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Clay minerals as palaeoenvironmental indicators in the Bathonian (Middle Jurassic) ore-bearing clays from Gnaszyn, Kraków-Silesia Homocline

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ABSTRACT:

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This paper reports the results of X-ray diffraction quantitative mineralogical studies of the clay-rich Middle Jurassic sedimentary rocks from Gnaszyn, central Poland and their palaeoenvironmental interpretation. The palaeoenvironmental interpretation is aided by the fact that the sediments have not been significantly altered by diagenesis. The mineral composition is uniform throughout the succession: quartz, K-feldspar, plagioclase, calcite, gypsum, anhydrite, pyrite, illite, kaolinite, chlorite, and glauconite. The clay assemblage is dominated by illite, which alone accounts for about 20 wt% of the total mineral content. Kaolinite amounts usually <10 wt% and chlorite and glauconite occur in subordinate quantities. The clay mineral assemblage is largely of detrital origin and indicates rather cool and/or dry climatic conditions favouring mechanical erosion of the source rocks.

Key words: Clays; Chlorite; Glauconite; Illite; Kaolinite; Mineral assemblage; X-ray diffraction quantitative analysis.

INTRODUCTION

Clay minerals in marine sediments are largely of detrital origin, reflecting the lithology of the source rocks, the climate in the surrounding areas and the direction of the prevailing marine currents (Chamley 1989; Weaver 1989). Thus, they can yield valuable palaeoenvironmental information provided their original assemblage and composition have not been significantly altered by diagenesis. In addition, there are several factors that may bias the clay mineral signature, e.g., the effect of erosion and transport, the time lag between the formation of the clay minerals on land and their arrival in the sedimentary basin (for review see Thiry 2000). Nevertheless, the analysis of clay mineral assemblages has proved to be a successful tool for palaeoenvironmental reconstruction in many differ-

ent sedimentary basins (e.g., Hein *et al*. 2003; Heroy *et al*. 2003; Ingles and Ramos-Guerrero 1995; Net *et al*. 2002; Tanner 1994). The following short review considers only those clays that were identified in the sediments from Gnaszyn.

Illite, illite-rich illite-smectite mixed-layer clay and chlorite are regarded as primary minerals in marine sediments in the sense that they are derived directly from the source rocks in the areas where a temperate, cold and dry climate supports extensive mechanical weathering (Chamley 1989; Weaver 1989; Net *et al*. 2002). Kaolinite, on the other hand, can be either primary or secondary, i.e., a product of chemical weathering of the source rocks. The illite (+chlorite)/kaolinite ratio can be used to reconstruct the history of chemical weathering versus physical erosion (e.g., Net *et al*. 2002; Heroy *et al*. 2003). However, the

climatic constraints of kaolinite (i.e., tropical weathering) are no longer valid without isotopic data due to the reported widespread cold kaolinitic weathering (Środoń 1999; Thiry 2000). Smectite and smectitic illite-smectite are derived into the sedimentary basins from soils developed on various kinds of rocks under a range of climatic conditions. However, smectite is more abundant in warm climatic zones (Weaver 1989). Smectite is also a product of postsedimentary transformation of volcanogenic material (Chamley 1989; Weaver 1989). Glauconite crystallizes at the sediment-water interface at depths from 60 to 1000 m under a wide range of climates (Weaver 1989; Środoń 1999).

MATERIAL

The mineralogical studies presented herein were performed on a set of clay-rich samples collected from the exposures of the Częstochowa Ore-bearing Clay Formation in the Gnaszyn clay pit (Text-fig. 1) as part of a multidisciplinary investigation of the palaeoecology and depositional environment of this formation (see Gedl *et al*. 2003; Gedl and Kaim 2012). The strata are dated as Middle and Late Bathonian (Matyja and Wierzbowski 2006; Gedl and Kaim 2012). A total of 38 samples were analyzed from three sections (Text-fig. 2). Detailed descriptions of the sections are given in Gedl and Kaim (2012).
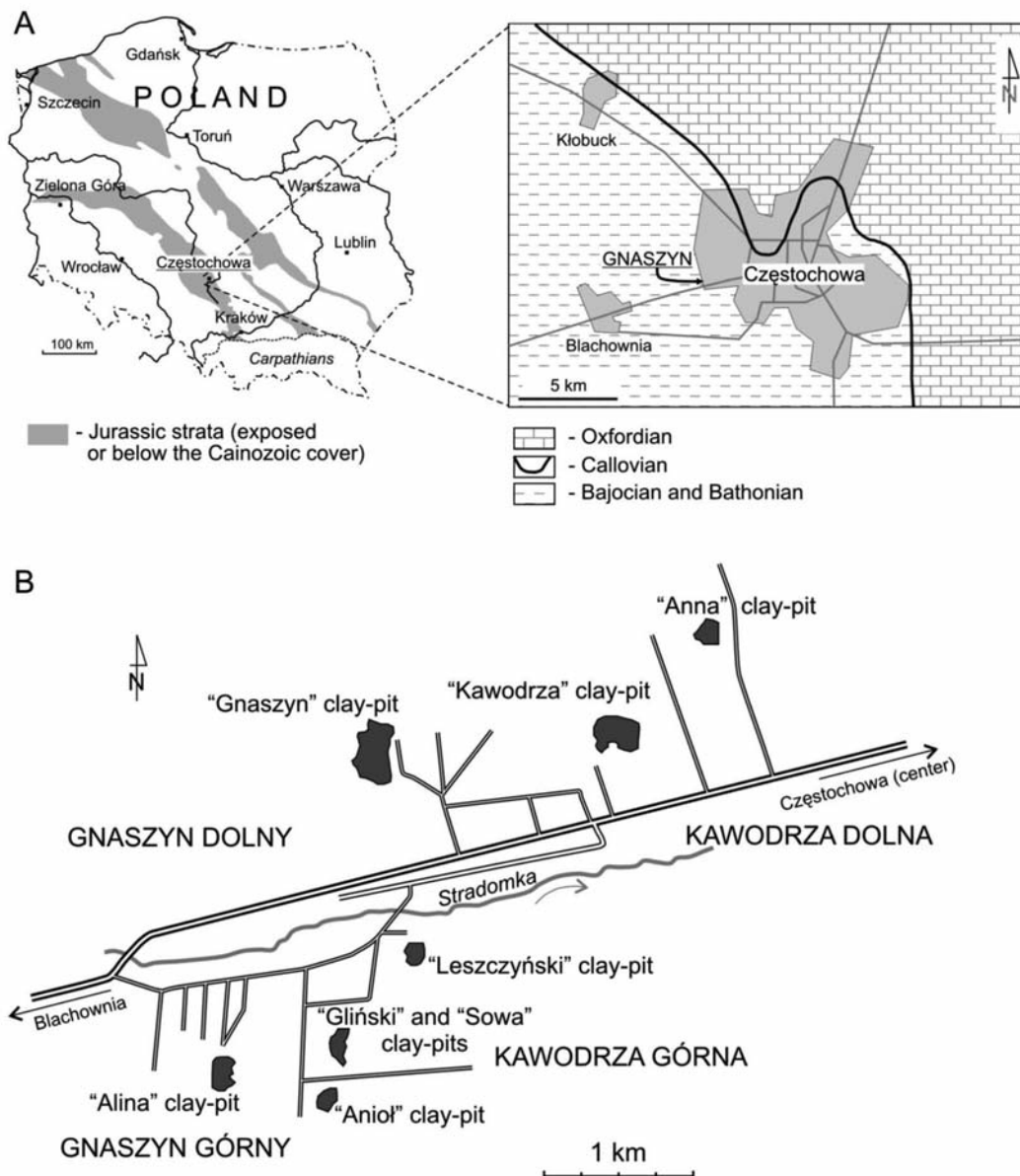

Text-fig. 1. Simplified geological map of the Częstochowa region (A – after Majewski 2000) and location of the Gnaszyn clay-pit (B – after Matyja and Wierzbowski 2003)

METHODS

The bulk rock mineral composition was quantified using the X-ray diffraction method (XRD) of Środoń *et al.* (2001). Sample preparation involved careful crushing, splitting, homogenization with zinc oxide (ZnO) used as an internal standard, and grinding in a McCrone micronizing mill. Random XRD preparations were made by side loading to ensure the absence of any preferred orientation of the clay particles. The analyses were recorded on a Philips diffractometer equipped with a Cu tube and a graphite monochromator. The preparations were scanned from 2 to 65 °2Θ with 0.02 °2Θ step and counting time 5s/step at 40 mA and 50 kV. The divergence and receiving slits were 1° and 0.6 mm, respectively. The mineral content was cal-

culated using equation 6 from Środoń *et al.* (2001) and the mineral intensity factors (MIF) given therein. The areas of the diagnostic reflections for each identified mineral were calculated by the peak fitting method using the Grams/AI(7.01) computer program. An example of an X-ray diffraction pattern of a representative sample from Gnaszyn (Gns18) is shown in Text-fig. 3. The following groups of clay minerals can be distinguished using the method described: kaolinite, dioctahedral 2:1 Al-rich clays (i.e., illite, illite/smectite, smectite, mica) – marked in Text-fig. 3 as "illite", dioctahedral 2:1 Fe-rich clays (glauconite), chlorites. An error in the measurements, marked by the departure of the sum of minerals from 100%, is due to a combination of various effects: presence of amorphous substances, slight misfit of the diagnostic peaks. Also, the
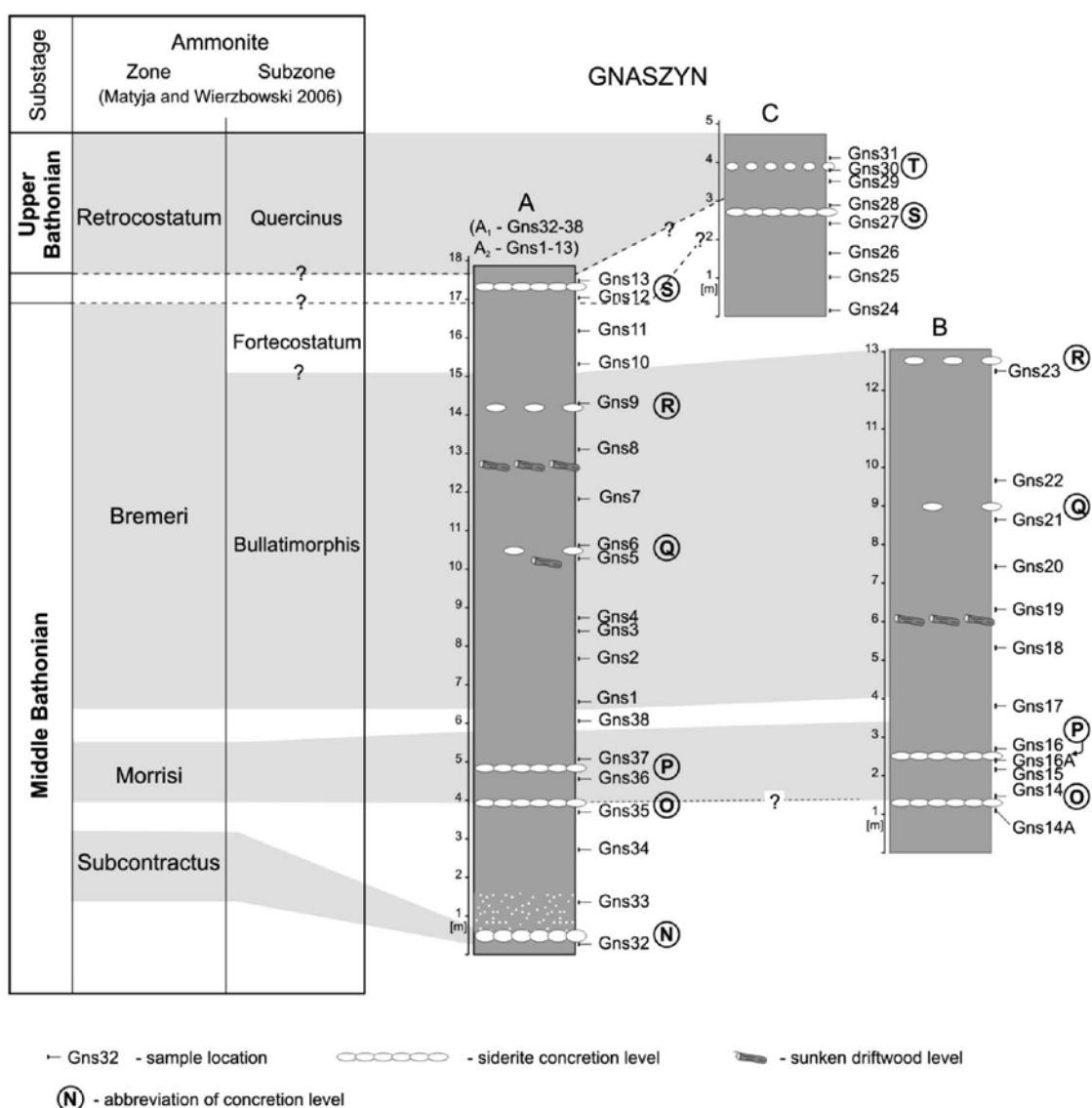
Text-fig. 2. Lithological logs of the Gnaszyn sections with sample positions indicated (from Gedl and Kaim 2012)
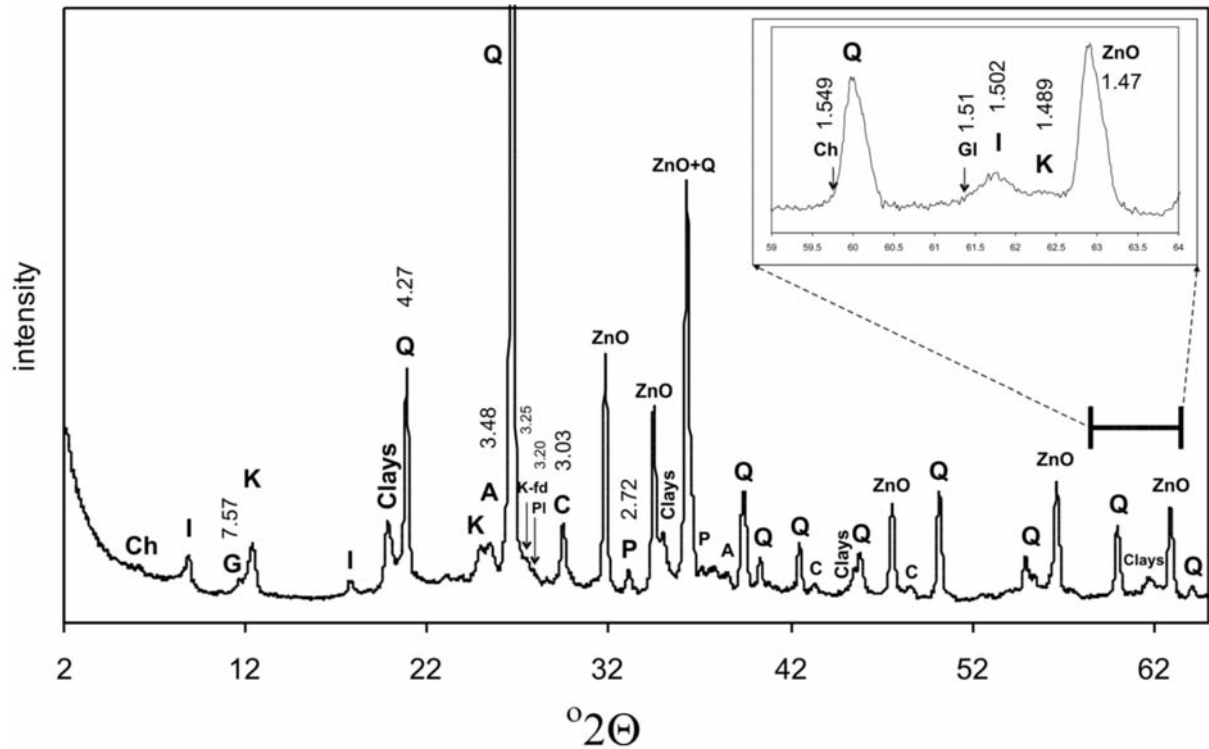
Text-fig. 3. Whole-rock XRD pattern of sample Gns18, which is representative of the sediments studied. C – calcite, G – gypsum, A – anhydrite, P – pyrite, Q – quartz, K-fd – potassium feldspar, Pl – plagioclase, K – kaolinite, I – illite, Gl – glauconite, Ch – chlorite, ZnO – zinc oxide (used as an internal standard). Peaks diagnostic for each mineral are marked with a value of d-spacing expressed in Å. Enlarged in the inset is a high-angle region (59–64 °2Θ) with peaks diagnostic for clay minerals. Chlorite and glauconite peaks cannot be seen well, but they are recognized after fitting the patterns

fact that the mineral standards were run on a different diffractometer from that used for the samples analyzed here could have contributed to the error.

RESULTS

The mineralogical composition of the rocks from Gnaszyn is presented in Table 1 and Text-fig. 4. In addition, Text-fig. 5 shows the quantitative relationship between the three groups of minerals in the samples arranged in ascending stratigraphical order. Quartz, the most abundant mineral, together with K-feldspar and plagioclase, accounts for about 50 wt% of the total mineral composition. Calcite, gypsum, anhydrite and pyrite total about 10 wt%. Clay minerals represent about 40 wt% of the bulk rock mineral content. Of the clay minerals, illite (and/or highly illitic illite-smectite) is by far the most common, accounting for about 20 wt% of the bulk rock composition (the second most abundant mineral after quartz). Although the method of quantitative analysis employed does not allow differentiating between illite, smectite and mixed-layer il-

lite-smectite, a small (or absent) low-angle peak characteristic of smectite-rich clay indicates negligible amounts of the smectite component. Therefore, in order to simplify the description, the "illitic clay" identified in Gnaszyn will be referred to as "illite". The average contribution of kaolinite is 7 wt%. Chlorite and glauconite occur in subordinate amounts (usually <5 wt%).

Text-fig. 5 reveals two trends in mineralogical composition. The content of quartz and feldspars fluctuates reciprocally with respect to the content of clay minerals. It is more diverse in sections A and C than in section B. The content of authigenic non-silicate minerals (calcite, gypsum, anhydrite and pyrite) increases towards the top in section A, and is uniform in sections B and C.

In Text-fig. 6, quartz content is plotted against the kaolinite/illite ratio. Illite is used here as internal standard because it is considered to be less sensitive to chemical weathering than other clay minerals (Ruffell *et al*. 2002). A broad negative trend indicates that kaolinite content increases (with respect to illite) with decreasing quartz content.

CLAY MINERALS OF MIDDLE JURASSIC ORE-BEARING CLAYS

	Gns1	Gns2	Gns3	Gns4	Gns5	Gns6	Gns7	Gns8	Gns9	Gns10	Gns11	Gns12	Gns13	Gns14	Gns15	Gns16	Gns17	Gns18	Gns19
Gypsum	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	3.1	0.0	1.9	0.0	2.6	3.4	2.7	4.3	2.4	3.3	4.9
Quartz	43.3	38.5	39.7	39.7	42.2	48.2	50.1	51.0	39.3	50.8	57.5	42.7	42.0	39.8	47.4	35.6	34.0	45.3	39.9
Anhydrite	4.3	3.7	4.4	4.0	3.5	4.0	3.9	4.5	4.2	4.1	4.0	4.7	4.0	3.5	3.5	4.1	3.1	3.9	3.5
K-feldspar	2.9	7.1	2.5	4.6	6.2	5.7	4.1	2.6	3.6	5.2	5.5	4.0	4.3	3.4	4.5	4.6	5.4	3.1	4.8
Plagioclase	1.2	0.6	1.5	1.5	1.3	1.1	1.2	2.5	1.4	1.1	1.6	2.3	1.7	1.3	0.8	1.0	1.2	1.6	1.8
Calcite	3.7	3.4	3.6	2.9	3.7	4.8	3.5	8.0	3.7	4.4	6.7	6.7	7.7	7.5	2.9	2.2	2.5	3.6	3.3
Pyrite	1.5	1.4	1.7	1.6	1.3	1.4	1.3	2.0	1.4	1.7	1.2	1.8	1.7	1.9	1.4	1.4	1.5	1.2	1.8
Chlorite	1.4	1.0	0.6	1.7	4.1	2.7	1.9	0.0	2.1	1.5	1.0	1.5	0.0	1.0	1.0	0.9	1.9	0.9	2.1
Glauconite	5.9	3.6	4.9	4.9	3.8	4.8	3.8	5.6	5.3	3.8	2.4	5.0	4.5	3.2	2.8	5.0	5.9	5.7	4.4
Illite	27.4	28.1	31.7	27.8	22.0	20.5	19.5	20.0	23.0	18.2	15.9	23.5	23.2	20.8	21.9	26.9	26.9	24.8	26.9
Kaolinite	9.9	8.0	9.5	12.1	12.5	9.6	7.8	3.6	11.6	7.7	4.9	7.8	4.8	7.3	7.0	13.6	15.6	8.7	11.3
sum	101.5	95.4	99.9	102.8	100.5	102.8	97.2	99.9	98.6	98.5	102.6	100.0	96.5	93.0	95.9	99.6	100.4	102.2	104.5

	Gns20	Gns21	Gns22	Gns23	Gns24	Gns25	Gns26	Gns27	Gns28	Gns29	Gns30	Gns31	Gns32	Gns33	Gns34	Gns35	Gns36	Gns37	Gns38
Gypsum	3.5	1.0	0.0	0.0	1.4	2.8	1.5	0.0	1.4	17.4	11.4	0.0	0.0	2.0	2.0	2.0	2.0	4.0	0.2
Quartz	34.8	42.1	46.8	43.7	49.9	51.1	51.7	45.6	44.9	36.0	39.1	55.3	60.0	56.0	63.0	54.0	62.0	67.0	44.1
Anhydrite	2.8	3.3	3.8	5.2	5.0	3.5	2.5	4.7	3.8	3.0	2.5	4.2	0.2	0.4	0.8	0.6	0.6	0.3	4.9
K-feldspar	4.2	4.8	3.6	4.7	3.0	4.8	5.8	5.5	5.2	7.2	4.1	3.8	2.0	2.0	2.0	4.0	1.0	4.0	0.5
Plagioclase	2.2	0.8	1.5	2.0	1.6	2.0	0.7	1.2	1.1	0.9	1.1	2.4	0.4	0.0	0.5	0.2	0.1	0.6	0.8
Calcite	3.5	4.7	7.1	3.8	4.6	3.5	10.4	4.9	17.2	2.4	2.9	5.0	1.0	1.0	2.0	3.0	3.0	3.0	0.3
Pyrite	1.6	1.6	2.0	1.5	1.1	2.0	1.0	1.2	0.7	0.8	0.7	0.7	2.0	0.9	2.0	2.0	1.0	1.0	1.0
Chlorite	1.6	2.0	0.9	2.0	0.0	1.5	2.3	2.3	0.0	1.2	2.0	0.0	0.0	0.7	0.3	0.4	0.5	0.0	0.3
Glauconite	6.6	5.3	4.7	3.0	2.7	3.0	3.9	2.1	6.1	3.2	4.8	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.7
Illite	26.1	22.9	22.6	23.7	22.7	17.0	12.9	22.1	15.3	22.8	20.4	22.9	26.0	29.0	20.0	25.0	24.0	17.0	38
Kaolinite	12.9	8.8	7.6	8.4	6.4	7.2	4.7	7.5	1.8	7.5	12.7	6.0	7.0	8.0	7.0	8.0	5.0	3.0	9
sum	99.8	97.3	100.5	97.8	98.5	98.3	97.3	97.3	97.4	102.3	101.9	104.1	98.6	100	99.6	99.2	99.2	99.9	99.8

Table 1. Mineral content (wt%) of the samples from Gnaszyn
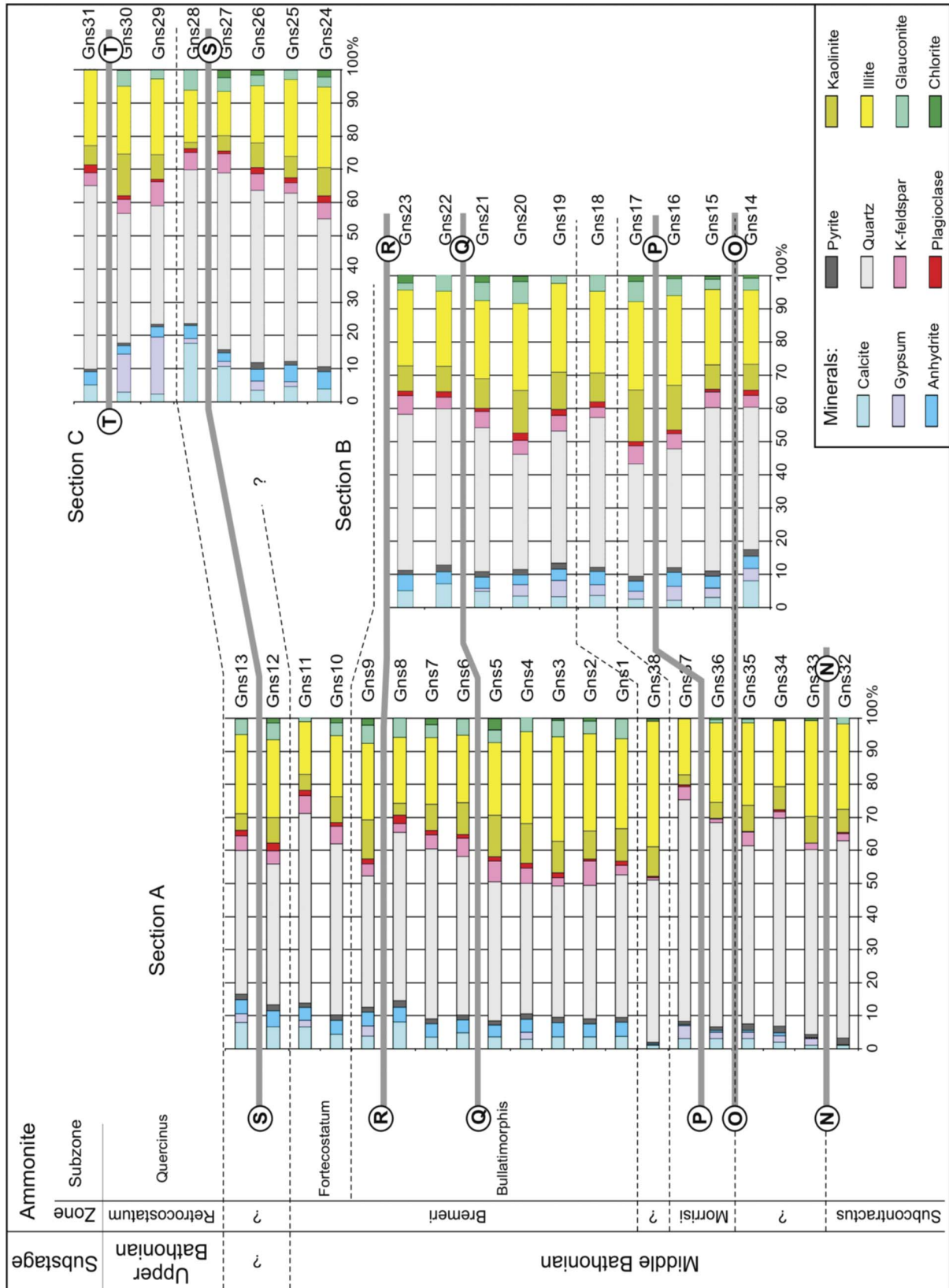
Text-fig. 4. Mineral content of the samples from Gnaszyn (graphic representation of Table 1)
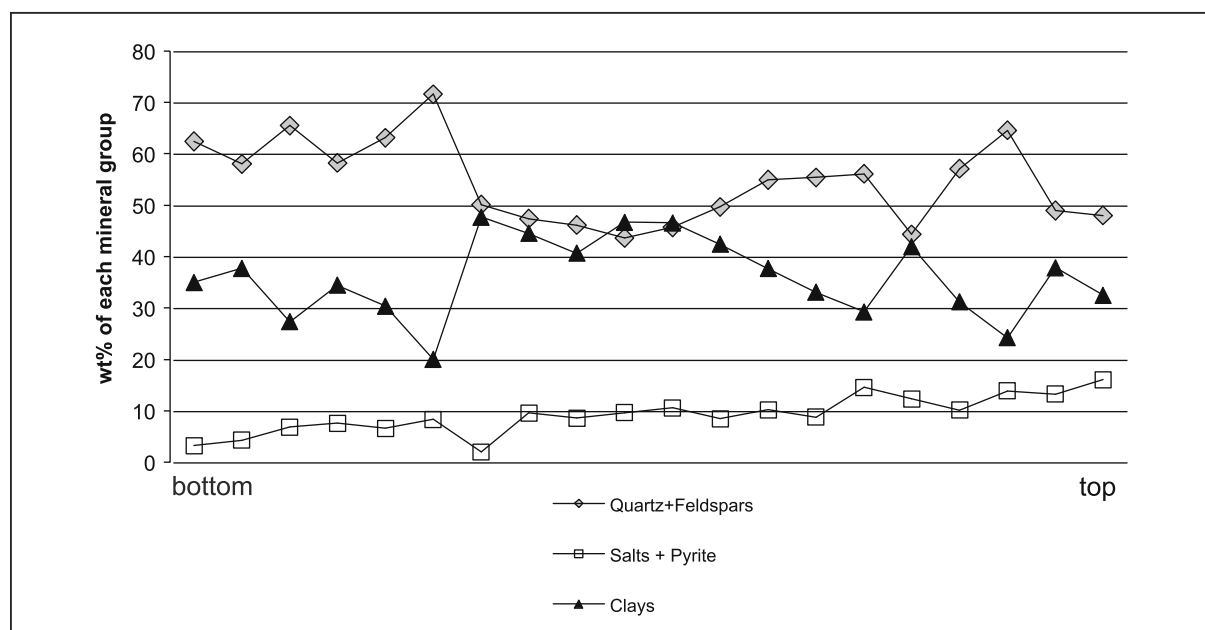
Text-fig. 5. Contents of the three mineral groups in the three sections (A, B and C) from Gnaszyn: diamonds: quartz + K-feldspar + plagioclase; squares: calcite + gypsum + anhydrite + pyrite; triangles: kaolinite + illite + glauconite + chlorite. The samples in each section are arranged in ascending stratigraphical order
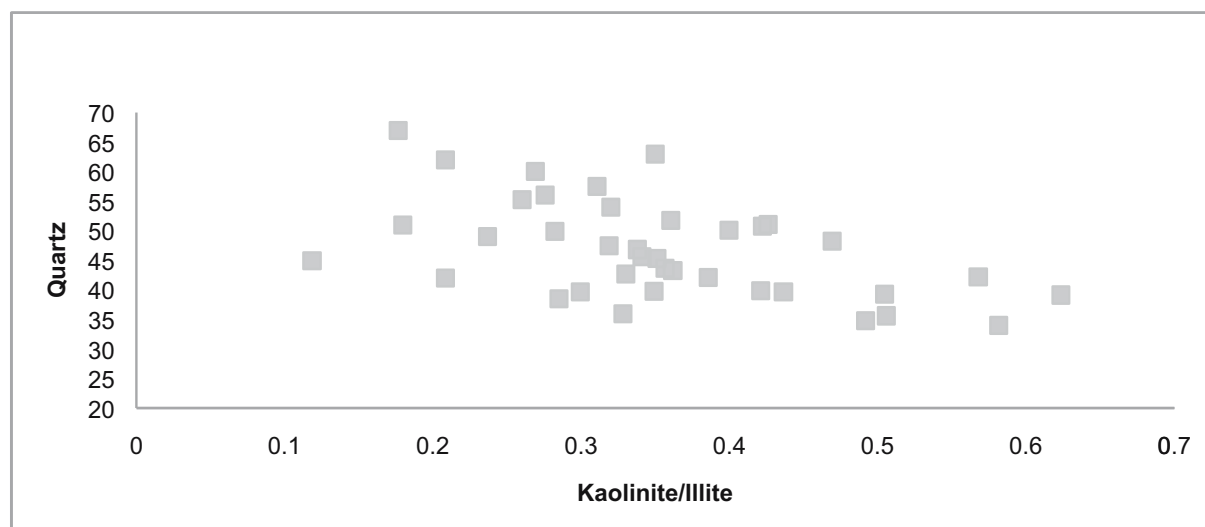
Text-fig. 6. Quartz content plotted against ratio of Kaolinite/Illite contents in all the samples studied

CONCLUSIONS

The sedimentary rocks from Gnaszyn are soft and plastic, indicating a very low degree of diagenesis. This is supported by the presence of K-feldspar, calcite and kaolinite, the minerals which disappear from sedimentary rocks during progressive diagenesis due to either dissolution or transformation (e.g., Boles and Franks 1979; Hower et al. 1976). It seems therefore that the abundant clays in the sediments studied have not been significantly altered since the time of their sedimentation and can be used in paleoenvironmental reconstruction.

The apparent dominance of illite over kaolinite in the sediments from Gnaszyn indicates that intensive mechanical breakdown of rocks prevailed in the source area. Such processes are favoured in temperate, cold and dry climatic conditions. The proportions of detrital clay minerals were similarly interpreted in the Quaternary sediments of the Bengal Basin (Heroy et al. 2003), where high illite and chlorite concentrations were reported from post-glacial deposits. Also, Net et

al. (2002), in their study of the Carboniferous Paganazo Group (Argentina), have noted the clay assemblages containing illite, chlorite with some kaolinite in those sequences that were associated with glacial conditions. Kaolinite in the rocks studied could have been derived directly from the source rock, along with illite and chlorite and/or it could be a product of limited chemical weathering in the source area. Text-fig. 6 shows that kaolinite is concentrated with respect to illite in the finer-grained samples. A similar trend was found in present-day soils from Limpopo Province in South Africa (Ekosse *et al*. 2011).

The mineralogical composition of the sediments from Gnaszyn can serve as an approximate constraint of the types of source rocks. The negligible amounts of smectite indicate very little (if any) volcanogenic input (Chamley 1989). On the other hand, the presence of quartz, feldspars, illite, and kaolinite, which together account for over 80 wt% of the total mineral composition of the sediments, indicates shales, schists, mudstones, loess, tills, sandstones and possibly magmatic and metamorphic rocks of felsic composition (granite, gneiss) as the most likely types of source rocks.

The palaeobathymetry of the basin can be defined as 60–1000 m by the presence of glauconite, if we assume that this mineral is authigenic.

At the section level, the reciprocal fluctuation of the quartz plus feldspars content with respect to clay minerals (Text-fig. 5) is probably linked to changes in grain size. This is most likely related to the changing depositional environment (especially sorting). Section B tends to be more uniform with regard to grain size than sections A and C. The increasing content of authigenic non-silicate minerals in section A represents changes in sedimentation conditions.

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