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BEHAVIOUR OF GARNETS IN DIAGENESIS OF CENOZOIC SEDIMENTARY ROCKS: EXAMPLES FROM POLAND

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ABSTRACT

The opposite trend between the contents of garnets and quantity of sulphides and organic matter was stated within Quaternary proglacial deposits in the Łomża region and Kurpie plain of NE Poland, as well as in certain Tertiary sediments. Diagenesis of the discussed deposits yielded new mineral assemblages, which changed chemical and physical characteristics of primary sediments. Such transformations, if not recognized properly, may lead to erroneous conclusions on the type of facies, in stratigraphy based on mineral assemblages, paleomagnetic considerations and paleogeographic interpretations.

Key words: *garnets, diagenesis, sulphides, organic matter, facies, stratigraphy, paleogeography, paleomagnetism, proglacial and glacial sediments, Quaternary, Tertiary, NE Poland.*

INTRODUCTION

Garnets are abundant heavy minerals in many clastic rocks. The investigations of these minerals have been performed for many tens of years during preparation of the detailed geological map of Poland (1:50,000), particularly in young, Tertiary and Quaternary sediments. The studies resulted in a set of data, which should be interpreted by taking into account proper genetic considerations.

The hypothesis concerning the diagenetic alterations and dissolution of garnets was formed during the studies of heavy minerals in Quaternary sediments, performed by the present author in the areas covered by the maps in the scale 1:50,000, the sheets: Zambrów, Zaręby, Lipowiec and Prabuty (Zawidzka 1995, 1996, 1997a, b). It was already outlined in an earlier publication (Zawidzka 1998).

A careful study of the published literature showed that the possibility of the diagenetic removal of garnets from sediments was commonly supposed. The research of the present author confirmed and documented this supposition, and yielded a possibility to reconstruct the pattern of the related diagenetic processes.

PREVIOUS CONSIDERATIONS

Among the papers of the Polish authors, the extensive discussion concerning the preservation of heavy minerals in sediments of various age and origin, published by Turnau-Morawska (1955), deserves a special attention. Reports of other authors, concerning Cenozoic (especially Quaternary) sediments in Poland, gave most spectacular examples confirming the present author's thesis on diagenetic behaviour of garnets.

In most of the sequences of the Quaternary deposits, the distribution of garnets is rarely ruled by a distinct scheme due to variable rock composition of the alimentation areas, multiple and selective remobilization, and redeposition of the clastic material. According to Racinowski (1992), the studies on heavy minerals do not allow to determine directly the lithostratigraphic levels of the Quaternary sediments. The distribution of garnets is most variable in glacial and fluvioglacial beds (Mycielska-Dowgiałło 1995).

A more consequent pattern of accumulation and distribution of heavy minerals, including garnets, was found in fluvial beds of the temperate climatic zone and, in lesser degree, in the lacustrine and aeolian sediments. Alluvia, in addition to the beach sands, are sediments enriched in heavy minerals, among which garnets are frequently the most common ones. However, the content of garnets, if compared to the content of *e.g.* zircon, decreases in the dust blown away from the sands of the river valley – the smaller grain size, the lower garnet content (Maruszczak, Racinowski 1968; Maruszczak, Morawski 1976). Similarly, the flood facies are poor in garnets: heavy minerals of flood sediments of the San River in Przemyśl (southern Poland) contain 18% of garnet, whereas the river bed sediments – 81% of this mineral (Racinowski 1976).

Thus, the primary enrichment of the sediments in garnets appears due to the commonly known processes. However, in many logs of the Cenozoic clastic rocks of various origin very distinct gradual increase of the garnet concentrations from older to younger sediments was observed. This feature was observed in various units, in which the deposition regime did not vary essentially or varied by cyclic mode within the unit ranges, and all gaps were recognized. Konecka-Betley and Majsterkiewicz (1973) found in dune and loess profiles with buried soils that the younger was the soil, the higher concentration of garnets it contained. Urbaniak-Biernacka (1975) determined garnet content as 19% of heavy minerals in the older dune level and 33% in the younger one in Wolin

Island (NW Poland). In the Pilica River bed (central Poland), the garnet content increased from 60 to 70% or from 38 to 50% of the total heavy minerals in the older and younger sediments, respectively (Rzechowski *et al.* 1975). The same tendency was found in other sandy deposits (Mycielska-Dowgiałło 1978, Florek *et al.* 1987), especially in Kampinos Forest near Warsaw (Kuźnicki *et al.* 1974). Decrease of garnet contents in soils and increase in the levels many times exposed to wind activity was noted by Cichosz-Kostecka *et al.* (1986). Numerous reports concerning loesses contain informations on the presence of garnets, albeit the changes of garnets during diagenesis, including limonite shells on garnet grains in old loess levels and fresh garnets in young loess, were indicated rarely (*cf. e.g*. Maruszczak, Morawski 1976).

In the Tertiary deposits in Warsaw (Miocene, Pliocene and pre-glacial sediments in the drilling core from Kasprzak Street), the lower heavy mineral assemblage contained 30% garnets but the upper one as much as 62% (Kociszewska-Musiał, Kosmowska-Ceranowicz 1976). Similar distribution of garnets was stated in the Oligocene-Pliocene sequence at Gołębin Stary (Wielkopolska Lowland) and in Miocene beds in Kętrzyn and Gdańsk, where the decrease of the garnets contents and their absence were interpreted as resulting from post-sedimentation chemical processes (Kosmowska-Ceranowicz 1979; Kosmowska-Ceranowicz, Buhmann 1982).

Fore-Carpathian Miocene yielded very good examples confirming the supposition that the contents of garnets in sediments of various age were influenced by duration of the diagenetic processes causing decay of these minerals. However, although it has been described *e.g.* in the Opolian and Tortonian beds from Przeciszów near Trzebinia (Krysowska 1966) that the younger beds usually contain higher amounts of garnets than the older ones, this feature has been interpreted in terms of primary accumulation, not diagenetic alteration. In the present author's opinion the existence of the diagenetic decomposition of garnets should result in serious corrections of the paleogeographic characteristics of the Fore-Carpathian depression.

The behaviour of heavy minerals during diagenesis was characterized by a number of authors, who consequently indicated diagenetic alterations of garnets (P. G. H. Boswell 1933, T. Smithson 1950 – *fide* Turnau-Morawska 1955, *moreover* Bramlette 1929, Pettijohn 1942). Bramlette (*op. cit.*) stated that most garnets disappear from sedimentary rocks under certain conditions, which may occur quite frequently. He described garnets with sequences of parallel planes resembling cleavage, and in his experimental etching of garnets he obtained the same effect. He concluded that this feature might appear in nature due to the joint partial dissolution and subsequent incomplete regeneration of garnets.

Garnets of the habit described by Bramlette (*op. cit.*) were found by the present author in Quaternary sediments from the environs of Zambrów, Zaręby, Lipowiec and Prabuty (Zawidzka 1995, 1996, 1997a, b). They were also reported from *Heterostegina* sands of the Fore-Carpathian Miocene beds

(Krysowska 1966) and from loess of the areas of Lublin and Przemyśl in SE Poland (Racinowski 1976).

A distinct decrease of the garnet-to-zircon ratio was recognized in Paleocene sandstones of North Sea. This feature was interpreted as the result of dissolution of garnets, with higher susceptibility of the calcic garnets to decay, because they disappeared at smaller depths than other garnet varieties ((Morton 1987). Similar disappearance of garnets due to corrosion was reported from the Eocene – Lower Oligocene McKee formation in New Zealand (Smale, Morton 1987) and from the Triassic sandstones of Spitsbergen; in the latter rock, pyrope-rich garnet disappeared first, what was accompanied by diagenetic silica cementation (Mørk 1999).

GARNETS IN QUATERNARY SEDIMENTS OF THE ŁOMŻA REGION AND KURPIE PLAIN

Taking into account the above described features of garnets and peculiarities of their distribution in sediments, their occurrence in the selected logs of the Quaternary sediments in NE Poland was investigated. The discussed problem could be presented best, when considered for the behaviour of garnets in the occurrences at Żabikowo near Zambrów in the Łomża region and Nowa Wieś near Ostrołęka in the Kurpie Plain.

Żabikowo near Zambrów

Characteristics of the sediments

The Quaternary sequence begins from thin bed of tills of the Narew Glaciation age. It is covered by 44 m thick complex of sandy sediments of an interglacial older than the Great one (Maksiak 1994), with subordinate muds and clays, and one layer of cobbles. These beds consist of various sedimentation cycles, frequently incomplete (Zawidzka 1995), *e.g.* typical of the proglacial rivers (Zieliński 1993). Nevertheless, the fine-grained sediments were deposited in lacustrine basins. The coarse-grained intercalations indicate either material from melting ice covering the basin, or more intensive erosion, probably connected with milder climate; this interpretation is confirmed by the presence of muds with plant debris and fragments of mollusc shells and phosphatized remnants of fishes.

The dark clayey muds and fine-grained sands are rich in finely dispersed organic matter. They bear high contents of sulphides, mainly pyrite (up to 80%), and/or authigenic chlorites (up to 40%) in the heavy mineral fraction, formed in periodically eutrophic lacustrine basin with high bacterial production of hydrogen sulphide from organic matter (Zawidzka 1995).

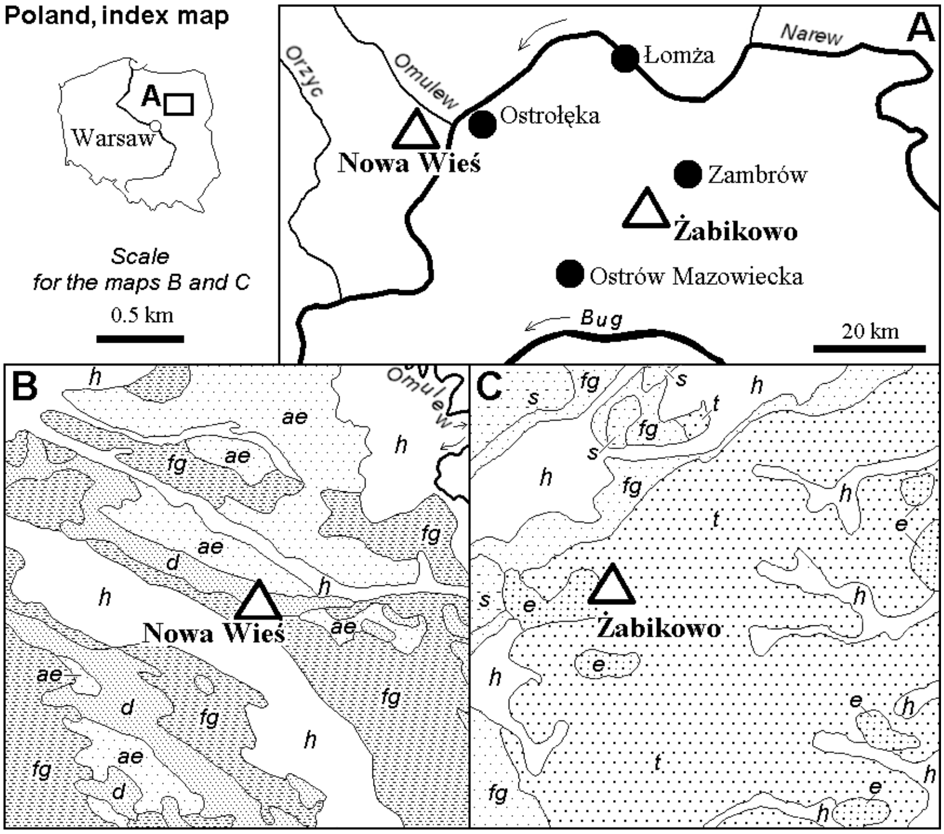

Fig. 1. Localization of the drillings at Nowa Wieś and Żabikowo (**A**) and simplified geological maps of the areas of Nowa Wieś (**B** – *after* Listkowska 1999) and Żabikowo (**C** – *after* Maksiak 2002); *h* – Holocene peats, and sands and silts of the river beds, *ae* – aeolian sands, *d* – dune sands, *fg* – fluvioglacial sands of the Baltic Glaciation in the map **B** or fluvioglacial sands and gravels of the Warta Glaciation in the map **C**, *e* – elluvial sands, gravels and clays of the Warta Glaciation, *s* – silts, sands and gravels of kames of the Warta Glaciation, *t* – tills of the Warta Glaciation.

These sediments are covered by a more than 10 m thick bed of various tills, attributed to the younger South-Polish Glaciation; the lowest gray till layer contains significant amounts of pyrite. The till bed is covered by clayey-muddy lacustrine sediments almost 20 m thick of Mazowsze Interglacial (Maksiak 1994), with detritus of mollusc shells, fish remnants and plant debris. The accumulations of organic matter are incrusted by sulphides of iron and possibly other metals (Zawidzka 1997b). Numerous tiny crystals of authigenic quartz occur in the sulphide aggregates. Upwards within this bed, sulphides disappear and the calcium carbonate concentration increases, marking the approaching cooling of climate.

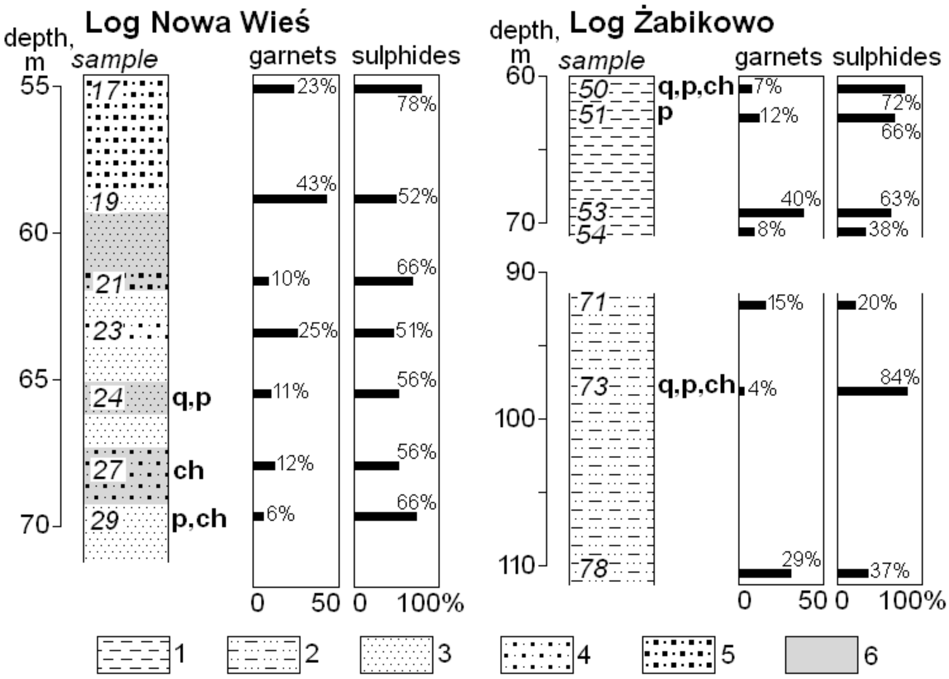

Fig. 2. Fragments of the logs of the drillings from Nowa Wieś and Żabikowo with the contents of garnets (percent of the total of transparent heavy minerals) and sulphides (percent of the opaque heavy fraction), log Nowa Wieś – proglacial sediments below the Odra Glaciation tills; log Żabikowo, upper part – probably Mazovian Interglacial, lower part – probably an interglacial older than the Great Interglacial; 1 – clayey silts, 2 – sandy silts, 3 – fine sands, 4 – sands of various grain size, 5 – sands of various grain size with gravels and boulders, 6 – humic and other fine organic matter, q – authigenic quartz, ch – authigenic chlorite, p – plant debris.

The upper part of the log consists of sediments comprising six levels of tills interbedded by sands, either the muddy ones, or with gravel, dated for Middle-Polish Glaciation (Maksiak 1994).

Distribution of garnets

Garnets are commonly present in the heavy fraction of the investigated sediments, however, their concentration varies strongly. Low amounts of garnets in the heavy fraction was stated in dark-gray muds and in dusty sands with thin layers of the organic substance, sedimented during an interglacial older than the Great Interglacial. Thus, at the depth of 112 m (sample 78) the garnet content is 29%, at 102 m (sample 73) – 4% and at 92 m (sample 71) – 15%. The low content of garnets coincides with the high amounts of sulphides and organic matter: the sample containing 4% garnets bears 84% sulphides and abundant organic matter, whereas samples with higher contents of garnets have low amounts of sulphides and organic matter (*see* Fig. 2). Low contents of garnets and high contents of sulphides, commonly with authigenic quartz, are accompanied by significant concentrations of apparently authigenic chlorites.

The same regularity concerns the distribution of garnets in the muddy-clayey sediments of the Mazowsze (Mazovian) Interglacial: the lowest concentrations of garnets (*ca* 7%) occur in the muddy clays with high concentrations of organic matter and 72% sulphides, more than 20% authigenic chlorites and abundant authigenic quartz (sample 50). The highest garnet contents (46%) occur in the clayey muds (sample 53), in which organic matter is not visible and chlorites are scarce (Fig. 2). In another sample of clayey mud, labelled as sample 51, garnets amount 12%, organic matter content is high and sulphide content reaches 66%.

In the Żabikowo log abundant garnets in heavy fraction coincide with high concentration of the clasts of the Scandinavian carbonate rocks; this was found in four samples from the six investigated ones (Zawidzka 1995). Such coincidence was also observed in other logs of the Quaternary sediments, the youngest units of the log from Nowa Wieś inclusively. In the latter one, at the depth of 183 m, one observed prevalence of garnets in the heavy fraction in presence of pyritized fauna, however, pyrite was coated by still non-dissolved Paleozoic limestone. Thus, probably carbonate occurrence counteracted acidifying of the pore waters of the sediments and protected garnets from decomposition.

Nowa Wieś near Ostrołęka

Characteristics of the sediments

The Quaternary sequence begins here with an over 140-metres-thick bed of strongly variable tills, which commonly bear Tertiary components and numerous and thick levels with boulders. These sediments were most probably accumulated by under- and intra-glacial flows.

The tills are covered by fluvial and limnic clays, muds and fine-grained sands with laminae of humus and plant detritus. Brown till with Tertiary components, and sand, gravel and green clay intercalations occur higher (Listkowska 1995); this part of the sediments was probably deposited aside the glacier ice. The mud-sandy and sandy sediments laying above, formed under lacustrine and proximal-deltaic conditions, in part during a climatic optimum of unknown rank, include laminae of organic matter, plant and thin-shell mollusc detritus, fish teeth and scales (Zawidzka 1996). This part bears a till intercalation covered by a 20-metres-thick layer of sand with plant remnants (Listkowska 1995).

The cyclic nature of the sediments is well expressed by alternation of sands with diagonal ripple-mark lamination, sands with horizontal lamination and sandy muds and clays with horizontal lamination in layers 1 to 1.5 m thick, occasionally with gravels at the base of some sediment cycles. The stagnation episodes in the basin yielded sediments enriched in organic matter, authigenic sulphides and chlorites.

The pyritized plant remnants have encrustations of authigenic quartz (Zawidzka 1996); garnets are scarce (11%), sulphides exceed 56% and samples from the directly underlying sediment contain abundant chlorites. The sediments formed in lacustrine basin supplied by rivers, but, on the other hand, periodically with waters low in oxygen.

Subsequent phases of the continental glacier transgression yielded increasing gravel amounts, high concentrations of calcium carbonate, abundant inflow of glauconite from the eroded Tertiary beds; the plant remnants almost disappeared (Zawidzka 1996). Thick tills overlying the described sediments have distinct prevalence of garnets in heavy fractions, sometimes as grains of two populations: rounded and angular. Slightly altered biotite, clasts of sericite-chlorite schists and abundant microfauna including Paleozoic conodonts occur in some till layers.

The profile from Nowa Wieś is finished by various sands with mud and gravel intercalations, bearing chips of rotten wood and red iron oxides (hematite?) – the latter may occupy up to 90% heavy mineral fraction. Fragments of metamorphic rocks and grains of kyanite, andalusite, sillimanite and epidote are very numerous; the heavy mineral fraction of the sands occurring directly under soil contains more than 60% garnets.

Distribution of garnets

The sediments investigated in the log from Nowa Wieś contained heavy mineral assemblages, which confirmed the regularity found in the glacial sediments of Żabikowo. The above-characterized sandy-muddy-clayey beds with repeating intercalation rich in humus substances and plant detritus (wood chips inclusively) commonly have garnets, however the content of this mineral group varies: layers rich in organic matter and sulphides are poor in garnets and the low or negligible content of the organic matter is accompanied by high amounts of garnets (Fig. 2).

DISCUSSION

Certain generalizations may be made on the basis of the above-presented characteristics of the Quaternary deposits:

a) In the proximal gravel, gravel-sandy and sandy facies of the fluvial sediments, the contents of garnets are generally poorly variable, having values of 20 to 30%. Quick covering by overlying material and small differences of lithologic features and physico-chemical conditions in the sediments did not stimulate the synsedimentary and diagenetic changes of the concentrations of garnets in the accumulated material.

b) Fine-grained sands and muddy sediments, which precipitated from suspension in waters of the distal areas of the outwash plains, contain abruptly variable amounts of garnets, from few to more than 50% in heavy mineral fraction, though the grain size and main mineral clastic components are the same or vary within very narrow limits.

c) The low contents of garnets in presence of high amounts of organic matter and/or sulphides, mainly authigenic pyrite, is very distinct in the proglacial sediments. This concerns also the coincidence of low contents of garnets and high amounts of authigenic chlorites and quartz. The high contents of garnets are associated with low amounts of organic matter, sulphides or authigenic chlorites.

d) In tills, the maximum concentrations of garnets are accompanied by very high contents of limestone pebbles.

It seems that the scheme of diagenetic processes in the investigated proglacial sediments may be outlined as follows:

The chemically decomposed garnets release iron, which is in the state of the bivalent ion, because most of the detritic garnets are almandine-rich, containing even above 40% FeO. Under favourable conditions, meaning here low Eh and moderately low pH, the released iron reacts with sulphur, forming iron sulphides, mainly pyrite. Sulphur might come either from sulphates reduced by anaerobic bacteria or from decomposition of organic matter. Under such conditions the mobilization of rare earth elements, and of uranium and thorium is also possible, as reported from other areas (Fralick, Miall, 1987). This diagenetic environment is also favourable for crystallization of pyrrhotite (both antiferro- and ferrimagnetic varieties), thyospinels like greigite, sulphides of the platinum group elements like smythyte and linnaeite, compounds of uranium like coffinite, various sulphides bearing copper, lead and zinc, as reported from the Keuper sediments by Dill (1988; *cf. also* Zawidzka 1996, 1997a, b, 1998a). Greigite and smythyte were recently found in the Miocene sediments of the Fore-Carpathian Deep and their origin was connected with the early diagenesis of the sediments under anoxic conditions (Król, Jeleńska 1999). Appropriate investigations of the Quaternary deposits would be reasonable.

The decomposition of garnets releases silica which crystallizes in the form of euhedral authigenic quartz, encrusting sulphide-organic clusters. Similar process occurred in the earlier mentioned Triassic sandstones in Spitsbergen, where dissolution of garnets was accompanied by extensive crystallization of quartz cement (Mørk 1999).

The investigated Quaternary deposits contain also iron-rich authigenic chlorites, which reach even 40% in heavy mineral fractions.

An important role in initiation and control of the described diagenetic processes is played by organic matter, increase of the content of which in the sediment causes the processes of its bacterial decomposition, leading to extensive use of all the electron acceptors present in the environment and stabilization of the reducing conditions.

Anoxic and acid medium increases the rate of dissolution of many alumosilicates and silicates bearing iron, as well as iron oxides putting iron in mobile form of bivalent ion (*cf.* Postma, Brockenhuus-Schack 1987). The results of such diagenetic processes are probably recorded in many sedimentary logs of various age. Probably the diagenetic phenomena that occurred in many cyclically variable sediments, *e.g.* in those investigated in the drilling core of the borehole Jamnica in the Fore-Carpathian Deep (Król, Jeleńska 1999), were similar to these described here.

Post-deposition changes of the detritic iron-rich silicates, alumosilicates and oxides in clastic rocks influence essentially properties of the rocks. The genetic considerations based on stratigraphic, paleogeographic and paleomagnetic studies, made without taking into account the above-indicated diagenetic processes, may lead to incorrect conclusions and wrong interpretations.

It was shown earlier that organic matter seriously influences the diagenetic processes. Almost every kind of organic matter has such importance. In the cyclic sapropel-bearing logs from the sediment Tertiary/Quaternary border in the area of North Sea, the most important minerals carrying magnetic information are destroyed above the sapropel layer, but below it the same minerals precipitate again (Langereis, Dekkers 1999).

Hydrocarbons, both ascending and produced by local diagenetic processes, common in the sedimentary rocks of the Tertiary and Quaternary age, influence the dia- and epigenetic environment, causing the possibility of precipitation of authigenic magnetite, hematite (specularite) and pyrrhotite from the solutions bearing iron ions. On the other hand, they may cause dissolution of authigenic hematite, resulting in relative increase of the content of the detritic iron minerals and thus their greater influence on the paleomagnetic properties (Kilgore, Elmore 1989).

The dissolution of some silicates and mobilization of iron from their structure may be caused by microorganisms – bacteria and fungi. In certain soils under oxidizing conditions at pH close to neutral, bacteria of the genus *Streptomycetes* produce in their metabolism siderophores, *i.e.* specific ligand compounds carrying iron released from iron silicates during decomposition of the minerals; these minerals are sources of microelements necessary for the bacteria (Liermann *et al*. 2000).

Behaviour of iron in soils yields examples, which may be extended to diagenesis as well. It was found that in soils new magnetic mineral phases may be formed (Sutton, Maynard 1993; Langereis, Dekkers 1999).

The yellow, brownish or reddish colours of the rock beds are usually interpreted as due to the formation of the rock in warm or tropical climate. However, the release of iron from silicates and oxides, and precipitation of FeOOH as goethite, lepidocrocite or ferrihydrite, with further alteration to hematite may extensively occur in temperate or cold climates, which are typical of the accumulation of the outwash sediments. Thus, after sufficiently long time, alteration to hematite is the inevitable final transformation of all the iron compounds precipitated during the diagenetic processes (Postma, Brockenhuus-Schack 1987; Waleńczak 1987; Langereis, Dekkers 1999).

Results of the activity of the diagenetic processes of the discussed type may be of special importance for climatic stratigraphy, when loess-buried paleosols, geosols, welded paleosols and pedocomplexes are considered. Apparently, pedocomplexes or/and geosols as well as welded paleosols in one region may be a chronostratigraphic equivalent of several paleosols interlayered by loess in another region (Bronger 1999). For example, one supposed that the Fe-soil from Stari Stankamen (Yugoslavia) formed in a climate much warmer than any Holocene climate in this area. However, in Karamaydan (Tadjikistan) such soil is of an age equivalent of several interglacial soils, interbedded by loess levels formed during 140,000 years. Thus, the advanced state of the diagenetic alterations depended there not on climate but on the duration of the process (Bronger 1999).

The examples given above illustrate the possible serious consequences (in facial, stratigraphic and paleomagnetic conclusions), which may appear if diagenetic processes were not taken properly into account. The influence of diagenetic behaviour of minerals on the final composition of the assemblages of heavy minerals should be considered to avoid possible misinterpretations.

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