Tatyana A. Kalinina

# Carbonate and sulphate evaporites of Perm Region: forming and weathering conditions

Specialization 25.00.06 – Lithology

**AUTHOR'S ABSTRACT**

of Dissertation to Candidate Thesis

(translated from russian)

Kazan 2015

The work was carried out at Geology of mineral deposit Laboratory of the Mining Institute of Ural Branch of Russian Academy of Sciences

| | |
|---|---|
| **Supervisor** | **Ph. Doctor Ilya I. Tchaikovsky**, Mining Institute of Ural Branch of Russian Academy of Sciences, Perm |
| **Opponents** | **Ph. Doctor Gunar A. Mizens**, Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg |
| | **Ph. Doctor Olga P. Goncharenko**, Saratov State University, Saratov |
| **Opponent Organization** | **Institute of Geology of the Komi Science Centre of the Ural Branch of the Russian Academy of Sciences, Syktyvkar** |

The defense is performed on 11th December 2015 at the PhD Council D 212.081.09 at Kazan Federal University: 420008, Kazan, Kremlyovskaya Str., 4/5, Institute of Geology and Petroleum Technologies.

The thesis manuscript can be found in the Nikolay Lobachevsky Scientific Library and on the site (www.kpfu.ru) of Kazan Federal University.

The authors' adstract was distributed on 5th October 2015.

Scientific secretary of
the PhD Council — Akhmet. A. Galeev

## TOTAL CHARACTERISTIC OF RESEARCH

**The importance of the research.** The Permian Period is one of most favourable periods for evaporite sedimentation during all history of the Paleozoic [Zharkov, 1978].Unique scales of evaporite processes and chemical differentiation led to accumulation of saliferous and sulphate thicknesses which are characterized by the great outcrop area. One of the largest Permian evaporite basin is East European basin – there are halogenous rocks which are developed on the area over 1,5 million $km^2$.

The wide-spread occurrence of Lower Permian carbonate and sulphate evaporites in the Perm Region has destined mineralogical specialization of this area. However opening of the Mazuyevskoe strontium deposit in 1996, which is largest one in Russia [Bolotov, 1997; Konopatkin, 1999], greatest scales of travertine-forming and numerous flows of fluorite [Abramovich, Nechayev, 1960] and borates testify to bigger mineralogical potential of these thicknesses [Iblaminov, Lebedev, 2004]. Actuality of evaporite researching is also connected with their easy solubility and delicacy to tectonic deformation that maybe used not only for paleotectonic reconstruction, but also for projection of raw materials' quality and spatial arrangement of minerals.

Despite long history of Lower Permian evaporite studying (more than 170 years) [Sofronitsky, 1973], still remains a number of the unresolved questions which are connected with formation and the subsequent hypergene reconversion of Lower Permian evaporites. This situation has led to a lack of date on the structure of the carbonate, sulphate and combined carbonate-and-sulfate massifs and chemical elements behavior at initial and ephebic hypergenesis of evaporites. All of these could increase efficiency of prospecting works.

**The basic purpose of the research** is to identify the conditions of formation and the post-sedimentation changes of carbonate and sulphate evaporate in the Perm Region.

**Research questions of the work:**

- to establish structural-and-textural types of sulphate and carbonate evaporites, sequences of their bedding, reconstruction of their conditions at the sedimento- and diagenesis stages;
- to study mineralogical, the litogeochemical and geochemical features of the initial and alterated sulphate and carbonate evaporites;
- to analyze the products of secondary alterations, staging reconstruction hypergene alteration of evaporates.

**Scientific novelty of the work.**

1. Complex lithologic, mineralogical and geochemical studying of carbonate and sulphate evaporites of the Perm Region is for the first time carried out.

2. It is established that formation of different structural-and-textural types of carbonate and sulphate evapories and their alternation on a section are caused by sedimentation recurrence and formation at regressive and transgressive stages.

3. Modern geochemical and isotope ($\delta^{13}C$ and $\delta^{18}O$) characteristic of carbonate and sulphate evaporites of the Perm Region (it is received for the first time) allowed to reconstruct sedimentation conditions in the Early Permian evaporite basin and processes of their hypergene alteration

4. It reveals specifics of anhydrite-contained evaporites hydration of the Perm Region and its influence on adjacent carbonates

5. The mineralogical, lithologic and geochemical studying of weathering products of carbonate and sulphate evaporites which allowed to reconstruct conditions of their hypergenesis is for the first time carried out.

**Practical value of the work.** The revealed structural and textural features of carbonate and sulphate evaporites can be used for a differentiation of Permian evaporite sections, quality evaluation of sulphate materials, safety evaluation of gypsum massifs, searches of the accompanying minerals (celestine, fluorite, borate) and prediction of karst and gypsum tectonics development.

**Structure of the manuscript.** The Candidate thesis manuscript is divided into 4 parts: Introduction, Main Body (three Chapters), Conclusion and References (218 items). The whole volume of the manuscript is 185 pages including 117 figures and 22 tables.

# CONTENTS

## 1. Lithology and formation processes of carbonate and sulphate evaporites

Carbonate and sulphate evaporites of the Perm Region are dated for east margin of the East European platform and the Pre-Ural foredeep. Its rocks are related to Philippovsky suite of the Philippovsky horizon and Irensky suite of the Irensky horizon of the Kungurian stage, and also lower part of Solikamsky suite of the Solikamsky horizon of the Ufimian stage of Permian Lower series. Irenskaya suite is subdivided [International …, 1991] into three carbonate (Nevolinskaya, Yelkinskaya, Tyuyskaya) and four sulphate (Ledyanopescherskaya, Shalashninskaya, Demidkovskaya, Lunezhskaya) members.

**Lithological characteristic.** Studying of structural features the Philippovsky and Irensky evaporites showed that carbonates are presented by calciferous dolomite with pelitomorphic texture and lamellar or massive oolitic structure. The alternation of these options in a section suggests a change of sedimentation conditions in the Early Permian basin: from well heating shallow with active hydrodynamics to more deep-water with passive hydrodynamics.

Solikamsky carbonates are presented by marls that can testify to intensification of the continental flow in sedimentation basin from the Urals. Lamellar texture of marls from the lower part of Solikamsky suite and presence of halite, halite-anhydrite and dolomite-anhydrite-halite interlayers there may indicate that carbonate sedimentation in Early Solikamsky time was in shallow isolated basin with higher salinity of waters and the passive hydrodynamics. Total absence of skeletal fauna in the lower part of Solikamsky suite can point at extremly unfavourable for life conditions of sedimentation.

Sulphate members are characterized by a cyclic structure: from the shevron in bottom to fine-crystalline massive or indistinctly laminated (center) and then nodular and-to-or lenticular-and-nodular in overlying bed. This member structure allows suggesting that sedimentation of sulphate materials began with formation of large gypsum crystals and their twins from undersaturated solutions [Warren, 1982]. Their alternation up a section by fine-crystalline material testifies to the following supersaturation of brines in the evaporite basin and large-scale sedimentation of pelitomorphic gypsum [Macdonald, 1953] or bassanite [Kinsman, 1965; Van Driessche et al., 2012] material. Massive texture of sulfates changing by nodular and lenticular-and-nodular ones is caused by clay and carbonate components increasing in the rock contents [Kopnin, 1996]. This can indicate the water demineralization and the terrigenous material introduction in paleobasin. Thus, observed change of shevron structure of gypsum by nodular and lenticular-and-nodular ones represents result of regular variation of water mineralization in basin at a sulphate stage of a cycle.

Consequently, the revealed material-and-structural features of carbonate and sulphate rocks allowed to retrace sedimentation evolution within each cycle and compose for them a typical idealized section (fig. 1). Some similarity in a structure of carbonate-and-sulphate is noted in a section of the Messinian (Upper Miocene) of the northern Apennines [Vai, Ricci-Lucchi, 1977], the Kangan formation (Lower Triassic) of the Persian Gulf [Zamannejad et al., 2013] and sedimentary cycle of modern saline soils of South Australia [Shreyber et al., 1990]. The formation of these evaporites is due to the subaqueous condition of shallow regional parts of the drying or closed to the sea salt lakes. Unlike the subaqueous sediments carbonate and sulphate rocks both modern (the district of Abu Dhabi, Persian Gulf [Shreyber et al., 1990]) and ancient (lower purbek (Upper Jurassic), Southern England [Shearman, 1966]) sebkhas don't show expressed cyclic structure.

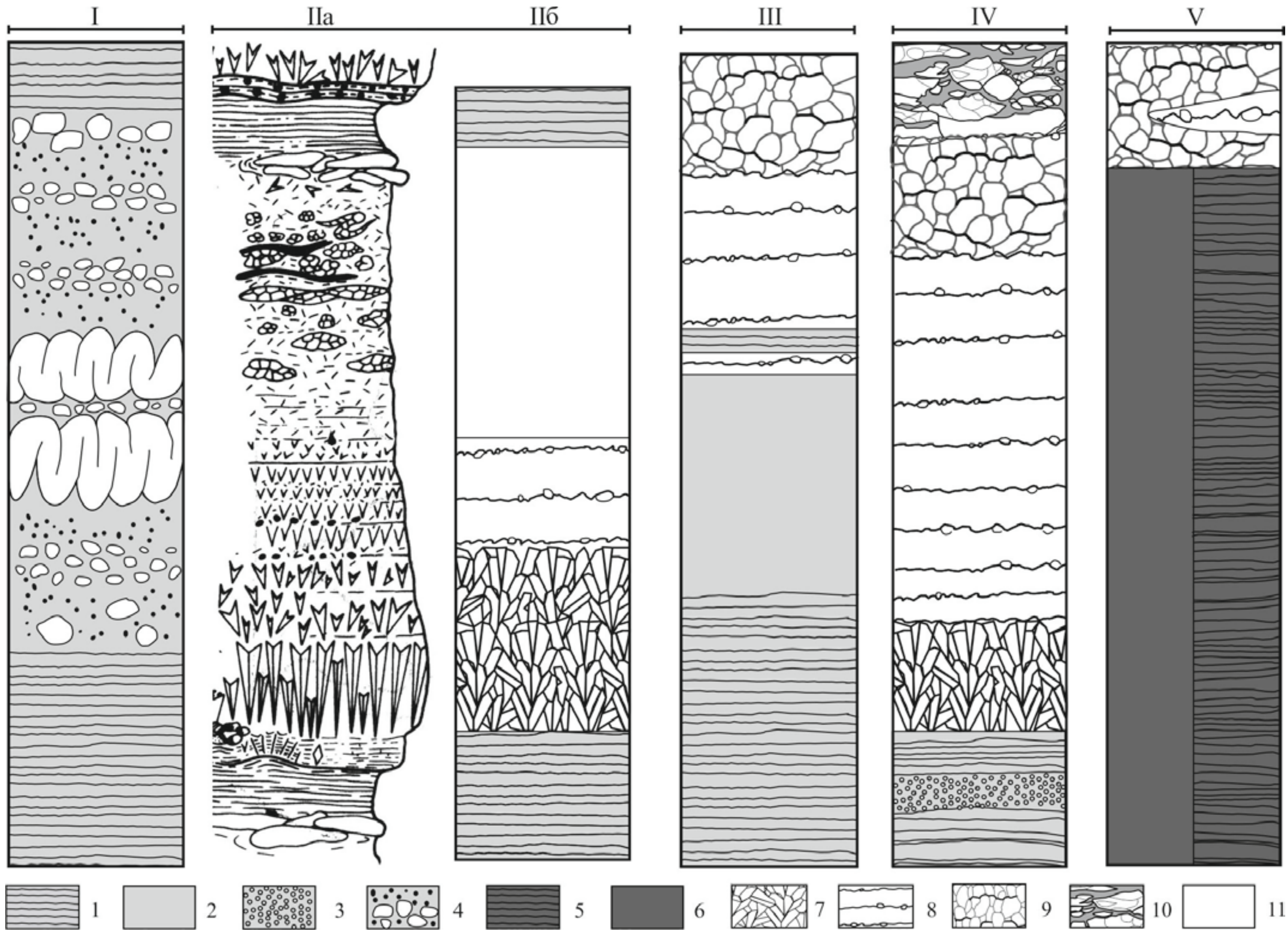


Fig. 1. Comparison of the schematized sections of a sebkha (I) and sedimentary cycles of the Messinian of the northern Apennines (IIa – by [Vai, Ricci-Lucchi, 1977]; IIb – by author of this abstracts), the Kangan formation (Lower Triassic) of the Persian Gulf (III); IV, V – the Lower Permian carbonate and sulphate evaporites of the Perm Region (IV – the Philippovsky-and-Irensky ones and Solikamsky evaporites on the platform part of the Perm Region; V – Solikamsky evaporites on the Solikamsk depression).Designations: 1-4 – structural-and-textural types of carbonates (1 – lamellar and pelitomorphic dolomite; 2 – organogenic detrital dolomite; 3 – massive oolitic dolomite; 4 – massive carbonate with dissipated sulphate nodules; 5 – lamellar marl; 6 – massive marl); 7-11 – structural-and-textural types of sulphates (7 – with a shevron structure; 8 – the massive; 9 –nodular; 10 –lenticular-and-nodular; 11 – chaotic)

***Accessory minerals.*** Except primary dolomite and anhydrite in carbonate and sulphate evaporites section of the Perm Region there are noticed celadonite and howlite.

Celadonite $(Mg_{1,63-2,10}Fe_{0,79-1,04})(OH)_2[Al_{0,19-0,35}Si_{3,61-3,85}O_5]\cdot K_{0,33-0,57}\cdot(H_2O)_n$ is characterized by the high content of potassium, iron and magnesium. This mineral is noted as a rock-forming mineral of low-power interlayers in dolomite members and as nest and veins in gypsum.

Howlite $((Ca_{1,69-1,82}Na_{0,04-0,02})B_5Si_{1,18-1,31}O_9Cl_{0-0,03}(OH)_5)$ is noted as concretions with fine-crystalline structure in the Ledyanopescherskaya gypsum member [Potapov, Parshina, 2010; Tchaikovsky et al., 2010; Kalinina et al., 2015].

***Geochemical characteristic.*** Chemical composition of the researching carbonate and sulphate evaporites showed that Philippovsky and Irensky rocks are characterized by simple composition ($SO_3$, CaO and MgO is near 95 wt. %) whereas Solikamsky evaporites have complicated composition. It is established that carbonates are enriched by potassium and sulfates – aluminum. It can suggest various extent of aluminum silicate material change.

Comparison of average composition of the investigated carbonate and sulphate rocks with clarkes of Earth crust, sea water and continental clays showed that the main geochemical specialization of trace elements is defined by presence of the terrigenous material. It is supposed that clastic material was formed by femic rocks crushing of the Urals.

The analysis of trace elements distribution on a Kungurian evaporites section showed that each cyclite is characterized by own geochemical specialization (fig. 2). Observed evolution can reflect the periods of water supersaturation by these elements (Sr, Co, Re, Te, Ni, Cu and Li in early stage, Ba in average one and W, Zn, Sn in finishing one), however it is assumed that at this time there could be a provenance reconstitution.

The analysis of trace elements distribution on a Solikamsky evaporites section showed that maximum concentration of the elements are dated mainly for the bottom and average parts (fig. 3). The observed picture is explained by trace elements sedimentation a result of their sorption by the clay minerals which came to the Kungurian paleobasin at the beginning of Solikamsky time. Maximum concentration of the elements in sulphate interlayers is connected with sedimentation of these elements as a result sulfate reduction (Ni, Cu, Mo, Re, I, Sb, Sn, Pb, Bi) and-to-or as isomorphic impurity in gypsum and carbonate minerals (Sr and Ba).

***Isotope characteristic.*** $\delta^{13}C$ and $\delta^{18}O$ distribution allowed to divide the Lower Permian carbonates into two groups. The first group is presented by Philippovsky and Irensky carbonates ($\delta^{13}C$=5,9÷7,5‰, $\delta^{18}O$=-6,9÷-1,3‰) and the second group is presented by Solikamsky ones ($\delta^{13}C$=(-6,9÷-1,4‰, $\delta^{18}O$=-11,5÷-3,0‰) (fig. 4). Such carbonate isotope composition is atypical for carbonates of the Quaternary evaporites ($\delta^{13}C$=-4,5÷5,5‰, $\delta^{18}O$=1,0÷5,0‰ [Hudson, 1977]) but is noted in the Lower Cambrian saliferous rocks in the Irkutsk amphitheater [Vinogradov et al., 2006] and the Devonian rocks in the Pripyat Trough [Makhnach et al., 1995; Makhnach et al., 2013]. Similar values of $\delta^{18}O$ are noted in the Zechstein evaporites [Clark, 1980; Botz, Muller, 1987; Below, 1992] and the Middle Permian (Kazanian) evaporites in east margin of the East European platform [Kuleshov, Sedaeva, 2009; Kuleshov, 2012; Sungatullin et al., 2014]. These data allow to believe that difference between Permian carbonate's oxygen isotopic composition and oxygen isotopic composition of Quaternary and more ancient carbonates is caused by distinction of Phanerozoe waters' oxygen isotope composition [Veizer et al., 1999; Came, 2007].

The Philippovsky and Irensky dolomites are characterized by high values of $\delta^{13}C$ (5,9-7,5‰) and $\delta^{18}O$ (-6,9÷-1,3‰). It is noted that the oxygen isotope composition of lamellar pelito-

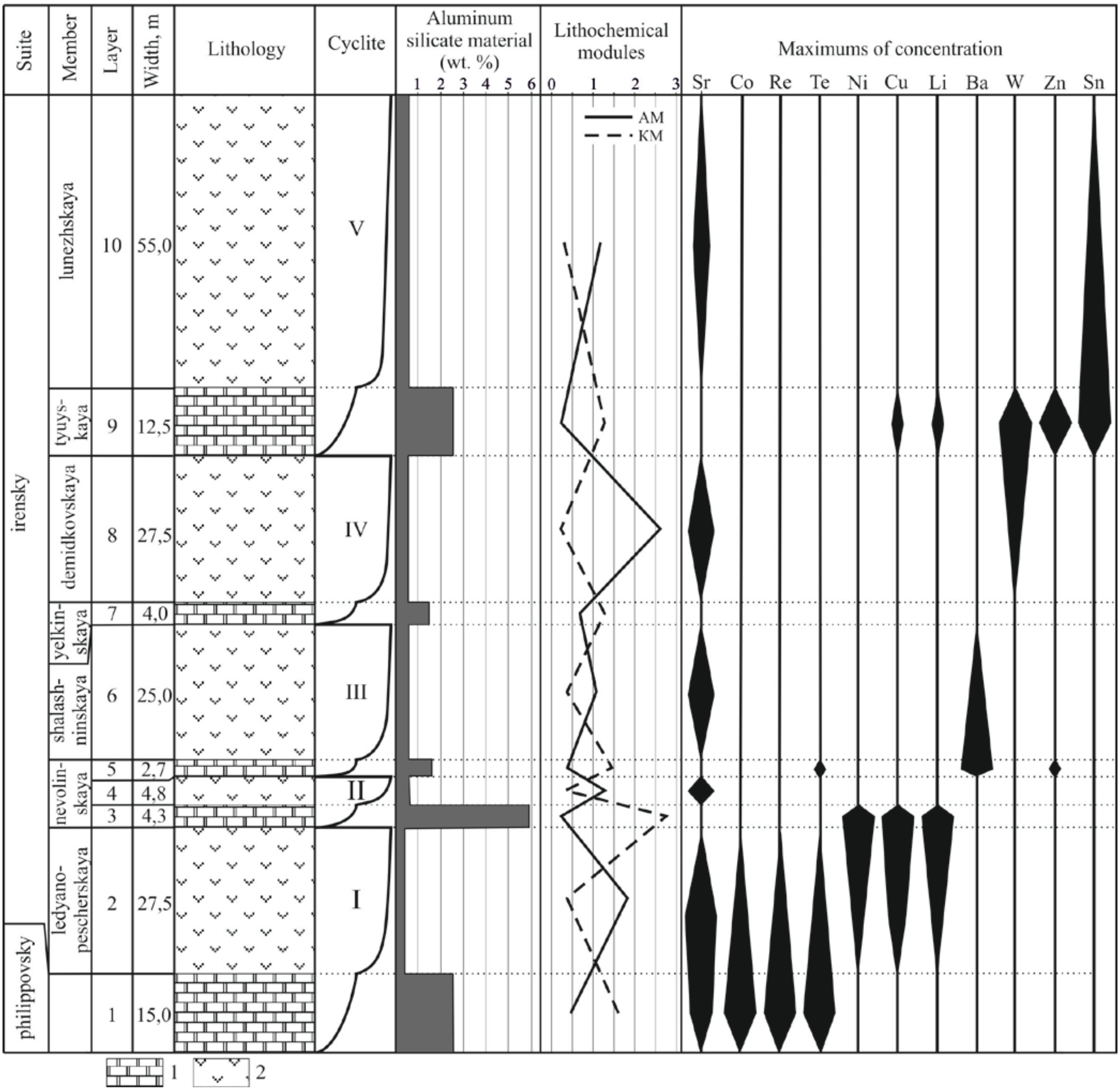


Fig. 2.Geochemical evolution of the Kungurian evaporites. Designations: 1 – carbonates; 2 – sulphates. Lithochemical modules (AM=$Al_2O_3/SiO_2$; KM=$K_2O/Al_2O_3$ [Yudovich, Ketris, 2000]) are normalized by average ones.

morphic dolomite ($\delta^{18}O$=-3,5÷-1,3‰) differs from massive oolitic one ($\delta^{18}O$=-6,9÷-3,6‰).These difference may be connected with sedimentation of these varieties in different part of the basin: such oolitic dolomite was formed in a zone of active waters circulation and at small depths, then pelitomorphic dolomite was formed in zone with passive hydrodynamics and at deeper and stagnant conditions.

Solikamsky carbonates differ from younger Kungurian ones in easier values of $\delta^{13}C$ (-6,0÷-1,4‰) and $\delta^{18}O$ (-11,5÷-6,6‰) that witness the major modification of sedimentation conditions in the Solikamsky evaporite basin. It is supposed that the reason of such low values of $\delta^{13}C$ and $\delta^{18}O$ can be gained of easy-isotopic surface water with dissolved soil carbonic acid. The high contents of terrigenous (aleuropelitic) material and attritus presence may witness it.

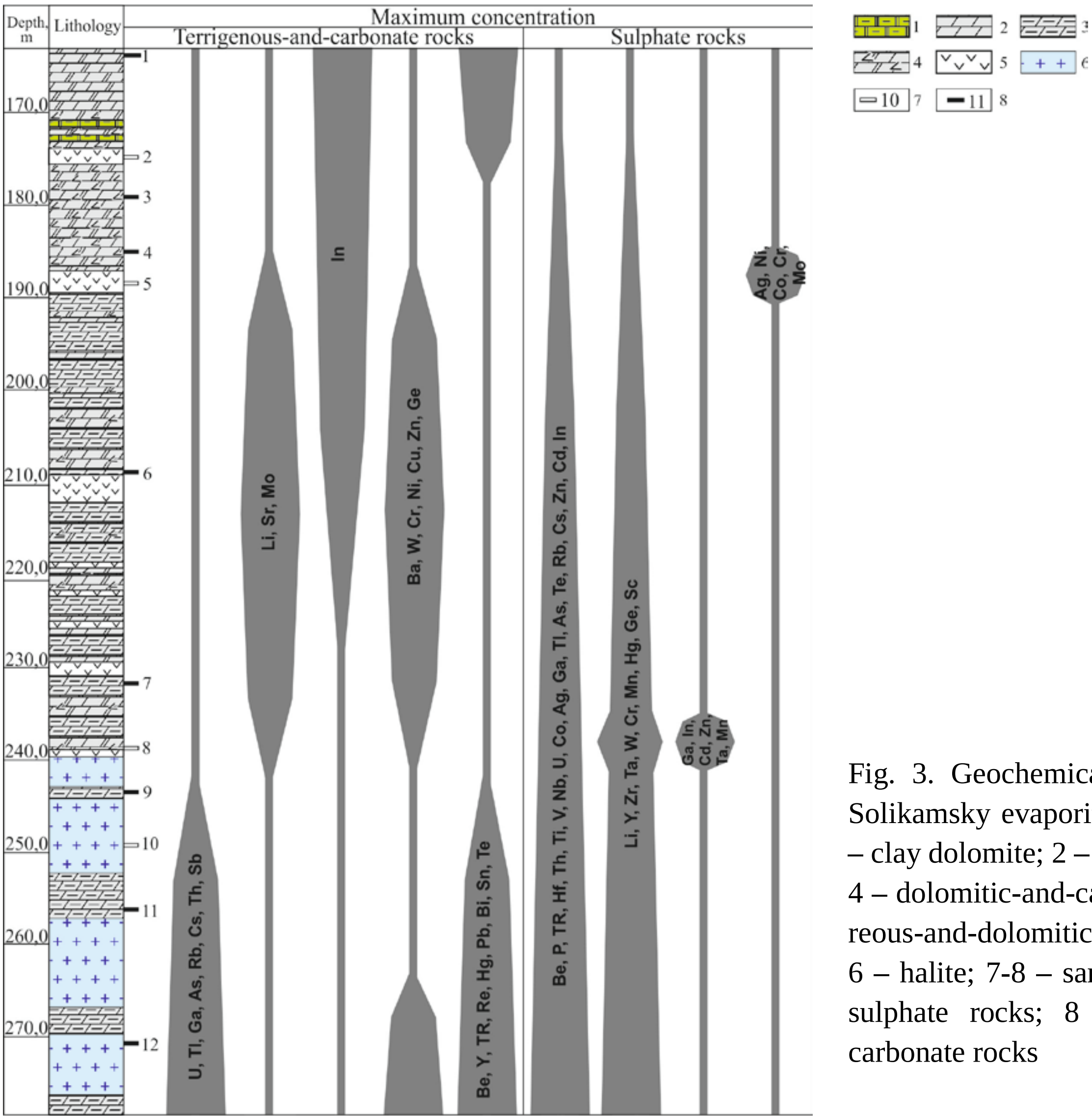


Fig. 3. Geochemical evolution of the Solikamsky evaporites. Designations: 1 – clay dolomite; 2 – marl; 3 – clay marl; 4 – dolomitic-and-calcareous and calcareous-and-dolomitic marl; 5 – gypsum; 6 – halite; 7-8 – samples numbers (7 – sulphate rocks; 8 – terrigenous-and-carbonate rocks

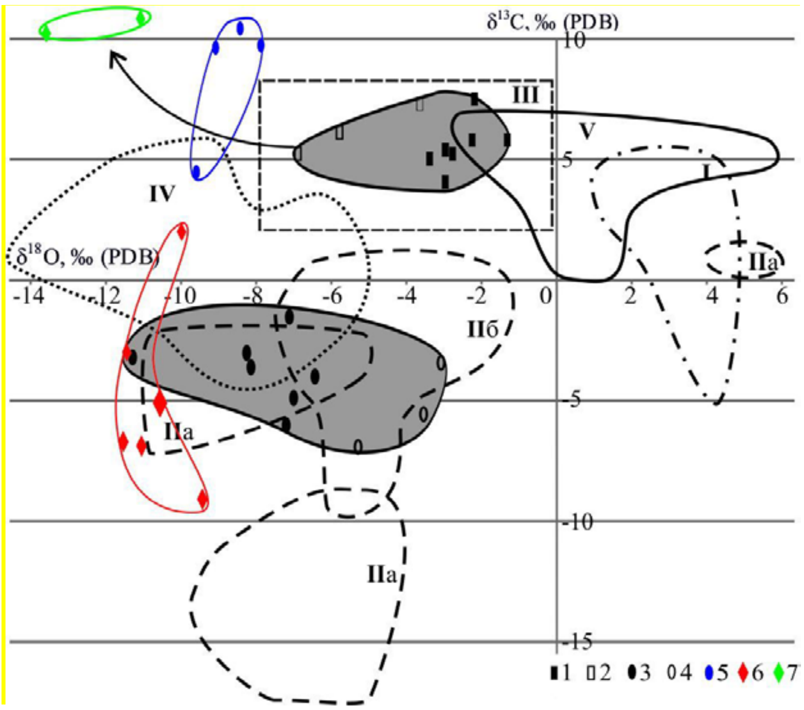


Fig. 4. Distribution of $\delta^{13}C$ and $\delta^{18}O$ values in primary and secondary carbonates of the Perm Region. Designations: 1, 2 – Philippovsky and Irensky carbonates (1 – pelitomorphic; 2 – oolitic); 3, 4 – Solikamsky carbonates (3 – the Solikamsky depression; 4 – platform part); 5 – recrystallized residual dolomite; 6 – incrustive dolomite; 7 – incrustive calcite; I-V – areas of carbonate isotopic composition (I – Quaternary evaporites (by [Hudson, 1977]); II – Devonian saliferous rocks of the Pripyat Trough (by [Makhnach et al., 1995; Makhnach et al., 2013]: a – not-salt rocks of a halite subformation of the Upper saline formation; б – a potassium subformation of the Upper saline formation); III – Zechstein carbonates (by [Clark, 1980; Botz, Muller, 1987; Below, 1992]); IV – Lower Cambrian saliferous rocks in the Irkutsk amphitheater (by [Vinogradov et al., 2006]); V – the Sakmarian-Kazanian dolomite of the East margin of the Russian plate (by [Sungatullin et al., 2014])

*Thus Philippovsky and Irensky evaporites of the Perm Region were formed in the extensive shallow basin during 5 cycles where each is characterized by regular alteration of pelitomorphic/oolitic calcareous dolomites by chevron, indistinctly laminated and nodular anhydrites. The evaporites chemical composition is defined by practically monomineralic sedimentation of talassophylic elements and trace elements concentration in aluminum silicate materials. The established range of maximum concentration of some trace elements (chalcophylic → chalcophylic-lithophylic → lithophylic ones) in Kungurian evaporites section can reflect sequential destruction of the Urals' femic rock complexes and then more sialic ones. The Solikamsky stage is connected with the gradual demineralization of the relict Kungurian lagoon occurring due to "avalanche" entry of a surface water and terrigenous material from the Urals. Connection with the boreal sea appeared only at the end of Solikamsky time as the evidenced by appearance of marine fauna. At the beginning of Solikamsky time clay material was introduced in the basin what led to occlusion of trace elements. Trace element accumulation in sulphate interlayers resulted due to their precipitation by reason of sulphate reduction (Ni, Cu, Mo, Re, I, Sb, Sn, Pb, Bi) and as isomorphic impurity in gypsum and carbonate minerals (Sr and Ba). Concentrating of Solikamsky sulphates by Zn, Bi, Te, Cd and In (that differ them from younger Kungurian carbonate and sulphate evaporites) can testify about both increasing of the Urals' volcanogenic materials in evaporite sedimentation and more reductive conditions in the Solikamsky basin which were favorable for sulfides sedimentation.*

## 2. Initial hypergenesis processes of carbonate and sulphate evaporites

The study of the sulphate thicknesses structure showed that gypsum is dated for the upper part of anhydrite members, to anhydrite-dolomite interlayer contact and local sites in anhydrite members. Gypsum thicknesses increases in the direction to water gap and narrow edges. Such sulphate massifs structure is coordinated with conclusions of the previous researchers [Howitt, 1964; Bailey, 1965; Darovskikh, Kudryashov, 2001] also confirms anhydrite hydration possibility by his interaction with down and interbedding water flows.

Anhydrite hydration happens in monomineralic anhydrite and sulphate-carbonate-clay rocks variously.

In monomineralic anhydrite rock gypsum meets along conformable and transverse cracks upon transition from anhydrite to gypsum. Then the massif range gradually stockwork and breccia structure. At the beginning of this process anhydrite relicts are characterized by acute-angled form, and at the end – by spherical ones. Marginal parts of anhydrite relicts are exfoliate that reflects increase in volume at hydration and permeable zone origin. It is noted in this case gypsum inherits lamination and clayed carbonate material distribution in previously anhydrite rocks.

Gypsum rock is characterized by net fabric structure: gypsum nodules are contorted and broken into blocks. It is connected with the strain distribution in hydration progress that accompanied with increase in volume

Structural supervision showed that anhydrite hydration leads to cleavage of anhydrite layers and carbonate interlayers, release fractures appear on valley-side slopes. Rock stratification can exists along carbonate interlayers at anhydrite hydration.

***Specifics of gypsum recrystallization processes.*** Secondary gypsum rocks are subdivided into three groups (fig. 5). The first group is characterized by massive structure and fine-crystalline texture, the second one – cellular structure, in the third one – sparry gypsum is devel-

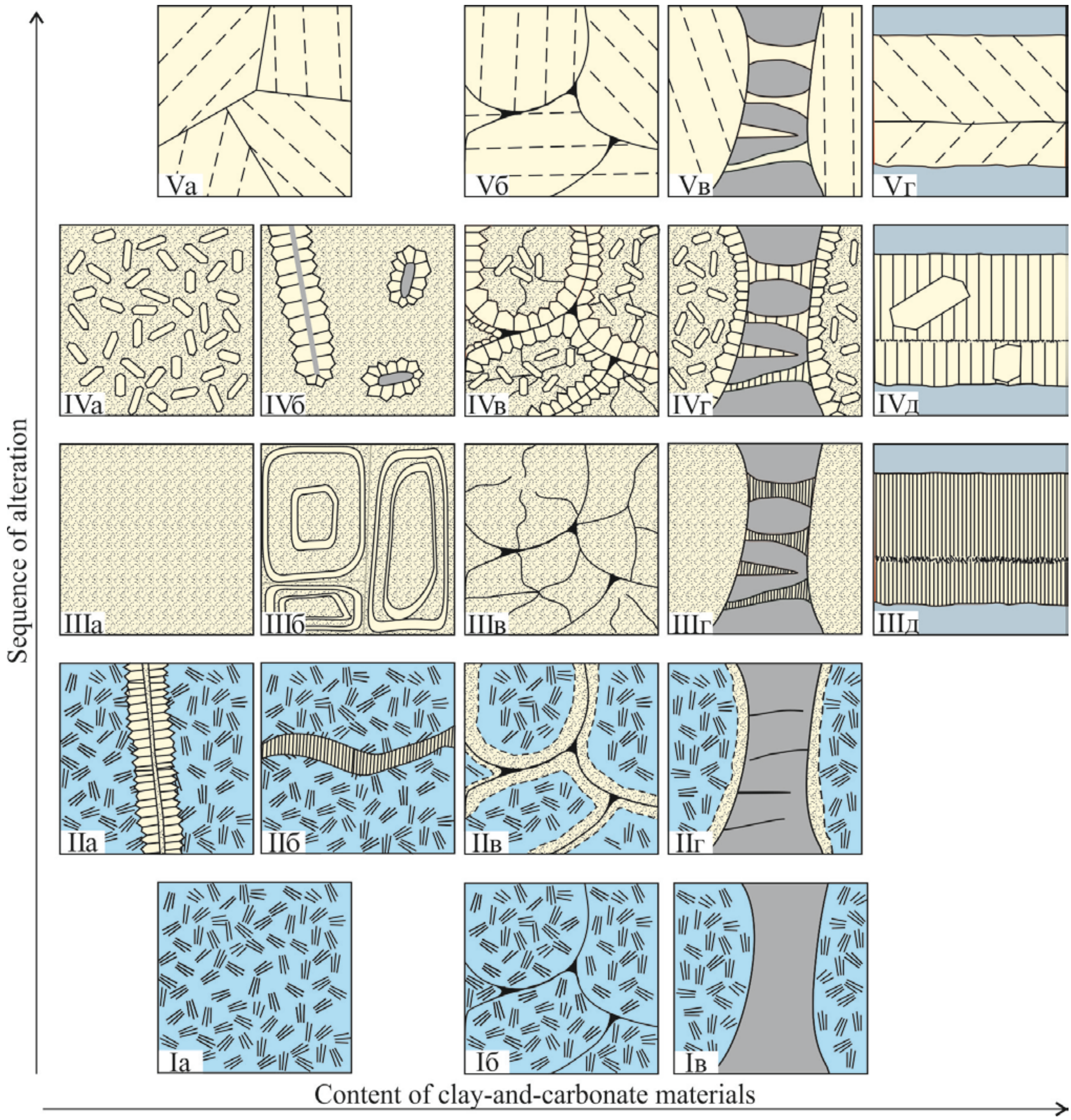


Fig. 5. Sequence of hydration and recrystallization of anhydrite-contained rocks: I – anhydrite rock (a – with massive structure; б – with nodular structure;в – rare nodules in a clay carbonate matrix); IIa –"metasomatic" gypsum veins; IIб – selenite veins without dog-hole; IIв-г – a fine-crystalline gypsum border; IIIa-в – gypsum rock (a – with massive; б – with cellular structure; в – with net fabric structure); IIIг – selenite veins without dog-hole; IIIд – selenite veins with dog-hole; IV – gypsum porphyroblasts (a – in basic mass; б – along clay interlayers and branching channels; в – in marginal parts and centre of nodules; г – in marginal parts of nodules and selenite veins; д – in selenite veins); Va-г – gypsum with coarse-crystalline and giant-crystalline structure

oped along clay interlayers and branching channels where it forms radial fibrous units. Thus noted structural-and-textural features of gypsum rocks of the Perm Region testify that recrystallization can happen differently: diffusive type – on all volume of the massif and from cracks to inside separate blocks – and infiltration one – along cracks. Such features testify to diffusive and infiltration gypsum recrystallization lead to forming of gypsum with coarse-crystalline and giant-crystalline structure.

The structural-and-textural analysis of gypsum nodules allowed to allocate some stages of its transformation and tectonic processes appearance.

In the mixed rocks there are noted selenite veins without a dog-hole, with one dog-hole and some dog-holes, shear zones, an orthogonal and slanting fibers arrangement. Veins shape can be simple, zigzag and branching. Such veins structure points at significant influence of tectonic movements which can be showed both during vein formation and after it.

Recrystallization processes can lead to formation of gypsum with coarse-crystalline and giant-crystalline structure. One of such sites is opened in the Khrustalny channel of Kungur Ice cave the where the gypsum crystal size is exceeds 50 cm.

Thus the structural analysis of the Lower Permian sulphate rocks in the Perm Region showed that their hypergene transformation scheme differs from hypergene transformation scheme of the Lower Purbek anhydrites [West, 1979]. Specifics of anhydrite hydration and the subsequent gypsum recrystallization are defined by contents and distribution of sulphate material in rocks and followed by formation of specific structures.

***Mineralogy of hydration zones.*** Accessory minerals of gypsum rocks are presented by celestine, fluorite and borates. The first is noted as single xenomorphic crystals and its segregations. The second composes small crystals with cubic habitus. Borates (probertite and studenitsite) composes small nodules with paniclemorphic and sheaf structure.

***Geochemistry of hydration zones.*** The pair correlation analysis of trace elements of anhydrite, gypsum-and-anhydrite and gypsum rocks allow to divide them into three groups. The elements of the first group (Fe, Ni, Ge, Sr, Zn, Ag, Tl, Bi, Be) are characterized by high content in anhydrite and lower one in gypsum. It may testify about mobility of these elements during hypergene sulphates alteration. The elements of the second group (Li, Ti, Co, Y, Zr, Sb, Cs, TR, Th, U) are characterized by the raised contents in gypsum-and-anhydrite rocks. Accumulation of these elements can be connected with the acid-alkali condition changing at anhydrite hydration frontier. The elements of the third group (Se, Cd, Hf) are characterized by chaotic distribution.

Comparison of coarse-crystalline and gian-crystalline gypsums with initial fine-crystalline ones showed that gypsum recrystallization is followed by Li, Rb, Cs, La-Ho carrying out and Sn, P, Cr, As, Mo, Er-Lu accumulation. Probably such lanthanides redistribution reflects alkaline composition of the solutions which led to gypsum recrystallization and La-Ho carrying out [Chemistry…, 1978]. Sn, P, Cr, As and Mo accumulation in gian-crystalline gypsum testify that gypsum recrystallization happened in hot oxidizing conditions.

The carbonate members dependency in a Kungurian evaporite section defines their mechanical and hydrochemical dependence on the processes happening in more soluble and deformable sulphates. Hypegene alteration of pelitomorphic and oolitic dolomites leads to calcite leaching, dolomite recrystallization and elements redistribution. Minerals presence with iron and manganese (carbonates and hydroxides) testify to nonequilibrium of conditions in which there was a initial rock alteration. Considerable variations of calcite, dolomite and siderite composition also can testify to it.

***Geochemical characteristic.*** Comparison of initial dolomite composition with secondary dolomite composition showed that dolomite hypegene alteration led to a carrying out of elements and also accumulation of Co, Cu, Zn, Se, Sr, Cd, Sb, Hg at recrystallization and B, Sc, Co, Cu, Se, Sr, Sn, Sb, Te, Re, Au, Hg, Pb, Bi at calcite leaching. The pair correlation analysis showed that trace elements lost correlation bond with petrogenic oxides that testifies to aluminum silicate and carbonate alteration and trace elements leaching. Finds a celestine, barite, borates and pyrite afford ground to suppose that some elements (Sr, Ba, B, Fe) forms independent phases whereas chalcophylic elements (Pb, Bi, Re, Te, Co, Sb, Cu) can be a part of sulfides. Some elements (Mn, Fe, W, Mo, Zn, As, Sn, P) can form secondary phosphates, molybdates, tungstates and hydroxides.

*Thus, specifics of anhydrite hydration and the subsequent gypsum recrystallization are defined by contents and distribution of sulphate material in rocks and followed by structural-and-textural alteration, selenite veins formation and deformations. There are calcite leaching of carbonate rocks and dolomite recrystallization. Elements redistribution happens in nonequilibrium conditions and repeatedly, it is followed by fluorite, celestine and borates formation.*

## 3. Ephebic hypergenesis processes of carbonate and sulphate evaporites

**3.1. Hypergenesis of sulphate rocks.** Structure of sulphate rock outcroppings is composed of three zones: country rock (fine-crystalline gypsum rock), structural eluvium (gypsum rock disintegrated into blocks with size more 25 mm), eluvium (loosely coupled gypsum material (1-25 mm) with aleuropelitic carbonate-and-sulphate particles) and linear wedge-shaped pockets. Such outcropping structure suggests that the main process of gypsum destruction is physical weathering which develops from a surface (as areal weathering crust) and to more intensive – along tectonic deformations. The incrusted aggregates recorded in a structural eluvium zone testify to a suffosion plays a significant role in the weathering.

Morphological analysis of authigene gypsum (fig. 6) allows to establish the main ways of gypsum alteration (pulverescent "sinter", grains of fine-crystalline gypsum rock and recrystallization veins) and educe specifics for them. All of them get through intergranular dissolution and grains release, the subsequent regeneration and further structural corrosion. Intermediate brecciated aggregates are sometimes formed. Such scheme of gypsum alteration reflects complexity of gypsum hypergenesis at the grain level.

Finds of barite, celestine, iron and manganese hydroxides testify that rock destruction leads to release and reaggregation of trace elements. Vanadium and molybdenum presence as a part of hydroxides point at gypsum alteration in oxidizing conditions of hot climate. Presence of galenite, native copper and silver on the hydroxide surface are associated with epigenetic redox exchange between solid manganese hydroxides and infiltration solutions [Silayev, 2008].

**3.2. Hypergenesis of carbonate rocks.** The surface of the Kazakovskaya Gora is covered by thick (60 m and more [Plusnin, 1947]) of dolomite and calcite-dolomite rocks with cavernous structure and relicts of initial pelitomorphic calcareous dolomites. Morphological studying of rock samples allows to track fragments of carbonate alteration and built the generalized sequence [Tchaikovsky et al., 2010] (fig. 7): 1) formation of dolomite recrystallization veins on system of cracks; 2) pelitomorphic material leaching with cavernous rock forming; 3) residual material compression with formation of the breccia with sublayered texture; 4) deposition of secondary crustified dolomite and calcite. Such structure reflects the secondary nature of the carbonates which were created due to leaching and recrystallization of calcareous dolomites.

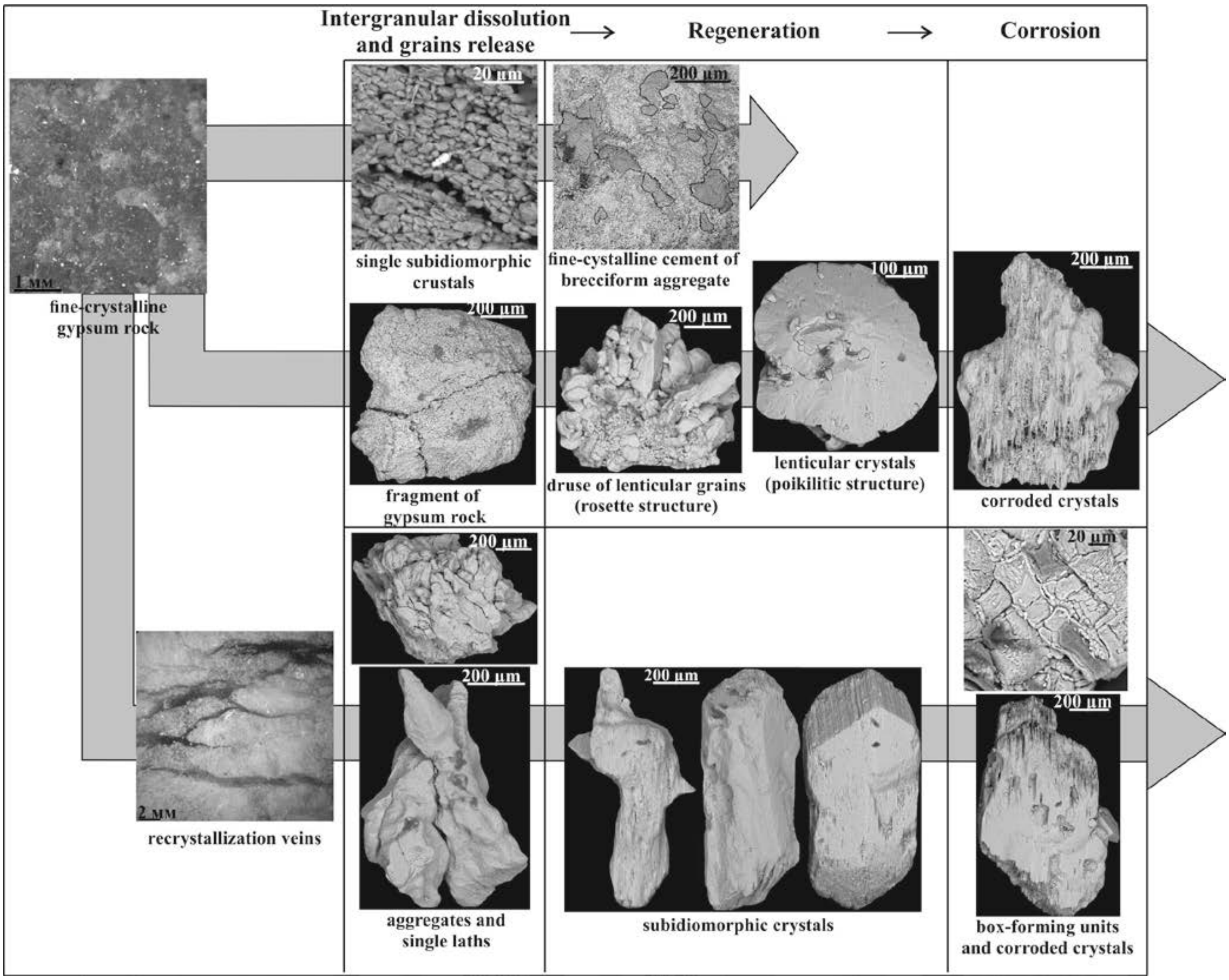


Fig. 6. Scheme of gypsum alteration

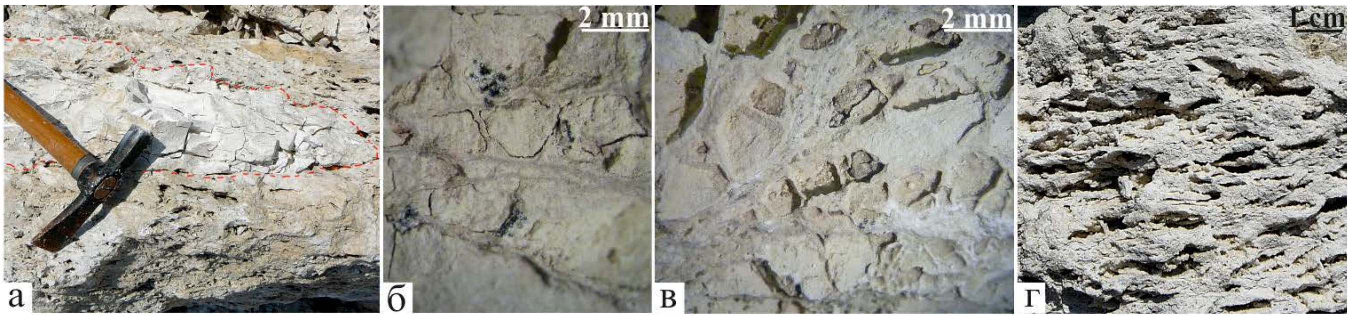


Fig. 7. The secondary carbonates of the Kazakovskaya Gora: а – relicts of initial pelitomorphic calcareous dolomites; б, в – leached carbonates; г – a breccia with sublayered structure

The similar structure of secondary carbonates is noted on the Shubino gypsum deposit that allows to assume the close scheme of its hypergene alteration. Positional relation of the revealed minerals in carbonate weathering crust allows to detach three zones a main and accessory mineralization. The surface of residual dolomite was complicated by the cuttings with authigene mineralization.

***Isotopic characteristic.*** Carbon and oxygen isotopic analysis of carbonates of weathering crust showed that dolomite is characterized by high values of $\delta^{13}C$ (4,4-10,8‰) and low– $\delta^{18}O$ (-13,5÷-8,4‰). Newly calcite is characterized by lower values of $\delta^{13}C$ (-9,2÷2,0‰) and lower $\delta^{18}O$ (-11,4÷-9,4‰) (see fig. 3). High values of $\delta^{13}C$ in dolomite may be connected with

Table

Mineralogical zonality of carbonate weathering crust of the Shubino gypsum deposit

| Mineral zone and subzone | | Main minerals and its morphology | Accessory minerals | |
|---|---|---|---|---|
| | | | Independent | On organic pelicles |
| Iron and manganese mineralization | Manganese hydroxides | Reniform aggregates | Barite, brass, iron (with Cr), copper silver, cassiterite, tenorite | |
| | | Single globules and dendrites | Barite, stannum, brass, celestine | |
| | Iron hydroxides | Ochreous iron hydroxides | Barite, pyrite, iron | |
| | | Reniform aggregates of iron-and-manganese hydroxides | Barite, celestine, brass | Sphalerite |
| | | Pelicles of iron-and-silicium hydroxides | Barite | |
| Calcite leaching | Dolomitic | Recrystallized dolomite | Barite, pyrite,zinc, gold | Bi |
| Calcite deposition | Calcite-dolomitic | Recrystallized dolomite with calcite nests | Barite, fluorite | |

carbon isotopes redistribution at hypergene alteration of pelitomorphic dolomite: $^{12}C$ was taken out with filterable waters whereas $^{13}C$ was preserved in secondary dolomite. Low values of $\delta^{18}O$ in secondary dolomite can testify about meteoric origin of filterable waters.

The relationship between dolomite and calcite testifies to temporary perturbation presence between their deposition that witness dolomite and calcite is not a products of one minerogenesis event or a stage. These conclusions allow to say that formation of carbonate weathering crust happened repeatedly at a atmospheric waters filtration. This condition could be realized in the semiarid climate.

**3.1. Hypergenesis of combined sulphate-carbonate-clayed rocks.** *Solikamsky suite of platform part of the Perm Region ("Chusovskaya Strelka" section).* Research of sulphate-carbonate-clayed rocks showed that in margin parts of gypsum nodules there are often are noted reniform units of newly metacrystalline quartz with poikilitic texture and crystallomorphic outlines. Their internal structure is defined by the oriented lamellar gypsum interpositions. Calcite, gypsum, pyrite, oxidic and native iron, manganese oxides, barite and celestine are recorded on a surface of the quartz. It is supposed that hypergene gypsum dissolution increased solution's aggression that leds to calcite leaching, alcalinity increasing and solution enrichment by silicon. The dissolved silicon dioxide was besieged on the margin parts of gypsum nodules which were serving as a geochemical barrier. Then the central part of gypsum nodules was leached and calcite was created on quartz crystals. Similar units were noted in over-salt series of the Verkhnekamskoe salt deposit where gypsum-quartz-calcite pseudomorphoses are localized only among marls of the Solikamsky suite. It is supposed that their formation happened at neotectonic raising of the territory [Tchaikovsky, Chirkova, 2011].

*Solikamsky suite of the Solikamsky depression* (over-salt series of the Verkhnekamskoe deposit, Polovodovo plot). Studying of a section of hypergene zone show that clay limestones and marl are displaced by clay marl and clays which are characterized by intense jointing (rocks are crashed to blocks with 1-1000 mm size). Besides there was noted a breccia forming of which contacts with rock volume reduction as a result of calcite leaching, collapse and letdown.

Secondary rocks are divided into four groups. The first group is presented by cavernous carbonate rocks (limestones, clay limestones) which were created due to dissolution of anhydrite nodules. The rocks of the second group have decalcified zones along layer-by-layer and near-vertical cracks. The rocks of the third group are presented by marls and clay marls with relicts of clay limestone. The rocks of the fourth group are characterized by the cellular-cavernous structure: vertical and layer-by-layer calcite partitions with clay remains between them. The local chemical analysis of initial and hypegene changed sites of these rocks allowed to establish carrying out to 55% a calcium or magnesium carbonate (fig. 8a).

Carbonatization zones are shown as Liesegang bandings appearance of which is defined by cracks system. Chemical composition research showed that rock decolorizing is caused by calcite or dolomite enrichment as a result of diffusive metasomatism (fig. 8b).

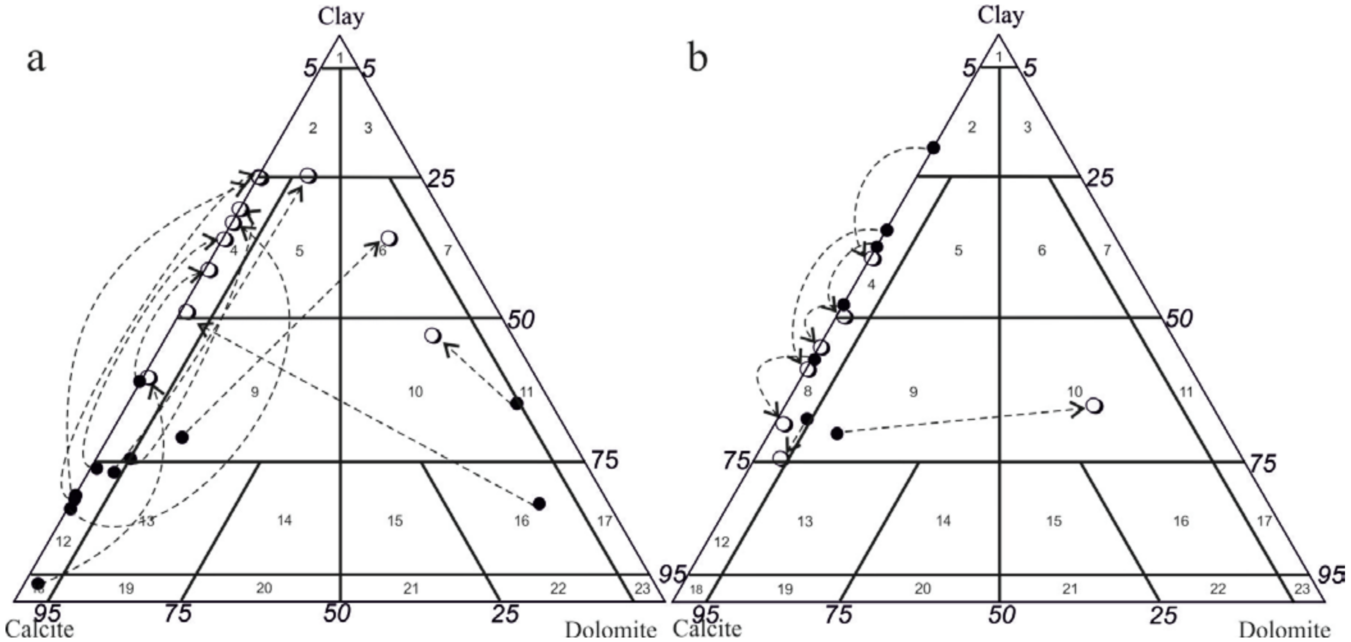

Fig. 8. A ratio of calcite, dolomite and clay in primary and altered sites of rocks from leaching (a) and carbonization (б) zones. Black circles – primary composition, unshaded circle – altered ones

*Solikamsky suite of the Solikamsky depression (over-salt series of the Verkhnekamskoe deposit, Bygelsko-Troitsky plot).*The top of the salt surface of the Verkhnekamskoe deposit and the underlying rock salt revealed breccia rocks of variable composition: lenticular and budinaged clasts and layers of gypsum rock, fragments and clusters of dolomite, and gypsum-bearing aggregates. Some clasts contain parallel-columnar gypsum stringers, and their fragments are also observed on the outer side of dolomite aggregates.

The enclosing mass has a heterogeneous composition because of the irregular distribution of carbonate-clayey material. It is saturated with lenticular gypsum xenoliths near gypsum aggregates and observed only as thin stringers inside the xenoliths. The material is characterized by foliated structure near sliding planes in the distal zones. The chemical composition of different sectors of rocks was examined with a scanning electron microscope. The results showed that the clayey–carbonate material inside the gypsum aggregates contains a higher amount of carbonate material than the enclosing mass located along sliding planes (Fig. 9).

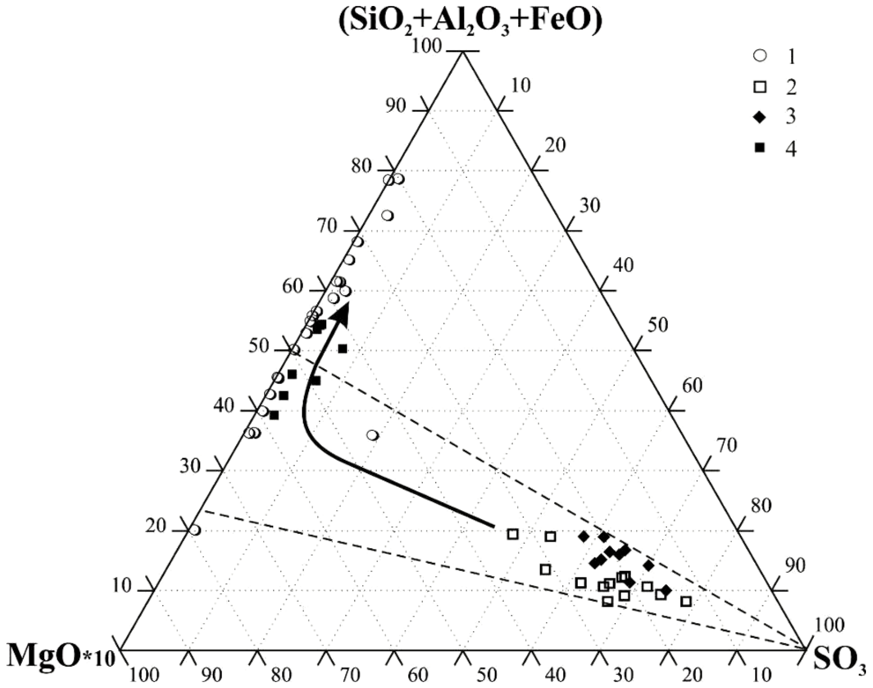


Fig. 9. Variations in the chemical composition of the studied breccias (wt %). (1) Local monomineral clayey sectors; (2, 3) gypsum segregations: (2) central portion, (3) marginal portion; (4) enclosing mass; (5) boundary of the inferred zone of the carbonate-clayed material alteration during the leaching of gypsum. Arrow shows the rock composition evolution

The lenticular and boudined structure of gypsum aggregates, aprons of the disintegrated carbonate material, selenite vein lets inside and on the surface of dolomite clasts, and the appearance of complex concentric dolomite–gypsum aggregates suggest their formation because of foliation in the contact zone between salt beds and overlying rocks along diagonal sliding planes, probably, owing to sliding of the supra-salt sequence over the salt sequence along a synsedimentary dip-slip of the Durinsk fault system. Percolation of groundwaters along the weakened zones during tectonic displacements promoted a significant compositional transformation of breccia rocks and their mineral-geochemical zonation.

*Thus, specifics of ephebic hypergenesis of the evaporires are defined by a substratum composition and the main processes are dissolution and leaching. The final weathering product of sulphates is gypsum powder, carbonates – dolomite rock with cavernous structure or calcite powder, combined sulphate-carbonate-clayed rocks – clay units with breccia structure. Evaporites destruction leads to trace elements release and forming of oxides, hydroxides, phosphates, vanadate, molybdates, sulphates, sulphides, native phases, fluorite both in oxidizing reductive and conditions. C and O isotopy of carbonates reflects that formation of carbonate weathering crust happened repeatedly and in condition of the semiarid climate.*

## Conclusion

The material given in work allowed to show difficult and long evolution of carbonate and sulphate evaporites of the Perm Region which due to easy solubility and deformability react to change of environment conditions and suffer considerable structural-and-material alterations. Summarizing the received results it is possible to draw the following conclusions.

1. During the Philippovsky and Irensky time extensive shallow periodically freshened basin with carbonate and sulphate sedimentation was on the territories of the Perm Region. Solikamsky evaporites were created in an initial stage of the last transgressive cycle of the Early Permian sea when there was gradual demineralization of the relict Kungurian lagoon. Structure of the sulphates is formed at a sedimentation and diagenesis stage and depends on not sulphatic materials content in rock and anisotropy of minerogenesis environment.

2. Comparison of the studied sections with other models of ancient and modern evaporites showed that Lower Permian evaporites are presented by frequent repeating full cycles (pelitomorphic/oolitic dolomite → anhydrite with a shevron structure → massive anhydrite → nodular anhydrite → lenticular-and-nodular anhydrite) that reflecting regular evolution of waters concentration in basin. It allows to consider Lower Permian evaporites of the Perm Region is a model of carbonate and sulphate evaporite sedimentation.

3. Trace elements of carbonate and sulphate evaporites are connected with clays. During anhydrite hydration and subsequent gypsum recrystallization there is a elements redistribution both in sulphate and carbonate layers with newly mineral phases forming.

4. Carbonate and sulphate evaporites of the Perm Region are characterized by specific poverty of the original minerals (gypsum, anhydrite, dolomite, celadonite, howlite) and a big variety of products of initial (probertite, studenitsite, fluorite, celestine, siderite etc.) and ephebic (manganese and iron hydroxide, fluorite, mirabilite, blodite, ulexite, Zn-contained saponite, barite, pyrite, cassiterite, tenorite, native gold, copper silver, zinc, iron, stannum, brass, vanadinite, powellite) hypergene alteration.

5. Hypergenesis of sulphate rocks leads to vulgar and linear weathering crusts forming where the main process of gypsum destruction is physical weathering and less physical and chemical one. Hypergenesis of carbonate rocks leads to weathering crusts forming which is put by *dolomite and calcite-and-dolomite rock with cavernous structure and mineralogical* zonality. Weathering of *combined sulphate-carbonate-clayed rocks* leads to sulphate and then carbonate (at first calcite then dolomite) with accumulation of clay rest. These are accompanied by rock volume reduction with breccias and carbonization zone (Liesegang bandings) forming. Imposing of tectonic processes leads to an intensification of hypergene processes and linear weathering crusts and breccias formation.