Journal de la Société Ouest-Africaine de Chimie

J. Soc. Ouest-Afr. Chim.

Code Chemical Abstracts : JSOCF2

Cote INIST (CNRS France) : <27680>

ISSN 0796-6687

17ème Année, Décembre 2012, N° 034

Site Web: http://www.soachim.org

Note

Mineralogy, geochemistry of clay raw material from Ivory Coast (West Africa) used as pharmaceutical products

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(Reçu le 23/06/2012 – Accepté après corrections le 15/12/2012)

Abstract: The present article aims to determine the geochemistry and the mineralogical compositions of clay samples from Aboutou's office that are used to heal affections of digestive system, skin diseases, wounds etc. The investigation made by X-ray diffraction, chemical analysis using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) shows that the clays AK1 and AK2 arise from different source rocks and are mainly composed by kaolinite, quartz and illite. The difference between the two clays is the presence of goethite in AK2 and a small amount of montmorillonite in AK1. Based on these compositions AK1 and AK2 can be used effectively as antidiarrheal, laxative, in the protection of intestinal mucous membrane and as skin protector.

Keywords: kaolinite, illite, quartz, geochemistry, mineralogy

Résumé : Ce présent article a pour objet de déterminer les compositions géochimique et minéralogique des échantillons d'argiles provenant de l'atelier d'Aboutou Poterie, utilisés pour guérir les maladies du système digestif, de la peau, les plaies etc.
Les investigations menées au moyen de la diffraction des rayons X (DRX), de l'analyse chimique par ICP-AES et ICP-MS, montrent que les argiles AK1 et AK2 proviennent de roches mères différentes et sont principalement composées de kaolinite, de quartz et d'illite. Ces deux argiles diffèrent par la présence de goethite dans AK2 et par une faible quantité de montmorillonite dans AK1. Du fait de leur composition minéralogique, AK1 et AK2 peuvent être utilisés effectivement comme antidiarrhéique, laxatif et comme protecteur dermatologique et gastrointestinal.

Mots clés : kaolinite, illite, quartz, géochimie, minéralogie

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1. Introduction

The use of clays for therapeutic purposes dates since prehistoric [1- 3]. In Africa and particularly in Ivory Coast [4, 5], clay is used alone or in association with sheets in traditional pharmacopeia.

However, these clays are unknown from the point of view of their geochemistry and mineralogical compositions.

This study deals with the determination of the geochemistry and the mineralogical composition of clays AK1 and AK2 that are used in the cure of digestive system, skin diseases, wounds etc. in order to estimate their possible therapeutic potential.

2. Materials and methods

2.1. Materials and geological setting

The two clays referenced AK1 and AK2 have been collected in Aboutou's Pottery office which is a center of naturotherapy recognized officially by the state of Ivory Coast since August 06th, 2009 under the number: MSHP /PNPMT / N° 2355. At Aboutou's office, AK1 and AK2 are used for affections of the digestive system, skin diseases, wounds, etc. as well by internal ways as external's.
They are from the Bocanda region in the center part of Ivory Coast (Figure 1). This area belongs to the Paleoproterozoic domain of the Man shield [6- 8]. It is composed of Paleoproterozoic formations, the so-called Birimian formations that form major parts of the West African craton [7]. The Birimian terranes form narrow sedimentary basins and linear or arcuate volcanic belts corresponding to a period of accretion between 2.25 and 2.05 Ga [9-12] during the Eburnean orogeny and was coeval with the emplacement of large granitoid plutons [13-15]. The Bocanda area is mainly composed of metaarenite with biotite bearing granitoid intrusions [16].

2.2. Experimental methods

- X-rays diffraction of the powder was carried out using oriented preparation by reflexion with a Brucker D8 device using the cobalt $K\alpha_1$ radiation.
- Bulk-rock chemical analysis was obtained by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for major elements and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) for trace elements, after fusion with $LiBO_2$ and dissolution in HNO_3. Analytical conditions and limits of detection are found by Carignan & al. [17].

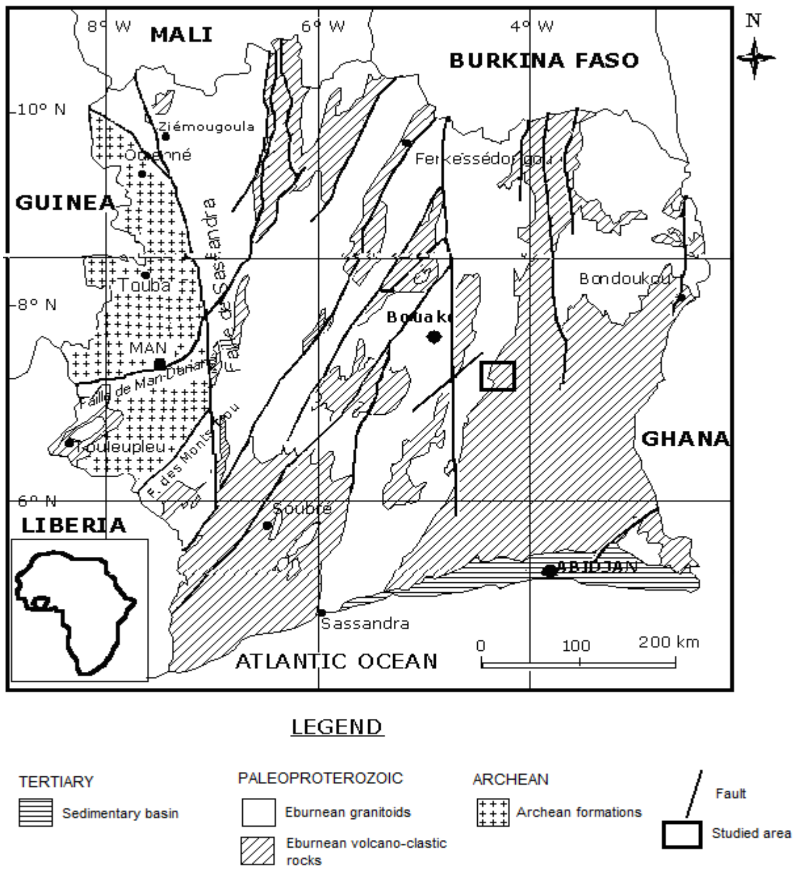

Figure 1: Geological map of Ivory Coast with location of the studied area [6,18]

3. Results and discussion

3.1. Geochemistry

The chemical composition of the two clay samples is variable (Table I, II and III). The clays exhibit very high values of LOI (9 and 11.8 wt%, Table I).

3.2. Major elements.

The two clay samples (AK 1 and AK 2) are mainly made of silica (62 and 52 wt% SiO_2), associated with an appreciable amount of alumina (16.8 and 22.1 wt% Al_2O_3) and iron (8.5% and 10.9 wt% Fe_2O_3) and feeble content of K_2O (2.14 and 1.59 wt %). These results let to think that quartz, alumino-silicates compounds and iron minerals seem to predominate in the samples. However, the two clays exhibit several compositions differences. In fact, sample AK1 clearly show higher content in SiO_2, MgO and K_2O than sample AK2. On the contrary, AK1 indicate lower contents in Al_2O_3, Fe_2O_3 and TiO_2.

3.3. Trace elements

Trace element contents are very variable in the two clay samples. This is true both for the elements considered as toxic (As, Ba, Cd, Co, Cu, Ni, Pb, Sb, Zn) [19-23] and those considered less dangerous (Cr, Mo, Rb, Sr, V, Zr, REE). The Th/Zr diagram (Figure 2) indicates that the two clays are different. Ba (361 and 299.5 ppm), W (296 and 183.4 ppm), Zr (125.1 and 254.3 ppm), V (122.9 and 135.3 ppm), Cr (120.5 and 122.5 ppm) and Rb (83.81 and 74.42 ppm) present the higher contents. The two clays show relatively low content in REE.(**Figure 3**) AK1 have REE content of 101 ppm higher than that of AK2 (ΣREE 80 ppm). Rare earth element patterns for the analyzed clays are similar and are weakly fractionated ($La_{[N]}/Yb_{[N]}$=6.5 and 7.3). They show negative minor Eu anomalies (Eu/Eu*=0.89 for AK1 and 0.77 for AK2). Y contents are also relatively weak.

It’s established that major elements such as Si, Na, K, Ca and some traces elements (such as Rb, Ba, Sr,…) are easily mobilized by alteration. However, elements like Al, Ti, Zr, Hf, Th, and rare REE are known to be relatively immobile during alteration.

Differences generally important in most of the immovable element (Zr, Th, Hf, Al, Ti) seem to indicate that these two clays arise from different source rocks.

Table I. Whole rock major element compositions (%) of clays from Bocanda

	SiO2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	PF	Total
AK1	61.99	16.78	8.47	0.02	1.23	0.15	0.13	2.14	0.77	0.06	8.96	100.69
AK2	52.24	22.13	10.85	0.03	0.23	0.28	0.06	1.59	0.93	0.09	11.79	100.22

Table II. Whole rock trace element compositions (ppm) of clays from Bocanda

	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Ga	Ge	Hf	In	Mo
AK1	20.56	361.3	1.06	0.25	<D.L.	56.24	120.5	3.33	54.39	19.37	1.79	3.41	<L.D	0.68
AK2	15.42	299.5	1.05	0.27	0.20	30.83	122.5	4.2	39.11	26.94	1.66	6.56	<L.D.	2.53

Table II (continued)**.** Whole rock trace element compositions (ppm) of clays from Bocanda

	Nb	Ni	Pb	Rb	Sb	Sn	Sr	Ta	Th	U	V	W	Y	Zn	Zr
AK1	5.81	47.82	10.26	83.81	0.22	1.23	64.7	1.35	3.67	1.19	122.9	296	16.08	64.32	125.1
AK2	14.02	26.45	14.34	74.42	1.51	2.29	66.76	1.74	9.75	2.64	135.3	183.4	11.32	32.97	254.3

< L.D :limite detection

Table III: Whole rock REE compositions (ppm) of clays from Bocanda

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
AK1	20.55	38	5.29	20.53	4.01	1.07	3.33	0.52	3.09	0.60	1.79	0.28	1.90	0.30
AK2	15.01	36.39	3.54	13.45	2.67	0.60	2.15	0.33	2.03	0.41	1.29	0.21	1.57	0.27

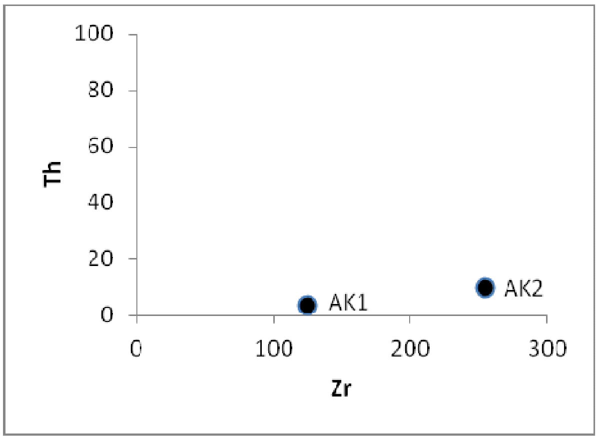

Figure 2: Plot of the clay samples Zr against Th

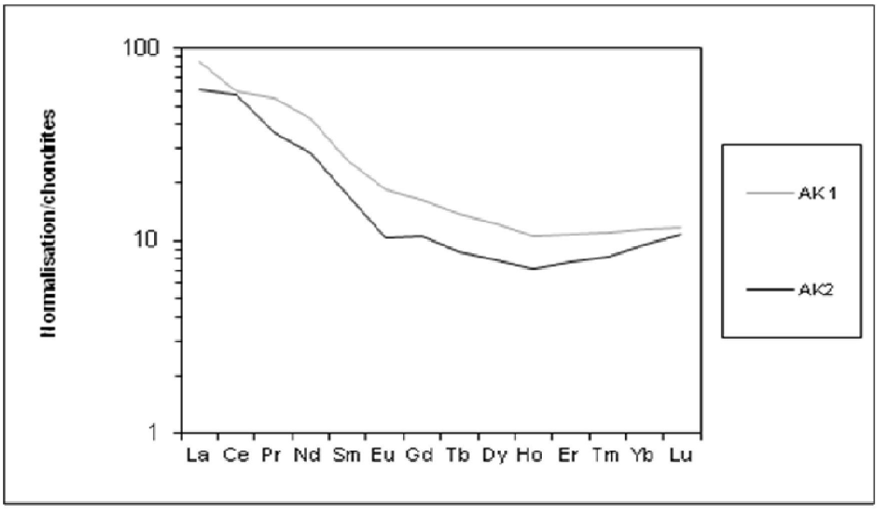

Figure 3 : Chondrite – normalized REE paterns of the two clay samples
Chondrite analysis are from Evensen and al.[24]

3.4. Mineralogy

3.4.1. X-rays diffraction

Figure 4, 5, 6 and **7** give diffractograms of raw and treated samples of AK1 and AK2.The diffractogram of raw material (figure 4, 5) permit, according to references [25,26] the detection of montmorillonite, illite, kaolinite associate to quartz for AK1 and kaolinite and illite associate to quartz and goethite for AK2. As we can note, these mineral phases are usually present in clay from Ivory Coast [27-32].

The diffractogram of treated samples indicates the presence of montmorillonite, illite and kaolinite in AK1's and the presence of kaolinite and illite in AK2's fine fractions. These results show that the mineral phases, kaolinite and illite, are the major minerals in the two samples. Montmorillonite is present only in AK1. Quartz and goethite, present in the samples, are present only in the unrefined granulometry.

3.4.2. Semi- quantitative composition of the crystallized mineral phases

The results of semi-quantitative composition were obtained according to Yvon's & al. methodology [33]. The method of calculation uses the composition of the mineral kaolinite $Si_2O_5Al_2(OH)_4$, quartz SiO_2 , montmorillonite $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2$, illite $KAl_2(Si_3Al)O_{10}(OH)_2$ and goethite FeO.OH. The crystalline mineral phases percentage contained in the sample is given at table IV. The result obtained shows that, the main minerals in AK1 and AK2 are kaolinite (22.6-43%) and illite (18-13.5%) which is in agreement with loss on ignition (9-11.8%) and the diffractograms. The proportion of quartz respectively 41% and 26% in AK1 and AK2 is important as we noted in the XRD diagrams. The amount of goethite (12%) present only in AK2 is appreciable and it is in agreement with what have been seen in the diffractograms. Montmorillonite amount (6.5%), present only in AK1, is noticeable.

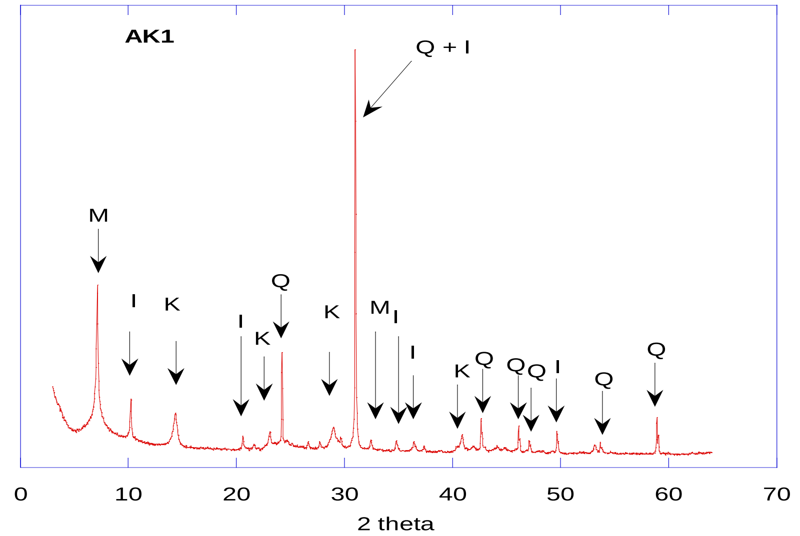

Figure 4: Diffractogram of raw fraction of sample AK1
I=illite, M=montmorillonite, K=kaolinite, Q=quartz

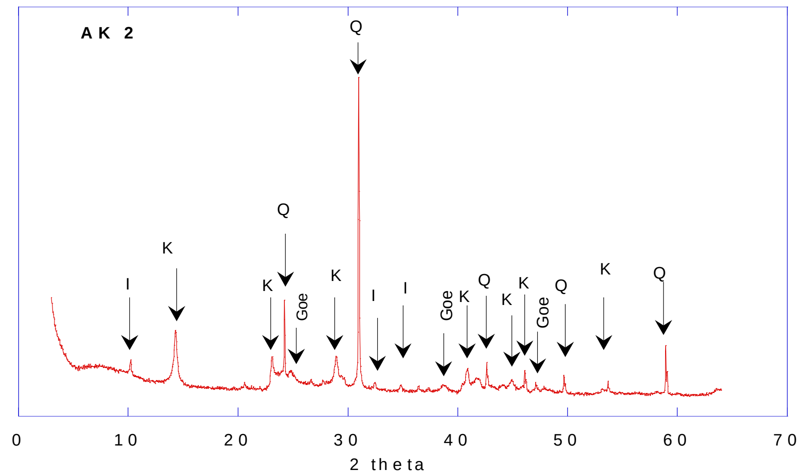

Figure 5: Diffractogram of raw fraction of sample AK2
Goe=goethite

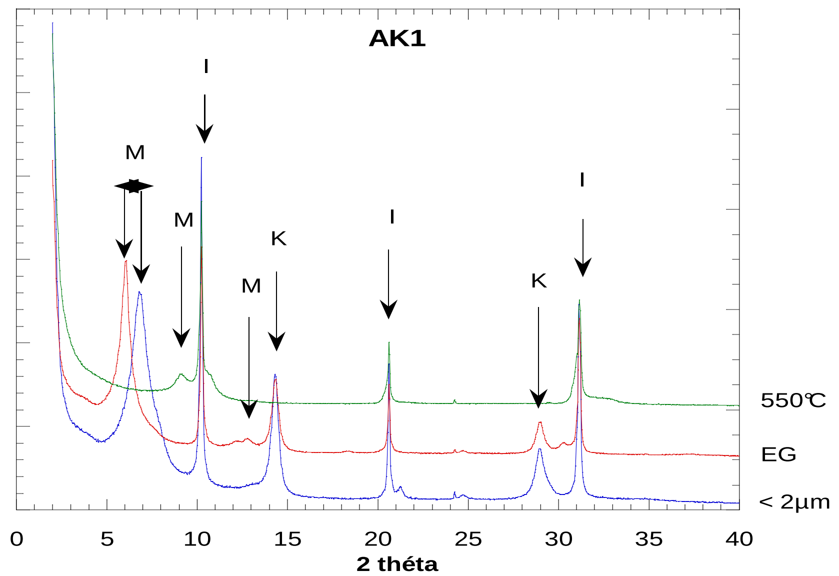

Figure 6 : Diffractograms of treated fractions of sample AK1
EG= ethylene glycol

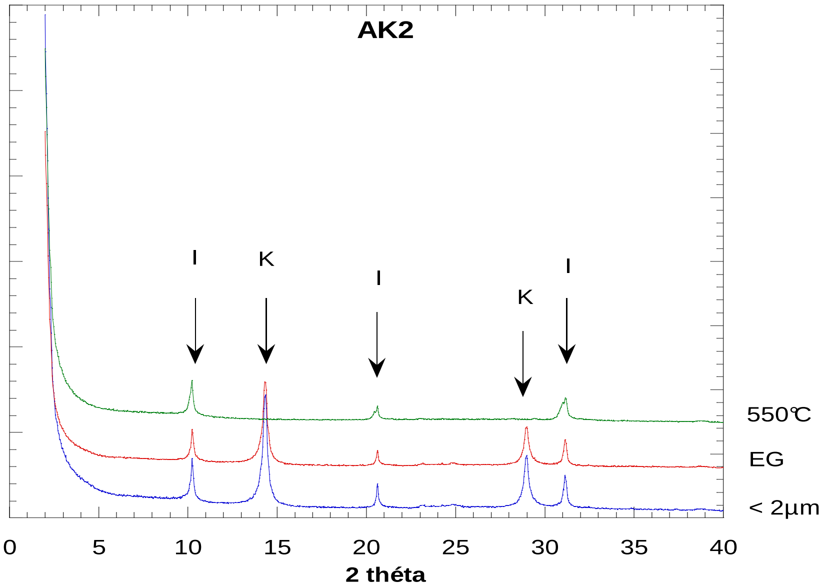

Figure 7 : Diffractograms of treated fractions of sample AK2

Table IV: the crystalline mineral phases percentage contained in AK1 and AK2

Sample	K	Quartz	Goethite	Illite	M	Total
AK1	22,58	41,14		18,098	6,528	88,346
AK2	42,96	26,16	12,074	13,44		94,634

4. Conclusion

The exploitation of the results obtained by using chemical analysis, X-ray diffraction show that the samples AK1 and AK2 arise from different source rocks and are mainly constituted of kaolinite (22.6-43%), quartz (41-26%) and illite (18-13.5%). Goethite (12%) is also present in AK2. Beside the proportion of montmorillonite in AK1 is in less importance (6.5%).

Because of the presence of kaolinite and illite in AK1 and AK2, these clays can be used effectively as gastrointestinal protectors and antidiarrhoeaics [1, 23]. They can also be used as cataplasm and participate in formulations used for topical applications in both dermopharmacy and dermocosmetics [23].

The presence of montmorillonite in AK1, can allow it use as antiseptic, excipients in the bioavailability of the active principle and remineralizing [1].

On the other hand, considering the important presence of quartz in AK1 and AK2 (41 % and 26 %), these raw materials have to be the object of a granular cut before their use.

The goethite in AK2 must be also kidnapped to avoid any poisonings which would be connected to the iron.

Acknowledgments

The authors thank the‘’ Programme d’Appui Stratégique à la Recherche Scientifique (PASRES)’’for it’s financial supports. They are grateful to the staff members of *the Laboratory of Environment and Mineralurgy (LEM) of National Polytechnic Institute of Loraine- Nancy (France) for their invaluable contribution to this work.*

References

[1] Carretero M.I, Applied Clay Science (2002) 21, 155–163.

[2] Carretero M.I., Gomes C.S.F., Tateo F., Clays and human health. In: Handbook of Clay Science (Bergaya, F., Theng, B.K.G., Lagaly, G. ,Editors) (2006) Pp. 717–741 Developments in Clay Science, 1, Elsevier, Amsterdam.

[3] Wilson M.J., Journal of Chemical Ecology (2003) 29, 1525–1547.

[4] Kikouama O. J. R., Sei J., Soro N., Abba-Touré A., Atindéhou E. et Bonnet J. P., Afrique Bio Médicale (2003) 7, 34-40.

[5] Amin, N. C., Andji Y.Y.J., Aké M., Yolou S. F., Touré A. A., Kra G., Journal des Sciences Pharmaceutiques et Biologiques (2009) 10, 21-30.

[6] Tagini B., Esquisse structurale de la Côte d'Ivoire. Essai de géotectonique régionale. Thèse de Doctorat 1971, Université de Lausanne.

[7] Bessoles, B., Géologie de l'Afrique : le craton ouest-africain, (1977) p 259-262, Mémoires du BRGM n° 88, Paris.

[8] Cahen L., Snelling N.J., Delhal J., Vail J.R., Bonhomme M., Ledent D., The West African Craton: the Guinea Rise. (1984) pp. 297–311. Edition Clarendon Press, Oxford.

[9] Abouchami W., Boher M., Michard A. & Albarède F., Journal Geophysical Research (1990) 95 (11), 17605-17629.
[10] Boher, M., Croissance crustale en Afrique de l'Ouest à 2.1 Ga. Apport de la géochimie isotopique. Thèse de Doctorat 1991, Université de Nancy I.
[11]Boher, M., Abouchami, W., Michard, A., Albarède, F., Arndt, N.T., Journal of Geophysical Research (1992) 97, 345-369.
[12] Taylor P.N., Moorbath S., Leube A., Hirdes W., Precambrian Research (1992) 56, 97-111.
[13] Leube A., Hirdes W., Mauer R., Kesse G.O., Precambrian Research (1990) 46 (1–2), 139-165.
[14] Cheilletz A., Barbey P., Lama C., Pons J., Zimmerman J. L., Dautel D., Comptes Rendus de l'Académie des Sciences série II (1994) 319, 435-442.
[15] Pons J., Barbey P., Dupuis D., Léger J.M. Precambrian Research (1995) 70, 281-301.
[16] Daouda B. Y., Lithostratigraphie et pétrologie des formations birimiennes de Toumodi-Fettêkro (Côte d'Ivoire) : implication pour l'évolution crustale du Paléoprotérozoïque du craton Ouest-Africain. Thèse de Doctorat 1998, Université d'Orléans-Géosciences.
[17] Carignan J., Hild P., Mevelle G., Morel J., Yeghicheyan D., Geostandards Newsletter (2001) 25, 187-198.
[18] Kouamelan A. N., Géochronologie et géochimie des formations archéennes et protérozoïques de la dorsale de Man en Côte d'Ivoire, implications pour la transition archéen protérozoïque. Thèse de doctorat 1996, Université de Rennes.
[19] Nieboer E., Sanford W.E. In: MAC Short Course Handbook (M.E. Fleet, Editor) (1984) Pp. 149–168 Mineralogical Society, 10, Canada.
[20] Lindh U., a. Biological functions of the elements. In: Essentials of Medical Geology: Impacts of the Natural Environment on Public Health (O. Selinus, B. Alloway, J.A.Centeno , R.B. Finkelman, R. Fuge, U. Lindh, P. Smedley, Editors) (2005) Pp. 115–160 Elsevier Academic Press, Amsterdam.
[21] Lindh U., b. Uptake of elements from the biological point of view. In: Essentials of Medical Geology: Impacts of the Environment on Public Health (O. Selinus, B. Alloway, J.A.Centeno , R.B. Finkelman, R. Fuge, U. Lindh, P. Smedley, Editors) (2005) Pp. 87–114 Elsevier Academic Press, Amsterdam.
[22] Combs Jr. G.F., Geological impacts on nutrition. In: Essentials of Medical Geology: Impacts of the Natural Environment on Public Health (O. Selinus, B. Alloway, J.A. Centeno, R. B. Finkelman, R. Fuge, U. Lindh, P. Smedley, editors) (2005) Pp. 161–177 Elsevier Academic Press, Amsterdam.
[23] Gomes C.S.F. & Silva J.B.P., Applied Clay Science (2007) 36 (1–3), 4–21.
[24] Evensen N. M., Hamilton P.J., O'nions R.K., Rare earth abundances in chondritic meteorites. Geochim. Cosmochim. Acta (1978) 42, 1199-1212.
[25] Brindley G.W. & Brown G., Crystal structures of clays minerals and their X- ray identification p 495. Mineralogical Society, London (1980).
[26] Bouchet A., Meunier A., Sardini P., Minéraux argileux: structure cristalline, identification par diffraction de rayons X, 136 p, volume 23 de Bulletin du Centre de Recherches Elf Exploration Production, Pau (2000).
[27] Sei J., Touré A. A., Olivier-Fourcade J., Quiquampoix H., Staunton S., Jumas J.C., Womes M., Applied Clay Science (2004) 27(3–4), 235-239.
[28] Sei J., Morato F., Kra G., Staunton S., Quiquampoix H., Jumas J.C., Olivier-Fourcade J., Journal of African Earth Sciences (2006) 46(3), 245-252.
[29] Konan K. L., Sei J., Soro N. S., Oyétola S, Gaillard J.M., Bonnet J.P. & Kra G., Journal de la Société Ouest –Africaine de Chimie (2006) 21, 35-43.
[30] Kikouama, O. J. R., Yagoubi N., Legendre B., Baldé L., Applied Clay Science (2007) 35, 1–10.
[31] Kpangny E.B., Andji J.Y.Y, Adouby K., Oyetola S., Kra G., Yvon J., Journal of Applied Sciences (2008) 8(5), 871-875.
[32] Andji J. Y.Y, Touré A.A., Kra G., Yvon J., Journal of applied sciences (2009) 9(7), 1238-1247.
[33] Yvon J., Garin P., Delon J.F., Cases J.M., valorisation des argiles kaolinitiques des charentes dans le caoutchouc naturel. Bulletin de Minéralogie (1982) 105.