Main Colouring Minerals in the 'Poznań Clays': Case Studies from the Upper Neogene in the Polish Lowlands

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Abstract

This article is devoted exclusively to three iron minerals that have a decisive influence on the colour of the 'Poznań Clays'. These are hematite, goethite, and jarosite. Their presence gives the 'Poznań Clays', which are the most common and best known Neogene lithostratigraphic unit in the Polish Lowlands, characteristic 'warm' colours ranging from yellow through orange to dark red. The presented results were mainly obtained using powder X-ray diffraction and 57Fe Mössbauer spectroscopy.

Keywords: case study, colouring minerals, neogene, polish lowlands

Introduction

The colour of sediments and rocks has been the object of great human interest for centuries. This also applies to clay sediments, the research results of which are presented below. Simply put, clays have been used for the production of varicoloured building materials, as well as pigments for colouring artistic works, paints, ceramics, and so on [1-3]. Today, in addition to the abovementioned practical uses, rock formations consisting of multicoloured clayey sediments are geotouristic attractions [4, 5], and they can also be used as indicators of palaeoenvironmental conditions [6-10].

The 'Poznań Clays' cover almost a quarter of the Polish territory, i.e., 75.000 km^2 (Figure 1a). They are exposed in many locations in the Polish Lowlands, both in small natural outcrops and in relatively large lignite opencasts. On the other hand, they have been extensively studied, mainly mineralogically [11-18]. In recent years, the 'Poznań Clays' have also been intensively examined sedimentologically [19-25]. Excluding our preliminary study [3], the colour of these sediments has not been the main subject of research in any of the abovementioned contributions. Therefore, the main aim of this study was to briefly characterise the most important mineral pigments found in the varicoloured 'Poznań Clays'.

Fig. 1. Location map; (a) studied exposures in the background of the 'Poznań Clays' extent; (b) detailed location of the Dymaczewo Stare outcrop; (c) detailed location of the Jóźwin IIB lignite opencast

Geological Setting

The examined 'Poznań Clays' contain so-called 'grey clays', as well as 'green and flamy clays' [11, 26]. The 'grey clays' belong to the Grey Clays Member which also hosts the first Mid-Polish lignite seam (MPLS-1), which is currently being exploited for electricity production, among others, in the Jóźwin IIB opencast. On the other hand, the 'green and flamy clays' form the Wielkopolska Member. Both of these members make up the Poznań Formation, which is the youngest Neogene lithostratigraphic unit in central Poland [16, 27-29].

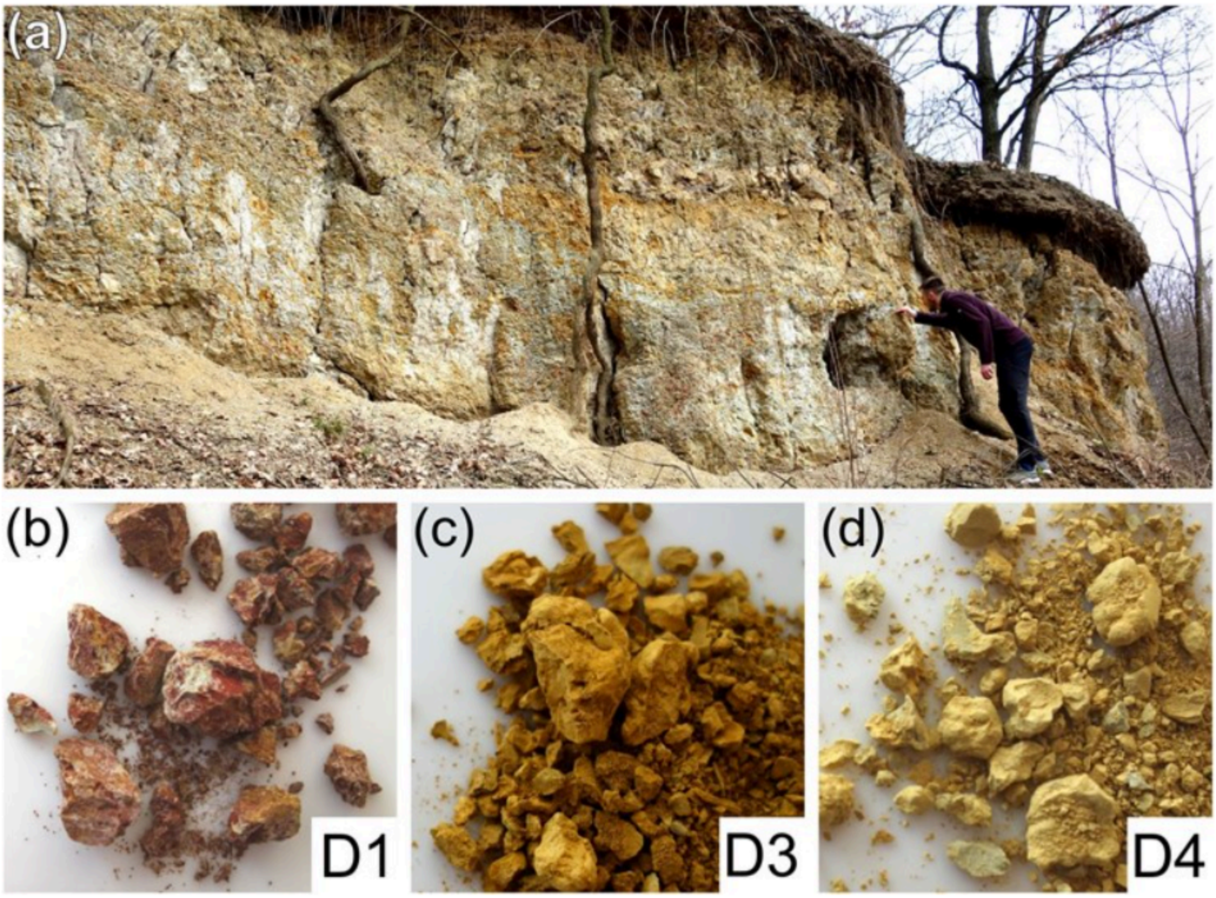

Fig. 2. 'Poznań Clays' at the Dymaczewo Stare outcrop; (a) broad view of the exposure; (b) dark red (cherry) sediment; (c) orange sediment; (d) yellow sediment

The 'grey clays' (Grey Clays Member) were deposited in shallow lakes that existed in Neogene backswamp (mire) areas [27, 28]. In other words, they provide a record of the final stage of the MPLS-1 accumulation that took place between 14.3–13.8 Ma [30, 31]. The 'green and flamy clays' (Wielkopolska Member), in fact, are mainly represented by multicoloured overbank muds (>95 vol.%), as well as channel-fill sands and muds (<5 vol.%). They were accumulated between approximately 13.8–5 Ma by an upper Neogene anastomosing or anastomosing-to-meandering river system [19-25, 30, 31].

Material and Methods

The sediments studied in this article were obtained from two sites located in west-central and central Poland. They are the Dymaczewo Stare outcrop (52°13'49.8''N, 16°47'28.7''E), located ~15 km south of the city of Poznań and ~3 km west of the town of Mosina (Figure 1b), and the Jóźwin IIB lignite opencast (52°24'25.7''N, 18°11'53.6''E), which is situated ~20 km north of the town of Konin (Figure 1c). Fieldwork was carried out at both sites during the first half of 2021 (Figures 2a, 3a, b).

During the fieldwork, 20 samples of various colours were collected, including six (D1–D6) from the Dymaczewo Stare and 14 (J1–J14) from the Jóźwin IIB. Nevertheless, we only selected five samples among these (i.e., D1, D3, D4, J8, J14) that contain the main colouring pigments characterised below (Figures 2b–d, 3c, d). The colours of the samples were, of course, determined macroscopically in the field and then digitised in a RGB (Red–Green–Blue) system using the CorelDRAW X8 computer program (Table 1).

The results presented here were obtained almost exclusively by powder X-ray diffraction (PXRD) and 57Fe Mössbauer spectroscopy (57Fe-MS). The first method enabled us to qualitatively identify the basic minerals present in the samples, whilst the second method allowed the determination of the relative contents of iron cations (Fe3+, Fe2+) in the Fe-bearing minerals. For more information on these two methods, the interested reader is invited to consult our other papers [3, 32, 33] and [3, 34, 35], respectively.

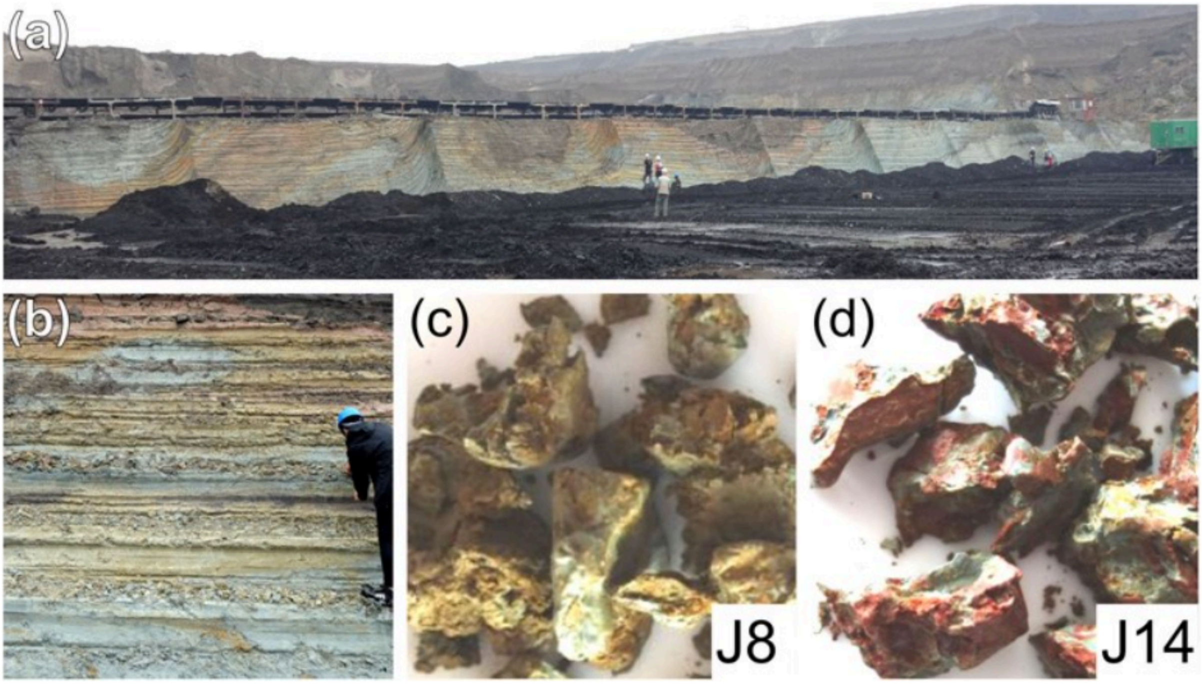

Fig. 3. ‘Poznań Clays’ at the Jóźwin IIB lignite opencast; (a) broad view of the exposure; (b) close-up view of the exposure; (c) yellow sediment; (d) red sediment

Results

Description of the ‘Poznań Clays’ Colour

The colours of the samples determined in the field and in the laboratory differ significantly (compare Figures 2, 3 and Table 1). This is due to their physical properties including moisture contents and grain sizes and, moreover, the colour will depend on the perception of the human eye [3]. Therefore, we additionally applied a more objective method than a macroscopic one to determine the colour of the investigated samples, i.e., the RGB system (Table 1).

Tab. 1. Colours of the ‘Poznań Clays’ determined in the field and digitised in the RGB system

Sample number	Colour in the field	RGB colour air-dried sample
D1	dark red (cherry)	brown (R:160 G:98 B:85)
D3	orange	sand (R:226 G:180 B:108)
D4	yellow	yellow pale (R:255 G:255 B:204)
J8	yellow	gold (R:188 G:145 B:87)
J14	red	reddish brown (R:206 G:108 B:89)

Mineralogy of the ‘Poznań Clays’

The mineral composition of the ‘Poznań Clays’, and especially of their clay fraction, is well known from many publications mentioned in the introductory chapters [e.g., 11-17]. It varies both regionally (i.e., in the Polish Lowlands) and locally (i.e., exposure, borehole profile). However, as in the examined samples, quartz is always the main mineral, and the clay fraction is dominated by minerals from the smectite group such as smectite and illite-smectite. Other major minerals may consist of calcite (sample D3), hematite and goethite (sample D1, and jarosite (sample D4) (Figure 4; Table 2).

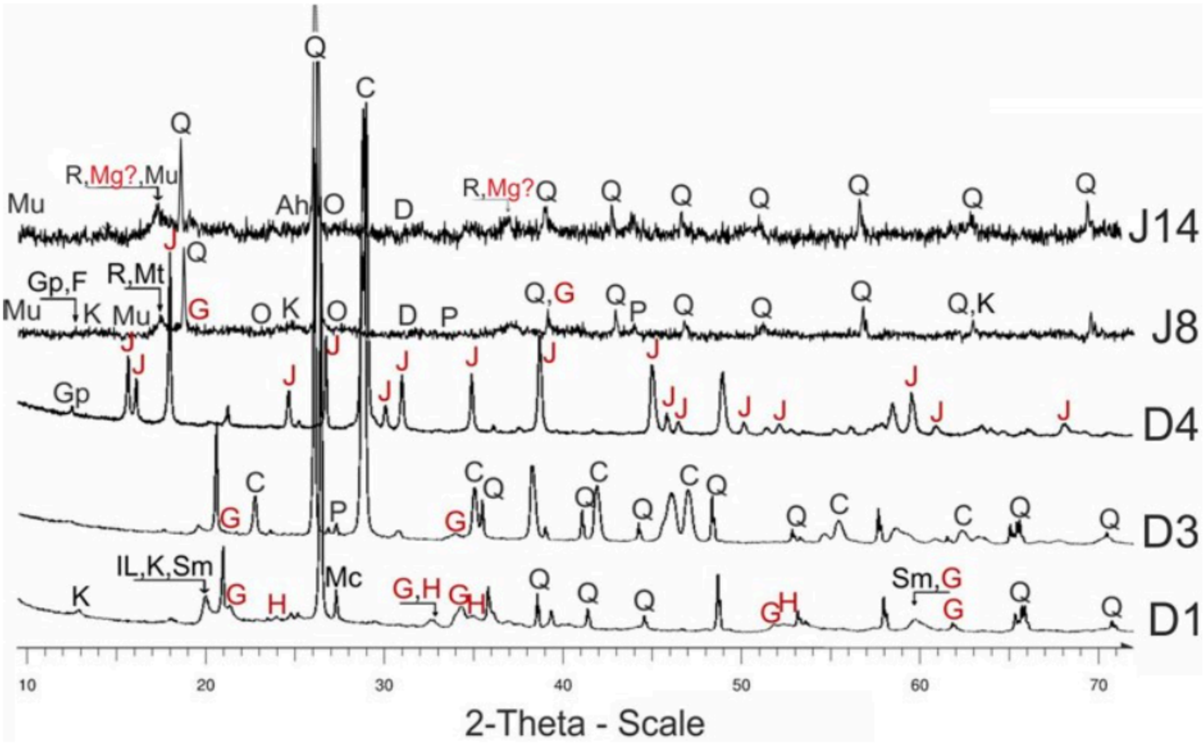

Fig. 4. Powder X-ray diffraction (PXRD) for 'Poznań Clays' from the Dymaczewo Stare and Jóźwin IIB sites with the main pigments marked in red; Ah – anhydrite, C – calcite, D – dolomite, F – fougerite (group species), G – goethite, Gp – gypsum, H – hematite, IL – illite, J – jarosite, K – kaolinite, Mc – microcline, Mg – magnetite, Mt – montmorillonite (smectite-group species), Mu – muscovite, O – orthoclase, P – plagioclase, Q – quartz, R – rectorite (illite-smectite), Sm – smectite; compare with data from Table. 2; the main colouring minerals are marked in red.

The minerals occurring in smaller amounts (minor minerals), include among others, orthoclase, plagioclase, and gypsum (samples D4 and J8) as well as muscovite ('illite') and kaolinite. These also include pigments, i.e., goethite (samples D3 and J8) and magnetite (sample J14). Nevertheless, the last case requires confirmation by other methods (e.g., SEM-EDS – scanning electron microscope-energy dispersive spectroscopy) because the 57Fe-MS results indicate the presence of hematite and not magnetite (compare Figures 4, 5 and Table 2). This discrepancy may possibly be related to a high sample heterogeneity.

Tab. 2. Compilation of mineral composition obtained by PXRD and 57Fe-MS methods; compare with Figures 4 and 5; the main pigments are in bold and italics

Sample no. and its colour	**PXRD**	**^{57}Fe-MS**
D1 dark-red, cherry	major minerals: quartz, ***hematite***, ***goethite***; minor minerals: microcline, 'illite', kaolinite, smectite-group species, orthoclase	***hematite***, ***nano-hematite***, other Fe^{3+} minerals
D3 orange	major minerals: quartz, calcite; minor minerals: plagioclase, microcline, orthoclase, ***goethite***, kaolinite, 'illite', smectite-group species	***goethite***, ***nano-goethite***, ***jarosite***, other Fe^{3+} minerals
D4 yellow	major minerals: quartz, ***jarosite***; minor minerals: gypsum, kaolinite, 'illite', smectite-group species, orthoclase	***jarosite***
J8 yellow	major minerals: quartz; minor minerals: ***goethite***, gypsum, kaolinite, muscovite, plagioclase, orthoclase, rectorite, dolomite, smectite-group species, fougèrite	***hematite***, Fe^{3+} and Fe^{2+} silicates
J14 red	major minerals: quartz; minor minerals: ***magnetite*?**, orthoclase, dolomite, muscovite/'illite', rectorite, anhydrite	***hematite***, siderite, Fe^{3+} silicates

Distribution of Iron Atoms in the 'Poznań Clays'

Trivalent and divalent iron atoms (Fe3+, Fe2+) were identified in each of the studied samples. In general, they occur in minerals such as hematite, goethite, jarosite, siderite, and Fe-bearing silicates. Hematite and nano-hematite predominate in samples D1, J8, and J14. Only jarosite was found in sample D4, whilst sample D3 hosted both goethite (and nano-goethite) and jarosite. Additionally, other iron minerals and silicates were found in samples D3, J8 and J14, although these were difficult to precisely identify by 57Fe-MS (Figure 5; Table 2).

In most cases, the results obtained by PXRD and 57Fe-MS are consistent with each other (samples D3 and D4) or similar (sample D1). Some differences in samples J8 and J14 may be explained by at least two reasons (compare Figures 4, 5 and Table 2). Firstly, the analysed pigments may be present in trace amounts in the sediments and thus their concentrations would be below the detection limit of the PXRD analysis (i.e., below 0.n wt%). Secondly, their trace amounts in iron oxides and hydroxides, and above all in Fe-bearing silicates, would make the determination of the exact minerals difficult by 57Fe-MS [36-38]. Another reason could be very low crystallinity of goethite, and possibly also hematite, making them indistinguishable from the PXRD background.

Original Colour and Possible Origin of the Studied Pigments

Jarosite, KFe3(SO4)2(OH)6, is a basic hydrous sulphate of potassium and ferric iron (Fe3+), which is typically yellow in colour with shades ranging from light to brownish. It can be formed by pyrite oxidation when jarosite could then transform into goethite [39].

Goethite, α-FeOOH, is a thermodynamically stable iron oxide (Fe-oxyhydroxide) in natural environments. Pure and powdered goethite is yellow in colour, but when its fine-grained form (nano-goethite) predominates, it is beige-brown [40, 41]. Thus, various combinations of goethite and/or jarosite can lend an orange colour to the sediment as is the case with sample D3 (compare Figures 4 and 5).

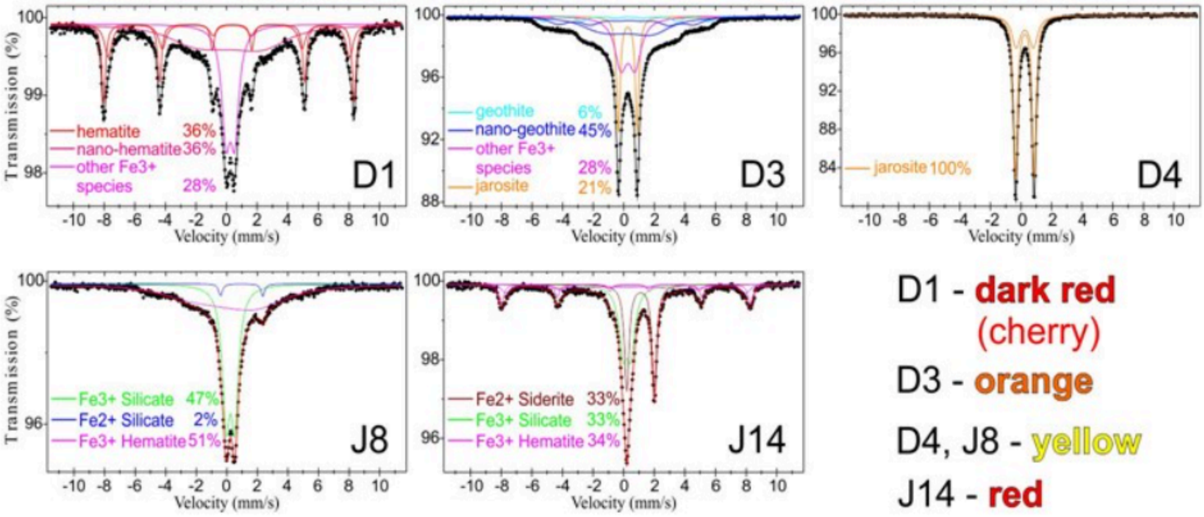

Fig. 4. ^{57}Fe Mössbauer (^{57}Fe-MS) spectra of the examined "Poznań Clays" from the Dymaczewo Stare and Jóźwin IIB sites with the relative distribution of the Fe atoms in iron-bearing minerals; compare with data from Table 2.

Hematite, α-Fe2O3, is one of the most common iron oxides found on the surface of the Earth, Mars, and the Moon, among others [41]. Because its formation is strongly related to temperature, humidity/aridity, acidity, and so on, it is often used in environmental studies of sediments and soils [7, 9]. Because hematite is very stable in nature, it is considered to be the end member of the transformation (weathering, oxidation, etc.) of other iron oxides and hydroxides, including jarosite and goethite [41]. However, in the context of this research, the most important textural feature is the characteristic red colour of hematite, both in its powdered form and in the sediment/rock [4-10].

Conclusion

The beauty of the multicoloured 'Poznań Clays' results mainly from the yellow, orange, and red interlayers and mottles (goethite and hematite) in a grey background of various shades. In this paper, it was confirmed that the main mineral pigments are iron minerals, where iron is solely or predominantly trivalent.

The yellow colour of the sediments is due to jarosite (sample D4) or alternatively, hematite with a large share of Fe-rich silicates (sample J8). The orange colour may be due to the presence of jarosite or goethite in the sediments, or a mixture of both (sample D3). The red colour of the studied samples (D1, J14) derives exclusively from hematite, but the presence of minerals with divalent iron (e.g., siderite) reduces the intensity of the red colour of the sediment (sample 14).

In the absence of the main colouring minerals (jarosite, goethite, hematite) or the presence of organic matter, the sediments have a 'cold' colour. In this case, the 'Poznań Clays' are grey with shades ranging from bluish to greenish, and even dark grey to black when the organic matter contents are greater. Such a colouration may be caused by the fougèrite-group species which in sample J8 is masked by other Fe minerals.

Finally, PXRD and 57Fe-MS methods should be considered complementary, but not fully sufficient to identify the main pigments affecting the colouration of the 'Poznań clays'. Therefore, extending the research methodology (e.g., to include SEM-EDS) would help provide further insights into this topic.

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