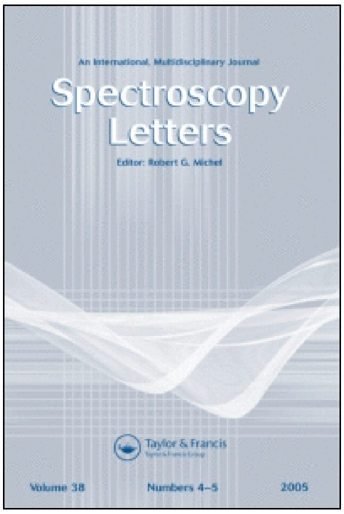
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Influence of the Fe^{3} -for - Al^{3} Octahedral Substitutions on the IR Spectra of Montmorillonite Minerals

Constantin Crâciun[a]
[a] Research Institute for soil Science and Agrochemistry, Bucharest 32, ROMANIA

To cite this Article Crâciun, Constantin(1984) 'Influence of the Fe^{3} -for - Al^{3} Octahedral Substitutions on the IR Spectra of Montmorillonite Minerals', Spectroscopy Letters, 17: 10, 579 — 590

To link to this Article: DOI: 10.1080/00387018408072640

URL: http://dx.doi.org/10.1080/00387018408072640

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 17(10), 579-590 (1984)

INFLUENCE OF THE Fe^{3+} - FOR - Al^{3+} OCTAHEDRAL SUBSTITUTIONS ON THE IR SPECTRA OF MONTMORILLONITE MINERALS

KEY WORDS; *Infrared spectra, montmorillonites, dioctahedral smectites*

Constantin Crăciun
Research Institute for Soil Science and Agrochemistry
B-dul Marasti 61, R-71331 Bucharest 32,
ROMANIA

ABSTRACT

The influence of octahedral replacement of Al^{3+} by Fe^{3+} on the infrared spectra of montmorillonites in the domain of OH vibrations is presented.

The obtained results suggest that in the domain of OH-bending vibration, the absorption band from 870 cm^{-1} (Al^{3+}-OH-Fe^{3+}) can not be detected in the spectra of montmorillonites when the octahedral Fe^{3+} content is below 0.10-0.15 (per half unit cell)

In the domain of OH-stretching, the increasing Fe^{3+}-for-Al^{3+} substitution in the dioctahedral series of smectites causes a continous shift of the absorption band ascribed to M^{3+} - OH - M^{3+} vibrations to lower frequencies.

0038-7010/84/1710-0579$3.50/0

INTRODUCTION

The presence of OH groups in smectite lattices determines the appearence of some characteristic absorption bands in the infrared spectra of these minerals. Vibrations involving proton (OH-stretching and bending) are very largely independent of the vibrations of silica and oxygen in the rest of the lattice[1] but are markedly affected by the ion to which these are coordinated and their environment[2]. Usually, for the montmorillonite minerals these ions are Al^{3+}, Mg^{2+}, Fe^{3+}. They constitute the octahedral population of the montmorillonite lattice. Generally there is little information refering to the influence of octahedral composition on the infrared spectra of montmorillonites.

The present study is an attempt to discuss the influence of octahedral substitutions, namely the Fe^{3+} - for - Al^{3+} of the infrared spectra of montmorillonites in the domain of OH vibrations, on the basis of some of our own results and literature data.

EXPERIMENTAL

A number of 19 montmorillonite samples were investigated by infrared spectrometry. The samples represent the fraction below 1 μ from Gurasada bentonite deposits[3]. The clay fractions were separated by the pipette method without any chemical treatment except the addition of 4% NaOH as a dispersing agent. For the infrared investigations the Ca-saturated samples were utilized. Randomly oriented preparations were obtained by the potassium bromide pressed-disk technique. Spectra were recorded using a sodium chloride prism for dispersion in the region

4000-700 cm^{-1} and a potassium bromide prism in the 700-400 cm^{-1} region. (UR - 20 JENA IR spectrophotometer).

RESULTS AND DISCUSSION

In the Gurasada region two montmorillonite varieties were reported[4] differentiated by their dehydroxylation reaction. According to Mackenzie[5] the samples which showed a single endothermic effect at 700-710°C were considered "normal" montmorillonites, while the samples which showed a double endothermic effect (550-570°C and 670-680°C) were defined as "abnormal" montmorillonites. Of the investigated samples 10 belong to the normal and 9 to the abnormal variety.

The X-ray diffraction patterns of oriented specimens indicated the presence of montmorillonite and cristobalite. The cristobalite content is higher for the normal samples.

From the chemical point of view the main difference between the normal and abnormal variety refer to the octahedral composition of the montmorillonite lattice.

From Figure 1 can be observed that the abnormal samples show higher Fe^{3+} - for - Al^{3+} substitutions and lower Mg^{2+} - for - Al^{3+} substitutions than normal samples. Differences also appeared in the infrared spectra.[6]

In Fig. 2 are presented the relationships between the OH bending vibrations from the IR spectrum and the octahedral sheet composition. The top three samples are normal and the bottom three abnormal. The peak at 790 cm^{-1} is due to cristobalite and is shown in the spectra only for comparaison purposes. From this figure one can see that an increase of the Fe^{3+}-for-Al^{3+} substitution determines an increase of absorption

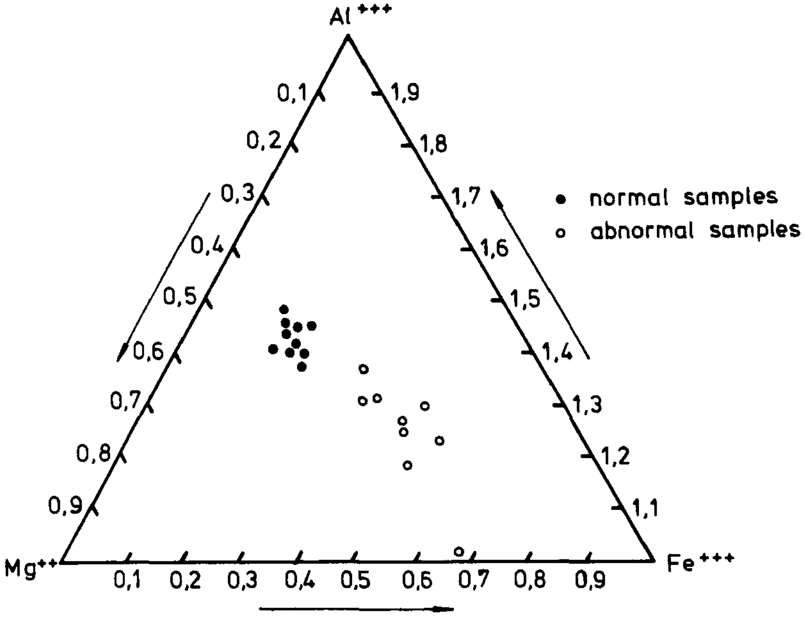


Figure 1 Octahedral composition of the studied montmorillonites

band intensity at 870 cm^{-1} due Al^{3+}-OH-Fe^{3+} librational vibrations[7,8] and a decrease of absorption band intensity at 915 cm^{-1} ascribed to Al^{3+}-OH-Al^{3+} librational vibrations[9]. The decrease of the intensity of the 840 cm^{-1} absorption band ascribed to Al^{3+}-OH-Mg^{2+} vibrations[9] is in accordance with the lower content of octahedral Mg for the abnormal samples.

The relationships between the intensity of 915 cm^{-1} absorption band and the isomorphous octahedral substitutions of the studied montmorillonites (Mg^{2+}, Fe^{3+} and Mg^{2+} + Fe^{3+}) is presented in Figure 3. As shown in this figure the Fe^{3+} - substitutions exert a stronger influence on this vibration mode than Mg^{2+} substitutions.

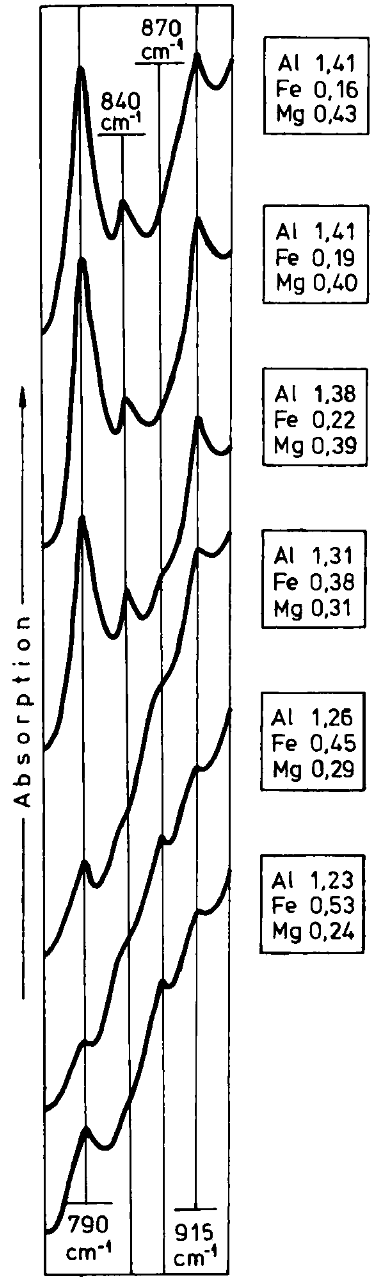


Figure 2 Infrared spectra - octahedral composition relationship for some Gurasada montmorillonites

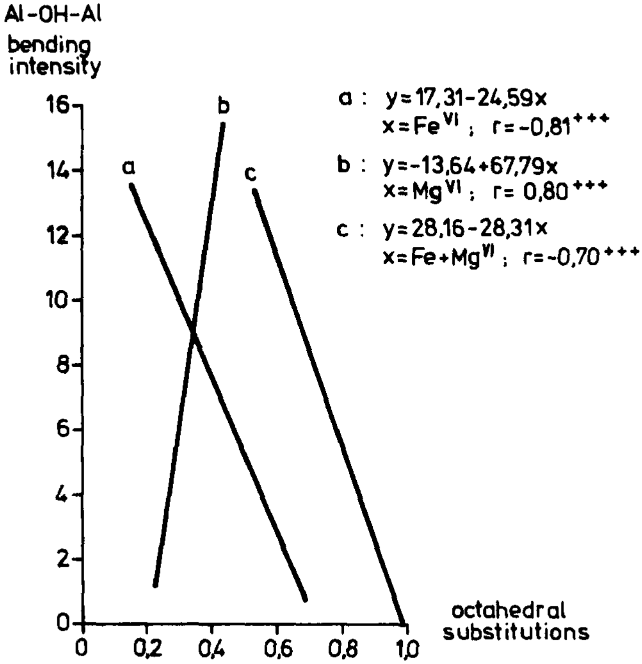


Figure 3 Relationships between intensity of the 915 cm^{-1} absorbtion band (Al^{3+}- OH - Al^{3+}) and isomorphous octahedral substitutions of investigated montmorillonites

In Figure 4 are presented the relationships between intensity and position of the absorption band due to Al^{3+}-OH-Fe^{3+} vibrations and octahedral Fe^{3+}content. In the correlations from this figure three normal samples are also included at which a vibrational mode Al^{3}-OH-Fe^{3+} can be observed. Also in the correlation from Figure 4B are included two so-called "reference samples" from Wyoming and Woburn presented by Farmer and Russell[9]. The data from Figure 4 suggest that in the case of a Fe^{3+} - for-Al^{3+} substitution below 0.10-0.15 octahedral Fe^{3+} (per 1/2 unit cell) the absorption band from 870 cm^{-1} can not be detec-

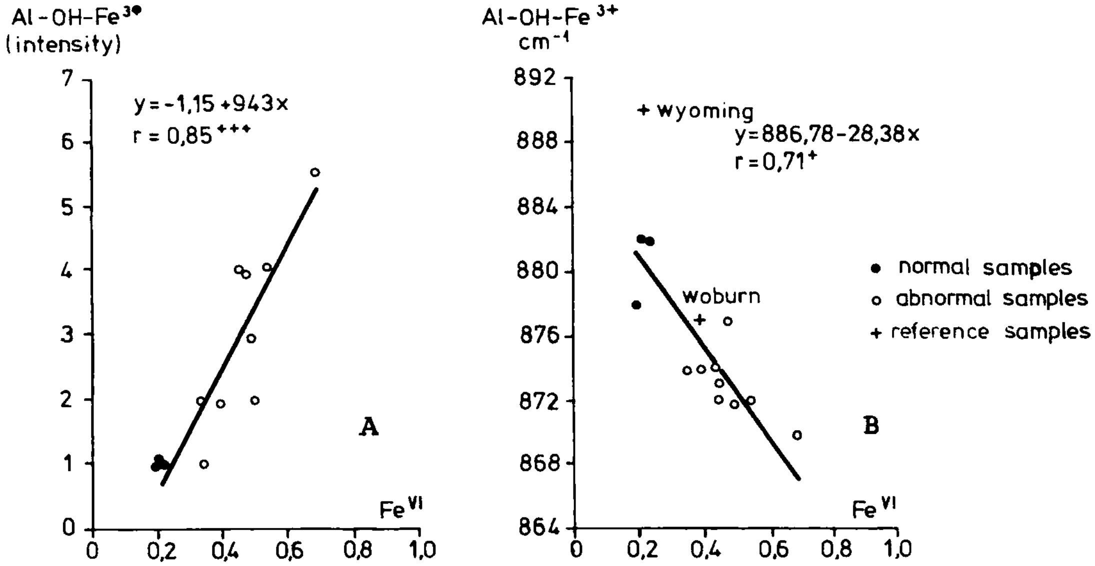


Figure 4 Relationships between intensity and position of absorption band due Al^{3+} - OH - Fe^{3+} librational vibrations and octahedral Fe^{3+} content of some montmorillonites

ted in the spectra of montmorillonites. This is in agreement with previous literature data. Such an absorption band could be observed in the spectra of montmorillonites from Wyoming (0.18 Fe^{3+})[9], Woburn (0.36 Fe^{3+})[9], Belle Fourche (0.17 Fe^{3+})[10] and Aberdeen (0.31 Fe^{3+})[11]. The same absorption band could not be detected in the spectra of Skyrvedalen montmorillonite (0.02 Fe^{3+})[9], Cheto montmorillonite (0.09 Fe^{3+})[11] of Otay montmorillonite (0.08 Fe^{3+})[10,11].

Farmer[12] showed that in the spectrum of montmorillonites, in the region of OH stretching vibrations, the presence of octahedral Fe^{3+} broadens the 3620-3630 cm^{-1} absorption band at the lower frequencies, the process terminating with nontronite.

We did not see such a broadening of the absorption band for the Gurasada montmorillonites, but rather a gradual shift of the band maximum towards lower frequencies with increase of $Fe^{3+} \longrightarrow Al^{3+}$ substitution. In this domain all investigated samples show an absorption band of medium intensity at 3610-3637 cm^{-1}. The peak of the absorption band is situated between 3625 and 3637 cm^{-1} for normal samples and between 3610 and 3621 cm^{-1} for abnormal samples. This difference can be ascribed to the higher octahedral Fe^{3+} content of the abnormal samples. Indeed from Figures 5 it can be seen that the ocahedral Fe^{3+} content correlates with the position of this absorption band. In the correlation from this figure some literature data concerning other dioctahedral smectites (so-called "reference samples"), were introduced. The octahedral composition of the used reference samples are presented in the Table 1. From Figure 5 it is evident that the increase of Fe^{3+} - for $-Al^{3+}$ octahedral substitution in dioctahedral series of smectites causes

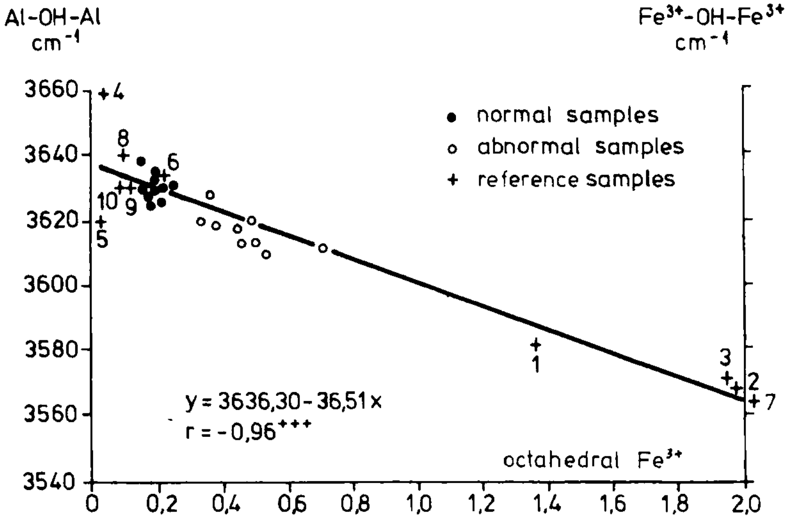


Figure 5 Correlation between stretching frequencies M^{3+} - OH - M^{3+} and octahedral Fe^{3+} content of dioctahedral smectites

a continous shift of the OH absorption band belonging to M^{3+}-OH - M^{3+} vibrations to lower frequencies. This absorption band is a fairly adequate indicator for the replacement of octahedral Al^{3+} by Fe^{3+} in the lattice of the dioctahedral smectites.

In the region below 500 cm^{-1} a significant difference between normal and abnormal samples must be mentioned. In this region Si-O bending vibrations contribute to absorbtion, but this absorption is sensitive to the nature of the octahedral cations[12]. All abnormal samples show an absorption band like a shoulder at about 420-425 cm^{-1}, which could not be identified in the spectra of normal samples. Reported in the spectra of Woburn montmorillonite[9] this absorption band was associated with the higher proportion of Fe^{3+} in octahedral sites. The presence of this absorption band in the spectrum of the abnormal samples is con-

Table 1

The octahedral composition of the "reference samples" used in the statistical correlation from Figure 5 ^{x}

Reference sample	octahedral composition	REF
1. Washington (USA) N.	Al 0,53 Fe 1.36 Mg 0.13	13
2. Garfield (USA) N.	Al 0.00 Fe 1.98 Mg 0.02	
3. Koegas Cape Province (SA)N.	Al 0.00 Fe 1.95 Mg 0.12	
4. Black Jack Mine Idaho (USA) B.	Al 1.93 Fe 0.02 Mg 0.01	9
5. Shyrvedalen (Norway) M.	Al 1.62 Fe 0.02 Mg 0.36	
6. Wyoming (USA)M	Al 1.56 Fe 0.18 Mg 0.19	
7. Georgia (USA)N	Al 0.03 Fe 2.02 Mg 0.00	
8. Hojun Mine Gumma Prefect. (Japan) M.	Al 1.72 Fe 0.09 Mg 0.19	11
9. Otay (USA) M.	Al 1.39 Fe 0.10 Mg 0.55	
10. Cheto (USA) M.	Al 1.38 Fe 0.09 Mg 0.54	

B = Beidellite M = Montmorillonite N = Nontronite

x) The iron content refers to Fe^{3+}.

sistent with the higher octahedral Fe^{3+} content in these samples and is a new evidence that this vibration mode is associated with this ion.

CONCLUSION

The established relationships between octahedral Fe^{3+} and infrared spectra of montmorillonites indicates that $Fe^{3+} \rightarrow Al^{3+}$ octahedral isomorphous substitutions can be positively identified and in some cases semiquantitatively evaluated by infrared absorption, using some absorption bands due OH bending and stretching vibrations.

REFERENCES

1. V.C.Farmer and J.D.Russell, Clays,Clay Minerals, 15, 121 (1967)
2. J.L.White, Soil Sci., 112, 1, 22 (1971)
3. C.Crăciun, Mineralogical study of the bentonite deposits from Gurasada. Ph.D.Thesis, University of Bucharest, (1984)
4. C.Crăciun, Studii Tehn.Ec., I, 14, 53 (1978)
5. R.C.Mackenzie, Differential Thermal Analysis, Academic Press, London, (1970)
6. C.Crăciun, Colocviul Nat. de Opticǎ (II) Bucureşti, 33, (1980)
7. J.M.Serratosa, Am.Miner., 45, 1101, (1960)
8. L.Heller, V.C.Farmer, R.C.Mackenzie, D.Mitchell and H.F.W.Taylor, Clay Miner.Bull., 5, 56, (1962)
9. V.C.Farmer and J.D.Russell, Spectrochim.Acta, 20, 1149 (1964)

10. L. Lerot and P. F. Low, Clays, Clay Minerals 24, 191, (1976)

11. R. Grim, G. Kulbicki, Am. Miner. 46, 1329 (1961)

12. V. C. Farmer, The infrared spectra of minerals, Mineralogical Society London, (1974)

13. B. A. Goodman, J. D. Russell and A. R. Fraser, Clays, Clay, Minerals, 24, 53 (1976)

Received: June 16, 1984
Accepted: July 18, 1984