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DICKITE AND NACRITE FROM THE LIEGE COAL BASIN (BELGIAN COAL MEASURES GROUP, WESTPHALIAN, UPPER CARBONIFEROUS)

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(6 figures, 1 table and 8 plates)

Abstract. Westphalian sediments of the Belgian Coal Measures contain two primary kaolinite populations, either well crystallised or badly crystallised. The proportion of these two populations was originally linked to the depositional environment but changed through diagenesis and atmospheric weathering. Dickite and nacrite, as polymorphs of kaolinite, occur frequently in the tectonised Liège coal measures where they are systematically associated to stress constraints (called tectoglyphs in the present paper). These tectoglyphs and their mineral phases are here described. Dickite fills small sized distensive fractures while sliding surfaces reveal nacrite. Authigenic dickite was precipited from interstitial solutions in open fractures and protected pockets after partial clay dissolution of the host rock. Microtextural relationships suggest that nacrite is a synkynematic mineral resulted of the polymorphic transformation of dickite under stress constraints. No direct relationships can be demonstrated between kaolinite and other polytypes.

Key-words. Dickite, nacrite, stress constrains, XRD, SEM, polymorphic transformation, Coal Measures, Liège, Belgium

Résumé. **La dickite et la nacrite du bassin houiller Liégeois (groupe houiller, Westphalien, Carbonifère supérieur)**. Les roches westphaliennes du bassin houiller belge renferme deux populations de kaolinite primaire, l'une bien cristallisée et l'autre mal cristallisée. La proportion relative des deux populations est originellement reliée au milieu de dépôt mais peut changer au cours de la diagenèse et des processus d'altération atmosphérique. La dickite et la nacrite, polymorphes de la kaolinite, sont observés fréquemment dans le bassin houiller liégeois et apparaissent systématiquement associés aux tectoglyphes. Ces derniers ainsi que les phases minérales associées sont ici décrites. La dickite remplit des fractures en extension alors que la nacrite occupe les surfaces glissées. La dickite authigène est précipitée à partir de solutions interstitielles dans des fractures ouvertes et des niches protégées suite à la dissolution des minéraux argileux de la roche hôte. Les relations microtexturales suggèrent que la nacrite est un minéral syncinématique résultant de la transformation polymorphique de la dickite sous contraintes tectoniques. Il n'y a pas de relation démontrée entre la kaolinite et les autres polymorphes.

Mots-clés. Dickite, nacrite, halloysite, contraintes tectoniques, DRX, MEB, transformation polymorphique, terrains houillers, Liège, Belgique

1. Introduction

Kandites are dioctahedral clays with a te-oc structure, no interlayer cations, a composition of $Al_2Si_2O_5(OH)_4$ and concern four species: kaolinite, dickite, nacrite, and halloysite, which differ by their crystal structures, and genetic conditions.

The kaolin sub-group shows three polytypes : kaolinite, dickite and nacrite. In this paper, we will use the term "kaolin" as general term to indicate these three polytypes. Kaolinite is far the most common, while dickite is rather uncommon; nacrite is the rarest polymorph known. Although dickite and nacrite have the same basic structure as kaolinite, the stacking sequence of layers is different in these former minerals. Whereas kaolinite consists of a one-layer stacking sequence with a triclinic symmetry, dickite has a two-layer stacking sequence with a monoclinic symmetry. The crystalline structure of nacrite was initially described as a 6-layer kaolin mineral with rotation of empty octahedral sites as to produce a spiral around the c axis. However, nacrite can be described as a monoclinic structure having two layers with a monoclinic symmetry but with a larger beta angle (Zheng & Bailey, 1994). Kaolinite and halloysite exhibit single-layer structure. Halloysite possesses water molecules between the te-oc sheets; its chemical formula is $Al_2Si_2O_5(OH)_4 \cdot 4H_2O$. Kaolinite, dickite and nacrite generally occur as plates. Halloysite, with a single layer of water between its layers, occurs with a tubular form. The distinction between these minerals is usually based

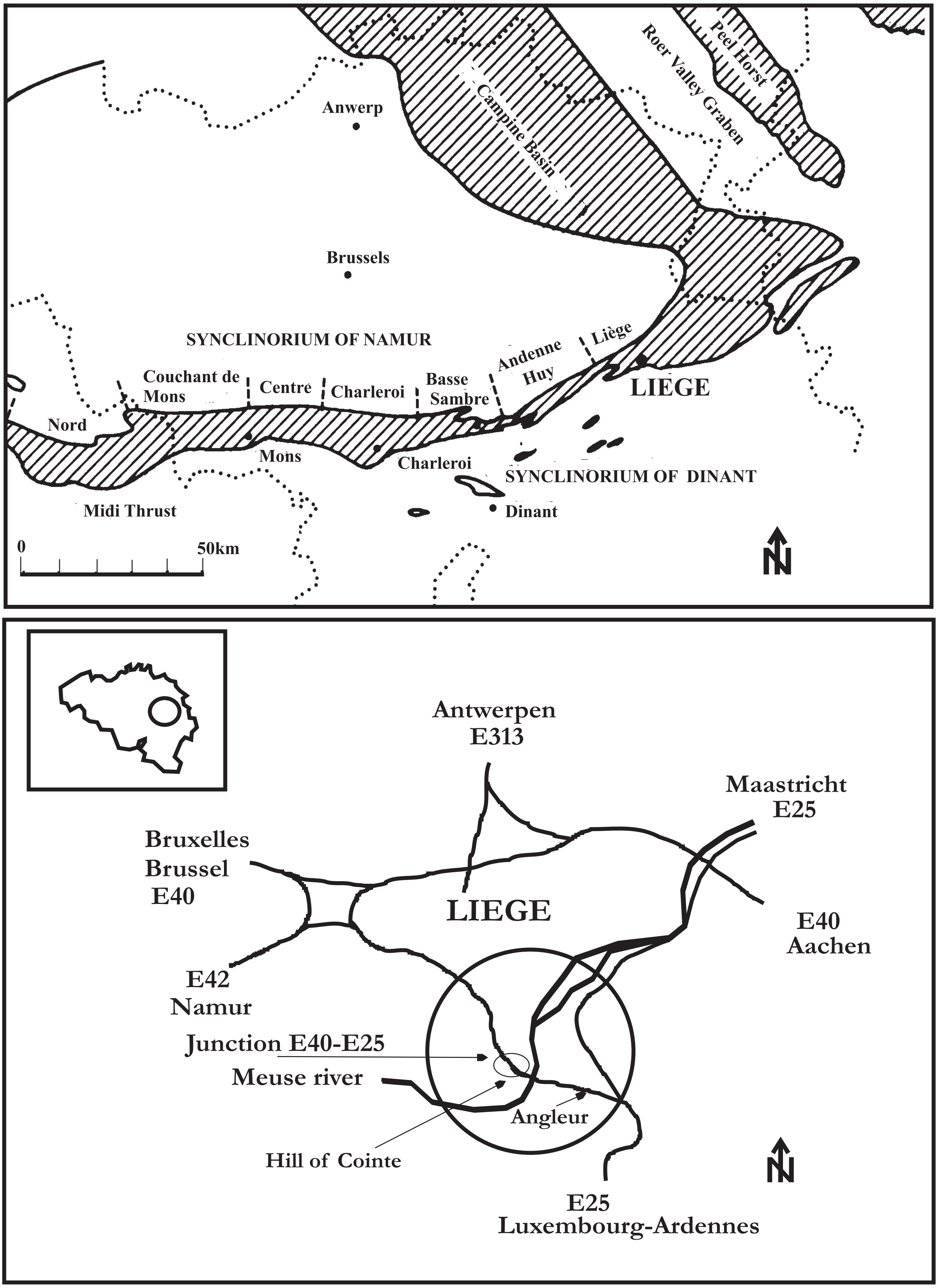

Figure1. a) Belgian coal mining districts map, modified after Paproth *et al*., 1983; b) Simplified location map of Liège with indication of the study area.

on X-ray diffraction (XRD). However, XRD patterns are often ambiguous because diagnostic non-basal reflections may be overlapped by reflections belonging other associated minerals (illite, illite-smectite mixed layer, chlorite, quartz and feldspars), and because of structural parameters such as polymorphism and order-disorder (Beaufort *et al.*, 1998). Complementary chemical and heating must be performed to reduce interferences of reflections.

Halloysite was never found in close association with Upper Carboniferous rocks. However, in Angleur (type-locality, in the vicinity of Liège), halloysite was formed in dolomitized crinoidal Tournaisian limestone, at the faulted and mineralised contact with Namurian pyrite-bearing black shales. In the particular tectonic context of thrust-wedges pinched in the Condroz overthrust, the source-rock for Al and Si was mainly a residual material, presumably derived from the leaching of illite and kaolinite minerals from the Namurian black shales (Goemaere & Hanson, 1997). Sulfuric acid solutions needed for halloysite genesis and karstification originated from sulphides fault mineralisation and pyrite-bearing Namurian black shales.

The tunneling of a subway through the hill of Cointe (Liège) (Lambert 72 Belgian coordinates X: 235.000 Km, Y: 146.000 Km), was completed for a motorway connection between E40 (Brussels-Liège) and E25 (Luxembourg-Liège) highways (Fig.1). The hill of Cointe, part of Liège Coal Basin, is geologically located at the northern side of the complex anticline of Cointe, with an E-W axial orientation. The geological cross-section of the tunnel (1.3 km long) shows a succession of oblique folds with weakly inclined northern flanks ("plateures") and steep southern flanks affected by longitudinal faults and fractured zones (Arnould, 1990). An extensive borehole program has been carried out and provided an opportunity to collect fresh samples.

Mineralogic analyses demonstrated the occurrence in these samples fo kaolinite, dickite and nacrite. Such an occurrence in the coal measures of Westphalian from Belgium but not been sufficiently checked until now. The aim of this paper is to demonstrate origin and transformation of clay minerals in peculiar geological conditions – stress conditions.

Furthermore, no halloysite has been identified in the Cointe hill. In the absence of limestone (neutralisation of acidity), black shales affected by strong acidic leaching observed in an old coal mine gallery involves the genesis of allophane, hydrobasaluminite and gibbsite (Goemaere, 2004).

2. Samples and methods

All the analysed kaolin minerals have been collected from core samples of mudstone, shale and sandy shale. Core samples were collected in numerous wells. A complete and very well-documented study about the clay mineralogical variation in sandstone near coal seams, shale and mudstone of the Westphalian of Campine basin (NE Belgium) has been published by Van Keer (1999). Samples of halloysite were collected in the type locality of Angleur, in the vicinity Liège (Fig.1).

The analysed samples cover fresh material (below the water table) and various types of tectoglyphs. Bulk rock samples were analysed by XRD as disoriented powders, scanning electron microscopy (SEM) and polarising microscopy. The <2µm and coarser size fractions were studied by XRD. Oriented aggregates of the <2 µm fraction were prepared according to the sedimentation onto glass method. They were sequentially analysed as air-dried (N), glycolated (ethylene-glycol - EG) and heated (4 hours, 490°C).

The mineral content of fractures, veins and sliding surfaces were picked up by hand. It was specifically investigated by XRD as oriented aggregates and random powders of the bulk material, and oriented aggregates of the <2µm, the latter after specific post-treatments: saturation with formamide, DMSO and hydrazine and complementary heating treatments: 550°C/4H, 600°C/4H. Also other method have been applied: IR, TGA, DTA, petrography and SEM. In some favourable cases, XRD was performed directly on sliding surfaces; SEM was used to investigate the morphology of dickite and nacrite crystallites occurring in various tectoglyphs.

There is no difficulty for identifying kaolin polytypes by XRD when occurring as pure monomineral phases, but practical problems arise when dealing with mixtures of polytypes with chlorite. Chlorite shares its (002) and (004) reflections with respectively the (001) and (002) reflections of kaolinite, as well as of dickite and nacrite. Moreover the (00l) reflections are more intense than the other (00l) reflections reflecting the high Fe content in chlorite. After heating (490°C), kaolinite is dehydroxylated. However, (00l) reflections of dickite and nacrite persist but with a decreased intensity, while the (001) of chlorite becomes modified being related to their chemistry and fresh state. Heating alone will not permit to distinguish kaolinite group minerals from chlorite because its (002), (003), and (004) peaks are also weakened by heat treatment at 490°C. Mixtures of chlorite and kaolinite group minerals remains difficult to resolve at the level of qualification and relative abundance. Complementary post-treatments are thus necessary, i.e. complete dissolution of Fe-chlorite by HCl (4N boiling) followed by heating at 490°C. A comparison between N-EG-490 diffractograms and HCl-490 diffractograms permits to discriminate chlorite, kaolinite and dickite/nacrite in mixtures. A minor presence of Al-Chlorite (pedogenetic origin) in some underclays adds a supplementary problem because this mineral sustains the HCl attack. Furthermore differentiation between dickite and nacrite cannot be achieved by an acid treatment at 490°C, a further heating at 550°C and 600°C is requested to identify nacrite beside dickite.

3. Kaolinite

XRD analyses of the bulk sediments indicate that quartz, illite, kaolinite, Illite/Smectite (I/S) random mixed layer and Fe-chlorite are the major minerals; minor feldspars and carbonates may also be present. The <2µm fraction is restricted to quartz, illite, kaolinite, I/S random mixed layer and Fe-chlorite. Kaolinite is ubiquist in all the sediments of the Westphalian coal measures (Scheere, 1963, 1968; Thorez & Van Leckwijk, 1967; Goemaere, 1991). Moreover this mineral forms the main component in cinerites - called tonstein in Belgium and Germany - (Scheere, 1957, 1958). In fresh material (cinerites being excluded), the relative content of kaolinite varies according to the lithology (kaolinite is more abundant in the coarser sediments), to the relative position in the sedimentary sequence, to the depositional environment, and to the paleopedogenetic overprint. The relative percentage of kaolinite, as obtained by XRD from the < 2µm fraction, ranges between 15 and 50%. The content of kaolinite increases through a complete and well-developed fining-upward sequence, reaching a maximum in the underclays. Kaolinite is the main component of the clay-fraction in sandstone. Moreover, Van Keer (1999) reported kaolinite and dickite of diagenetic origin occluding intergranular pores of sandstone. The other clay minerals show complementary, both quantitative and qualitative evolutions but with a decreasing crystallinity of illites and an increasing contribution of vermiculitic or smectitic layers respectively in chlorite-vermiculite and I/S random mixed-layers.

Iron chlorite dissolution by boiled HCl_{4N} unravels the kaolinite abundance and allows a relative quantification of chlorite *versus* kaolinite. Subsequent hydrazine saturation permits to estimate the crystallinity of kaolinite. A complementary heating treatment (500°C/4H) inducing the dehydroxylation of kaolinite indicates the absence or presence of dickite and nacrite as these two kaolinite polymorphs sustain the heating. Indeed their temperatures of dehydroxylation (under the same laboratory conditions) occur at 550°C and 600°C, respectively. The saturation with hydrazine vapours during 7 days at 65°C distinguishes a well-crystallised kaolinite (K_T) which incorporates hydrazine in its interlayer space, and a poorly crystallised kaolinite (Kd = Type IV of Range (1969)) which remains insensitive to this treatment (Fig.2). Relative to all forms of kaolinite, the percentage of K_T ranges between 50 and 80%. The relative proportion of the two populations is directly connected to the position of the samples in the sedimentary sequence. The proportion of Kd decreases progressively downward off the coal seam. The sandstone, enriched in kaolinite relatively to other lithologies, con-

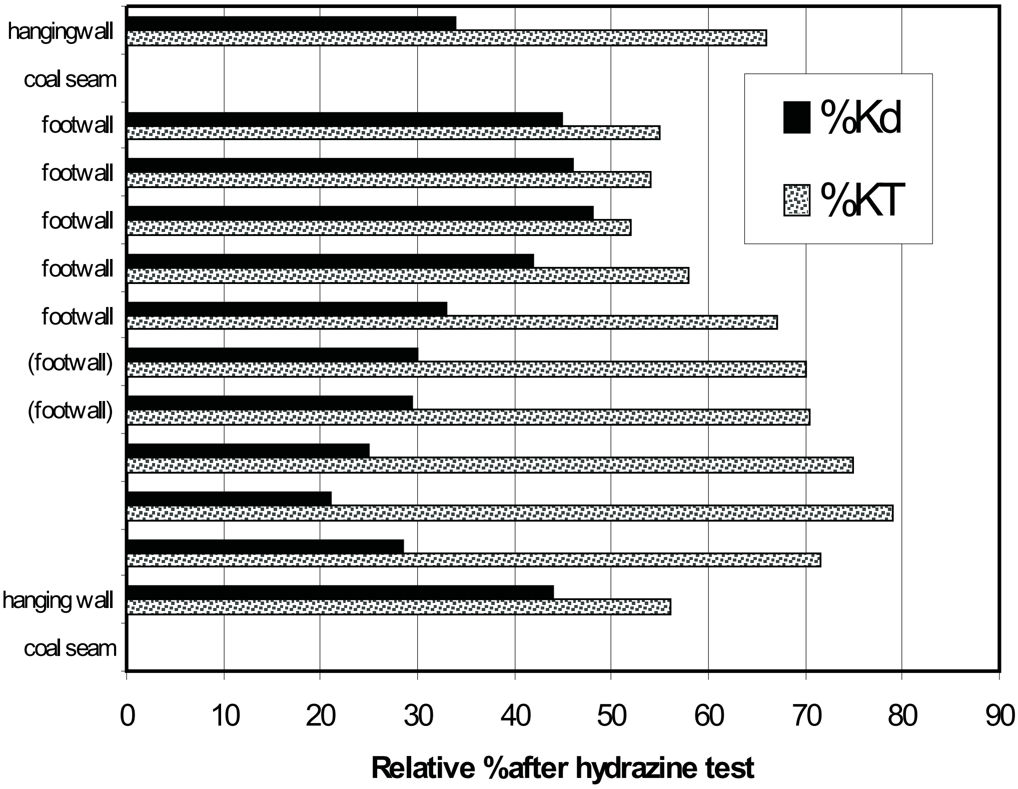

Figure 2. Relative proportions of the two populations of detrital kaolinite (in the <2µm fraction) calculated from hydrazine test. Samples are located between two main coal seams.

tains a higher percentage of Kd specifically when having affected by pedogenesis. Footwalls and hangingwall are richer in poorly crystallised kaolinite than the other lithologies Such a trend is amplified when the coal seam is thick and the corresponding footwall well developed. Carbonate cemented rocks present the highest content of well-crystallised kaolinite. In weathered profiles, the abundance of well crystallised kaolinite (fine-grained crystals) increases in the leached horizons above the water table. The mineral is abundant as pore-filling cement and replaces feldspars, micas and also rocks fragments. The crystallinity and the abundance of kaolinite have thus four origins : detrital, (paleo)pedogenetic, diagenetic (in sandstone) and weathering (current) with, for the first two, a strong control of the depositional environment.

4. Dickite and nacrite

In Belgium, dickite has been recognised since a long time. It was named "pholérite" by the miners. Pholérite is a Belgian mining term indicating a white kaolin material observed on sliding surfaces or slickensides. The Belgian literature concerning dickite is relatively scarce and dickite is generally considered as a rare mineral (Bourguignon, 1964; Fransolet & Bourguignon, 1978, Van Keer, 1999). However, personal field observations and correlative XRD analysis show that dickite is often present in grey or black Belgian Palaeozoic clayey series. In contrast, only one occurrence of dickite associated with Givetian dolomites has been recognised as filling material of dissolution cavities and fossil moulds. Shiny snow-white colour and a powdery aspect of dickite, almost both similar for kaolinite, are probably responsible of frequent erroneous macroscopic determinations.

Only three nacrite occurrences has been reported in Belgium, always in Carboniferous shales (Aderca, 1962; Van Tassel, 1962; Goemaere, 1991). The scant information about nacrite occurrence of is not only related to the scarcity of this species but is also due to the difficulty in identifying polytypes of kaolinite by conventional methods, especially when nacrite occurs in subordinate amounts or is associated with other kaolin mineral (Prost *et al.*, 1989, Ruiz Cruz, 1996).

Observations from numerous coal dumps in Liège coal basin show the frequency of the dickite and the relative scarcity of nacrite. In a similar way, drilling descriptions and coal dump observations in the coal basins of Charleroi, Centre and Couchant de Mons attest the frequent presence of 'pholérite'. In all these basins, dickite and nacrite were identified and always associated in the same microstructures as described in the present paper. However, drillings carried out in the Campine coal basin seldom revealed pholérite. Dickite in sandstone near coal

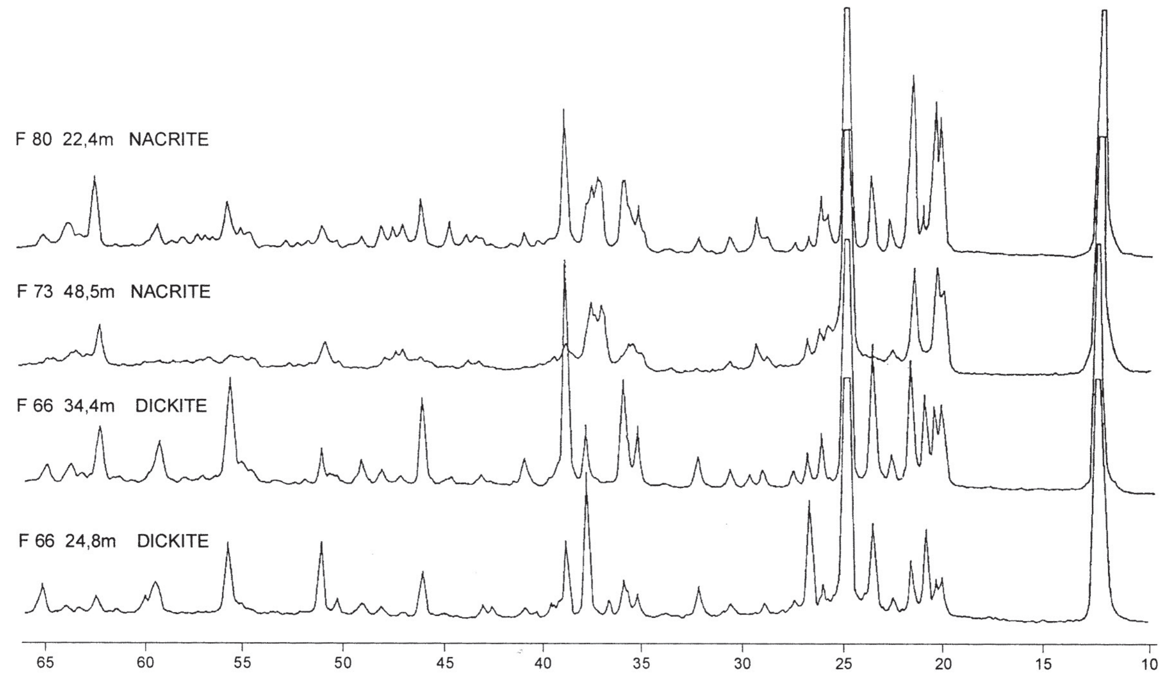

Figure 3. X-ray powder diffraction pattern *versus* 2θ, degrees: Cu Kα radiation. Dickite and nacrite were collected from borehole samples, Cointe of Hill, Liège, Belgium.

seams, shales and mudstones in the Westphalian of the Campine Basin has been assessed by Van Keer (1999). The coalification rank in the Campine Basin is well known (trough collieries and from numerous coal exploration well in the eigthies) and corresponds to the catagenesis stage (Pillement, 1982, Van Keer, 1999). The variation of the coalification follows the depth and is closely dependant of the various local heat flows, the thickness of overlying sediments and the tectonic deformations, indicating complex subsidence and thermal histories (Van Keer, 1999). In the southern basins, recent vitrinite-reflectance (%R_0) data are lacking, because the soon closure of collieries, in the sixties and the seventies. The last coal mine in the Liège basin (Argenteau-Trembleur) stopped its underground mining activities in 1980. In the southern basins, the coalification rank is higher than in the Campine basin. It varies from the catagenesis stage to the lower metagenesis stage and Pillement (1992) concluded that this rank was obtained before to the Variscan deformation in the Asturian times. In the "Cointe Anticlinal" structural unit (part of the Basin of Liège), the vitrinite-reflectance of the Malgarnie coal seam (Westphalian A) fluctuates between 2.4 and 2.5.

XRD analyses of oriented and unoriented mounts indicate that dickite and nacrite are absent in whole fine rocks. X-ray diffraction patterns and crystallographic parameters of dickite and nacrite are presented respectively at the Fig.3. & in the → Table 1. These minerals are always linked to different tectonic microstructures, called tectoglyphs like: pure extension fractures, oblique extension joints, tension joints; shear joints; shear normal joints with finite displacement and sliding surfaces of different morphologies (planes with filled scratches) (Pl.1/1; Pl.2/3-5; Pl.7/4); plans with nacrite maculae with cylindrical development - at sample scale -, surfaces with scratches of slip, oblique extension joints, shear joints with refraction over resistant layers, and accretion staircases (Fig.4) (Pl.3/1-4; Pl.6/2; Pl.8/1-3). The main structures only contain dickite. Nacrite is restricted to flat or slightly undulating sliding surfaces and is always associated with dickite. In the Westphalian sandstone of Campine, dickite typically occurs both in secondary pores and veinlets; dickite can be texturally distinguished from kaolinite by its more block habits (Van Keer, 1999). Both polarizing and electron microscopy examined the morphology and related petrographic properties of the clays (see photographic plates).

Pure extension joints are frequent in sandstone and silty sandstone layers where open spaces became partially filled by dickite (Pl.1/1). Dickite shows here a shiny snow-white to translucent colour and appears as loose, porous, friable powder. Each crystal face reflects the natural light. Sometimes mm to cm fragments of sandstone are embedded (cemented) by dickite (Pl.1/1, 2 & 4). In thin-sections of coarse sandstone, the fracture borders are rough with dickite showing the best automorphic

mineral	**dickite**	**dickite**	**dickite**
borehole number	66	80	Wérister (1)
depth	34.4m	60.5	Collieries
a (Å)	5.150 ± 0.001	5.150 ± 0.002	5.156 ± 0.002
b (Å)	8.937 ± 0.001	8.935 ± 0.002	8.944 ± 0.002
c (Å)	14.421 ± 0.002	14.432 ± 0.003	14.431 ± 0.003
ß	96°46'50" ± 70"	96°46'00" ± 1'12"	96°46' ± 1'
V (Å3)	659.2 ± 0.1	659.5 ± 0.2	661 ± 1
a:b:c	0.576:1:1.614	0.576:1:1.615	0.576:1:1.613
mineral	**nacrite**	**nacrite**	**nacrite**
borehole number	80	80	80
depth	33.7	22.4	60.5
a (Å)	8.910 ± 0.001	8.922 ± 0.005	8.915 ± 0.007
b (Å)	5.159 ± 0.001	5.162 ± 0.003	5.173 ± 0.005
c (Å)	15.672 ± 0.002	15.659 ± 0.007	15.660 ± 0.010
ß	113°33'42" ± 36"	113°37'06" ± 2'36"	113°33'48" ± 3' 43"
V (Å3)	660,3 ± 0.1	660,8 ± 0.4	661.9 ± 1
a:b:c	1.727:1:3.038	1.728:1:3.034	1.723:1:3.027

$Pb(NO_3)_2$ as internal standard

Cu Kα radiation

(1) Fransolet & Bourguignon, 1978

Table 1. Crystallographic parameters of dickite and nacrite from Cointe (Liège).

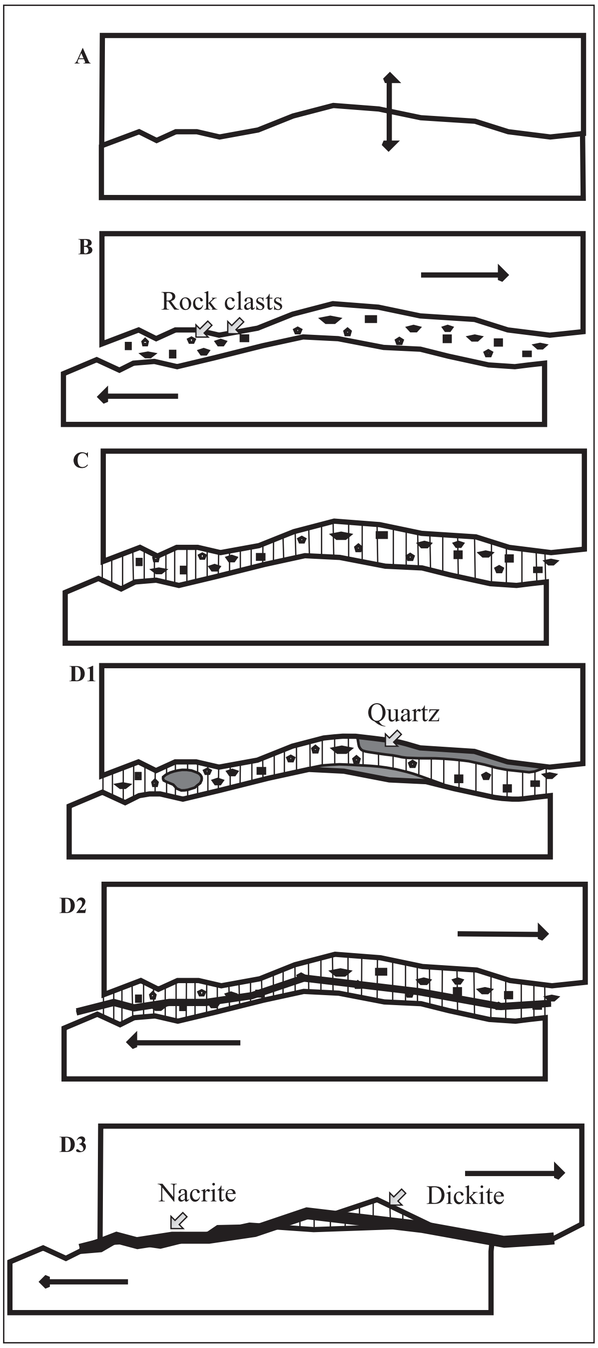

Figure 4. Schematic diagrams (strongly modified after Power & Tullis, 1989) illustrating the inferred development sequence for fracture and slickenside microfault surfaces in the hill of Cointe. Successive episodes of both discontinuous and continuous deformation are responsible for textural and mineralogical features. (a) irregular fracture or microfault surface (or sliding surface); (b) opening and translation of the surfaces relative to one another caused limited cataclasis and dilation along the surfaces; (c) dickite precipitation (well-developed isolated elongated crystals or vermicular dickite) from interstitial solutions; (d1) crystallisation of poekilitic quartz which includes dickite booklets; (d2) shearing: new translation (with new cataclasis for irregular fractures) with closing of the space inducing polymorphic transformation of dickite to nacrite. Dickite is preserved (with a blocky habit) in protected cavities; (d3) thin planar sliding surface with nacrite.

development (Pl.1/3, Pl.4/6) with a length until of 300 µm. Dickite crystals are elongated platelets parallel to the a-axis (elongation parallel to the pinacoid edge). Chen *et al.* (2001) report that such an elongated habit is common for hydrothermal dickite; however no traces of hydrothermalism have been found so far in Liège Basin.

Joints in extension with displacement affect sandstone, argillaceous sandstone and siltite. Generally, in the main extension joints and oblique extension joints with a weak displacement of mm to cm in length, the whitish (snow white), powdery dickite occurs as friable veinlets or as thin coatings within the fractures affecting the interbedded sandstone and siltstone beds (Pl.2/3-5, Pl.7/4). In thin-sections, dickite shows typical accordion-like to book-like aggregates of platelets, from 10 to 100µm length (Pl. 2/2, Pl.4/1, 2, 4 &5). The 'rouleaux' of platelets are generally randomly oriented. Smaller vermicules are located along the borders of the joint. Vermicules are laid out in all directions and are frequently sinuous. Each vermicule is composed of subhexagonal plates with a thickness of 800Å to 2000Å on average, often divided into four or five crystallites; each plate is composed of 100 to 300 dickite layers. The colour is white; the small individual size of crystallites, integrated in accordion-like books does not allow reflection of the light. Dickite is either directly in contact with the host rock, or is separated from the latter by a thin crystallisation of micrometric xenomorphic quartz crystals (Pl.1/2&4). Locally, this quartz edge is better developed and can reach a thickness of 1mm. The quartz includes then short vermiculated dickite crystals consisting of one to ten hexagonal plates (Pl.2/1-2). Rarely, a late crust of calcite can be observed after a re-opening of the fracture Pl.2/4). The following sequence of processes can be suggested: fracturing and cataclasis ➔ quartz and dickite precipitation ➔ dickite precipitation ➔ re-opening of the fracture ➔ calcite precipitation. When the shear component is more important, dickite presents a blocky aspect: vermicules of dickite are then more compacted and shorter in dimension, the stacking is also stronger and the plates do not appear so automorphic (Pl.4/1). The average size of the plates decreases while their number in each vermicule increases (until forty plates).

In the strongly folded and/or faulted zones, the argilaceous rocks are often strongly sheared with shiny, curved shearing fracture planes) on which slickensides or striations developed (Pl.3/2-4). Two main types of shear veins are observed: planar surfaces (sometimes cylindrical) (Pl.3/4; Pl.8/1-3) and accretion stairs (Pl.6/2). The accretion stairs are observed on very oblique joints (to the stratification plane) (Pl.6/1). They mainly developed in argilaceous rocks composed by thin layers of siltite or sandstone, and in siltites interlayered by (pluri)millimetric sandstone sheets. The accretion stairs (Fig.5) consist of blocky (slight powdery) dickite; the accordion-like books are short and strongly compacted, with a partial imbricated structure of plates and locally folded plates

(Pl.5/2-5). Surfaces of stairs and rises consist of pearl luster and/or translucent thin coatings of nacrite. Nacrite is composed of fine subhexagonal plates (seldom visible) (Pl.6/4), generally welded, oriented parallel to the sliding surface, and resulting into quite indurated platy aggregates, even not friable under water. Frequently, no individual crystallites are not developed. In cross section, one observes the morphological passage from dickite to nacrite (Pl.6/1, 3; Pl.7/1-3). This zone of transition is underlined by imbricated vermicules composed by coalescent xenomorphic particles (puzzle structure), then by the development of an oriented 'fibrous' fabric (with disappearance of stacking), and finally by thin sheets of pure nacrite at the surface. Optical and SEM observations show the progressive shearing, deformation, lamination and reorientation of dickite crystallites. This arrangement preferentially affects vermicules characterised by the more oblique stacking relatively to the shearing direction. Still in the zone of transition, from the heart of the stairs (dickite) to the surface (nacrite), diffractograms show a badly crystallised dickite (i.e. modified relative intensities of the reflections) and a mixture of both minerals respectively. But in some samples, corresponding diffractograms cannot discriminated to dickite from nacrite or mixtures of both minerals. Shutov *et al.* (1970) and Ruiz Cruz (1996) attributed these occurrences to mixed-packets and possible dickite-nacrite mixed-layers respectively. Ruiz Cruz (1996) also suggested that the intermediate phases could be considered as disordered phases. SEM and optical observations and related diffractograms patterns of dickite and nacrite are more consistent with the presence of translation defects and of an increasing level of structural disorder.

Sliding surfaces (Fig.4) parallel or almost parallel with the stratification plane form reflective planar (Pl.8/3) or undulatory surfaces with both maculae of 0.1 to 0.2 mm thick of white to translucent nacrite (typical pearly aspect) and green areas showing orientation and recrystallisation of chlorite and muscovite flakes under stress. The spots of nacrite do not individualise nacrite particles even by SEM. The maculae are generally of elliptic forms, which the large axis parallel with the direction of displacement. Such surfaces appear in all fine-grained lithologies or at the contact between two different lithologies. Beside the nacrite maculae, chlorite and illite are also oriented with their (001) plane parallel to the sliding surface (<1mm thick zone). Furthermore, the disappearance of I/S random mixed-layers in the diffractograms, and the increasing intensity of the smooth reflections of both chlorite and illite (Fig.6), indicate the improvement of the crystallinity of these minerals. Sliding surfaces appear brilliant and of deep green colour. A section perpendicular to the slid-

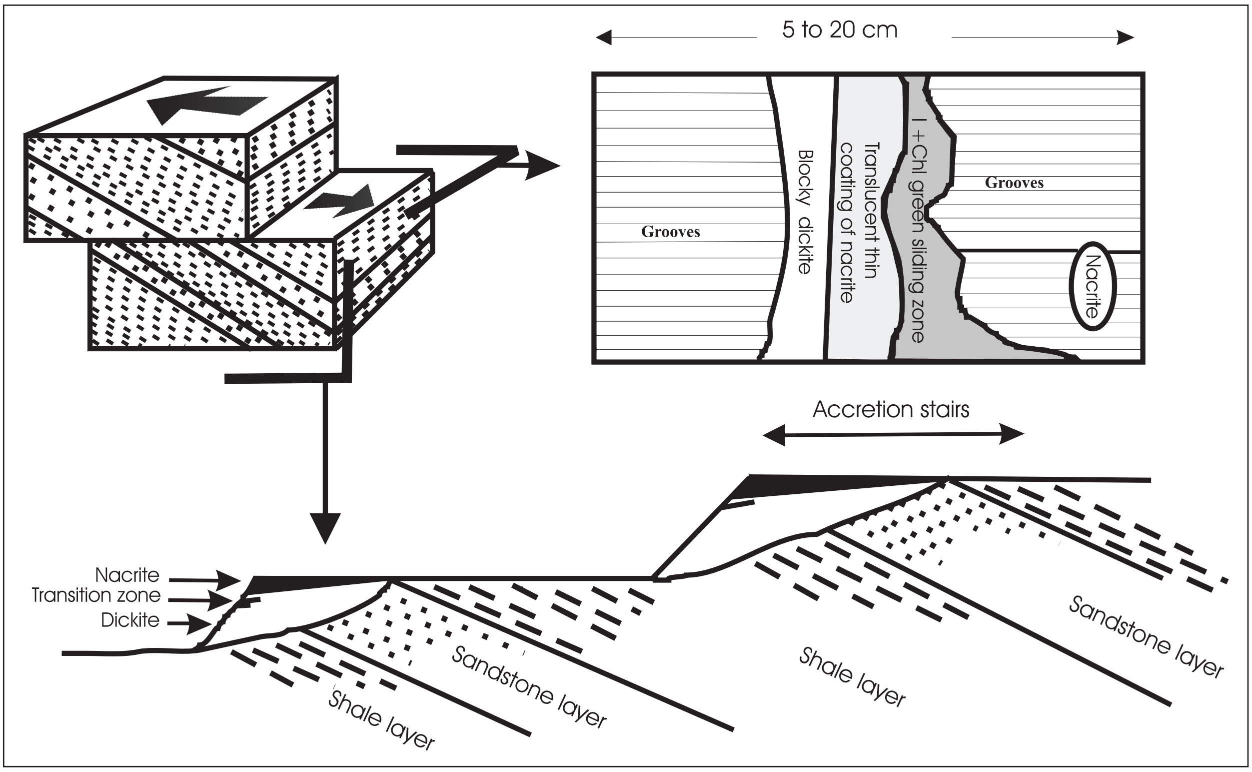

Figure 5. 3D partial view of a slickenside with formation of accretion staircases. Vertical view: section through stair with blocky dickite, zone of transition between dickite and nacrite, thin sheet of nacrite and refraction of the fracture over sandy layers. View of he plane of fracture: blocky dickite, thin coating of nacrite, sliding (glassy white) surface both with thin coating of nacrite and orientation of phyllites under shearing; sliding surface (glassy and deep green) with orientation and recrystallisation of chlorite and muscovite flakes under stress, oriented grooves.

ing surface reveals a discontinuous film of nacrite beside reoriented chlorite and illite flakes. Dickite occurs in small 'protected' pockets generated by the fracturing and dissolution under pression as exemplified by microstairs of sandy laminae, and abrasion of siderite nodules just below the surface. When shear zones affect underclays embedding siderite concretions, the petrographical observations show a rotation of the nodules, underlined by a correlative, tangential orientation of micas and chlorite flakes and by an ultrathin layer of nacrite occurring against the upper and lower parts of the nodule. Booklets of dickite fill the internal fractures after palisadic calcite has crystallised.

In the terrigenous rocks or carbonates respectively, slickensides are usually covered by calcite or quartz crystallisations but the deformed coal measures of the Liège coal basin are exceptional by the exclusive presence of kandites. The slickenside surfaces consist of compact and short vermicules of dickite. The hollow parts of the grooves are filled with dickite whereas the ridges are covered by nacrite. Such a microstructural pattern is typical for joints originally formed by extension, complemented by shearing with rupture of the bridges of rock, abrasion and probable dissolution of irregularities, yielding a planar surface filling the depressions.

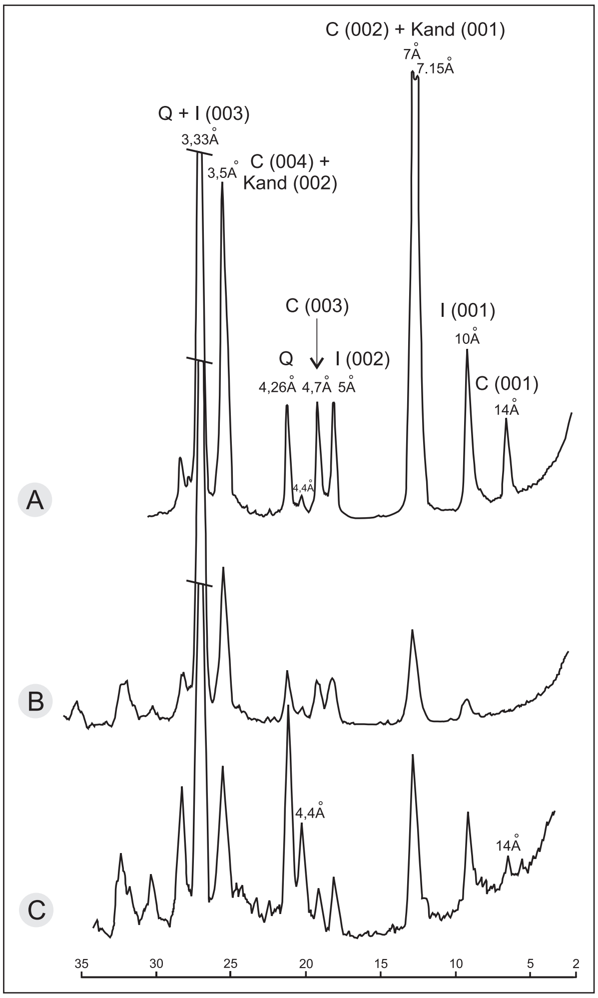

Figure 6. X-ray diffraction (Cu Kα radiation; degrees 2θ as horizontal scale) patterns performed on different surfaces of a monster a) sliding surface, b) unaffected surface, c) oriented powder obtained from scraped and crushed sliding surface. I: Illite; C: Chlorite; Kand: kandites; Q: Quartz

If in recent years, considerable attention has been given to the genesis of dickite and nacrite in sedimentary conditions, their origin and genesis are still a matter of debate. If dickite is generally considered to be a relatively high-temperature polytype, many other occurrences have been reported in hydrothermal and diagenetic environments, indicating that the genetic conditions of formation of are less restrictive than are envisaged initially. Indeed the kaolinite-dickite transition is now recognised as a major diagenesis indicator in sandstones. Goemaere (1991) and Van Keer (1999) drawed up a list of possible origins, respectively for dickite & nacrite and dickite alone: precipitation from hydrothermal solutions; neoformation; diagenetic processes; different models of transformation of kaolinite to dickite (with K/D mixed-layers as intermediate; progressive replacement of kaolinite by dickite with an increase in stacking order; continuous dissolution of kaolinite and subsequent and progressive precipitation of dickite), and transformation of dickite into nacrite.

Nacrite is usually considered as a high temperature polymorph; most reported occurrences support a hydrothermal or a pneumatolytic origin (Zheng & Bailey, 1994) but its formation during advanced diagenesis and through incipient metamorphism has also been described (Shutov *et al.*, 1970). However, Bühman (1988) and Ushatinsky *et al.* (1973) in Zheng & Bailey (1994) reported nacrite in sediments for which an authigenic or a low-temperature (<80°C) hydrothermal origin was postulated.

Lin & Wang (1997) described dickite in strictly localized fractured and/or disturbed zones along (over)thrust faults but concluded that dickite is mostly formed in situ in the interstices of country rocks, although partly resulting of hydrothermal alteration of the wall rocks.

In agreement with Van Keer (1999), there is no evidence for hydrothermalism and transformation of kaolinite into dickite. K/D mixed-layers are totally absent. In our geological environment, the absence of obvious relationships between kaolinite and dickite is shown by diffractometric analyses and petrographical studies. We suggest that dickite has been precipitated in our case from interstitial solutions. Van Keer (1999) suggested a link between organic matter maturation and the precipitation of dickite. This author concluded that dickite precipitated from Si and Al-saturated fluids in secondary pores (of sandstone) and veinlets. Combined oxygen and hydrogen stable isotopic data suggested that dickite formed from marine derived waters by assuming a precipitation temperature comprised between 120° and 150°C. Furthermore, the variable concentration of interstitial solutions could explain the various morphologies observed for the dickite particles, which could be correlated to the kinetic of the crystal growth.

The Westphalian coal-bearing strata of the Liège Basin underwent a complex diagenetic and deformation history, involving the formation of authigenic clay minerals, quartz and carbonate and organic maturation. Tectonic deformation of the Liège Basin during the Hercynian orogeny is at the origin of the numerous microstructures of deformations.

5. Conclusions

Because of the complexity of the clay assemblages, especially as mixtures of chlorite, kaolinite, dickite and nacrite, specific post-treatments before XRD investigations were required. Kaolinite is one of the main clay minerals of the Westphalian rocks. Its crystallinity varies according to sedimentary environments, proximity of coal seams, diagenesis and later atmospheric weathering. In the Liège Coal Basin, dickite and nacrite, polytypes of kaolinite, occur only in peculiar tectonic microstructures whereas no geothermal process can be invoked to explain their crystallisation. Dickite crystallised in extension joints and in protected pockets. Its origin is to be searched in a crystallisation process starting with solutions enriched in silica and alumina and containing a low content in alkaline and alkaline-earth ions. The Upper Carboniferous sediments are rich in alumina and silica. A reducing medium and an acid pH make it possible to put in solution the primary phyllosilicates of bulk rocks. These conditions became fulfilled thanks to the presence of sulphides associated with the organic matter during diagenesis. The presence of dickite, only in the tectonised zones, suggests its formation being associated with deformation (Buatier *et al.*, 1997). SEM data and optical observations confirmed that dickite crystals underwent deformation as supported by sheared vermicules, curved crystallites and stacking strain. Dickite is thus related to fluid-sediment interaction and to deformation in Hercynian folded and faulted zones. The dissolution by pressure solution in shearing zones may also have fed the neoformation of dickite in protected zones. The mechanism of nacrite formation here described is different from those generally proposed for sedimentary rocks. Nacrite is only associated in sheared planes where the constraints have been enhanced. Much evidence (optical and electronic observations, XRD) makes it possible to propose a polymorphic transformation of dickite into nacrite under shearing constraints. We think that both dickite and nacrite crystallisations are directly related to the Hercynian deformation, taking place in Al, Fe and C-rich sediments and associated with tectoglyphs. Dickite and nacrite are effectively rare in the Campine foreland basin and "relatively" abundant in the Liège basin at the variscan front. Strain can be an important factor promoting mineral reactions (Buatier *et al.*, 1997) and we hope that this study will stimulate further investigation about the role of deformation on mineral genesis.

6. Acknowledgements

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7. References

ADERCA, B.M., 1962. Contribution à la tectonique houillère : fentes penniformes avec présence de nacrite. *Annales de la Société géologique de Belgique*, 85 : 309-317.

ARNOULD, R., 1990. Géologie, stabilité et exécution de deux tunnels autoroutiers en site urbain (Liège, colline de Cointe). *Revue française de Géotechnie,* 52 : 67-84.

BEAUFORT, D., CASSAGNABERE, A., PETIT, S., LANSON, B., BERGER, G., LACHARPAGNE, J.C. & JOHANSEN, H., 1998. Kaolinite-to-dickite reaction in sandstone reservoirs. *Clay Minerals*, 33 : 297-316.

BOURGUIGNON, P., 1964. Dickite du Silurien et du Houiller de Belgique. *Annales de la Société géologique de Belgique*, 86, 1962-1963, 9, B519-534.

BUATIER, M., TRAVE, A., LABAUME, P. & POITEVIN, J.-L., 1997. Dickite related to fluid-sediment interaction and deformation in Pyrenean thrust-fault zones. *European Journal of Mineralogy*, 9 : 875-888.

BUHMANN, D., 1988. An occurrence of authigenic nacrite. *Clays and Clay Minerals*, 36 : 137-140.

CHEN, P.Y., WANG, M.K. & YANG, D.S., 2001. Mineralogy of dickite and nacrite from northern Taiwan. *Clays and Clay Minerals*, 49, 6 : 586-595.

FRANSOLET, A.-M. & BOURGUIGNON, P., 1978. Pyrophyllite, dickite et kaolinite dans les filons de quartz du Massif de Stavelot. *Bulletin de la Société royale des Sciences de Liège*, 47° année : 213-221.

GOEMAERE, E., 1991. Révision critique de l'analyse par diffraction des rayons X de matériaux et minéraux argileux: applications à quelques problèmes géologiques et pédologiques à intérêt géotechnique. Volume IV : Etude des matériaux du Houiller belge et conclusions générales. *Liège University,: unpublished PhD-thesis*, 150p.

GOEMAERE, E., 2004. Hydrobasaluminite : a new occurrence in Belgium. *Geologica Belgica*, 7/1-2 : 71-76.

GOEMAERE, E. & HANSON, A., 1997. New data about the halloysite from Angleur type-locality, Belgium. *Geologica Carpathica* – Series Clays, 6, 1 : 11-25.

LIN, S.B. & WANG, Y.-R., 1989. Mineralogy and tectonic implication of the dickites from Hung-Chun Peninsula, Souther Taiwan. *Acta Geologica Taiwanica*, 27 : 19-32.

PAPROTH, E., DUSAR, M., BLESS, M.J.M., BOUCKAERT, J., DELMER, A., FAIRON-DEMARET, M., HOULLEBERGHS, E., LALOUX, M., PIERART, P., SOMERS, Y., STREEL, M., THOREZ, J. & TRICOT, J., 1983 : Bio- and lithostratigraphic subdivisions of the

Silesian in Belgium, a review. *Annales de la Société Géologique de Belgique*, 106 : 241-283.

PILLEMENT, P., 1982. La houillification des formations carbonifères de Belgique. Sa place dans l'histoire sédimentaire et structurale varisque. Unpublished third cycle PHD thesis, Aix-Marseille University, 220p.

POWER, W.L. & TULLIS, T.E., 1989. The relationship between slickenside surfaces in fine-grained quartz and the seismic cycle. *Journal of Structural Geology*, 11, 7 : 879-893.

PROST, R., DEMEME, A., HUARD, E., DRIARD, J. & LEYDECKER, J.P., 1989. Infrared study of structural OH in kaolinite, dickite, nacrite, and poorly crystalline kaolinite at 5 to 600K. *Clays and Clay Minerals*, 37 : 464-468.

RUIZ CRUZ, M.D., 1996. Dickite, nacrite and possible dickite/nacrite mixed-layers from the Betic Cordilleras (Spain). Clays and Clay Minerals, 44, 3 : 357-369.

SCHEERE, J., 1957. La pétrologie des tonstein du Houiller belge. A l'occasion de la présence d'un tonstein dans la couche 40 d'Eisden. *Bulletin de la Société belge de Géologie*, 66, 3 : 300-316

SCHEERE, J., 1958. La kaolinite du Houiller belge. *Journée internationale d'étude des argiles de l'Association belge pour favoriser l'étude des verres et des composés siliceux*, 11p.

SCHEERE, J., 1963. Etude micrographique de l'évolution diagénétique des roches du Houiller belge. *Bulletin de la Société belge de Géologie*, 72 : 295-370.

SCHEERE, J., 1968. Les minéraux des argiles de la zone de Genk (Westphalien A supérieur) de la Campine. *Bulletin de la Société belge de Géologie*, 77 : 5-13.

SHUTOV, V.D., ALEKSANDROVA, A.V. & LOSIEVSKAYA, S.A., 1970. Genetic interpretation of the polymorphism of the kaolinite group in sedimentary rocks. *Sedimentology*, 15 : 69-82.

THOREZ, J. & VAN LECKWIJK, W., 1967. Les minéraux argileux et leurs altérations dans le Namurien inférieur de Belgique (synclinal de Namur). *Annales de la Société géologique de Belgique*, 90, 4 : B329-B379.

THOREZ, J., 1975. Phyllosilicates and Clay Minerals. A laboratory handbook for their X-ray diffraction analysis. G. Lelotte Ed., Dison, Belgium, 579p.

THOREZ, J., 1976. Practical identification of Clay Minerals. G. Lelotte Ed., Dison, Belgium, 90p.

USHATINSKIY, I.N., BABITSYN, P.K. & KIESLEVA, F.P., 1973. Dickite and nacrite in Mesozoic deposits of western Siberia. *Akad. Nauk SSSR, Doklady Earth Sciences Section*, 209 : 107-109.

VAN KEER, I., 1999. Mineralogical variations in sandstone sequences near coal seams, shales and mudstones in the Westphalian of the Campine Basin (NE-Belgium) : its relation to organic matter maturation. *Katholieke Universiteit Leuven, unpublished PhD-thesis*, 190p.

VAN TASSEL, R., 1962. Occurrence de nacrite dans les fissures de veinules de charbon. *Annales de la Société géologique de Belgique*, 85, 1961-1962, 8 : B320-321.

ZHENG, H. & BAILEY, S.W., 1994. Refinement of the Nacrite Structure. *Clays and Clay Minerals*. 42, 1 : 46-52.

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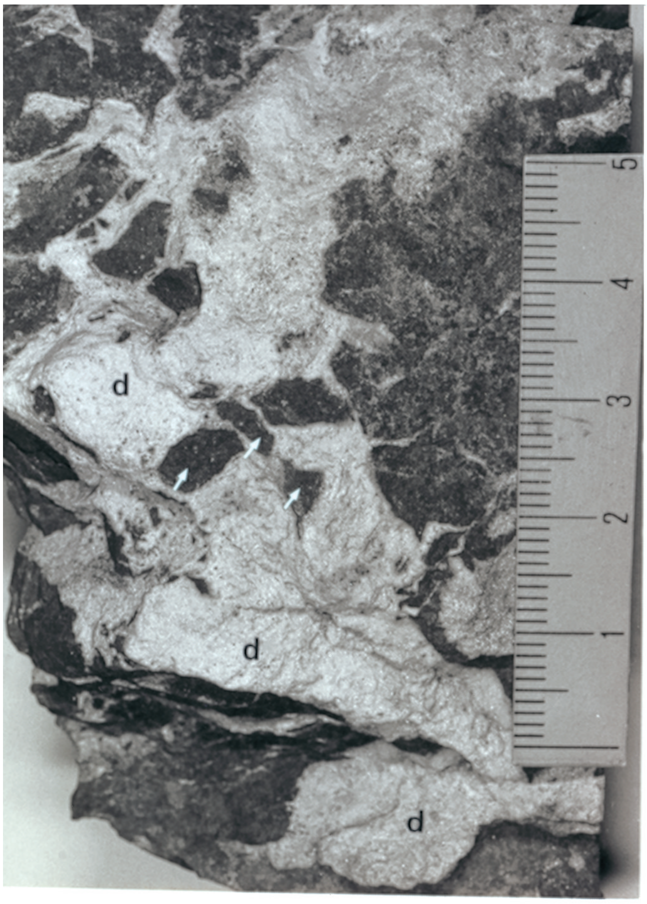
Plate 1. Dickite in sandstones

(1) Sandstone with a dense network of fractures. Powdery snow-white pearly dickite (d) embedded angular rock fragments – white arrows;
(2) Photomicrograph of a thin section trough an open joint in a siltstone. Mosaic of dickite (d) and angular rock fragments (r) - Transmitted light;
(3) Elongated crystals of dickite from a pearly powder with loose crystals;
(4) Idem (2). Rim of quartz (q) around rocks fragments – Crossed nicols



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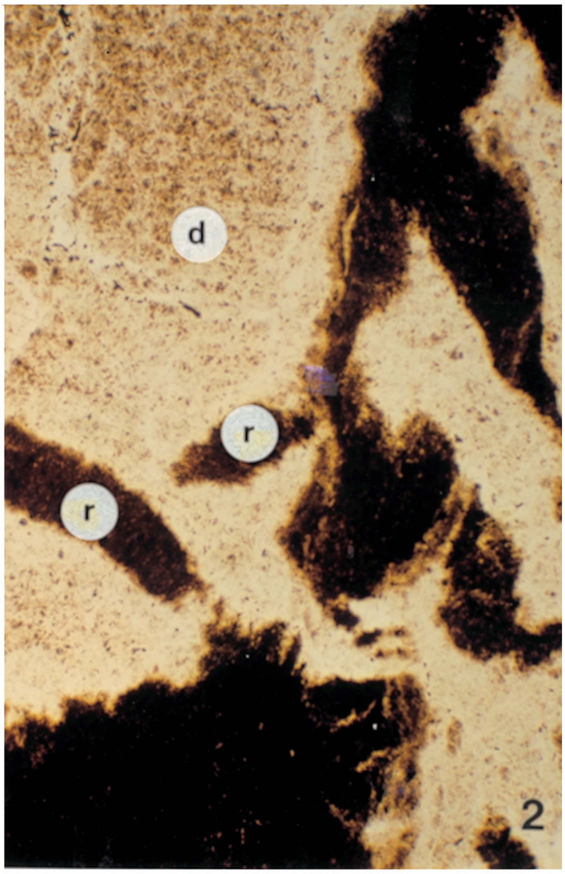
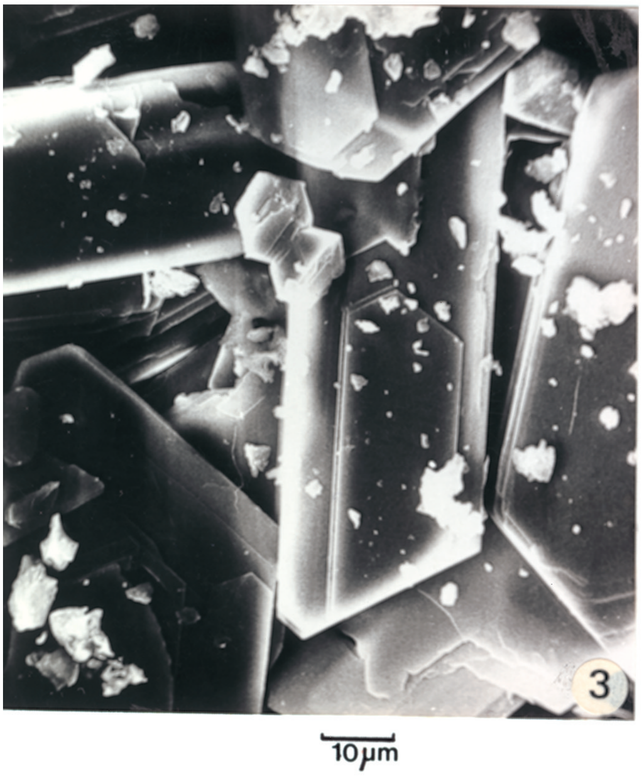




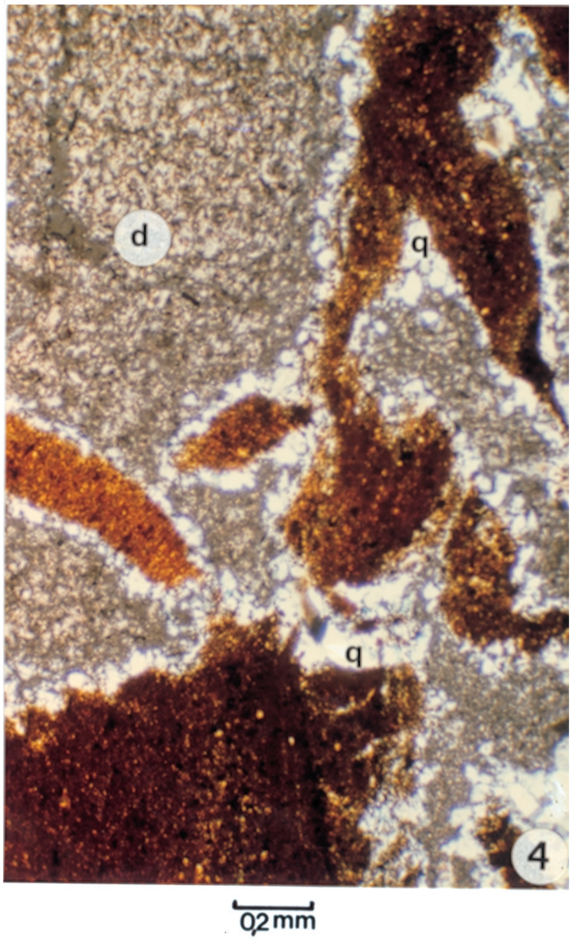
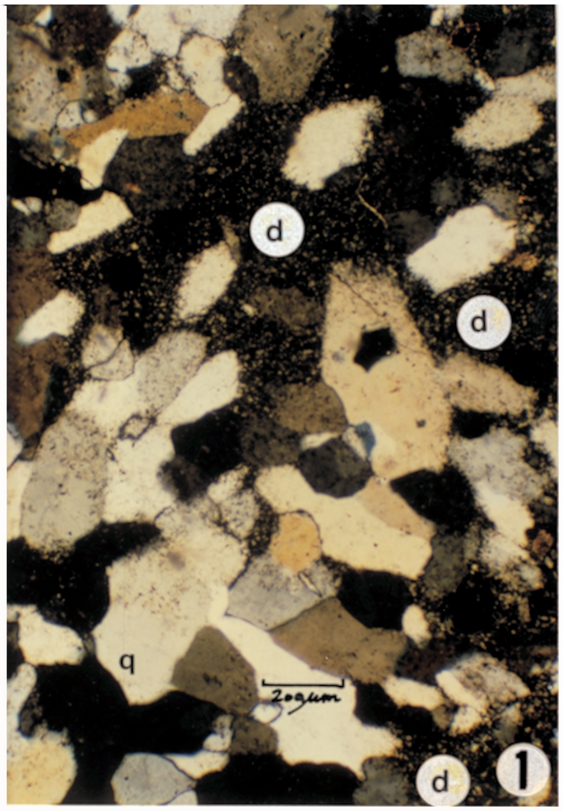
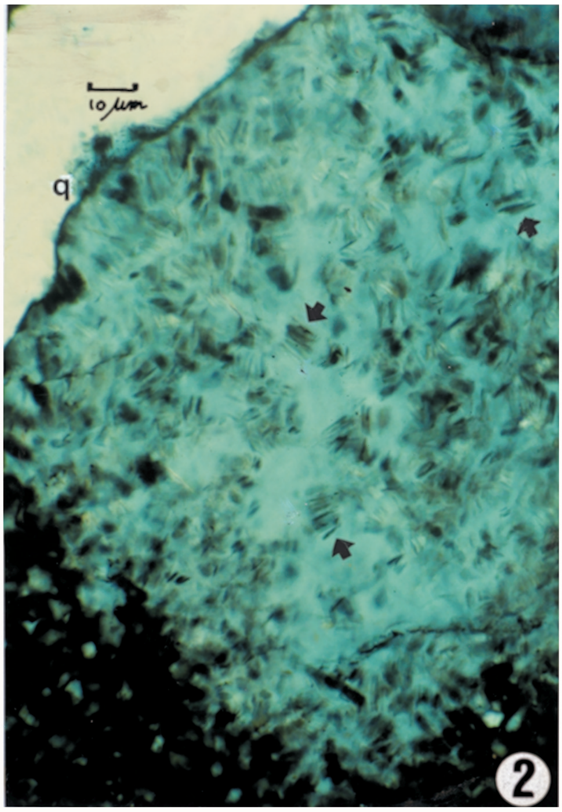


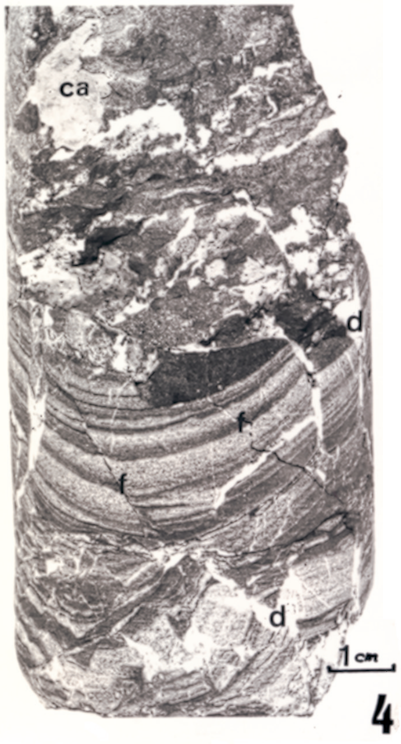
Plate 2: Dickite in open joints

(1) Mosaic of quartz with a shiny aspect mainly in the upper part of the micrograph – crossed nicols;
(2) Two grains of quartz including numerous short vermicules of dickite. Stacking and book-like aggregates are clearly observable – transmitted light;
(3) Strongly fractured core sample with regular alternation of siltstone (grey) and sandstone layers (white). Millimetre-thick veins and open joints are respectively filled and coated with white-snow dickite (d);
(4) Other view of the same core sample showing veins filled with dickite (d), empty fractures (f) and crust of calcite (ca);
(5) Core sample of massive sandstone with network of veins filled with white powdery dickite. Note the brilliant undulating sliding surface parallel to the stratification plane at the base of the core.


d
d
q
20 µm
d
1


10 µm
q
2


d
d
1 cm
3


ca
d
f
f
d
1 cm
4


1
2
3
4
5
d
d
5

Plate 3: Fractures with kandite minerals

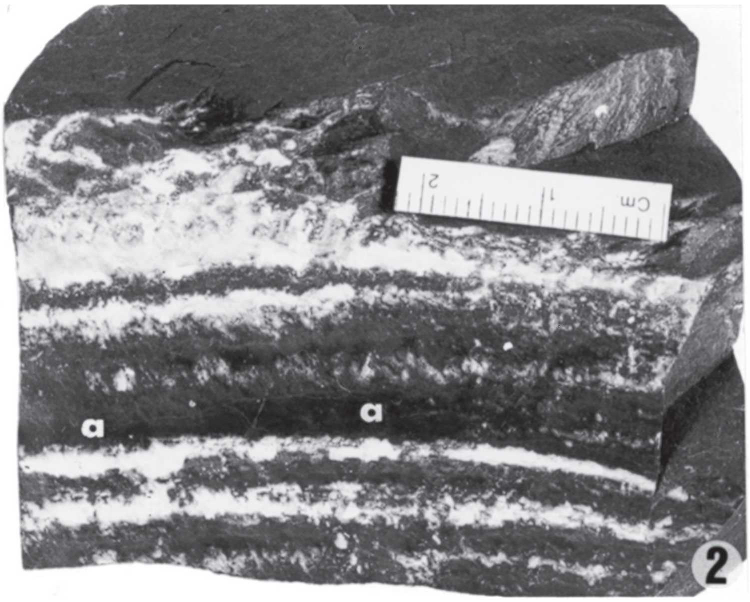
(1) Core sample of a fine sandstone with an irregular fracture strongly oblique to the stratification plane (little black arrows). The displacement (indicated with large arrows) induces many microstairs with felting of white dickite;

(2) Core sample of a siltstone interlayered by coarse siltstone layers. The fracture has a curved surface (left to right) with alternation of crystallisations of dickite (snow-white), dickite and nacrite (translucent white) and black polished surfaces (a). This zonation is strongly related with refraction over coarse siltstone layers.

(3) Undulating polished surface through a siltstone with orientation (and enhancement of crystallinity) of clay minerals (illite, chlorite) and organic matter, parallel to the sliding plane. The green black colour is due to chlorite and organic matter

(4) Core sample of sandstone. Variation in grain size indicates the plane of stratification (So). Two conjugated fractures cut the sandstone. The sliding surface (upper surface) is strictly parallel to the stratification plane and shows white-translucent nacrite thin coatings (b) and black areas (oriented both clay minerals and organic matter). Note the two different generations and orientations of striations. The rough oblique surface carries striations of dickite (a) at the lower surface. Furthermore, note three thin veins filled of dickite (d).

1



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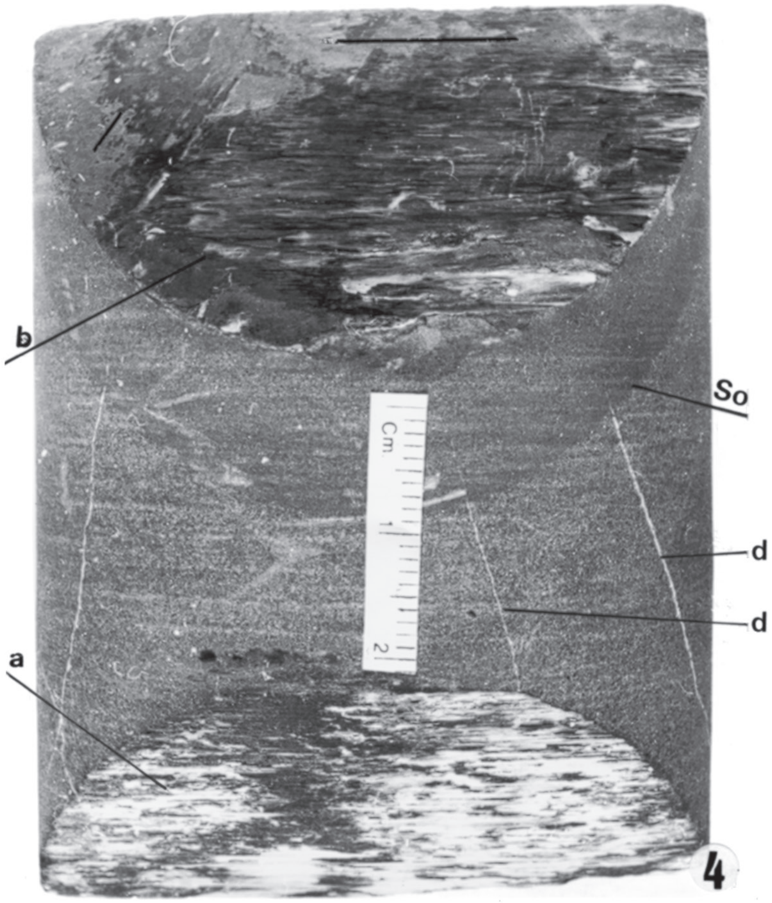
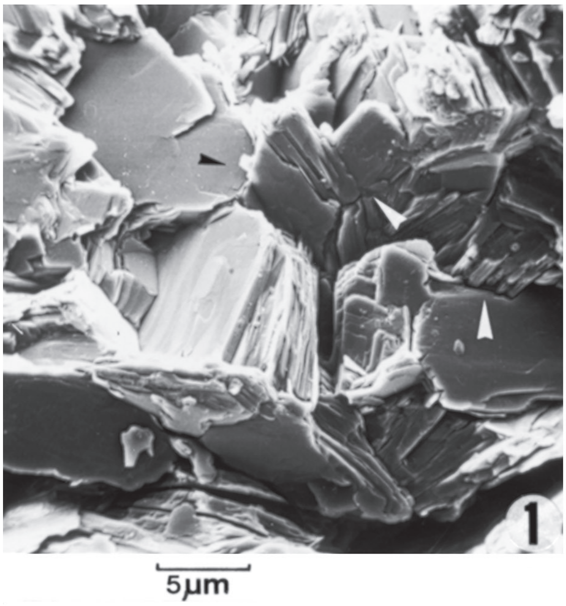


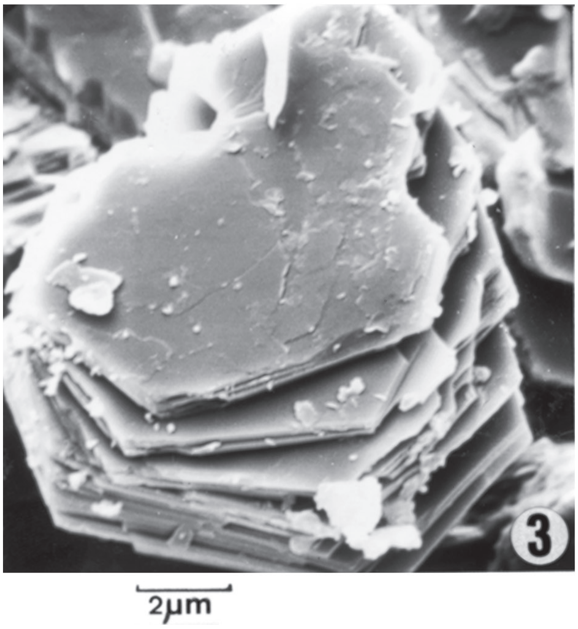
4

Plate 4: Scanning electron micrographs of dickite. Fractured surfaces of specimens

(1) Blocky dickite. Vermicules are short, compact and without any orientation. The hexagonal habit of the platelets is affected by an imbricated structure (see arrows).
(2) Close-up of micrograph 4 showing the compact disposition and thickness (100 to 200 angstroms) of the platelets.
(3) Vermicular dickite stack with hexagonal platelets. Note the limited translation and rotation of crystallites after shearing.
(4) Blocky dickite with book-like aggregates. Vermicules are short and compact. The hexagonal habit of the platelets are affected by an imbricated structure.
(5) Blocky dickite with book-like aggregates and without orientation of vermicules.
(6) Powdery dickite showing "giant" elongate crystals. See some elongated lath-shaped platelets of dickite (a). Wérister coal mine.


1
5µm


2
1µm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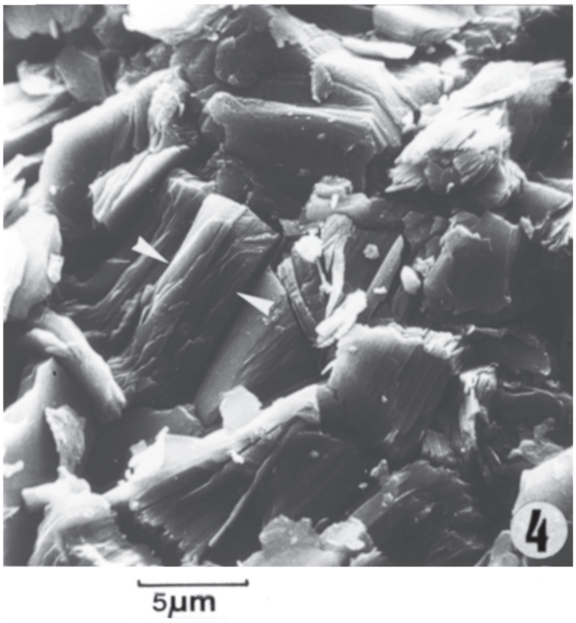
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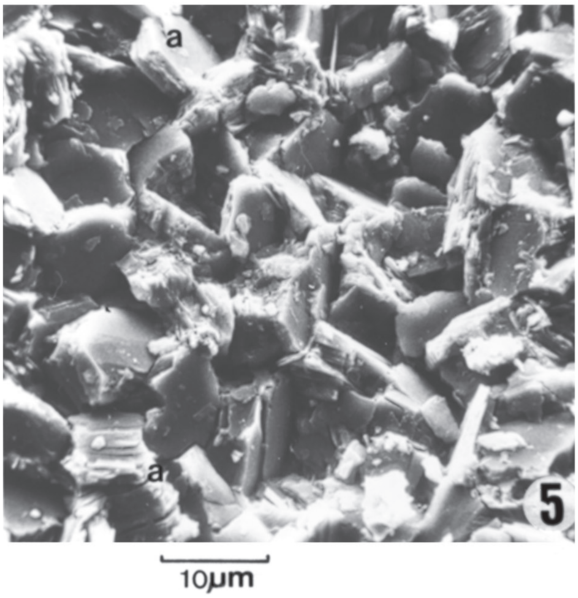
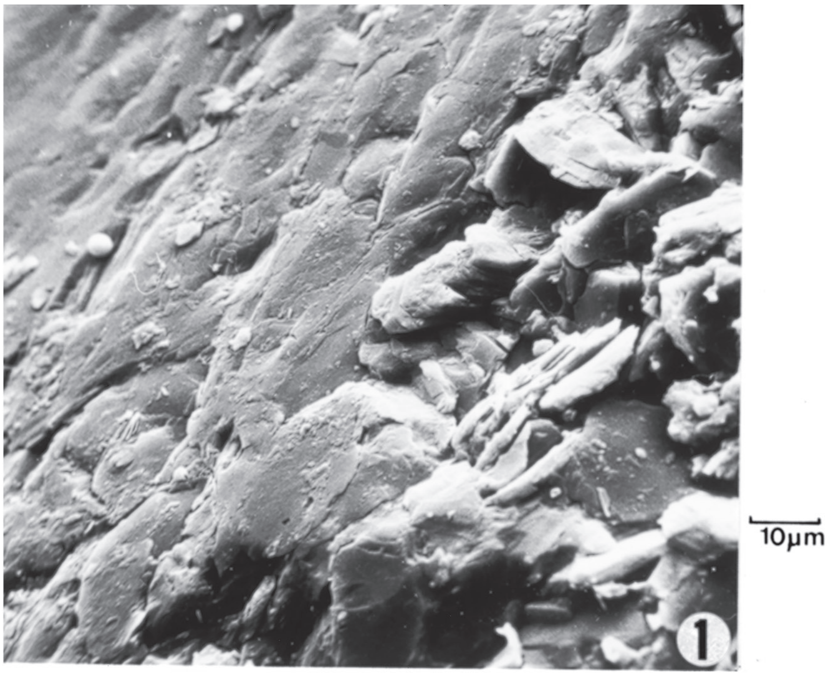
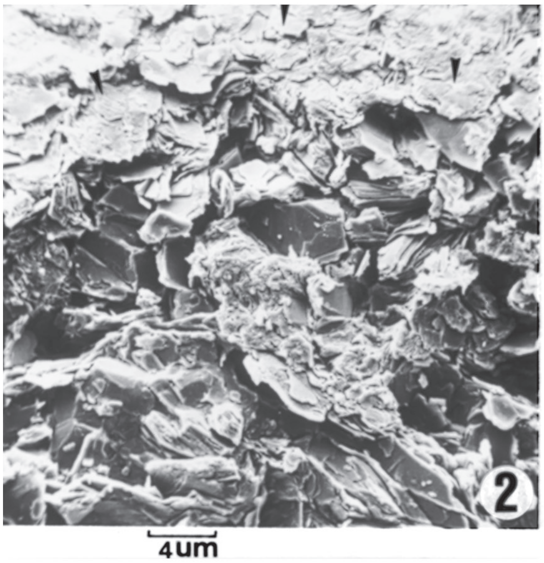

a
a
5
10µm

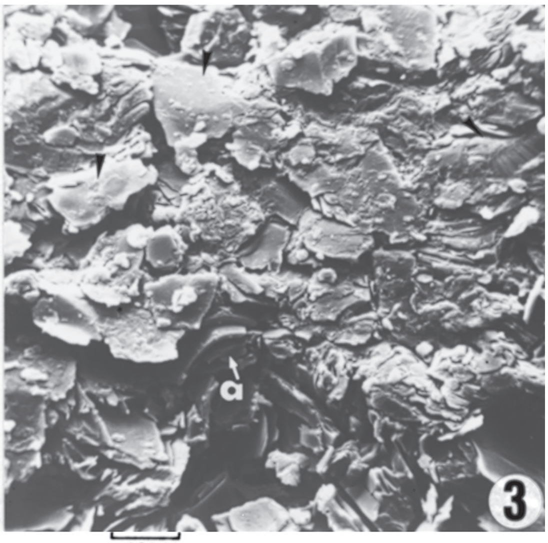

a
6
50µm

Plate 5: Scanning electron micrographs on accretion stairs

(1) Irregular upper surface of an accretion stairs. Note the abraded aspect of the surface (left part) with intimate interpenetrating of xenomorphic crystallites. Note the disturbance of the particles and the disappearance of the vermicular aspect (right part).
(2) Near the upper sliding surface, the upper part of the photo shows the orientation of nacrite particles, the disturbance of the platelets and the disappearance of the vermicular aspect (dickite-nacrite transition zone) which reach a maximum. See the irregular border of the individual platelets.
(3) Idem (2) showing the curved aspect of the particles (a) and their strongly irregular shape and edges.
(4) Close-up of a folded rouleau of dickite (sliding surface from upper right to lower left). The opening of the sheets at the border and the tightening in the axis of the microfold are observable.
(5) Other detail showing deformation of the platelets accompanying the orientation of crystallites under stress.


10µm
1


2
4um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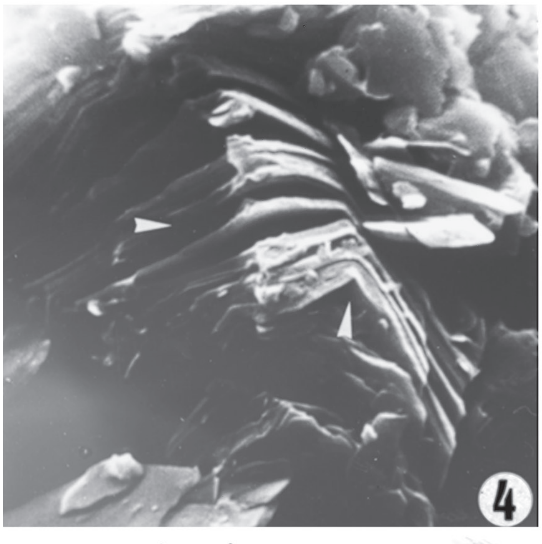
3
4um


4
0,75µm


5
2,1µm

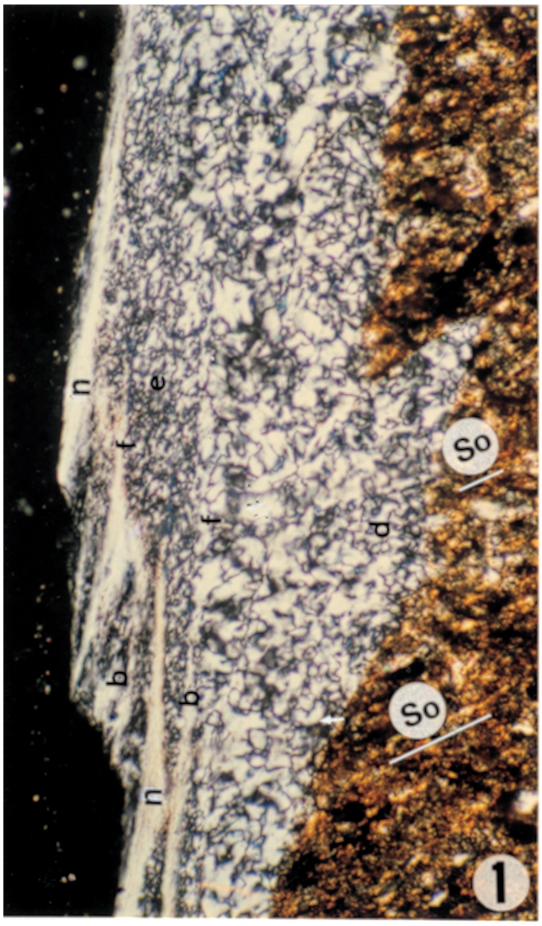
Plate 6: Accretion stairs

(1) Thin vertical section through a complex accretion stair developed on shale. So: stratification plane; n: sliding plane composed of nacrite sheets, b: nacrite sheets and transition dickite-nacrite; d: slightly deformed dickite zone, f: strongly deformed dickite zone, e: transition zone between dickite and nacrite

(2) Macroscopic view of a shale with numerous white accretion stairs (n) and striations (s). Direction of displacement is from bottom to top. The more translucent white areas are composed of nacrite exclusively while pure white zones are composed of dickite with a thin cover sheet of nacrite

(3) Thin section through a stairs of accretion showing shale (upper left corner), rouleaux of dickite (d) –arrows show internal stacking, and nacrite sheets (n)

(4) Electron micrograph of hexagonal platelets of nacrite – sliding surface.


n
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So
b
b
n
1
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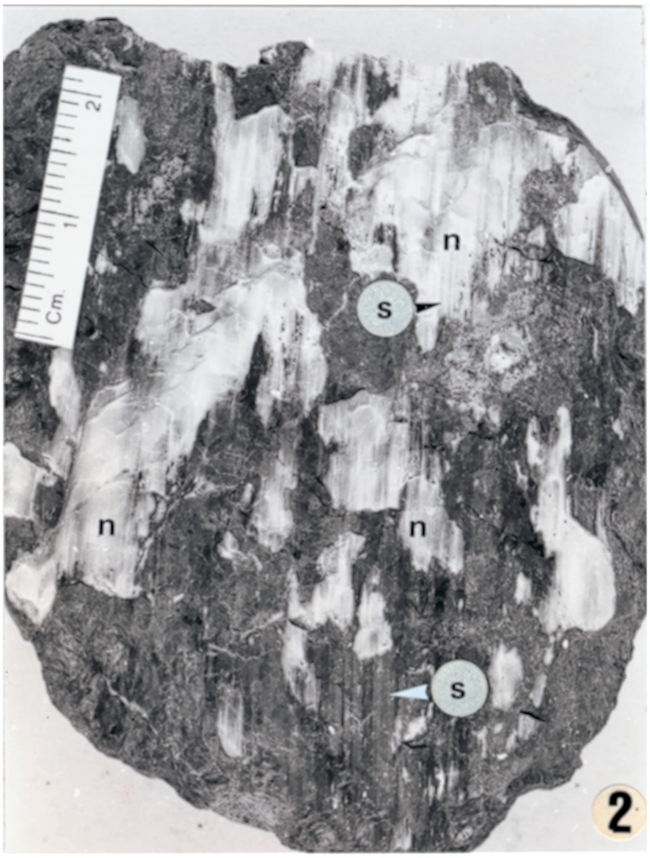
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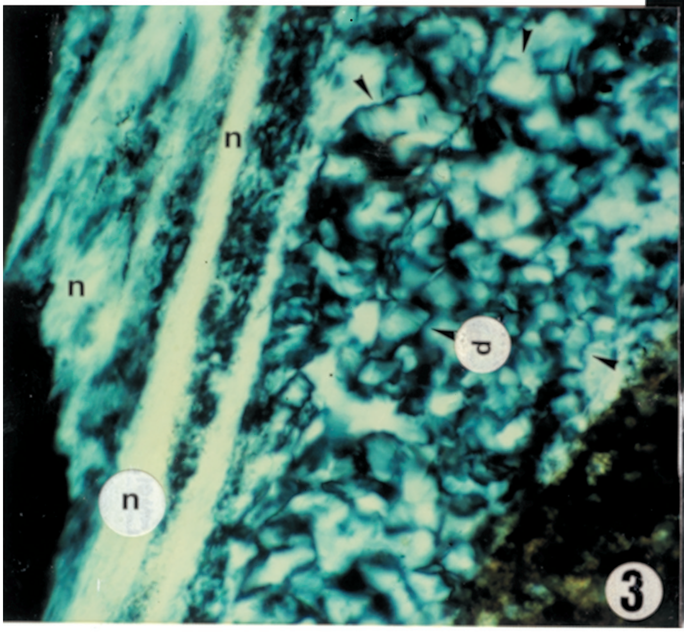
s
n
n
s
2


n
n
n
d
3
10µm


b
a
b
4
200µm

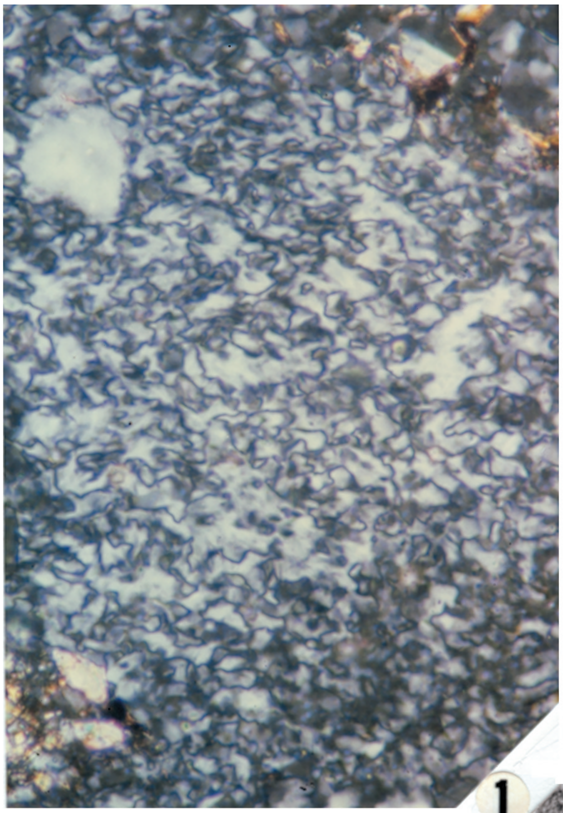
Plate 7: Dickite and nacrite transition zone

(1) Thin section through the internal (furthest away from sliding plane) transition zone between pure dickite zone and pure nacrite zone. Compared with the photo 3, illustration of the reduction of the size of crystallites, their puzzling aspect with a strong interpenetrating and in some places a coalescent of crystallites. The internal stacking in the rouleaux only persists at rare places.

(2) Thin section through the external (nearest the sliding surface) transition zone between pure dickite zone and pure nacrite zone. Compared with photos 1 & 3, the shearing aspect and the systematic orientation of poorly crystallised nacrite as showing by the stretching of white and grey areas.

(3) Typical dickite zone showing short unoriented compacted rouleaux with typical internal stacking.

(4) Core sample of laminated sandstone strongly affected by fracturation. Fractures are filled with dickite - white snow - (d) or dickite plus nacrite – grey white and translucent) (d,n)



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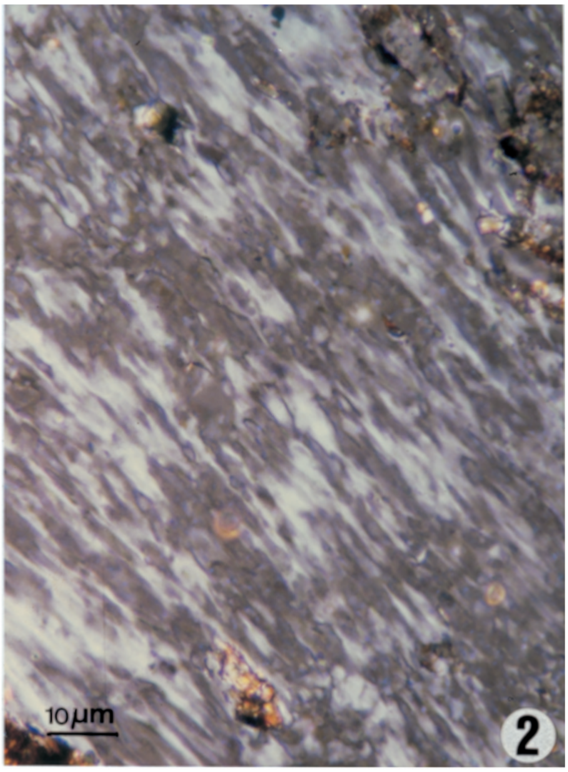


2

3

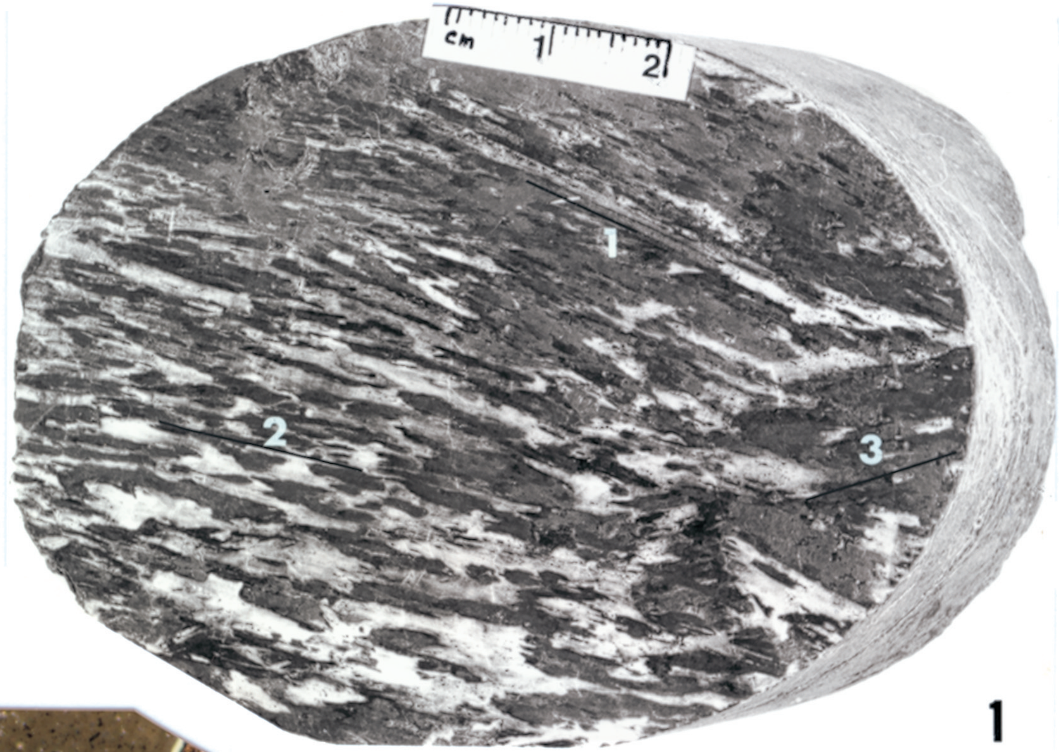
4

Plate 8: Nacrite

(1) Hand specimen of core sample showing a planar sliding surface developed parallel to the stratification plane. Note three directions of striations. White translucent areas are constituted of nacrite, while white areas contained dickite in cavities covered by a thin sheet of nacrite. Black areas are characterised by oriented clay minerals and slipped organic matter while grey surfaces represents unaffected host rock.

(2) Thin section through a siltite with a sliding surface materialised by pelicular nacrite. The stratification plane is strongly oblique with the sliding plane.

(3) Flat sliding surface with a strong orientation of clay minerals correlative with an improvement of their crystallinity. White and translucent thin coatings are constituted of nacrite.



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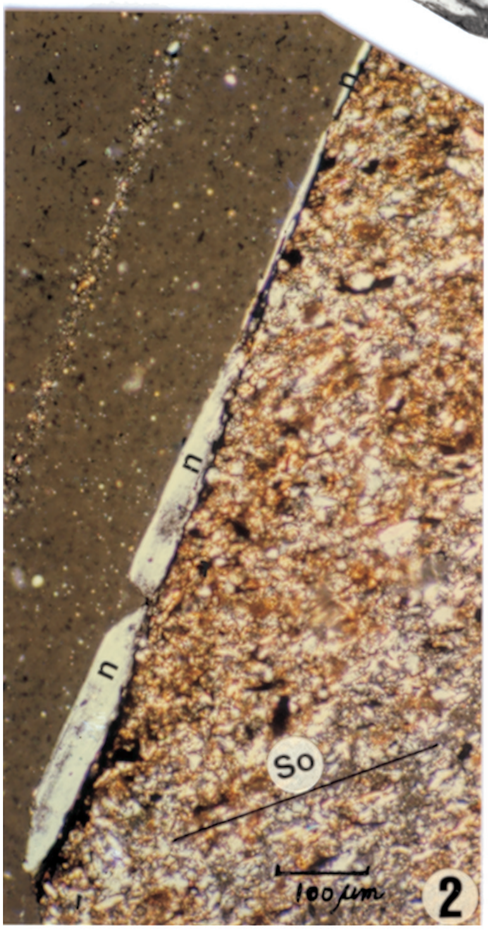

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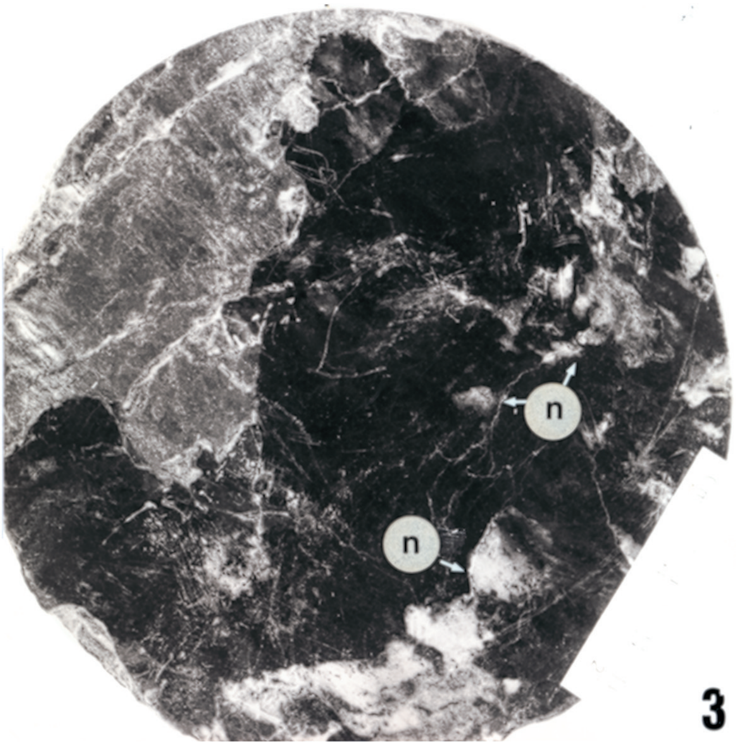

3