Clays and Clay Minerals, Vol. 58, No. 2, 164–173, 2010.

A MÖSSBAUER SPECTROSCOPIC STUDY OF ALUMINUM- AND IRON-PILLARED CLAY MINERALS

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Abstract—The placement of metal oxide pillars between clay mineral layers modifies their physical-chemical properties, including surface area, acidity, and catalytic activity. Aluminum is the most commonly used pillar cation, but the use of Fe offers a distinct opportunity to expand the range of catalytic behavior. The purpose of this study was to prepare Fe-pillared Laponite and montmorillonite and to characterize the resulting Fe phase(s). Laponite or montmorillonite suspension was mixed with different pillaring solutions containing Al oligomer and/or Fe oligomer with Fe:(Al+Fe) percent ratios ranging from 0 to 100%. The Al oligomer was obtained by hydrolysis of $AlCl_3 \cdot 6H_2O$ with NaOH at pH 4.4 and the Fe oligomer was prepared by $FeCl_3$ hydrolysis with Na_2CO_3 at pH 2.2. The pillared clay was obtained by adding the oligomer to the clay suspension, then heating to 300ºC for 3 h. The Fe oligomer and the pillared clay minerals were characterized by variable-temperature Mössbauer spectroscopy, X-ray powder diffraction, and chemical analysis. The unheated Fe oligomer was akaganeite, an Fe oxyhydroxide phase. Heating the Fe oligomer to 300ºC transformed the akaganeite to hematite, but heating it in the presence of the clay protected it, at least partially, from this transformation, creating instead a phase which resembled a more poorly ordered akaganeite or a mixture of akaganeite and poorly ordered hematite. Mixing of Al and Fe oligomers in the pillaring solution had no effect on the magnetic hyperfine field of the Fe pillars, indicating that Al forms separate pillars rather than substituting for Fe in the pillar. A small fraction (4%) of the Fe pillar resisted reductive dissolution by citrate-bicarbonate-dithionite.

Key Words—Akaganeite, Aluminum, Iron, Laponite, Montmorillonite, Mössbauer Spectroscopy, Pillared Clay.

INTRODUCTION

The presence of metal-oxide pillars in clay minerals induces important changes in their catalytic behavior which can be tailored toward specific industrial needs. Aluminum is the most commonly studied and used metal, forming the Keggin ion (Al_{13}), but Fe, though much less studied than Al, is also of considerable interest because it expands the possible range of pH- and/or redox-catalyzed reactions (Carriazo *et al.*, 2003; Chirchi and Ghorbel, 2002).

Techniques such as Mössbauer spectroscopy, Temperature Programmed Reduction (TPR), Nuclear Magnetic Resonance (NMR), and Transmission Electron Microscopy (TEM) have been used to determine the nature, location, and redox properties of Fe in these pillars. Lee *et al.* (1989) used room-temperature Mössbauer spectroscopy to follow reduction and oxidation of Fe pillars in montmorillonite and found that metallic iron (Fe^0) could be formed upon heating in H_2 at 723 K, which was greatly enhanced by the addition of a Pt catalyst. Bakas *et al.* (1994), using a mixed Al/Fe intercalant solution and redox-controlled conditions, showed that both the precursor and the pillared clays (PILC) contained Al-substituted lepidocrocite as the major Fe phase, in addition to distorted octahedral Fe(III) sites in the clay structure. Heating converted this hydroxide to Al-substituted maghemite. Doff *et al.* (1988) observed a two-component sextet in both the Fe-intercalated precursor and the Fe-pillared montmorillonite, in which the magnetic hyperfine fields of the two components were separated by ~5 T (47.1 and 42. 4 T in the intercalated precursor and 49.6 and 44.9 T in the pillar, respectively).

Different pillaring procedures lead to different Fe phases in the pillars. Zurita *et al.* (1996), using Fe acetate as the precursor solution, obtained only small amounts of hematite after heating the PILC. This phase was formed from free Fe outside the structure of the pillared clay. No transformation of the pillars was observed.

Gangas *et al.* (1985) discovered that intercalation of Fe into ferruginous smectite (sample SWa-1 from the Source Clays Repository of The Clay Minerals Society) at 552ºC produces a magnetic bridge between superimposed smectite layers and raises the magnetic ordering temperature of structural Fe(III) in the layers from ~2 K to ~40−60 K. The authors explained this phenomenon as being due to the lifting of the magnetic frustration that

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DOI: 10.1346/CCMN.2010.0580203

normally exists in Fe-rich smectites (Ballet and Coey, 1982; Lear and Stucki, 1989).

Bergaya and Barrault (1990) reported that the structure of mixed Al/Fe-PILCs is similar to Al-PILC if the Fe:(Al+Fe) percent ratio is $\leqslant 50\%$, indicating isomorphic substitution of Al by Fe in the Keggin ion (Al pillar). Komadel *et al.* (1994) studied the stability of Al/Fe- and Fe-pillared montmorillonite during treatment with acids and complexing or reducing agents. Iron was more difficult to remove from the mixed Al/Fe-pillared montmorillonite than from the Fe-pillared montmorillonite, suggesting that Fe substituted for Al in the mixed Al/Fe pillars. Using a standard Wyoming montmorillonite (sample SPV from Comptoir des Minéraux et Matières Premières), Mandalia *et al.* (1998) observed large interlamellar spaces in Al/Fe-pillared clays. Increasing the percentage of Fe decreased the surface area and created mesoporosity between the particles, leading to large interlayer repeat distances. Nanostructural analysis of this mixed pillared montmorillonite using High-Resolution Transmission Electron Microscopy (HRTEM) revealed different layer stackings depending on the Fe/(Al+Fe) ratio and the probability that various chemical species were present within a single interlayer space (Clinard *et al.*, 2003). This was explained by the difference in pH of the Al and Fe oligomers used as precursors for the pillars, which could be a controlling factor in their decomposition. The alternating stacking sequence of small particles (few clay mineral layers) and Fe aggregates in the interlamellar space accounted for the large interlayer distances observed by X-ray powder diffraction (XRD).

The purpose of this investigation was to gain a better understanding of these factors by systematically studying pillared Laponite and montmorillonite under controlled conditions in which Fe, Al, or a mixture of the two was used to form the pillars.

MATERIALS AND METHODS

Two smectites were used in this study: (1) a synthetic hectorite: Laponite, RD, from Laporte, England. This trioctahedral clay was deliberately chosen as the starting material because it is devoid of Fe (Bergaya *et al.*, 1993). The structural formula is $Na_{0.671}K_{0.001}Si_{7.953}Al_{0.049}[Mg_{5.482}Li_{0.364}Ti_{0.007}]O_{20}(OH)_4$. (2) Wyoming montmorillonite (SPV) was used as received from Comptoir des Minéraux et Matières Premières (Paris, France). Its formula in the Na-saturated form is $Na_{0.59}K_{0.03}Si_{7.89}Al_{0.11}[Al_{3.11}Fe^{3+}_{0.38}Mg_{0.49}]O_{20}(OH)_4$. Impurities are quartz and feldspar (Frini *et al.*, 1997).

The oligomer-pillaring solutions were prepared by the following methods: (1) Al_{13} oligomer – a solution containing Al hydroxide oligocations with an OH:Al ratio of 2.2 was prepared from 0.4 mol L^{-1} $AlCl_3.6H_2O$ and 0.4 mol L^{-1} NaOH, then aged for 7 days at room temperature before use. (2) Fe oligomer, following the procedure of Rightor *et al.* (1991), Na_2CO_3 powder was added gradually to an aqueous solution of 0.2 mol L^{-1} $FeCl_3$, up to a CO_3:Fe ratio of 2. The resulting fresh oligomer was used immediately without aging.

The PILCs were prepared by adding different amounts of Al and Fe oligomers simultaneously to a 2% suspension of the clay to give a metal:clay ratio of 10 mmol g^{-1}. The suspension was aged for 1 day at room temperature and then the clay products were centrifuged and washed until free of Cl^- (conductivity test). The intercalated clay mineral was dried by evaporation at room temperature and heated at 300ºC for 3 h. Sample labels of 100% Al, 100% Fe, 50% Fe, *etc.*, represented the Fe:(Fe+Al) percent ratio of the oligomers added. The actual percentages of Al and Fe in the resulting pillars or within the clay interlayers were not determined but were assumed to be relatively similar.

Sub-samples were treated by the oxalate or citrate-bicarbonate-dithionite (CBD) method. In the former, 0.250 g of clay was extracted with a mixture of 0.2 mol L^{-1} of ammonium oxalate and 0.2 mol L^{-1} of oxalic acid at pH 3 in the dark for 4 h (Schwertmann, 1964). In order to remove poorly crystalline Fe(III), CBD extraction was performed following the Mehra and Jackson (1958) procedure to remove all free Fe(III) (oxyhydr)oxides.

Mössbauer spectra were acquired in 1024 channels in transmission mode using a spectrometer supplied by Web Research, Inc. (Edina, Minnesota, USA), with a drive system operating with a triangular waveform, thus giving mirror-image spectra which were then folded to produce a horizontal background. The gamma-ray source was ^{57}Co, dispersed as 10% in a Rh foil, with a nominal strength of 50 mCi (1.85 GBq) (Ritverc GmbH, St Petersburg, Russia). The sample temperature was controlled at 4, 77, or 298 K with a Janis Model SHI-850-5 (Janis Research Co., Inc., Wilmington, Massachusetts, USA) closed-cycle cryostat. Experimental data were fitted using Lorentzian-shaped lines and Gaussian distributions of magnetic hyperfine fields and/or quadrupole splittings or shifts; isomer shifts were calculated relative to a 7 μm thick αFe foil at room temperature.

X-ray diffraction patterns were obtained using a Philips Model PW 1830 X-ray generator (CuKα radiation) and PW3020/2 goniometer equipped with a proportional counter detector. The freeze-dried oligomer unheated and heated under the same pillaring conditions were analyzed using steps of 0.04º at 4 s/step in the range of 10 to 80º2θ.

RESULTS AND DISCUSSION

Fe oligomer

The room-temperature (298 K) Mössbauer spectrum for the unheated Fe oligomer powder exhibited a doublet which was fitted with component sub-spectra representing three sites (Figure 1). The Mössbauer hyperfine

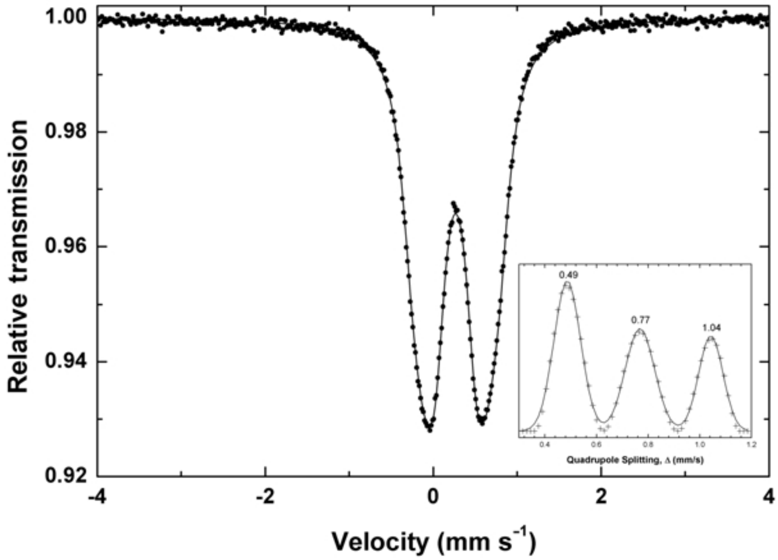

Figure 1. Mössbauer spectrum of unheated Fe oligomer at 298 K.

parameters (Table 1) are consistent with akaganeite, where Fe is in an octahedral configuration. The quadrupole spliting values are related to the proximity of the Fe(III) site to the halide anion; the more positive the value of the quadrupole splitting, the closer the location of the Fe site to the halide. Fitting with two sites according to Chambaere *et al.* (1978), Gotic *et al.* (1994), and Saric *et al.* (1998), for example, failed to give satisfactory results. Childs *et al.* (1980) fitted the spectra of a fluoride-containing akaganeite with three components having similar quadrupole splittings, although they recommended a 2-site fit. Their third component could be explained by a large distortion in the component responsible for the outer doublet. Chambaere *et al.* (1979) also reported one fluoride-containing akaganeite with a third component with a more distorted octahedral site (Table 1).

At 4 K, the Mössbauer spectrum of the unheated Fe oligomer (Figure 2) was dominated by a magnetically ordered pattern with a small paramagnetic phase contributing only 10% to the total area, which was probably due to impurities in the undialyzed oligomer. The spectrum was fitted with three hyperfine field distributions, according to the RT Mössbauer spectrum, ranging from 47.2 T to 48.5 T (Table 1).

The XRD pattern of the unheated Fe oligomer (Figure 3) confirmed the formation of akaganeite upon drying. The initial conditions of the oligomer solution

Table 1. Mössbauer parameters of unheated Fe oligomer at 4, 77, and 298 K.

T (K)	Assignment	δ (mm/s)	Δ or ε (mm/s)	B_{hf}**(T)	*A* (%)
4	Akaganeite	0.51 0.47 0.51	−0.61 −0.15 −0.02*	47.2 47.3 48.5	23 36 31
	Doublet	0.49	0.46	–	10
77	Akaganeite	0.51 0.48 0.47	−0.02* −0.11 −0.72	47.6 46.2 45.1	18 49 22
	Doublet	0.50	0.37	–	11
298	Akaganeite	0.38***	0.49 0.77 1.04	– – –	37 36 27

δ: isomer shift; Δ: quadrupole splitting or shift; ε: quadrupole shift; B_{hf}: hyperfine field; *A*: sub-spectrum relative area.
* Fixed parameter in the fitting; ** Position of peak maximum in hyperfine field distribution; *** Average value from distribution.

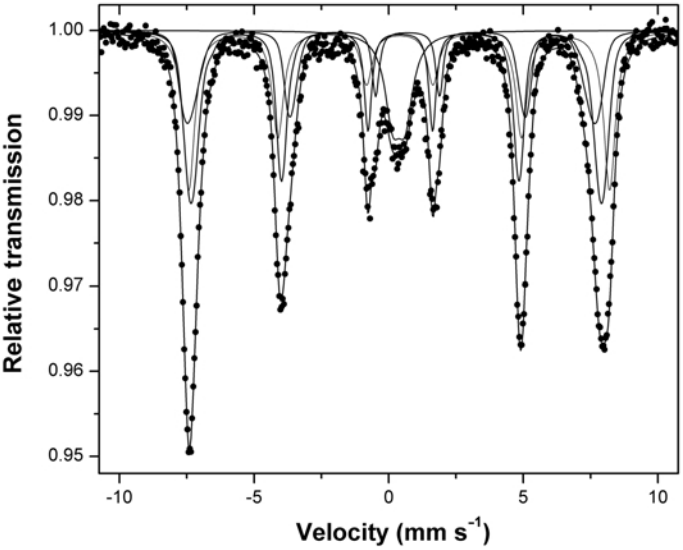

Figure 2. Mössbauer spectrum of unheated Fe oligomer at 4 K.

(low pH and high chloride concentration) also favored stabilization of the akaganeite structure. Sodium chloride was present because the product was undialyzed.

Heating the oligomer at 300ºC for 3 h (the same conditions used in the pillaring process) transformed the akaganeite to hematite (α-Fe_2O_3) (Figure 3; Mössbauer

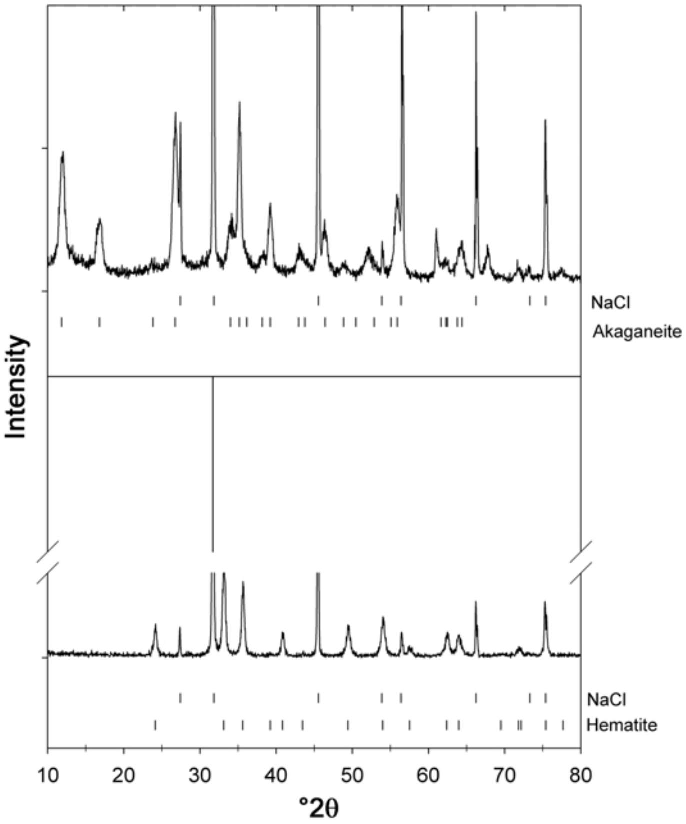

Figure 3. Powder XRD traces of unheated (upper) and heated (lower) Fe oligomer.

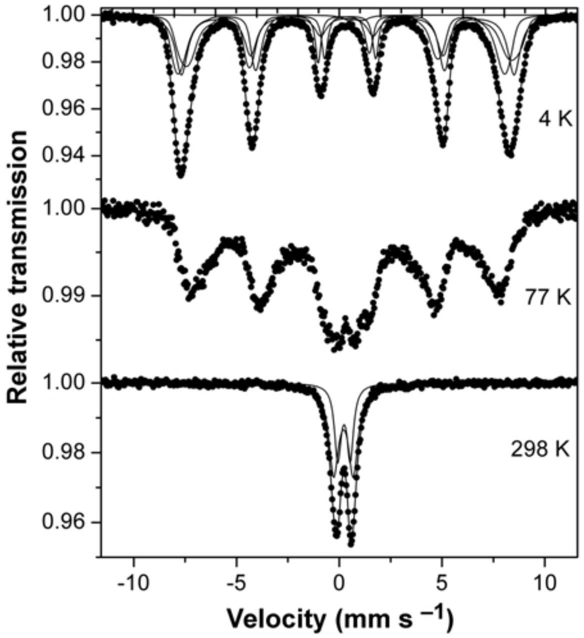

Figure 4. Mössbauer spectra of 100% Fe-pillared Laponite at 4, 77, and 298 K.

spectrum not shown), with Mössbauer parameters, at room temperature, of $B_{hf} = 51.57(5)$ T, $\delta = 0.360(3)$ mm/s, and $\varepsilon = -0.22(1)$ mm/s. This transformation was also reported by Post *et al.* (2003).

Pillared Laponite

Pillaring of Laponite yielded a basal spacing of ~1.8 nm after aging in suspension (see fig. 4 in Bergaya *et al.*, 1993) and the oligomer structure appeared to be preserved during the pillaring process. The room-temperature Mössbauer spectrum of 100% Fe-pillared Laponite (Figure 4) was similar to the spectrum of the unheated oligomer, consisting of an inner (less distorted site) and outer (more distorted site) quadrupole doublet having parameters consistent with akaganeite (Table 2). Attempts to fit with three sites were unsuccessful. The intensity ratios of these two sites in the unheated oligomer and Fe-pillared samples were also similar, indicating that the structures were similar; so, the oligomer structure was largely preserved during the pillaring process. The quadrupole splittings of the outer doublets were also similar, but the inner-doublet quadrupole splitting increased upon pillaring, probably due to some increased distortion because of the loss of water and chloride.

At 77 K, the Mössbauer doublets were only partially magnetically ordered in the pillared sample, whereas complete magnetic order was observed in the unheated oligomer. At 4 K, complete magnetic order was achieved in both samples. These differences in magnetic behavior between oligomer and the Fe phase in the pillared clay indicate that the magnetic domains in the pillars are much smaller and more poorly ordered than in the unheated oligomer, causing a decrease in the magnetic ordering temperature. The hyperfine parameters (Table 2) are consistent with a mixture of akaganeite and poorly ordered hematite in the interlayer space or adsorbed onto the surface of Laponite. Heating the oligomer in the presence of the clay thus inhibited the facile transformation from oxyhydroxide (akaganeite) to oxide (hematite), as was observed with the isolated Fe oligomer. These observations indicate that the structure of the intercalated oligomer may be more preserved during heating than was previously thought (Pinnavaia, 1983).

Extraction with oxalate and CBD

Oxalate extraction had no apparent effect on the Mössbauer spectrum of Fe-pillared Laponite (Figure 5), even though the chemical analysis (Table 3) reported that this treatment removed ~7 wt.% of the Fe. Evidently the dissolution by oxalate was homogeneous and thus largely undetectable by the Mössbauer spectra.

Table 2. 100% Fe-pillared Laponite at 4 and 298 K (see Figures 4 and 6).

Pillared Laponite	*T* (K)	Assignment	δ (mms^{-1})	Δ or ε (mms^{-1})	B_{hf} (T)	*A* (%)
Untreated	4	Hematite	0.34	0.25	48.5	34
		Akaganeite	0.50	0.04	50	33
			0.44	−0.42	49.4	32
			0.90*	0.70*	–	1
	298	Fe(III)	0.34	0.61	–	36
		Akaganeite	0.32	0.95	–	64
CBD-treated	4	Fe(III)	0.48	0.89		94
		Fe(II)	1.21	3.02		6

δ: isomer shift; Δ: quadrupole splitting; ε: quadrupole shift; B_{hf}: hyperfine field; *A*: sub-spectrum relative area; * fixed in the fitting.

Table 3. Effects of oxalate and CBD treatments on Fe content of 100% Fe-pillared Laponite.

Sample	Treatment	Total Fe (wt.%)
Pillared Laponite 100% Fe	None	29.7
	Ammonium oxalate	23.2
	CBD	3.8

Treatment of the pillared Laponite with CBD removed almost all the Fe (~96 wt.%) from the sample (Table 3), leaving only a low-intensity paramagnetic Mössbauer spectrum at 4 K (Figure 6) fitted with two doublets, one for Fe(III) and one for Fe(II). The Fe(II) doublet clearly derives from the reduction treatment with CBD. The location of the residual Fe(III) remains unclear but the parameters show that the Fe is in an octahedral configuration and the relatively large quadrupole splitting of the Fe(III) doublet may represent a strongly distorted site. The fact that it resisted CBD dissolution and lacked magnetic order at 4 K indicates that it could well be an interlayer Fe(III) species that is strongly bound to the clay layer, possibly by coordination through the structural OH and/or basal oxygens. If this is true, one could also envision this Fe being a remnant from the binding site of the pillar to the clay mineral layer. The hyperfine parameters may also be consistent with an Fe(II) sulfide mineral, which could have formed during CBD treatment, but the presence of citrate in CBD to chelate dissolved Fe makes this only a remote possibility.

Effect of aluminum

The maximum magnetic hyperfine field (B_{hf}) of the Fe pillars in Fe/Al-pillared Laponite was unchanged by the Fe/(Al+Fe) ratio within the error range (Figure 7, Table 5), indicating that separate Fe and Al pillars were formed rather than Al substituting for Fe in the pillared Fe structure. The results of Murad and Schwertmann (1983, 1986) and many others support this conclusion because they clearly demonstrated that Al-for-Fe substitution in Fe (oxyhydr)oxides decreases the magnetic hyperfine field. The absence of a shift in the magnetic hyperfine field in the present study when Al was included in the pillars is, therefore, direct evidence for discrete and separate phases of Al and Fe species in the pillars, as proposed by Lee *et al.* (1989), but differs from the conclusion reached by Komadel *et al.* (1994). The

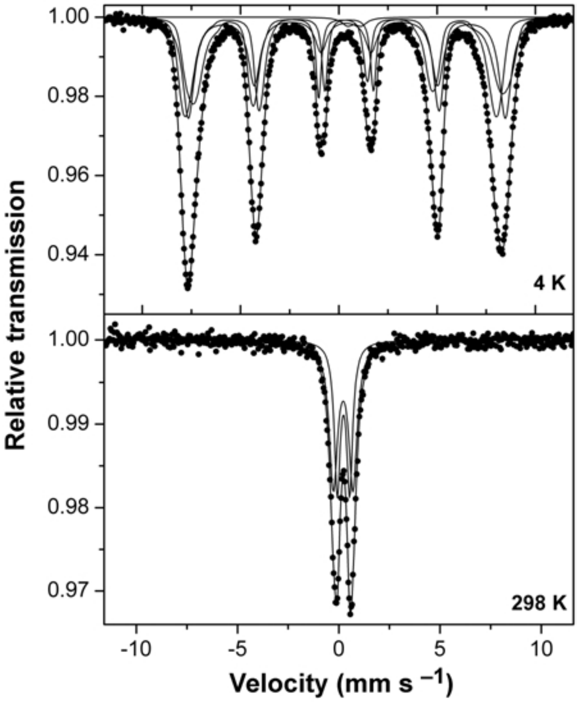

Figure 5. Effect of oxalate treatment on Mössbauer spectra of 100% Fe-pillared Laponite at 298 K and 4 K (compare with Figure 4).

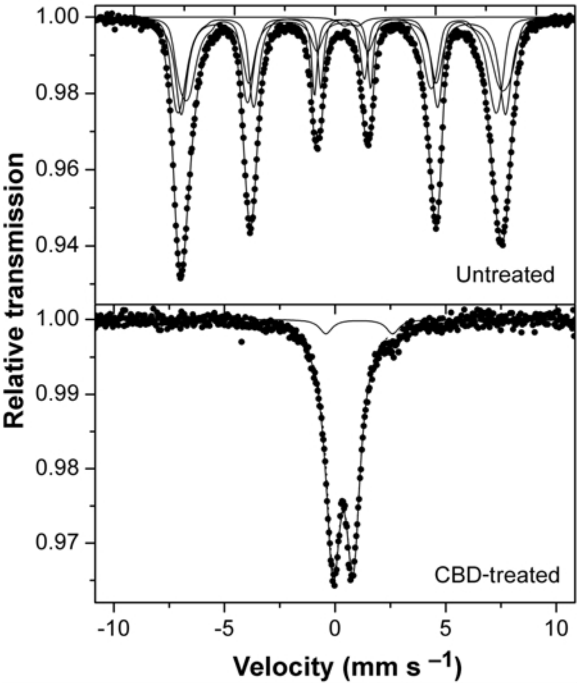

Figure 6. Effect of CBD treatment on Mössbauer spectra of 100% Fe-pillared Laponite at 4 K.

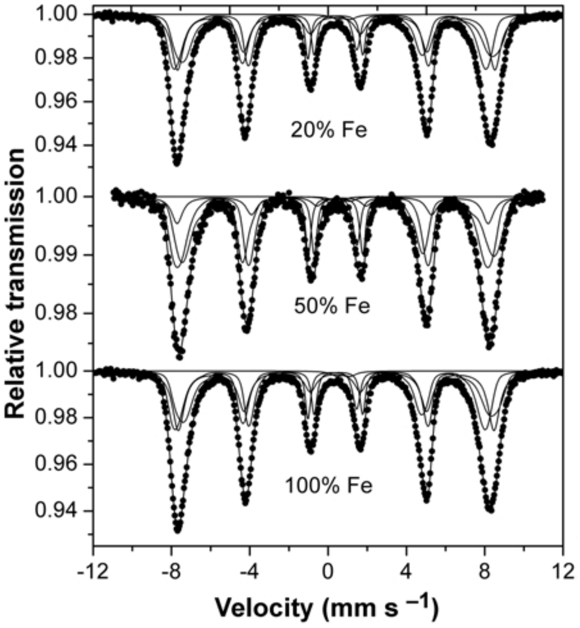

Figure 7. Effect of the Fe/(Al + Fe) ratio on the Mössbauer spectra at 4 K of Al/Fe-pillared Laponite.

reasons for differences between the present results and those of Komadel *et al*. (1994) are probably related to the pillaring preparation method.

Unpillared montmorillonite

At 298 and 77 K, the Mössbauer spectra of unpillared and unheated SPV montmorillonite (Figure 8, spectra a and b) consisted of two doublets; one for Fe(III) and one for Fe(II). At 4 K (Figure 8, spectrum c), a broad, magnetically ordered sextet appeared, comprising ~16% of the spectral area. The six-line pattern was fitted with two sites having Mössbauer parameters of $\delta = 0.44$ mm s^{-1}, $\varepsilon = 0.24$ mm s^{-1}, and $B_{hf} = 54.1$ T for the first site, attributed to superparamagnetic hematite, and the second site attributed to maghemite ($\delta = 0.45$ mm s^{-1}; $\varepsilon = -0.09$ mm s^{-1}, and $B_{hf} = 50.6$ T).

In order to understand the behavior of montmorillonite with heating in the absence of the oligomer, *i.e.* heating with no pillaring, the sample without oligomer was heated to the pillaring temperature. This decreased the relative intensity of the Fe(II) doublet and introduced some magnetic order into the spectrum at 77 K (Figure 8, spectrum e). The loss of intensity in the Fe(II) doublet could be interpreted as either re-oxidation or formation of a magnetically ordered Fe(II) phase. The former interpretation is favored because a magnetically ordered Fe(II) phase should have different hyperfine parameters than the Fe(III) (oxyhydr)oxide phase and, except for the apparent increase in magnetic ordering temperature, the spectrum lacks such additional complexity. The heating process apparently led to the transformation of the original, indigenous Fe (oxyhydr)-oxide phase which was present in this sample into larger or better ordered clusters, probably by oxidation and dehydration of these species, which would account for the onset of magnetic order in the sample at a greater temperature (77 K instead of 4 K), as evidenced by the sextet pattern at 77 K.

Chemical treatment of pillared montmorillonite

Mandalia *et al.* (1998) observed a basal spacing for Fe/(Al + Fe) = 100% at 7.6 nm, hinting that intercalation of the Fe species was successful. However, those authors further showed by HRTEM that the structure is apparently more complex than a classic periodic pillared structure. They concluded that globular Fe aggregates inserted in mesopores between particles could have been responsible for this large basal spacing ‘seen’ by XRD, corresponding in fact to a correlation length within these aggregates and the particles (Clinard *et al*., 2003).

The 4 K Mössbauer spectrum of 100% Fe-pillared montmorillonite (Table 6; Figure 9, untreated spectrum) was successfully fitted with three spectral components that are consistent with akaganeite (Childs *et al*., 1980). Oxalate treatment removed ~10% of the Fe from the sample (Table 4), which apparently was from the magnetically ordered phase because the relative intensity of the sextet to the doublet decreased (Figure 9). After CBD treatment, the spectrum had three components; one due to a small residuum from the magnetically ordered Fe pillar, one due to structural Fe(III) in the clay mineral, and one due to structural Fe(II) in the

Table 4. Iron content of Fe-pillared montmorillonite before and after oxalate and CBD treatments.

Sample	Treatment	Total Fe (wt.%)
Pillared montmorillonite 100% Fe	None	31.1
	Ammonium oxalate	21.3
	CBD	2.8
Untreated montmorillonite	None	2.4
	Ammonium oxalate	2.5
	CBD	2.3

Table 5. Effect of Fe/(Al + Fe) pillaring ratio on Mössbauer parameters in Laponite.

Sample	Assignment	δ (mm/s)	Δ (mm/s)	B_{hf} (T)	*A* (%)
Laponite 50% Fe	Akaganeite	0.57	−0.45	49.21	14
	Hematite	0.38	0.27	51.0	42
		0.49	−0.29	48.6	43
	Doublet	0.90*	0.80*	–	1
Laponite 20% Fe	Hematite	0.49	−0.21	49.5	40
		0.44	0.38	51.5	29
	Akaganeite	0.40	−0.49	49.4	29
	Doublet	0.90*	0.80*	–	2

* parameter fixed in the fitting

clay mineral. The enhanced intensity of the structural Fe(II) component relative to structural Fe(III) from 0.32 to 0.52 was due to chemical reduction by CBD (Table 6). With regard to the other Fe(III) component, the same attributions may be made as in the CBD treated-100% Fe-pillared Laponite, *i.e.* interlayer Fe(III) strongly bound to the clay layer.

The Mössbauer spectra of 100% and 50% Fe-pillared montmorillonite revealed, as with Laponite, that no Al was incorporated into the structure of the Fe pillar, as

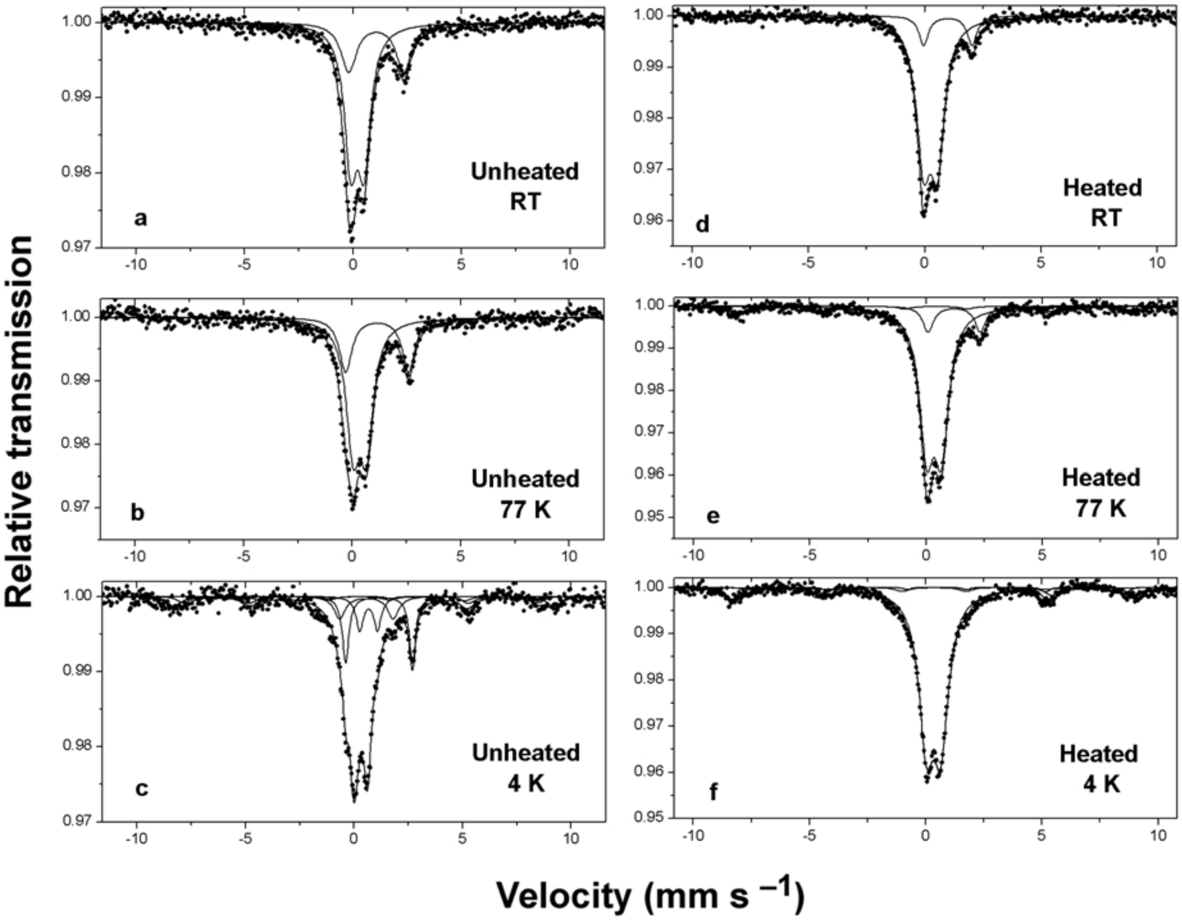

Figure 8. Mössbauer spectra of unpillared SPV montmorillonite at 298 K (a and d), 77 K (b and e), and 4 K (c and f). Spectra a, b, and c from unheated; and spectra; d, e, and f from heated samples.

Table 6. Mössbauer parameters of 100% Fe-pillared montmorillonite (SPV) at 4 K for different chemical treatments and Fe/(Fe + Al) ratios

Sample	Assignment	δ (mm/s)	Δ (mm/s)	B_{hf} (T)	*A* (%)
SPV 100% Fe untreated	Akaganeite	0.40	−0.48	49.5	27
	Hematite	0.40	0.27	50.4	41
		0.52	−0.16	50.1	28
	Doublet	0.44*	0.70*	–	4
SPV 100% Fe oxalate	Akaganeite	0.39	−0.46	49.4	27
	Hematite	0.39	0.31	50.2	35
		0.53	−0.16	50.2	31
	Doublet	0.44*	0.70*	–	7
SPV 100% Fe CBD	Fe^{2+}	1.25	3.09	–	35
	Fe^{3+}	0.58	0.76	–	36
		0.27*	0.73*	–	29
SPV 50% Fe untreated	Akaganeite	0.39	−0.52	48.7	26
	Hematite	0.44	0.33	49.1	38
		0.52	−0.11	50.1	31
	Doublet	0.44	0.70	–	5

* parameter fixed in the fitting

evidenced by the hyperfine field being unaffected by the Fe/Al ratio.

CONCLUSIONS

The main component of the isolated Fe oligomer was akaganeite, its structure being stabilized by the chloride in solution at the favored pH of 2.2. As the oligomer was heated it underwent a phase transformation from akaganeite to hematite, but if heated in the presence of Laponite or montmorillonite, *i.e.* during the pillaring process, this transformation was inhibited and, instead, formed a phase resembling poorly ordered akaganeite and/or poorly ordered hematite. Altering the Fe/(Al+Fe) ratio in the pillaring process yielded no change in the magnetic hyperfine field (B_{hf}) of the pillared Laponite or montmorillonite, indicating that no Al substitution occurred in the Fe pillars and that Al and Fe formed separate pillars or phases in the clay interlayer.

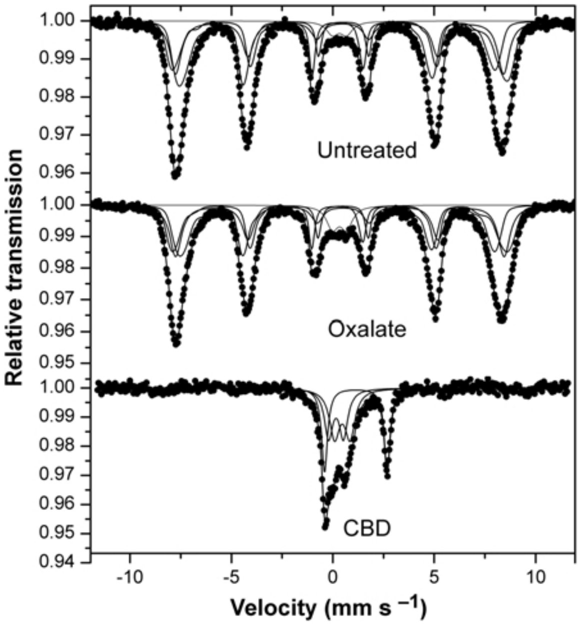

Figure 9. Effect of oxalate and CBD treatments on Mössbauer spectra at 4 K of 100% Fe-pillared montmorillonite.

Pillars largely resisted dissolution by chemical treatment with oxalate, but CBD treatment dissolved most of the Fe in the pillars in both samples. In Laponite, the small proportion of Fe that remained (4%) after CBD treatment was probably due to residual Fe(III) from the pillar that was bonded to structural OH groups in the clay octahedral sheet and/or basal oxygens. In the case of montmorillonite, after CBD treatment, a similar residual Fe(III) component was observed as in Laponite, except that it was largely obscured by structural Fe(III) and Fe(II) in the octahedral sheet of the montmorillonite. The increased amount of structural Fe(II) occurred because of chemical reduction by CBD.

ACKNOWLEDGMENTS

The authors acknowledge financial support for the use of Mössbauer spectroscopy facilities at the University of Illinois by the National Science Foundation, Division of Petrology and Geochemistry, Grant No. EAR 01-26308; and the Environmental Remediation Sciences Program

(ERSP), Biological and Environmental Research (BER), U.S. Department of Energy, Grant No. DE-FG02-07ER64374.

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(*Received 15 December 2008; revised 23 October 2009; Ms. 261; A.E. W.P. Gates*)