KAOLIN TONSTEIN OF VOLCANIC ASH ORIGIN IN THE LOWER ORDOVICIAN OF THE CANTABRIAN MOUNTAINS (NW SPAIN)

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TRABAJOS DE GEOLOGIA

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A kaolin bed about 65 cm thick was deposited over at least 1.800 km² of the Central Asturias region (NW Spain) in the Lower Ordovician, interbedded within the Armorican Quartzite-Barrios Formation. Two closely related varieties, type G «coarse grained» and F «fine grained» kaolin, have been differenciated, displaying both petrographic and sedimentologic distinctive properties. Based on field, petrographic and mineralogic characters, it is interpreted as a «kaolinite tonstein» originated by «in situ» diagenetic alteration of a volcanic ash-fall tuff.

Una capa de caolín de unos 65 cm de espesor medio se depositó durante el Ordovícico Inferior, intercalada en la Cuarcita Armoricana-Formación Barrios, sobre gran parte de la región centro-asturiana (NW España), cubriendo al menos una extensión de 1.800 km². Se han diferenciado dos variedades íntimamente relacionadas entre sí, caolín tipo G «grano grueso» y F «grano fino», con caracteres petrográficos y sedimentológicos específicos. A partir de características de campo, petrográficas y mineralógicas, se interpreta como un «tonstein de caolinita» formado por alteración diagenética «in situ» de una toba de cenizas volcánicas de transporte eólico.

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A laterally persistent kaolin bed 55-75 cm thick occurs in the middle part of the «Armorican Quartzite» (Barrios Formation, Lower Ordovician) of Central Asturias (Cantabrian Mountains, NW Spain: Figs. 1 to 4, «Sierra del Pedroso Bed». It lies in interbedded shales and quartzites intensively bioturbated by large number of vertical *Skolithos* burrows. Upper and lower contacts are always sharp. It is extended at least 1.800 km² and can be traced along 80 km. The palinspastic restauration probably results in a more widespread distribution. Both composition and geometry agree with the classical concept of «tonstein» s.l.

The bed has been intensively exploited from 1946 as a raw for the refractary industry, and a number of working and abandoned mines are seen all around the region.

KAOLIN TYPES

Two varieties of kaolin are recognized:

TYPE G «COARSE GRAINED KAOLIN»

Medium gray, compact, breaking with a hackly fracture (Fig. 5 a). In thin sections it is seen to be composed of medium to fine sand kaolinite and quartz grains in a well ordered (Fig. 6 e, f) fine grained kaolinite matrix. Kaolinite grains are rounded, pseudomorphic euhedrals, fibrouses or vermiculars. Quartzs are typically very angular and elongated according to the stratification (Fig. 6 a). Rare anatase is present. This type generally occurs in thin levels less than 6 cm, locally up to 24 cm thick. Most of them are placed in the lower half of the kaolin bed, ranging from 19 to 45 percent of total. Graded bedding and parallel to low angle lamination are common (Fig. 5 c, d, e).

TYPE F «FINE GRAINED KAOLIN»

Light gray, compact, breaking with conchoidal fracture (Fig. 5 b), it is mainly composed of

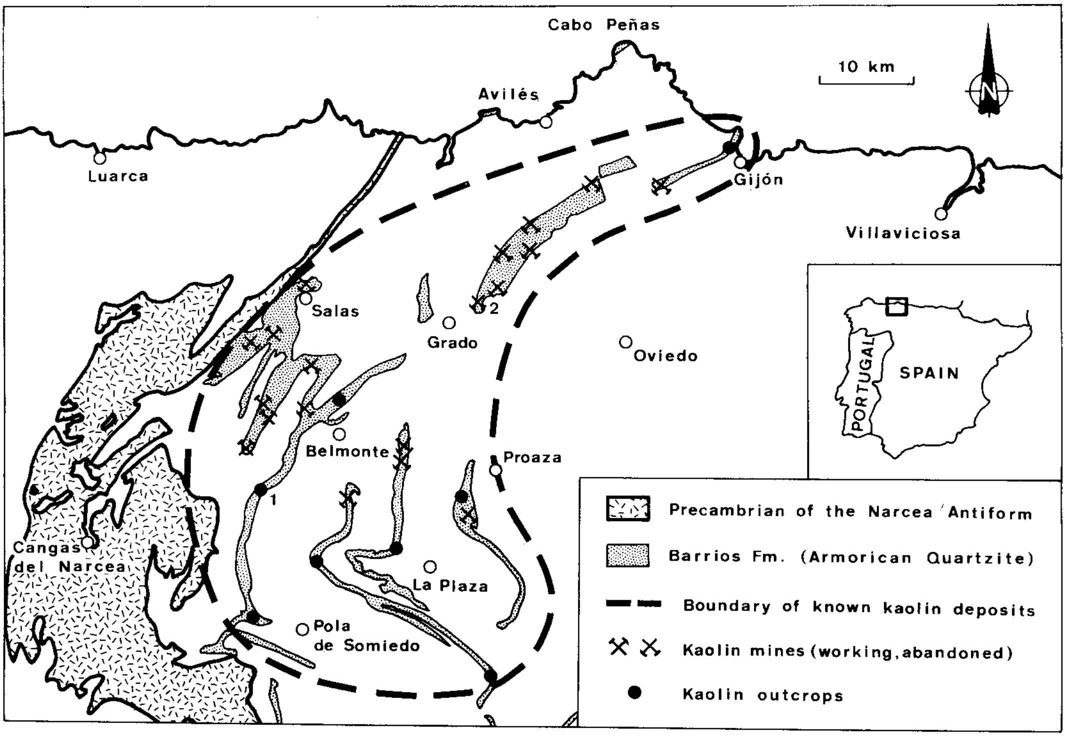

Fig. 1.–Location map of the kaolin deposits in the Lower Ordovician of Central Asturias. 1: Abedul; 2: Peñaflor.

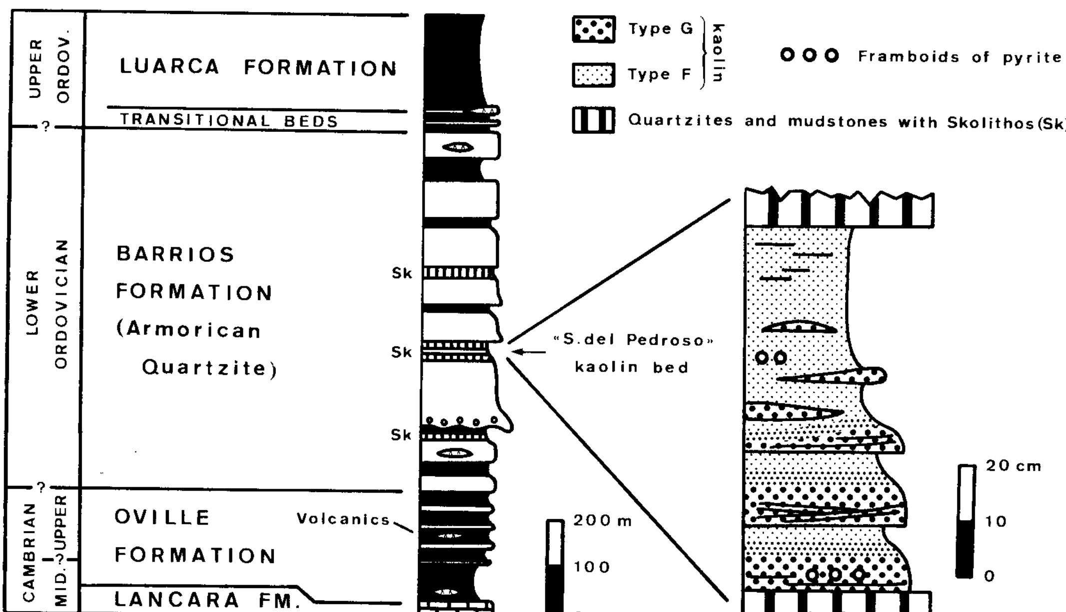

Fig. 2.–Generalized stratigraphic section of the Cambro-Ordovician rocks in Central Asturias, and detail of the kaolin bed.

Fig. 3.–Representative section of the Barrios Formation in the Abedul locality.

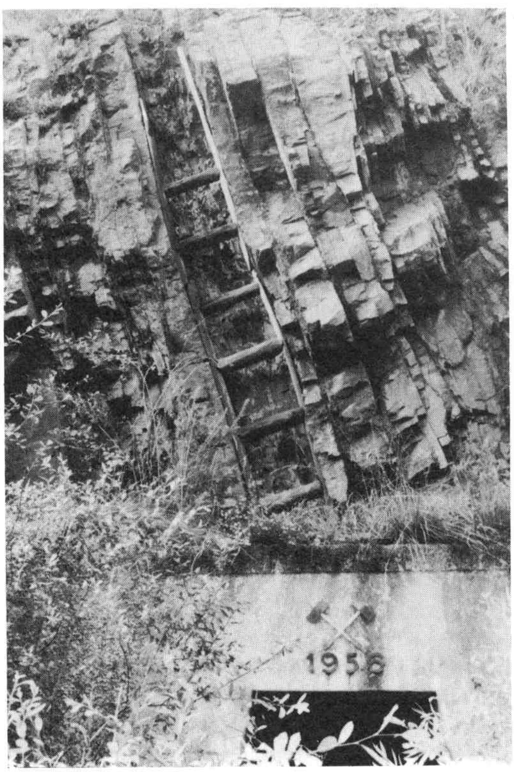

Fig. 4.–The kaolin bed at a mining entrance in the Peñaflor locality. Bed is 65 cm thick.

kaolinite (Fig. 6 b, d) and quartz grains (both similar in shape to those of type G, althought less and smaller quartz grains are present here), silt and sand sized, in a well ordered fine-grained kaolinite matrix («flint clay»). Frequent plane lamination is present, composed of pyrite or heavy minerals alignements (Fig. 5 f); pyrite is also commonly present as framboids, in type G and F. Fine grained kaolin make up 55 to 81 percent of total, and it is mostly located in the upper half of the bed.

Small quantities of mixed-layer illite-montmorillonite and some traces of zeolites have bean found in both types.

In an ideal section of the kaolin bed (Fig. 2) the close relation between types G and F is shown. The whole bed displays a positive sequence of decreasing grain size, all over the studied region.

OTHER ORDOVICIAN KAOLINS IN SPAIN

Some other similar levels are known in the Ordovician of the Cantabrian Mountains. A kaolin bed outcrops discontinuously, interbedded in the Armorican Quartzite, in the North of the Province of León (Barrios de Luna, Getino, etc.). Its changing characteristics have not been

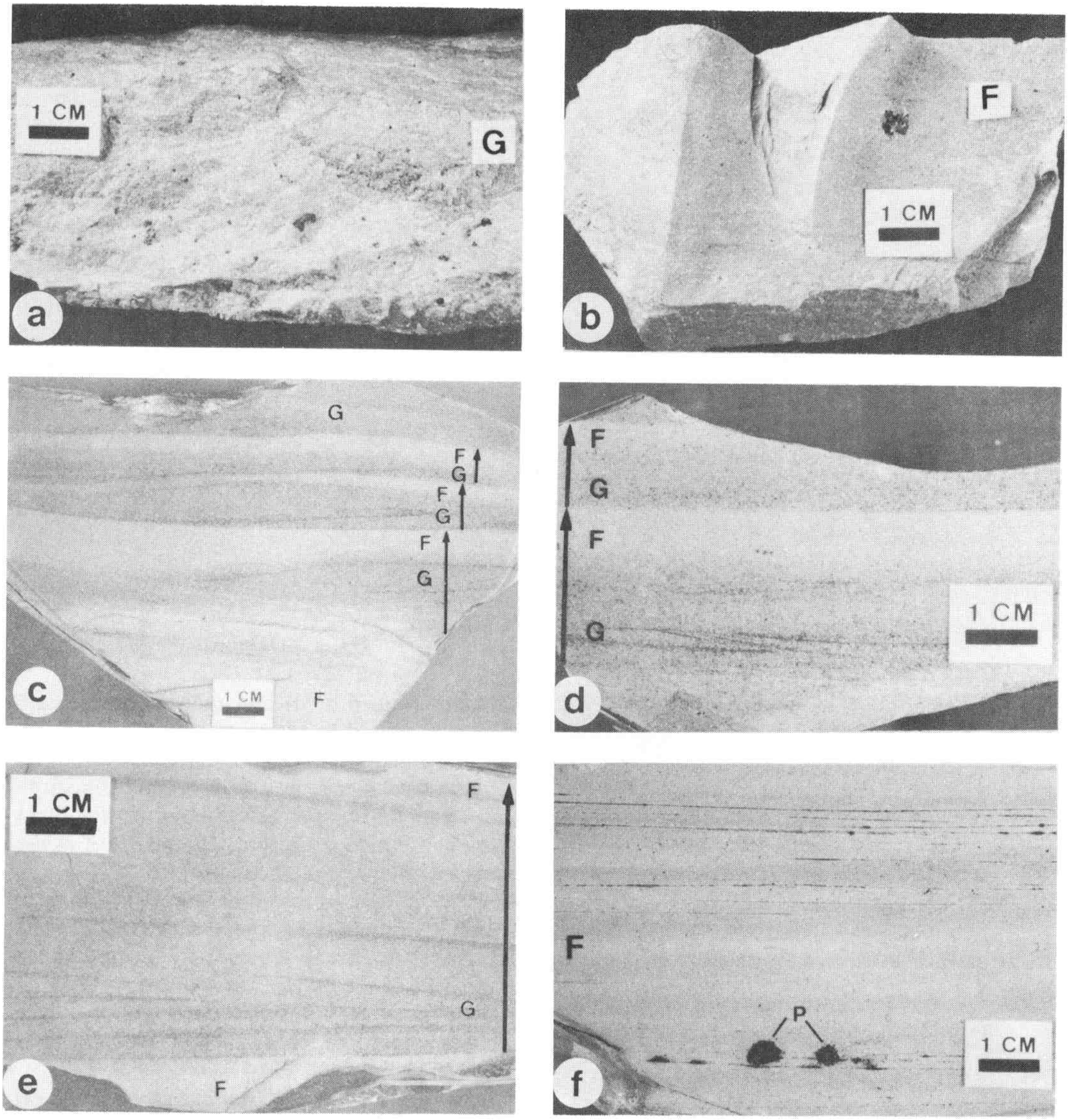

Fig. 5.–Macroscopic features: a) Freshly broken specimen of type G kaolin. Note the characteristic hackly fracture. b) Freshly broken specimen of type F kaolin. Note the conchoidal fracture, characteristic of a «flint clay». c), d), e) Polished sections showing the typical alternation of type G and F kaolins, ordered in normal graded microsequences. Plane lamination to low angle cross lamination commonly occur in type G. f) Polished section of type F kaolin with plane lamination and framboidal pyrite (P).

well studied yet. It consits in compact, light to medium gray, fine to coarse grained kaolin, in one bed 30 to 50 cm thick, with sharp upper and lower contacts. A 30 cm level, similar in aspect and structure to the «Sierra del Pedroso Bed» is interbedded in the Middle Ordovician Black Shales at Cabo Peñas. Its composition is changed, in this case, to illite-clorite due to the low-range regional metamorphism, probably representing a metabentonite.

West of the Narcea Antiform (Fig. 1) some dispersed kaolin outcrops occur in the Cam-

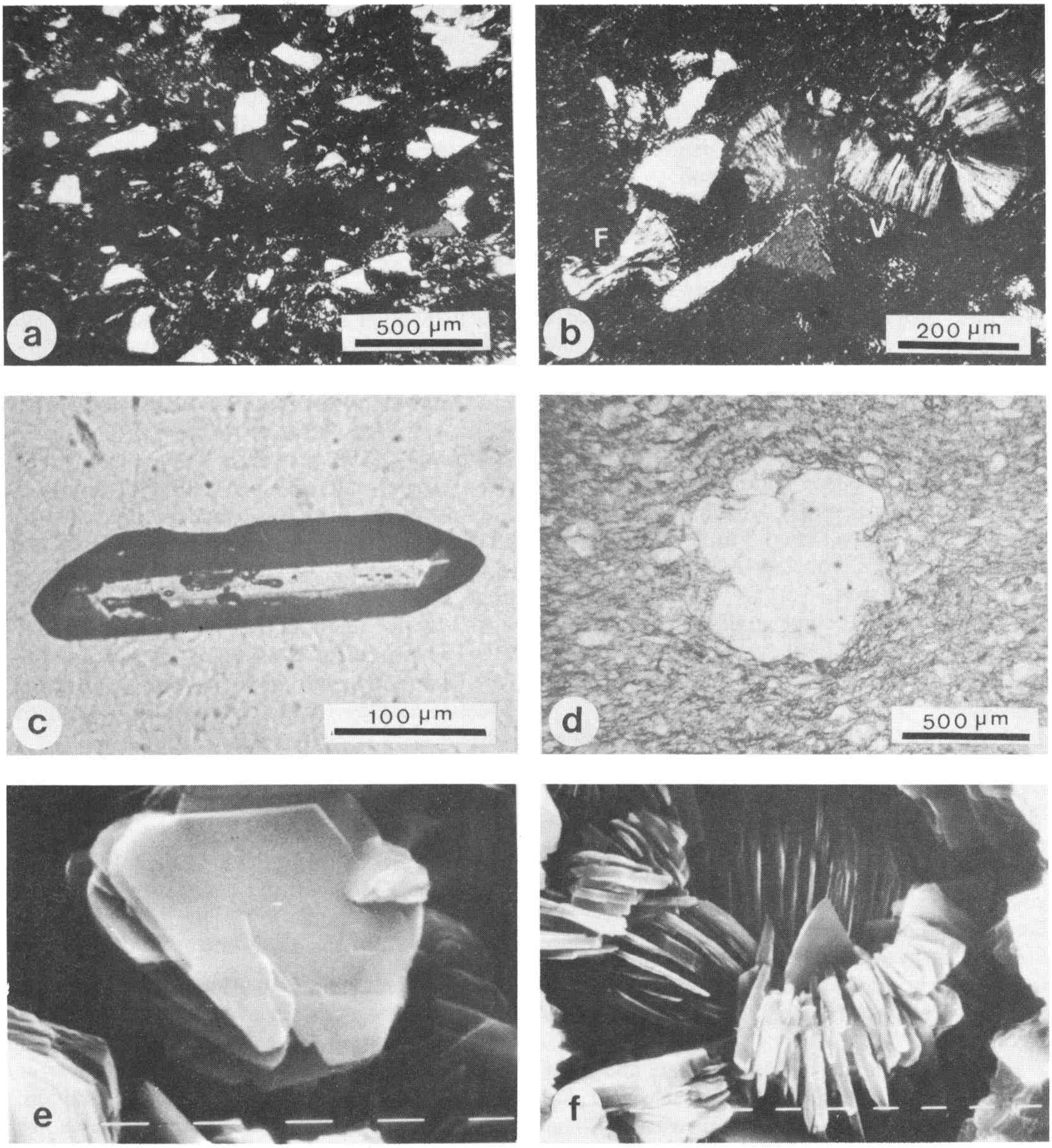

Fig. 6.–Microscopic characters: a) Very angular quartz grains («splinters») in a fine grained kaolinite groundmass. Type G kaolin. Crossed nicols. b) Two characteristic kaolinite aggregates: vermicule (V) and «double fan-like» (F). Type G kaolin. Crossed nicols. c) Elongated idiomorphic zircon. Plane polarized light. d) Kaolonite ovoid or «rouleau» in a fine-grained kaolinite groundmass («graupen tonstein»). The ovoid is internally formed of several kaolonite vermicules in a fine-grained kaolinite matrix. Type F kaolin. Plane polarized light. e) SEM photomicrograph of an idiomorphic kaolinite crystal. Every scale bar is 1 micron. f) SEM photomicrograph of a vermicular aggregate or «book» of kaolinite. Every scale bar is 1 micron.

bro-Ordovician Cabos Group: Grandas de Salime, Navelgas, Soto de Luiña, etc. A kaolin bed 1,5 m thick is reported in the Lower Ordovician of Badajoz, South Spain (Galán 1973-1975).

ORIGIN AND SIGNIFICANCE

Previous workers (Gómez de Llarena 1955; Galán 1973-1975; Galán and Espinosa 1974) consider that the «Sierra del Pedroso Bed» was primarily originated in the source area through kaolinitization of igneous rocks or recycling of older kaolin and then transported and deposited at its present place.

However, our statements support an alternative interpretation by «in situ» diagenetic kaolinitization of a volcanic ash-fall tuff:

1) Tabular geometry of the bed, similar to «tonsteins»: widespread distribution with slightly variable thickness. The contacts with the overlying and underlying rocks are sharp. Other mudstone levels interbedded in the Armorican Quartzite have frequent lateral changes and grade sometimes into quartzites.

2) Homogeneous clay mineral composition (kaolinite). Illite is prevailing in other mudstone levels (Galán 1973-1975; Brime 1981).

3) The whole bed constitute a fining-upward sequence, with frequent small second order graded beddings in it (Fig. 5 c, d, e). It can be seen as a single vulcano-sedimentary event, with minor impulses.

4) Bioturbation is generally absent in the kaolin. However it is intensive in the adjacent beds, with very frequent *Skolithos* and some *Cruziana*.

5) Characteristical mineral components: very angular quartz grains («splinters»), unstrained, with rare vacuoles; some of them are idiomorphic or show embayments. Other components include frequent vermicules of autigenic kaolinite (Fig. 6 b), elongated idiomorphic zircons (Fig. 6 c), mixed-layer illite-montmorillonite clays and traces of zeolites.

6) Other volcanic rocks are commonly interbedded in the Cambro-Ordovician of this area (trachytes, tuffs, etc.), ranging from 0,5 to 200 m thick.

Kaolinitization was nearly complete and most of the characteristical components in volcanic ashes have been destroyed. However, some kaolinitized grains seem to be pseudomorphic feldspars.

Similar kaolin levels, interpreted in an analogous way, are reported from the Carboniferous of Great Britain (Eden *et alt.* 1963; Barnsley *et alt.* 1966; Price and Duff 1969; Spears 1970; Spears and Rice 1973) and other areas of Europe (Francis 1983), the Appalachian Basin of North America (Seiders 1965; Bohor and Triplehorn 1981; Chesnut 1983), Australia (Diessel 1983), USSR (Zaritsky 1983) and Indonesia (Harrison *et alt.* 1983), the Upper Cretaceous and Tertiary of the Rocky Mountains (Bohor *et alt.* 1976; Ryer *et alt.* 1980), etc. Generally volcanic ashes are said to have been deposited in a continental or transitional (coal-bearing delta plain) environment; the fresh-water occurrence (Price and Duff 1969) and/or humus abundance (Williamson 1970) provide a low pH which facilitate an early alteration to kaolinite. Preservation of these thin beds was favoured by the characteristic slow sedimentation of this facies, as compared with the greater probability of contamination and erosion within higher energy deposits of the adjoining levels. A similar transitional environment is assumed for the Armorican Quartzite levels including the «Sierra del Pedroso kaolin» (Aramburu and García-Ramos 1984).

Volcanic ash fall tonsteins will provide in the future the most valuable time-stratigraphic marker in the Armorican Quartzite of the Cantabrian Mountains, where no guide fossils have been found. More distant correlations are even possible with the Serie de los Cabos (Cabos Group), west of the area showed in this paper.

Kaolinite tonstein here studied constitute one of the thickest beds reported in the past. Comparable thickness have been noted by other authors: 30 cm (Kimpe 1966), 40 cm (Ryer *et alt.* 1980), 43 cm (Chesnut 1983). In addition, this bed is remarkable because, as far as we know, no other precarboniferous kaolinite tonstein has been previously described.

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REFERENCES

Aramburu, C. and García-Ramos, J. C. (1984).–Cambro-Ordovician alluvial and marine sedimentation in the Cantabrian Zone, North Spain. *5th European Regional Meeting of Sedimentol.*, I.A.S., Abs., 30-31, Marseille 1984.

Barnsley, G. B., Clowes, J. M. and Fowler, W. (1966).–Kaolin tonsteins in the Westfalian of North Staffordshire. *Geol. Mag.*, 103, 508-521.

Bohor, B. F. and Triplehorn, D. M. (1981).–Volcanic origin of the flint clay parting in the Hazard n.º 4 (Fire Clay) coal bed of the Breathitt Formation in eastern Kentucky. In: J. C. Cobb, Chesnut, D. R. Hester, N. C. and Hower, J. C. (Eds.), *Coal and coal-bearing rocks of eastern Kentucky.* Annual Geol. Soc. Am. Coal Division Field Trip, 1981. *Kentucky Geol. Survey*, 11, 49-54.

——, Hatch, J. R. and Hill, D. J. (1976).–Altered volcanic ash partings as stratigraphic marker beds in coals of Rocky Mountain Region (abs.). *AAPG Bull.*, 60, 651.

Brime, C. (1981).–Postdepositional transformation of clays in Palaezoic rocks of Northwest Spain. *Clay Miner.*, 16, 421-424.

Chesnut, D. R. (1983).–Source of the volcanic ash deposit (flint clay) in a coal of the Appalachian Basin. *X Int. Congr. of Carboniferous Stratigr.* & Geol., Abs., 34, Madrid 1983.

Diessel, C. F. K. (1983).–Tuffs, tonsteins and palaeosols in the Coal Measures of New South Wales, Australia. *X Int. Congr. of Carboniferous Stratigr.* & *Geol.*, Abs., 333, Madrid 1983.

Eden, R. A., Elliot, R. W., Elliot, R. E. and Young, B. R. (1963).–Tonstein bands in the coalfields of the East Midlands. *Geol. Mag.*, 100, 47-58.

Francis, E. H. (1983).–Use of tonsteins for palaeovolcanic reconstructions. *X Int. Congr. of Carboniferous Stratigr.* & *Geol.*, Abs., 332, Madrid 1983.

Galán, E. (1973-1975).–*Caolines españoles: geología, mineralogía y génesis.* Soc. Esp. Cerámica y Vidrio, Madrid, 152 pp.

—— and Espinosa, J. (1974).–*El caolín en España.* Soc. Esp. Cerámica y Vidrio, Madrid, 230 pp.

Gómez de Llarena, J. (1955).–Un yacimiento de caolín sedimentario en la Cuarcita Armoricana de la Sierra del Pedroso (La Reigada, Avilés, Asturias). *Not. y Com. Inst. Geol. Min. Esp.*, 37, 73-93.

Harrison, R. K., Addison, R., Land, D. H. and Young, B. R. (1983).–A comparison of tonsteins from the Tertiary Coal Measures of Kalimantan, Indonesia, with Carboniferous tonsteins of the United Kingdom. *X Int. Congr. of Carboniferous Stratigr.* & Geol., Abs., 337, Madrid 1983.

Kimpe, W. F. M. (1966).–Occurrence, development and distribution of Upper Carboniferous tonsteins in the paralic West German and Dutch coalfields, and their use as stratigraphical marker horizons. *Meded. Geol. Sticht.* (N. S.), 18, 3-10.

Price, N. B. and Duff, P. Mc L. (1969).–Mineralogy and chemistry of tonsteins from Carboniferous sequences in Great Britain. *Sedimentology,* 13, 45-69.

Ryer, T. A., Phillips, R. E., Bohor, B. F. and Pollastro, R. M. (1980).–Use of altered volcanic ash falls in stratigraphic studies of coal-bearing sequences: An example from the Mancos Shale in central Utah. *Geol. Soc. Am. Bull.*, 91, 579-586.

Seiders, V. M. (1965).–Volcanic origin of flint clay in the Fire Clay Coal Bed, Breathitt Formation, eastern Kentucky. *U. S. Geol. Survey Prof. Paper,* 525D, D52-D54.

Spears, D. A. (1970).–A kaolinite mudstone (tonstein) in the British Coal Measures. *Jour. Sed. Petrol.*, 40, 386-394.

—— and Rice, C. M. (1973).–An Upper Carbonifeorus tonstein of volcanic origin. *Sedimentology,* 20, 281-294.

Williamson, I. A. (1970).–Tonsteins– Their nature, origins and uses (second part). *Mining Mag.*, 122, 203-211.

Zaritsky, P. V. (1983).–A review of the study of tonsteins in the Donetz Basin. *X Int. Congr. of Carboniferous Stratigr.* & *Geol.*, Abs., 336, Madrid 1983.