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THE STUDY OF SOME NORMAL AND ABNORMAL MONTMORILLONITES BY THERMAL ANALYSIS AND INFRARED SPECTROSCOPY

CONSTANTIN CRĂCIUN

Institutul de Cercetări pentru Pedologie şi Agrochimie, B-dul Mărăşti 61, R-71331, Bucharest 32 (Romania)

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ABSTRACT

The use of thermal analysis in conjunction with infrared spectroscopy permitted us to obtain information concerning the nature of differences between normal and abnormal (giving a double dehydroxylation reaction) montmorillonites.

The established relationships between thermal and infrared data were interpreted as evidence for the implication of Fe^{3+} in the differences between the two species of montmorillonite and for the ability of the infrared technique to distinguish between these montmorillonite varieties.

INTRODUCTION

In the case of certain dioctahedral clay minerals such as pyrophyllite, illite and montmorillonite, dehydroxylation occurs in so-called "abnormal" species at temperatures different from those associated with "normal" species [1]. Thus, the so-called normal montmorillonite shows a medium-small endothermic peak at about 700 °C while on the other hand, samples of the abnormal variety give curves with either two relatively small endothermic peaks at about 550 and 650 °C or a single peak at about 550 °C in place of the normal 700 °C peak [2].

From the standpoint of natural occurrence, the normal variety constitutes the principal component of most bentonite deposits (except metabentonites) while the abnormal variety with a single dehydroxylation reaction appears to be more widespread in soils. In the case of the abnormal variety giving two peaks, it is difficult to talk about a certain trend because its reported occurrences include different situations such as: bentonite deposits [2,3], soils [4,5] and weathered volcanic deposits [6].

This paper aims at a comparative study using thermal analysis and infrared spectroscopy of some normal and abnormal (giving a double dehydroxylation reaction) montmorillonites from Gurasada (Romania) ben-

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tonite deposits. The purpose of this study is to obtain information on the nature of the differences between normal and abnormal montmorillonite varieties and to investigate the possibility of using the infrared technique as a differentiation tool for the two varieties.

EXPERIMENTAL

Nineteen montmorillonites from the Gurasada bentonite deposits were investigated by thermal and infrared methods (ten normal and nine abnormal). These were examined in the form of < 1 μm fractions separated from the original material by the pipette method without any chemical treatment except the addition of 4% NaOH as a dispersing agent. For this study the Ca-saturated samples were utilized, obtained by using 1N $CaCl_2$ solution, with subsequent removal of excess chloride by centrifugation and washing [7].

DTA, TG and DTG curves were obtained with a MOM-OD-103 Derivatograph, with differential thermocouple (Pt–Pt/Rh) and ceramic crucibles. A heating rate of 10 °C min^{-1} was used.

Infrared spectra were recorded with a UR-20 JENA spectrophotometer (400–4000 cm^{-1} range). Randomly oriented preparations for infrared investigations were obtained by the potassium bromide pressed-disk technique.

RESULTS AND DISCUSSION

Thermal analysis

On the DTA curves, the thermal effects appear in three distinct temperature ranges. In Table 1 are presented the temperatures of these effects and the accompanying percentage weight losses.

The 20–300 °C range Generally, montmorillonite minerals show in this range a low-temperature peak due to loss of sorbed moisture, the shape and size of which, depend on the saturating cation [2]. Such a peak can be observed for all investigated samples. Its temperature varies between 160 and 170 °C (Table 1). The weight loss specific to this reaction varies between 8.8 and 12.5%. This effect is accompanied by a broad inflexion at 200–210 °C atributable to water bound to exchangeable cations. The weight losses characteristic to this effect are below 3.5%. In Table 1 the weight losses due to hygroscopic moisture are presented totalized for the two effects.

The 300–800 °C range In this range, which is characteristic for clay mineral dehydroxylation, clear differences between the samples can be observed (Table 1). The "normal samples" (1–10) show a single dehydroxylation effect with the temperature between 697 and 708 °C. The corresponding

TABLE 1

The temperatures of thermal effects and accompanying weight losses for the investigated samples

No.	Dehydration		Dehydroxylation					Structural change		
	Endo (°C)	WL (%)	Endo (°C)	WL (%)	Endo (°C)	WL (%)	WL_t (%)	Endo (°C)	Exo (°C)	T (°C)
1	157	14.1			697	3.2	3.2	870	1000	130
2	165	13.2			701	3.1	3.1	870	980	110
3	160	11.1			702	3.1	3.1	872	1000	128
4	170	14.1			707	3.3	3.3	870	1000	130
5	160	13.7			700	4.4	4.4	870	1000	130
6	161	13.5			704	3.4	3.4	863	1000	137
7	168	14.2			692	3.3	3.3	872	995	123
8	160	13.6			695	3.3	3.3	860	990	130
9	160	11.8			696	3.0	3.0	877	1000	123
10	170	12.2			708	3.3	3.3	866	1000	134
11	165	15.7	581	1.6	670	1.9	3.5	848	905	57
12	167	14.4	580	2.0	672	1.8	3.8	848	905	57
13	162	14.4	572	2.0	680	1.8	3.8	846	910	64
14	160	13.7	550	1.3	675	1.6	2.9	850	910	60
15	160	14.2	540	2.6	670	2.1	4.7	850	905	55
16	167	15.3	581	1.7	686	1.3	3.0	845	907	52
17	170	12.4	570	1.9	685	1.4	3.3	850	920	70
18	167	14.0	580	1.7	688	2.1	3.8	833	900	67
19	160	12.7	568	2.0	680	1.6	3.6	846	910	64

Endo, endothermic effect; Exo, exothermic effect; WL, weight loss; WL_t, total dehydroxylation weight loss; T, temperature difference between endothermic and exothermic effects.

weight loss varies between 3.0 and 4.4%. The "abnormal samples" (11–19) give a double dehydroxylation peak at 540–581 °C (weight loss between 1.3 and 2.0%) and at 670–688 °C (1.3–2.1% weight loss).

Regarding the dehydroxylation, two aspects must be noted: (1) the amplitude of the single endothermic peak ("normal samples") is higher than for each of the two peaks ("abnormal samples"); (2) the weight loss for the "abnormal samples" (obtained by adding the two dehydroxylation effects) is similar to the one which appears for the "normal samples".

The 800–1000 °C range In the high temperature range, the montmorillonite minerals give a small S-shaped endothermic–exothermic peak system at about 850 and 950 °C due to structural change [2].

The "abnormal samples" show such a system composed from two distinct peaks: an endothermic peak at 833–850 °C and an exothermic peak at 900–910 °C. The difference of temperature between the two effects is 52–70 °C. The temperatures of the two effects in the case of "normal samples" are 860–870 °C and 980–1000 °C and above 1000 °C for the endothermic and exothermic peaks, respectively. The temperature difference between them is greater than 100 °C.

The results from Table 1 indicate significant differences between the two montmorillonite species concerning the dehydroxylation and endothermic–exothermic inversion domain.

In order to verify whether the first dehydroxylation reaction (540–580 °C) belongs to montmorillonite or arises from illite, which was made evident in similar quantities in both varieties [7], some additional experiments were carried out.

Investigation by DTA of the illite–normal montmorillonite mechanical mixtures

Figure 1 allows a comparison between the DTA curve of such a mixture and the DTA curve of an abnormal montmorillonite. In the case of the mixture the two effects belonging to the dehydroxylation of the two clay minerals are distinct and symmetrical, while for the abnormal montmorillonite they are asymmetrical and partialy overlapped. Furthermore, there are differences concerning the temperature of the effects (see Fig. 1).

Investigation by DTA of the submicronic fractions of the bentonites

In these fractions the illite crystallites are less abundant [8].

DTA curves of these fractions are presented in Fig. 2 in comparison with those of the coarser clay fractions. On all DTA curves of clay fractions the double dehydroxylation reaction is present, indicating a small increasing trend in finer fractions.

The results of these additional experiments indicate that the first dehydroxylation peak arises from montmorillonite.

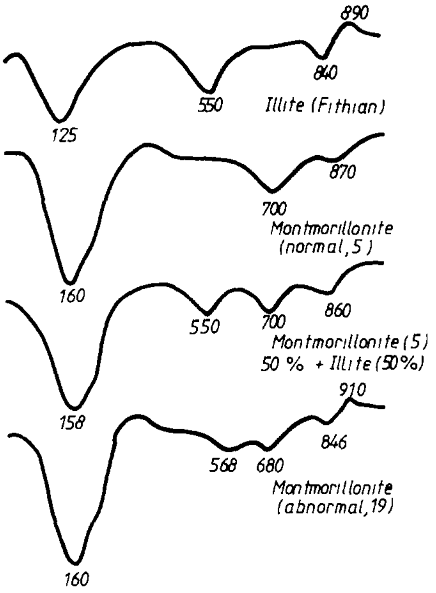

Fig. 1. DTA curves of the normal montmorillonite–illite mechanical mixture and abnormal montmorillonite.

The differences concerning the dehydroxylation reaction which appears between normal and abnormal montmorillonites must be related in some manner to the energy with which the hydroxyl groups are bound in the

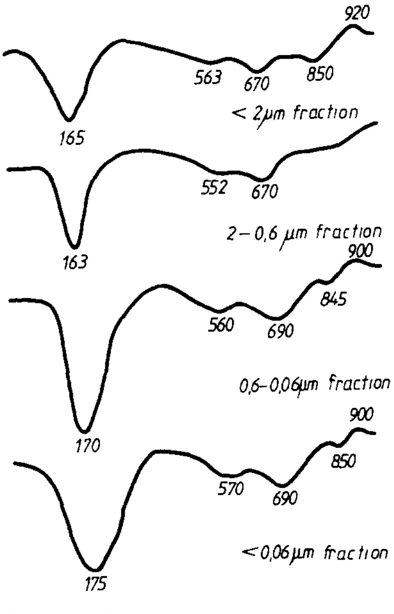

Fig. 2. DTA curves of the different clay subfractions of the abnormal montmorillonite.

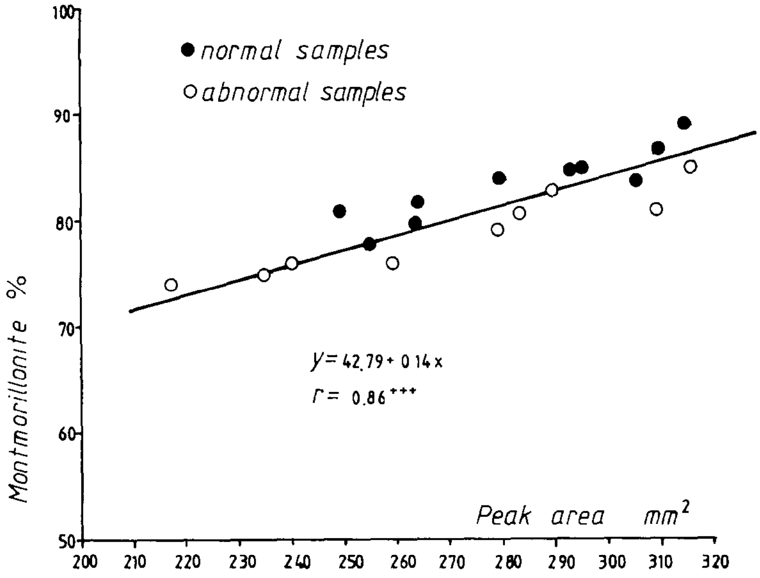

Fig. 3. Relationship between area of dehydroxylation peak or peaks and montmorillonite content (determined by X-ray diffraction) for the investigated samples.

lattice [2]. It is interesting to note that the energy required for dehydroxylation as determined from the areas of a single or double peak is similar for all samples, confirming the results of Mackenzie [2] (Fig. 3).

The differences between the two montmorillonite species, which appear in the temperature range characteristic for structural change have already been mentioned. Temperature of the effects from this range which appears to be associated with entropy changes [9] may well be affected by bulk composition [4,10].

The high-temperature compounds are identified by corroboration of the results of DTA (to 1500 ° C) and X-ray diffraction of the samples heated to 800, 900, 1000, 1100, 1200 and 1300 ° C. The analytical data show that all investigated montmorillonites develop the same crystalline phases on heating. These are formed in the following order given by the increase of temperature: cristobalite (high), mullite and spinel. The last is not present in all samples, but it appears unimportant whether the sample is normal or abnormal.

The montmorillonite structure is preserved to 830–850 ° C where it is lost abruptly in a temperature interval of about 50–70 ° C in the case of abnormal samples. Cristobalite and mullite develop at about 950 ° C and 1050 ° C, respectively. In the case of normal samples the montmorillonite structure persists to about 870 ° C, where it is lost. Cristobalite and mullite develop at about 1000 (and above 1000) and 1100 ° C, respectively.

The behaviour of the montmorillonite at high temperatures can give useful information regarding their structure and composition. As is known [11], the first nucleation stage of phases that appear above a certain temperature is dependent on the structure of the original mineral. Thus, a certain high temperature compound can be promoted by the certain arrangement of an ion in the lattice.

The data obtained by thermal analysis suggests that some structural and chemical differences are involved in the differences between normal and abnormal montmorillonites. Anyway, the similarity of the high temperature phases suggests that chemical differences are not so pronounced probably due to differences between lattice substitutions. On this account, we resorted to infrared spectroscopy (see following section).

INFRARED ANALYSIS

All investigated samples exhibit a dioctahedral composition. However, IR spectra made evident some differences between the two montmorillonite species in the range of vibrations of structural hydroxyls and lattice vibrations.

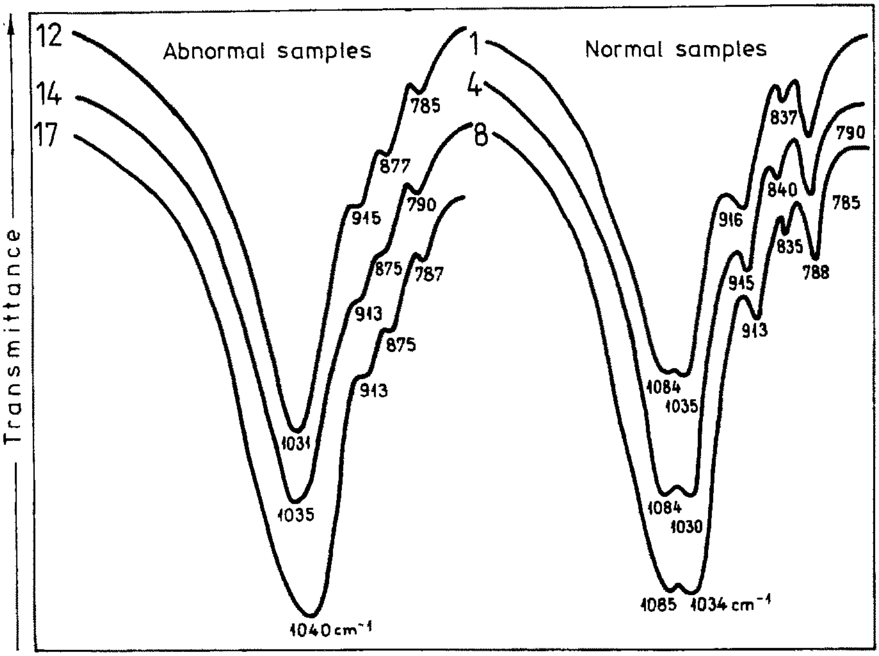

Fig. 4. The infrared spectra of some normal and abnormal montmorillonites in the range 700–1200 cm^{-1}.

Vibrations of structural hydroxyls

In the range characteristic to OH stretching vibrations, all samples show a medium absorption band in the interval of 3610–3637 cm^{-1} which was interpreted as arising from the hydroxyl coordinated to (Al, Al) pairs [12]. For the "normal samples" the interval of values is 3625–3637 cm^{-1} while for the abnormal samples it is 3610–3621 cm^{-1}. In the light of the established relationship between IR spectra of dioctahedral smectites in this domain and their octahedral composition [13] these results suggest some differences concerning the Fe^{3+}-for-Al octahedral substitutions between the two varieties. The differences of this kind are more significant in the domain of bending vibrations of the OH groups (800–950 cm^{-1}). As shown in Fig. 4, the normal samples show two absorption bands at 915 and 840 cm^{-1} atributable to (Al, AlOH) and (Al, MgOH) grouping, respectively [14]. The abnormal samples give spectra in which the intensity of these two absorption bands is lower (the last band becomes an inflexion and sometimes can not be observed). However, an absorption band is then developed at 870–875 cm^{-1} which is ascribed to (Al, Fe^{3+}OH) grouping [15,16]. In some situations this absorption band could be observed in the spectra of normal samples (samples 3, 6, 7 which indicated the highest Fe^{3+} octahedral content).

Lattice vibrations

In the 950–1200 cm^{-1} region in which appear the stretching vibrations involving Si and O ions, all samples give a very strong absorption band at 1030–1040 cm^{-1} ascribed to in-plane Si–O–Si vibrations [12]. This is accompanied by another absorption band at 1080–1090 cm^{-1} (Fig. 4), but only in the case of normal samples. Considered as an in-plane Si–O stretching vibration [17] whose origin seems uncertain, this absorption band, which is not characteristic to montmorillonite, always appears in the spectra of minerals belonging to the SiO_2 group [18]. The presence of the above absorption band in the spectra of normal samples suggests the existence of such minerals in higher quantities.

In the 400–600 cm^{-1} range the Si–O bending vibrations contribute to the absorption, but this absorption is more sensitive to the nature of octahedral cations [17]. No significant differences between the samples regarding the two absorption bands at 465 and 520 cm^{-1} ascribed to the Si–O bending vibration [17] and Si–O–Al^{VI} vibration [19], respectively, were noted. However, a difference between samples must be mentioned: all abnormal samples showed an absorption band resembling a shoulder at about 420–425 cm^{-1} which could not be observed in the spectra of normal samples. Reported in the spectra of Woburn montmorillonite [12], this band was associated with the higher proportion of Fe^{3+} in octahedral sites. Farmer

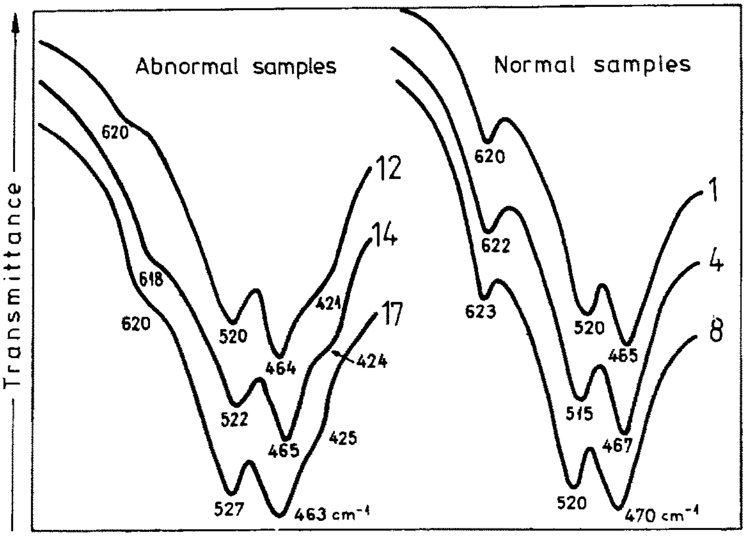

Fig. 5. The infrared spectra of some normal and abnormal montmorillonites in the range 400–700 cm^{-1}.

and Palmieri [20] mentioned that the intensity of this absorption band was proportional with Fe^{3+} content of the nontronites.

Some differences were observed in the 600–800 cm^{-1} range. In this interval the spectra of normal samples contain two absorption bands at 620 cm^{-1} (Fig. 5) and 790 cm^{-1} (Fig. 4), while in the spectra of the abnormal samples the intensities of these bands is reduced or they do not appear at all. The absorption band at 790 cm^{-1} is characteristic to minerals from the SiO_2 group, except quartz which gives a doublet at about 780–800 cm^{-1} [17]. Among other minerals belonging to this group only cristobalite presents the absorption bands at 790 and 622 cm^{-1} [17,18].

The results of IR spectroscopy indicate some mineralogical and chemical differences between normal and abnormal montmorillonites and from this point of view the spectral findings are consistent with the data obtained by X-ray diffraction and chemical analysis [7]. Thus, the higher content of cristobalite in normal samples is conformable with the higher intensity of the absorption bands at 620, 790 and 1080 cm^{-1}. In the cases where these absorption bands have a reduced intensity or are not found in the spectra (as of abnormal samples) the X-ray diffraction results indicated a lower content or no cristobalite content, respectively.

The higher Fe^{3+}-for-Al octahedral substitutions in abnormal samples are consistent with the following spectral changes: the appearance of the inflexion at about 425 cm^{-1} and development of the absorption band at 870–875 cm^{-1}; the displacement of the Al, AlOH stretching vibrations to lower frequences; the decrease of the absorption band intensity belonging to the Al, AlOH bending vibrations.

The higher octahedral Al and Mg content in normal samples is in agreement with the displacement of the Al, AlOH stretching vibrations to higher frequences, the increase of the 915 cm^{-1} absorption band intensity and with the increase of the 840 cm^{-1} absorption band intensity, respectively.

Summarizing, the data obtained by the two techniques indicate some mineralogical, chemical and structural differences between normal and abnormal montmorillonites. Among these, the mineralogical differences can not be involved in the differences which appear between the two montmorillonite species refering to the behaviour with thermal treatment. The chemical difference suggested by thermal analysis are emphasized by IR spectroscopy. The established relationships between thermal data and spectral data (Fig. 6) constitute an evidence for the influence of Fe^{3+}-for-Al octahedral substitutions on the dehydroxylation reaction temperature of montmorillonites and for the implication of this substitution in the differences between the two montmorillonite varieties. The relationship became more closed when, for this correlation, the chemical parameter (octahedral content of Fe^{3+}) was directly used (Fig. 7) In this respect, these data confirm the results obtained previously by ESR spectroscopy [21].

No relation could be established between spectral data and thermal data refering to the first peak of dehydroxylation. This can be interpreted as a proof for the implication of some structural differences (besides those chemical) in the differences between normal and abnormal montmoril-

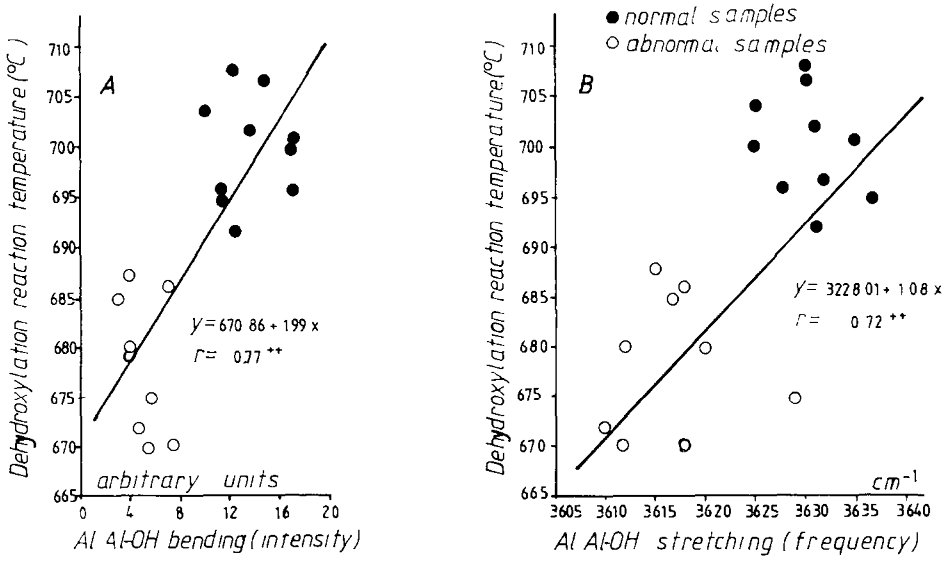

Fig. 6. Relationships between dehydroxylation temperature and Al, AlOH bending (A) and stretching (B) vibrations for the investigated montmorillinites.

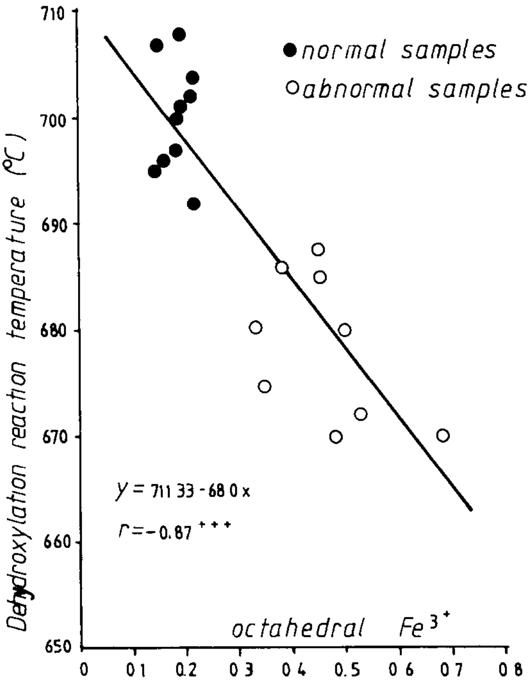

Fig. 7. The influence of the Fe^{3+} octahedral content on the dehydroxylation temperature of the studied montmorillonites.

lonites. Differences of this kind, which can influence the montmorillonite lattice stability and the temperature at which some of the high temperature crystalline phases are formed, were already suggested by the thermal analysis. As a matter of fact, the octahedral substitutions, especialy Fe^{3+}-for-Al in montmorillonites involve some structural changes or differences, such as tetrehedral rotation [7] or the *b* parameter [7,22].

CONCLUSION

(1) The use of thermal analysis in conjunction with infrared spectroscopy allows us to obtain information concerning the nature of differences between normal and abnormal montmorillonites.

(2) The chemical differences suggested by differential thermal analysis are more clearly made evident by the infrared method. This demonstrates the ability of this technique to distinguish between the two species of montmorillonite from Gurasada bentonite deposits.

(3) The established relationships between thermal and infrared data can be interpreted as an evidence for the implication of Fe^{3+} in the differences between the two montmorillonite varieties.

(4) The chemical differences refering to octahedral substitutions can involve some structural differences between normal and abnormal montmorillonites. At present it is very difficult to interpret the structural implications, but further work is in progress in the author's laboratory to elucidate other as yet unknown facets of the stated problem.

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