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Abstract

Talc of different origins has been examined to determine if low temperature talc exists. Spectroscopic studies show that, in hydrothermal talc, only ferrous iron is present and is located in octahedral M₂ sites. In talc from weathering profiles, both ferrous and ferric iron exist in the M₂ sites. The oxygen isotope compositions of the two kinds of talc are completely different (+ 10 ‰ and + 20 ‰, respectively). The high δO₁₈ values of weathering talc cannot be explained by post formational oxygen isotope exchange between high temperature talc and meteoric water. Using the fractionation factors of Escande (1983) and a δO₁₈ value of — 5 ‰ for the meteoric water, the temperature obtained for talc from weathering profiles is between 25 and 50 °C. A possible mechanism of formation for low temperature, ferric talc is the recrystallization of a ferrous talc, immediately followed by a more or less complete and very fast iron oxidation. A similar evolution has been observed for smectites in natural and experimental studies.

Résumé

Des échantillons de talc d'origines diverses ont été étudiés dans le but de vérifier si une origine de basse température est possible. Des études spectrométriques montrent que, dans le talc hydrothermal, le fer est à l'état ferreux dans les sites octaédriques M₂. Dans le talc provenant de profils d'altération, le fer existe sous forme ferreux et ferrique dans les mêmes sites. Les compositions isotopiques de l'oxygène des deux groupes sont complètement différentes ($\delta\text{O}_{18} = + 10 \text{ ‰}$ et $+ 20 \text{ ‰}$ respectivement). L'enrichissement en O₁₈ du talc d'altération ne peut pas être expliqué par un échange entre eaux météoriques et talc hydrothermal après sa formation. En utilisant les facteurs de fractionnement d'Escande (1983) et une composition isotopique des eaux météoriques de — 5 ‰, on obtient pour les talcs de profils d'altération, une température de 25 à 50 °C. Un processus de formation possible pour ce talc météorique ferrique est la cristallisation de talc ferreux, immédiatement et rapidement suivie par une oxydation plus ou moins complète du fer. Un tel phénomène est observé dans certaines smectites ferrifères naturelles ou de synthèse.



Spectroscopic and oxygen isotopic evidence for low and high temperature origin of talc

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Abstract. — Talc of different origins has been examined to determine if low temperature talc exists. Spectroscopic studies show that, in hydrothermal talc, only ferrous iron is present and is located in octahedral M_2 sites. In talc from weathering profiles, both ferrous and ferric iron exist in the M_2 sites. The oxygen isotope compositions of the two kinds of talc are completely different (+ 10 ‰ and + 20 ‰, respectively). The high δO^{18} values of weathering talc cannot be explained by post formation oxygen isotope exchange between high temperature talc and meteoric water. Using the fractionation factors of Escande (1983) and a δO^{18} value of - 5 ‰ for the meteoric water, the temperature obtained for talc from weathering profiles is between 25 and 50 °C. A possible mechanism of formation for low temperature, ferric talc is the recrystallization of a ferrous talc, immediately followed by a more or less complete and very fast iron oxidation. A similar evolution has been observed for smectites in natural and experimental studies.

Key words : talc, Mössbauer spectroscopy, optical spectroscopy, oxygen isotopes, weathering.

Mise en évidence de talc de haute et basse température. Une étude spectroscopique et isotopique.

Résumé. — Des échantillons de talc d'origines diverses ont été étudiés dans le but de vérifier si une origine de basse température est possible. Des études spectrométriques montrent que, dans le talc hydrothermal, le fer est à l'état ferreux dans les sites octaédriques M_2 . Dans le talc provenant de profils d'altération, le fer existe sous forme ferreux et ferrique dans les mêmes sites. Les compositions isotopiques de l'oxygène des deux groupes sont complètement différentes ($\delta O^{18} = + 10\text{‰}$ et + 20 ‰ respectivement). L'enrichissement en O^{18} du talc d'altération ne peut pas être expliqué par un échange entre eaux météoriques et talc hydrothermal après sa formation. En utilisant les facteurs de fractionnement d'Escande (1983) et une composition isotopique des eaux météoriques de - 5 ‰, on obtient pour les talcs de profils d'altération, une température de 25 à 50 °C. Un processus de formation possible pour ce talc météorique ferrique est la cristallisation de talc ferreux, immédiatement et rapidement suivie par une oxydation plus ou moins complète du fer. Un tel phénomène est observé dans certaines smectites ferrifères naturelles ou de synthèse.

Mots-clés : talc, spectrométrie Mössbauer, spectrométrie optique, isotopes de l'oxygène, altération météorique.

I. INTRODUCTION

Talc is generally described as the result of hydrothermal alteration of ultrabasic rocks or of magnesium metasomatism of quartzite and dolomitic rocks (Chidester, 1962 ; Naldrett, 1966 ; Ildefonse, 1980 ; Moine, 1982 ; Moine *et al.*, 1982 ; Beaulieu, 1983 ; Hemley *et al.*, 1977). But talc is also often present in lateritic profiles on basic or ultrabasic rocks (Delvigne, 1965, 1983 ; Trescases, 1975 ; Nicolas and Sagon, 1966 ; Bernardelli *et al.*, 1983 ; Menegotto and Formoso, 1983 ; Nahon *et al.*, 1982 ;...) and the question is whether such talc is a relic of a previous hydrothermal alteration or the result of weathering ? The existence of meteoric talc has

been suggested by several authors (Wackermann, 1975 ; Pion, 1979 ; Fontanaud, 1982 ; Nahon *et al.*, 1982 ; Colin, 1984) but has never been proved. In this paper we report spectroscopic and isotopic analyses of different talc samples, in an attempt to prove a low-temperature origin for talc of supposed meteoric origin and to find criteria to distinguish between hypogene and supergene talc.

II. PETROLOGY AND GEOLOGICAL OCCURRENCES OF SAMPLES

The samples studied have several origins. Sample BR22 is from the metamorphosed ultra-

basic massif of Bragança (Portugal). This Precambrian peridotitic body was metamorphosed (about 900 m.y. old) from greenschist to amphibolite facies (Anthonioz, 1972). Talc occurs as small lenses, often associated with chlorite and sometimes quartz. Talc and chlorite form the matrix of the rock in which big pyroxenes are completely transformed to amphiboles. Samples PO5D and CF13 are from the Precambrian (Low to Middle Proterozoic) serpentinized ultrabasic massif of Campo Formoso (Brazil). The talc occurs as a replacement product of antigorite and chlorite, or is associated with carbonates. These two occurrences are interpreted as different phases of an hydrothermal alteration of the serpentinites (Boukili *et al.*, 1983 ; Boukili, 1984). Sample "TRIMOUNS" comes from the talc ore of Trimouns in the Pyrénées Mountains (France). The talc deposit is found between crystalline formations at the wall and chlorito-graphitic epimetamorphic series, with dolomitic intercalations at the roof. Talc was formed by a late Hercynian magnesian metasomatism at 250 to 300 °C (Fortuné *et al.*, 1980). Samples 13-77, 95-77 and 106-77 come from two lateritic profiles on dunites and pyroxenites at Moyango and Sipilou, Ivory Coast (Mathez, 1976 ; Nahon, 1977, 1978). In sample 13-77, talc is associated with nickeliferous chlorite-vermiculite in a silcrete (Noack and Colin, in press). In samples 95-77 and 106-77, talc occurs as alteration of orthopyroxene or as filling of small veins in the transitional horizon of the profile (Nahon *et al.*, 1982). Sample "GABON" has a completely different origin. It is a sedimentary talc formed at the contact between dolomite and sepiolite in the Upper Proterozoic Nyanga synclinal, in southeastern Gabon. This deposit is interpreted to have formed through interaction of sepiolite and water at pH below 8 (Dubinska, 1984).

III. EXPERIMENTAL STUDIES

1. Mineralogy and crystallography

Samples PO5D, CF13, TRIMOUNS, BR22 and GABON are very pure talc with no detectable amounts of other phases by X-ray diffraction. Sample 13-77 contains talc and about 5 % of quartz and is red-colored, suggesting the occurrence of iron oxides. Sample 106-77 consists of

talc, about 3 % of quartz and trace amounts of chlorite. Sample 95-77 is a mixture of about 30 % talc and 70 % smectite. Cell parameters for all the talc samples studied have been calculated using the crystallographic computer program of Tournarie (1969) on the basis of a triclinic unit-cell (Table I). Because the talc particles are lamellar, it is sometimes difficult to obtain desoriented powder samples and then (hkl) reflections in XRD pattern. The precision obtained is not good for these samples. The calculated crystallographic parameters are close to each other for all the samples, except 106-77 which has a smaller unit-cell volume.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
BR 22	5.268 ±0.007	9.142 ±0.005	9.475 ±0.013	91.43 ±0.21	99.56 ±0.37	89.70 ±0.16	449.8 ±0.7
PO 5D	5.249 ±0.007	9.158 ±0.005	9.442 ±0.010	89.72 ±0.10	98.10 ±0.14	90.75 ±0.12	449.3 ±0.8
CF 13	5.150 ±0.061	9.161 ±0.003	9.452 ±0.018	90.79 ±0.92	98.52 ±0.67	89.61 ±0.40	440.7 ±5.3
TRIMOUNS	5.252 ±0.009	9.144 ±0.004	9.444 ±0.013	91.43 ±0.21	98.42 ±0.42	89.70 ±0.15	448.7 ±0.9
13-77	5.265 ±0.005	9.157 ±0.007	9.493 ±0.009	90.81 ±1.00	99.75 ±0.10	90.12 ±1.00	451.0 ±0.6
95-77	5.269 ±0.022	9.182 ±0.002	9.460 ±0.025	90.49 ±0.95	98.86 ±0.96	90.26 ±0.36	452.2 ±1.8
106-77	5.106 ±0.055	9.155 ±0.003	9.455 ±0.012	89.89 ±0.44	98.34 ±0.41	89.82 ±0.65	437.2 ±5.7
GABON	5.252 ±0.004	9.140 ±0.004	9.454 ±0.006	90.88 ±0.12	98.60 ±0.12	89.71 ±0.10	448.7 ±0.4
(1) MINNESOTAITE	5.623	9.419	9.624	85.21	95.64	90.00	
(2) Fe ³⁺ -PYROPHILLITE	5.26	9.10	19.1	95.5			

TABLE I. — Unit-cell parameters (with standard deviations) of studied talc. 1) Guggenheim & Bailey (1982) ; 2) Monoclinic unit-cell, Chukhrov *et al.* (1979).

Paramètres cristallographiques (avec incertitudes) des échantillons de talc étudiés. 1) Guggenheim & Bailey (1982) ; 2) Maille monoclinique, Chukhrov *et al.* (1979).

2. Chemistry

The chemical composition of the talc samples were determined by atomic absorption spectrophotometry, electron microprobe and SEM with a Si-Li detector (Table II). Bulk analysis and analysis of isolated particles of talc by SEM are similar. The iron content varies widely from 0 to 12 % Fe₂O₃ as total iron. The analysis of separated particles from the same sample shows that the iron content varies little. The Al₂O₃ content is generally low except for samples 95-77 and 106-77. High Al₂O₃ contents (as measured by

	BR22(1)	PO5D(1)	CF13(1)	TRIMOUNS	13-77 ⁽²⁾	95-77 ⁽³⁾	106-77 ⁽³⁾	GABON(1)
SiO ₂	61.50	63.00	61.21	62.69	61.19	62.43	64.00	60.15
Al ₂ O ₃	0.50	0.20	0.08	0.49	0.38	1.92	1.30	0.55
Fe ₂ O ₃	3.58 ^x	1.36 ^x	1.01 ^x	0.76 ^x		7.97 ^x	12.10 ^x	0.06 ^x
FeO					1.70 ^x			
MgO	28.00	30.00	31.37	29.93	30.31	25.60	18.80	33.20
CaO	0.25	0.20	0.30	0.30		0.11	0.90	0.06
Na ₂ O	0.05	0.05	0.02	0.03		0.32	0.35	0.10
K ₂ O	0.01	0.01	0.01	0.02		ND	0	0.01
NiO	0.08	0.04	0.23		0.14	ND	1.47	ND
Cr ₂ O ₃	0.01	0.04	0	ND	ND	ND	1.08	ND
H ₂ O	5.68	5.78	5.24	5.48	ND	ND	ND	5.50

TABLE II. — *Chemical analysis of the studied talc.*

x : Total iron ; ND : not determined. (1) Atomic absorption spectrophotometry ; (2) Electron microprobe ; (3) SEM with Si-Li detector. Analysis recalculated to 100 %.

Analyses chimiques des échantillons de talc étudiés.
x : Fer total ; ND : non analysé. (1) Spectrophotométrie d'absorption atomique ; (2) Microsonde électronique ; (3) MEB avec détecteur Si-Li. Analyses recalculées à 100 %.

SEM) correspond to small quantities of chlorite detected by XRD. The same method shows that the NiO and Cr₂O₃ contents in the samples from lateritic profiles are associated with talc particles.

3. Mössbauer spectroscopy

Mössbauer spectra were recorded in 512 channels of an Elscint AME 40 spectrometer in the

triangular mode. A ⁵⁷Co source in a rhodium matrix of nominal strength 25 mCi was used with a NaI scintillator as γ ray detector. Velocity calibration was made using a high grade metallic iron lamina. Spectra were collected at room temperature until 4 to $5 \cdot 10^6$ counts per channel were accumulated. All data were computer fitted with Lorentzian components by a least squares program. All samples were analyzed, except GABON, which is too low in iron. The Mössbauer spectra for the talc analyzed are of two kinds. Those of talc having an obvious high-temperature origin (BR22, PO5D, CF13, TRIMOUNS) have only one Fe²⁺ doublet, more or less asymmetric (Figure 1). The experimental spectra can be well fitted by one Lorentzian line with Mössbauer parameters characteristic of Fe²⁺ in octahedral sites (Coey, 1980 ; Heller-Kallai and Rozenson, 1981) (Table III).

The linewidths are narrow, close to the instrumental resolution. Spectra contain only one doublet and their asymmetry can be attributed to an orientation of talc particles in the samples. The large value of the quadrupole splitting is classically attributed to Fe²⁺ in M₂ sites. For PO5D sample a broadened absorption line having a very low intensity (less than 5 % in surface) is observable at 0.395 mm/s. This feature has been attributed to Fe³⁺ atoms in octahedral sites but no acceptable fit was obtained using Lorentzian curves. On the basis of these results, it's not

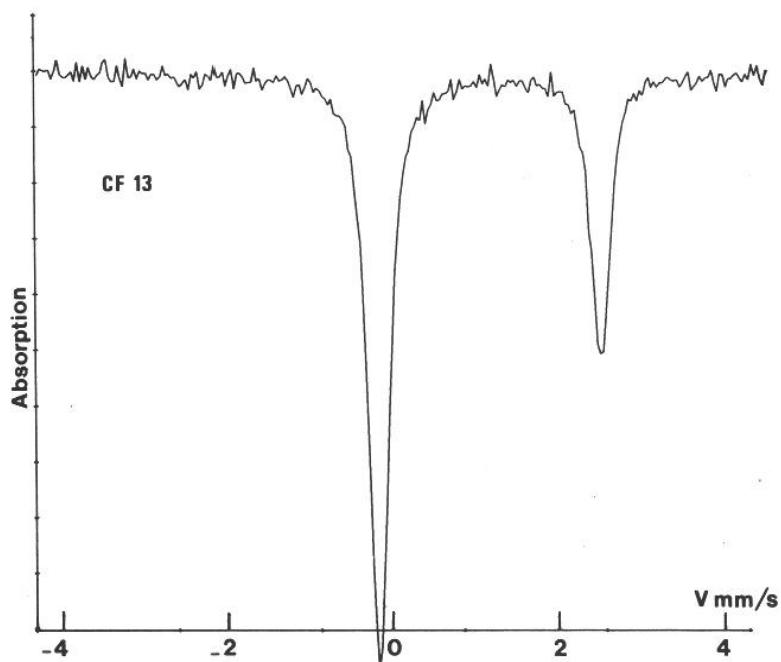


FIG. 1. — *Mössbauer spectrum of hydrothermal talc (sample CF 13).*
Spectre Mössbauer de talc hydrothermal (échantillon CF 13).

Site	Fe ²⁺					Fe ³⁺					Samples and references
	I.S.	Q.S.	Γ	S	Site	I.S.	Q.S.	Γ	S		
M2	1.14	2.60	0.30	-	M2	0.48	0.58	0.48	-		Heller-Kallai & Rozenson 1981
M2	1.13	2.60	0.30	100	M2						Blaauw et al. 1980
M2	1.13	2.63	0.30	100	M2						Coey 1980
M2	1.39*	2.60	0.14	100	M2						Hogg and Meads 1970
<hr/>											
M2	1.135	2.630	0.285	100	M2						POSD
M2	1.153	2.640	0.256	100	M2						TRIMOUNS
M2	1.154	2.630	0.293	100	M2						BR 22
M2	1.127	2.625	0.269	100	M2						CF 13
M2	1.114	2.564	0.447	28	M2	0.367	0.533	0.466	72		106-77
M2	1.13	2.692	0.278	18	M2	0.366	0.601	0.440	82		13-77
					M2	0.365	0.540	0.404	100		95-77

TABLE III. — Mössbauer parameters of studied talc (in mm/s). I.S. = Isomer shift ; Q.S. = Quadrupole splitting ; Γ = Line width ; S = Relative area of the doublet. I.S. relative to iron metal except* relative to nitroprusside.

Paramètres Mössbauer des échantillons de talc étudiés (en mm/s). I.S. = Déplacement isomérique ; Q.S. = Ecart quadripolaire ; Γ = Largeur du doublet à mi-hauteur ; S = Surface relative du doublet. Les déplacements isomériques sont mesurés par rapport au fer métal sauf* mesuré par rapport au nitroprusside.

possible to localize either in the talc structure or in a separate phase this amount of iron atoms, which represents about 0.06 weight percent of the sample.

Mössbauer spectra of talc samples with a supposed meteoric origin (13-77, 95-77, 106-77) are quite different, the main feature being an intense doublet with parameters typical of ferric iron in octahedral sites (Figure 2 and table III). The spectrum for sample 106-77 can be fitted with two doublets : the first corresponds to Fe²⁺ located in octahedral M₂ sites, as above ; the second can be attributed to Fe³⁺ in M₂ sites, according to the small value of the quadrupole splitting of this doublet (Rozenson and Heller-Kallai, 1977 ; Coey *et al.*, 1984). The spectrum of sample 13-77 is very similar to the previous one, but contains a broad modulation of the baseline which cannot be fitted by one Lorentzian line, and can be attributed to iron oxides, amorphous or in very small particles (Kundig *et al.*, 1966). About 40 % of total iron is located in this phase. For both samples the Fe²⁺/Fe^{total} ratio in talc is low : 18 % for 13-77 and 28 % for 106-77. No evidence was found of tetrahedrally coordinated Fe³⁺ in these minerals. Linewidths are larger than for high temperature talc but in the range of values found for equivalent doublets in Mössbauer spectra of smectite (Rozenson and Heller-Kallai, 1977 ; Bart *et al.*, 1980). Broade-

ning of Lorentzian lines is generally attributed to iron atoms located in octahedral sites with similar but not identical Mössbauer parameters. In the samples studied here, broadening of the lines in correlated with the incorporation of Fe³⁺ atoms in the talc structures.

The Mössbauer spectrum for samples 95-77 has only one doublet which can be fitted by one Lorentzian line corresponding to Fe³⁺ atoms in octahedral M₂ sites. There is no indication of ferrous iron and thus Fe²⁺/Fe^{total} < 0.02. On the basis of SEM data about 8 % of the iron is located in the talc structure of sample 95-77. Mössbauer results indicate that neither the smectite phase nor the talc phase contains detectable amounts of ferrous iron.

Relatively few talc Mössbauer data are available (Hogg and Meads, 1970 ; Coey, 1980 ; Blaauw *et al.*, 1980 ; Heller-Kallai and Rozenson, 1981) and none of these papers gives the geological origins of the samples. In three cases (Table III), Mössbauer spectra have been fitted only with a Fe²⁺ doublet, and in only one case is a Fe³⁺ doublet mentioned, but without the Fe²⁺/Fe^{total} ratio. Mössbauer parameters are similar to those we report in this paper. There are few reports of Fe³⁺-bearing talc in the literature probably because of the difficulty in separating appreciable amounts of talc from weathering profiles.

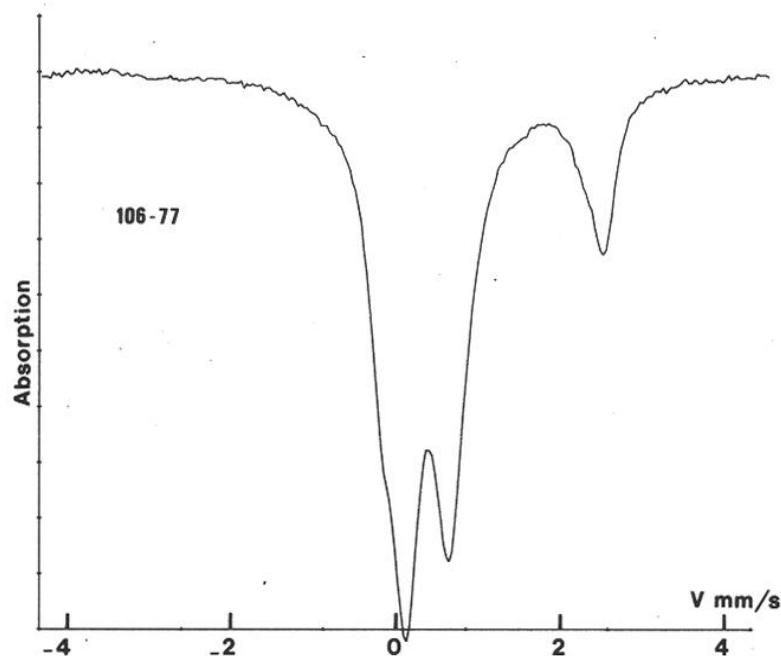


FIG. 2. — Mössbauer spectrum of talc from weathering profile (sample 106-77).
Spectre Mössbauer de talc de profil d'altération (échantillon 106-77).

4. Optical spectroscopy

Optical measurements were performed using a Cary 17D spectrophotometer with a diffuse reflectance attachment. Reflectance values were converted into remission function $F(R)$ according to the formalism of Kubelka and Munk (in Wendlandt and Hecht, 1966). Three samples (PO5D, BR22 and 106-77) were examined and spectra are given in figure 3. The optical spectrum of BR22 consists of three main absorption features each having a specific origin. The sharp peaks at 7190 cm^{-1} and 10750 cm^{-1} are overtones of the OH stretching mode at 3677 cm^{-1} . The visible range is dominated by a tail from a strong absorption centered in the ultraviolet region and which originates from a Fe-O charge transfert absorption. Lastly, the absorption band at about 10500 cm^{-1} is characteristic of six-fold coordinated Fe^{2+} atoms and corresponds to spin-allowed electronic transitions towards the E_g state of Fe^{2+} . This band splits into two components at 10000 cm^{-1} and 11400 cm^{-1} . By comparison with spectra of other Fe compounds this splitting may arise from four configurations (Burns, 1970 ; Blazey, 1977 ; Smith, 1980 ; Rossman, 1984 ; Amthauer and Rossman, 1984) :

- Presence of Fe^{2+} in both the M_1 and M_2 sites.
- $\text{Fe}^{2+}\text{-Fe}^{3+}$ interaction (Intervalence Charge Transfer-IVTC) and Fe^{2+} within the M_1 or the M_2 site.

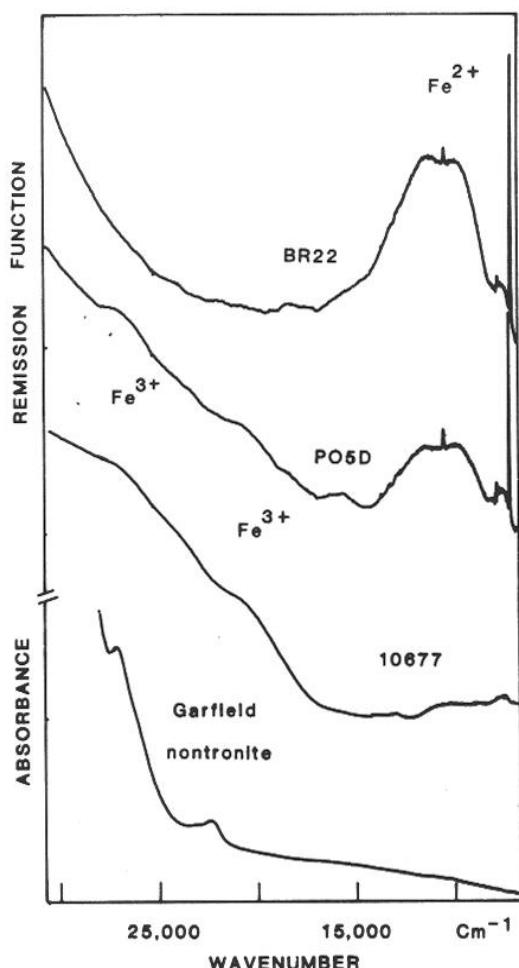


FIG. 3. — Optical spectra (diffuse reflectance spectroscopy) of samples BR22, PO5D and 106-77.
Spectres optiques (réflectance diffuse) des échantillons BR22, PO5D et 106-77.

- Fe atoms in a very regular octahedron (point symmetry O_h).
- Distortion of the Fe site.

The Mössbauer results preclude the first two assignations as Fe atoms are found to occupy a single site, and there is no evidence for ferric iron. As Fe^{2+} atoms are located in a high symmetry octahedron, the upper levels e g splits *during the electronic transition*. This so-called dynamic John-Teller effect occurs because the lifetime of the transition (about 10^{-13} s) is considerably smaller than the period of frequencies of vibrational modes so that the $[FeO_6]$ octahedra are not actually distorted. Such a phenomenon is known only in the periclase structure ($MgO:Fe^{2+}$) and has been never observed in other minerals as their 6 coordinated site is always more or less distorted. Finally, these two absorption maxima are attributed preferentially to a distortion of the Fe^{2+} site so that the upper level e g is separated into two discrete energy levels *in the groundstate*. Fe^{2+} in a site of low symmetry is known to produce two absorption bands in the near-infrared portion of optical spectra of silicates but these bands are generally not recognized in TOT phyllosilicates — in spite of the frequent trigonal distortion of octahedra — because of the mixing of the oxidation states and site occupancy (M_1 , M_2) which occur in sheet silicates.

The absorption features of the ferrous talc BR22 are also observed on the spectrum of PO5D. This latter has two additional shoulders at 27000 cm^{-1} and about 21200 cm^{-1} which are superimposed upon the charge transfer tail. These weak peaks are centered approximately at the same energy as those of the nontronite (Bonin *et al.*, 1985) and can be unambiguously assigned to the 4_{Ag} (4_D), $4_{Alg}-4_{Eg}$ (4_G) levels of the octahedral Fe^{3+} . This amount of Fe^{3+} was not easily detected by Mössbauer spectrometry at 295 K.

The optical spectrum of sample 106-77 is characterized by two shoulders of six-fold coordinated Fe^{3+} in the visible range. The Fe^{2+} features located in the near infrared are not resolved and are probably overlapped by the $4_{T1g}-4_{T2g}$ (4_G) transitions of octahedral Fe^{3+} .

5. Oxygen isotopes

Sample 95-77 was not isotopically analysed because its smectite content is too high. Before

analysis samples were set into a dry box for 24 hours in order to eliminate absorbed water (Savin and Epstein, 1970). Oxygen was extracted from the samples by reacting with BrF_5 and then converted to CO_2 for mass spectrometric analysis, following the procedure described by Clayton and Mayeda (1963). Some samples were isotopically exchanged before analysis as described by Labeyrie and Juillet (1982). This last procedure gives the proportion of easily exchangeable oxygen atoms. Isotopic analyses were made on a Micromass 602 D mass spectrometer. All results are given in the δ notation versus the SMOW standard using NBS 28 and Caltech Rose Quartz calibration. The standard analytical deviation is $\pm 0.11\text{ ‰}$.

Analytical data reported in table IV show that there are two groups of talc isotopic compositions. For talc with an obvious high temperature origin the oxygen isotopic composition range from ≈ 8.6 to 10.2 per mil, whereas for talcs with a supposed meteoric origin the range is between 18.6 and 22.3 per mil.

In order to discuss the thermometric significance of the measured O^{18}/O^{16} ratios fractionation factors between talc and water are required. Available fractionation factors for sheet silicates are given in table V. None of them can be directly applied to talc systems. However, because talc is closer to smectite than to mica, we prefer to use the results of Yeh and Savin (1977), Kulla (1978) and Escande (1983). In addition the latter two papers give results for magnesian smectites. Kulla (1978) found the same experimental fractionation factor for saponite and

Sample	δO^{18}	Exchangeability (%)*
PO 5D	8.6	0
TRIMOUNS	9.3	0
CF 13	8.8	0.15
BR 22	10.2	0.20
GABON	21.7	-
105-77	18.6	1.3
13-77 T	22.32	
13-77 Q	29.74	

TABLE IV. — *Oxygen isotope analysis of studied talc.*

* Atomic ratio of exchangeable oxygen atoms in the procedure of Labeyrie and Juillet (1982).

Analyses des isotopes de l'oxygène des échantillons de talc étudiés. * Rapports atomiques des atomes d'oxygène échangeables dans la procédure de Labeyrie and Juillet (1982).

Mineral	Temperature range (°C)	$10^{-6} A$	B	References
Muscovite	400-650	2.38	-3.89	O'Neil and Taylor 1969
Illite	160-270	2.48	-4.82	Eslinger and Savin 1973
Smectite	0-270	2.67	-4.82	Yeh and Savin 1977 (A)
Montmorillonite	170-320	2.21	-2.82	Kulla 1978 (C)
Saponite				
Stevensite	25-95	3.31	-4.82	Escande 1983 (B)
Saponite				

TABLE V. — *Mineral-water isotope fractionation factors expressed in the form : $\delta^{18}\text{O} = AT^{-2} + B$; T = temperature in K.*

Facteurs de fractionnement isotopique minéral-eau sous la forme : $\delta^{18}\text{O} = AT^{-2} + B$; avec T = température en K.

aluminium rich smectites. Escande (1983) gives an experimental calibration curve for oxygen isotope exchange between stevensites, saponites and water for the range 25-95 °C.

It is possible that post formational oxygen isotope exchange takes place between talc formed at elevated temperature and surfacial waters (Savin and Epstein, 1970). Previous experimental work shows that for clay minerals the exchange rates are low and controlled by accessibility of water to the interlayer region (O'Neil and Kharka, 1976 ; James and Baker, 1976). In talc minerals which are sheet silicates without interlayer water, this phenomenon should not take place to any appreciable degree, and can probably be neglected. Our results are consistent with this assumption. The talc samples analysed have very few exchangeable oxygen atoms (Table IV) compared to smectites (Escande, 1983 ; Escande *et al.*, 1984). So the difference of about 10 per mil found between the two kinds of talcs can be interpreted as resulting from different genetic environments.

Despite the various geological origins of different samples of "hot" talc their oxygen isotope compositions are nearly the same, and can perhaps be related to similar conditions of genesis. On the basis of petrologic and geochemical investigations, the formation temperature of Trimouns talc has been estimated to range between 300 °C (Fortuné, 1971) and 450 °C (Moine, 1982). Using the above available geothermometer it is possible to determine the isotopic composition of paleowater from which this talc precipitated. In this range of temperature the three selected fractionation factors give approximately the same answer : $\delta^{18}\text{O}$ values of water that would have been in equilibrium with

this talc range from ≈ 1 to 9 per mil. These values are consistent with other calculated isotopic composition of paleohydrothermal water (Sheppard, 1977 ; Wenner and Taylor, 1971).

The high $\delta^{18}\text{O}$ values measured for other talc samples are typically those of low temperature clays (Savin and Epstein, 1970 ; Hassanipak and Eslinger, 1985). The above results show clearly that "hot" talcs can retain their original isotopic compositions, even over times of several hundred millions years. High $^{18}\text{O}/^{16}\text{O}$ ratios cannot be interpreted as caused by post-formational oxygen isotope exchange between talc with low $\delta^{18}\text{O}$ values and meteoric waters.

The Gabon talc occurs as a diagenetic replacement of sepiolite in Precambrian dolomite that shows no evidence of hydrothermal alteration or burial metamorphism (Devigne, 1959). It is not possible to date the diagenetic transformation of sepiolite to talc. On the basis of geological evidence this mineral has an undoubted sedimentary origin which is corroborated by its oxygen isotope composition.

Samples 106-77 and 13-77 come from a weathering profile developed during the Quaternary (Mathez, 1976). Previous works of Lawrence and Taylor (1971-1972) show that the oxygen isotope compositions of clays (smectite and kaolinite) in Quaternary soils and weathering profiles are independent of those of the parent rocks, and clearly correlate with $\delta^{18}\text{O}$ values of corresponding present-day meteoric waters. They conclude that these clay minerals are in isotopic equilibrium with their local meteoric waters.

The $\delta^{18}\text{O}$ values of samples 106-77 and 13-77 are similar to those of montmorillonite from the Big Sea weathering profile (California) developed on a hornblende quartz diorite (Lawrence and Taylor, 1972). These results confirm the hypothesis of a low temperature genesis for these samples of talc. A quantitative estimate of temperature can be obtained using the fractionation factors given above. We can use for the isotopic composition of present-day precipitation those measured in Ghana (which has the same latitude as the neighboring Ivory Coast) which have a mean value of $\delta^{18}\text{O} \approx -5\text{‰}$ (Akita, 1980). By another way we must also take into account the possible isotopic effect due to iron atoms in clays. Lawrence and Taylor (1972) found that an increase of 3.3 % in Fe_2O_3 of two

smectites involves a decrease of 2.8 ‰ in $\delta^{18}\text{O}$ values. Temperatures of talc genesis have been so calculated using the three available fractionation factors with and without an iron isotopic effect of 2 ‰ (Table VI). The estimated temperature for the genesis of this talc are obviously those of weathering. This result is confirmed by the isotopic composition of quartz associated with talc in the silcrete (sample 13-77Q).

Sample	Fractionnatiion factors			
	A	B	C	D
106-77	37°	72°-55°*	20°-4°*	
13-77T	15°	48°	about 0°C	
13-77Q				25°

TABLE VI. — *Estimated temperature (°C) of talc genesis using various fractionation factors.* A,B,C see Table V ; D silica-H₂O (Clayton *et al.*, 1972) ; * Estimated temperatures taking in account iron effect.

Températures estimées (°C) de formation des échantillons de talc en utilisant les différents facteurs de fractionnement. A,B,C, voir tableau V ; D silice-H₂O (Clayton *et al.*, 1972) ; * Températures estimées en tenant compte de l'effet du fer.

IV. DISCUSSION

In the introduction, we posed the question about the possible low-temperature origin of talcs. The oxygen isotope analyses allow us to distinguish two groups of minerals :

- The samples of hydrothermal talc all have $\delta^{18}\text{O}$ values ranging from 8.6 to 10.2 ‰.
- The talc from either lateritic profiles or produced by diagenesis have $\delta^{18}\text{O}$ values from 18.6 to 22.3 ‰.

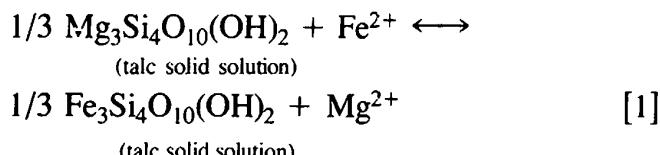
The gap in isotopic composition is sufficiently large to think that the $\delta^{18}\text{O}$ values measured were probably established at the time of crystallization and have not changed since. The hydrothermal talcs are Precambrian to Paleozoic and it seems that their isotopic compositions change little with time. Therefore, the isotopic composition of the other samples of talc studied cannot be interpreted as the result of post-formational isotopic exchange. Using the present-day isotopic composition of rain waters in Africa, the talc from weathering profiles appears clearly to have a low temperature origin. It cannot be considered as a relic of hydrothermal alteration. Conse-

quently, for talc found in weathering profiles on ultrabasic rocks and interpreted as relics of high-temperature, pre-weathering events (Trescases, 1975 ; Delvigne, 1983) the possibility should be reassessed that they instead formed during weathering.

It is also possible to distinguish talc of various origins by its crystallographic and chemical characteristics (Mössbauer and optical spectrometry). Hot talc has a low iron content only in the ferrous form. The substitution of Fe²⁺ for Mg²⁺ is too low to cause modifications of unit-cell parameters detectable by XRD. Lateritic talc has relatively high total iron content, principally in the ferric form and also detectable amounts (about 1 % weight) of NiO and Cr₂O₃. The unit-cell volume of the sample with the higher iron content (106-77) is significantly lower than that of pure magnesian talc (Table I). The only diagenetic talc we have studied is only magnesian and contains no detectable amounts of other metals (Fe, Ni, Cr).

The geochemical conditions of formation of hydrothermal talc are well known (Hemley *et al.*, 1977 ; Moine, 1982). In the weathering profiles, the incorporation of iron in the talc structure is related to the state of iron in the environmental solution. In these geochemical environments, iron in solution can exist essentially in the ferrous form. A possible mechanism of formation for the Fe³⁺-rich talc is substitution of ferrous iron for magnesium, immediately followed by a more or less complete and very fast iron oxidation within the mineral structure. A similar evolution was described for the synthesis of ferrous and ferric smectites (Decarreau, 1983 ; Decarreau and Bonnin, 1986) and in natural transformations of similar smectites in Red Sea sediments (Badaut *et al.*, 1985).

On the basis of this mechanism, incorporation of ferrous iron in the talc structure can be described by the following equilibrium reaction :



the equilibrium constant of reaction [1] is :

$$K_{\text{Fe-Mg}} = \frac{(\text{Fe}^{2+}/\text{Mg}^{2+}) \text{ solid solution}}{(\text{Fe}^{2+}/\text{Mg}^{2+}) \text{ aqueous phase}}$$

The measured value of the corresponding experimental distribution coefficient for stevensite is : $\log K_{\text{Fe-Mg}} = 2.37$ at 25 °C, which shows a strong tendency for ferrous iron to substitute for magnesium in the smectite structure (Decarreau, 1983, 1985). The effect of temperature on the value of $K_{\text{Fe-Mg}}$ can be estimated using the thermodynamic data for talc and minnesotaite (Fritz, 1981). So calculated, theoretical partition coefficients for reaction [1] decrease from $\log K_{\text{Fe-Mg}} = 4.77$ at 25 °C to $\log K_{\text{Fe-Mg}} = 3.69$ at 300 °C. This calculation confirms the strong tendency of Fe^{2+} to substitute for Mg^{2+} in the talc structure. For equivalent geochemical conditions, the stabilization of Fe^{2+} will be ten times higher at 25 °C than at 300 °C. This result can explain the high iron content of low temperature talc in weathering profiles.

The partition coefficient $\text{M}^{2+}\text{-Mg}$ in synthetic stevensites is almost constant from the magne-

sium end member to the M^{2+} end member and the solid solutions, except for Cu^{2+} , are complete (Decarreau, 1983). We can expect the same thing for talc. But in natural talc, a $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio between .30 and .70 has never been found and the existence of a complete Fe-Mg solid solution for talc must be reconsidered.

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REFERENCES

- AKITI, T.T. (1980). — Etude géochimique et isotopique de quelques aquifères du Ghana : gneiss de la plaine d'Accra ; calcaires de la plaine au sud-est de la Volta ; granites de la haute-région. Thèse Univ. Paris-Sud, 232 p.
- AMTHAUER, G., ROSSMAN, G.R. (1984). — Mixed valence of iron in minerals with cation clusters. *Phys. Chem. Miner.*, 11, 37-51.
- ANTHONIOZ, P.M. (1972). — Les complexes polymétamorphiques précambriens de Morais et Bragança (N-E du Portugal) : étude pétrographique et structurale. *Mém. Serv. Géol. Port.*, 20, 192 p.
- BADAUT, D., BESSON, G., DECARREAU, A., RAUTUREAU, R. (1985). — Occurrence of a ferrous, trioctahedral smectite in recent sediments of Atlantis II deep, Red Sea. *Clay Minerals*, 20, 389-404.
- BART, J.C., BURRIESCI, N., CARIATI, F., MICERA, G., GESEA, C. (1980). — Spectroscopic investigations of iron distribution in some bentonites from Sardinia. *Clays Clay Miner.*, 28, 233-236.
- BEAULIEU, P. (1983). — Contribution à l'étude géologique des gisements de talc du Val-Malenco (Alpes Italiennes). Thèse 3^e cycle, Besançon, 301 p.
- BERNARDELLI, A., MELFI, A.J., OLIVEIRA, S.M.B., TRESCASES, J.J. (1983). — The Carajas nickel deposits. Proc. II Intern. Seminar on Laterization Processes, São Paulo, 1982, Melfi and Carvalho Eds., 107-118.
- BLAAUW, C., STROINK, G., LEIPER, W. (1980). — Mössbauer analysis of talc and chlorite. *J. Phys. C*, 1, 411-412.
- BLAZEY, K.W. (1977). — Optical absorption of MgO:Fe . *J. Phys. Chem. Solids*, 38, 671-675.
- BONNIN, D., CALAS, G., SUQUET, H., PEZERAT, H. (1985). — Sites occupancy of Fe^{3+} in Garfield nontronite : a spectroscopic study. *Phys. Chem. Miner.*, 12, 55-64.
- BOUKILI, H. (1984). — Pétrologie, minéralogie et géochimie des altérations des roches ultrabasiques à chromite de Campo Formoso, Brésil. Thèse 3^e cycle, Strasbourg, 130 p.
- BOUKILI, H., NOVIKOFF, A., BESNUS, Y., SOUBIES, F., QUEIROZ, C. (1983). — Pétrologie des produits de l'altération des roches ultrabasiques à chromites de Campo Formoso, Etat de Bahia, Brésil. Proc. Intern. CNRS Col. "Pétrologie des Altérations et des Sols". Nahon et Noack Eds., *Sci. Géol., Mém.*, 72, 119-328.
- BURNS, R.G. (1970). — Mineralogical application of crystal field theory. Cambridge University Press, 224 p.
- CHIDESTER, A.M. (1962). — Petrology and geochemistry of selected talc bearing ultramafic rocks and adjacent country rocks in north-central Vermont. *U.S. Geol. Surv. Prof. Pap.*, 345, 207 p.
- CHUKHROV, F.V., ZVYAGIN, B.B., DRITS, V.A., GORSHKOV, A.I., ERMIOVA, L.P., GOILO, E.A., RUDNITSKAYA, E.S. (1979). — The ferric analogue of pyrophyllite and related phases. In Proc. VI Intern. Clay Conf., Oxford, 1978, Mortland M.M. and Farmer V.C., Eds., *Develpt. Sedim.*, v. 27, Elsevier, 55-64.

- CLAYTON, R.N., MAYEDA, T.K. (1963). — The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analyses. *Geochim. Cosmochim. Acta*, 27, 43.
- CLAYTON, R.N., O'NEIL, J.R., MAYEDA, T.K. (1972). — Oxygen isotope exchange between quartz and water. *J. Geophys. Res.*, 77, 17, 3057-3067.
- COEY, J.M.D. (1980). — Clay minerals and their transformations studied with nuclear techniques : the contribution of Mössbauer techniques. *Atomic Energy Review*, 18, 1, 73-124.
- COEY, J.M.D., CHUKHROV, F.V., ZVYAGIN, B.B. (1984). — Cation distribution, Mössbauer spectra and magnetic properties of ferri-pyrophyllite. *Clays Clay Miner.*, 32, 198-204.
- COLIN, F. (1984). — Etude pétrologique des altérations des pyroxénites du gisement nickélifère de Niquelandia (Brésil). Thèse 3^e cycle, Paris VII, 136 p.
- DECARREAU, A. (1983). — Etude expérimentale de la cristallogénése des smectites. Mesure des coefficients de partage smectite trioctaédrique/solution aqueuse pour les métaux M²⁺ de la première série de transition. *Sci. Géol. Mém.* 74, 185 p.
- DECARREAU, A. (1985). — Partitioning of divalent transition elements between octahedral sheets or trioctahedral smectites and water. *Geoch. Cosmochim. Acta*, 49, 1537-1544.
- DECARREAU, A., BONNIN, D. (1986). — Synthesis and crystallogenesis of ferric smectites. Experiments in partially reducing conditions. *Clay Minerals*, (sous presse).
- DELVIGNE, J. (1965). — Pedogenèse en zone tropicale. La formation des minéraux secondaires en milieu ferrallitique. *Mém. ORSTOM*, Paris, 13, 177 p.
- DELVIGNE, J. (1983). — Micromorphology of the alteration and weathering of pyroxenes in the Koua Bocca ultramafic intrusion, Ivory Coast, Western Africa. In Proc. Intern. CNRS Col. "Pétrologie des Altérations et des Sols", Nahon & Noack Eds, *Sci. Géol. Mém.* 72, 57-68.
- DEVIGNE, J.P. (1959). — Le Précambrien du Gabon occidental en Afrique Equatoriale Française et régions limitrophes. *Bull. Direction Mines et Géologie*, 11, 315 p.
- DUBINSKA, E. (1984). — Sepiolites and talc-like minerals from Szklary near Zabkowice Slaskie (Lower Silesia). *Archiwum Miner.*, XXXIX, 2, 53-99.
- ESCANDE, M.A. (1983). — Echangeabilité et fractionnement isotopique de l'oxygène des smectites magnésiennes de synthèse. Etablissement d'un géothermomètre. Thèse 3^e cycle, Orsay, 150 p.
- ESCANDE, M., DECARREAU, A., LABEYRIE, L. (1984). — Etude expérimentale de l'échangeabilité des isotopes de l'oxygène des smectites. *C.R. Acad. Sci. Paris*, 299, 11, 707-710.
- ESLINGER, E.V., SAVIN, S.M. (1973). — Mineralogy and oxygen isotope geochemistry of the hydrothermally altered rocks of the Ohaki-Broadlands, New-Zealand geothermal area. *Am. J. Sci.*, 273, 240-267.
- FONTANAUD, A. (1982). — Les faciès d'altération supergène des roches ultrabasiques. Etude de deux massifs de lherzolite (Pyrénées, France). Thèse 3^e cycle, Poitiers, 103 p.
- FORTUNÉ, J.P. (1971). — Contribution à l'étude minéralogique et générique des talcs pyrénéens. Thèse Sci., Toulouse, 227 p.
- FORTUNÉ, J.P., GAVOILLE, B., THIEBAUT, J. (1980). — Le gisement de talc de Trimouns près de Luzenac (Ariège). 26^e CGI, E 10, 43 p.
- FRITZ, B. (1981). — Etude thermodynamique et modélisation des réactions hydrothermales et dia-génétiques. *Sci. Géol. Mém.* 65, 197 p.
- GUGGENHEIM, S., BAILEY, S.W. (1982). — The superlattice of minnesotaite. *Can. Mineral.*, 20, 579-584.
- HASSANIPAK, A.A., ESLINGER, E. (1985). — Mineralogy, crystallinity, O¹⁸/O¹⁶ and D/H of Georgia kaolins. *Clays Clay Miner.*, 33, 2, 99-106.
- HELLER-KALLAI, L., ROZENSON, I. (1981). — The use of Mössbauer spectroscopy of iron in clay mineralogy. *Phys. chem. Minerals*, 7, 223-238.
- HEMLEY, J.J., MONTOYA, J.W., CHRIST, C.L., HOSTETLER, P.B. (1977). — Mineral-equilibria in the MgO-SiO₂-H₂O system : I. Talc-chrysotile-forsterite-brucite stability relations. *Am. J. Sci.*, 277, 322-351.
- HOGG, C.S., MEADS, R.E. (1970). — The Mössbauer spectra of several micas and related minerals. *Mineral. Mag.*, 37, 289, 606-614.
- ILDEFONSE, J.P. (1980). — Recherches sur le transport du silicium et du magnésium en conditions hydrothermales. Thèse Sciences, Orléans, 131 p.
- JAMES, A.T., BAKER, D.R. (1976). — Oxygen isotope exchange between illite and water at 22 °C. *Geochim. Cosmochim. Acta*, 40, 235-239.
- KULLA, J.B. (1978). — Oxygen and hydrogen isotope fractionation factors determined in experimental clay-water systems. Ph. D., Thesis, Urbana, Illinois.
- KUNDING W., BOMMER, H., CONSTABARIS, G., LINQUIST, R.H. (1966). — Some properties of supported small α-Fe₂O₃ particles determined with the Mössbauer effect. *Phys. Rev.*, 142, 2, 327-333.
- LABEYRIE, L., JUILLET, A. (1982). — Oxygen isotopic exchangeability of diatom value silica ; interpretation and consequences for paleoclimatic studies. *Geochim. Cosmochim. Acta*, 46, 967-975.
- LAWRENCE, J.R., TAYLOR, H.P. (1971). — Deuterium and oxygen 18 correlation : clay minerals and hydroxides in quaternary soils compared to meteoric waters. *Geochim. Cosmochim. Acta*, 35, 993-1003.
- LAWRENCE, J.R., TAYLOR, H.P. (1972). — Hydrogen and oxygen isotope systematics in weathering profiles. *Geochim. Cosmochim. Acta*, 36, 1377-1393.
- MATHEZ, G. (1976). — Prospection des indices de nickel de Moyando (Lefoi) et de Foungouesso (Extensions E et NE). Unpub. rept. SODEMI,

- Abidjan, 361, 55 p.
- MENEGOTTO, E., FORMOSO, M.L.L. (1983). — Geochemical study of the weathering of the ultrabasic Pedras Petas Massif, Sao Sepe, Brazil. Proc. II Intern. Seminar Lateritization processes, Sao Paulo, 1982, Melfi and Carvalho Eds, 317-329.
- MOINE, B. (1982). — Géochimie des transformations métasomatiques à l'origine du gisement de talc et chlorite de Trimouns (Luzenac, Ariège, France). II. Approche des conditions physico-chimiques de la métasomatose. *Bull. Minéral.*, 105, 76-88.
- MOINE, B., GAVOILLE, B., THIEBAUT, J. (1982). — Géochimie des transformations métasomatiques à l'origine du gisement de talc et chlorite de Trimouns (Luzenac, Ariège, France). I. Mobilité des éléments et zonalités. *Bull. Minéral.*, 105, 62-75.
- NAHON, D. (1977). — L'altération des roches ultrabasiques de la région de Biankouma (C.I.). I. Le massif de Sipilou Nord. Rapport Sci. de la Terre, Univ. Abidjan, n° 21, 22 p.
- NAHON, D. (1978). — L'altération des roches ultrabasiques de la région de Biankouma (C.I.) II. Le massif de Moyango. Rapport Sci. de la Terre, Univ. Abidjan, n° 22, 16 p.
- NAHON, D., PAQUET, H., DELVIGNE, J. (1982). — Lateritic weathering of ultramafic rocks and the concentration of nickel in the Western Ivory Coast. *Econ. Géol.*, 77, 1159-1175.
- NALDRETT, A.J. (1966). — Talc-carbonate alteration of some serpentined ultramafic rocks south of Timmins, Ontario. *J. Petrol.*, 7, 3, 489-499.
- NICOLAS, J., SAGON, J.P. (1966). — Altération en talc d'une diabase au sud de Quintin (Côtes du Nord). *Bull. Gr. Fr. Argiles*, XVIII, 14, 47-50.
- NOACK, Y., COLIN, F. (1986). — Chlorites and "chlorite-like" minerals in ultrabasic rocks of Moyango (Ivory Coast) and Angiquinho (Brazil). *Clay Minerals*, sous presse.
- O'NEIL, J.R. and TAYLOR, H.P. (1969). — Oxygen isotope equilibrium between muscovite and water. *J. Geophys. Res.*, 74, 6012-6022.
- O'NEIL, J.R. and KHARAKA, V.K. (1976). — Hydrogen and oxygen isotope exchange reactions between clay minerals and water. *Geochim. Cosmochim. Acta*, 40, 241-246.
- PION, J.C. (1979). — Altération de massifs cristallins basiques en zone tropicale sèche. Etude de quelques toposéquences en Haute-Volta. *Sci. Géol.*, Mém. 57, 220 p.
- ROSSMAN, G.R. (1984). — Spectroscopy of micas. *Review in Mineralogy*, vol. 13, Bailey S.W., Ed., Mineralogical Soc. of America.
- ROZENSON, I., HELLER-KALLAI, I. (1977). — Mössbauer spectra of dioctahedral smectites. *Clays Clay Miner.*, 25, 94-101.
- SAVIN, S.M., EPSTEIN, S. (1970). — The oxygen and hydrogen isotope geochemistry of clay minerals. *Geochim. Cosmochim. Acta*, 34, 25-42.
- SHEPPARD, S.M.F. (1977). — The Cornubian batholith, SW England : D/H and O¹⁸/O¹⁶ studies of kaolinite and other alteration minerals. *J. Geol. Soc. London*, 133, 573-591.
- SMITH, G. (1980). — Evidence for optical absorption by Fe²⁺-Fe³⁺ interactions in MgO:Fe. *Phys. Stat. Sol.*, (a), 61, K191, K195.
- TOURNARIE, M. (1969). — Programme d'affinement statistique, version K par régression non linéaire. *J. Phys.*, 10, 737.
- TRESCASES, J.J. (1975). — L'évolution géochimique supergène des roches ultrabasiques en zone tropicale. Formation des gisements nickélières de N-Calédonie. *Mém. ORSTOM*, Paris, 78, 259 p.
- WACKERMANN, J.M. (1975). — L'altération des massifs cristallins basiques en zone tropicale semi-humide. Etude minéralogique et géochimique des arènes du Sénégal Oriental. Conséquences pour la cartographie et la prospection. Thèse Science, Strasbourg, 373 p.
- WENDLANDT, W.W. and HECHT, H.G. (1966). — Reflectance spectroscopy. Interscience Publishers, 298 p.
- WENNER, D.B., TAYLOR, H.P. Jr. (1971). — Temperature of serpentization of ultramafic rocks based on ¹⁸O/¹⁶O fractionation between coexisting serpentine and magnetite. *Contrib. Mineral. Petrol.*, 32, 165-185.
- YEH, E.W. and SAVIN, S.M. (1977). — Mechanism of burial metamorphism of argillaceous sediments. O isotope evidence. *Geol. Soc. Am. Bull.*, 88, 1321-1330.