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Iron Speciation in the Clays Consummated in Côte d'Ivoire: A Transmission Mössbauer Spectroscopy Study

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ABSTRACT

Iron is present in clay minerals under various forms and influences their properties by virtue of changes in its redox state in their crystal structure. The purpose of this work was to determine the iron statutes in the clays consummated in Côte d'Ivoire for their therapeutic virtues. We used ^{57}Fe Transmission Mössbauer Spectroscopy which is a powerful method to characterize local environment of Fe in iron-bearing minerals. In the green clay of Anyama (AVA) dominated by chlorite, illite and quartz with minor amounts of other minerals including smectite, Mössbauer spectra showed that at least 60% of the total iron was present as Fe^{2+} in two different octahedral sites characterized by δ = 1.09-1.13 mm sec^{-1} and ΔE_q = 2.34-2.65 mm sec^{-1}. For Fe^{3+} cation, the fit revealed two distorted octahedral (δ = 0.28-0.43 mm sec^{-1} and ΔE_q = 0.78-1.1 mm sec^{-1}) and one tetrahedral (δ = 0.15 mm sec^{-1} and ΔE_q = 0.16 mm sec^{-1}) sites. The clays from Bingerville (LBF, LVF and LJFF) were dominated by kaolinite with relative important amounts of quartz, illite and goethite. Their room temperature Mössbauer spectra were characterized by a broad doublet indicating that iron was present as Fe^{3+} in octahedral site (δ = 0.37-0.4 mm sec^{-1} and ΔE_q = 0.45-0.58 mm sec $^{-1}$). Samples LBF and LVF contained small amounts of Fe^{2+} while an intermediate valence was observed in sample LVF. Sample LJFF was rich in goethite presenting a superparamagnetic behaviour at room temperature but order magnetically at liquid nitrogen temperature.

Key words: ^{57}Fe Mössbauer spectroscopy, chlorite, illite, kaolinite, intermediate valence

INTRODUCTION

Iron is a very widespread element in the earth's crust and usually occurs in clay materials. It exists under various form and influence on certain of their crystallographic, physicochemical and mechanical properties (Mestdagh *et al*., 1980; Sei *et al*., 2002; Andji *et al*., 2009). Iron can belong to the clay network in substitution to the elements Al^{3+}; Si^{4+}; Mg^{2+}: it is structural iron. It can also exist at the state of free phases. These very iron rich phases exist also under various forms. Some of them, having a micronic size, are in coating on the clay particles surface and generally constitute the principal colouring of the clays. They are accessible to the extraction treatment such as dithionite citrate bicarbonate (Sei *et al*., 2003).

Other phases (oxides, oxyhydroxides nanometric and ferric gel) with superparamagnetic behaviour can be trapped in clay particles. They are sometimes badly crystallized and are little detectable by X-ray diffraction. These phases are not accessible to extraction treatment (Malengreau *et al.*, 1994).

For several applications such as paper manufacturing, ceramic production, the presence of iron in the clay can cramp but for others such as geophagy, the presence of iron is beneficial because of its biological activity role. Moreover, previous studies showed that iron rich clay minerals have large surface specific area and have large phosphate adsorption capacity (Borggaard, 1982, 1983; Sei *et al.*, 2002).

The samples which are the subject of this study, come from two different deposits in the Côte d'Ivoire: Anyama and Bingerville respectively situated 10 km North-West and 12 km South-West of Abidjan.

Although, Kikouama *et al.* (2002) have characterized the clays of Bingerville in terms of structure, grain size, crystallinity and chemical composition, no further analysis concerning their iron speciation has been carried out so far. Neither does the clay of Anyama.

The aim of this study is to characterize the different forms of iron contained in these samples. We have used ^{57}Fe Mössbauer spectroscopy which provides useful information on the oxidation state, coordination number, site occupancy of iron and which is particularly appropriate to discriminate between the structural iron and the iron contained as impurity.

MATERIALS AND METHODS

Materials: The clays used in this study (Fig. 1), come from two deposits of the district of Abidjan (Côte d'Ivoire): Anyama and Bingerville. These localities are situated in the sedimentary basin and the clays are supposed to be formed after sedimentation of alluvial products eroded from the uppermost layer of the Precambrian shelf (Le Bourdiec, 1958).

Fig. 1(a-d): Photography of (a) Green clay of Anyama (AVA), (b) Yellow Lokpo (LJFF), (c) Purple Lokpo (LVF) and (d) White Lokpo (LBF) in a traditional oven for thermal treatment

The green clay of Anyama, situated in a plateau area, is commercialized by the local population for its therapeutic virtues. It is used by internal way and also by external way to treat many diseases such as whitlow, athlete foot and stomach disease. It is also used for soap production. For this study, the only one sample (labelled AVA), has been collected to about 2 m of depth from mineral deposit and dried in air as that sold. For the different analyzes the sample has been dried at 40°C during 24 h in a steam room and ground.

The clays of Bingerville, situated in the coastal lagoon, have the particularity to be eatable (generally by pregnant women) after manning. They are also used for soap preparation and other beauty care. The samples were taken from the site of exploitation according to their color; suffer the same heat treatment as those sold commonly called "Lokpo". This treatment involves heating the sample in an oven built in clay and powered by firewood for 3 to 5 days. This operation often gives the clay material a pleasant and smells appetizing. The three investigated samples are labeled as; LBF: White Lokpo, LVF: Purple Lokpo and LJFF: Yellow Lokpo.

Methods

X-Ray diffraction: X-ray diffraction patterns were recorded on a Brucker D8 diffractometer that uses Co-K_α monochromatic radiation (λ = 1.7889 Å) at ambient temperature over the domain $2 \leq 2\theta \leq 40$. Both random and oriented powder samples were investigated. The latter was obtained by the sedimentation of the clay suspension on a slide support allowing the (001) reflection intensities of the various clay minerals to be amplified in order to ease their identification.

Chemical analysis: The chemical analysis in total rock was carried out by Inductively Coupled Plasma-Atomic Emission Spectroscopy for major elements. The quantitative mineralogy was estimated using the method proposed by Yvon *et al.* (1990).

The total adsorbed and structural (structural OH) water content was determined by thermogravimetric analysis at 1200°C.

Mössbauer spectroscopy: Mössbauer spectra were recorded in standard transmission geometry in the constant acceleration mode. The source was ^{57}Co in a Rh matrix. The velocity scale was calibrated with the room temperature six-line spectrum of α-iron and all isomer shifts are given with respect to the centre of this spectrum. Low-temperature measurements were carried out in a liquid nitrogen flow cryostat.

The absorbers were prepared from approximately 1.5 g of sample powder and placed in a lead sample holder (25 mm diameter, 2 mm thick). Data were analysed by fitting Lorentzian lines to the absorption spectrum, using the ISO least-squares fit program (Kundig, 1969).

RESULTS

X-Ray diffraction

Sample of Anyama (AVA): X-ray diffraction of randomly oriented powder (Fig. 2a) showed that the sample was a mixture of chlorite (characteristic peaks at 7.3° (14.13 Å), 14.65° (7,09 Å), 21.98° (4,98 Å), 29.46° (3,54 Å)), illite (peaks at 10.27° (10 Å), 20.70° (5 Å)) and quartz (peaks at 24.30° (4,25 Å), 31.26° (3,33 Å)).

The X-ray pattern of the oriented sample (Fig. 2b) showed in addition a diffraction peak at 6.66° (15.16 Å) characteristic of smectite. The saturation of the sample with ethylene glycol provoked the swelling of the clay and the displacement of the peak to 6.02° (17 Å) with a high intensity (Fig. 2c). Note that no iron oxide was detected in the sample.

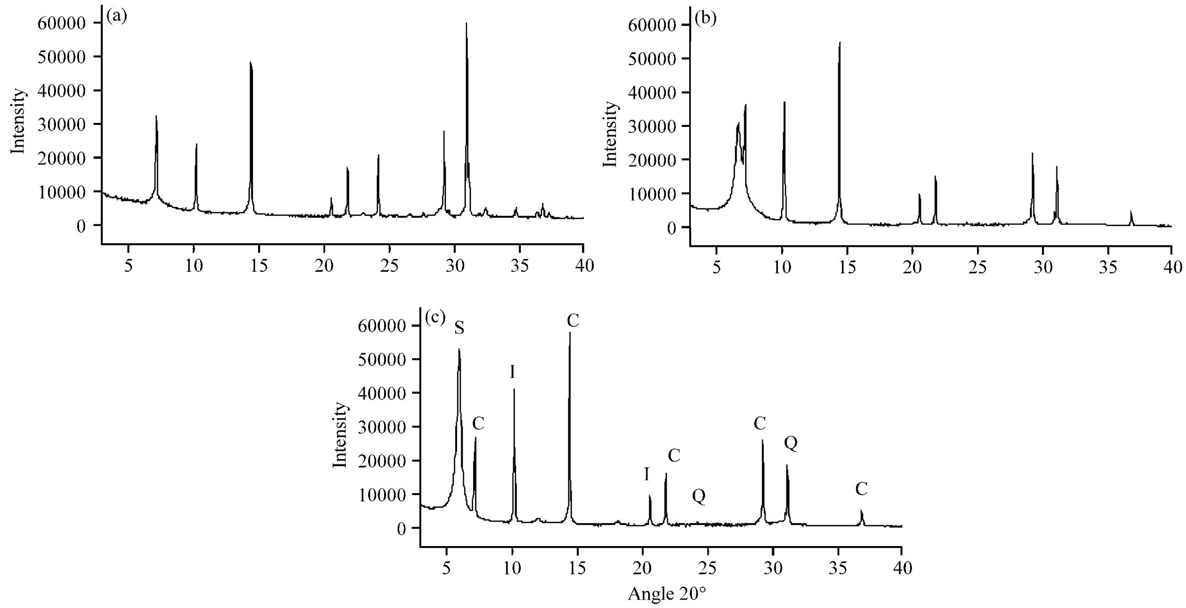

Fig. 2(a-c): Diffractograms of (a) Powder sample (b) Oriented sample and (c) Sample AVA saturated with ethylene glycol, S: Smectite, C: Chlorite, I: Illite, Q: Quartz

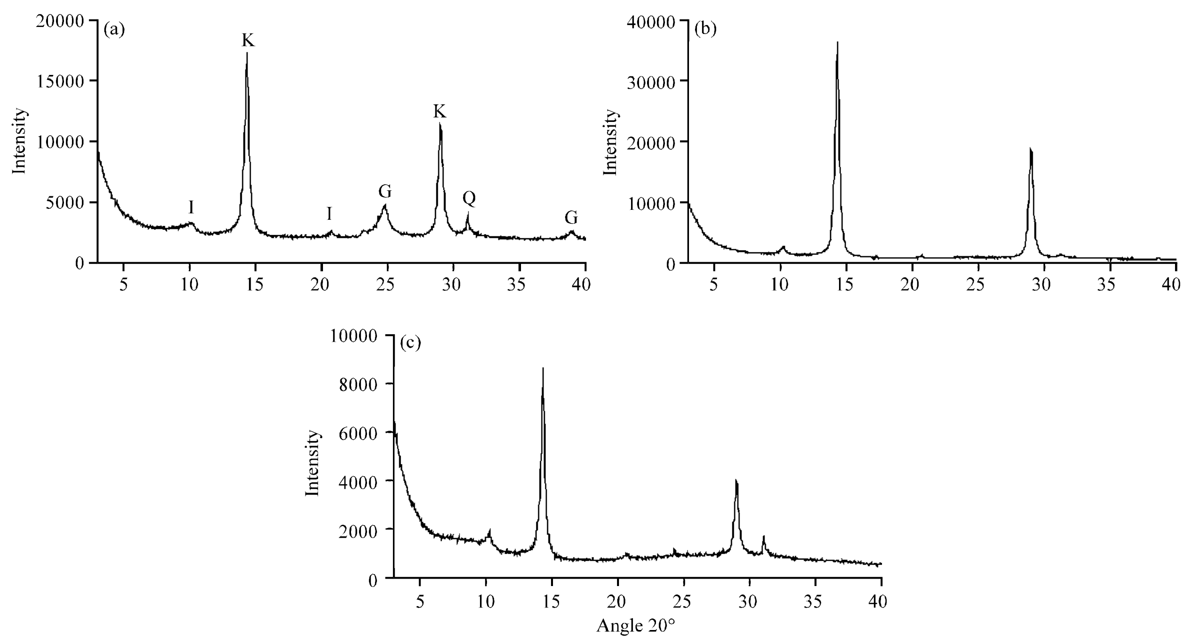

Fig. 3(a-c): Diffractograms of (a) LJFF, (b) LVF and (c) LBF samples from Bingerville, I: Illite, K: Kaolinite, G: Goethite, Q: Quartz

Samples of Bingerville (LBF, LVF and LJFF): X-ray diffraction of the oriented samples (Fig. 3) showed that kaolinite (peaks at 14.38° (7.15 Å) and 29.06° (3.58 Å)) was the dominant mineral phase in all samples with impurities of quartz and illite. Sample LJFF showed additional reflections of goethite (α-FeOOH).

Chemical analysis: The major elements found in all samples were Si, Al and Fe (Table 1). Sample AVA contained significant quantity of Mg and K due to the presence of chlorite, smectite and illite. The high quantity of Si can be explained by the presence of quartz as supported by X-ray diffraction.

Sample LJFF was particularly iron rich (26% Fe_2O_3). This was due to the important quantity of goethite detected by X-ray diffraction.

Quantitative analysis: On the basis of the results of X-ray diffraction and chemical analysis, the mineral composition calculated for each sample is given in Table 2.

The quartz was very abundant in the sample AVA whereas illite and chlorite were in proportion 2:3. Although the sample contained important quantity of iron (7.4% Fe_2O_3), no iron oxide was detected. The smectite composition was lower comparatively to illite and chlorite.

The samples from Bingerville were dominated by kaolinite. LVF was richer in kaolinite followed by LBF and finally LJFF. The later was very rich in goethite.

^{57}Fe Mössbauer spectroscopy: The two main hyperfine parameters of Mössbauer spectroscopy are the isomer shift δ and the quadrupole splitting ΔE_q.

The isomer shift δ is a direct measure of the total electronic density at the probe nucleus (Rancourt, 1998). It is sensitive not only to oxidation state but also to the coordination number of the ions. For Fe^{3+}, δ decreases with a decrease in coordination number as a result of an increase in the covalent character of the bonding (Goodman *et al.*, 1976). Room temperature isomer shifts (relative to metallic α-Fe) for the main valence states are: $\delta(Fe^0) \approx 0.0\text{-}1.3$ mm sec^{-1}; δ $(Fe^{3+}) \approx 0.2\text{-}0.4$ mm sec^{-1}.

The quadrupole splitting ΔE_q, is a measure of the electric field gradient at the ^{57}Fe nucleus and so, has a strong relation to site symmetry and local structure (Goodman *et al.*, 1976). Room temperature ΔE_q ranges are: ΔE_q (Fe^{2+}) = 1.5-3.0 mm sec^{-1} and ΔE_q (Fe^{3+}) = 0.0-0.15 mm sec^{-1}.

Mössbauer spectra of phyllosilicates consist of one or more doublets ensuing from Fe in di-or trivalent state and, where, applicable, on different structural sites (Murad, 1998). Fe^{3+} can not only

Table 1: Chemical composition of the samples

		Conc. (Wt. %)										
Samples	Colour	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	H_2O
AVA	Green	61.58	17.21	7.42	0.08	3.84	0.04	0.46	2.38	0.75	nd	5.74
LBF	White	52.83	29.74	2.34	nd	0.29	nd	0.11	1.17	1.06	0.08	12.03
LVF	Purple	45.73	34.41	4.92	nd	0.07	nd	0.06	0.57	1.12	0.09	13.12
LJFF	Yellow	42.71	18.33	26.02	nd	0.14	nd	0.05	0.63	0.87	0.12	11.69

Nd: Not determined, AVA: Green clay of Anyama, LBF: White Lokpo, LVF: Purple Lokpo, LJFF: Yellow Lokpo of Bingerville

Table 2: Relative quantification of minerals in the samples

	Minerals composition (%)						
Samples	Kaolinite	Illite	Chlorite	Smectite	Quartz	Goethite	Others
AVA	...	20.17	29.53	2.5	40.5	-	7.27
LBF	66.79	9.73	-	-	17.06	2.34	4.08
LVF	83.61	4.74	-	-	4.43	4.92	2.41
LJFF	41.86	5.28	-	-	20.67	26.02	6.17

AVA: Green clay of Anyama, LBF: White Lokpo, LVF: Purple Lokpo, LJFF: Yellow Lokpo of Bingerville enter the octahedral but also substitute to some extent for Si^{4+} (ionic radius 26 pm) in the tetrahedral. Fe^{2+} has a significant larger ionic radius and therefore fits only in the octahedral.

Sample from Anyama (AVA): The room temperature Mössbauer spectrum of the sample (Fig. 4) is characterized by asymmetry of two strong resonance absorption lines, corresponding to ferrous iron Fe^{2+} in two distorted octahedral sites characterized by $\delta = 1.13$ mm sec^{-1} and $\Delta E_q = 2.65$ sec^{-1} for the first; $\delta = 1.09$ mm sec^{-1} and $\Delta E_q = 2.34$ mm sec^{-1} for the second (Table 3). Part of asymmetry

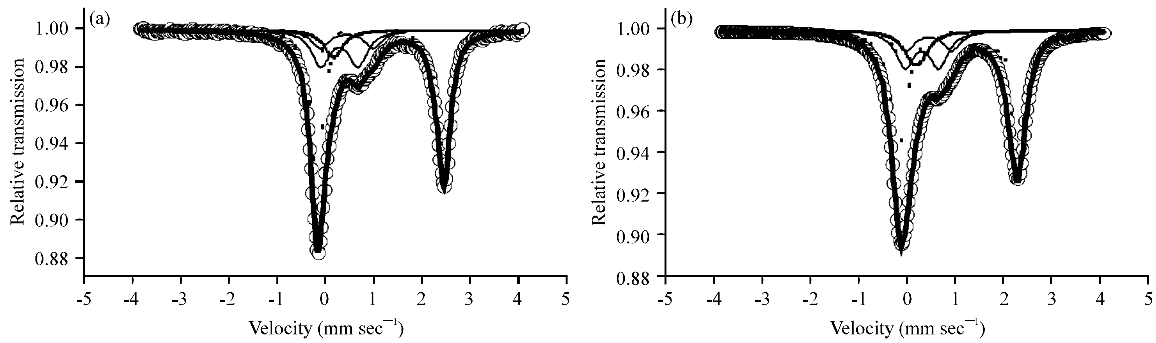

Fig. 4(a-b): ^{57}Fe Mössbauer spectra of the sample AVA recorded at (a) 300 and (b) 80 K, Scatter points: Experimental data, Thick solid line: Fitted curve, Thin solid line: Fitted doublets Fe^{3+} ions, Short Dot: fitted doublets Fe^{2+} ions

Table 3: ^{57}Fe Mössbauer parameters of the samples

Samples	Temp. (K)	δ (mm sec^{-1})	ΔE_q (mm sec^{-1})	2Γ (mm sec^{-1})	C (%)	H (T)	Assignment
AVA	300	0.434	1.106	0.457	10.0	...	Str. Fe^{3+}
		0.277	0.776	0.457	19.4	...	Str. Fe^{3+}
		0.150	0.161	0.457	7.7	...	Str. Fe^{3+}
		1.131	2.651	0.313	55.4	...	Str. Fe^{2+}
		1.093	2.343	0.312	7.5	...	Str. Fe^{2+}
	80	0.510	1.115	0.538	9.2	...	Str. Fe^{3+}
		0.338	0.822	0.538	16.7	...	Str. Fe^{3+}
		0.187	0.223	0.538	9.5	...	Str. Fe^{3+}
		1.224	2.927	0.465	49.1	...	Str. Fe^{2+}
		1.206	2.600	0.464	15.6	...	Str. Fe^{2+}
LBF	300	0.369	0.576	0.424	93.4	...	Str. Fe^{3+}
		1.026	2.387	0.285	6.6	...	Str. Fe^{2+}
	80	0.419	0.501	0.790	94.25	...	Str. Fe^{3+}
		1.247	2.807	0.284	5.75	...	Str. Fe^{2+}
LVF	300	0.411	0.454	0.552	78.21	...	Str. Fe^{3+}
		0.653	1.479	0.476	12.94	...	$Fe^{2.5+}$ (i.v.)
		1.060	2.502	0.504	8.84	...	Str. Fe^{2+}
	80	0.461	0.425	0.629	81.23	...	Str. Fe^{3+}
		0.793	1.763	0.671	8.28	...	$Fe^{2.5+}$ (i.v.)
		1.119	2.779	0.671	10.49	...	Str. Fe^{2+}
LJFF	300	0.367	0.529	0.663	100	...	Fe^{3+}-O_6
	80	0.433	0.551	0.642	40	...	Str. Fe^{3+}
		0.474	-0.131	0.613	47.84	48	α-FeOOH
		0.493	-0.124	0.613	11.15	44	α-FeOOH

Str.: Structural, δ: Isomer shift with respect to α-Fe at room temperature, ΔE_q: Quadrupole splitting, 2Γ: Full width at half maximum, C: Relative contribution of subspectrum to total absorption, H: Magnetic hyperfine field in Tesla (T), i.v. denotes an intermediate valeuce state +2.5

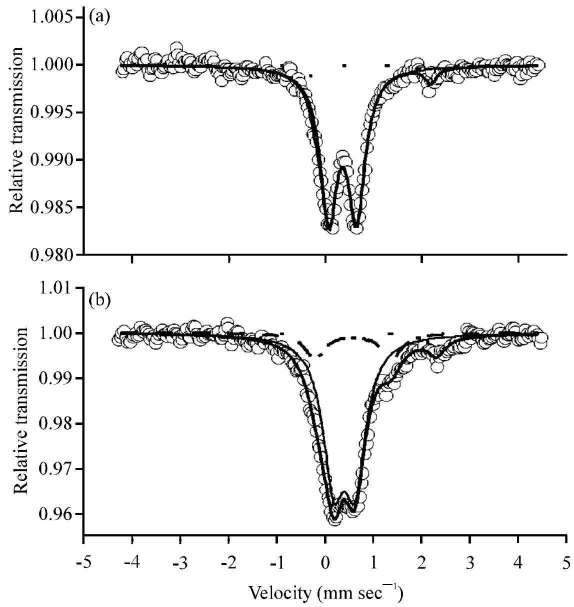

Fig. 5(a-b): ^{57}Fe Mössbauer spectra of the samples (a) LBF and (b) LVF recorded at 300 K, Scatter points: Experimental data, Thick solid line: Fitted curve, Thin solid line: Fitted doublets Fe^{3+} ions, Short Dot: Fitted doublets Fe^{2+} ions, Dash dot: Fitted doublets $Fe^{2.5+}$ ions

due to ferric contributions that can be fitted using 3 doublets representing 37% of the total absorption. It corresponded to ferric iron Fe^{3+} in two distorted octahedral sites characterized by $\delta = 0.43$ mm sec^{-1} and $\Delta E_q = 1.1$ mm sec^{-1} for the first; $\delta = 0.28$ mm sec^{-1} and $\Delta E_q = 0.78$ mm sec^{-1} for the second and a tetrahedral site of low contribution with $\delta = 0.15$ mm sec^{-1} and $\Delta E_q = 0.16$ mm sec^{-1}. The room temperature Mössbauer spectra of Illite-Chlorite recorded by Wagner *et al.* (1990) were dominated by Fe^{2+} with minor contribution of Fe^{3+} and is like that of AVA which is also dominated by illite-chlorite. No significant change was observed in the spectra recorded at liquid nitrogen temperature.

Samples from Bingerville

Samples LBF and LVF: Mössbauer spectra of samples LBF and LVF are shown in Fig. 5. The most intense doublet was characteristic of Fe^{3+} located in a distorted octahedral environment of oxygen anions. A further doublet, of low contribution (6-8%) and characterized by an isomer shift of $\delta = 1.03$ mm sec^{-1} and a quadrupole splitting of $\Delta E_q = 2.4$ mm sec^{-1} for LBF ($\delta = 1.06$ mm sec^{-1} and $\Delta E_q = 2.5$ mm sec^{-1} for LVF) (Table 3), corresponded to a structural Fe^{2+} in a distorted octahedral site.

A third doublet, representing about 13% of the total absorption, was clearly resolved in the room-temperature spectra of LVF. The Mössbauer parameters of $\delta = 0.65$ mm sec^{-1} and $\Delta E_q = 1.48$ mm sec^{-1} are unusual for iron in kaolinite. We attributed this doublet to an intermediate valence state of +2.5 resulting from a rapid electron exchange between Fe^{2+} and Fe^{3+} sites. This assignment is supported by the fact that its hyperfine parameters δ and ΔE_q are exactly the arithmetic average of the Fe^{2+} and Fe^{3+} hyperfine parameters of the sample. Moreover, the compilation of ^{57}Fe isomer shifts in a large number of oxides (Menil, 1985) showed that the values of $\delta = 0.60$ mm sec^{-1} lie well outside and exactly between the typical domains for Fe^{2+} and Fe^{3+}.

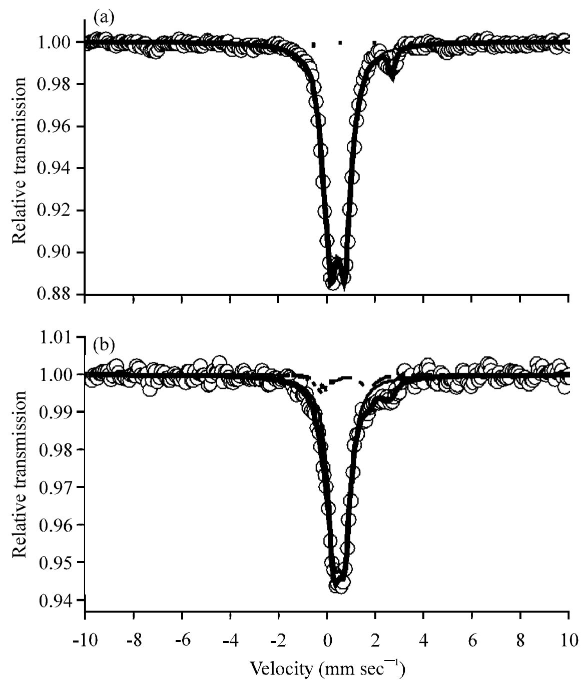

Fig. 6(a-b): ^{57}Fe Mössbauer spectra of the samples (a) LBF and (b) LVF recorded at 80 K, Scatter points: Experimental data, Thick solid line: Fitted curve, Thin solid line: Fitted doublets Fe^{3+} ions, Short dot: Fitted doublets Fe^{2+} ions, Dash dot: Fitted doublets $Fe^{2.5+}$ ions

An interpretation of this subspectrum as a sextuplet with low hyperfine magnetic splitting as would be observed in the case of relaxation effects in small particles of iron oxides/hydroxides can be ruled out. No tendency towards an increased six-line splitting is observed at liquid nitrogen temperature (Fig. 6).

Sample LJFF: The sample differed from the two others by its high iron content. The room temperature Mössbauer spectrum recorded is shown in Fig. 7. It consisted of a broad doublet upon the curved base line. The parameters of the doublet are typical for Fe^{3+} octahedrally coordinated by oxygen. The curved baseline is caused by the super paramagnetic behaviour of small particles of α- FeOOH (goethite) showed by X-ray diffraction to be present in considerable concentration. This was illustrated by the spectrum recorded at 80 K where, in additional to the doublet, a broad and asymmetric (in particular the outer ones) six-line spectrum characteristic of poor crystallised goethite was obtained. The latter can be fitted using two subspectra characterized by isomer shift δ = 0.474-0.493 mm sec^{-1} and ΔE_q = 0.124-0.131 mm sec^{-1} and hyperfine magnetic field H = 44-48 T.

The reported magnetic hyperfine splitting for pure goethite at 77 K is 439.8 T (Menil, 1985). The lower value with respect to this data can be explained by a distribution of particle sizes with some particles still exhibiting super paramagnetic behaviour and/or the presence of aluminium atoms substituting for iron in the goethite lattice which also reduces the local magnetic field at the iron nuclei (Golden *et al*., 1979; Goodman and Lewis, 1981; Murad, 1982; Fysh and Clark, 1982).

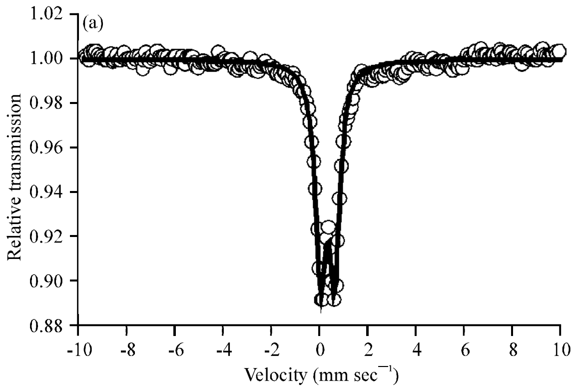

Fig. 7(a-b): ^{57}Fe Mössbauer spectra of the samples LJFF recorded at (a) 300 and (b) 80 K, Scatter points: Experimental data, Thick solid line: Fitted curve, Thin solid line: Fitted doublets Fe^{3+} ions, Very thin solid line: Fitted sextets (α-FeOOH)

DISCUSSION

The clays of the two investigated deposits showed differences in their mineralogy and their iron statutes, thus reflecting different weathering conditions.

Ferric and ferrous iron are known to exist in many layer silicate minerals. Their exact lattice position however, is difficult to determine.

The sample of Anyama, situated in a plateau area, is characterized by 2:1 minerals with dominant ferrous ions. Chlorite, the dominant clay mineral observed in the sample is unusual in humid tropical regions where kaolinite is by far, the occurred clay mineral (Velde, 1992).

The best fit of Mössbauer spectra revealed Fe^{2+} in two octahedral sites with $\delta = 1.13$ mm sec^{-1} and $\Delta E_q = 2.65$ mm sec^{-1} for the first; $\delta = 1.09$ mm sec^{-1} and $\Delta E_q = 2.34$ mm sec^{-1} for the second and Fe^{3+} in two octahedral sites with $\delta = 0.43$ mm sec^{-1} and $\Delta E_q = 1.1$ mm sec^{-1} for the first; $\delta = 0.28$ mm sec^{-1} and $\Delta E_q = 0.78$ mm sec^{-1} for the second and one tetrahedral site with relative low contribution (7.7%) characterized by $\delta = 0.15$ mm sec^{-1} and $\Delta E_q = 0.16$ mm sec^{-1}.

The parameters obtained agreed very well with those found in literature (Taylor *et al*., 1968; Kodama *et al*., 1982; Menil, 1985; Grave *et al*., 1987).

According to Rancourt *et al*. (1992) spectral components of Fe^{3+} in tetrahedral position should be characterized by an isomer shift $\delta = 0.17$ mm sec^{-1} and quadrupole splitting $\Delta E_q = 0.5$ mm sec^{-1} with respect to α-Fe standard. The isomer shift found in our study ($\delta = 0.15$ mm sec^{-1}) agreed with this value but the quadrupole splitting $\Delta E_q \approx 0.2$ mm sec^{-1} is lower, indicating that the tetrahedral site is less distorted. Ferrage *et al*. (2003) also found a small quadrupole splitting at ≈ 0.25 mm sec^{-1} for tetrahedral Fe^{3+} in the chlorite of Piemont (Italy).

Because chlorites are minerals which have many varieties, their Mössbauer spectra present slight differences. Manning *et al*. (1980) and Das *et al*. (1986) conclude that iron in chlorite is present in the Fe^{2+} state. Malczewski *et al*. (2004) and Kodama *et al*. (1982) solved their spectra with Fe^{2+} ions in two octahedral sites and Fe^{3+} in one octahedral site. Shabani (2009) fitted with Fe^{2+} in one octahedral site and Fe^{3+} also in one octahedral site. For his part, Taylor *et al*. (1968) detected Fe^{3+} in both octahedral and tetrahedral sites of the studied chlorites. Goodman and Bain (1979) also found tetrahedrally coordinated Fe^{3+} in some chlorite samples. Ferrage *et al*. (2003) found more tetrahedral Fe^{3+} (23%) than octahedral Fe^{3+} (9%) in the chlorite of Piemont (Italy). Present results that are a sort of synthesis of these observations, support and complete these previous works.

In layer silicate minerals both Fe^{2+} and Fe^{3+} ions occupy octahedral sites (in rare cases, there may also be tetrahedral Fe^{3+}) in these minerals where one distinguishes a total of three M sites per formula unit in the octahedral sheet: Two M1 sites in which the hydroxyls occupy the corners of the octahedral (trans) and one M2 site in which they are adjacent to another (cis).

In the dioctahedral species such as illite, two of the three sites are filled, leaving the M2 site vacant. In trioctahedral minerals such as talc, all three M sites are occupied.

In the case of chlorite, there is another octahedral site M3 in the interlayer hydroxide sheet.

Some authors (Grave *et al.*, 1987; Pal *et al.*, 1992; Lougear *et al.*, 2001) attribute Fe^{2+} in M1, M2 and M3 in chlorite and ignore Fe^{3+} distribution because of it's relative small amount. We think that these assignments are problematic and must be supported by X-ray or electron diffraction which indicates the nature and the proportion of the sites occupied.

As previously mentioned, chlorites have many varieties. There are dioctahedral chlorites and trioctahedral chlorites which also differ by the character of the interlayer sheet. We share the viewpoint of Rancourt (1994): no definitive conclusion can be drawn about the relative occupation of these sites.

Samples from Bingerville were dominated by kaolinites as clay minerals. Kaolinites, $Si_2Al_2O_5(OH)_4$, usually have relatively low iron contents. Their Mössbauer spectra generally consisted to a doublet characteristic of trivalent iron in octahedral coordination, isomorphous substituting for Al^{3+}. Certain samples presented a few contribution of divalent iron (Rozenson *et al.*, 1979; Coey, 1980; Tim *et al.*, 1992).

Mössbauer spectra recorded for these samples agreed with these observations and generally consisted to a broad doublet more or less asymmetric characteristic of Fe^{3+} in distorted octahedral site. Except LJFF, Fe^{2+} ions were observed in the two others samples.

The observation of the intermediate valence characterized by δ = 0.653 mm sec^{-1} and ΔE_q = 1.479 mm sec^{-1} in the purple Lokpo (LVF) is quite original because this degree of oxidization is unusual in the clay minerals.

The isomer shifts and quadrupole splittings obtained for Fe^{2+} (δ = 1.03-1.06 mm sec^{-1}; ΔE_q = 2.4-2.5 mm sec^{-1}) and Fe^{3+} (δ = 0.37-0.4 mm sec^{-1}; ΔE_q = 0.45-0.58 mm sec^{-1}) agreed very well with those found for numerous other natural kaolinites (δ = 0.3-0.53 mm sec^{-1} and ΔE_q = 0.4-0.7 mm sec^{-1} for Fe^{3+} and δ = 1.0-1.3 mm sec^{-1}, ΔE_q = 2.1-2.4 mm sec^{-1} for Fe^{2+}) (Bonnin *et al.*, 1982; Fysh *et al.*, 1983; Murad and Wagner, 1991; Tim *et al.*, 1992; Castelein *et al.*, 2002).

Cuttler (1980) showed that the ΔE_q of structural Fe^{2+} in kaolinite never exceeds 2.54 mm sec^{-1} and we supposed that the observed Fe^{2+} ions are structural.

Most of the samples (except LJFF) are designed to hold only structural iron. Research is underway to estimate the amount of structural iron.

CONCLUSION

This study permitted us to obtain information on the statutes of iron in the clays of the two investigated deposits. The clays differed by their mineralogy and their iron chemical state.

Although the green clay of Anyama contained significant amount of iron, it's very poor in iron oxides. It is dominated by illite-chlorite and is characterized by the predominance of divalent iron in octahedral coordination. The Fe^{3+} ions representing 37% of the total absorption are localized in both octahedral and tetrahedral sites. The absence of iron oxides allowed us to conclude that the majority of iron belongs to the clay network.

The clays from Bingerville present a high diversity. Contrary to LBF and LVF, sample LJFF is very rich in iron and contains important quantity of goethite. All the samples are dominated by kaolinites and are characterized by the predominance of trivalent iron in distorted octahedral site. The presence of iron oxides in these samples allowed us to conclude that only a few part of the total iron belongs to the kaolinite structure.

On the basis of their mineralogical and their chemical differences, we can admit that the clays of the two localities differ by their genesis conditions and the properties of their mother rocks.

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