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MÖSSBAUER ANALYSIS OF GLAUCONITES OF DIFFERENT BELGIAN FINDING PLACES

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Résumé.- Vingt échantillons naturels de glauconite de différents lieux d'origine et d'âge différent sont étudiés par spectroscopie Mössbauer. Les spectres sont analysés en ajustant cinq doublets paramagnétiques. Deux doublets sont assignés aux ions Fe^{3+} , deux autres aux ions Fe^{2+} , tous deux répartis sur les sites octaédriques M_1 et M_2 . L'attribution du cinquième doublet aux ions de fer en sites tétraédriques est douteuse; peut-être doit-elle être assignée à des complexes de fer situés entre les couches. Nous avons trouvé une corrélation entre la couleur des échantillons et la proportion de Fe^{2+} et de Fe^{3+} . Une corrélation entre l'âge des échantillons et les paramètres hyperfins, dérivés de leur spectre Mössbauer, ne se manifeste pas.

Abstract.- The Mössbauer spectra of twenty different glauconite samples from different origin and age are discussed. The spectra are fitted with five doublets: two doublets must be ascribed to Fe^{3+} , two others to Fe^{2+} (both in octahedral sites (M_1 and M_2)). The assignment of the fifth doublet to ferric ions in tetrahedral sites is doubtful; interlayer iron complexes can not be excluded. The correlation between the green colour of the samples and the ferrous to ferric ratio is very clear. A correlation between the age of the samples and their hyperfine parameters, derived from the Mössbauer spectra, could not be observed.

1. Introduction.- Glauconite is a dioctahedral mica. The formula can be represented by $(\text{Na}^+\text{K}^+\text{Ca}^{2+})[\text{Al}^{3+}\text{Fe}^{3+}\text{Mg}^{2+}\text{Fe}^{2+}\text{Ti}^{4+}]_2\{\text{Si}^{4+}\text{Al}^{3+}\}_4\text{O}_{10}(\text{OH})_2$. The ions between []-brackets are on the octahedral sites and those between the { }-brackets on the tetrahedral sites. Some authors /1/ mentioned that there can also be some iron on the tetrahedral sites. Glauconite minerals occur almost exclusively in marine sediments, particularly in green sands. Sometimes they are even found in volcanic deposits. In Belgium they are frequently found in sands from the Mesozoikum and Kenozoikum. The green glauconite pellets are easily separated from other minerals by a magnetic separator. Several Mössbauer studies on glauconite have been published until now but the interpretations of the spectra are rather controversial. Raclavsky et al. /2/, /3/ resolved their spectra into three doublets, two for Fe^{3+} and one for Fe^{2+} . Annersten /4/ describes his spectra with only one ferric doublet and two ferrous doublets. Rolf et al. /5/ and Coey /6/ made use of four doublets: two for Fe^{3+} and two for Fe^{2+} on the octahedral sites. The assignment of these doublets is recently discussed by Rozenson /7/.

2. Experimental results.- The Mössbauer spectra of twenty different glauconite samples at room temperature were collected using a constant acceleration drive unit in connection with a 1024-multichannel analyser. The velocity of the source, ^{57}Co embedded

in a Pd matrix, ranged from +4 to -4 mm s^{-1} . A few samples were measured between room temperature and liquid nitrogen temperature. The purity of the samples was controlled with an X-ray diffractometer. Most of the samples were dated with the K-Ar method. In figure 1 typical Mössbauer spectra at room temperature are shown. The first spectrum, referring to a sample which contains only Fe^{3+} , is well fitted with three doublets. The χ^2 was reduced by 50% compared to a two doublet fit. Spectra of samples which contain ferric and ferrous iron are fitted with five doublets and the obtained Mössbauer parameters are classified, according to the age of the sample in table I. Due to the strong overlap of the doublets the computer program of Chrisman and Tumolillo /8/ does not converge sufficiently. Therefore we made use of a program based on the simplex iteration /9/. The only constraints were that widths and areas of the two lines within a doublet were equal.

3. Discussion and conclusions.- A three- or four-doublet fit /3/, /4/, /5/ of glauconite spectra does not give a consistent behaviour of the hyperfine parameters as a function of temperature. With five doublets however normal variations of the isomeric shifts and quadrupole splitting are obtained and the areas of the different doublets are found to be constant as a function of temperature. The two most intense doublets (in the spectra of figure 1) correspond to Fe^{3+} ions in M_2 and M_1 sites. The M_2 and

Table I : Mössbauer parameters of the glauconite samples classified according to their age.

CLASSIFICATION Finding place age	Fe ³⁺									Fe ²⁺						Fe ³⁺	Fe ²⁺	Fe ³⁺ IL %	
	M2(cis)			M1(trans)			IL			M2(cis)			M1(trans)			(M ₁) (M ₂)	(M ₁) (M ₂)		(Fe ²⁺) (Fe ³⁺)
	IS	QS	Γ	IS	QS	Γ	IS	QS	Γ	IS	QS	Γ	IS	QS	Γ				
KENOZOIKUM																			
POEDERLIAN																			
Lichtaart +1 5 milj.y	0.14	0.35	0.40	0.13	0.75	0.37	0.38	0.69	0.42								0.81		14.16
SCALDISIAN																			
Antwerp +2 milj.y	0.16	0.33	0.38	0.15	0.72	0.34	0.42	0.75	0.40	0.89	2.68	0.28	0.99	1.87	0.29	0.81	0.39	0.059	6.44
DIESTIAN																			
Averbode + 5 milj.y	0.15	0.36	0.41	0.12	0.79	0.37	0.37	0.77	0.40							0.76			14.20
ANTWERPIAN																			
Terhagen +25 milj.y	0.17	0.41	0.44	0.17	0.81	0.40	0.46	0.91	0.53	0.98	2.67	0.38	1.03	1.96	0.38	0.54	0.40	0.097	2.32
PANISELIAN																			
Egem +47 milj.y	0.17	0.34	0.42	0.13	0.77	0.38	0.45	0.80	0.40	0.98	2.81	0.33	1.00	1.82	0.33	0.52	0.65	0.088	9.48
IEPERIAN																			
Zwevegem +49 milj.y	0.15	0.32	0.37	0.13	0.73	0.36	0.45	0.76	0.36	0.98	2.78	0.29	0.95	1.77	0.35	0.52	1.11	0.059	9.36
LANDENIAN																			
- Hoegaarden	0.14	0.36	0.36	0.12	0.78	0.39	0.46	0.73	0.30	0.94	2.81	0.16*	1.03	1.82	0.31	0.93	0.38	0.023	14.17
- Mesvin	0.14	0.36	0.40	0.12	0.78	0.36	0.45	0.73	0.35	0.94	2.82	0.27	1.00	1.79	0.30	0.59	4.42	0.037	11.83
- Nalinnes	0.12	0.35	0.37	0.10	0.72	0.35	0.41	0.69	0.37	0.81	2.45	0.25	0.87	1.54	0.27	0.71	0.74	0.037	17.94
- Chercq A	0.14	0.34	0.39	0.13	0.76	0.35	0.45	0.68	0.41	0.97	2.74	0.29	0.94	1.71	0.35	0.40	1.48	0.062	9.94
B	0.14	0.35	0.39	0.12	0.80	0.34	0.46	0.69	0.30	0.98	2.79	0.44	1.00	1.80	0.35	0.48	2.10	0.041	8.67
C	0.14	0.37	0.40	0.11	0.80	0.34	0.46	0.70	0.30	0.98	2.82	0.41	1.00	1.80	0.30	0.40	1.51	0.029	10.15
D	0.14	0.37	0.40	0.11	0.81	0.32	0.47	0.70	0.26							0.36			9.89
- Angre + 55 milj.y	0.12	0.34	0.36	0.08	0.73	0.34	0.42	0.72	0.34				0.96	1.62	0.26	0.57		0.020	18.84
MESOZOICUM																			
MAASTRICHTIAN																			
Ciply + 68 milj.y	0.15	0.33	0.39	0.13	0.72	0.39	0.44	0.75	0.28	0.93	2.74	0.12*	1.03	1.80	0.31	0.91	0.41	0.021	8.89
TUROON																			
Maisières + 88 milj.y	0.16	0.34	0.39	0.15	0.75	0.37	0.48	0.76	0.27	0.95	2.73	0.35	0.94	1.97	0.28	0.60	0.64	0.127	5.02
CENOMAN																			
Nimy + 90 milj.y	0.17	0.31	0.39	0.17	0.67	0.38	0.45	0.68	0.53	0.94	2.63	0.21*	0.94	1.68	0.32	0.63	0.94	0.097	4.25
ALBIAN																			
Bracquagnies + 95 milj.y	0.16	0.35	0.41	0.15	0.73	0.40	0.43	0.79	0.46	0.96	2.73	0.35	0.93	1.72	0.31	0.91	0.32	0.084	9.68

IS : isomer shift, relative to Pd

QS : quadrupole splitting ; Γ peak width all in mm/s

* : the too small value of Γ is due to the very low intensity of these lines.

M₁ positions in glauconite can be considered as the cis and trans isomers of an octahedron FeO₄(OH)₂. The expected ratio of the quadrupole splittings for such cis and trans octahedral ferric ions is 1:2/10/. The results in table I agree well with this value. Fe²⁺ is not a spherically symmetric ion and the q-valence term cannot be neglected. In general the quadrupole splitting is proportional with the distortion, so the splitting will be the largest for Fe²⁺ ions which occupy the more distorted M₂ sites. The crystallographical assignment of the fifth dou-

blet cannot be done straight forwardly. Two hypotheses are possible. As we mentioned earlier, substitution of Fe³⁺ for Si⁴⁺ is reported by some authors.

The observed hyperfine parameters, however, do not agree with the values usually obtained for Fe³⁺ ions in a tetrahedral position, particularly the isomeric shift is too high. On the other hand significant amounts of interlayer hydroxy iron, aluminium, magnesium complexes are proved to exist in glauconites /11/. We prefer to assign the fifth doublet

(I.L. in the table) to these interlayer iron compounds. The concentration of these compounds then seems to vary from sample to sample. The possibility and the influence of removing these "free" iron oxihydroxides is still under investigation.

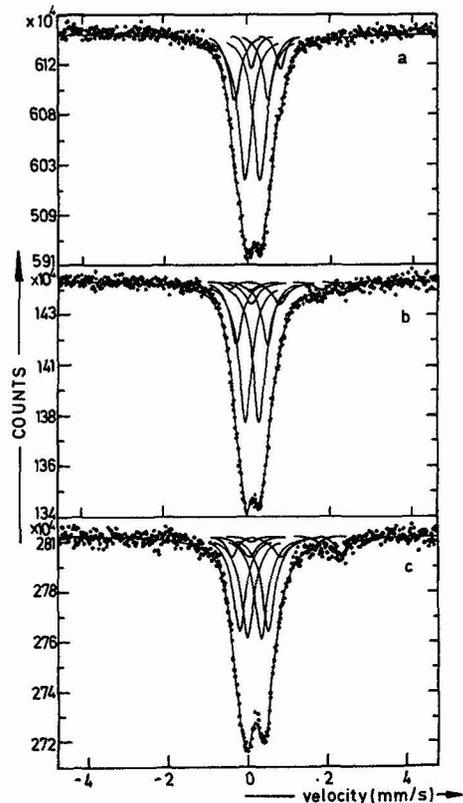


Fig. 1 : Mössbauer spectra at room temperature of three naturally occurring glauconite samples.
 a : Landenium Chercq D light-green fraction
 b : Landenium Chercq A dark-green fraction
 c : Albian-Bracquegnies

The samples which are indicated in table I as Landenian Chercq A, B, C, D are of the same origin. They are separated from the same calcareous green sand according to their colour. The colour is varying from dark green (A) to very light green (D). The only influence we notice in the Mössbauer pattern is the decrease of the ferrous content. The green colour of glauconite can be explained by a charge transfer transition between Fe^{2+} and Fe^{3+} in a neighbouring octahedral position. When the number of Fe^{3+} - Fe^{2+} pairs increases, the intensity of the absorption band in the red part of the spectrum increases and so does the intensity of the green colour of the mineral.

In contradiction with the assertions of Malysheva /12/ we do not observe any correlation between the Fe^{3+} hyperfine parameters and the age of formation of the samples. The quadrupole splitting and the line widths are rather constant. The variation of these parameters mentioned by others /5,7/ is, in our opinion, due to their fitting model. The observed variation of $\frac{M_1}{M_2}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the area of the interlayer doublet is the result of the different forming processes (low and high energetic) and the different weathering history of the samples.

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References

- /1/ Odin, G.S., Les glauconites, Thèse de doctorat d'état, Paris 1975.
- /2/ Raclavsky, K., Sitek, J. and Lipka, J., Proc. Int. Conf. Mössb. Spec. 2 (1973) 368.
- /3/ Cimbalnikova, A., Raclavsky, K. and Lipka, J., 6th Conf. Clay Mineral. Petrol.Geologica, Praha, (1973) p 57.
- /4/ Annersten, H., Neues Jahrb. Mineral, Monatsch. 8 (1975) 378.
- /5/ Rolf, R.M., Kimball, C.W. and Odom, I.E., Clays & Clay Minerals 25 (1977) 131.
- /6/ Coey, J.M.D., Proc. Int. Conf. Mössb. Spec. 2 (1975) 333.
- /7/ Rozenson, I. and Heller-Kallai, L., Clays & Clay Minerals 26 (1978) 173.
- /8/ Chrisman, B.L. and Tumollillo, T.A., Comp. Phys. Comm. 2 (1971) 322.
- /9/ Dauwe, C., Dorikens, M. and Dorikens-Vanpraet, L., Appl. Phys. 5 (1974) 45.
- /10/ Rozenson, I., and Heller-Kallai, L., Clays & Clay Minerals 25 (1977) 94.
- /11/ Thompson, G.R. and Hower, J., Clays & Clay Minerals 23 (1975) 289.
- /12/ Malysheva, T.V., and Kazakov, G.A., Proc. Int. Conf. Mössb. Spec. 1 (1975) 475.