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RUBIDIUM-STRONTIUM AND POTASSIUM-ARGON RADIOMETRIC DATATIONS ON GLAUCONITES OF THE "BANDE NOIRE" (BASE OF THE ASSE CLAY) FROM THE BELGIAN EOCENE[1]

by

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(3 figures and 4 tables)

RESUME.- La méthode Rb-Sr a été appliquée à une douzaine d'échantillons provenant de huit points de prélèvements en Belgique et dans le Nord de la France, représentant la "Bande Noire" (base de l'argile d'Asse, correspondant à NP 15). L'influence de la granulométrie, des propriétés minéralogiques et du traitement avant analyse a été prise en considération. Dans la plupart des cas, un bon accord est obtenu entre âges apparents Rb-Sr et K-Ar (en utilisant les constantes recommandées par l'IUGS en 1976), si les grains glauconieux sont soumis à un nettoyage supplémentaires aux ultrasons, avant analyse Rb-Sr. Il semblerait, au moins dans le cas présent, que la présence de matériaux hérités influence davantage les âges apparents Rb-Sr que les âges apparents K-Ar. L'âge obtenu, en ne prenant en considération que les résultats K-Ar ainsi que les résultats Rb-Sr sur glauconies "propres", est de 41.5 m.a., différent des 44 m.a. (avec les constantes utilisées dans ce travail) acceptés généralement pour la limite Eocène Moyen - Eocène supérieur (BERGGREN 1972).

ABSTRACT.- A dozen glauconite samples from eight localities in Belgium and Northern France, representing the "Bande Noire" (base of the Asse Clay, corresponding to NP 15) have been analyzed with the Rb-Sr method and some of them with the K-Ar method. The possible influence of grain size, mineralogy and handling procedure before analysis has been investigated. In most cases and provided that the glauconite pellets are submitted to additional ultrasonic cleansing before analysis with the Rb-Sr method, good agreement is observed between the apparent ages obtained by the K-Ar and Rb-Sr methods, using the decay constants recommanded by the IUGS in 1976. Present investigation suggests that inherited material has a greater influence on the Rb-Sr apparent ages than those obtained by the K-Ar method. The figure thus obtained, considering the K-Ar data and the Rb-Sr data on "clean" glauconite only, is 41.5 m.y. This is at variance with the generally accepted absolute age for the Middle Eocene to Upper Eocene transition, i. e. 44 m.y., as based on the same decay constants as used in the present paper (BERGGREN 1972).

SAMENVATTING.- Een twaalftal monsters, afkomstig van acht verschillende plaatsen in België en Noord Frankrijk, van de "Bande Noire" (basis van de Klei van Asse, die overeenkomt met NP 15) werden met de Rb-Sr methode onderzocht. Op sommige werd ook de K-Ar methode toegepast. De invloed van korrelgrootte, mineralogie en behandeling vóór analyse werd nagegaan. Op voorwaarde dat de glaukonietkorrels met ultrasone trillingen werden gereinigd alvorens met de Rb-Sr methode te worden onderzocht, is er over het algemeen een goede overeenstemming tussen K-Ar en Rb-Sr ouderdommen; mits gebruik te maken van de vervalkonstanten die door het IUGS in 1976 werden aangeraden. De Rb-Sr schijnbare ouderdommen blijken, althans in deze studie, meer dan die bekomen met de K-Ar-methode, te worden beïnvloed door de aanwezigheid, in het glaukoniet, van geërfd materiaal. De K-Ar resultaten en de Rb-Sr resultaten van "zuivere" glaukonieten geven een ouderdom van 41.5 m.j. Dit cijfer verschilt van de algemeen aangenomen absolute ouderdom van 44 m.j. (met de hier gebruikte vervalkonstanten) voor de grens Midden-Boven Eoceen. (BERGGREN 1972).

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INTRODUCTION

GEOLOGY

The Asse Clay (a compact, partly sandy and mostly glauconitic clay) can be found in the whole western and central part of Belgium (see fig, 1), where it overlies either the Wemmel Sands or the older Lede Sands. Notwithstanding the occasionally important variations in its thickness, sand and glauconite content, the Asse Clay is easy to identify and can be followed throughout the country. In particular, the so-called "Bande Noire" (= black strip), a thin (from a few decimeters to more than 1 meter), highly glauconitic layer, wich forms at most places, the base of the Asse Clay, is one of the key-beds of the Belgian Eocene.

Being the base of a transgressive formation, this "Bande Noire" can be considered as isochronous, within the limits of error of our datation methods, wich are, in this case of about 1 to 2 m.y. It is fossiliferous, containing a.o. *Pecten (amusium) corneum* and *N. Orbignyi* = *N. Wemmelensis.*

Different authors suggest an autochtonous rather than an allochtonous origin for the glauconite pellets from the Asse clay (KAASSCHIETER, 1961; ODIN, 1972). However, the high content (up to about 50 %) in glauconite of the "Bande Noire" might be considered as an indication of mechanical enrichment. Nevertheless some arguments can be put forward for the authigenic character of at least part of this glauconite which is very heterogeneous in colour, shape and grain size. (They will be discussed in the section "material", where those characteristics are given for all investigated samples).

To sum up, the probable authigenic (or "sub-authigenic") character of the glauconite, the fact that fresh samples can easily be collected in outcrops and bore-holes from many locations, the presence of different sorts of glauconite, the probable isochronous character of this key-bed and the absence of burial diagenesis, make this case interesting for the geochronologist.

METHODOLOGY

The use of glauconite in absolute dating is subject to a certain number of limitations, that are mainly concerned with the origin and subsequent evolution of both glauconite and sediment. These problems have been discussed in different papers (HERZOG *et al.*, 1958; HURLEY *et al.*, 1960; ODIN, 1975 ; a.o.). The earlier attempts to use glauconite in absolute dating have caused a certain scepticism among geochronologists. On the other hand, it has been argued (ODIN, 1975) that a homogeneous glauconite that has never been exposed to temperatures over 150°C, and that contains more than 7 % K_2O, yields K-Ar ages that are, within 5 %, comparable with data obtained on high temperature minerals. However, some glauconites, that do not fulfil all of these requirements still seem to give acceptable ages. Thus, it appears that the criteria to decide whether or not a glauconite is a good chronometer are not yet fully established, and that the question deserves further investigation.

From a pragmatic point of view, it is clear that the comparison of Rb-Sr with K-Ar results on the same sample, may help to solve some of the remaining uncertainties. Agreement of Rb-Sr with K-Ar dates, is an argument - though not decisive - to consider that glauconite acted as a closed system since its constitution, whether or not the "constitution" so defined, corresponds to the time of "sedimentation".

STRATIGRAPHY

In the classical understanding of the Belgian Eocene, the Asse clay forms, either together with the Wemmel Sands or independently, the lower and more important part of the Belgian Bartonian (GULINCK, 1965; GULINCK & HACQUAERT, 1954). In the latter case the Wemmel Sands are considered to be a chronostratigraphical unit (stage) on their own. This is what appears from the propositions of correlation between neighbouring basins, made at the Colloquia in Bordeaux, 1962 (Paleocene) and Paris, 1968 (Eocene). According to these correlations, the Asse clay should correspond with the Barton Beds in England and with the Marinésien and Auversien in the Paris Basin. The Wemmel Sands are supposed to be correlated with the Upper Bracklesham Beds and with the Upper-Lutétien (BLONDEAU *et al.*, 1965; CURRY *et al.*, 1969).

However, the similitude of the fossil content from the Asse clay with that of the Wemmel Sands has been pointed out repeatedly (GLIBERT, 1938; LERICHE, 1943; MARTINI & MOORKENS, 1969) and to some authors the Wemmel Sands are the coastfacies corresponding to the off-shore Asse clay (KAASSCHIETER, 1961; LERICHE, 1943; DROOGER, 1969). According to recent micropaleontological investigations (MARTINI & MOORKENS, 1969; MARTINI, 1969) both the lower part of the Asse clay and the Wemmel Sands form one single biostratigraphic zone (showing assemblages of the NP 15, or *Chiphragmalithus alatus (= quadratus)* zone), which should be older than the Barton Beds. Much ear-

lier, GLIBERT (1938) reported in a macropaleontological investigation the Wemmel Sands to be slightly older than the lowermost Barton Beds.

PREVIOUS GEOCHRONOLOGICAL DATA

Previous geochronological measurements, made on samples from the "Bande Noire" are reported in Table I, using the decay-constants, mentioned in row (x). According to the recommendation made by the I.U.G.S. subcommission on Geochronology (Subcommission on Geochronology, 1976), in the present study the constants mentioned in row (y) have been used.

In order to be able to compare some of the previous results with our own, the first have been recalculated with the new constants in row (y). The first reported data on samples G-54, G-132 and G-134, have been used by BERGGREN (1972) to confirm the absolute time-scale for the Tertiary, previously proposed by him, on the base of other data obtained in other localities (BERGGREN, 1969). However, subsequent measurements (made in Bern), revealed the first to be grossly incorrect. A re-investigation of the case is therefore justified. In this paper, more analytical details are given than customary : past experience shows it necessary.

II.- MATERIAL

SAMPLING

Altogether 9 samples - 5 from bore-holes (dry deep-drillings using spire-drills without water-flushing) and 4 from outcrops - were collected. Data on sample location are given in Table II, together with the glauconite content of the total rock and the K_2O-content of the glauconite. The sampling places are shown on the map (fig. 1).

SEPARATION, CLEANING AND SELECTION OF THE GLAUCONITES

In the process of mineral separation, care must be exercised to obtain pure glauconite samples, free of inclusions, coating, etc... Moreover, all operations which may cause loss of either parent or daughter isotopes should be avoided. With this in mind, only physical methods were used to separate the glauconites from the sediment and a temperature of 90°C was never exceeded. The applied procedure was not the same for all samples. A detailed description of the adopted methods is given in appendix I.

In nearly all samples the fraction below 100 μ, appeared to consist for the greater part out of fragments of glauconite grains (very often pale green), and of other minerals, mostly joined to small glauconitic pellets. Probably, most of this fraction has been released from the larger glauconite grains during their cleaning by washing in water or by ultrasonic treatment. The fraction over 100 μ, consists essentially of green to dark green grains; the largest attaining a diameter of 200 to 250 μ. Their shape is irregular and often angular. In samples DB-79, DB-90, C-1 and C-2, in addition to some impurities and the green grains that form the major part of the glauconite sample (about 90 o/o, 98 o/o, 80 o/o and 95 o/o respectively), a second and very different kind of glauconite grains could be found. They are very dark green to black, round or bean-shaped, with a smooth, regular surface. They are also much larger (200 μ to 400 μ) than the above mentioned green irregular grains.

The presence of two completely different kinds of glauconite can be considered as an argument for the authigenic character of at least one of them. Both kinds of glauconite are very different in grain size and are embedded in a clay matrix, together with the rest of the sand fraction, which has a completely different grain size distribution. We do not rule out short distance transportation (subauthigenic glauconite). But we can rule out that all the glauconite originates by a natural, mechanical concentration process from older, eroded deposits, with much lower glauconite concentration. This would imply much better granulometric sorting. The question arises even whether glauconite can stand such erosion and mechanical concentration implying a long transportation process because of its softness.

From sample DB-79, C-1 and C-2 we could separate enough of the coarse black glauconite grains, to date them separately. Fig. 2 shows very schematically the glauconite content of each sample. The vertical bars (full black for Rb-Sr; open for K-Ar) indicate the fractions upon which datations were carried out.

MINERALOGY

The pure monomineral glauconite (a hydrous, iron-alumino silicate; ferrifereous homeotype of illite) is rather rare. According to different investigators (HOWER, 1961; BURST, 1958; BENTOR and KASTNER, 1964; WARSHAW, 1957), about all glauconites are interlayered materials, built - up of various proportions of non-expandable 10 Å - layers and expandable

TABLE I - PREVIOUS GEOCHRONOLOGICAL DATA

USED DECAY CONSTANTS \ NR. SAMPLE (USED METHOD)	G-54	G-132		G-134		G-54 (2) (Rb-Sr glauconite +total rock isochron)	MIDDLE-UPPER EOCENE TRANSITION	
	A(1)	A(1)	B(1)	A(1)	B(1)		BERG-GREN 1972	ODIN 1975
(x) $^{40}K/K = 1.19\ 10^{-4}$ $^{40}K_{\lambda\beta} = 4.72\ 10^{-4}\ y^{-1}$ $^{40}K_{\lambda e+\lambda e'} = .584\ 10^{-10}\ y^{-1}$ $^{87}Rb_{\lambda} = 1.47\ 10^{-11}\ y^{-1}$	41.8 ±3.0	44.4 ±3.0	39.8 ±2.0	44.0 ±3.0	38.3 ±2.0	45.2	43	39
(y) $^{40}K/K = 1.167\ 10^{-4}$ $^{40}K_{\lambda\beta} = 4.962\ 10^{-10}\ y^{-1}$ $^{40}K_{\lambda e+\lambda e'} = .5811\ 10^{-10}\ y^{-1}$ $^{87}Rb_{\lambda} = 1.42\ 10^{-11}\ y^{-1}$			41.1 ±2.0		39.5 ±2.0	46.6	44	40

(1) All results in columns A should be discarded because of an error in the atmospheric argon correction (personal communication, G.S. Odin). Some of them have been re-investigated in better conditions at the Mineralogisches Petrographisches Institüt der Universität Bern (Odin, 1975.) giving the results in columns B.

(2) Ref. : Bonhomme et al., 1968

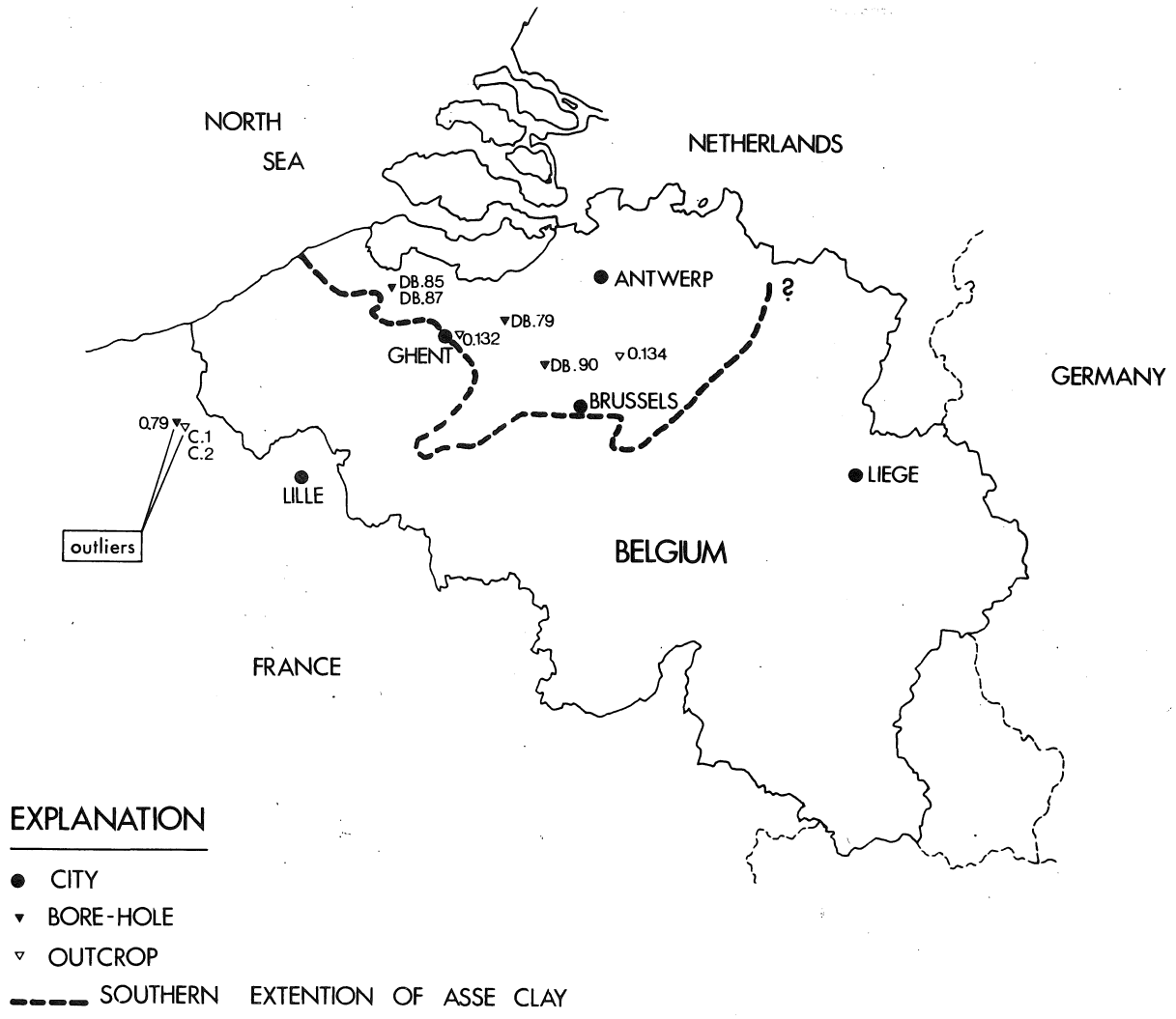


Figure 1.- Sampling location (1 cm = 26,6 kms)

(smectitic) layers. Several propositions have been made to subdivide the continuous series of glauconites (containing from less than 5 to over 40 o/o of expandable layers) into different mineralogical classes. The amount of expandable layers appears to be inversely proportional to the K_2O-content (Mc RAE and LAMBERT, 1968; MANGHNANI and HOWER, 1964; VELDE and ODIN, 1975; HOWER, 1961).

Inasmuch as post-depositional diagenesis involving K-enrichment is ruled out, the less expandable layers a glauconite contains, the more it is supposed to be adequate for use in geochronological work. Indeed, it is easier to imagine a change in the content of one or more of the ions (or atoms), with which the datation methods deal, in a more open K-poor lattice than in a more closed K-rich one. This point of view has been advocated by OWENS and SOHL (1972) and ODIN (1975).

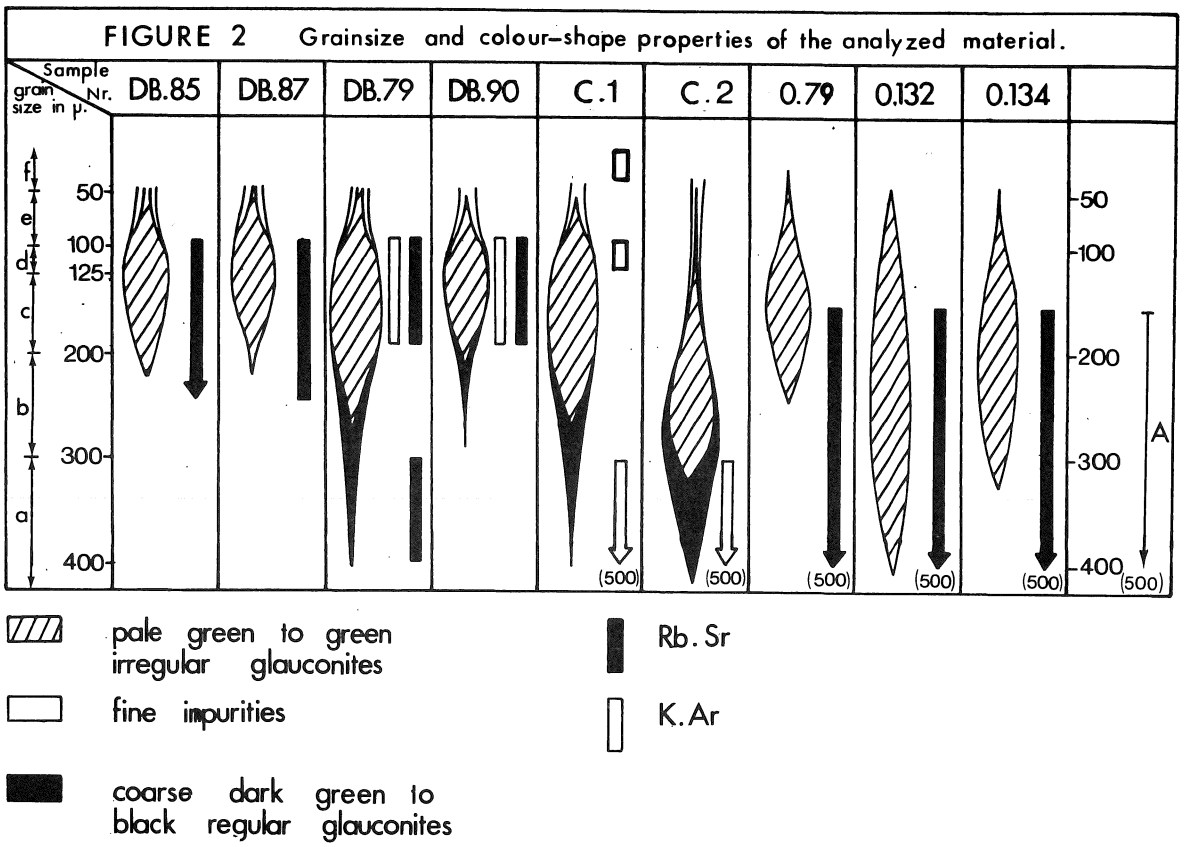
In order to have a rough estimate of the amount of expandable layers in each sample, we have applied a method developped by ODIN (1974). It consists in an X-ray-diffraction analysis of a slightly oriented powder specimen. The position and shape of the (001)-"10 Å"-peak, the importance of the $(11\bar{2})$- and (112)-peaks in comparison to the (003)-peak, and the neatness of the $(11\bar{1})$- and (021)-peaks in respect to the more important (020)-peak, are indications of the degree of disordering and of the amount of expandable layers. Hence, these informations give a rough idea of the K_2O-content.

Among all analysed samples only DB-79.a (>300 μ) may be considered as a well ordered 1M-glauconite,

TABLE II DATA ON SAMPLING SITES, CONDITIONS OF SAMPLING AND SAMPLED MATERIAL.

SAMPLE NR.	LOCALITY	OUTCROP OR DRILL (with NR. and LEVEL in m)	"Bande Noire" overlies	(in m) HEIGHT OF SAMPLE ABOVE BASE OF ASSE CLAY	GLAUCONITE CONTENT in %	K_2O CONTENT OF GLAUCONITE in %	COLLECTED BY
C-1	MONT DES RECOLLETS (FR.)	old refreshed outcrop	LEDE SANDS	0	51.3	7.61	E. ELEWAUT V.U.B. Brussels
C-2	MONT DES RECOLLETS (FR.)	old refreshed outcrop	LEDE SANDS	0	72.0	7.49	E. ELEWAUT V.U.B. Brussels
DB-85	MALDEGEM	Drill -38.5 133.DB 12	WEMMEL SANDS	1.80	41.8	ca.8.0	W.DE BREUCK & P.JACOBS R.U.G. Ghent
DB-87	MALDEGEM	Drill -39.5 133 DB 12	WEMMEL SANDS	.80	43.8	ca.7.5-8.0	W.DE BREUCK & P.JACOBS R.U.G. Ghent
DB-90	ASSE TER HEIDE	Drill -31.0 235 DB 1	WEMMEL SANDS	0	21.0	7.53	W.DE BREUCK & P.JACOBS R.U.G. Ghent
DB-79	LOKEREN	Drill -33.6 148 DB 60	WEMMEL SANDS (?)	0	43.0	7.42	W.DE BREUCK & P.JACOBS R.U.G. Ghent
O-79	MONT CASSEL (FR.)	Drill -21.5	LEDE SANDS	4.3 *	ca. 18	ca.7.5	G.S. ODIN Université de Paris VI
O-132	GENT	fresh artificial outcrop	WEMMEL SANDS	0	ca. 32	7.96	S. GEETS R.U.G. Ghent
O-134	ZEMST	fresh artificial outcrop	WEMMEL SANDS	0	ca. 36	8.02	M. GULINCK Geological Survey of Belgium

*At the Mont Cassel the "Bande Noire" consists of a complex of more or less glauconitic layers. On a whole it is less glauconitic (from 12 up to 25 %) than in general, but much thicker (4.5 to 5 m).



fitting in BURST's (1958) "first group" and in BENTOR and KASTNER's (1964) "class Ia". All the other samples appear to be more or less disordered and can be considered as to be similar to the better ones of BURST's second group, and certainly do not contain more than 20 °/o of expandable layers. Even sample DB-90.cd, which gives undeniably the worst X-ray pattern still has a K_2O-content (measured by flame photometry) of 7.53 °/o, which should correspond to an amount of expandable layers of hardly 10 °/o (Mc RAY and LAMBERT, 1968; MANGHNANI and HOWER, 1964; HOWER, 1961). According to BURST (1958) "ordered stacking becomes less apparent . . ., when the K-atom equivalent falls below approximately 1.4 per unit cell" (which corresponds with a K_2O-content of about 7.7 °/o) and "disordering begins when fewer than two out of every three possible potassium positions are filled" (1.33 per unit cell corresponds with a K_2O-content of about 7.0 °/o). All our K_2O-figures are above 7 °/o.

III.- K-Ar METHOD - RESULTS AND DISCUSSION

Argon was analysed on a Varian Mat GD 150 mass spectrometer, on line with a glass extraction system described by PURDY (1972).

The spike was calibrated against P207 muscovite, using a value of 28.15×10^{-6} cc ^{40}Ar rad/gr STP.

Potassium measurements were made by X-ray fluorescence. The apparatus, being calibrated by use of several well known rock standards, gives a mean of 9.53 °/o$K_2O \pm 0.05$ (2 σ) for the Bern Biotite 4B (analyst : Miss DUREZ and Mr. DELVIGNE; Royal Museum for Central Africa, Tervuren). The measurements were spread over a period of 18 months. During this period, measurements on the above mentioned standards showed no systematic variation.

Nevertheless, in the table of analytical data, time gaps between groups of analyses are marked by a double line.

From repeated measurements of standards and samples, errors on the apparent ages are estimated to 3 °/o at the 95 °/o analytical intralaboratory confidence level.

In addition to this statistical error estimation, a specific uncertainty must be mentioned when dealing with glauconites; namely : the influence of air moisture on the sample weight.

Different conditions of temperature and humidity during preparation and storage of the samples bear influence on the hygroscopic water content of the glauconite pellets.

Trying to put forward a quantitative appreciation of this particular effect seems at this very moment impossible. Indeed, experience taught us that different types of glauconite pellets also show different hygroscopic "attitudes".

On the other hand, drying of the samples above 90°C makes the mineral especially sensitive to water absorption; the sample weight thus becomes definitely unstable.

Still, some degree of stabilisation could be obtained by :

1. using glauconites that never in the course of separation and preparation have been exposed to temperatures higher than 90°C;
2. weighing the samples under standard atmospheric conditions and at room temperature.

The analytical constants are given in table I row (y).

A plausible explanation for the discrepant apparent age, measured on the fraction C-1.f (< 50 μ) is to be found in the sample treatment. Sample C-1, unlike C-2, contained an appreciable amount of carbonaceous debris. Therefore, C-1 underwent a treatment of ten minutes ultrasonic cleaning in water, to obtain a complete disaggregation of the sediment material.

OBRADOVICH (1964, p. 20) noted that the size fractions obtained after ultrasonic treatment are no longer representative for the size fraction of the original sample, but that they are instead the result of this treatment; i.e. a breaking down of the pellets is involved.

More recently, ODIN (1976) reported measurements on the G1-O powder (glauconite reference material) that clearly demonstrate an argon loss in comparison with G1-O pellets.

This means that the low apparent age of C-1.f could be due to argon loss caused by the sample treatment. Thus, the apparent ages of both C-1.f (< 50 μ) and C-1, total glauconite - partially consisting of C-1.f (< 50 μ) - should be discarded. They have been omitted when calculating the mean apparent age of the "Bande Noire" glauconites.

It would appear that the analytical errors alone can account for the spread in apparent ages (though the limited number of the results does not allow the formal statistical treatment which only could establish this).

TABLE III. K-Ar data

	% radiogenic	$x10^{-6}$ cc ^{40}Ar rad/ gr STP	% K	age in million years
DB-79	82.98	9.97	6.16	41.1±1.0
DB-90	83.38	10.15	6.25	41.2±1.0
C-1 total glauconite	83.78	9.63	6.23	(39.3±0.9) (1)
C-1f (< 50 µ)	76.37	8.41	5.80	(36.8±1.0) (1)
C-1d (100-125 µ)	75.73	9.97	6.19	40.9±1.1
C-1a (> 300 µ)	81.14	10.17	6.45	40.0±1.0
C-2 total glauconite	84.77	9.94	6.22	40.5±1.0
C-2a (> 300 µ)	85.05	10.53	6.38	41.9±1.0
	Mean :			40.9±0.5 (2σ)

(1) Not used for calculating the mean.

In appendix III the analytical data on glauconite sample G1-O, obtained in the same conditions, are given. Though this standard cannot be used neither for K, Ar, Rb, Sr absolute amounts, it may well be used as a standard in radiometric age (1).

IV.- Rb-Sr METHOD - RESULTS AND DISCUSSION

Rubidium and Strontium measurements were carried out by mass spectrometry using the isotope dilution method. For more technical details we would like to refer to Appendix II. Results are given in Table IV.

The stated errors correspond to the reproducibility at the 2σ level. It is based on the reproducibility, determined in each case, of spiking, aliquoting, mass spectrometry, etc . . . The errors on each of these operations considered as independant are combined statistically (root of the sum of the squares).

Too few repeated measurements on standards have been done in the considered period of time to allow an independent determination of the over-all reproducibility on each age determination. In the case of the repeated measurements on samples DB-90-cd and O-132-A it is important to note that the aliquoting of the glauconite sample occured before the final ultrasonic treatment in acid and that this may cause a larger spread in the data, inasmuch as a perfect standardization of this operation is possible. It has been assumed that the common strontium present is isotopically similar to that of open sea water at the time of glauconite formation. This would thus correspond to $^{87}Sr/^{86}Sr = .7086$ (HOFMANN *et al.*, 1972, PETERMAN *et al.*, 1970, DASH and BISCAYE, 1971). The notion of closed basin does not seem to have to be considered in the present case, the presence of authigenic glauconite being itself an argument for open sea environment. The calculated ages, for the acid-washed samples, are relatively unsensitive to the choice of this initial common strontium.

The treatment given to the sample before analysis needs to be precised for, as observed from the data presented in table IV and fig. 3 the radiometric ages measured depend on it. A final cleaning-up of all samples with ultrasons in acidic medium (1 N HCl) was judged necessary. The sonic vibration removes impurities which often carry excess ^{87}Sr (inherited clay, etc. . .) and the acid dissolves carbonates which contain considerable amounts of common strontium. Moreover, the easily exchangeable ions are presumably removed too; namely common strontium. But previous experiments (PASTEELS *et al.*, 1976) show that neither the mechanical vibration nor the chemical effects of the acid, alter significantly the rubidium or radiogenic strontium contents of the glauconite itself. Apparently thus the $^{87}Sr^{++}$-ion produced by radioactive decay remains in the same, non-exchangeable site as its progenitor $^{87}Rb^{+}$.

In order to confirm the conclusions of this earlier study, untreated splits of the same samples, mentioned as fractions N in table IV and fig. 3, were also analysed. These fractions N have thus been prepared as described in Appendix I, without further treatment.

We observed that for samples O-79.A, DB-79.cd and DB-79.a the apparent Rb-Sr ages on HCl ST, and N fractions respectively are in excellent agreement. These ages on different samples also agree with each other and with the K-Ar apparent ages in general. These cases are of straightforward interpretation and one is inclined to give some credit to these data, on very first inspection at least.

Other cases however are less clear, yielding age indications which are evidently or presumably unreliable. For samples DB-85.cd and DB-87.cd, a lowering of the apparent ages follows the HCl treatment. Thus the starting material, the so-called fractions N, obviously needed further purification. The fact that after the sonic treatment the apparent ages remain somewhat on the high side raises the question whether the further purification has been sufficient. The possibility may indeed be considered that some inherited clay with excess ^{87}Sr is still present, affecting by its presence the result of the radiometric ages on HCl ST fractions too.

So far, all the discussed cases fit well with the notion of inherited clayish material removed by the sonic treatment, carrying or not excess of radiogenic strontium, and a lowering of the common strontium content, in all case, as a consequence of the use of an acidic medium for this final cleaning. The rubidium contents are slightly increased, corresponding to the elimination of rubidium-poor material. There is no suggestion of a leaching-out of rubidium from the glauconite. If on the other hand radiogenic strontium was leached out one would expect to observe, in at least one case out of

(1) In this case, preferentially to biotite samples without weighting problems.

TABLE IV. Rb-Sr Data

SAMPLE NUMBER		Rb (in p.p.m)	Sr (in p.p.m)	Rad. Sr 87 (in p.p.b.)	$Sr87/Sr86$	t_{Rb-Sr} (in m.y.) ($\lambda=1.42\ 10^{-11}y^{-1}$)
O-79.A	N	259.2	14.48	44.08 ± .24	.73909 ± .00017	42.0 ± .9
	HCl.ST.	265.1	1.619	43.80 ± .14	.99195 ± .00037	40.9 ±1.0
O-132.A	N	248.5	10.48	42.1 ±1.3	.7491 ± .0011	41.8 ±1.5
	HCl.ST.I	255.2	1.665	43.90 ± .14	.9845 ± .0015	42.6 ±1.1
	HCl.ST.II	254.1	1.249	45.09 ± .15	1.09030 ± .00074	43.6 ±1.0
O-134.A	HCl.ST.	265.2	2.125	45.63 ± .46	1.0044 ± .0031	41.8 ±1.0
DB-85.cd	N	259.3	19.00	50.0 ±1.5	.73486 ± .00037	47.5 ±1.8
	HCl.ST.	266.3	3.520	46.53 ± .23	.84471 ± .00049	43.2 ±1.0
DB-87.cd	N	245.9	18.53	46.7 ±1.9	.7337 ± .0010	46.8 ±2.4
	HCl.ST.	255.0	3.336	44.40 ± .16	.84562 ± .00020	42.8 ±1.0
DB-90.cd	N	239.8	18.16	43.0 ±1.5	.7321 ± .0013	44.2 ±1.9
	HCl.ST.I	235.1	3.838	42.69 ± .26	.82281 ± .00024	45.0 ±1.0
	HCl.ST.II	235.6	2.961	41.40 ± .56	.85269 ± .00090	43.4 ±1.4
DB-79.cd	N	243.5	22.82	43.6 ±3.0	.7268 ± .0013	42.6 ±3.1
	HCl.ST.	248.0	3.338	42.6 ±1.3	.83993 ± .00034	42.1 ±1.0
DB-79.a	N	269.6	15.23	44.9 ±1.1	.73812 ± .00073	41.2 ±1.4
	HCl.ST.	277.0	2.893	45.97 ±0.24	.8726 ± .0019	41.0 ±1.3

all those considered, a Rb-Sr apparent age lower than the mean of the K-Ar age.

The remaining undiscussed cases are that of 0-134.A; BD-90.cd; 0-132.A. The first one has not been analysed before treatment, the HCl ST fraction yielding an apparent age in agreement with the "a priori acceptable" date found on 0-79.A, DB-79.cd, DB-79.a. Sample DB-90.cd exhibits a 2 °/o lowering of the rubidium content as a consequence of the sonic treatment in HCl (this difference remaining however within error limits). The apparent age remains on the "high" side after treatment. Detrital components may be present which cannot be removed by ultrasonic cleaning as in other cases. From the X-ray diffraction pattern, this sample has the highest content of expandable layers of the whole collection and thus may be, cautiously, discarded, on the base of this sole argument. The last sample to be discussed, 0-132.A has also relatively high Rb-Sr apparent ages, not reduced upon ultrasonic cleaning, what may tentatively be attributed to inheritance of detritic material, though reworking of the glauconite may be considered also. The potassium-argon apparent age of the same sample (Table I, row y) is the lowest found. However, this discrepancy remains unexplained. There is no objective reason, based on mineralogy, for example, to discard this sample.

All in all, the interpretation of the Rb-Sr data is less evident than that of the K-Ar data, and some results have to be discarded. Taking into account the conclusions of previous studies (PASTEELS *et al.*, 1976; ODIN *et al.*, 1974) we may tentatively conclude that the presence of small amounts of inherited material, of clay or silt size, filling the cracks of glauconite pellets presumably, influences more the Rb-Sr than the K-Ar ages and that the highest Rb-Sr ages have to be discarded. The mean of the Rb-Sr apparent ages of HCl ST fractions DB-79.cd, DB-79.a, 0-132.A, 0-134.A, 0-79.A, is 41.8 ± 8 m.y.. This figure changes little if sample 0-134.A is included, or sample 0-132.A. excluded.

CONCLUSIONS

A rather good agreement is observed between Rb-Sr and K-Ar apparent ages. Should they be considered as representing real ages, this would imply that the absolute time-scale of BERGGREN (1972) needs revision. Indeed, the Middle to Upper Miocene transition is set at 43 m.y. ago, which becomes, with the presently used decay constants, 44 m.y. ago. This is uncompatible with a deposition time 41 to 42 m.y. ago for the Asse Clay, whether this deposition occured during the late Lutetian or early Bartonian, a point not yet fully established.

However, to propose a revision of the absolute time-scale on the base of the data presented here only is probably unrealistic. Since the earliest attempt to establisch an absolute time-scale based on radioactivity, the transition Eocene-Oligocene, set at 38 m.y. ago by A. HOLMES in 1947, has oscillated between 35 and 40 m.y. ago, finding back its original position in BERGGREN's time scale 1972. This figure may still be incorrect by some 1 to 2 m.y., this being the subsisting uncertainty in dating sediments in the most favourable case.

The presently investigated case is certainly favourable : unaltered, unheated, authigenic glauconites yielding consistent Rb-Sr and K-Ar ages (with however some not fully explained exceptions). Thus the 41 to 42 m.y. figure obtained corresponds at least approximately to the deposition time of the sediment. By approximately it is meant : closer than 5 °/o or 2 m.y., which may be considered as encouraging in view of the poor reputation of glauconite as material for datation.

Nonetheless, in order to reduce this subsisting 5 °/o uncertainty to essentially zero, considerable work may still be necessary. To this problem is also linked that of the usefulness of radiometric dates on glauconites for interbasin correlations. Further attention should namely be devoted to the particular problem of sample selection, since no relations at all, except in a disputable case (DB-90.cd), has been found between apparent Rb-Sr or K-Ar ages and the observable mineralogical properties of the samples, which all had a moderate content in expandable layers. Thus the criteria for selection defined by ODIN (1975) : absence of burrial, oxydation, authigenic character and low content in expandable layers are essentially valid and no other could be found. However the best selected glauconites do not demonstratively yield apparent ages which can be accepted without discussion.

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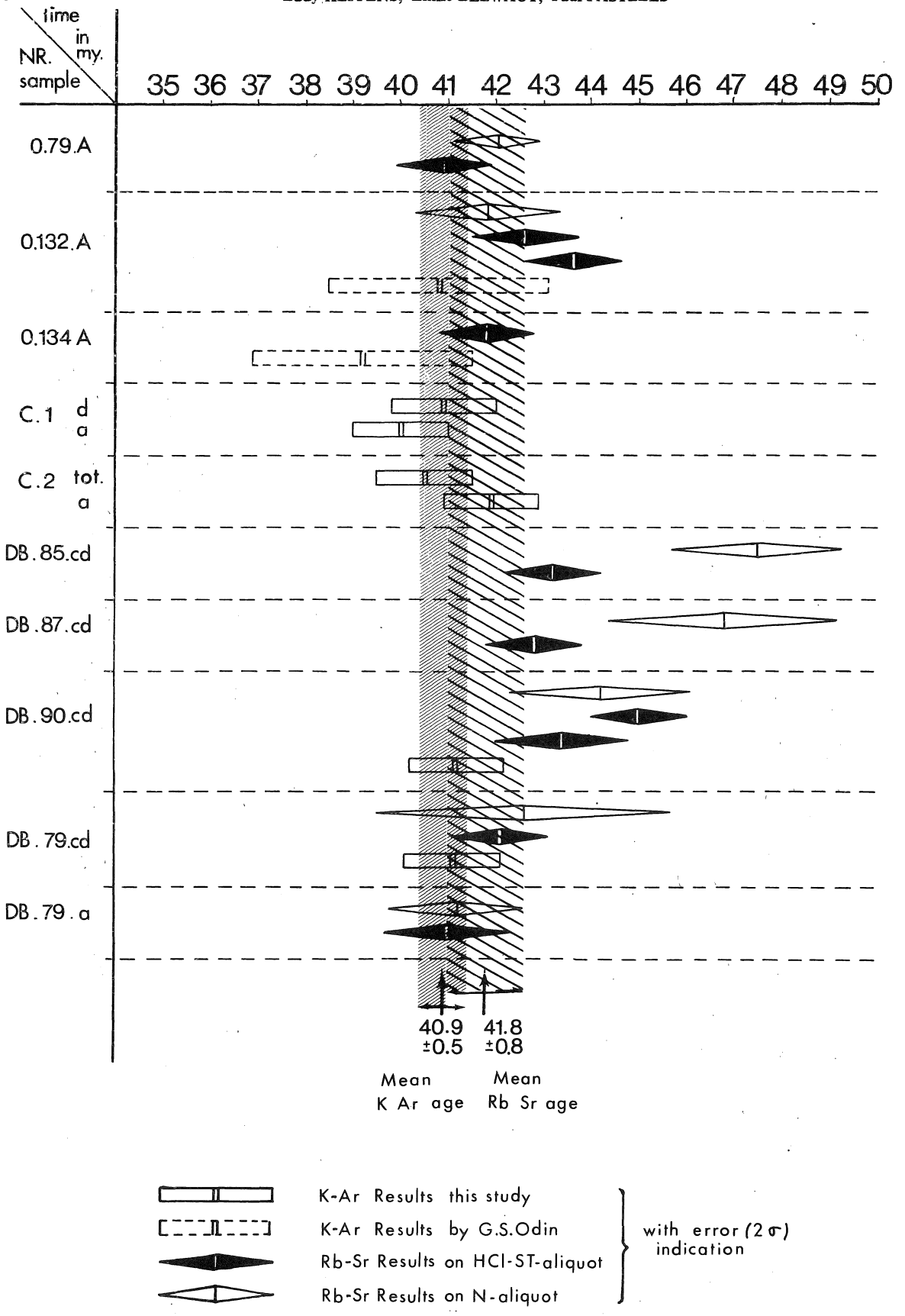

Figure 3.- Comparison of the Rb-Sr and K-Ar results

K-measurements were performed by Miss DUREZ and Mr. DELVIGNE of the "Royal Museum for Central Africa", Tervuren, Belgium.

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APPENDIX I

PROCEDURE FOLLOWED TO SEPARATE THE GLAUCONITES FROM THE SEDIMENT

For Samples O-79, O-132 and O-134

The sediment was washed with water and sieved wet on a 50 μ sieve. The sand fraction was dried and sieved dry on 100 μ, 160 μ and 500 μ sieves. From the fraction called A (from 160 μ to 500 μ) the glauconite was magnetically separated. The resulting glauconite fraction was purified by hand-picking and finally cleaned by ultrasonic vibrations in distilled water. (The resulting glauconite corresponds to the N-aliquot).

For Samples DB-85, DB-87, DB-90 and DB-79

The sediment was first treated with an ultrasonic device in water, then sieved wet on a 50 μ sieve. From the dried (90°C) sand fraction the glauconites were magnetically separated. Subsequently they were sieved on 100μ, 210μ, 250μ, 300μ and 350μ sieves. The fractions to be analysed (see Fig. 2) were finally purified by hand-picking (The resulting glauconite corresponds to the N-aliquot).

For samples C-1 and C-2

The sediment was sieved wet on a 50 μ sieve. From the resulting sand fraction, the glauconites were magnetically separated and subsequently cleaned by ultrasonic vibrations in water. An aliquot was analysed as such, while another aliquot was split into different granulometric classes by dry sieving on 50μ (to eliminate the fraction under 50μ resulting from the ultrasonic treatment), 100μ, 125μ and 300μ sieves. After cleaning by hand-picking some of the thus obtained size fractions were analysed as it is noted in Fig. 2.

APPENDIX II

ANALYTICAL PROCEDURE OF THE Rb Sr METHOD;

Samples were brought into solution and strontium was separated using standard ion-exchange procedure. The concentration and isotopic composition of strontium were measured by isotope dilution (using a 99.78 °/o ^{84} Sr-spike) and mass spectrometry with a TH5 Varian MAT mass spectrometer (21.4 cm. radius and 90° magnetic sector) the samples being loaded on a single Re-filament. Ion currents collected on a Faraday cup were amplified with a 401 Cary electrometer and the resulting potentials measured with a Hewlett Packard digital voltmeter. Final processing was accomplished on the 6400 or 6500 CDC computer of the Free University of Brussels Computer Center.

Concentrations of rubidium were measured by isotope dilution (using a 99.64 °/o ^{87} Rb-spike) and mass spectrometry on an ATLAS CH4 mass spectrometer (25 cm. radius and 60° magnetic sector). Ion currents were collected on a 17 steps electron multiplier. Spectra were obtained on a strip-chart recorder after manual peak switching. The mass spectrometric analyses of rubidium are less precise and accurate than those of strontium by a factor of almost ten.

A mean Sr 87/Sr 86 value (over 8 analyses during the last 5 years) of .70807 ±.00020 (2σ) was found for the Eimer and Amend ($SrCO_3$) Standard. For the NBS.987 Standard a Sr 87/Sr 86 ratio of .71031 ±.00038 (2σ) was measured.

APPENDIX III

K-Ar RESULTS ON G1-O

Argon

14 measurements giving a mean of 24.70 ±25 10^{-6} $cm_3STP^{40}Ar$ Rad/g.;

Potassium

several measurements over a period of 6 months vary between 7.95 and 8.00 °/o K_2O

mean : 7.98 ±0.02 °/o K_2O

apparent age for G1-0 : 93.2 ±1.2 10^6 j.