AUTOTRANSFORMATION OF H-SMECTITES IN AQUEOUS SOLUTION
The Effect of Octahedral Iron Content

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Abstract: H-smectites, with protons covering over 80 % of cation exchange capacity (CEC), were prepared from Jelšový Potok (Slovakia), Upton (Wyoming, USA) and Horní Dunajovice (Czech Republic) montmorillonites, and SWa-1 ferruginous smectite (Grant County, Washington, USA) using H-OH-H resin columns. The number of strong acid sites decreased and the number of the weak ones increased in course of aging of H-smectites in suspension. Iron was released in the process of autotransformation into the exchangeable positions of H-montmorillonites similarly to aluminium and magnesium. Increased amounts of exchangeable Mg, Al and Fe were found after repeated passage of the H-smectite through the resins. Highest relative amounts of Mg were found in all fresh H-smectites, however, in montmorillonites higher proportions of Al and Fe than of Mg were released in course of aging. The order of relative amounts of cations in exchangeable positions Mg>Al>Fe was not changed in course of aging of ferruginous smectite.

Key words: smectite, montmorillonite, acid site, potentiometric titration.

Introduction

Acid activation of clays is a common procedure to produce materials of various applications including catalysts or catalyst supports (Adams 1987; Breen 1991; Rhodes et al. 1991; Rhodes & Brown 1992, 1993; Kantam et al. 1993), bleaching earths (Siddiqui 1968), carbon less copy paper (Fahn & Fenderl 1983). Exchange of interlayer cations for protons is a fast reaction compared to dissolution of the layers. H-montmorillonites are unstable materials undergoing autotransformation to (H, Al, Mg)-forms (Coleman & Craig 1961; Barshad & Foscolos 1970). Various procedures for preparation of H-montmorillonites have been examined to ensure maximal saturation by protons and stability of the samples. These properties were found to depend strongly on treatment procedure and source bentonite. Best results yielded H-montmorillonite with less then 5 % exchangeable aluminium (Aldrich & Buchanan 1958). Barshad (1969) used a train of H-OH-H resins to remove all free salts and/or acids from the suspension of prepared H-clay.

Barshad & Foscolos (1970) reported that the rate of the autotransformation reaction, i.e. the interchange of adsorbed H^+ with octahedral Mg^{2+} and Al^{3+}, was directly proportional to the magnesium content and CEC of the samples. Acidic properties of H-clays were tested in aqueous and/or organic solvent systems on possible Al^{3+}-adsorbed hydrolytic reactions and salt induced hydrolysis (Shainberg & Dawson 1967; Loeppert et al.

1986). The role of temperature and aluminium and/or magnesium in the process of autotransformation was frequently investigated (Coleman & Craig 1961; Davis et al. 1962; Banin & Ravikovitch 1966; Mitra & Kapoor 1969; Barshad & Foscolos 1970). However, little is known concerning the role of iron or other cations in this process (Kaddah & Coleman 1967).

The aim of this work was to investigate the acid sites in the process of aging of four H-smectites containing various amounts of iron.

Materials and methods

Four dioctahedral smectites - three montmorillonites and a ferruginous smectite were used in this study: 1 - montmorillonite Jelšový Potok (JP, Slovakia); 2 - montmorillonite Horní Dunajovice (HD, Czech Republic); 3 - montmorillonite Upton (WY, Wyoming, USA) and 4 - ferruginous smectite SWa-1 (WA, Grant County, Washington, USA, from the Source Clay Minerals Repository of The Clay Minerals Society). The clays were Ca-saturated, fractionated to $<2\,\mu m$, washed free of excess ions, dried at 60 °C and ground to pass a 0.2 mm sieve. Their chemical analyses are presented in Tab. 1. X-ray diffraction patterns showed that smectite was the dominant mineral in these fine fractions of bentonites, however, admixtures of quartz were identified in all of them. Structural formulas were calculated by method of Kelley (1955) using the data given in Tab. 1. Traces of quartz in

Table 1: Chemical composition of $<2\mu$m fractions of Ca saturated smectites used for preparation their H-forms.

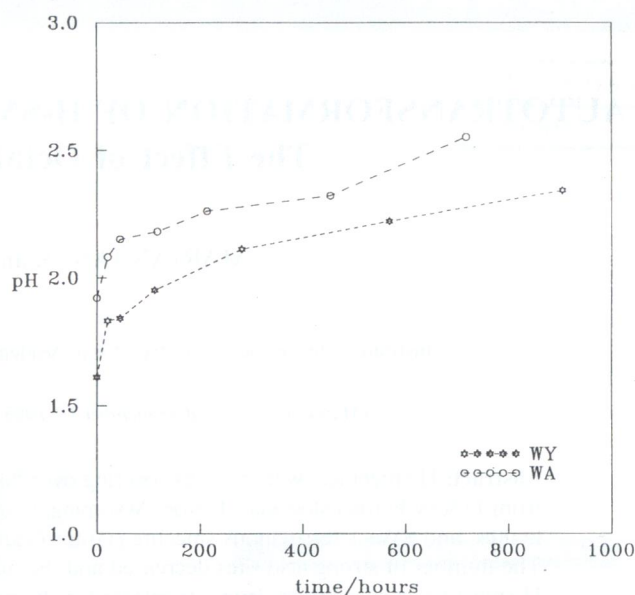| Sample	JP	HD	WY	WA
SiO_2	59.37	60.06	64.74	50.44
Al_2O_3	19.86	19.96	19.42	9.23
Fe_2O_3	2.55	4.23	4.07	26.97
FeO	-	0.17	0.14	-
TiO_2	0.11	0.38	0.11	0.51
MgO	3.56	4.00	2.48	1.28
CaO	2.93	3.00	2.42	2.70
Na_2O	0.04	0.07	0.03	0.09
K_2O	0.11	0.59	0.03	0.02
l.i.	10.95	7.61	6.41	8.24

l.i. = loss of ignition

Fig. 1. Changes of pH on aging of H-smectite suspensions Wyoming and Washington.

JP, HD and WA, estimated to be less then 3 mass % in any of these samples, were neglected in the calculation. Higher amount of quartz was found by XRD in WY, chemical analysis (UNIGEO Brno), gave 9.46 % of crystalline SiO_2. This amount was substracted from the total SiO_2 content in structural formula calculation. The structural formulas are given in Tab. 2.

Materials for preparation of H-forms were Na saturated by 1M NaCl solution, washed free of excess ions using water and ethanol, air dried at 60 °C, and ground to pass a 0.2 mm sieve. Then the samples were treated first with a solution of 1M NaCl + 0.1M $Na_2C_2O_4$ + 0.1M HCl for 30 minutes in a shaker. The solid was separated three times by centrifuge and resuspended in 1M NaCl + 0.1M $Na_2C_2O_4$ solution, washed to remove excess ions with water and ethanol and finally resuspended in redistilled water to make about 1% suspension. All treatments were finished within 48 hours. The suspension was passed under applied suction through a train of three columns where the first and the last were H-resins and the middle one was an OH-resin (Barshad 1969). The suspensions of H-smectites were left aging at room temperature. Two 100 ml aliquots were repeatedly removed from the suspensions, the first pair immediately after the H-smectite preparation was finished. One of them was titrated with 0.1 M NaOH, the portions were added in two minutes intervals. The resident exchange cations were replaced using 1 M KCl in the second one. Extracts were analyzed for Al^{3+} and Fe^{3+} spectrophotometrically and for Mg^{2+} by atomic absorption.

Results and discussion

Typical curves showing the changes of acidity of H-smectites on aging are shown in Fig. 1. The pH of all investigated clays was slowly increasing in course of aging, showing alteration of the acid sites. Technique of potentiometric titrations was employed for further investigation of this process. Titration curves of all freshly prepared H-clays are given in Fig. 2. Highly saturated H-forms have potentiometric curves typical for titration of strong acids (Aldrich & Buchanan 1958; Shainberg & Davson 1967). Buffered parts on curves were attributed to exchangeable aluminium (Aldrich & Buchanan 1958; Davis et al. 1962; Mitra & Kapoor 1969; Rich 1970). Hydrated protons cover about 95 % of CEC for JP and WY montmorillonites, while 90 and 80 % were found for HD montmorillonite and WA ferruginous smectite, respectively. These values are in accordance with the reported impossibility to prepare a completely pure H-form (Aldrich & Buchanan 1958; Coleman & Craig 1961; Barshad & Foscolos 1970), however, yet unknown is the reason of different saturation of fresh prepared samples with protons. Exchangeable protons are assumed to form strong acidic Brönsted sites on the clay surface. Their amount decreased with aging due to autotransformation (Coleman & Craig 1961; Davis et al. 1962; Foscolos & Barshad 1969; Mitra & Kapoor 1969). Decrease of the strong acid sites and increase of the weak ones (Figs. 3, 4) in the process of aging was observed in all four investigated smectites. Titration curves of JP and HD samples (not shown) were similar to WY (Fig. 3), however, freshly prepared H-form of HD was less saturated with H_3O^+ than the JP or WY and its alteration was finished after about 450 hours, compared to more than 900 hours for both WY and JP (Fig. 3). The weak acid sites were attributed to exchangeable aluminium which react with added base (Mitra & Kapoor 1969; Rich 1970; Loeppert et al. 1986).

Other inflections on potentiometric titration curves became distinguishable for WA, the sample with higher
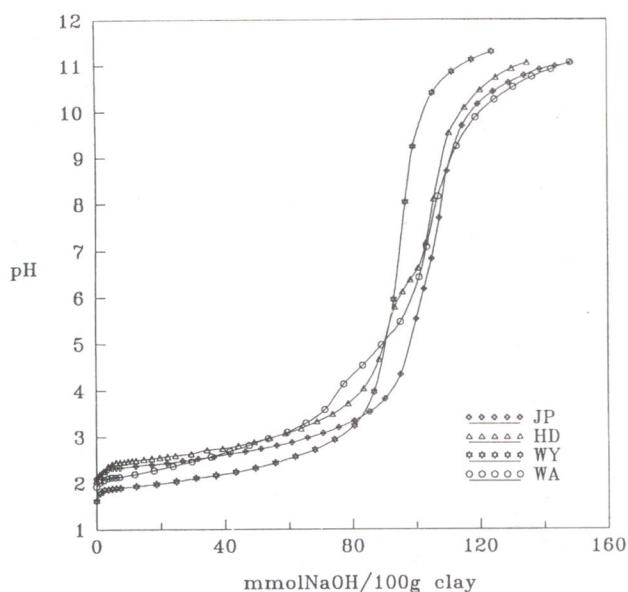
Fig. 2. Potentiometric titration curves of fresh H-smectites Jelšový Potok, Horní Dunajovice, Wyoming and Washington.

Fig. 3. Potentiometric titration curves of fresh and aged H-montmorillonite Wyoming.

iron content (Fig. 4). The buffered parts of the titration curves show complex reactions of the exchangeable cations in the system with the added base, where various hydroxy complexes might be formed (Baes & Mesmer 1976). The results reported in previous studies did not determine the exact ionic forms of exchangeable cations (Banin & Ravikovitch 1966; Mitra & Kapoor 1969; Rich 1970; Loeppert et al. 1986). It is supposed that hydrated cations prevail only in fresh H-clays, where the pH is below 2.5 (Baes & Mesmer 1976), and are not removed by the resin (Aldrich & Buchanan 1958) because of their higher ionic potential (charge/size ratio). This suppositions was confirmed using the Na-form of sample HD, which was passed through the train of the H-OH-H resins twice and 1M KCl extracts of thus prepared H-smectite were analyzed. The amount of cations increased slightly after the second passage of the suspension through the resins - aluminium 30.0 and 36.7 meq/100 g, magnesium 1.68 and 2.16 meq/100 g and iron 1.44 and 1.80 meq/100 g. When the pH value is incremented (Fig. 4) in the course of the potentiometric titration, consumption of base and/or hydrolysis reactions may occur,

depending on kind of the cation. This makes the potentiometric method inefficient for direct estimation of exchangeable aluminium (Aldrich & Buchanan 1958; Shainberg & Davson 1967; Mitra & Kapoor 1969), and is probably the cause of the more complicated shapes of the titration curves for the ferruginous smectite WA (Fig. 4).

Extraction in 1M KCl was used to investigation the nature of the exchangeable cations. The amounts released from the clay structure for samples JP and WY are given in Fig. 5. The values for aluminium and magnesium are similar to those reported previously for various H-smectites (Coleman & Craig 1961; Foscolos & Barshad 1969; Barshad & Foscolos 1970), but no data for iron were published. The results indicate that iron is released from the octahedral sheet in course of aging of H-smectites in a manner similar to that for aluminium and magnesium (Figs. 5 to 7). Sample HD (Fig. 6) reached stable values of the exchangeable cations after aging for 450 hours, which is in agreement with the results obtained from the potentiometric titrations.

A different situation was found for WA (Fig. 7). The initial high rate of aluminium and magnesium release from the layers in fresh H-smectites decreased rapidly and reached a constant value after approximately 150 hours. Conversely, the initially low release of iron increased substantially after about 60 hours, and was the highest at the end of the experiment (Fig. 7). Two different reaction rates for the autotransformation were attributed to a fast dissolution of aluminium from readily soluble phases and/or edges of the smectite particles, and from the layers, respectively (Banin & Ravikovitch 1966; Barshad & Foscolos 1970). The results in Fig. 7 suggest that the release of some aluminium and/or magnesium leads to a substantial increase in the rate of release of iron. Mössbauer investigation of SWa-1 ferruginous smectite (Murad 1987) showed less than 3 % of total Fe

Table 2: Structural formulas of smectites recalculated from the chemical analyses (Tab. 1).

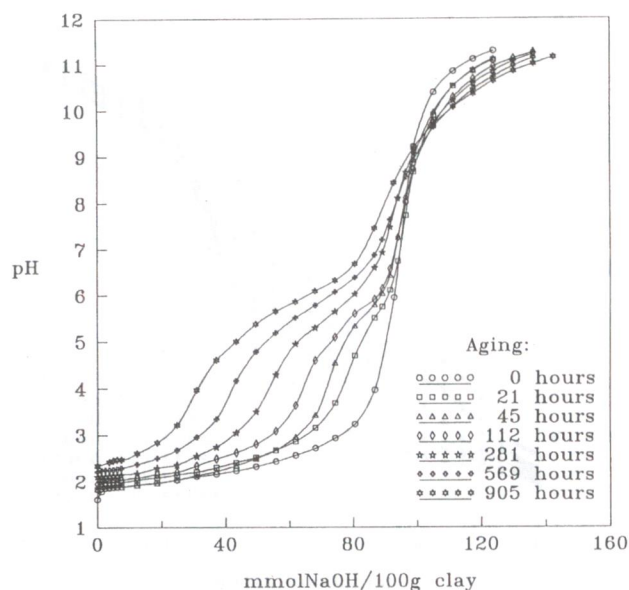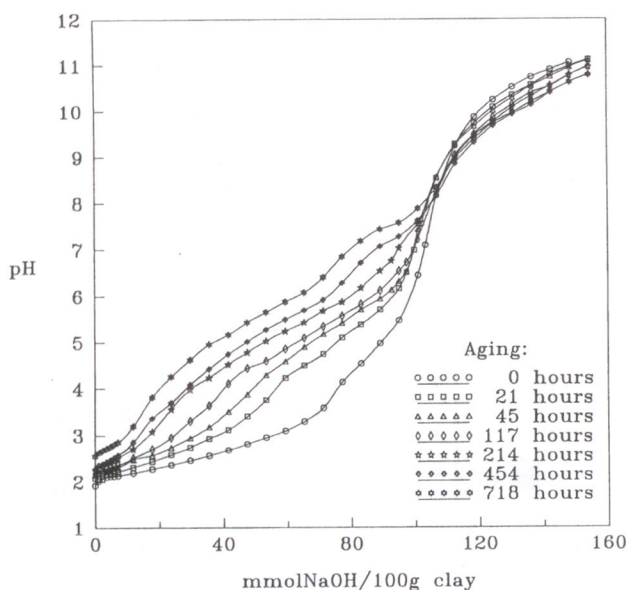| Sample	tetrahedra		octahedra				interlayer
	Si	Al	Al	Fe^{3+}	Fe^{2+}	Mg	Me^+
JP	7.90	0.10	3.02	0.26	-	0.71	0.87
HD	7.78	0.22	2.82	0.41	-	0.77	0.95
WY	7.80	0.20	3.03	0.43	0.02	0.52	0.70
WA	7.27	0.73	0.84	2.93	-	0.28	0.87

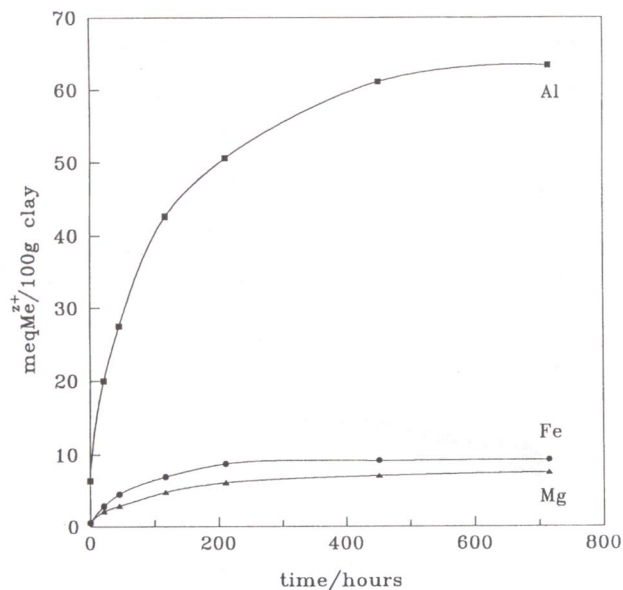**Fig. 4.** Potentiometric titration curves of fresh and aged H-smectite Washington.

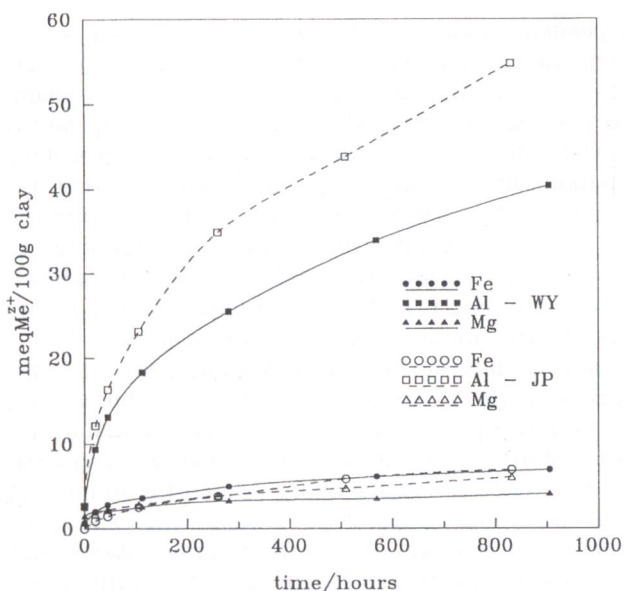**Fig. 6.** Content of exchangeable cations in fresh and aged H-montmorillonite Horní Dunajovice.

Fig. 5. Content of exchangeable cations in fresh and aged H-montmorillonites Jelšový Potok and Wyoming.
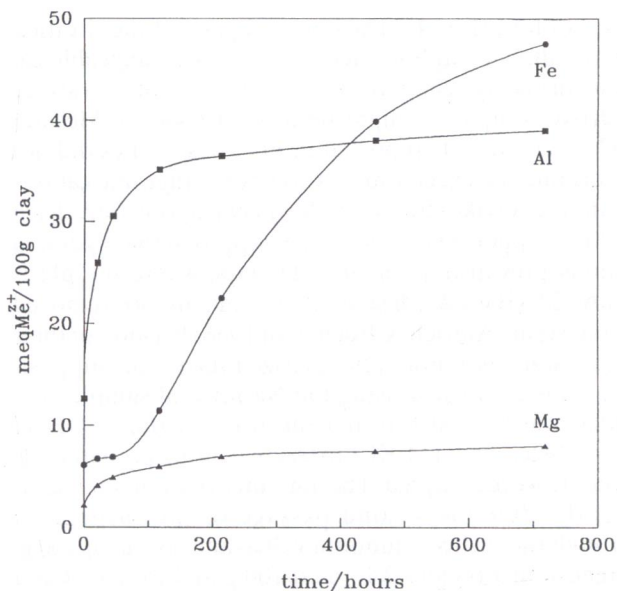

Fig. 7. Content of exchangeable cations in fresh and aged H-smectite Washington.

bound in goethite. However, in the results reported here the two rates for iron release cannot be attributed to the presence of two iron phases because the initial treatment with 1M NaCl + 0.1M $Na_2C_2O_4$ + 0.1M HCl and 1M NaCl + 0.1M $Na_2C_2O_4$ was employed to remove goethite.

Relative amounts of exchangeable cations (in % of the total interlayer cation content in the respective Ca-smectite, Tab. 2) are shown in Figs. 8 and 9. Obtained results for samples HD and JP (not shown) were similar to those for WY (Fig. 8). Highest relative amounts of magnesium were found in these fresh H-smectites. However, later the relative amount of released Al and even more Fe increased with aging of H-montmorillonites

(Fig. 8). As much as 12.6 % of total Mg was found in exchangeable positions after 700 hours of aging in the iron-rich sample WA, while the respective amounts of Al and Fe were much lower (7.2 and 4.7 %, respectively). The order of relative amounts of cations in exchangeable positions Mg > Al > Fe has not changed in course of aging of the ferruginous smectite (Fig. 9).

Conclusions

H-smectites with protons covering over 80 % of CEC were prepared from four Na-smectites using H-OH-H
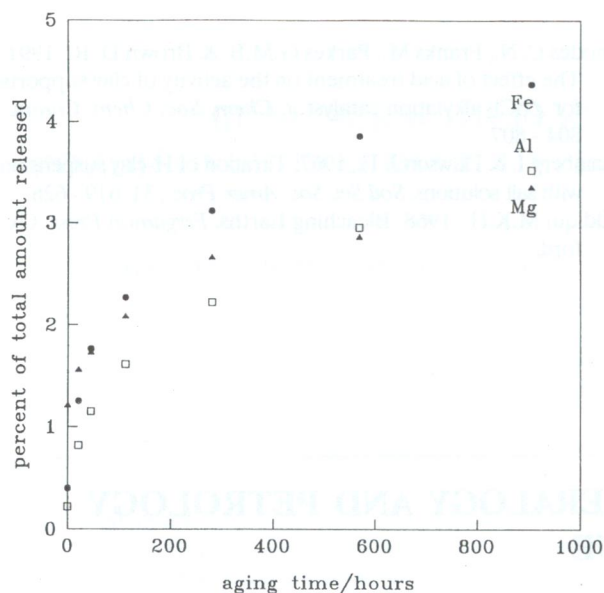
Fig. 8. Relative amount of exchangeable cations in fresh and aged H-montmorillonite Wyoming.
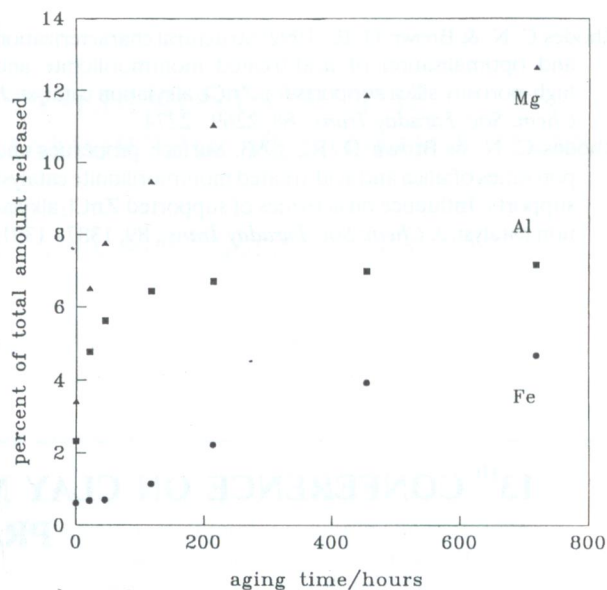

Fig. 9. Relative amount of exchangeable cations in fresh and aged H-smectite Washington.

resin columns. Number of strong acid sites decreases and number of the weak ones increases in course of aging of H-smectites in suspension. Iron was released in the process of autotransformation into the exchangeable positions of H-montmorillonites in a manner similar to that for aluminium and magnesium. Increased amounts of exchangeable Mg, Al and Fe were found after repeated passing of H-smectite through the resins. Highest relative amounts of Mg were found in all fresh H-smectites, however, in montmorillonites higher proportions of Al and Fe than of Mg were released in course of aging. The order of relative amounts of cations in exchangeable positions Mg>Al>Fe has not changed in course of aging of ferruginous smectite.

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Dr. Karel Melka, PhD
General Chairman