

Mössbauer study of the effect of rare earth substitution into montmorillonite

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Abstract Novel montmorillonites were prepared by the exchange of the interlayer cations with a series of rare earth cations (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er) and characterized by XRD, XRF, SEM, chemical analysis and ⁵⁷Fe Mössbauer spectroscopy. An unexpected magnetically split component, assigned to iron being in the interlayer space, was observed in the Mössbauer spectra at 78K in some rare earth cation exchanged montmorillonite. This paper is the initial report about this observation. The transition of iron from the octahedral site to the interlayer and possible incorporation of rare earths in sites different from those which are in the interlayer space was concluded.

Keywords Rare earth substitution · Bentonite · Mössbauer-spectroscopy · Interlayer Fe

1 Introduction

The intercalation of drugs into the interlayer space of clay minerals is one of the possible ways for drug delivery [1–3]. The occurrence of rare earths in several products can improve their applicability due to advantageous properties of lanthanoides like unique electron con-

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figuration, fluorescence, high refractive index, high magnetic anisotropy, high electrical conductivity and high oxygen storage and release capacity. The exchange of the interlayer cations of montmorillonite with the ions of rare earth elements is an effective approach to obtain catalysts, catalyst supports, sensors and adsorbents [4–6]. Mössbauer spectroscopy has been widely applied [7–9] to study the microenvironments of iron atoms occurring in montmorillonite. The ^{57}Fe Mössbauer spectra of montmorillonites generally show a paramagnetic broadened Fe^{3+} component and, in some cases, a minor Fe^{2+} resonance. ^{57}Fe Mössbauer spectroscopy has also been successfully applied to show the incorporation of Fe ion into the interlayer space of montmorillonites [10, 11] and Na-bentonite via treatment with FeCl_3 dissolved in acetone [12].

To develop tailored design of the medical therapies for specific diseases is very important. For this purpose the efficient and controlled drug delivery and uptake in the patients' organism play an extremely important role. The distant future goal is to elaborate more efficient drug delivery by the help of montmorillonite intercalated drugs. In previous works [1–3] montmorillonites, having mainly Na ions in the in the interlayer space, have been used to deliver e.g. ibuprofen, vitamin B₁ and antibacterial agents. We can expect a more efficient or novel drug delivery and uptake by applying montmorillonites in which the interlayer cations are exchanged for rare earths. To check this hypothesis we should be supplied by rare earth substituted montmorillonites. Therefore, the immediate aim of our work is to prepare novel montmorillonites by the exchange of the interlayer cations with a series of rare earth cations and to characterize their structural changes upon the rare earth cation exchange. For these studies X-ray diffractometry (XRD), X-ray fluorescence analysis (XRF), scanning electron microscopy (SEM), chemical analysis and ^{57}Fe Mössbauer spectroscopy are applied. During our study an unexpected magnetically split component in the Mössbauer spectra at 78K is observed in some rare earth cation exchanged montmorillonites. This paper is the first report about this observation.

2 Experimental

The original Ca-montmorillonite was obtained from Ca-bentonite collected in the region of Istenmezeje, Hungary. Elemental analysis of the original Ca-bentonite resulted in the following composition: 73.29 % SiO_2 , 18.71 % Al_2O_3 , 1.48 % Fe-oxide, 2.29 % CaO and 4.23 % MgO.

Rare earth (REE) montmorillonites were prepared from Ca-montmorillonite by several cation exchange: Ca^{2+} -montmorillonite (2 g) was suspended in 10 cm³ of $\sim 8.10^{-2}$ mol/dm³ REECIO₄ (REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er) solution at pH \sim 5.5 (equilibrium pH of suspension). The solutions were shaken for 5 hours, then centrifuged, washed, and dried at room temperature. REECIO₄ were prepared by dissolving REE oxides (purchased from Johnson, Matthey & Co., pro anal, with no Fe content (checked)) in cc. HCl. In our previous work performed with different cations in the interlayer space [13], we have experienced that the equilibrium of the cation exchange can be achieved within 0.5-1 hour. Here we selected longer time in order to observe any other chemical reactions if they would occur. The cation exchange capacity of montmorillonites was determined with the so-called "ammonium acetate" method [14].

XRD diffractograms were recorded using a Philips PW1710 powder diffractometer equipped with a $\text{CuK}\alpha$ source and a graphite monochromator.

XRF analyses were obtained with an energy dispersive X-ray fluorescence system. The parts of the system were: radioactive source (185 MBq ^{241}Am), Si(Li) detector with 20 mm²

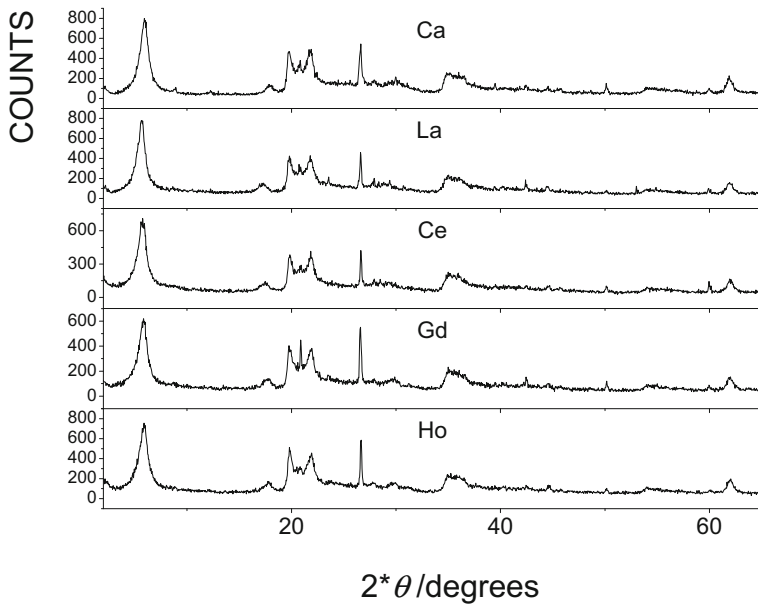


Fig. 1 XRD patterns of original Ca bentonite and rare earth bentonites

surface, 3.5 mm evaporated layer, Canberra DSA 1000 digital spectrum analyzer, Canberra Genie 2000 3.0 spectroscopy software.

SEM-EDX measurements were performed with a scanning electron microscope (Hitachi S4300 CFE).

^{57}Fe Mössbauer measurements were performed in transmission geometry at 78 K and 298 K using a JANIS He cryostat and 20 mCi activity $^{57}\text{Co}/\text{Rh}$ sources. The Mössbauer spectra of second series of samples were recorded more than 18 months later than the first series with decayed activity sources. The isomer shifts are given relatively to $\alpha\text{-Fe}$. The Mössbauer spectra were evaluated by least-square fitting using the MOSSWINN program.

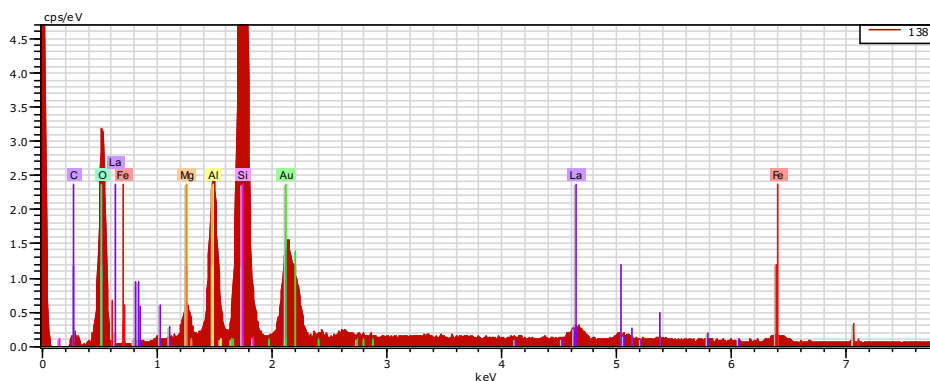
3 Results and discussion

XRD patterns of original Ca bentonite and selected REE-bentonites are depicted in Fig. 1.

The diffraction patterns of all rare earth substituted bentonites are quite similar to each other, reflecting that no essential changes occur in the crystal structure and in mineral composition upon incorporation of the rare earths in the bentonites. This result is consistent with those reported previously for La-substitution [3]. At the same time, the differences observed in the corresponding peak positions in the XRD patterns of REE-montmorillonites indicated change in the (001) basal plane distances for the different rare earths (Table 1). The difference in the basal lattice spacing between La- and Ca montmorillonites is similar to (even somewhat higher than) that reported in [3]. The increase of (001) basal spacing of rare earth montmorillonites compared to that of Ca-montmorillonite indicates the successful incorporation of rare earths into the structure and confirm the realisation of the ion exchange.

Table 1 Basal spacing and intensity of (001) reflection of rare earth substituted and Ca montmorillonites

Sample	$d_{001}/\text{\AA}$	I_{001}
La-bentonite	15.357	717
Ce-bentonite	15.357	564
Ho-bentonite	14.769	626
Ca-bentonite	14.656	733

**Fig. 2** SEM-EDX spectrum of La-bentonite**Table 2** Rare earth content of bentonites, measured by SEM-EDAX and by XRF

rare earth-bentonite	c[mol/g]	
	XRF	SEM
La-bentonite	3.90×10^{-4}	3.06×10^{-4}
Ce-bentonite	2.85×10^{-4}	3.10×10^{-4}
Gd-bentonite	3.10×10^{-4}	2.74×10^{-4}
Lu-bentonite	2.26×10^{-4}	2.17×10^{-4}

In the SEM-EDX spectrum of La-bentonite (Fig. 2), the appearance of La peaks can be well seen; and no peaks of Ca could be detected. Therefore, we can establish that all Ca present in the original Ca-bentonite have been exchanged to La.

Similar results were obtained in the case of other rare earth bentonites, too, indicating the realisation of the cation exchange in all cases.

Elemental distribution maps obtained by SEM-EDAX showed homogeneous distribution of the rare earths in these bentonites.

Rare earth concentration values measured by SEM-EDAX and by rare earth analysis performed by XRF are given in Table 2 for selected samples.

The rare earth concentrations are near to or slightly greater than the total cation exchange capacity (2.72×10^{-4} mol/g) calculated for trivalent rare earths. The concentration data greater than the cation exchange capacity indicate that rare earth cations can be incorporated not only into the interlayer space, but also other substitutions has to be supposed. The difference between the rare earth content measured by the two methods (Table 2) can

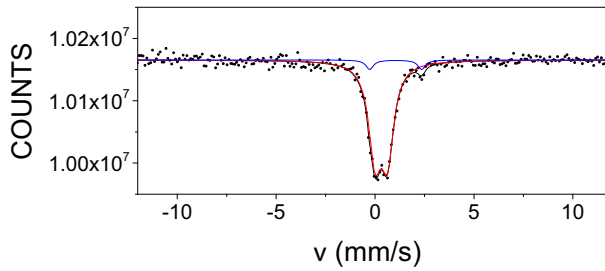


Fig. 3 Room temperature Mössbauer spectra of La-bentonite

Table 3 Room temperature Mössbauer parameters of Ca-bentonite and rare earth bentonites

	Component	δ (mm/s)	Δ (mm/s)
Ca-bentonite	D1	0.31	0.60
	D2	1.07	2.61
La-bentonite	D1	0.32	0.59
	D2	1.06	2.64
Ce-bentonite	D1	0.32	0.62
	D2	1.08	2.65
Dy-bentonite	D1	0.35	0.65
	D2	1.07	2.57

be explained because SEM-EDAX measures the surface but XRF gives information rather about the bulk.

The results of XRD, SEM-EDAX and XRF measurements revealed the successful preparation of rare earth montmorillonites from Ca-bentonite via cation exchange.

The room temperature ^{57}Fe Mössbauer spectra of both the original Ca-bentonite and the rare earth substituted bentonites showed a doublet envelope which was well decomposed into 2 doublets. The major doublet, with average Mössbauer parameters of $\delta = 0.32$ mm/s and $\Delta = 0.60$ mm/s for Ca-bentonite, was assigned to Fe^{3+} at the octahedral sites, while the minor doublet, with $\delta = 1.07$ mm/s and $\Delta = 2.64$ mm/s for Ca-bentonite, was attributed to Fe^{2+} being at the octahedral sites in montmorillonite; these data are in good agreement with previous literature data for the montmorillonites [3–6]. We have found no essential differences between the room temperature Mössbauer spectra (Fig. 3) and between the corresponding Mössbauer parameters (Table 3) of original Ca-bentonite and rare earth substituted bentonites. The small differences between the corresponding parameters are within the reproduction errors. Consequently, on the basis of room temperature ^{57}Fe Mössbauer spectra it is not possible to observe the effect of rare-earth substitution in Ca-montmorillonite.

The 78 K Mössbauer spectrum (Fig. 4, d) of original Ca-bentonite is similar to the room temperature spectrum, consisting of the two doublets having only the regular temperature dependent changes in their isomer shifts and quadrupole splitting values.

However, unexpectedly, we have observed the appearance a magnetically split component in the Mössbauer spectra of some rare earth montmorillonites recorded at liquid nitrogen temperature.

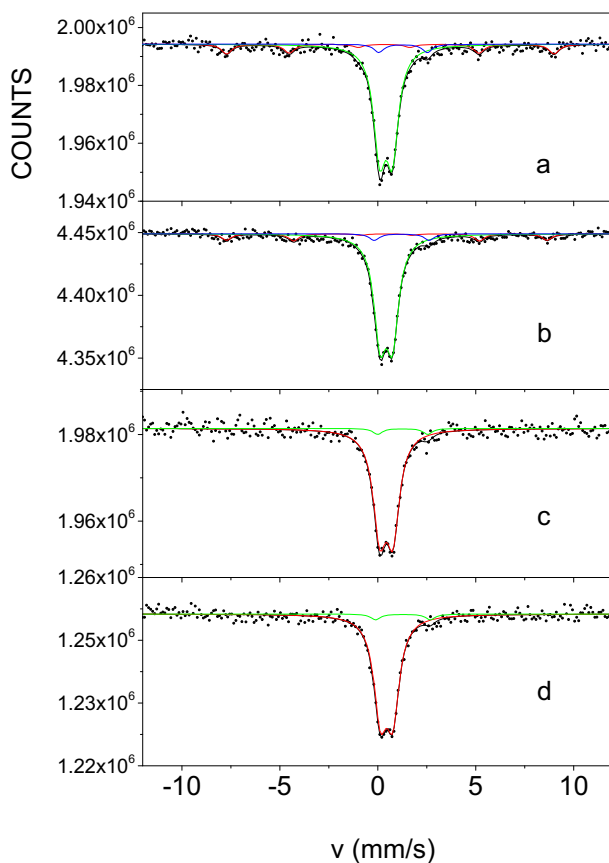


Fig. 4 78 K ^{57}Fe Mössbauer spectra of rare earth bentonites La (a), Ce (b), Ho (c) and Ca-bentonite (d)

Figure 4 illustrates that a sextet component is also present in the 78K spectra of La and Ce exchanged bentonites but this component was not observed in the case of Ho-bentonite.

The Mössbauer parameters of the sextet component at 78 K were found in the range of $\delta = 0.44\text{--}0.48$ mm/s, $\Delta = -0.08 - 0.09$ mm/s and $B = 49\text{--}51$ T. Based on previous Mössbauer studies [7–9], this sextet component corresponds to Fe^{3+} located in the interlayer space in montmorillonite. Consequently, we assigned the sextet components appearing in the rare earth bentonites to Fe^{3+} cations, coordinated to water molecules and hydroxide ions, in the interlayer space of montmorillonite.

Our results show that a part of the iron occurs in the interlayer after the ion exchange when Ca was exchanged to some rare earth like La and Ce. We know that iron occurred only in the octahedral sites in the original Ca-bentonite, its Mössbauer spectrum also reflects the corresponding paramagnetic contribution at low temperatures. On the other hand, no traces of iron were detected in any components used at the exchange of rare earth ions. Consequently, no other iron source, than iron ions being in the octahedral sites in the original Ca-montmorillonite, existed for creating the new iron microenvironments in the interlayer in the observed extent at the rare earth exchange. Therefore, we can conclude that a part of iron ions transferred from the octahedral positions to the interlayer space when Ca was

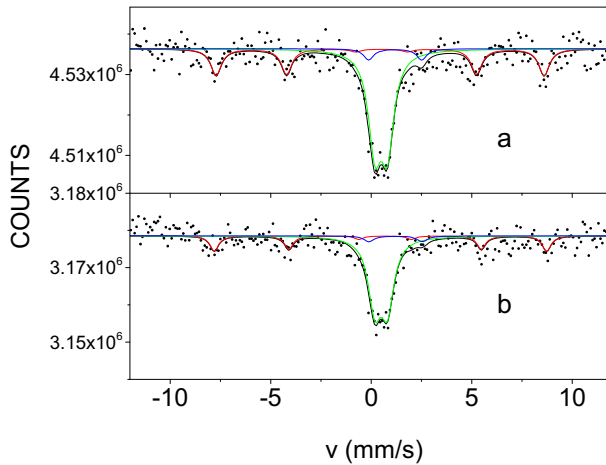


Fig. 5 78K Mössbauer spectra of La-bentonites prepared with different La content: 3.9×10^{-4} mol/g (a) and 2.9×10^{-4} mol/g (b)

exchanged to La or Ce. Such an outcome of iron ions from octahedral site occurs at temperatures higher than room temperature or at conditions different from our present ones. Mineral phase transformations in La-bentonite have been found, until now, only under annealing or pressure effects [6]. In our present case, however, no phase transition or phase segregation were observed by XRD after the rare earth exchange. Our result cannot be well explained by taking into consideration the known background of chemical, diffusion and mineralogical processes at the conditions of our rare earth cation exchange.

In order to get further information, we have measured a new series of rare earth substituted Ca-bentonites prepared at different rare earth concentration. Figure 5 shows the 78 K Mössbauer spectra of La-bentonites with higher and lower La content. Similarly to the previous measurements, both spectra exhibit the appearance of sextet. Furthermore, the relative sextet area is higher (31 %) for La-montmorillonite with higher La content (3.9×10^{-4} mol/g) than that (22 %) belonging to La-bentonite of lower La concentration (2.9×10^{-4} mol/g). This confirms the previous results; and moreover reveals that the occurrence of interlayer iron is the consequence of the cation exchange.

Furthermore, we have found a correlation between the extreme high concentration of rare earths and the appearance of sextet in the Mössbauer spectra of their bentonites. Namely, the chemical analysis indicated a rare earth content being considerable higher that would correspond to the total cation exchange capacity when a part of the iron atoms moved from the octahedral site to the interlayer space. Taking into account the composition of our original Ca-montmorillonite maximum 27.2 milliequivalent of trivalent rare earths could be accommodated in the interlayer space. In contrast, the analysis showed more than 30 % ‘over substitution’ in the case of La and Ce and 15 % in the case of Gd. In the one hand, this indicates that rare earth can occupy sites different from those being in the interlayer space, and on the other hand, it supports our finding that iron needs to move from the octahedral sites since the montmorillonite is ‘oversubstituted’ with rare earth. A question arises: where are the rare earths which are out of the interlayer space? Some may certainly be accommodated in other minerals of bentonite, mainly in silicates. However, even if it might occur, this would be negligible compared to the analytical data of ‘oversubstitution’, considering the

low occurrence of silicates other than montmorillonite in these bentonites. Looking at the correlation between the relative area of Mössbauer sextet and the corresponding analytical data of 'oversubstitution', one can speculate that the incorporating rare earth can push out the iron atoms from their octahedral position during the cation exchange process; and rare earth cations can also be incorporated at sites different from those in the interlayer space, and might substitute for Fe in the octahedral positions.

The partial occupation of octahedral site by rare earth ions can be considered as an unexpected phenomenon at the applied cation exchange process. The background of this considering the conditions of cation exchange [1–3] has not been understood yet. However, our present experimental study would suggest the possibility of such a phenomenon. To prove the existence and clarify the background of a rare earth substitution in the octahedral sites of montmorillonite needs further investigation.

4 Conclusions

XRD, XRF, SEM and chemical analysis revealed the successful preparation of rare earth montmorillonites (for rare earths: La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er) from Ca-bentonite via cation exchange, suspended in corresponding rare earth perchlorate solution.

An unexpected magnetically split component was observed in the ^{57}Fe Mössbauer spectra of certain rare earth (e.g. La, Ce) cation exchanged montmorillonite at 78K. This magnetically split component was assigned to iron being in the interlayer space. The chemical analysis showed that these samples contained about 15–30 % more rare earth cations than the cation exchange capacity. Its correlation with the fraction of interlayer iron may suggest the conclusion that rare earth cations can also be incorporated at sites different from those in the interlayer space, and they might substitute for Fe in the octahedral positions, clarification of which needs further studies.

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