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# CLAY MINERALOGY OF SOME CLAYEY INTERVALS IN THE THERMAE 2002 BOREHOLE (VALKENBURG A/D GEUL, THE NETHERLANDS)

by

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(6 figures and 2 tables)

## 1. INTRODUCTION

Apart from unconsolidated clayey sediments in the Upper Cretaceous sequence (Vaals and Aachen formations), the Thermae 2002 borehole in Valkenburg a/d Geul has penetrated several other clayey intervals in the Dinantian which have been partly investigated on their clay mineral contents (fig. 1).

The first interval (184-236 m) consists of a kaolinic paleosol capping uppermost Visean black shales. Part of this interval (186-199 m) has been studied for the present report (samples 6763 to 6772 ; fig. 2, tables I and II).

The Gamma Ray (GR) log has revealed the presence of several thin clayey intercalations in the sequence of sometimes partly to completely silicified, bituminous limestones between 236 and 381.5 m. Two of these at 302-303 m and 375-376 m have been investigated on their clay mineral composition (samples 6773 and 6774 ; fig. 5-6, table I).

## 2. METHOD OF STUDY

Qualitative and semi-quantitative analysis of the clay composition of the less than 2 $\mu$m fraction by X-ray diffraction (XRD) has been carried out on oriented aggregates following the method used at the Liège Laboratory. Samples have been studied in their air-dried (normal) state after solvation with vapors of ethylene glycol and after heating to 500°C. No post-treatments (i.e. cationic saturations), HCl attack and hydrazine saturation) have been carried out. Apart from the identification of the clay components further crystallochemical data were yielded by the evaluation of the «crystallinity» of the smectite component. This evaluation is based on Biscaye's (1965) v/p ratio (valley/peak intensity ratio measured on the 17 Å (001) reflection of the glycolated smectite) and on homogeneity classes A to E of Thorez (1976). Illite/quartz (I/Q) ratio, kaolinite/quartz (K/Q) ratio and Hydrolysis Index (H.I.) (Thorez 1985) have been calculated for the samples from the partly weathered interval between 186 and 199 m. The H.I. yields a quantitative figure of the global and final weathering intensity that has or may have affected the parent material in the course of an atmospheric, pedogenetic and even hydrothermal weathering.

## 3. RESULTS OF XRD ANALYSIS

### 3.1. WEATHERED INTERVAL

The 186-199 m interval consists of a clayey matrix with abundant silicified limestone fragments and downward decreasing amounts of authigenic quartz crystals (Krings et al. 1987). The less than 2 $\mu$m fraction contains several clay minerals (fig. 2, table I). X-ray patterns for two representative samples (6763 and 6766) are shown in figures 3 and 4. Figure 2 shows the vertical changes in the clay mineral composition and in the I/Q and K/Q ratios in this interval.

Between 199 and 195.3 m (samples 6772 to 6769) the clay fraction virtually consists of a monomineralic illite phase with traces of a mixed-layer illite/chlorite ($10\text{-}14_c$). This randomly interstratified structure is built up by distended illitic layers (10) with interlayers resembling chlorite ($14_c$) in the identification tests. The illite mineral either belongs to the variety with enlarged peak (foot) ($I_{LP}$) or to a degraded (open) illite (Trauth et al. 1968), and shows the presence of some distended interlayers. Genetically this predominant illitic material may represent the clay mineral of the black shale that resulted from the diagenetic phase prior to the weathering process.

The interval between 195.3 and 190 m is characterized by an association of illite and kaolinite. Illite (of the open, degraded variety) decreases upwards and is replaced by well-crystallized kaolinite that becomes predominant between 192 and 190 m. Other clay minerals - chlorite : degraded chlorite as mixed layer chlorite/vermiculite or ($14_c\text{-}14_v$) ; mixed layers ($10\text{-}14_v$) and ($10\text{-}14_{sm}$) with interlayers behaving respectively as vermiculite ($14_v$) or smectite ($14_{sm}$) - occur in low amounts. Presumably illite is a residual component developed during a karstic dissolution of Visean limestone and physico-chemical weathering of the black shales. The upward increase of kaolinite indicates the progressive influence of the weathering of the parent illite that has produced the neoformation of kaolinite because of intensive leaching within an open system.

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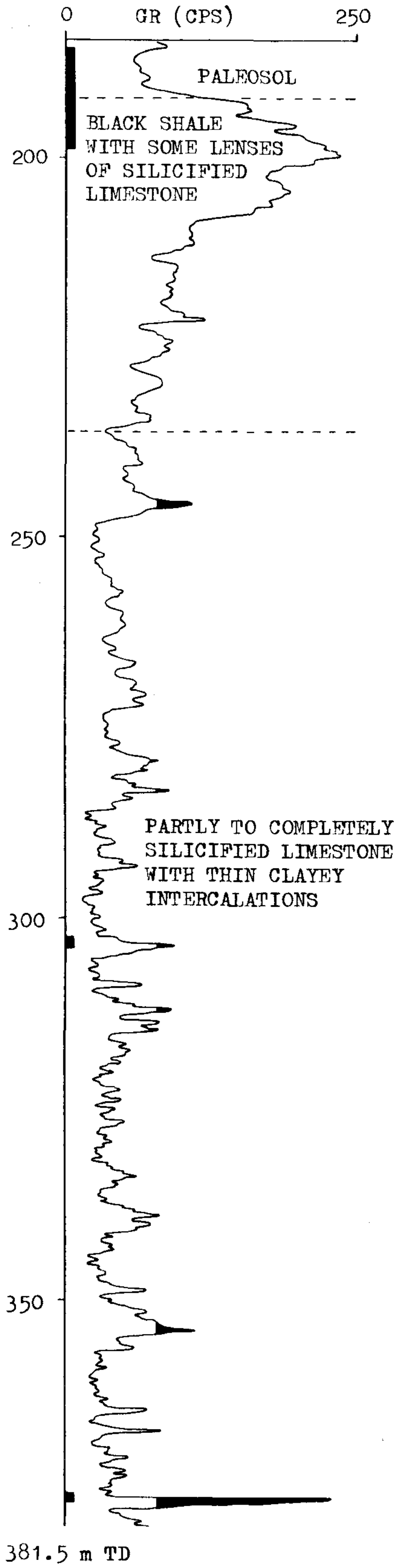


*Figure 1 - Gamma-Ray log and lithology of the Dinantian sequence in Thermae 2002.*
*The position of the here studied intervals is indicated.*

Transitory stages between the parent illite and the end-formed kaolinite are represented by traces of mixed layers of the types ($10\text{-}14_v$) and ($10\text{-}14_{sm}$). The ($10\text{-}14_{sm}$) variety usually characterizes products of atmospheric and/or pedogenetic weathering of either illite/chlorite-bearing Paleozoic shales or dissolution products of Dinantian limestones in Belgium (Thorez & Bourguignon 1973). These transitory phases predominate in karstic conditions where illite and kaolinite are subordinate. The weathering under the warm-wet conditions of the Jurassic to Lower Cretaceous which produced the paleosol between 184 and 199 m in Thermae 2002 must have been more severe than the weathering of carbonates in Belgium under warm-humid conditions of Tertiary times (Thorez & Bourguignon 1973).

The change in clay composition between 199 m (uppermost Visean black shales) and 190 m matches the change in the I/Q and K/Q ratios (fig. 2), and also the change in the H.I. values which grade from 1 to 1.3 in the black shales (199-195.3 m) to 103.4 at the top of the weathered interval at 190 m (sample 6768 ; table II).

The upper portion of the studied interval between 190 and 186 m is characterized by the absence of illite, predominance of kaolinite over smectite and vermiculite, and by traces of ($10\text{-}14_c$). Vermiculite, smectite and kaolinite are genetically «antagonistic» minerals. Kaolinite is formed only under conditions of intense leaching and weathering in a warm, humid climate with heavy rainfall. Vermiculite may develop under warm, temperate or even cool conditions provided that the average annual rainfall is at least 1000 mm. Smectite is a degraded by-product of the weathering of e.g. illite and chlorite. It is also a further stage in the weathering (degradation) of vermiculite (Thorez 1985). Smectite preferably develops in a climate with long dry and short wet periods with a maximum annual rainfall of 300 m. Therefore it is difficult to believe that these three «antagonistic» clay minerals form a «natural» mixture. Maybe the association of kaolinite, smectite and vermiculite is the result of reworking of the kaolinic paleosol with clays of the Aachen Formation. Or the observed mixture is the result of contamination of the kaolinic paleosol cuttings with material derived from the Vaals and Aachen Formation during the drilling. Only a detailed study of the clay mineralogy of these formations may solve this question. The K/Q ratio (fig. 2) clearly suggests a «reworking» effect for the 190-186 m interval. The association of kaolinite, smectite and vermiculite along with the absence of illite is responsible for the extremely high H.I. values in table II.

### 3.2. POTASSIUM-BENTONITES

Potassium-bentonites (or K-bentonites) in the Visean sequence of Thermae 2002 are characterized by pronounced peaks in the GR log. The clay composition of these layers bears the hall mark of a completely different association than the monomineralic illite of the black shales in the upper portion of the sequence.

The less than 2 $\mu$m fraction of sample 6773 (302-303 m) consists of an association of aluminan

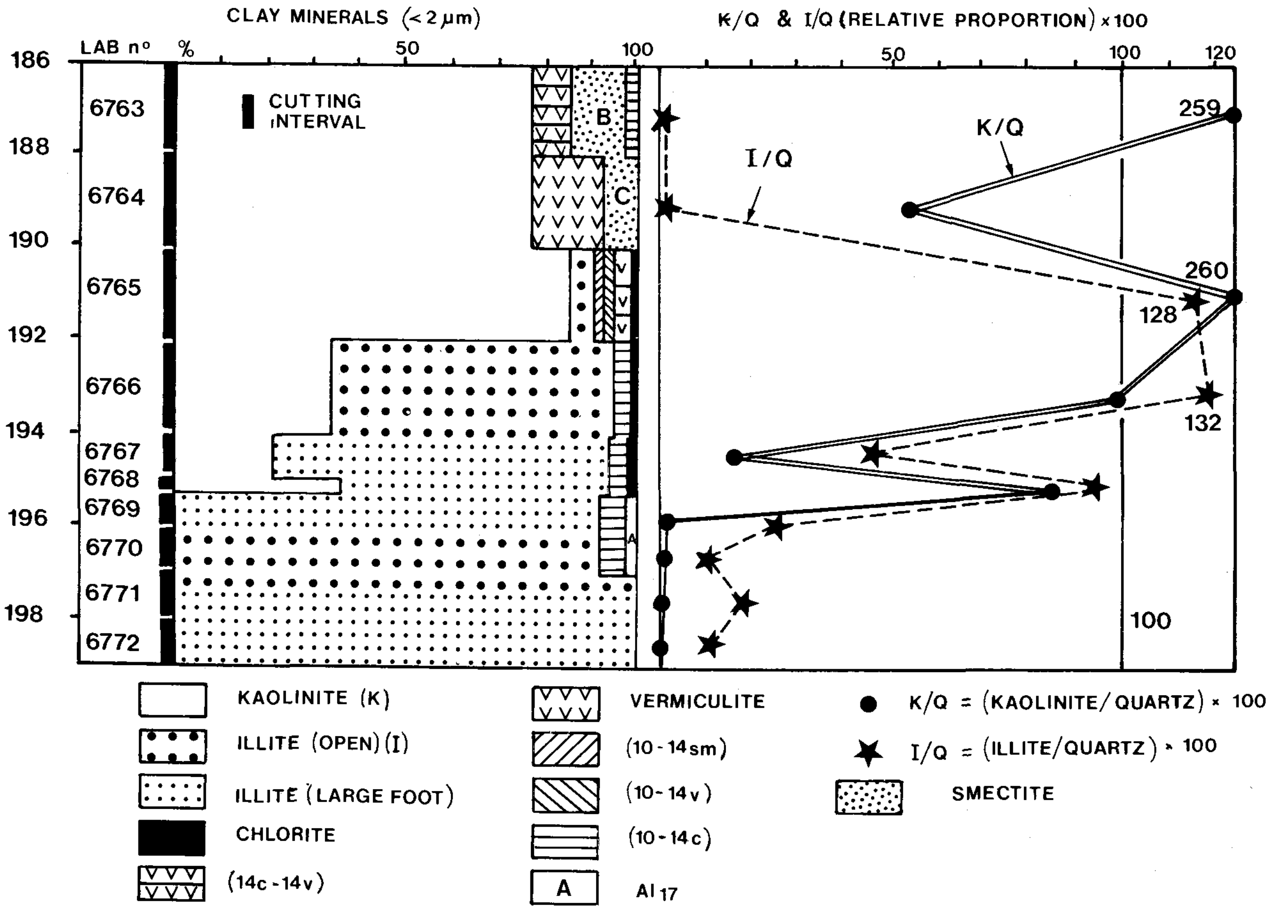


*Figure 2 - Clay mineral evolution and other mineralogical characteristics of weathered interval between 186 and 199 m in Thermae 2002.*

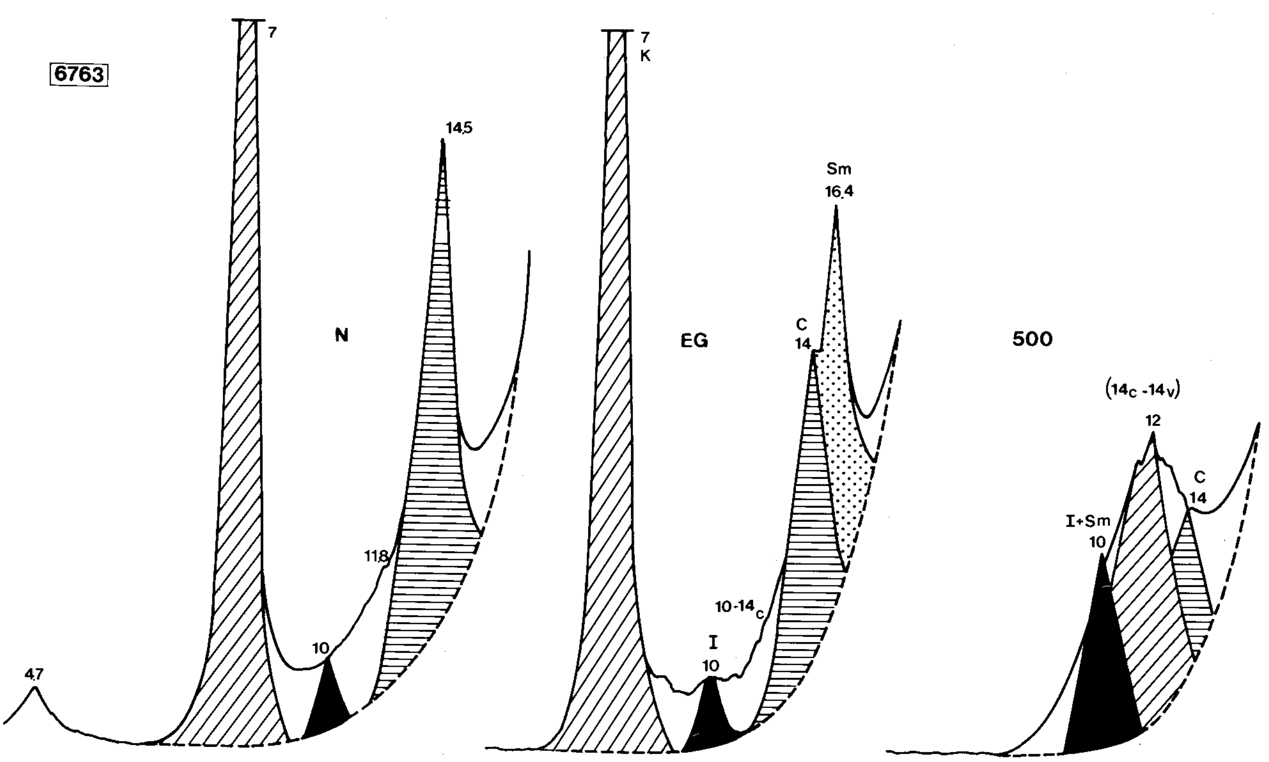


*Figure 3 - Trace of X-ray pattern for clay fraction extracted from sample 186-188 m (sample 6763). Oriented aggregate. N = air dried (normal) state ; EG = glycolated state ; 500 = 500° C heating treatment.*

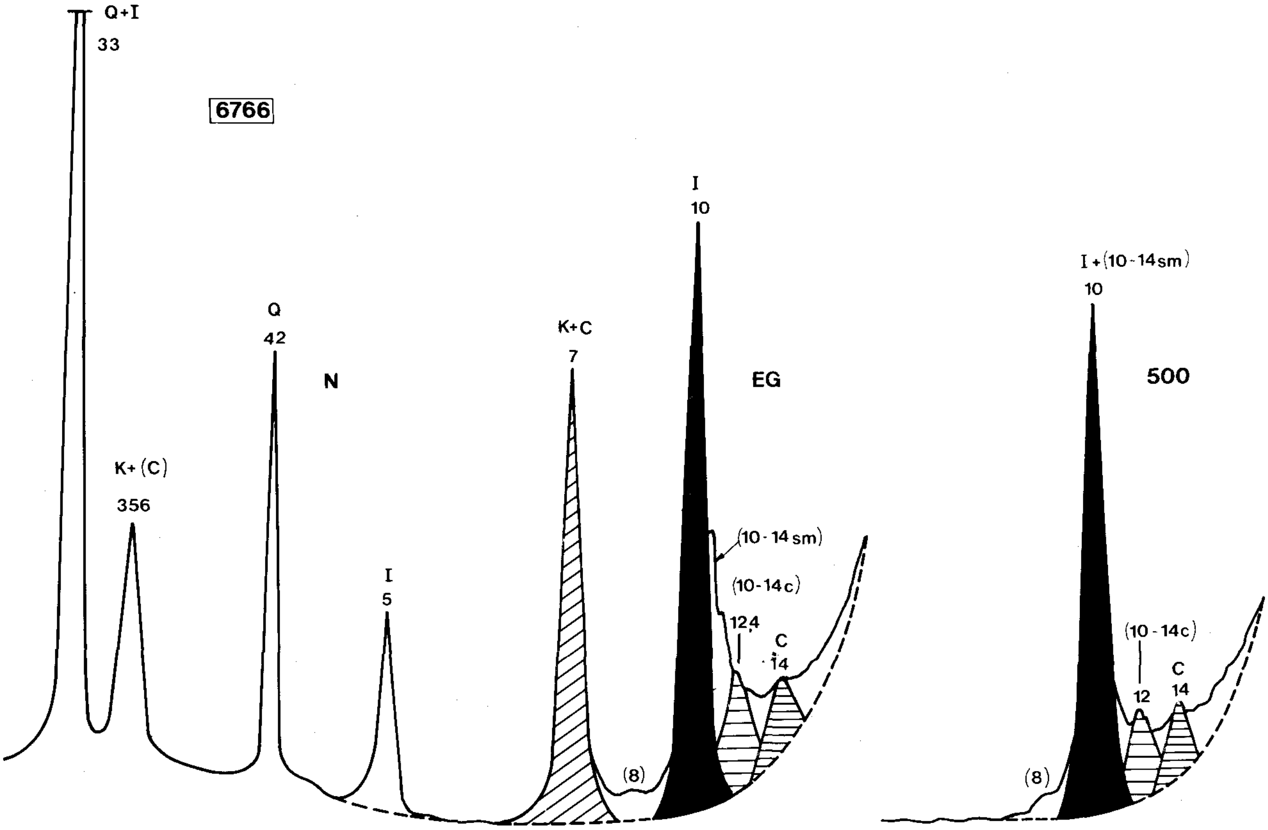


*Figure 4 - Trace of X-ray pattern for clay fraction extracted from sample 192-194 m (sample 6766). Oriented aggregate. N = air dried (normal) state ; EG = glycolated state ; 500 = 500° C heating treatment.*

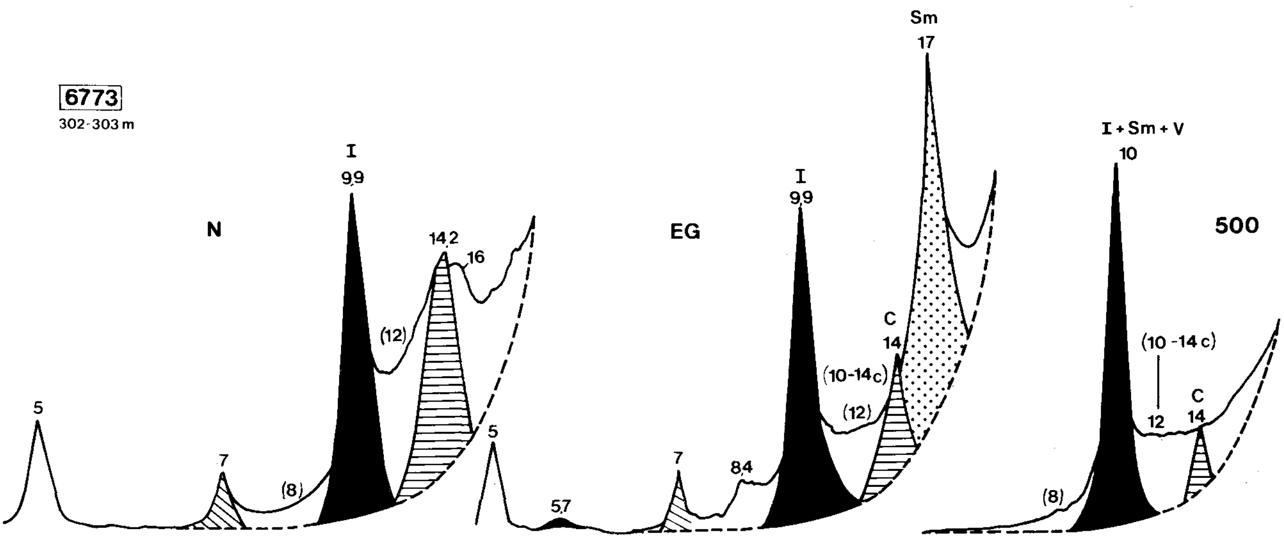


*Figure 5 - Trace of X-ray pattern for clay fraction extracted from sample 302-304 m (sample 6773). Oriented aggregate. N = air dried (normal) state ; EG = glycolated state ; 500 = 500° C heating treatment.*

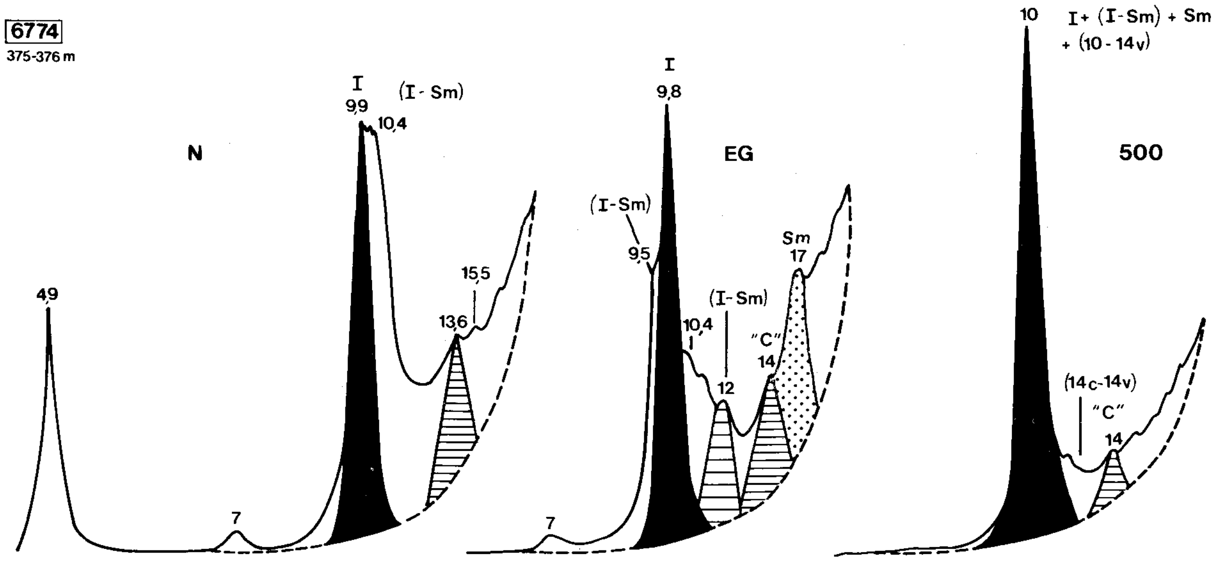


*Figure 6 - Trace of X-ray pattern for clay fraction extracted from sample 375-376 m (sample 6774). Oriented aggregate. N = air dried (normal) state ; EG = glycolated state ; 500 = 500° C heating treatment.*

*Table I - Clay mineral composition of the intervals 186-199 m, 302-303 m and 375-376 m in Thermae 2002. $I_{LP}$ = illite with large peak (foot) ; $I_0$ = open (degraded) illite ; $(10\text{-}14_{Sm})$ = illite-smectite mixed layer ; $(10\text{-}14_V)$ = randomly interstratified illite-vermiculite structure ; $(10\text{-}14_C)$ = randomly mixed layer illite-vermiculite ; C = chlorite ; $(14_C\text{-}14_V)$ = randomly mixed layer chlorite-vermiculite ; V = vermiculite ; Sm = smectite ; $Al_{17}$ = naturally «swollen» smectite with Al-hydroxyl «pillars» in interlayers ; K = kaolinite.*

| Depth of samples | Lab. n° | Clay mineralogy ( oriented aggregate of the less than 2 m ) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $I_{LP}$ | $I_0$ | $(10\text{-}14_{Sm})I$ | $(10\text{-}14_V)$ | $(10\text{-}14_C)$ | C | $(14_C\text{-}14_V)$ | V | Sm | $Al_{17}$ | K |
| 186 -188 | 6763 | - | - | - | - | - | - | 7,5 | | 14,5 | - | 77 |
| 188 -190 | 6764 | - | - | - | - | - | - | - | 15,7 | 7,3 | - | 77 |
| 190 -192 | 6765 | - | 6 | 1,8 | 2,6 | - | - | 2,8 | - | 1,7 | - | 85,3 |
| 192 -194 | 6766 | 60,4 | - | - | - | 3,6 | 1,2 | - | - | - | - | 34,8 |
| 194 -195 | 6767 | 74 | - | - | - | 3 | 1,8 | - | - | - | - | 21,2 |
| 195 -195,3 | 6768 | 59,6 | - | 3,5 | - | - | 1,2 | - | - | - | - | 35,7 |
| 195,3-196 | 6768 | 91,5 | - | - | - | 5,2 | - | - | - | - | 3,2 | - |
| 196 -197 | 6770 | - | 91 | - | - | 9 | - | - | - | - | - | - |
| 197 -198 | 6771 | - | 100 | - | - | - | - | - | - | - | - | - |
| 198 -199 | 6772 | - | 100 | - | - | - | - | - | - | - | - | - |
| 302 -304 | 6773 | 64,3 | - | 3 | - | 5,2 | - | 7,3 | - | 14,8 | 5,5 | - |
| 375 -376 | 6774 | 48,2 | - | 36,6 | 5,4 | - | 1,9 | 2,7 | - | 2,3 | 2,9 | - |

illite (with large peak, $L_{LP}$), relatively well-crystallized smectite (v/p ratio 0.53, crystallinity-homogeneity class C) with subsidiary randomly mixed layers ($10\text{-}14_c$) and ($10\text{-}14_{sm}$), chlorite (C) and degraded chlorite ($14_c\text{-}14_v$) (fig. 5 ; table I).

The clay assemblage of sample 6774 (375-376 m) contains an association of illite and a S=0/S=1, more or less regularly mixed layer illite-smectite. The (002) of the latter is about 10.4 Å (N state) and characteristically splits into two peaks. One peak is about 9.5 Å and appears as a hump on the 10 Å illite peak and corresponds (in the glycolated state) to the (003) peak of the mixed layer. The other «peak» (002) is better developed as a diffraction band between 10 and 13 Å. This behaviour upon glycolation points to a IMII illite-smectite mixed layer with about 25 to 30 % swelling layers. Other components identified in this clay assemblage are a badly crystallized smectite (class C-D) and some chlorite, a part of which has been weathered into a mixed layer chlorite-vermiculite or ($14_c\text{-}14_v$) (fig. 6 ; table I).

*Table II*
*Illite/Quartz (I/Q x 100), Kaolinite/Quartz (K/Q x 100) ratios and Hydrolysis Index (H.I.) in the interval 186-199 m of Thermae 2002.*

| Depth of samples | Lab. n° | I/Q X 100 | K/Q X 100 | H.I. |
|---|---|---|---|---|
| 186 -188 | 6763 | 0 | 259 | 671 |
| 188 -190 | 6764 | 0 | 54 | 622 |
| 190 -192 | 6765 | 128 | 260 | 103,4 |
| 192 -194 | 6766 | 132 | 100 | 5 |
| 194 -195 | 6767 | 45 | 16 | 3 |
| 195 -195,3 | 6768 | 96 | 84 | 5,2 |
| 195,3-196 | 6769 | 26 | 0 | 1,3 |
| 196 -197 | 6770 | 10 | 0 | 1,2 |
| 197 -198 | 6771 | 19,3 | 0 | 1 |
| 198 -199 | 6772 | 16 | 0 | 1 |

The clay assemblages of these two samples match those of many former volcanic ash layers (cf. potassium-bentonites or K-bentonites) in the Visean rocks of Belgium (Thorez & Pirlet 1978). It is suggested that other peaks on the GR log (fig. 1) of the Visean sequence of Thermae 2002 also represent K-bentonite layers. This hypothesis needs to be checked by further investigations.

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