Proc. Estonian Acad. Sci. Geol., 1995, 44, 2, 111—118
https://doi.org/10.3176/geol.1995.2.04

SCANNING ELECTRON MICROSCOPY OF FERRIFEROUS MINERALS IN THE QUATERNARY DEPOSITS OF THE BALTIC STATES AND BELARUS

Svetlana SHIMANOVICH[a], Tatyana KOLOSOVA[a], and Anto RAUKAS[b]

[a] Акадэмія навук Беларусі Інстытут геалогii (Institute of Geological Sciences, Belarus Academy of Sciences), Жодінская 7, 220141 Мінск, Беларусь (Belarus)
[b] Eesti Teaduste Akadeemia Geoloogia Instituut (Institute of Geology, Estonian Academy of Sciences), Estonia pst. 7, EE-0100, Tallinn, Eesti (Estonia)

Received 27 June 1994, accepted 20 October 1994

Abstract. The surface microtopography of ferriferous minerals (magnetite, pyrite, siderite, a.o.) of various origin was studied. Differentiation of these minerals, which are widely spread in the Quaternary deposits of the Baltic states and Belarus, is attempted based on micromorphological features. Ferriferous minerals impart valuable information on sedimentation processes and contribute to precise correlation of the deposits of different age and genesis. The concentrations of extraterrestrial magnetite globules and platelets in certain horizons of sediments probably favour the establishment of telecorrelations over rather vast areas.

Key words: micromorphology, ferriferous minerals, extraterrestrial magnetite globules and platelets, Quaternary deposits, Baltic states, Belarus.

INTRODUCTION

Ferriferous minerals (magnetite, pyrite, siderite, a. o.) enclosed in sediments impart valuable information on the genesis and secondary transformations of the Quaternary cover. The knowledge of typomorphological varieties of these minerals contributes to the reconstruction of geochemical and palaeoclimatic conditions of lithogenesis and offers good possibilities for lithostratigraphic correlations. Ferriferous minerals, even if present in low concentrations, provide new ideas about sedimentation processes and palaeoenvironments.

Our earlier paper (Shymanovich et al., 1993) dealt with meteoritic matter and microtektites in the surroundings of the Kaali meteorite craters (Saaremaa Island, Estonia). These craters were studied with an aim of contributing to the knowledge of extraterrestrial ferriferous spherules to help differentiate them from spherules of terrestrial origin. This paper discusses the results of a research into ferriferous minerals of different origin. Attempts are made to establish their similarities and differences and to develop some criteria for the differentiation of extraterrestrial formations and for establishing the role of some concrete exogenous agents in the transformation of ferriferous minerals. Higher concentrations of extraterrestrial magnetite globules and platelets in certain sedimentary sequences are helpful in finding chronostratigraphic guide levels. As to the Kaali meteorite impact on Saaremaa Island, we hope to find traces of that catastrophic event in the peat and marine sediments around.

Unfortunately, the long-term preservation of the meteoritic matter in sediments has proved possible only under favourable natural conditions and this hampers investigation.

In the Kaali area the soil both in the craters and around them contains, apart from meteoritic fragments, great amounts of pulverized and partly metamorphosed meteoritic matter. The areas of elevated concentrations of extraterrestrial matter also occur east of Kaali, and even on the Estonian mainland (Tiirmaa, 1984; Тийрмаа, 1988). Viiding (1965) found globules of meteoritic dust from Estonian Devonian and Cambrian sediments. These occurred in especially big amounts at a depth of 320 m in the Lower Cambrian sandstone in the Viru-Roela borehole. Such high concentrations of small magnetite—iocite globules (Ø 20—450 μ) or shell-like fragments (Ø up to 2—3 mm) warrant the supposition that a giant meteorite could have fallen in that area some 530 million years ago. The most complete Quaternary section in the East European Plain is in Belarus. It provides the best possibilities for finding some evidence of a meteorite fall in the area during the Quaternary and contributing to the knowledge of the impact activity through the history of the Earth.

The paper focuses on the PACT interdisciplinary research elucidating the environmental development and events that have been of importance in the prehistory and history of the Baltic region.

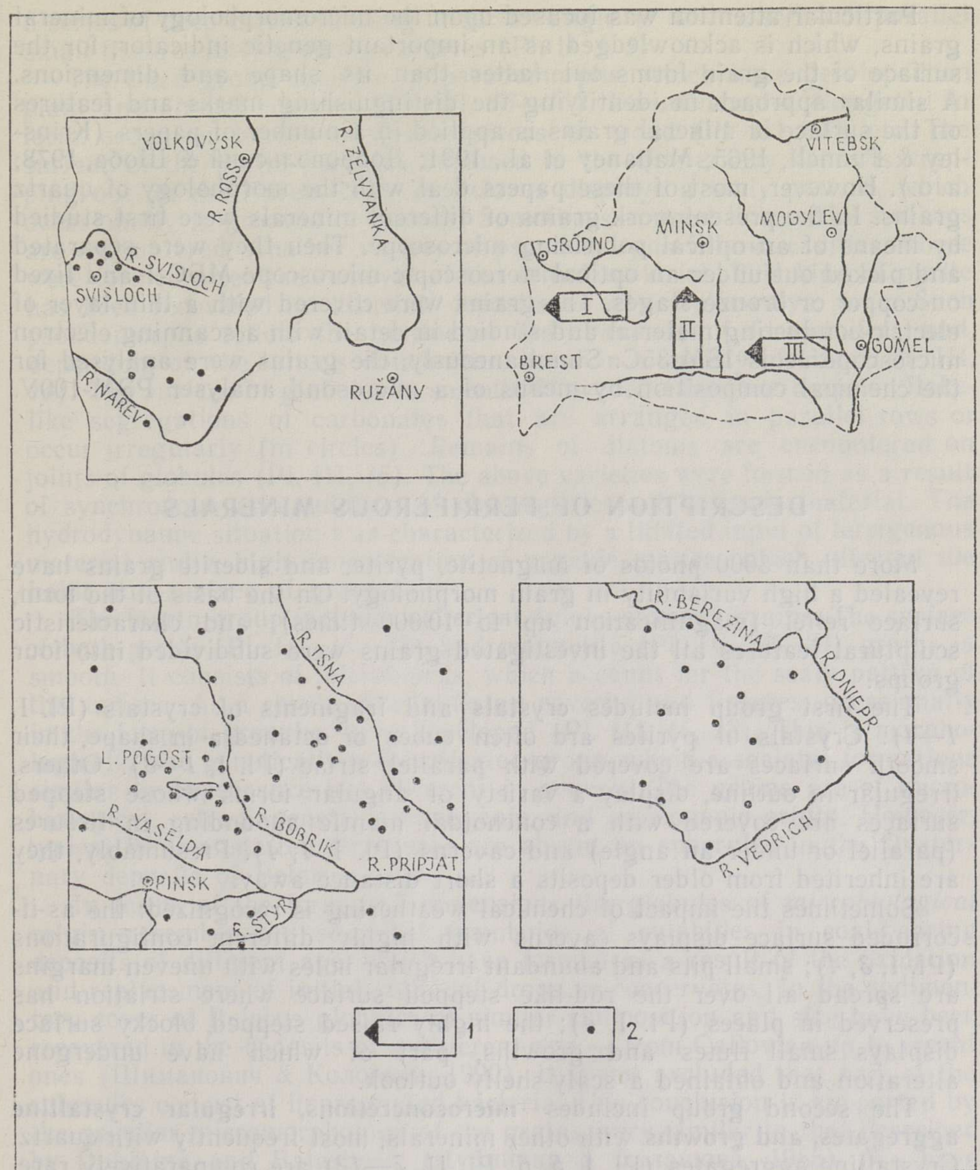
A SHORT DESCRIPTION OF SEDIMENTS AND MINERALS OF THE STUDY AREA

The territory of Belarus has a complicated geological structure and history. The Quaternary cover is up to several hundred metres thick and consists of glacial, glaciofluvial, lacustrine, alluvial, eolian and several other genetic types of deposits. All these deposits have been studied in considerable detail. Their mineralogical and geochemical peculiarities have been discussed in many papers. Both allothigenic and authigenic minerals occur in these deposits. A large variety of authigenic, mainly iron-bearing, minerals occur in lake and bog deposits but also in the flood-plain facies of alluvium. Though several researchers have been involved in the study of ferriferous minerals, the related problems are far from being settled.

The presence of more than half a hundred minerals and mineral groups has been ascertained in the Quaternary sediments of Belarus. The predominating minerals are quartz and feldspars. Micas and carbonates or clay—carbonate aggregates are also quite common. The associations of minerals in the heavy subfraction (>2.89 Mg/m^3) are represented by amphiboles, garnets, ilmenite, metamorphic minerals (disthene + sillimanite + staurolite), and epidote.

A number of general tendencies observed in the distribution of various minerals provide an excellent basis for solving stratigraphic problems. The content of garnets, amphiboles and epidote increases towards younger sediments and that of metamorphic minerals, ilmenite, leucoxene and, partly, zircon towards the older deposits. The greatest amount of authigenic minerals—pyrite, siderite, limonite, phosphates and carbonates (calcite + dolomite)—is concentrated in Lower Quaternary sediments, particularly lacustrine deposits. This is predominated by ferriferous minerals (pyrite, siderite, hematite, and hydrohematite, and magnetite), whose content ranges from low values in glaciofluvial deposits up to 83.6% (from the yield of the heavy subfraction of fine sand) in lacustrine deposits. A great variety of morphological types of minerals have been recorded. They differ in deposits of different genesis.

Mineral grains were studied in three areas shown in the Figure.



Areas of investigation (*1*) and location of the sampling sites (*2*). I, Narev—Svisloch; II, Pinsk; and III, Vedrich area.

METHODS OF INVESTIGATION

Ferriferous minerals, which, on the one hand, are capable of long-term preservation of traces of exogenous impact and, on the other, undergo morphological changes due to the alteration of the agent of weathering, were studied using various methods. In the field, the colour, form, and the state of the surface of larger particles were estimated visually or studied by means of a magnifying glass. Thin sections of consolidated rocks were analysed for colour, dimensions, form, surface pattern, character of micro-aggregates packing, etc.

Particular attention was focused upon the micromorphology of mineral grains, which is acknowledged as an important genetic indicator, for the surface of the grain forms out faster than its shape and dimensions. A similar approach in identifying the distinguishing marks and features on the surface of mineral grains is applied in a number of papers (Krinsley & Funnell, 1965; Mahaney et al., 1991; Добровольский & Шоба, 1978; a. o.). However, most of these papers deal with the morphology of quartz grains. In the present work grains of different minerals were first studied by means of an optical polarizing microscope. Then they were separated and picked out under an optical stereoscopic microscope МБС-1 and fixed on copper or bronze stages. The grains were covered with a thin layer of electric-conducting material and studied in detail with a scanning electron microscope Jeols ISM-35C. Simultaneously, the grains were analysed for the chemical composition by means of a microsond analyser РЭМ-100У.

DESCRIPTION OF FERRIFEROUS MINERALS

More than 3000 photos of magnetite, pyrite, and siderite grains have revealed a high variability in grain morphology. On the basis of the form, surface relief (magnification up to 10 000 times), and characteristic sculptural features all the investigated grains were subdivided into four groups.

The first group includes **crystals** and fragments of crystals (Pl. I, *1—4*). Crystals of pyrites are often cubes or octahedra in shape, their smooth surfaces are covered with parallel striae (Pl. I, *1—3*). Others, irregular in outline, display a variety of angular forms whose stepped surfaces are covered with a conchoidal mantle abounding in fissures (parallel or under an angle) and caverns (Pl. I, *1*, *4*). Presumably, they are inherited from older deposits a short distance away.

Sometimes the impact of chemical weathering is recognized: the as-if-corroded surface displays caverns with highly different configurations (Pl. I, *3*, *4*); small pits and abundant irregular holes with uneven margins are spread all over the rod-like stepped surface where striation has preserved in places (Pl. I, *4*); the highly raised stepped blocky surface displays small flutes and growths, part of which have undergone alteration and obtained a scaly-shelly outlook.

The second group includes **microconcretions, irregular crystalline aggregates, and growths** with other minerals, most frequently with quartz. Crystalline aggregates (Pl. I, *5*, *6*; Pl. II, *7—12*) are comparatively rare. Scanning electron microscopy views show the layered structure of the elongated prismatic formations accounting for the specific "ribbed" pattern of aggregate surfaces. Often hollows are found on the surfaces. Twinning usually takes place at the early stage of crystallization when two or more crystals grow into each other. The pyrite particles in Pl. I, *5*, *6* and Pl. II, *7*, *8* consist of intergrowths. Alteration of environmental conditions causes destruction and peeling of plates. This is followed by gradual smoothing of the surface up to the disappearance of apexes. The space between separate components increases. The lamellae surface of the pyrite in Pl. II, *7*, *8* displays tubercles that occur on different grains coating them almost entirely. Gradually the "emery" surface obtains a smooth block appearance. The appearance of the microconcretions and aggregates reflects the medium and conditions in which they were formed. Microconcretions may be rounded, prolate-rounded, or kidney-shaped (Pl. II, *9—11*). Aggregates and growths display a large variety of forms: angular, flattened, shapeless with irregular elongated block varieties, prolate with a series of deep cracks running under an angle, or with a series of parallel small fissures having emery surfaces (Pl. II, *1*, *2*).

The third group consists of **pseudomorphs**, which have developed on plant and animal remains (Pl. III, *13—15*). Pseudomorphs, elongated in form, occur on blades of grass, pieces of wood (Pl. III, *13*), etc. The surface of the pyrite particles enclosed in the Quaternary deposits cropping out on the Narev River in Belarus displays a scaly pattern, which occasionally is grooved or porous. Sometimes rugged lichen-like surfaces are encountered. Another variety of pseudomorphs fills in cavities. These were formed after the removal of the initial material. This kind of pyrite has been recovered in alluvial deposits of the Dobrovalya area. Such pseudomorphs follow the outline of the chambers of foraminifers and, depending on the latter's dimensions, occur in a variety of sizes (Pl. III, *14*). The surface of globules is smooth. However, there are drop- or flake-like segregations of carbonates that are arranged in parallel rows or occur irregularly (in circles). Remains of diatoms are encountered on joints of globules (Pl. III, *15*). The above varieties were formed as a result of synchronous accumulation of chemogenic and biogenic material. The hydrodynamic situation was characterized by a limited input of terrigenous material and a high concentration of organic matter, which affected the habit and surface of grains.

The fourth group includes **spherical** (globe-shaped) grains. The surface of both pyrite (Pl. III, *16—18*) and magnetite (Pl. IV, *19—24*) grains is smooth. It consists of microblocks, which account for the scaly pattern of the surface. As a result of weathering caverns and fissures, occasionally in the form of growths, have developed (Pl. III, *16*, *18*). This is morphologically and genetically a complicated group, which associates formations similar in appearance but different in genesis. The grains are of microbiological, retrodiagenetic, technogenic, and cosmogenic origin. However, typical Widmanstatten structures are absent on spherules in the Quaternary deposits of Belarus.

In terms of the form and dimensions the globules of *microbiological* origin resemble the so-called framboids of sulphides in coal-bearing deposits of different age, which have formed as a result of the oxidation and replacement of initial colloidal drops or coacervates. In the sedimentary cover of Belarus globules of similar composition and size have been recovered in the deposits of a different age — from Callovian up to recent ones (Шиманович & Колосова, 1990). It is not excluded that part of the spherules consist of impregnated bacteria. This conclusion is supported by the peculiar micromorphology of the grains, very similar to that described by Dubinina and Balashova (Дубинина & Балашова, 1985). We have detected this kind of magnetite very rarely. Besides, the scanning electron microscopy studies (Киршвинк et al., 1989) have shown that only the magnetosensitive bacteria are capable of forming magnetite crystals, the size of which ranges from 0.05 to 0.1 mm. These dimensions, as shown in the works dealing with the magnetism of rocks, correspond to a single magnetic domain.

Conditions are ideal for the formation of *retrodiagenetic ferriferous minerals* (Pl. III, *17*) when together with the newly-formed aqueous ferric oxide also ferrous oxide ions occur in the solution. The slower the rate of oxidation, the more complete and effective is the process of crystallization. As is known, this is promoted by weakly alkaline environmental conditions and a slight temperature rise. However, retarded synthesis can also take place in neutral and even slightly acid solutions.

Occasionally, the formation of magnetite is preceded by metastable phases of "green rust", which may arise either during the slow oxidation of ferrous oxide (solid phase) or precipitation of the corresponding carrier compounds whose further transformation is controlled by environmental conditions. The formation and development of Fe_3O_4 takes place when $Fe(OH)^+$ ions with a hydrocomplex of trivalent iron precipitate slowly within the thin layer outlining the embryonic nuclei. Outside this layer Fe_3O_4 oxidizes little by little up to the formation of magnetite. Such conditions are often created by industrial flows. We classified the globules formed in this way as technogenic. T. Kolosova and S. Shimanovich detected such globules in the embankment of the underground track in the town of Minsk, where they studied Quaternary deposits. They differ from each other in terms of anatomy, micromorphology, and internal structure (Pl. IV, *19*, *23*, *24*).

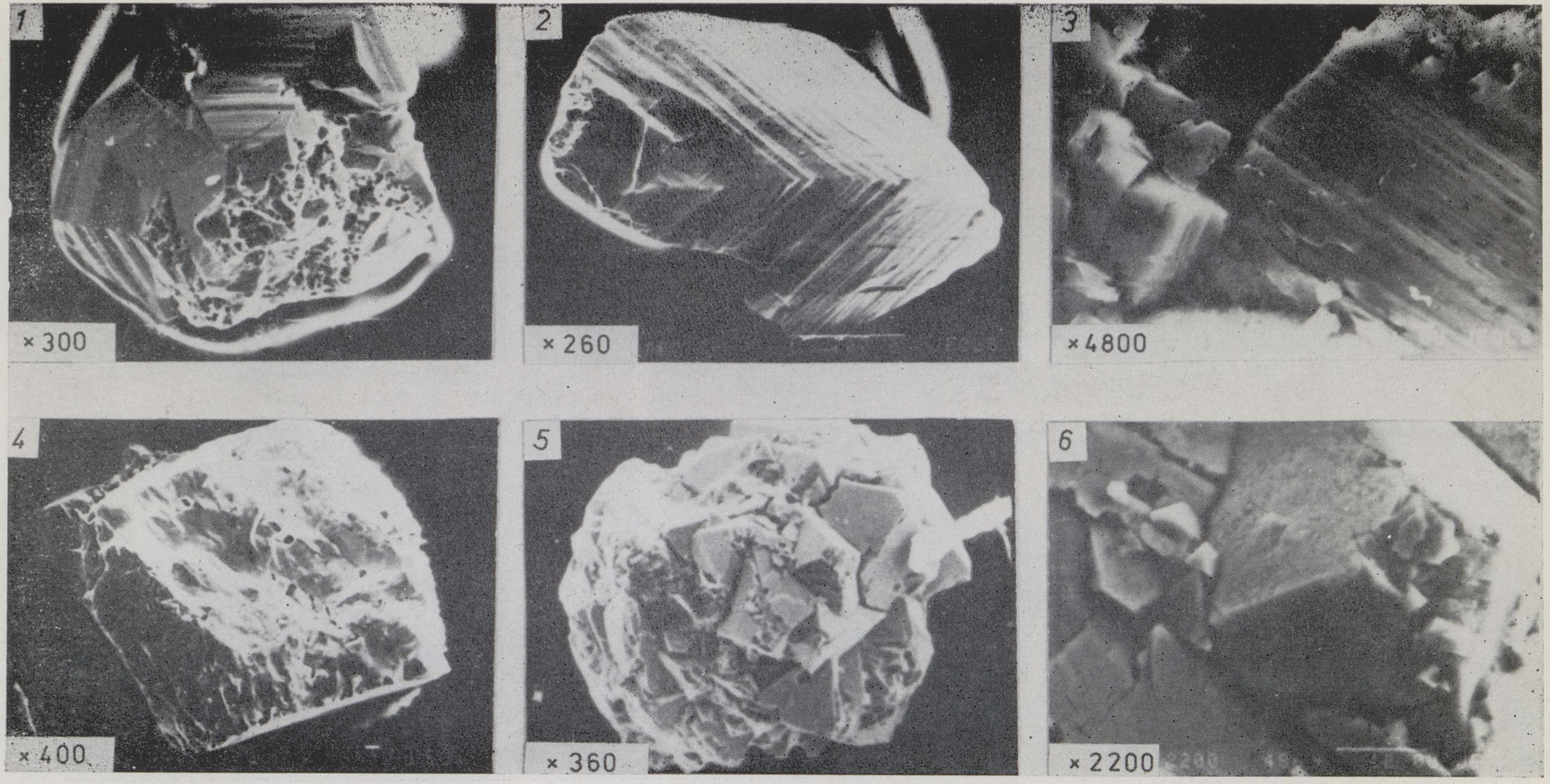
Part of the globules in the Kaali area of Estonia have a specific Widmanstatten surface indicative of their extraterrestrial origin. According to Dobrovolsky (Добровольский, 1988), spherules of magnetic iron oxide account for 10% of the (2—5) · 10^6 t of fine dispersed cosmic matter that reaches the Earth annually. Their size varies from microns to a few millimetres. According to Florensky (Иванов & Флоренский, 1969), (1—2) · 10^5 t of spherules (0.2—0.4 kg/km^2) falls from the outer space onto the Earth every year. Yudin and Kolomensky (Юдин & Коломенский, 1987) maintain that meteoric dust is formed during the movement of meteoric bodies in the atmosphere at a cosmic speed. Krinov's (1976) research showed the dust-tail of a bolide to be an accumulation of solidified drops—globules blown off from the melting surface of a meteoric body into the Earth's atmosphere. The spherules of the size of fine sand and silt, which we refer to this group of extraterrestrial matter, often have undergone corrosion. Such spherules are rather frequent and may provide a key to the correlation of sedimentary sequences in different regions.

Magnetite globules both in the surroundings of the Kaali meteoritic crater in Estonia and in the Quaternary deposits of Belarus vary in roundness, internal structure, and microsculpture of the surface (Pl. IV). Many of them are rather similar to extraterrestrial spherules in glacial sediments in the Beardmore glacial area in the East Atlantic (Hagen et al., 1990). The following varieties can be distinguished: spherical, rounded, elliptic, ovate-tubercular, oolitic or drop-like resembling a lemon. Occasionally, strongly crusted forms are encountered. In all likelihood, these are remains of elliptic globules. In terms of internal structure, the following forms can be distinguished:

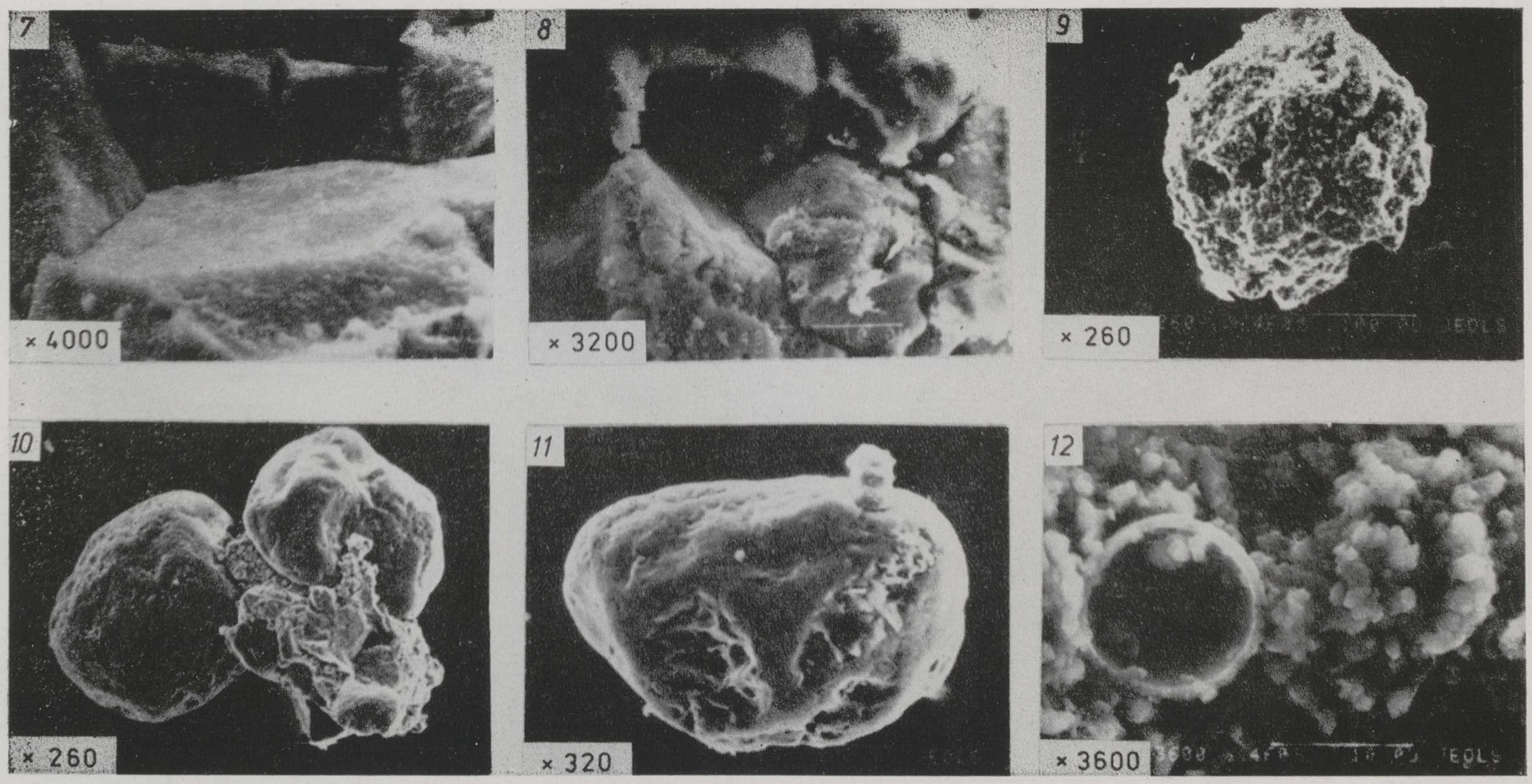
— hollow magnetite globules whose surfaces are covered with slightly irregular plates;
— compact globules with metallic nucleus, which may have Widmanstatten structures or be rod-like (elongated), resembling a prism structure;
— hypothetically rounded forms whose surfaces are covered with a pattern of regular moonlets resembling craters.

It should be stressed that if Widmanstatten structures are absent, it is hard to differentiate extraterrestrial ferriferous spherules from those of some other origin, e.g. products of volcanic eruption or sometimes even from spherules generated by industrial pollution. In that case labour-intensive microsond studies should be conducted to determine the composition of spherules.

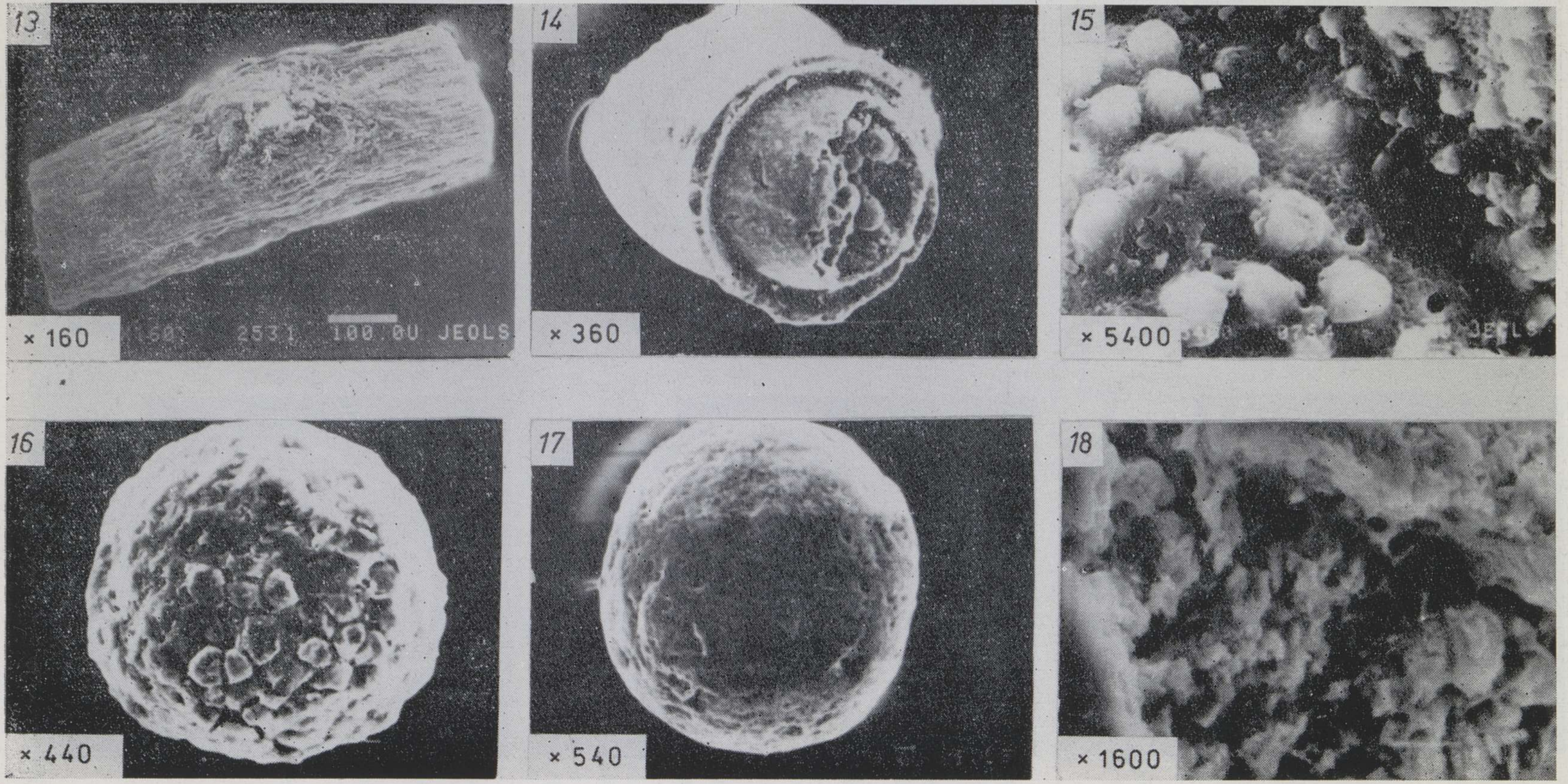
Research into ferriferous minerals has revealed great diversity of forms due to different facial and physico-chemical conditions under which they were formed. The studied morphotypes of grains and the character of changes on their surfaces are mostly determined by mechanical and chemical processes. Comparison of ferriferous minerals from different



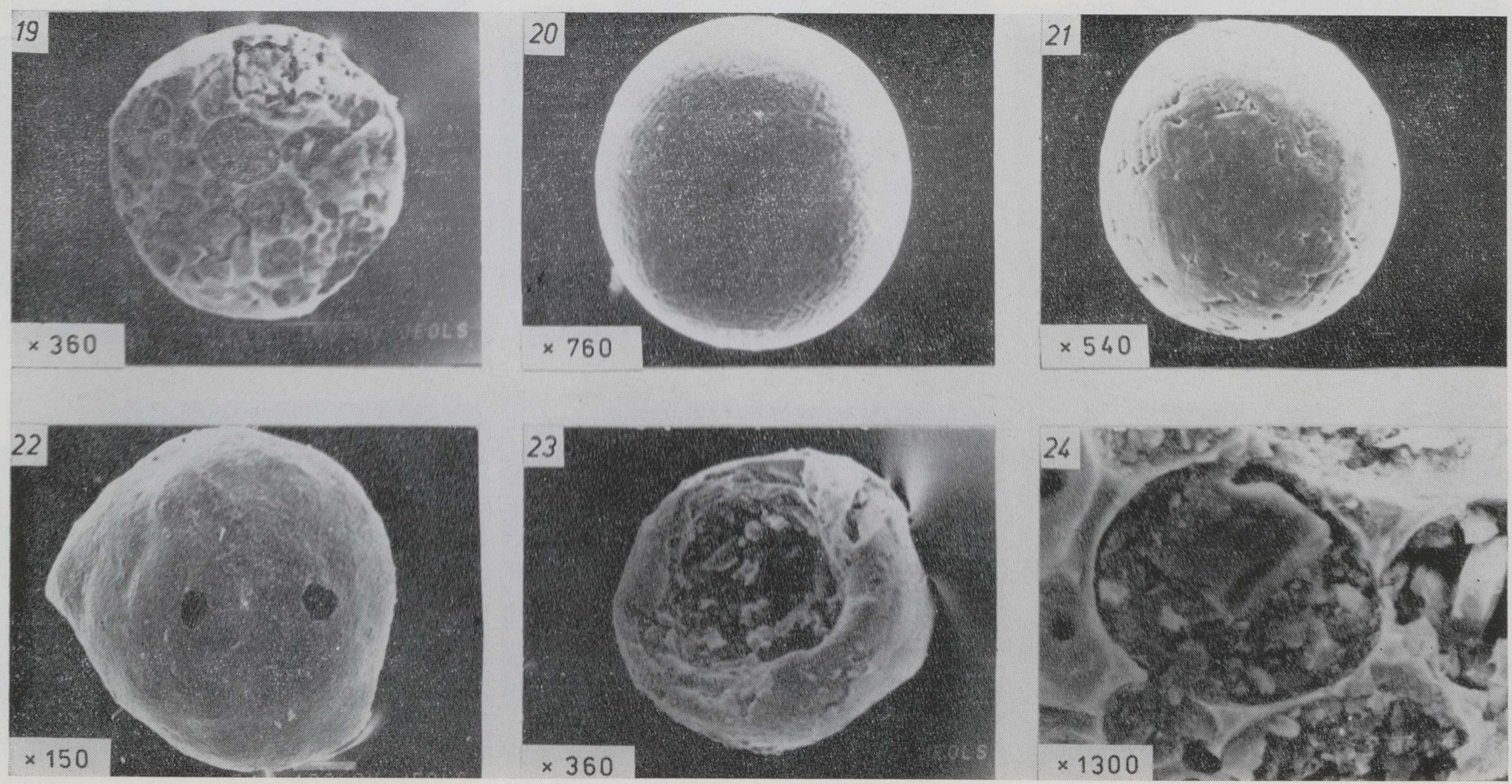
Forms of crystals and crystal particles of pyrites (*1*, *2*), their typical surface morphology (*3*, *4*), and characteristic crystalline aggregates of pyrite (*5*, *6*).



The characteristic surface morphology of crystalline aggregates of pyrite growths (*7, 8*), varieties of siderite aggregates (*9—11*), and their surface morphology (*12*).



Pseudomorphs of pyrite on organic matter and necroplankton (*13*, *14*) and their surface morphology (*15*); rounded forms of pyrite (*16*, *17*) and their surface morphology (*18*).



Varieties of magnetite spherules of different genesis (*19—23*) and their microtopography (*24*).

regions based on their micromorphological indices has enabled us to elucidate similar features, particularly in magnetites that are spherical in outline. The differentiated morphotypes facilitate correlation of deposits devoid of fauna. They also contribute to the resolution of problems related to the elucidation of the stages of volcanic and cosmic activity, determination of palaeogeographic situations of sedimentation, and further transformation of sediments in the course of lithogenesis.

ACKNOWLEDGEMENTS

The authors wish to thank Peter Kalinovsky for his help with microphotos and Helle Kukk for her help with the English language.

REFERENCES

Hagen, E. H., Koeberl, C. and Faure, G. 1990. Extraterrestrial spherules in glacial sediment, Beardmore glacier area, Transarctic mountains. — Contributions to Antarctic Research I. Antarctis Research Series 50, 19—24.

Krinov, E. L. 1976. Forms of nonterrestrial dust on the Earth. — Meteoritics, **11**, 1, 43—50.

Krinsley, D., Funnell, B. 1965. Environmental history of sand grains from the Lower and Middle Pleistocene of Norfolk, England. — Quart. J. Geol. Soc. London, **121**, 435—561.

Mahaney, W. C., Vaikmäe, R. and Vares, K. 1991. Scanning electron microscopy of quartz grains in supraglacial debris, Adishy Glacier, Caucasus Mountains, USSR. — Boreas, **20**, 395—404.

Shymanovich, S., Kolosova, T., Raukas, A. and Tiirmaa, R. 1993. Extraterrestrial spherules in the surroundings of Kaali meteorite craters (Saaremaa Island, Estonia). — Proc. Estonian Acad. Sci. Geol., **42**, 3, 127—133.

Tiirmaa, R. 1984. Kaali meteoriidiainet otsimas. — Eesti Loodus, 9, 571—576.

Viiding, H. 1965. Vanima meteoorse tolmu leid Eestis. — Eesti Loodus, 5, 293—296.

Добровольский Г. В. 1988. Биохимия — поиски и проблемы. — Природа, 2, 68—73.

Добровольский Г. В., Шоба С. А. 1978. Растровая электронная микроскопия почв. Изд-во Моск. ун-та, Москва.

Дубинина Г. А., Балашова В. В. 1985. Микроорганизмы, участвующие в круговороте железа и марганца и их применение в гидрометаллургии. — In: Биогеотехнология металлов. ГКНТ, Москва, 145—161.

Иванов А. В., Флоренский К. П. 1969. Мелкодисперсное космическое вещество из нижнепермских солей. — Астрономический вестник, **3**, 1, 45—49.

Киршвинк Дж., Джонс Д., Мак-Фадден Б. (eds). 1989. Биогенный магнетит и магнеторецепция. Новое о биомагнетизме. Мир, Москва. (Translated from English.)

Тийрмаа Р. 1988. Площадное распределение распыленного вещества метеорита Каали. — Изв. АН ЭССР. Геол., **37**, 1, 43—46.

Шиманович С. Л., Колосова Т. Е. 1990. Микроморфология минералов железа плиоцен-плейстоценовых отложений Белоруссии. — In: Мелкие ценные минералы и их народнохозяйственное значение. Минск, 31—32.

Юдин И. А., Коломенский В. Д. 1987. Минералогия метеоритов. УНЦ, Свердловск.

BALTIMAADE JA VALGEVENE KVATERNAARISETETES LEIDUVATE RAUAMINERAALIDE MIKROMORFOLOOGIA VÕRDLEV ANALÜÜS SKANEERIVA ELEKTRONMIKROSKOOBI ABIL

Svetlana ŠIMANOVITŠ, Tatjana KOLOSSOVA, Anto RAUKAS

Püriit, sideriit, magnetiit ja teised rauda sisaldavad mineraalid aitavad korreleerida settekivimeid ning selgitada möödanikus olnud paleogeograafilisi tingimusi. Mineraalide uurimine skaneeriva elektronmikroskoobi abil võimaldas esile tuua arvukaid morfoloogilisi erimeid. Eriti huvitavad on pihustunud meteoriitse ainese leiud, mis võimaldavad täpseid telekorrelatsioone.

СРАВНИТЕЛЬНЫЙ АНАЛИЗ МИКРОМОРФОЛОГИИ ЖЕЛЕЗИСТЫХ МИНЕРАЛОВ ЧЕТВЕРТИЧНЫХ ОТЛОЖЕНИЙ ПРИБАЛТИКИ И БЕЛАРУСИ С ПОМОЩЬЮ СКАНИРУЮЩЕГО ЭЛЕКТРОННОГО МИКРОСКОПА

Светлана ШИМАНОВИЧ, Татьяна КОЛОСОВА, Анто РАУКАС

Пирит, сидерит, магнетит и другие железистые минералы — это характернейшие и очень информативные компоненты вещественного состава четвертичных отложений Прибалтики и Беларуси. С их помощью могут быть оценены некоторые геохимические и палеоклиматические условия литогенеза, проведены корреляционные построения. Встречаясь даже в небольших количествах, они служат ценным источником сведений о характере осадконакопления. В то же время особенности строения и сложная иерархическая организация структуры исследованных минералов обусловливают необходимость применения специфических подходов к их изучению. Последнее стало возможным благодаря растровой электронной микроскопии, позволяющей проводить исследования на микроуровне.

В работе рассматриваются формы эпигенетической концентрации железистых минералов (магнетита, пирита, сидерита и др.), в частности особенности морфологии их поверхности. Делается попытка сопоставить эти повсеместно встречаемые минералы из четвертичных отложений Прибалтики и Беларуси по микроморфологическим признакам.