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MODERN MINERAL FORMATION IN EXOGENOUS SYSTEMS OF CRIMEAN PENINSULA

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СУЧАСНИЙ МІНЕРАЛОГЕНЕЗ В ЕКЗОГЕННИХ СИСТЕМАХ КРИМСЬКОГО ПІВОСТРОВА

Propagation, morphology and mineral composition of the main systems of modern water-chemogenic mineral formation in the Crimea is investigated. The features of this process in the salt lakes, mud volcanoes, caverns and in areas of chemical weathering of volcanic rocks of Cape Fiolent are reviewed. In the composition of modern exogenous polymineral formations there are 38 mineral types.
Keywords: mud volcanoes, salt lakes, water-chemogenic mineral formation, polymineral aggregates, Crimean Peninsula.

Досліджено поширення, морфологію та мінеральний склад основних систем сучасного водно-хемогенного мінералогенезу на території Криму. Розглянуто особливості цього процесу в солених озерах, грязьових вулканах, карстових порожнинах та на ділянках хімічного вивітрювання вулканітів мису Фіолент. У складі сучасних екзогенних полімінеральних утворень встановлено 38 мінеральних видів.
Ключові слова: грязьові вулкани, солені озера, водно-хемогенний мінералогенез, полімінеральні агрегати, Кримський півострів.

INTRODUCTION

Crimea is a region of active development processes of modern water-chemogenic and supergene mineral formation. These processes accomplish in different systems of mineral formation and are characterised by different mineral associations. On the one side, mineral formation is controlled by regional factors behind the plane tectonic and deep factors, but on the other side – features of lithological content and intensity of exogenous processes.

Previous researches prove that mud volcanoes, distributed on land and in the waters of the Black and Azov seas, have significant influence on the processes of modern mineral formation. They supply enormous amount of terrigenous clastic material, gases and mud treatment at discharge zone. Products of mud volcanoes affect both the course of chronicle and under favorable conditions, become a source of many water-chemogenic polymineral neocrystallisation.

One of the favorable factors of modern chemogenic mineral formation in the Crimean region is climate. It creates an opportunity of deposition of mineral aggregates from supersaturated solutions and accelerates the process of dissolution, hydrolysis and hydration, that is also supported by new mineral creation.

Processes of modern mineral formation specify the activity of geological processes of the region and open opportunities of reconstructing the development of territory in the past.

RESEARCH METHODOLOGY

The authors conducted field work in mountainous and steppe Crimea, Kerch Peninsula and seaside zones of the Black and Azov seas during 2008-2013 years. Research covered mud volcanoes, salt lakes, oxidation zone of cape Fiolent volcanoes and Crimea mountain karst cavities. The most attention was paid to Kerch Peninsula, as a territory with the most expressed processes of modern water-chemogenic mineral formation. During the works all active mud volcanoes and salt lakes of peninsula were examined.

Samples (over 200 pieces) for the laboratory studies were taken particularly in the spots of mineralization and packed in hermetic glass containers for reservation and transportation. Choosing the samples was obligatorily supported by measuring air and water temperatures.

Laboratory studies were based on macro- and microscopical study, X – ray diffraction analysis, dissolution and crystallisation experiments, chemical analysis of waters and gases, electronic microscopical research.

Macro and microscopical research were held in Taras Shevchenko National University of Kyiv using binocular (MBS-9) and polarization microscopes (Polam S-112). Immerse method was widely used for fine – grained formations diagnostics. Experiments of dissolution and crystallization were held under the temperature of 20 degrees C° and pressure 760 mm. Distilled water was used for dissolution.

X-ray diffraction analysis was held in the laboratories of Taras Shevchenko National University of Kyiv (analyst candidate of geological sciences S.P. Saveniuk) and Institute of Geochemistry, Mineralogy and Ore Formation NAS of Ukraine (analyst candidate of geological and mineral sciences O.Y. Hrechanovska). Research was performed by diffractometer DRON -3 with copper anodes. For mineral phases diagnostics American etalon card file PCDFWIN v.2.0 (ICDD, JCPDS 1998 and 2001 yrs.) was used. The complexity of diagnosing of hydrate mineral phases was that during the sample preparation it was grated in a mortar, what led to partial loss of crystallization water.

Electronic microscopical research was held in Institute of Geochemistry, Mineralogy and Ore Formation NAS of Ukraine (JSM-6700F, operator I.V. Hurnenko), Institute of Geological Sciences (JSM-6490 LV, operator – V.V. Permyakov) and Institute of Geology and Mineralogy at Siberian Department of Russian Academy of Sciences (SEM – LEO 1430VP, operator A.T. Titov). Samples under investigation were treated with carbon, gold and platinum ions.

RESULTS AND ANALYSIS

The main modern exogenous mineral formation systems of Crimea are salt lakes and mud volcanoes. In the supergene zone modern minerogenesis appears less.

Salt lakes. Currently in Crimea there are about 300 salt lakes. According to genetical signs they are divided into two types: inner and coastal. Territorially they are divided into four major groups: Eupatorian, Tarhankut, Perekop and Kerch group (Dzens-Litovskiy, 1962).

In salt lakes of Crimea water-chemogenic mineral formation is fixated almost ubiquitously. Mineralization of Crimean salt lakes varies from 40 to 300 g/l. Less mineralization is a characteristic for coastal lakes, but more frequent for inner lakes.

As a landfill object for the investigation of processes of modern minerogenesis in salt lakes a group of lakes in Kerch Peninsula, as a region with most contrasty demonstration of this process has been chosen.

Activisation of mineral formation in lakes comes during hot and draining periods of year. At the surface of division of bottom deposits and water, the salt leakage in a form of shiny and smooth crusts, membranes, granular, flourlike and even crystallic masses appear. In separate lakes such formations occupy the complete water surface. The thickness of salt cover can vary from few millimeters to 5 cm and more. It's output grows from coastline to central parts. In most drying lakes salt formation captures also the upper layer of sludge and therefore new formed minerals pierce through and cement feeble sediment under the depth of 10 cm.

The color of secretions is mainly white, rarely pink with different shades, sometimes grayish -blue. Coloristic zonality is often noted, and it is objected in change of color of the salt layer from edging parts to the centre of the water.

Water-chemogenic new formations of salt lakes have polymineral content, utility quantities correlation of certain mineral phases for different types of waters is variable.

In the composition of Kerch Peninsula salt lakes polymineral aggregates 6 minerals were diagnosed: halite, gypsum, mirabilite, thenardite, astrakhanite, hydroglauberite (Nesterovskiy, Deyak, 2010; Nesterovskiy, Deyak, 2011). Main forms of their output are shown on Fig. 1.

In inner lakes dominates mainly sulfate mineral formation, and in coastal – halide.

Mud volcanoes. Crimea is included in one of the biggest mud volcanic provinces of the world — Kerch – Tasman. It has more than 80 mud volcanoes. There are 17 active mud volcanoes in Kerch Peninsula. They all are in gas – gryphon stage of development. They supply the surface of the ground with liquid mud, gas and water. The last of mentioned is unloaded on the slopes of the hills, flows down to the lowered parts of relief. The debit of hill waters in a whole is negligible, but their mineralisation varies from 2,4 to 25 g/l and more. The saltiest are the waters of Bulganatsky volcano, with mineralization up to 47g/l. All hill waters are boron enriched (0,1-4g/l). pH of hill waters is 6,9-8,5, the average temperature at the exit of a crater is about +19-21°C. The summer temperature of the air near volcanoes riches 45-50°C(July).

Water-chemogenic formations are concentrated around hill craters, salses, gryphons, water sources and along the unloading flows. They have quite a various morphology and are represented by crusts, flower – like and cluster – like aggregates, dendrites, earthy compounds (fig.2).

In the composition of the new polymineral aggregates of the Kerch Peninsula mud volcanoes there are 20 minerals established. They are represented by borates (borax, tincalconite, probertite), carbonates (calcite, dolomite, northupite, gaylussite, pirssonite, nesquehonite, trona), sulfates (gypsum, astrakhanite, epsomite, hexagydrite, pentahydrite, sanderite, thenardite, mirabilite), nitrates (nitratine), chlorides (halite).

Mineral associations for different volcano groups are different, but they mainly correlate to the

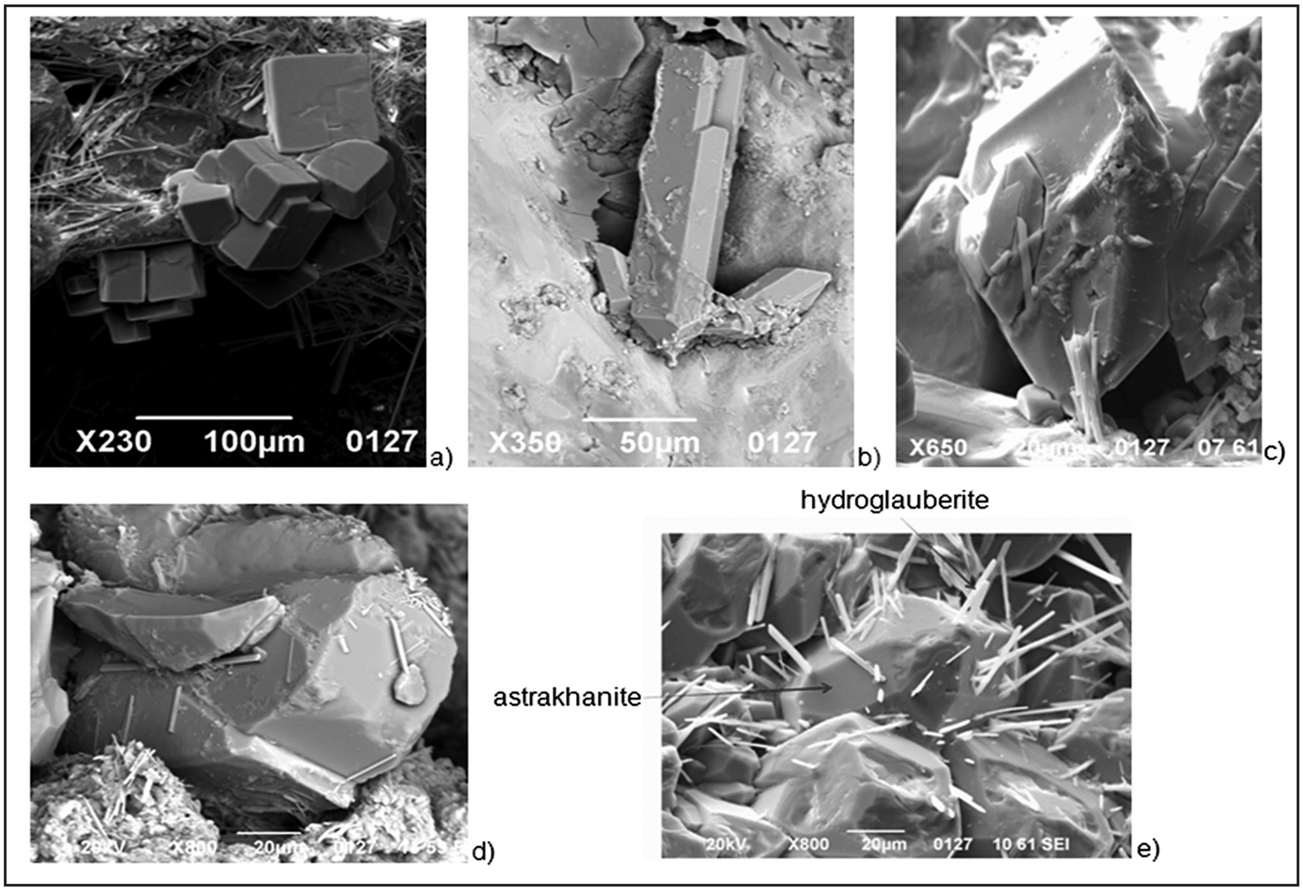

Fig. 1. Salt lakes minerals of Kerch Peninsula:
a – halite; *b* – gypsum; *c* – thenardite; *d* – astrakhanite; *e* – hydroglauberite.

chemical composition of hill waters. For the major types of hill waters of the Kerch Peninsula we have determined such mineral associations as:1) chloride-hydrocarbon- sodium – calcite, dolomite, borax, thenardite, halite, trona, northupite, pirssonite, gaylussite, nitratine; 2) hydrocarbon – chloride – sodium – calcite, borax, thenardite, halite, trona, northupite, pirssonite, gaylussite;3) sulfate – chloride – magnesium – epsomite, hexagydrite, halite, gypsum; 4) chloride-sulfate-hydrocarbon – sodium – epsomite, hexagydrite, halite, gypsum; 5) hydrocarbon -nitrate – sodium – epsomite, hexagydrite, halite, thenardite, gypsum; 6) sulfate – hydrocarbon-sodium – magnesium – epsomite, hexagydrite, halite, gypsum.

The most spreaded types of hill waters in the Kerch Peninsula are chloride-hydrocarbonate- sodium and hydrocarbon – chloride -sodium. The maximal quantity of mineral associations is connected to them particularly. The constant component of polymineral aggregates of all types is halide.

Among the minerals studied – northupite, gaylussite, pirssonite, nesquehonite, sanderite are rare and new for the Ukrainian territory (fig. 3).

Mineral formation in volcanic oxidation zone. In recent years, in borders of Mountainous Crimea numerous formations of modern various crystalline hydrates and main sulfate salts Na, K, Ca, Mg, Mn, Zn, Al, Ba, Cu, Pb etc, connected to the oxidation zone of sulfide mineralisation in hydro – thermally changed volcanic of jurassic period. The most expository region of modern seasonal mineral formation is surroundings of cape Fiolent (South – Western Crimea).

Cape Fiolent is found in the furrows of Herakleian volcano – tectonic structure in South – Western Crimea and is situated in the hub intersection of Sevastopol -Nyzhnyogorod break zone and Bechka-Kardagsky subaltitutional deep fault. Fragments of volcanic apparatus of central type, crypto-volcanic and numerous dyes separate their layers on the coast cliff of cape Fiolent in 5 km distance (Shatalov, 1990). Volcanosedimentary complex of dogger consists of layers of lava flows of alkaline basalts, andesito-basalts, microdiabase, acidic tuffs with layers of liparites, felsite, andesito-dacites, andesite, andesitic porphyries mafics tuffs. During the geological measuring work in 1974-76 in lava breccias among feline – porphyry the sulphide polymetallic mineralization was established, which was represented by thin streaks of pyrite, galena, blende and chalcopyrite. In the oxidation zones of this mineralisation secondary minerals: covellite, chrysocolla, bornite, goethite, manganic oxide are developed (Borisenko, 1981). On their basis the new formed minerals represented by sulfates are being unfold.

According to the estimation data (Zinchenko, 2008) the general number of new formed mineral kinds on Crimea is over 38. However, the number of

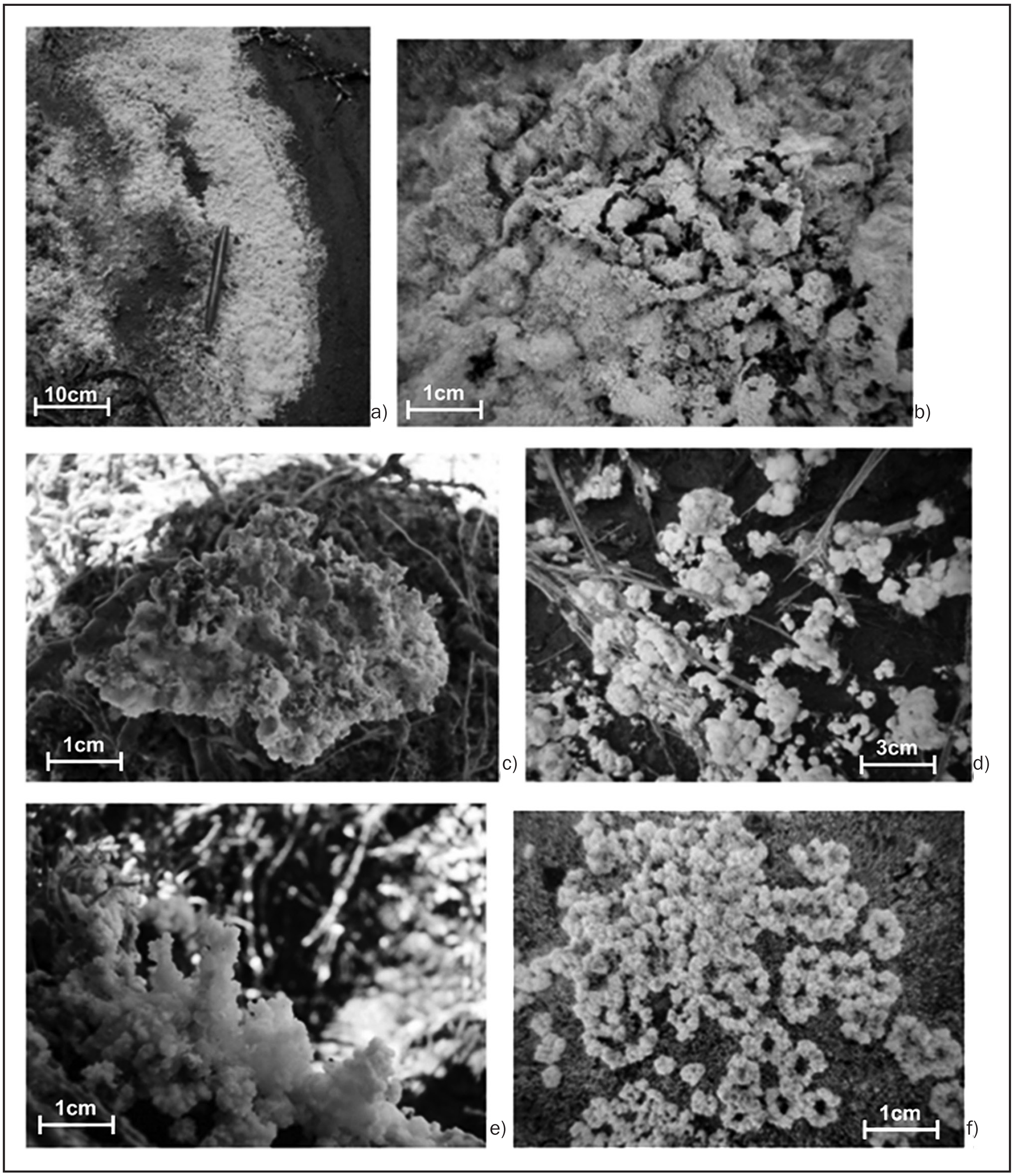

Fig. 2. Water-chemogenic aggregates morphology of the mud volcanoes:
a – massive crusts (Konchek); *b* – noncoherent crusts (Burulkay); *c* – pore crusts (Ak-Tube); *d* – botryoidal aggregates (Suyurtash); *e* – dendrites (Ak-Tube); *f* – flower-shaped aggregates (Vladislavovka).

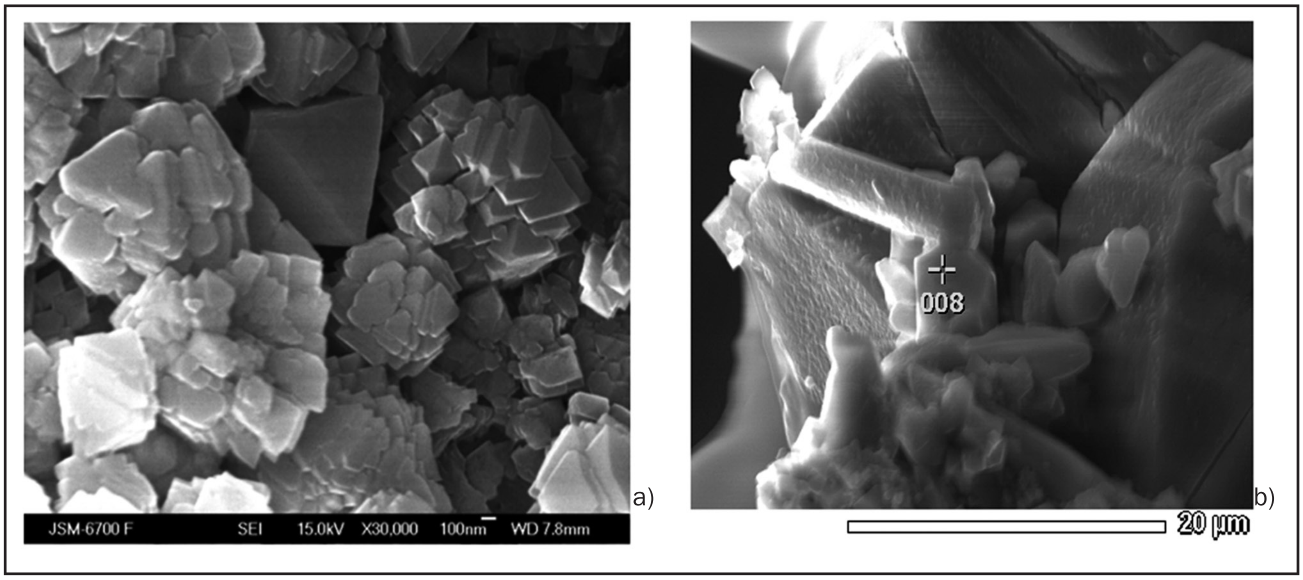

Fig. 3. Morphology of northupite and gaylussite crystals:
a – northupite; *b* – gaylussite.

laboratory research and diagnosis of these minerals is not high. In the scientific literature the data about their chemical composition and structure features is almost absent. First of all, it is associated with the complexity of mineral aggregates structure, their micrigrainity, polyphase and hydration. The most complete study of sulfate ensembles of cape Fiolent was held by researchers of Taras Shevchenko National University of Kyiv, headed by O.V. Zinchenko.

The main forum of water sulfate polymineral formations allocation is cluster-like aggregates – coralites. They are the chimeric joints of open or closed spherulites with diameter 2-3mm. Open spherulites are edged with numerous needle like and plate – spikelet diaphanous crystals, powdered with yellowish – brown dustlike material. Closed spherulites have dense rough crust like surface. The size of coralites is from 10 – 15 mm to 10 cm and more. The colouring of coralites is milky white, light-grey with yellow shade, rarely spotty bright up to deep-orange.

With the help of complex of laboratory investigation (Zinchenko, 2009) in the composition of polymineral coralites such sulfates were established: pikerengite – $Mg,Al_2(SO_4)_4 \cdot 22H_2O$, ferric pikerengite, hexagydrite – $MgSO_4 \cdot 6H_2O$, starkeyite – $MgSO_4 \cdot 4H_2O$, epsomite – $MgSO_4 \cdot 7H_2O$, alunogen – $Al_2(SO_4)_3 \cdot 17H_2O$, botryogen – $MgFe^{3+}(SO_4)_2(OH) \cdot 7H_2O$, yarosite – $KFe_3^{3+}(SO_4)_2(OH)$, copiapite – $Fe^{2+}Fe_4^{3+}(SO_4)_2(OH) \cdot 20H_2O$, gypsum – $CaSO_4 \cdot 2H_2O$. The availability of pentahydrate, butleryt etc is assumed. Except sulfates in the composition of sulfate new formations quartz, gypsum, amorphous SiO_2, allofan, illite potassium, chloride, kaolin items, etc are established. These minerals are contained in coralites in different ratio, creating certain paragenetical associations (fig.4).

In the following list new are starkeyite and botryogen.

Earlier the new formated sulfate minerals in Crimea were established by Y. V. Sobolevskiy (1976) in the weathering crust of Chekur-Koyaskiy and Sultanivsky sulfur deposits in Kerch Peninsula. He has described halotrichite – $Fe, Al_2(SO_4)_4 \cdot 20H_2O$, hexagydrite – $MgSO_4 \cdot 6H_2O$, hydrargillite – $Al(OH)_3$, sderotil – $FeSO_4 \cdot 5H_2O$, basaluminite – $Al_4(OH)_{10}SO_4 \cdot 3,3\text{-}5H_2O$.

Mineral formation in karst cavities of Mountainous Crimea.

A striking example of modern subaqueous authigenous and alothigenous mineral formation is karst cavities of Mountainous Crimea.

Within the Mountainous Crimean karst area of 1180km2 there are 16 karst regions, where more than 1000 karst cavities are found. Sediments of the upper structural floor are mainly karsted: late jurassic carbonate breeds, presented by limestone of oxford, kimmeridge and tyton storeys. They for numerous exits to the surface, extending with intermittent strip from Feodosya to Balaclava and they form almost all peaks in modern relief of the main ridge of the Crimean Mountains (Dublyansky, 2002).

The most intense karst processes in this region had place during the Late Chalk, Paleogene, Neogenea and Antropogene. The favorable conditions for that were: much relief disjoint, availability of local tectonic cracking zones, which impale almost all the thickness of structural floor. The most important are vertical cracks; significant power of carbonate breeds; hydrochemi-

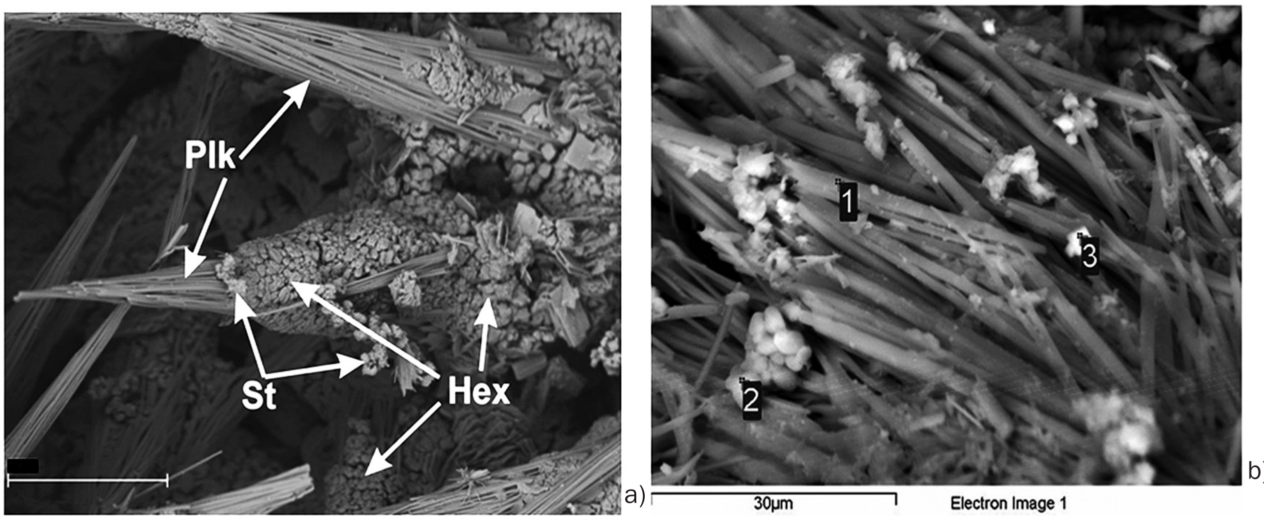

Fig. 4. Sulfates minerals from cape Fiolent coralites (Zinchenko, 2009):
a – sulfates aggregates on the coralites surface; *b* – bar- shaped pikerengite crystals with starkeyite and natroyarosite powder.

cal activity of karst waters and big amount of instant carbon dioxide in them; scattered infiltration of atmospheric sediments and concentrated stock of underground and surface waters; durability of karst period.

The intensity of carbonate karst development is much influenced by lithological features of breeds: composition, the content of insoluble impurities, texture, structure, level and character of diagenetic changes, presence of organic substance and sulfides.

A favourable factor for karst formation is vegetation, which promotes the accumulation of moisture, regulates warmth and provides uniformity of karsting the surface of mountains in time and space. Atmospheric fall – outs, that come through the layer of ground and vegetation enlarge their aggressive features due to the it saturation by organic acids.

Karst cavities are filled with material with different composition and origin. According to the classification (Dublyansky, 1977) in karst caves of Mountainous Crimea there are following types of sediments : remaining, landslide(thermogravitational, landslide – gravitational, fail – gravitational), water-mechanic (underground rivers and lakes, drifted from outside), water-chemogenic ((stalactites, fringe, helictites, stalagmites, stalagnates, pillar, covers, shield, karolity, film, zberegy, gury, oolites, calcite crystals, correlativus deposits, ice), organogenic (guano, bones clusters), anthropogenic.

Significant contribution to the study of processes of speleogenesys and Crimean karst evolution was made by V.M. Dublyansky, B.O. Vakhrushev, O.I. Tyschenko (Dublyansky, 1977; Dublyansky, 2002; Dublyansky, Lomaev, 1980; Tyshchenko, 2001; Tyshchenko, 2006; Tyshchenko, 2008). However the level of study of different types of karst formations is not same. The most researched are water-mechanic sediments. In pelite fraction they are dominated by mixed-layered silicates like illite-montmorillonite or illite. As the impurity there are kaolin, quartz, feldspars, goethite, calcite. Polymineral creations of authigenous and alothigenous origin are significated. Among them, hornblende, anatase, apatite, barite, brookite, galena, hematite, goethite, hydrogoethite, glauconite, almandine, native iron, gold, ilmenite, padolit, cassiterite, kyanite, cinnabar, corundum, leucoxene, magnetite, marcasite, monazite, moissanite, pyrite, pyroxene, pyrolusite, psilomelane, rutile, native plumbum, siderite, sillimanite, biotite, hydrobiotite, hydromuscovite, staurolite, sphalerite, tourmaline, chalcopyrite, chlorides, chromite, zircon, spinel, epidote. Majority of the minerals has no concentration and is presented by solitary signs.

Nowadays in the world's caves about 200 mineral kinds are known. Most of them are rare or connected to ore-hydrothermal processes or oxidation zones. In «cold» caves there are about 60 mineral kinds (Dublyansky, 2002). Mineralogy of water-chemogenic karst cavities new formations in Crimea is not well studied. There are only aragonit, gypsum, goethite, illite, calcite, quartz, kaolin, pyrolusite, psilomelane, sodium and potassium nitrate established. However, in our opinion, the list is not full and it can be significantly supplemented due to using modern laboratory equipment.

Aragonite is found in wandering formations, and beidelite, goethite, quartz and kaolin are fixed in composition of the cave pearls (Andreenko, 1987). Gypsum locations are known in the caves Partyzanska, Ayu-Teshyk, Stvarykayska, Chervona (Red), Marmurova (Marble) etc (Dublyansky, Lomaev, 1980). Gypsum forms separate prismatic crystals up to 8 cm, small crystallic crusts, membranes, gypsum «flowers», helictites etc.

The most wide spread mineral of water-chemogenic formations in Crimean caves is calcite.

It is described in many caves, but it is roentgenometrically established only in sediments of the Chervona (Red) cave (Dublyansky, 2002). Calcite is found in the form of small granules aggregates, druzes and separate individual crystals, as well as skeletal and Iceland spar.

Pyrolusite in the form of small granules crusts is found 30 underground in Kaskadna mine. In caves Chervona (Red) and Soldatska crusts of psilomelane were described (Dublyansky, 2002; Dublyansky, Ivanov, 1985).

In some caves there are pseudomorphs of hydroxide of iron and manganese, gypsum, calcite, carbonatapatit found by the remnants of fauna. Among them, detally studied is carbonat-hydroxylapatit hydroxylapatite from the karst caves Eni-Sala and Skel'na (Rocky), where it forms pseudomorphs of vertebrates' teeth, bones and koprolyte replacement.Potassium nitrate is found in artificial caves of Inkerman, Chufut-Kale, Mangup-Kale etc. It forms flour like fluffy raids on the walls and ceiling of the caves. On the walls of one of the Mangup-Kale grottos the mineral is found in the shape of small dirty – white crystals. In scientific literature there are also emissions of hair – like aggregates of potassium nitrate up to 20 cm length are described (Tyshchenko, 2008).

Sometimes sodium selitra (nitratine) is marked in the composition of potassium nitrate's aggregares. It was identified in the artifical caves and natural holes wich occur in the maastrichtian and danian rocks of the Mount Bakla. In 2008 O.I. Tyschenko found impurities nitromagnesite $Mg(NO_3)_2 \cdot 6H_2O$ among potassium nitrate aggregates in the same outcrop. Yu. Palkanov (1981, 1985) found aqueous calcium oxalate – whewellite $Ca(C_2O_4) \cdot H_2O$ – as part of the composition of fine-grained crusts in the natural holes of the «cave towns» Chufut-Kale, Kachi-Kalon.

CONCLUSIONS

1. The territory of Crimea is a region with active processes of modern exogenous mineral formation.

2. The main natural systems of modern mineral formation are mud volcanoes, salt lakes, karst and the sections of chemical weathering in the places of sulfide mineralisation.

3. Favourable conditions for exogenous mineralohenesis are geographical location, climate, character of mineralisation and composition of water solutions, lithological features of the breeds.

4. In most cases, modern new formations create polymineral aggregares of crypto- and thin-granuled construction.

5. The most distributed forms of polimineral aggregates emission are crusts, flower-like and cluster – like formations, dendrites, muddy masses, leaks, membranes, coralites.

6. In the composition of modern exogenous polymineral formations there are 38 mineral types. They are presented by berates borates (borax, tincalconite, probertite), carbonates (calcite, aragonite, dolomite, northupite, gaylussite, pirssonite, nesquehonite, trona), sulfates (gypsum, astrakhanite, epsomite, hexagydrite, pentahydrite, sanderite, thenardite, mirabilite, hydroglauberite, pikerengite, ferric pikerengite, starkeyite, alunogen, botryogen, yarosite, copiapite, butleryte), nitrates (nitratine, potassium nitrate, nitromagnesite), chlorides (halite), oxides and hydroxides (goethite, pyrolusite, psilomelane), silicates (illite, kaolin), organic compounds (whewellite).

Such minerals as northupite, gaylussite, pirssonite, sanderite, nesquehonite are new for the Ukrainian territory, and hydroglauberite and nitromagnesite – for the Crimean region.

7. In general context, in the composition of polymineral new formations preferable are hydrates, carbonates, sulfates and borates. The most spreaded mineral of salt lakes and mud volcanoes in Crimea is halite, and of karst cavities and places of hydrocarbon gases unloading-calcite. In oxidation zone of sulfate mineralisation of cape Fiolent volcanites the main development was gained by water sulfates of iron, magnesium and aluminium.

8. Most new formated minerals of mud volcanoes, salt lakes and volcanoes' oxidation zones are instant. Under the influence of atmospheric fallouts they transform into the solution and, under the good conditions, fall to the ground layer, causing its salting.

9. Minerals of karst cavities are saved in the shape of different wandering forms, creating great underground architectural ensembles.

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