Glaukonite from Deposits of Different Age in Mountain Crimea

A F Georgievskiy1, V M Bugina1
1Peoples’ Friendship University of Russia (RUDN University), Moscow, Russia

E-mail: georgievskiy-af@rudn.ru

Abstract. The article describes glauconites, which in stratigraphic section of the Crimean Mountains, are mainly localized among Alb-Cenomanian, Maastricht-Danian and Eocene deposits. The study of isolated mono fractions made possible to identify the characteristics of glauconites of different ages and different generations. Three generations are distinguished, reflecting a sequential series of glauconite transformation at different stages of sedimentary rock formation. Generations differ in density, electromagnetic, structural, and chemical properties. Together, they allow to consider glauconites as heterogeneous illite formations with a variable content of swelling smectite layers, replaced by “hard” illite packets. This led to stabilization of the glauconite structure and their self-purification from Mn, Ti, V, Cr, Ni, Co, Cu, Zn. At different stratigraphic levels glauconites also differ in trace contaminants. In Alb-Cenomanian glauconites V, Cu, Zn accumulate above Clark. Danian varieties are enriched in Cr and a little in V, and Eocene glauconites - Mn, Ni, Co, and B. The glauconite formation was an intermittent, multi-stage, recycling process. Their main mass was formed during diageneric crystallization of Al-Fe-Si gel. The process was repeatedly interrupted by sediments' rewashing and roiling by waves and currents. Then the glauconites formation renewed again in the form of microconcretions or of outgrowths, coatings, and shells over rewashed glauconite grains. The maximum concentration of glauconite occurred at elevated offshore areas during erosion and rewashing of glauconite-containing sediments, as well as in depressions below the wave erosion base. Diagenetic glauconite formation was optimally combined with the accumulation of glauconite grains, transported by sea heaving and currents.

1. Introduction

One of the potential industrial minerals of Crimea is glauconite, which is used in agriculture, in construction, in paint and varnish production, in medicine, and as technical sorbents. Dozens of domestic and foreign scientists have been studying that mineral. Thanks to their efforts, the basic structural and chemical features of glauconite became clear, possible depositional environments and conditions of their formation are shown [1-17]. According to modern concepts, glauconites occur at the main stages of lithogenesis, from the accumulation of sediments to their diageneric and catagenetic changes. However, the majority of glauconites are authigenic diageneric minerals from reduced sediments level [8, 18].

Among the platform complex of deposits of the mountain Crimea, Alb-Cenomanian, Maastricht-Danian and Eocene levels of glauconite accumulation stand out. Glauconite is concentrated in sandstones, concretionary phosphorites and limestones, where its amount varies from 10 to 60%
The aim of this work is a comparative analysis of the glauconites of different stratigraphic levels, as well as understanding their depositional environment and conditions of their accumulation. The factual material was sixty samples of Cretaceous-Paleogene rocks taken from bedrock of the northern slopes of the Crimean Mountains from Inkerman to Belogorsk.

2. Materials and methods

Samples of glauconite-containing sandstones, phosphorites and limestones were leached with weak acids with the release of insoluble residues, which, after mechanical screening and subsequent separation in heavy liquids, were subjected to magnetic and electromagnetic separation. The obtained glauconite fractions were studied by microscopic, chemical, spectral and X-ray methods. For analytical purposes, we used a POLAM L213M polarizing microscope, a DRON-4 diffractometer, a DFS-8 spectrograph, a Levenhuk 720B binocular microscope, and a SIM-1 separator. Analysis were performed in the laboratories of the RUDN University and the Alexandrov Experimental Methodological Expedition.

3. Results and discussion

Glauconite is represented by rounded grains, pseudo morphoses and microconcretions 0.01-0.7 mm, usually 0.15-0.25 mm in diameter. Light, bright, and dark green differences are distinguished, which differ in content of swelling smectite layers – packets in their crystal structure. From light green to dark green glauconites, the degree of their structure’s ordering increases, smectite layers are replaced by illite. It affects differences in chemical composition, density properties, magnetic susceptibility, and refractive index.

3.1. Glauconite with a density of 2.75 - 2.85 g/cm³

It is represented by dark green, almost black isometric grains and their fragments with a glossy surface, some of which are partially, and sometimes completely, covered with films of pale green or yellowish green glauconite substance. Grains are mainly rounded, but many of them have a “paw-like” or “bunch-like” structure, and traces of mud cracks. In thin sections, glauconite grains are brownish-green, with iron hydroxides illinitations, in polars crossed grains often have a pronounced microaggregate extinction and often surrounded by a thin pale green crystallized border. During electromagnetic separation using a SIM-1 separator, glauconite accumulates as an independent fraction at a current strength of 0.2 A. By the ratio of Fe and Al oxides, it can conditionally be attributed to a highly ferrous variety (Fe₂O₃/Al₂O₃ >> 2) of the mineral. The above noted morphological features allow us to consider this modification of glauconite as formations, most of which are rewash at place of their formation or redeposited from underlying sediments.

Two reflections with d = 10.10.2 Å and 3.32 - 3.34 Å which are reflections with indices 001 and 003, are distinguished on the diffractometric curves of glauconite. The second order is weakly expressed, which is typical for mica with a high content of Fe in the octahedra, and the presence of interplanar spacing d060 ~ 1.50 Å indicates the dioctahedral nature of the mineral [2, 12].

The observed first reflection with the values d(001) = 10.1–10.2 Å has a somewhat asymmetric shape with a fuzzy outline in the direction of small angles. When the sample is saturated with ethylene glycol, the parameter d(001) becomes equal to 9.9 Å. After the calcination, peak 001 acquires a symmetrical shape, and the interplanar distance (d(001)) increases to 10.0 Å. Given this, we can assume the presence of an insignificant (~ 10-15%) number of swelling layers in the mineral structure.

Consequently, according to the results of X-ray diffraction studies and considering chemical data, the considered glauconite is a highly ferrous dioctahedral hydromica (illite) of a 1M polymorphic modification containing about 10-15% montmorillonite packets.

3.2. Glauconite with a density of 2.6-2.75 g/cm³

It is bright green, observed in the form of light-colored microconcretions - globules, redeposited microconcretionary grains, mineral and biogenic pseudo morphoses, and it also fills the channels of
sponge spicules, cavens from leached foraminifera, and cracks in quartz grains. Microconcretions have an irregularly isometric shape, a bunch-like or kidney-shaped structure complicated by syneresis cracks. In thin sections, they are “paw-like” and have distinct aggregate polarization. Some of them have traces of compression, while others have a crystallization rim along the periphery. The same rim, but in relics form, is preserved in rewash glauconite microconcretions. The rounded and sometimes the elastic shapes are typical for them. Glaucnite bio morphoses has the same aggregate polarization as in microconcretions and repeats to the smallest detail structural elements of substituted shells of various foraminifera. Sometimes it develops in the pores and channels of the remnants of echinoderms and spicules of the sponges, or it occurs in the form of small balls - casts from single-chamber foraminifera. Mineral pseudomorphs of glauconite on mica scales and plagioclase grains look differently. In these cases, the mineral is characterized by weak pleochroism, single crystal extinction, and birefringence within the range of Ng - Np = 0.027. When interacting with electromagnetic fields, bright green glauconite is separated at a current strength of 0.3 - 0.4 Å. By the ratio of Fe and Al oxides, it can conditionally be considered as a ferruginous variety of the mineral (Fe₂O₃/Al₂O₃ ~ 2.0). On the X-ray diffractograms of the oriented natural preparations, a distinct asymmetric, which flattens towards small angles, is recorded, the first reflection 001 with values of 10.5–11.2 Å. When saturated with ethylene glycol, two reflections with maximum of 17.2-17.5 Å and 9.5-9.7 Å arise. Calculation of the samples leads to a decrease in interplanar distance to 10 Å while maintaining the reflection of 3.33-3.34 Å. Such features of the diffraction patterns indicate that this type of glauconite is heterogenous and is a mixed layer illite - montmorillonite formation with an ordered structure of the 1M polytype, where phases with a swelling packet content of about 40-50% dominate [21,22].

3.3. Glaucuite (glaucinite-like mineral) with a density of 2.55 - 2.6 g/cm3
It is characterized by a pale and yellowish-green colour and forms poorly formed roundish or incorrectly isometric microconcretions - globules that are closely associated with secretions of clay matter. In thin sections, they are yellowish-green, with microaggregate polarization, sometimes almost isotropic, often with syneresis cracks, often have fuzzy “blurry” contours. In some cases, there are grains - microconcretions with signs of rewashfing. On the SIM-1 separator, glauconites are separated into an independent fraction at a current strength of 0.4–0.5 Å. The study by x-ray methods showed that the latter are complex heterogeneous formations, as evidenced by the nature of the diffractometric curves. In their analysis, along with the reflex typical of mica (d = 10 Å - 10.09 Å), the development of distinct basal reflections with dₘ(001) = 12.7 - 29.2 Å in small angles is observed. Saturation of samples with ethylene glycol increases interplanar spacings to 17.0 Å – 33.0 Å, and causes the conjugate appearance of additional reflexes with maxima in the range of 9.65 Å – 9.99 Å. After calcination the samples, the opposite effect occurs, and high-order reflections are compressed to 10.1 Å - 9.89 Å. Moreover, sample processing does not affect the shape and location on the profile of the diffraction patterns of the reflex with d ~ 10 Å. So, it should be concluded that the glauconite fraction with a density of 2.55 - 2.6 g/cm3 consists of a mixture of particles of illite, smectite and mixed-layer clay minerals. X-ray powder studies show that illites belong to the 1M and 1Md modifications (reflections 4.3, 3.65, 3.1 Å). The content of the noted clay phases in glauconites as a first approximation can be estimated by the ratio on the diffractometric curves of the areas occupied by the peaks of the main basal reflections (001) with d (001) = 10 Å, 12 Å - 17 Å, 27 Å - 29 Å [10]. The performed calculations show that the number of different phases varies markedly even within the same sample. At the same time, a tendency toward greater development of the smectite component in glauconites of the Alb-Cenomanian level is outlined, while at higher stratigraphic horizons, the illite (micaceous) part of them becomes the dominant phase of glauconite deposits. An additional idea of the nature of glauconites is given by the chemical composition of the fraction 2.55 - 2.6 g/cm3. They are low ferruginous formations where Fe₂O₃/Al₂O₃ ratio (1.0–0.4) reflects the fractional participation of smectite and illite phases in the structure of glauconite globules. Another important feature of glauconites is the internal heterogeneity of grains, reflecting the multi-stage history of their formation. In thin sections and under
the binocular, along with homogeneous grains, grains consisting of several varieties of glauconite are observed. Most often, in the central part of grains, dark green ferruginous glauconite is developed, which partially or completely grows bright or pale from the surface its green low-iron varieties (Figure 1). Often, the colour of the mineral and, consequently, the density and other properties change in the contours of one grain (Figure 2), and a thin (0.01-0.015 mm) crucifix of light coloured crystallized glauconite is formed along its periphery. There are also cases where the central part grain is composed of a glauconite-like clay mineral, and the outer shell is a glossy dark green, often almost black glauconite (Figure 3). Finally, glauconite grains and their fragments are found, in which a repeated cycle of substance growth is noticeable (Figure 4).

Figure 1. Pale bright and dark green varieties (generations) of glauconite. White quartz grains. Thin section. Plain polarised light. Field of view 2mm.

Figure 2. Complex transitions inside the grain of different phases of glauconite substance during its diagenetic and catagenetic changes. Thin section. Plain polarised light. Field of view 1mm.

Figure 3. An angular-rounded grain. Its central part is pale, and its edges are dark-coloured glauconite substance. Thin section. Plain polarised light. Field of view 1.5 mm.

Figure 4. A rounded grain of dark green glauconite, with a clear newly formed border of bright green glauconite. Thin section. Polar crossed. Field of view 0.25mm.

Glauconites of varying degrees of conversion and various stratigraphic levels differ in microelement composition. In Alb-Cenomanian deposits, glauconites above Clark accumulate V, Cu, Zn. At the Danian, they are enriched in Cr and, to a little in V, and in the Eocene sediments - Mn, Ni, Co, and B. However, in general, Crimean glauconites are comparable in terms of trace amounts to glauconites from other regions [23].

The behaviour of trace elements during the formation of glauconite microconcretions is different. Light green glauconites differ from bright green in increased concentrations of all other trace elements, except for Ga and B. This trend persists for dark green glauconites, which is clearly seen in Ti and V. At the same time, alignment with other elements is observed their contents or even some concentration (Cr, Cu, B). Thus, when light green glauconites turn into bright and dark green, they self-clean from microelements at the beginning, and then, at the stage of conversion of bright green glauconites to dark green, they accumulate again. The highest concentration of many trace elements in the light green differences is due to the high proportion of swellable layers of packets with impurities in the interlayer space. As the structural homogeneity increases and the mineral transforms into bright green glauconite, the swellable layers are replaced by compact hard micaceous packets, which leads to the “squeezing” of trace elements from the inter-packet space. Their enrichment of already dark green glauconites is probably associated with the sorption of trace elements on the surface of glauconite particles.

The most of glauconites, by their origin, are microconcretionnairy formations and passed the gel stage, being initially in a colloidal state. This is evidenced by globular and colloiform characteristic of many glauconite microconcretions in the form of “paws”, “kidneys”, “trefoils” with syneresis cracks. They generated in non-lithified heavily flooded silts, the waters of which, along with other elements, were saturated with molecular and colloidal solutions of Fe, Si and Al oxides. These compounds
mutually coagulated and precipitated each other with the subsequent formation of mixed gels in the form of gelatinous micro bunches. During their deposition, colloids captured pelitomorphic particles of the sediment and, therefore, the resulting gel glauconite coagulate were a complex mixture of chemically and mechanically deposited components. Depending on the nature of the depositional environment and under the influence of surface tension, the coagulates took various rounded colloform globular forms or repeated the forms of the filled pore space. Subsequent aging of the glauconite gel was accompanied by its compaction and partial crystallization, resulting in the formation of several mixed-layer (illite - smectite) clay formations and the generating microconcretions were cleaned of foreign particles.

The maximum concentration of glauconite was achieved in elevated areas of the seabed during erosion and "rewashing" of glauconite-containing sediments, as well as in lowering of the relief below the wave erosion base. Diagenetic glauconite formation was optimally combined with the accumulation of glauconite grains, which were carried there by waves and currents. Glaucnite formation ended with the formation of branching thin veinlets and veins of glauconite mineral, which, crossing the rock, bend or envelop its dense inclusions (small pebbles, gravel and sand grains, as well as phosphate concretions and organic residues). Such morphological features of the veins show that they were most likely formed in the initial stages of catagenesis, when microcracks appeared in the dehydrated pelitomorphic cement substance of newly formed rocks. Squeezed silt solutions with colloidal Al-Fe-Si matter entered within those cracks and formed the veins.

4. Conclusions

- The formation of glauconites was an intermittent, multi-stage, recycling process. The globular and colloform glauconites indicate that its secretions passed through the gel stage and were initially in a colloidal state.

- Glaucnite is a heterogeneous illite formation with a variable content of swelling (smectite) packets. While ordering its crystal structure, the proportion of those packets in the mineral structure decreases. Glaucnites with a density of 2.55 - 2.6 g/cm³ make up an isolated group. They are a two- or three-phase finely divided mechanical mixture of smectite, mixed-layer and illite clay minerals.

- The established relationship between the density, electromagnetic, and structural properties of glauconites indicates that as the density in the chemical composition of minerals increases, the ratio between the oxide and nitrous forms of iron progressively increases. This, obviously, reflects a slight increase in the medium of glauconite formation of the redox potential, which stimulates the occurrence of weakly oxidative processes.

- Since glauconites with different density properties can spatially separate not only within one layer, but even in a thin section, the conclusion is drawn about the extremely unbalanced state of the sediment and the extremely various, almost dotted changes in its values of Eh during the period of glauconite accumulation.

- The close association of different glauconite phases with each other (intergrowths, growths, shells, rims) shows that, during their formation, sediments, along with Eh, also remained very heterogeneous and mobile in relation to pH, cationic composition and concentrations of silt waters.

- The placement of practically significant concentrations of glauconite was controlled by geomorphological features of the bottom of the sea basin.

5. References

[1] Gorbunova L I 1973 Glaukonit fosforitonsnyh otlozhenij mezozoja central'nyh rajonov Russkoj platformy in Genetic types of sedimentary mineral deposits (Moscow: Publishing House Nedra) pp 61-75 https://search.rsl.ru/ru/record/01007255477

[2] Dric V A, Saharov B A 1976 X-ray diffraction analysis of mixed-layer minerals (Moscow: Publishing House Nauka) 255 p https://search.rsl.ru/ru/record/01006931685
[3] Shutov V D, Kac M Ja et al 1975 Kristallohimija glaukonita kak indikatora facial'nyh uslovij ego obrazovaniya i posledstvennogomnogno izmenenija in Crystallochemistry of minerals and geological problems (Moscow: Publishing House Nauka) pp 74-80 https://search.rsl.ru/ru/record/01006990933

[4] Ivanovskaja T A et all 2015 Globuljarnye sloistye silikaty glaukonit-illitovogo sostava v otlozhenijah verhnego proterozoja i nizhnego kembrija Lithology and Mineral Resources №6 pp 510-537 https://www.elibrary.ru/item.asp?id=24187449

[5] Kazakov A V 1991 Geochemistry of minerals and geologicheskei usloviya obrazovaniya glaukonitov i ih indikatornoe znachenie v osadochnom processe Trudy Gosudarstvennogo instituta gornohimicheskogo syr'ja N81 pp 56-85 http://webirbis.spsl.nsc.ru/irbis64r_01/cgi/cgiirbis_64.exe?P21DBN=GG&I21DBN=GG_PRIN T&S21FMT=fullw_print&C21COM=F&Z21MFN=475585

[6] Kossovskaja A G, Dric VA 1971 Voprosy kristallohimicheskoj i geneticheskoj klassifikacii sljuzistyh mineralov osadochnyh porod in Epigenesis and its mineral indicators (Moscow: Publishing House Nauka) pp 71-95 https://search.rsl.ru/ru/record/01007048290

[7] Nikolaeva I V 1977 Minerals of the glauconite group in sedimentary formations (Novosibirsk: Publising House Nauka) 332 p https://search.rsl.ru/ru/record/01007691514

[8] L.S. Dric VA 1974 Glaukonit kak diageneticheskoe obrazovanie reducirovannyh zony okeanicheskih osadkov Lithology and Mineral Resources №6 pp 3-19

[9] Logvinenko N V, Nikolaeva I V, Orlova L V 1988 K voprosu o genezise glaukonita in Composition and properties of clay minerals and rocks (Novosibirsk) Issue 4 pp 53-60 https://search.rsl.ru/ru/record/01001433046

[10] M. Zh 1968 Clay geology (Leningrad: Publishing House Nedra) 359 p http://www.geokniga.org/books/7057

[11] Georgievskiy A F, Bugina V M 2005 K voprosu ob uslovijah obrazovaniya glaukonitov Gornogo Kryma Bulletin of RUDN University Engineering Researches 2 pp 120-123

[12] Rateev M A, Gradusov B P 1971 Tipy smeshannoslojnyh obrazovanij sljuda – montmorillonitovogo rjada v metabentonitah silura – ordovika Pribaltiki Lithology and Mineral Resources 2 pp 74-94 https://www.elibrary.ru/item.asp?id=9934406

[13] Burst J F 1958 Mineral heterogeneity in «glauconite» pellets. Amer. Mineralogist vol. 43 5-6 http://www.minsocam.org/msa/collectors_corner/amtoc/toc1958.htm

[14] Richard C Selley, Robin M Cocks, Ian R Plimer 2005 Encyclopedia of Geology (Elsevier) pp 542–548 https://b-ok.cc/book/571447/68d628

[15] López-Quirós, Adrián & Sánchez-Navas, A. & Nieto, Fernando & Escutia, Carlota 2020 New insights into the nature of glauconite American Mineralogist 105 674-686 https://www.researchgate.net/publication/338629533_New_insights_into_the_nature_of_glauconite

[16] Malstrom N, Grandstaff D 2018 X-ray diffraction analysis of glauconite interlayer thickness: a new method of assessing glauconite maturity https://gsa.confex.com/gsa/2018NE/webprogram/Paper311177.html

[17] Zhang Xiaoke & Cai, Yuanfeng & Jiang, Dongmei & Zhang, Yang & Pan, Yuguang & Bai, Liujuan 2017 PREPUBLICATION: An experimental study on transforming montmorillonite to glauconite: implications for the process of glauconitization Clays and Clay Minerals 65 10.1346/CCMN.2017.064081 https://www.ingentaconnect.com/content/ccm/2017/00000065/00000006/art00006

[18] Strakhov N M 1962 Fundamentals of the theory of lithogenesis (Moscow: Publishing Youse of the Academy of Sciences of the USSR) V1 133 p https://search.rsl.ru/ru/record/01008287994

[19] Bugina V M 2007 Perspektivy fosforitonosnosti i osobennosti litologicheskogo sostava otlozhenij mel- paleogenovogo osadochnogo chehla Gornogo Kryma Moskva avt dis 240 p
https://www.dissercat.com/content/perspektivy-fosforitonasnosti-i-osobennosti-litologicheskogo-sostava-otlozhenii-mel-paleogen

[20] Shehotkin V V 1977 Litologiya pogranichnykh otlozhenij mela i paleogena gornogo Kryma i svjazannye s nimi poleznye iskopaemye Khar’cov avt dis 258 p https://search.rsl.ru/ru/record/01009558238

[21] Kubler B 1961 Sur guelgues interstratifies irreguliers mica-montmorillonite Bull.Serv. Carte geol. Alsace et Lorraine t.14 4 https://www.persee.fr/doc/sgeol_0037-2560_1961_num_14_4_1237

[22] Lucas J 1962 La transformation des mineraux argileux dans la sedimentation etudies sur les argiles du trias Memoires du serv.Carte geol. d Alsace et Lorraine 23 https://www.persee.fr/doc/sgeol_0080-9020_1962_mon_23_1

[23] Arhipenko D K, Nikolaeva I V 1981 Mineralogy and Geochemistry of Glauconites (Novosibirsk: Publishing House Nauka) 120 p http://www.geokniga.org/bookfiles/geokniga-mineralogiya-i-geohimiya-glaukonita.pdf