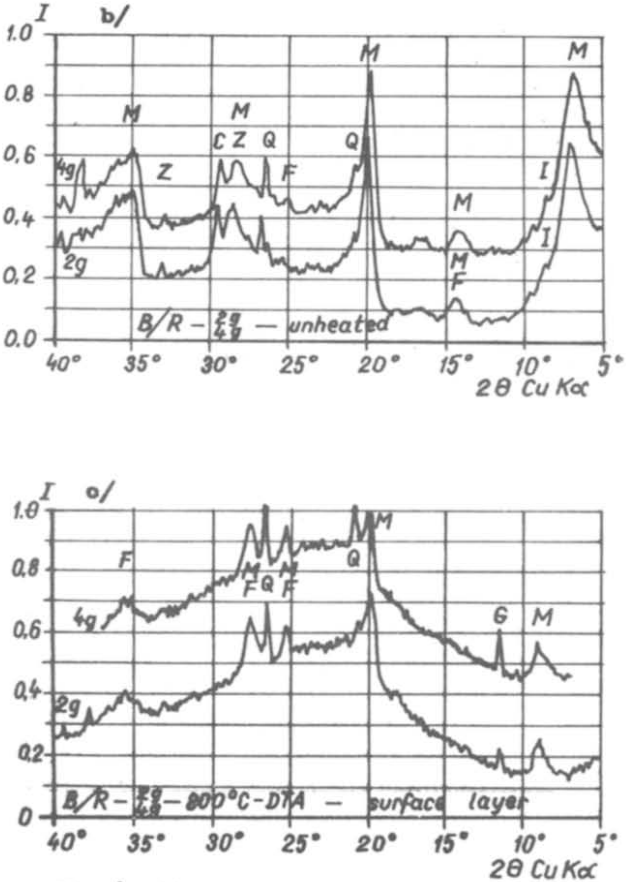


Fig.5 B/B-9b-800°C-1h





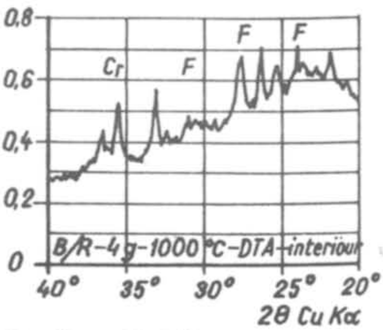


Fig.4 XRD: F - feldspar, Cr - cristobalite, Q - quartz

XRD was studied of the surface part and of the internal part of some samples, series b, heated at 800°C, i.e. B/R-2b-,-4b-, B/B-6b-, -8b- and -9b-800°C-1h. All the peaks observed may be interpreted as /Fig. 3, 4a/:

/1/ dehydrated montmorillonite

/2/ feldspar: small 6.4 Å peak, peaks at 4.0 Å, 3.2 Å, 3.0-2.97 Å and others at 3.75, 3.49-3.5, 2.89, 3.69-3.78 Å. In B/R samples they were closer to low albite, in B/B samples - to high albite. Feldspar-like grains were observed in sample B/B-9d-800°C-18h, Fig. 7. Some grains of morphology and chemical composition of feldspar were found by SEM in unheated samples 1g, 2g, 3g, 4g and 10g. A grain of morphology of sanidine "in statu nascendi" was observed in cluster structure of sample B/R-2 /Fig. 7/.

/3/ cirstobalite, especially in surface layers /4.13-4.2, 2.5-2.6 Å/. Grains of cristobalite morphology and chemical composition were observed by SEM in some samples. Also quartz peaks /4.27 Å, 3.35 Å/ and grains were found.

/4/ a gypsum peak at 7.6-7.7 Å was detected in all the B/R heated samples, which peak was not present in the unheated ones, Gypsum grains were identified by SEM in sample B/R-4b.

/5/ some small, possibly zeolite peaks /phillipsite/ were found in B/B-2b, surface layer /4.98, 3.27, 3.19, 2.7 Å, Fig. 4a/. Also small, possibly amphibole peaks are visible /8.7, 3.06, 2.69 Å/.

In all the B/B samples,series b, feldspar peaks were comparatively higher in the brown core than in the yellow surface layer, including internal yellow grains, see Fig. 3.

Relative intensities of feldspar peak 3.2 Å /G.Kranz, ZIAC, Berlin, Fig. 2b/ were compared in: /1/ Berkbent powder /I=5%/, /2/ that heated at 800°C /I=10%/ and both /3/ yellow crust /I=11%/ and /4/ brown core /I=16%/ of the sample B/B-9b-800°C-1h. Appreciable quartz peak appeared in sample /2/ and a weak one in sample /3/. It should be noted that the first order montmorillonite peak disappeared after heating of the powder sample /2/, it indicated a very low intensity in sample /3/, or a broad band was found beteen 7.7 and 9.8 Å in the unground sample [9]. The intensity of this peak was somewhat higher in sample /4/, Fig. 2a.

Increase in weight loss Δ G/110°C-800°C/ was observed in

TABLE 1

Thermogravimetric behaviour of dried bentonite suspensions in static heating /series b/, in DTA /series g/ and in DTG /series f/

Sample	Series b stored 4 months G/110-800°C/ %	DTA, series g, stored 8 months Dehydration:		ΔG %	Heat mV.min/G	Dehydroxylation: T_{defl} °C	T_{min} °C
			T_{min} °C				
B/R-1	6.27						
-2	6.12	surf		11.7	65.3	567	658
		int	120	13.7	71.6	564	656
-3	5.61						
-4	6.28	surf	111	9.4	44.0	559	645
		int	113	10.1	56.3	569	645
		"	112	9.7	56.1	569	
B/R-powder	4.65						

		DTG, series f, stored 8 months				
		G_0mg	Dehydration: T/completion/ °C	ΔG %	Dehydroxylation: T/inflection °C	ΔG %
B/B-5	6.82	29	103	12.5	507	5.5
B/B-6	7.16	32	102	13.9	523	5.5
B/B-7	6.36	11	83	14.0	501	6.0
B/B-8	7.31					
B/B-powder	4.58					

surf - surface layer, int - internal part.

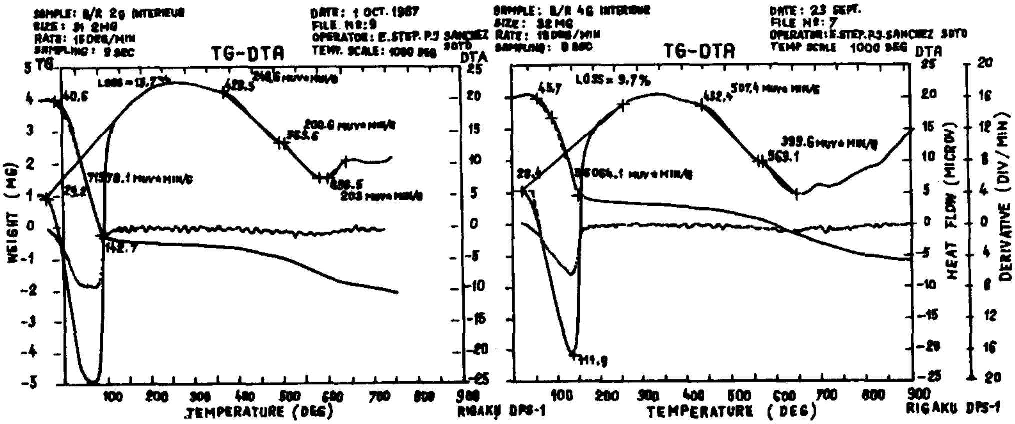


Fig. 6

series b in comparison to powder samples. It may be due to increase in temperature of dehydration /see [12]/, but also phase transformations mentioned above may be of importance. Both effects depend on microstructure.

The value of Δ G increased with the increase in stirring energy of the initial suspension and it varied also with its concentration /Table 1/.

In samples series f and g heated in DTG /f/ or DTA /g/ different TG behaviour was detected. These differences between series may be due either to /1/ a longer storing time /different microstructure/ and a shorter heating time or to /2/ smaller sample size /here ca. 30 mg/ in form of minute scratched crumbs. The influence of sample size and of microstructure on water sorption was reported in [9].

Also different XRD patterns were observed in samples series g heated in DTA than in samples series b heated statically, compare Fig. 4a and c. Surface layers and internal cores of samples 2g and 4g after heating at 800°C in DTA gave very similar XRD patterns, except the very high background of sample 4g-surface /amorphous matter/, which indicates the influence of stirring energy and the segregation of suspension during drying /Fig. 4b and c/. Besides the peaks of dehydrated montmorillonite /9.7 Å, 4.48 Å etc./, there were present quartz peaks of high intensity /4.27 Å and 3.34 Å/. This corresponds to a deflection on DTA curve about 560-570°C, Fig. 6. Feldspar XRD peaks were weak, they were probably masked by the high background. In unheated B/R samples series g also weak feldspar peaks are present and zeolite /phillipsite/ is possible.

Analysis of SEM results /selected samples series 0, a, b, d, f and g/ indicates that: feldspar grains were not observed by SEM in suspensions stored for a short time /series 0 and a/. Grains of feldspar morphology were found in /1/ series b and d, stored for 4 months and heated statically at 800°C,/2/ in series g stored for 8 months; here also the chemical composition was estimated in SEM, indicating feldspar. In both cases cristobalite and/or quartz grains were observed.

A big grain of the size of ca. 0.5 mm of feldspar-like morphology and characteristic twinning was found in the cluster structure of sample B/B-9d-800°C-18h /Fig. 7/. On the surface of this grain outlines of separate smectite particles are visi-

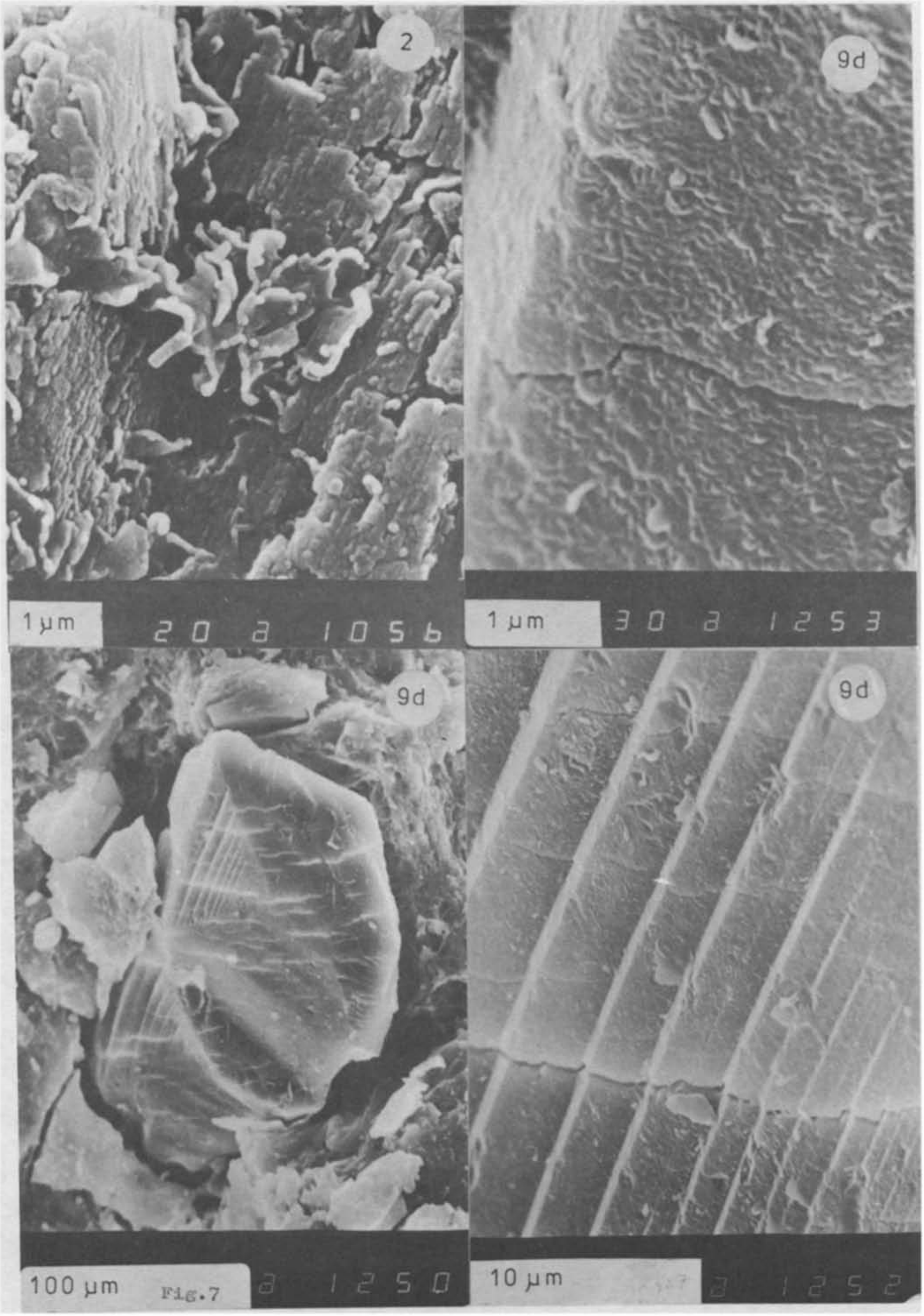


Fig.7

TABLE 2

Feldspar peaks /Å/ in heated samples

2b-yellow-4b		4g interiour	
800°C		800°C	1000°C
6.37			
4.03	4.004		4.036
3.83	3.86		3.88
3.75			
3.69			3.69
3.49	3.49	3.53	3.49
3.34Q	3.33Q	3.34Q	3.354Q
3.20	3.187	3.229	3.206
3.06			
2.998			
	2.508	2.526	2.519
	2.455		2.459

Low albite /?/

6b-yellow-8b		6b-brown-8b	
800°C		800°C	
4.00		4.004	
3.85	3.85	3.87	3.88
3.69	3.70	3.74	3.78
3.50			
3.335Q		3.34Q	3.335Q
3.275	3.27	3.24	3.24
3.206		3.21	3.206
3.005	3.008	2.97	2.97
2.891	2.88		
2.611		2.696	2.696
2.59		2.519	2.519
2.47	2.47	2.47	2.453
2.348	2.34		

High albite /?/

Zeolite peakes /Å/, possibly phillipsite in B/R-2b-800°C-1h yellow surface layer:
4.983, 4.27, 4.17, 4.03, 3.75, 3.49, 3.27
3.19, 3.058, 2.876, 2.805, 2.698, 2.629

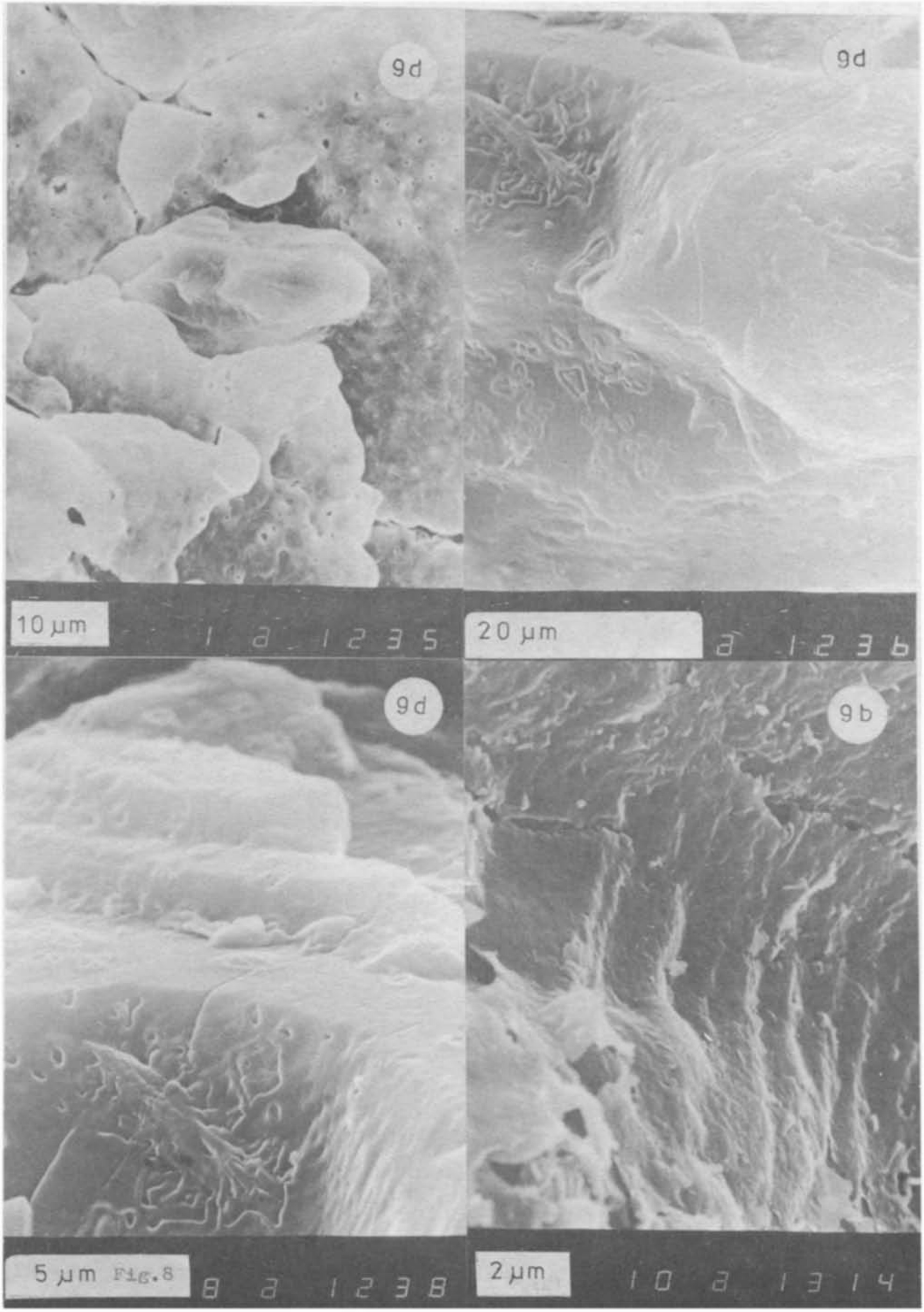


Fig.8

ble and their arrangement in a dense cluster structure may be seen, compare [5].

Another feldspar grain was found within the parallel structure of the surface part of the sample B/B-9d-800°C-18h. Here although the twinning is also visible, the surface morphology is different but it is characteristic of feldspar as well /Fig. 8/, compare [3].

A replica of twinning or a feldspar grain "in statu nascendi" was observed in sample B/B-9b-800°C - 1h, Fig. 8, as a "wavy" structure of the "wavelength" of ca. 5 μm as compared to the double size of twinning steps, Fig. 7 c and d, equal to ca. 5 - 6 μm.

In figures 9, 10 and 11 some other examples of feldspar grains are shown and their chemical composition is indicated.

SUMMARY

Study presented above indicates that feldspar may form in bentonite suspensions:

/1/ during drying at room temperature or at 110°C, if the energy necessary is supplied by decrease in internal energy /ΔV_A/ of the final dense packing of particles and structural elements,

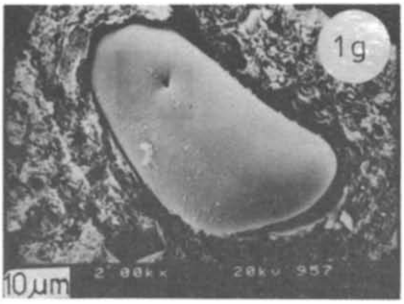
/2/ during heating at elevated temperature: in this case phase transformation depends on storing time prior to drying and on sample size and form,

/3/ during prolonged storage /8 months/ followed by drying,

/4/ cluster structure gives in Berkbent bentonite the highest probability of development of feldspar due to suitable arrangement of clay particles.

Thus both postulates, i.e. dependence of phase transformation on microstructure and on action /energy x time/ found some verification.

High stirring energy of a bentonite suspension resulted in desintegration of particles into amorphous matter, which migrated to sample surface during drying. It may transform into some crystal structure of silica /cristobalite observed in big samples and quartz observed in small samples/. This amorphous silica created the possibility of formation of feldspar in silica saturated solution.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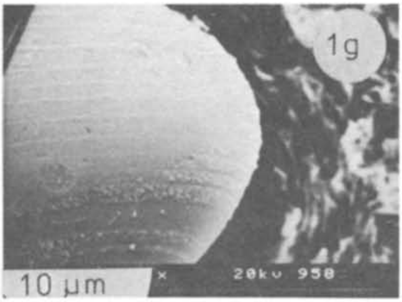
2.00kx
20kv 957

Fig. 9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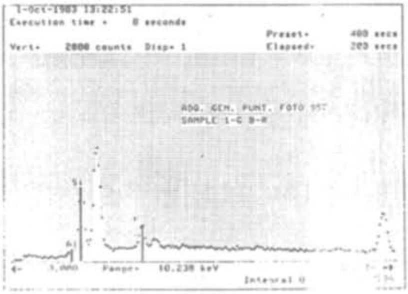
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K
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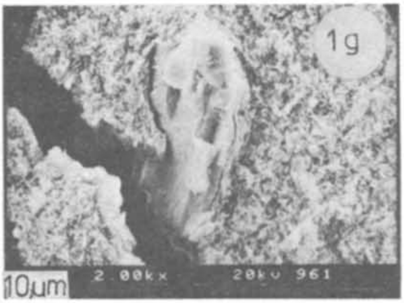
Integral 0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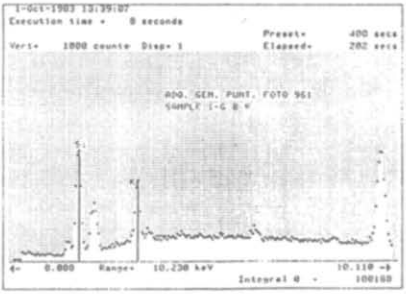
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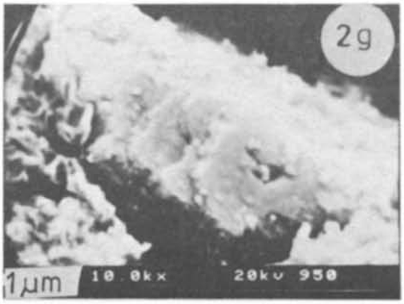
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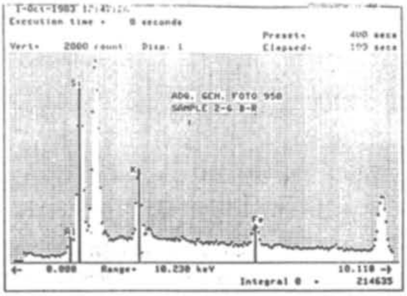
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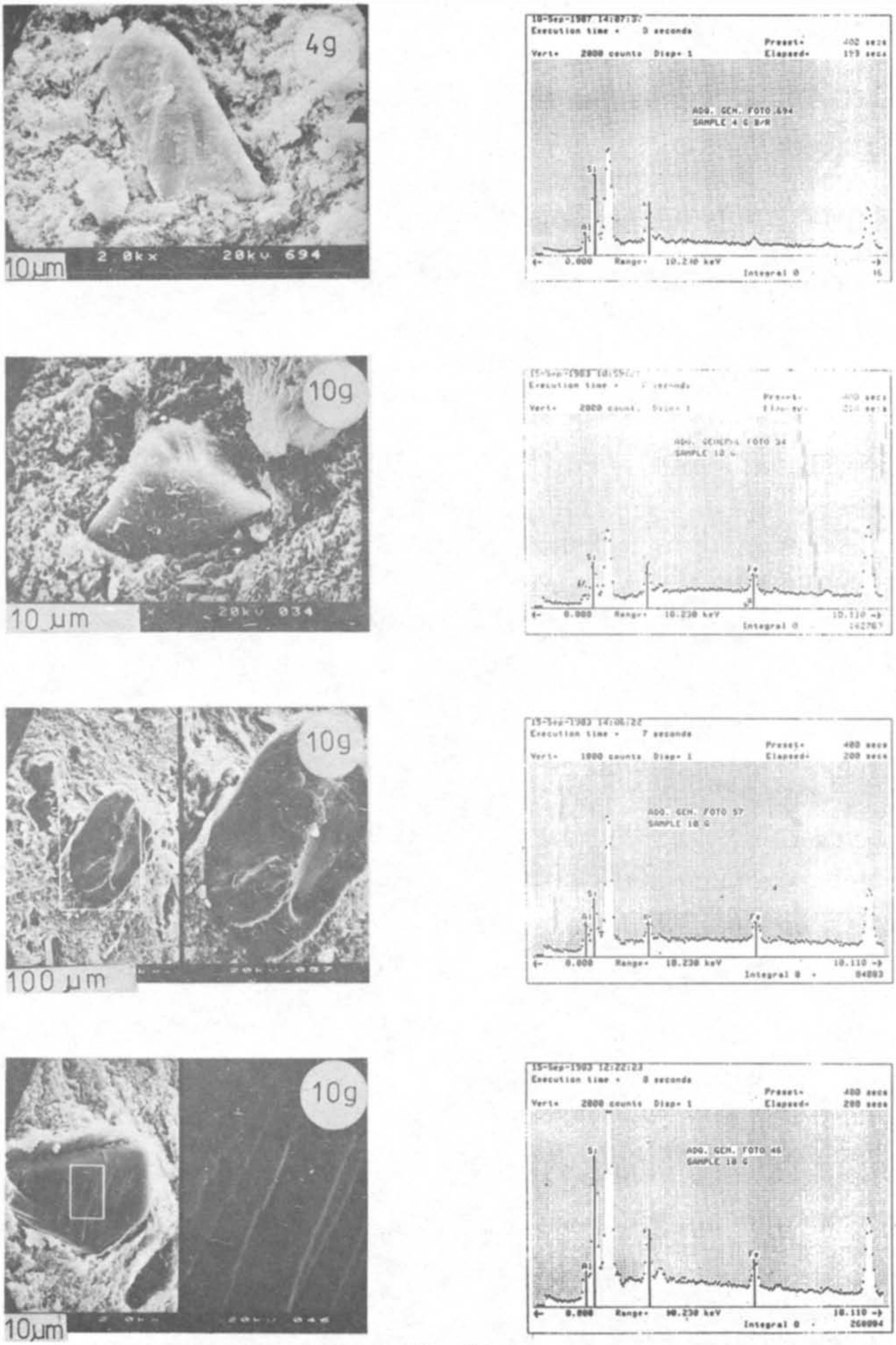
4g
10µm
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10g
10 µm
20kv 034
10g
100 µm
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10µm
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Fig.10

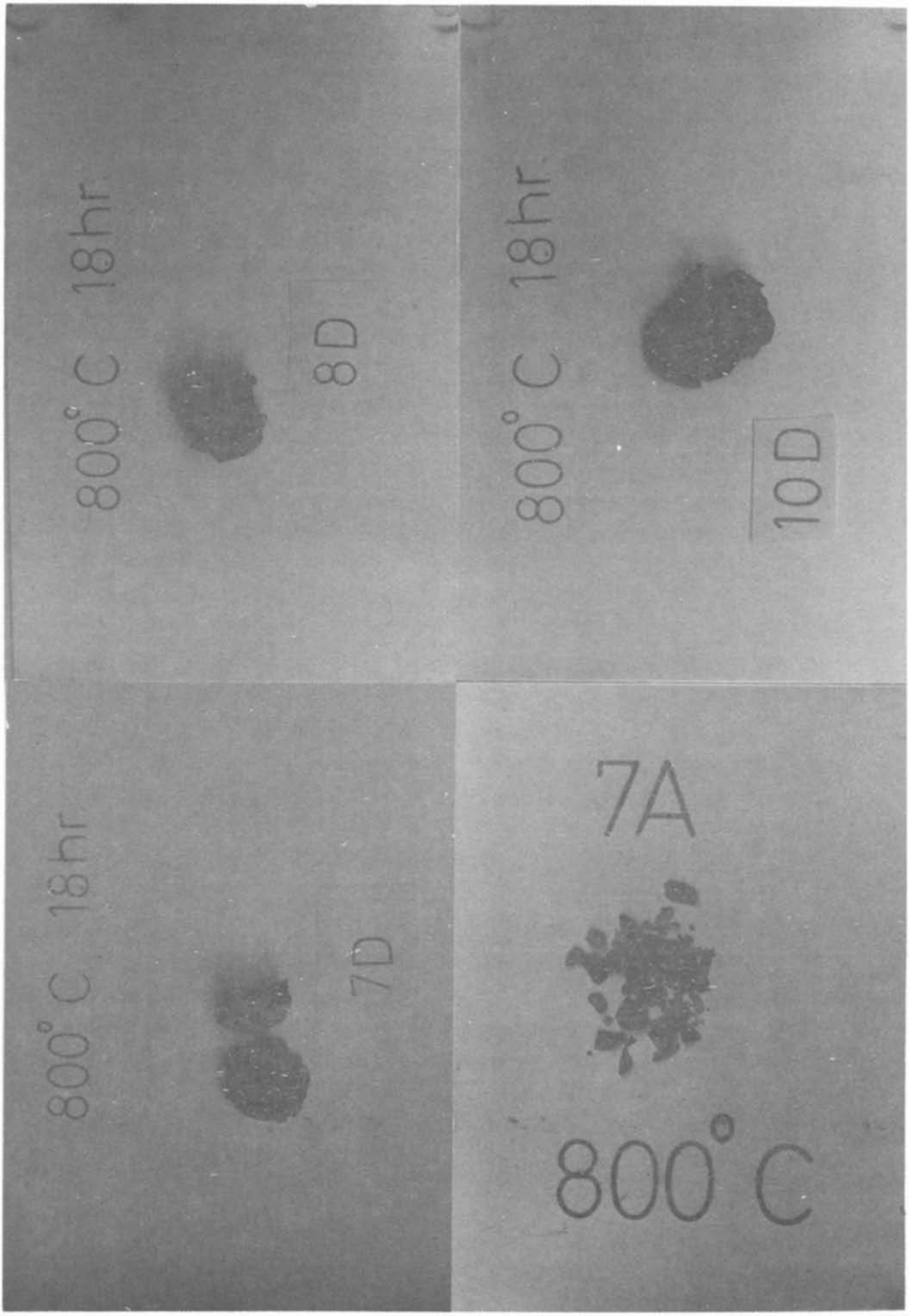

Fig. 11

ACKNOWLEDGEMENTS

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REFERENCES

1. R.L. Hay, Natural Zeolites, Pergamon Press, 1978, Ed. L.B. Sand and F.A. Mumpton, p. 135
2. A. Iijima, as above, p. 175
3. C.V. Jeans, R.J. Merriman and J.G. Mitchell, Clay minerals, 12 /1977/ 11
4. F. Lippmann, N.Jb. Miner. Abh., 136 /1979/ Nr 3, p. 287
5. A.C. MacKenzie and J. Zussman
6. E.E. Senderov, Natural Zeolites, 1985 Budapest, Akademiai Kiado, Budapest 1988, Ed. D. Kallo and H.S. Sherry, p. 111
7. H. Seyama and M. Soma, Clays and Clay Minerals, 34 /1986/ 672
8. E.T. Stępkowska, Archiwum Hydrotechniki, 29 /1982/ 469
9. E.T. Stępkowska, and S.A. Jefferis, 7th ICTA, Kingston, 1982, Przegląd Geologiczny /1983/ Nr 3, 156
10. E.T. Stępkowska and S.A. Jefferis, Archiwum Hydrotechniki, 30 /1983/ 193
11. E.T. Stępkowska, Natural Zeolites, 1985 Budapest, Akademiai Kiado, Budapest 1988, Ed. D. Kallo and H. S. Sherry, p. 149
12. E.T. Stępkowska, 9th ICTA, Jerusalem 1988
13. E.J. W. Verwey and J. Th. G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier Publ. Co. 1948