

HYDROBASALUMINITE: A NEW OCCURRENCE IN BELGIUM.

Eric GOEMAERE

(1 figure, 3 tables and 1 plate)

Royal Belgian Institute of Natural Sciences, Geological Survey of Belgium, Jenner Street. 13, B-1000 Brussels, Belgium; E-mail : eric.goemaere@naturalsciences.be

ABSTRACT. We report the first Belgian occurrence of hydrobasaluminite as a weathering product in the waste deposits of an old mined coal seam. Basaluminite was identified after 'natural' laboratory dehydration. A description of the depositional setting and the mineralogy together with a brief discussion about the origin of this hydrated aluminium sulphate mineral is presented.

KEYWORDS: hydrobasaluminite, basaluminite, Westphalian, coal seam, weathering, X-ray diffraction, Liège.

RESUME. **L'hydrobasaluminite: une nouvelle occurrence en Belgique. Courte note.** Cette note présente la première occurrence belge d'hydrobasaluminite, produit d'altération associé aux déchets issus d'une veine de charbon déhouillée. La basaluminite est acquise par déshydratation 'naturelle' dans les conditions du laboratoire. La description du dépôt, sa minéralogie et une brève discussion sur l'origine de ce sulfate d'aluminium hydraté sont présentées.

MOTS-CLES: hydrobasaluminite, basaluminite, Westphalien, veine de charbon, altération, diffraction des rayons X, Liège.

1. Introduction

Since the original discovery and the description of both hydrobasaluminite, $Al_4SO_4(OH)_{10} \cdot 12-36H_2O$, and basaluminite, $Al_4SO_4(OH)_{10} \cdot 5H_2O$, from joint-faces coating of Jurassic Ironstone deposits in England, by Bannister & Hollingworth (1948), these minerals have been found in many locations (England, Italy, Poland, USA, - see Tab. 1 - France and Russia).

Hydrobasaluminite is also known to dehydrate irreversibly to basaluminite, even after a short (a few days) exposure in the laboratory. As a consequence, main occurrences of basaluminite are related to dry material, directly collected in the field or transformed in the laboratory environment.

2. Geographical and geological setting

The boring of a subway through the hill of Cointe, Liège, establishes a motorway connection in the city between the motorways E40 (Brussels-Liège) and E25 (Luxembourg-Liège) (Fig. 1). This 2-ways twinned tunnel bored the hill between the Guillemins railway station and the Val-Benoit (Fagnée). The hill of Cointe is geologically located at the northern side of the complex anticline of Cointe, with an E-W axial orientation. A large borehole prospection was performed. The geological cross-section of the tunnel (1.3 km long) published by Arnould (1990) shows a succession of oblique folds

with weakly inclined northern flanks ("platteures") and steep southern flanks affected by longitudinal faults and fractured zones.

The section of gallery in which hydrated sulphates were observed is framed by cored vertical drillings F95 and F90, with respectively the follow coordinates (Lambert Belgian network 1974) X1: 234653, Y1: 146103, Z1: 125m and X2: 234549, Y2: 146407, Z2: 129.5m, at an altitude of approximately +60 m, 65 m under the topographic surface. The water table level oscillates between +75 and +85m. At this place, the motorway tunnel crosses a zone that was mined at the end of the 18th century or beginning of the 19th century by way of chambers (room timbering) and coal pillars. If numerous coal seams were mined in Liège since the Middle Ages, the main activity started at the end of the 18th century with the development of numerous collieries but first and old mine mapping is lacking. The coal seam concerns the Bomebac coal seam (Mons Member, formerly known as « Assise de Genk » or « Zone de Genk », Formation of Charleroi, Upper Westphalian A (Upper Bashkirian)). At this place, the Bomebac coal seam (60-90 cm width) was mined on the slightly inclined NW flank of a syncline while the almost vertical northern flank remained unmined. The coal mined zone is cut by the tunnel between 895m and 935m measured from the entrance Avenue of Gerlache (Val Benoît).

Room timbering was locally preserved and chambers were filled by extraction wastes (black and

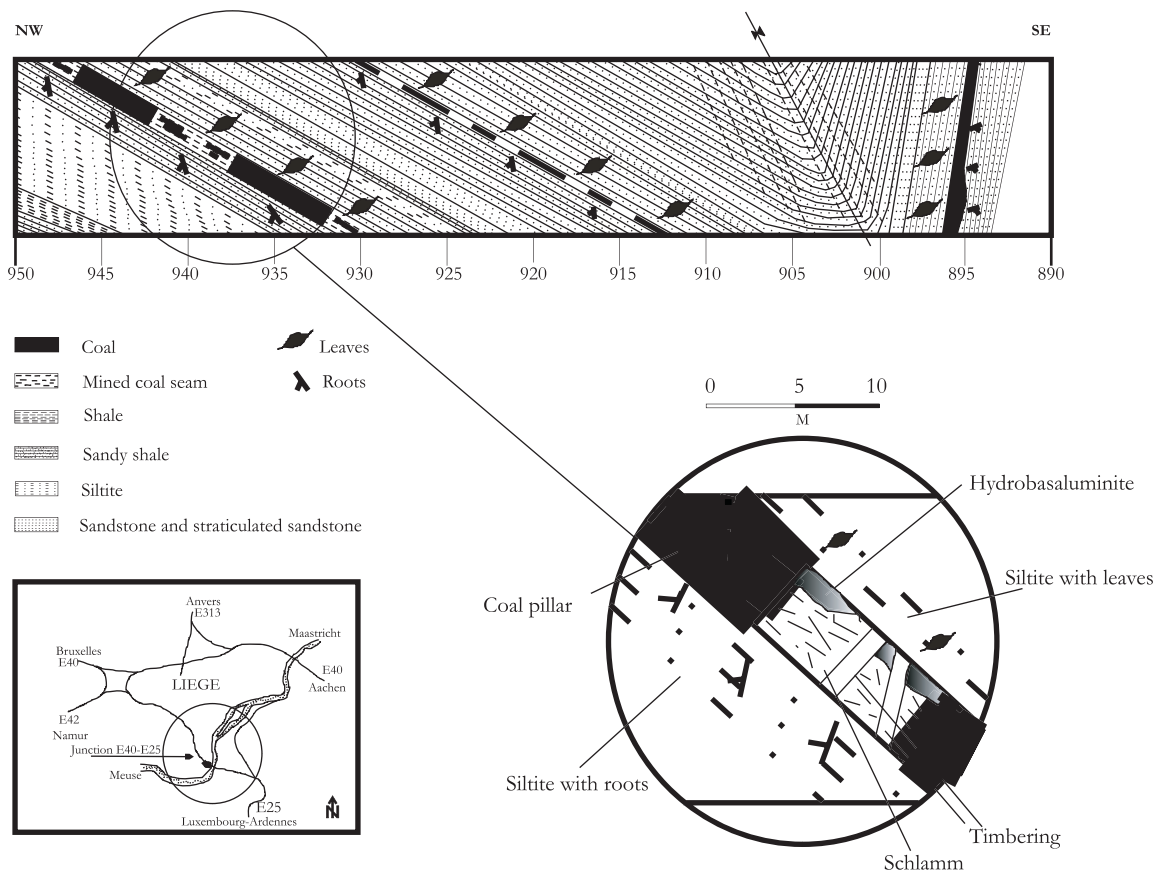


Figure 1: Schematic location map and section of hydrobasaluminite occurrence. Cointe hill tunnel. Liège. Belgium.

grey shales stained along fractures by yellow-brown iron hydroxides). Goethite was identified by X-ray. An unctuous mass of a few cm to more than 50 cm wide is located between the top of the irregular surface of the waste heap and the plane contact with the hanging wall (carbonaceous shale with leaves) (plate 1, photo B). Clay-like mineralisation is concentrated with hydrobasaluminite, allophane, traces of gibbsite and amorphous iron hydroxides (plate 1, photo A). The upper shales apparently were unaffected by collapse after mining, but some stratification or fracture planes are coated by iron hydroxydes. Quartz, feldspar, illite, kaolinite, irregular illite-smectite mixed-layers, iron chlorite and pyrite are usually the major constituents of the unweathered shale.

3. Methods and results

The mineral is extremely fine grained and admixed with variable amounts of impurities. These features combined with the property of an easy dehydration made chemical analyses and optical investigations rather difficult. Analytical results were thus restricted to the recording of X-ray powder diffraction patterns obtained with a Phillips (PW 1730) diffractometer, using a Ni-filtered Cu K_α radiation. The following XRD method was applied for the collected samples. The latter

were kept humid until the X-ray diffraction powder method was performed. Humid hydrobasaluminite was packet into a 2 mm deep glass sample holder and immediately X-rayed. Samples were naturally dried at room temperature, gently crushed and homogenized in a hand mortar. The finely ground powder was then mounted in a shallow cavity of a glass sample holder in order to prevent any preferred orientation.

Table 1: Main occurrences of hydrobasaluminite described in the literature

- *Hollingworth & Bannister (1950)*
Hydrobasaluminite as mineral coating joint-faces in quarries (Lodge pit) in the Nortampton ironstone, Irchester, Northamptonshire, UK. "Sulphates of aluminium suggest the solution of alumina by acid waters derived from the oxidation of pyrite which is a widespread constituent of the unweathered ironstone".
- *Milton et al. (1955)*
In geodal cavities and thin seams in a residuum between the Chattanooga shales and the underlying limestone. Action of H₂SO₄ (derived from oxidised pyrite) on the Chattanooga shales, Nashville Basin, 5 localities, Tennessee and Kentucky, USA.
- *Tien (1968)*
Hydrobasaluminite above the Fleming coal and below a marine shale, (Crawford County, Kansas, USA) on a draining gully leading to an abandoned strip. Gypsum

and iron oxides. Basaluminite found as debris on dry slopes.

- Sunderman & Beck (1969)
Hydrobasaluminite in an abandoned halloysite prospect tunnel (Shoals, southwestern Indiana, USA). Hydrobasaluminite + allophane + gibbsite + hydrated iron and manganese oxides. Clay seam at the Mississippian (limestone)-Pennsylvanian (conglomerate) unconformity. Alteration of reworked residual clay (halloysite and allophane). Hydrobasaluminite dehydrates to basaluminite at room temperature and under X-ray beam.
- Wieser (1974)
Hydrobasaluminite as felt-like clusters of fibres penetrating allophane accumulations. Basaluminite (after dehydration) as coatings and crack or joint infillings in Hieroglyphic beds (dry slopes of shales), Upper Eocene, Polish Flysch Northern Carpathians, village Sienna, dam-lake Roznow, Poland. Interaction of sulphuric acid produced by pyrite decomposition with kaolinite-rich sediment. Accompanying minerals : gibbsite, allophane, gypsum, hydrated Fe and Mn oxides, and jarosite.
- Clayton (1980)
Weathering zone of the Oxford Clay at Chickerell, Dorset, UK. Occurs as a reaction rim surrounding carbonate concretions, resulting from neutralization of aluminium-bearing acid sulphate solutions formed by oxidation of pyrite and subsequent leaching of clay (pyritic bituminous shales). Basaluminite is formed on the field as a dehydration product.
- Forti (1997) reported by Polyak & Provencio (1998)
Alum Cave, Sicily, Italy. Oxidation of fumerole gas (containing minor H₂S) and acid weathering of volcanic ash and tuff.
- Polyak & Provencio (1998)
By-product of the H₂S-H₂SO₄ speleogenesis of Cottonwood Cave (Guadalupe Mountains of southeastern New Mexico, USA). Clay-rich seams in dolostone altered in hydrobasaluminite, alunite, hydrated halloysite, minor gibbsite and amorphous silica. Basaluminite not detected in the caves samples but results to room dehydration of hydrobasaluminite.

4. Description

Hydrobasaluminite from the Cointe tunnel occurs in two main habits : a) white, opaline to porcelaneous pure lenses of hydrobasaluminite with a plastic clay-like texture (toothpaste consistency) and b) pale yellow to yellowish-brown, porcelaneous to earthy (plate 1, photo A). The latter consists of a mixture or a thin interlayering of iron hydroxides and allophane. Locally, a clear coloured zonation related to monomineralic layer can be observed. In polymineralic layers, beside hydrobasaluminite, associated minerals are goethite, gibbsite, as identified by XRD and allophane. Basaluminite was not found in the tunnel samples. Hydrobasaluminite was found to be unstable at 20-22°C and 55-65% RH (laboratory conditions), converting into

basaluminite in a few days (or in a few hours after X-rayed). Cracks of retraction appeared in the material and its coherence disappeared. Hydrobasaluminite crumbled to a fine white powder which did not regain its plastic character when wetted. The conversion was irreversible. After drying, white or yellowish colours were most pronounced and especially along desiccation cracks.

The optical polarising microscope was used for direct observations of the basaluminite morphology. Individual crystallites of basaluminite are so small that optical properties could not be determined but micrometric rhomb-shaped platelets were observed.

Powder diffraction data for hydrobasaluminite and basaluminite from the Cointe Hill are given in Table 2 and compared with data collected from the literature. The X-ray beam generates rapid dehydration of the crystals and the structures begin to collapse and change during the measurements. This behaviour is typical for hydrated sulphate minerals and explains the lack of high quality X-ray powder data for most of these sulphate minerals.

Allophane was identified (SEM) in a mixture with hydrobasaluminite, but also as thin millimetric yellow (corn colour and waxy aspect) layers interbedded in zonal texture. The material was carefully handpicked under a 50X binocular lens. A wet chemical analysis was performed only of the homogeneous material, free of impurities, after drying it at 110°C. The results are compared with the data collected from the literature in Belgium (Tab. 3).

5. Discussion

Hydrobasaluminite of the Cointe tunnel in Liège is the first occurrence of the mineral in Belgium. Unfortunately, the original sampling site totally disappeared a few hours after the initial observation due to the concrete projection of the walls and the continuous progress of the tunnel boring. Consequently any further sampling was impossible.

The Cointe mineralisation and its depositional setting show many similarities with other occurrences described in the literature (see Tab. 1), but it is the first time that hydrobasaluminite is described in a close association with a coal seam. According to several authors (Hollingworth & Bannister, 1950; Milton *et al.*, 1955 in Mitchell, 1970; Tien, 1968; Wieser, 1974; Clayton, 1980), the minerals invariably occur in the weathering zone, usually as a consequence of the oxidation of pyrite. They are commonly associated with gypsum, allophane, gibbsite and iron oxides. However, pockets of alteration of the hill of Cointe differ from others because they mainly consist of hydrobasaluminite and allophane with minor amounts of gibbsite and without jarosite, gypsum, halloysite and alunite. The absence of gypsum could be related to the absence of carbonates in the wastes and in the above lying shales.

Hydrobasaluminite (1) + amorphes Cointe			Hydrobasaluminite (2) + amorphes			Hydrobasaluminite Hollingsworth & Bannister -1950		Hydrobasaluminite Clayton - 1980	
I/lo	d(A)		I/lo	d(A)		I/lo	d(A)	I/lo	d(obs)
100	12,27		100	12,80		100	12,60	100	12,59
15	9,98	illite	6*	9,80-10,1	illite ?	50	8,08	3	8,08
11	7,86		9	8,07		70	6,18	1	7,81
16	6,28		18	6,32		70	5,29	2	7,62
10	5,86		18	5,94		70	4,70	10	6,30
14	5,23		9	5,64		60	4,23	3	6,21°
7	4,80	gibbsite	23	5,30		60	4,00	9	5,91
19	4,65		83	4,83	gibbsite	70	3,73	3	5,67°
10	4,34	gibbsite	35	4,69		50	3,43	4	5,62°
19	4,18	goethite	7	4,51		30	3,21	8	5,33
15	3,93		54	4,36	gibbsite	70	3,07	10	5,26
19	3,64		19	4,22		40	2,83	1	5,00
12	3,42		19	3,95		50	2,57	11	4,693
7	3,31	illite	7	3,87		50	2,41	2	4,656°
8	3,20		32	3,69		50	2,25	1	4,601
6	3,07		15	3,47		30	2,22	3	4,511
6	2,80		8	3,39		60	2,10	1	4,420
5	2,70	goethite		3.30-3.39	**	30	2,06	9	4,205
11	2,53		10	3,23		40	1,96	3	4,169°
6	2,42	goethite	14	3,07		60	1,835	3	4,127
11	2,37		9	2,96		50	1,793	1	4,044
8	2,27		10	2,81		40	1,729	11	3,960
6	2,23		6	2,73		10	1,680	4	3,877
			4	2,70		60	1,625	11	3,681 ^b
			3	2,64		5	1,560	1	3,523
			11	2,53		30	1,500	4	3,472
			16	2,45	gibbsite	50	1,445	1	3,437°
			24	2,39	+ gibbsite	10	1,408	2	3,404
			4	2,33		10	1,382	1	3,361
			9	2,27		10	1,349	3	3,218
			13	2,24				1	3,192°
			12	2,18				2	3,152
			6	2,11				3	3,094
			5	2,09				4	3,061
			10	2,07				2	3,033
			11	2,04				1	3,000
			5	2,00	gibbsite			3	2,948°
			5	1,96				1	2,910
			5	1,92				1	2,831°
			7	1,82				2	2,813
			9	1,80				1	2,745°
			6	1,73				1	2,727
			6	1,69	??			1	2,700
			7	1,61				1	2,660
								1	2,635
								1	2,558
								3	2,539 ^b
								1	2,483
								1	2,452
								1	2,430
								1	2,416
								4	2,383
								1	2,364
								1	2,335 ^b
								1	2,300
								1	2,274
								1	2,257°
								2	2,240°
								1	2,226°
								2	2,211°
								1	2,197°
								2	2,186
								1	2,158
								1	2,116
								2	2,088
								3	2,064
								1	2,040
								1	2,020°
								1	2,002
								1	1,955
								1	1,878

(1) : slightly yellowish sample
(2) : white opaline sample

* broad
** band

° = overlapped
^b = broad

Table 2: X-ray powder data of hydrobasaluminite and basaluminite from Cointe. Comparison with data from Hollingsworth and Bannister (1950)

The field evidence thus suggests that the formation of hydrobasaluminite is controlled by weathering. Hydrobasaluminite and allophane accumulation results from a combination of circumstances which could have produced unusual favourable conditions such as clayey source rocks, pyrite in adjacent coals, mining rock-wastes and black shales, circulation of water through fractures (of tectonic or anthropic origin) in a local drainage system and voids created by an incomplete infill of the mine galleries or by the compaction of the wastes. Field relations suggest that weathering, texture and nature of wastes and mineralogy of country rocks control the formation of hydrobasaluminite and associated minerals. Hydrobasaluminite is derived from an intense hydrolysis of silicates in acid medium. Acidity of water can be found in oxidation of pyrite, abundant in the roof of the coal veins. During circulation, clay minerals, feldspars and carbonates are decomposed by hydrolysis. Hydrobasaluminite and associated minerals were deposited from these solutions. Acidic solutions migrated along bedding planes, fractures and through coal seams and probably accumulated due to the space created by the sealing of the rock-wastes. As observable on the field photo, many rock fragments (carbonaceous shale) are embedded in a matrix of Al-sulphates and allophane stained by iron hydroxides, suggesting the in-situ hydrolysis of rock wastes. The clay fraction, prepared from the rock fragments and investigated by XRD, shows the disappearance or marked degradation of iron chlorite, the decreasing of crystallinity of kaolinite and illite minerals. Internal structures, like mineral zonation, banded allophane, cracks, veins, patches, lenses and deformation planes suggest a complex genesis with time, variable hydrochemical conditions and internal compaction effects.

	Cointe (this work)*	Angleur (**)	Namur (**)	Blaton (**)
Al ₂ O ₃	34.06	31.12	39.6	34.0
SiO ₂	16.65	33.96	24.2	17.9
Fe ₂ O ₃	0.25			Traces
CaO	0.94	2.26		
MgO	0.13		2.2	
K ₂ O	0.01			
Na ₂ O	0.12			
H ₂ O+	21.83	12.84		
H ₂ O-	26.03	20.28		
P ₂ O ₅	n.d.			6.8
H ₂ O total			33.4	40.9
Total	100.02	100.46	99.4	99.6

Table 3: Chemical analyses of allophane granules.

(*)Analyst: J.-M. Speetjens; n.d. = not determined. (**) Melon. J. *et al.* (1976).

6. Acknowledgements

Wet chemical analyses were performed by J.M. Speetjens (Laboratory of Mineralogy, University of Liège). The author is grateful to I. Cocinas Garcia, geologist who has been in charge of the follow-up for the boring of the tunnels. He also wishes to express his thanks to Prof. A.-M. Fransolet (University of Liège) and Prof. F. Fontan (University Paul-Sabatier, Toulouse), for critically reading the manuscript and for their helpful comments. Dr. C. Baeteman kindly revised the English.

7. References

- ARNOULD, R., 1990. Géologie, stabilité et exécution de deux tunnels autoroutiers en site urbain (Liège, colline de Cointe). *Revue française de Géotechnique*, 52: 67-84.
- BANNISTER, F.A. & HOLLINGWORTH, S.E., 1948. Two new British minerals. *Nature. London*, 162: 565.
- CLAYTON, F., 1980. Hydrobasaluminite and basaluminite from Chickerell, Dorset. *Mineralogical Magazine*, 43: 931-937.
- HOLLINGWORTH, S.E. & BANNISTER, F.A., 1950 : Basaluminite and hydrobasaluminite. two new minerals from Northamptonshire. *Mineralogical Magazine*, 29: 1-17.
- MELON, J., BOURGUIGNON, P. & FRANSOLET, A.M., 1976 : Les minéraux de Belgique. *Editions G. Lelotte, Dison, Belgique*: 282 pp.
- MILTON, C., CONANT, L.C. & SWANSON, V., E., 1955. Sub-Chattanooga residuum in Tennessee and Kentucky. *Bulletin of the Geological Society of America*, 66: 805-810.
- MITCHELL, R.S., 1970. An occurrence of basaluminite in Maryland. *Mineralogical record*, 1, 127-128.
- POLYAK, V.J. & PROVENCIO, P., 1998. Hydrobasaluminite and aluminite in caves of the Guadalupe Mountains, New Mexico. *Journal of Cave and Karst Studies*, 60 (1): 51-57.
- SUNDERMANN, J. A. & BECK, C. W., 1969. Hydrobasaluminite from Shoals, Indiana. *American Mineralogist*, 54: 1363-1373.
- TIEN, P.-L., 1968. Hydrobasaluminite and basaluminite in Cabaniss Formation (Middle Pennsylvanian), Southeastern Kansas. *American Mineralogist*, 53: 722-732.
- WIESER, T., 1974. Basaluminite in the weathering zone of Carpathian flysch deposits. *Mineralogia Polonica*, 5: 55-66.

Manuscript received 14.03.2003, accepted for publication 20.06.2003.

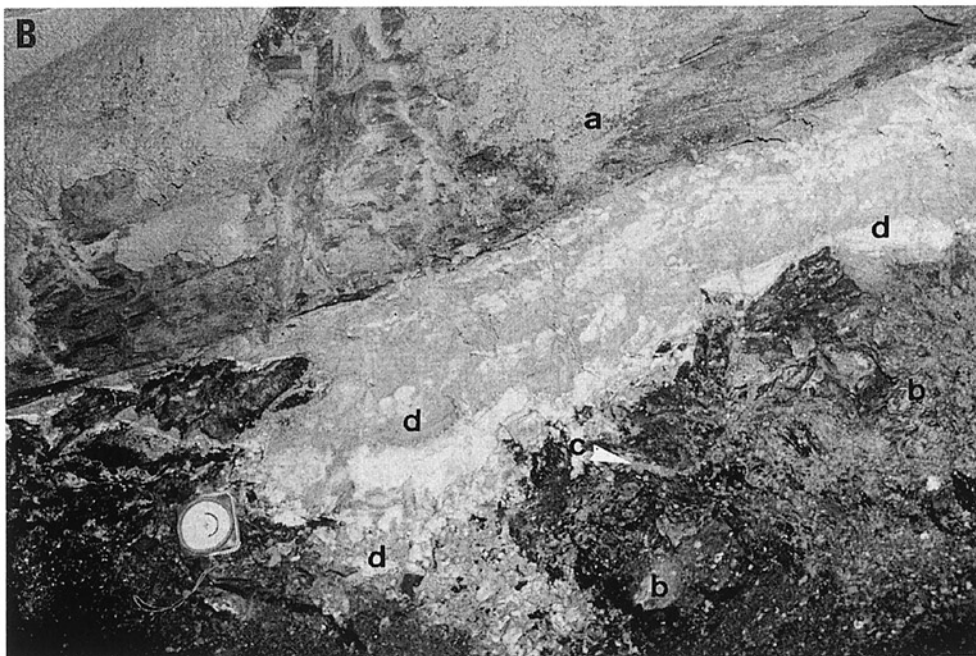
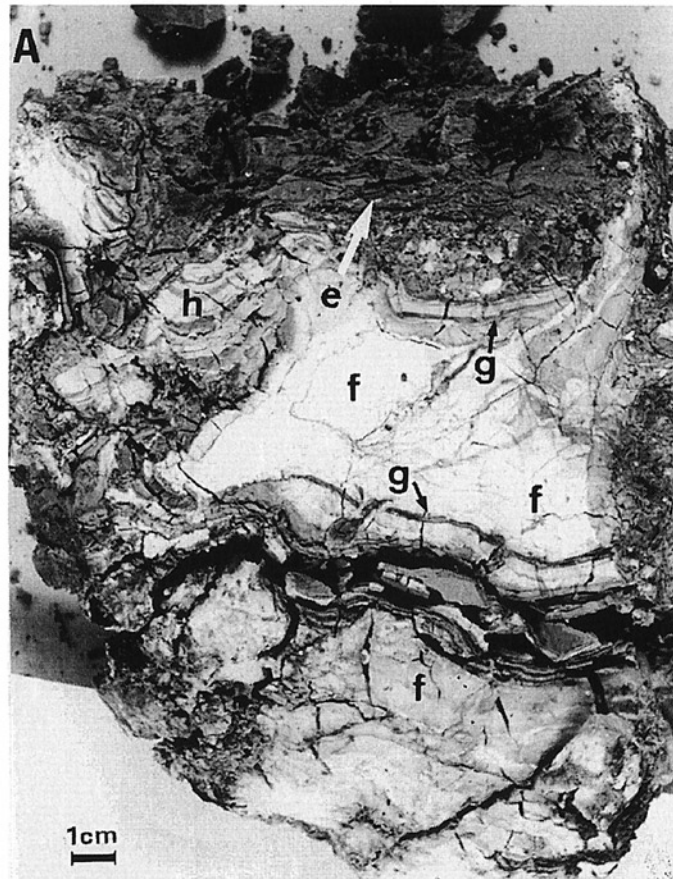


Plate 1

Photo A: complex layered and zonal structure of a pocket sample. Photo taken 36 hours after sampling. Fracturation related to the partial dehydration of the hydrobasaluminite to basaluminite affects coherence of the material. e) allophane, goethite and iron hydroxydes. f) partial dehydration of hydrobasaluminite. g) pure allophane layer (corn color). h) microlayering.

Photo B: partial view of the mineralised pocket. a) black shales at the top of the mined Bomebac coal seam. b) waste deposits with black shales and impure coal. c) iron hydroxydes stained material and d) hydrobasaluminite (white patches) and mixture of hydrobasaluminite and allophane (yellow patches). The compass gives the scale.