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Sulfur isotopic composition of sulfur deposits in Ural karst caves

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The subject of the study is the sulfur isotopic composition of sulfate deposits (minerals) of caves. The purpose of the study is the construction of mineral and speleogenesis model based on sulfur isotope study of primary and secondary mineral deposits. Authors conducted sampling of sulfate mineral formations for research in the Kungur and Kinderlinsk caves. Mineralogical and isotopic studies were done at the Institute of Mineralogy, Ural Branch of Russian Academy of Sciences (Miass). Diagnosis of minerals was made on diffractometer DRON-2.0, CuK α -emission. Determination of the isotopic composition of sulfur was carried out on a mass spectrometer DeltaPlus Advantage, manufactured by Thermo Finigan, and linked to the elemental analyzer EA Flash1112 with interface ConFlo III. The analysis error is 0,27 ‰ CDT. Authors studied the isotopic composition of sulfur of secondary sulfate minerals formed in two caves of the Urals – sulfate karst in the Kungur cave and carbonate karst in Kinderlinsk cave. Primary chemogenic-sedimentary rocks (gypsum and anhydrite) in the Kungur cave have the isotopic composition $\delta^{34}\text{S}$ ranging from 10,09 ‰ to +12,32 ‰, CDT, which corresponds to a typical composition for the Lower Permian marine evaporites. In the newly formed sulfate minerals (gypsum, mirabilite) were no significant changes in the isotopic composition of sulfur in comparison to sulfate of bedrock, which indicates their formation in the process of dissolution and re-deposition of primary sedimentary sequence. In the Kinderlinsk cave newly formed sulfate minerals are characterized by a slight sulfur isotopic composition $\delta^{34}\text{S}$, ranging from -23,51 ‰ to -15,288 ‰ CDT. A similar lighter sulfur isotopic composition is typical for mineral formations that are products of bacterial sulfate reduction. Authors assume formation of secondary gypsum from compounds of organically bound sulfur of bituminous substance of accommodating limestone, which oxidizes in oxygen conditions to sulfates with participation of sulfur-oxidizing (thionic) bacteria.

Keywords: isotopes of sulfur; sulfates; secondary mineral formations; carbonate and sulfate karst caves; sulfate reduction; sulfuric acid speleogenesis; genesis of minerals.

Introduction to the problematics

During studying the mineralogy of speleological objects [1–6], one eventually comes to the necessity of solving the genetic problems both in terms of mineral and crystallogenesis and in terms of speleogenesis. Solving these problems is possible with the use of isotope geochemistry methods [7–9], which we used for two objects (caves) – sulfate karst of the Kungur cave and carbonate karst of the Kinderlinsk cave. The study of psychogenesis is important not only in the fundamental sense, but also in the applied sense, because speleogenesis often involves the formation of mineral deposits [10].

As is well known, there are several speleogenesis agents, one of which is sulfuric acid. The role of sulfuric acid formed by oxidation of hydrogen sulfide and sulfide minerals in dissolution of carbonate rocks is well known [11, 12]. The first model of sulfuric acid speleogenesis was proposed by S. Egemeyr in year 1981 [13] in order to explain the genesis and evolution of cave Lower Kane, Wyoming, USA. Currently, a number of major cave systems demonstrated mostly sulfuric acid origin: it is the cave Villa Luz in Mexico [14] and the caves of Guadalupe Mountains in New Mexico, USA [15], the cave system Frasassi in Italy [16], the cave Krauskhülle in Austria [17], and the caves of the Cerna valley in Romania [18]. Sulfuric acid speleogenesis usually refers to the formation of cavities during the massive dissolution of carbonate rocks by sulfuric acid formed during the oxidation of sulphide water in the aeration zone. The cause of H₂S typically are bacterial sulfate reduction processes, occurring anaerobically in the lower hydrodynamic zone in the presence of marine evaporites (gypsum, anhydrite) and hydrocarbons in a cross-section [10]. In the caves having mainly epigenous origin (formed by dissolving meteoric water with carbonic acid of biogenic origin), the elements of the sulfuric acid corrosion might be present during the oxidation of the grains of sulphides (mainly pyrite) contained in the host rocks, but the process usually gets a secondary role in speleogenesis [18, 19]. However, certain cases involve a significant role of this factor (sometimes called “pyrite-effect”) in the genesis of cavities and their subsequent evolution [20]. The main product of the sulfuric acid dissolution and re-deposition of limestone is gypsum – CaSO₄ × 2H₂O. Therefore, one can consider the carbonate karst presence of gypsum in the cavities as a potential indicator of sulfuric acid speleogenesis process.

Sulfate minerals in carbonate karst caves have one of the four possible sources: the oxidation of sulfides and sulfide waters, redeposition of marine evaporites in the field of nutrition, the expansion of bat guano, and migration

of deep gases during postvolcanic activity [21]. Reliably determining the source of gypsum in some cases is problematic. Reliably determining the source of gypsum in some cases is problematic. In the diagnosis of sulfuric acid corrosion, it is necessary to exclude the possibility of re-deposition of gypsum from sea sulfates in the context of host rocks (which may not always be displayed on the available geological maps and cuts, especially in areas with a complex tectonic structure).

One of the most informative methods for establishing a source of sulfate is the study of isotopic composition of sulfur [18, 19, 22]. Sulfur has nine isotopes, four of which are stable (³²S, ³³S, ³⁴S, ³⁶S). They differ in the number of neutrons in the nucleus, which, respectively, determines their mass, causing subtle differences in the physical and chemical behavior. Most of the stable isotopes of sulfur in the compounds are represented by ³²S (95%) and ³⁴S (4,22%), two other isotopes are less common, and are rarely used in the analysis [23]. The isotopic composition of the sample is given in the unit $\delta^{34}\text{S}$ and is expressed as a ratio of ³⁴S and ³²S in ‰, normalized to the universal standard (troilite of iron meteorite Canyon Diablo, Canon Diablo Troilite: CDT).

Authors show the average isotopic composition for various sulfur-containing mineral formations in Fig. 1 [24]. Overall, the average values of $\delta^{34}\text{S}$ varies widely: from $\delta^{34}\text{S}$ –50 to +35 ‰. Sulfur of magmatic, volcanic and hydrothermal origin is usually slightly heavier relative to CDT (i. e. close to the sulfur of meteorites). Residual unreduced sulfates in ocean waters, and as a result, evaporites, formed from them, have a heavier isotope composition of sulfur, which is in the geological history of the Earth significantly varied over a wide range with a maximum of $\delta^{34}\text{S}$ +30 ... + 35 ‰ in the Cambrian and Ordovician and minimum of $\delta^{34}\text{S}$ +9 ... + 13 ‰ in the Permian. The isotopic composition of sulfur of modern marine sulphates is $\delta^{34}\text{S}$ +21,0 ± 0,2 ‰ [22]. The most significant factor responsible for the fractionation of stable isotopes of sulfur is a bacterial sulfate reduction, which has a negative “shift” around $\delta^{34}\text{S}$ –30 ‰ for the resulting hydrogen sulfide. The physical essence of the phenomenon lies in the fact that the light isotope ³²S has a less strong chemical bonds in the sulfate than the heavier isotope ³⁴S, so these bonds break first of all (in this case, the residual sulphate reservoir gets enriched with the heavy isotope). The isotopic composition of sulphide and sulfur formed during biological reduction processes varies widely, averaging at $\delta^{34}\text{S}$ –12 ‰ [24].

Authors examine the features of the isotopic composition of sulfur in the primary sedimentary sulfates (gypsum and anhydrite) and secondary speleothemes (newly formed mineral sulfate minerals) on the example of the Kungur and the Kinderlinsk caves.

Research methods

Collection of samples of sulfate mineral formations was conducted in the framework of fieldwork in 2008, 2012–2013, in the Kungur and the Kinderlinsk caves. Mineralogical and isotopic studies were done at the Institute of Mineralogy, Ural Branch of Russian Academy of Sciences (Miass). Diagnosis of minerals was made on diffractometer DRON-2.0, CuK α -emission. Determination of the isotopic composition of sulfur was carried out on a mass spectrometer DeltaPlus Advantage, manufactured by Thermo Finigan, and linked to the elemental analyzer EA Flash1112 with interface ConFlo III. The analysis error is 0,27 ‰ CDT. The research results include 19 analyzes of the sulfur isotopic composition of sulfate minerals from the caves.

Kungur Cave: redeposition of marine evaporites

Cave Kungur (Perm, Kungur town) is located in the Middle Urals. The main part of the cavities lies in the ice cave pack of irensk horizon of Kungurian stage of the Lower Permian (^{ir}_{ld}-P_{1k}^{ir}). It mostly contains of anhydrites, gypsum is less common [25].

Kungur cave is one of the largest karst caves in the European part of Russia, laid in gypsum and anhydrite. The cave is located at the contact of the lower (Filippov) horizon of Kungurian stage, composed by limestones and dolomites, and the upper (irensk) horizon, mainly composed of gypsum and anhydrite. Karsting of sulphate rocks increases rapidly on the border with carbonate strata. Authors explain strengthening of karst by the arrival of low-mineralized bicarbonate-calcium waters of the carbonate sequences to the easily soluble sulfate rocks. As result of activity of meteoric water, there is a dissolution of sedimentary rocks (limestone, dolomite and gypsum-anhydrite

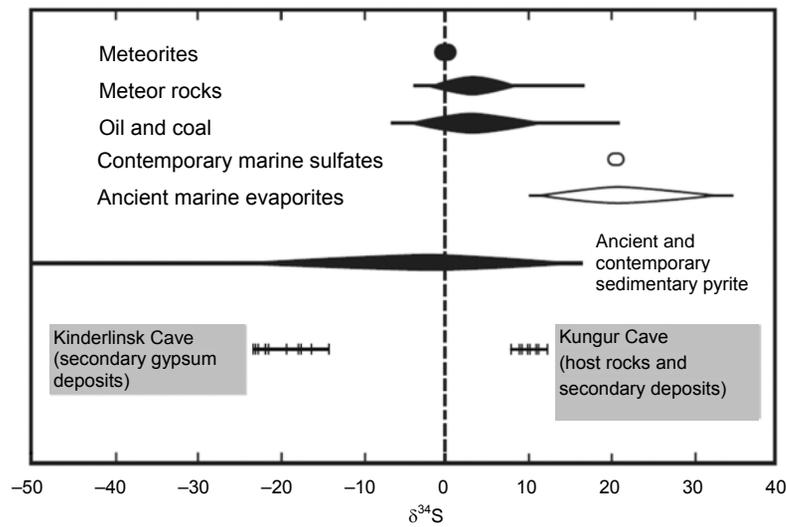


Figure 1. Variations of $\delta^{34}\text{S}$ for various mineral formations by R. R. Seal [24] and the data of our study of the isotopic composition of sulfur and sulfate minerals of the Kungur and the Kinderlinsk.

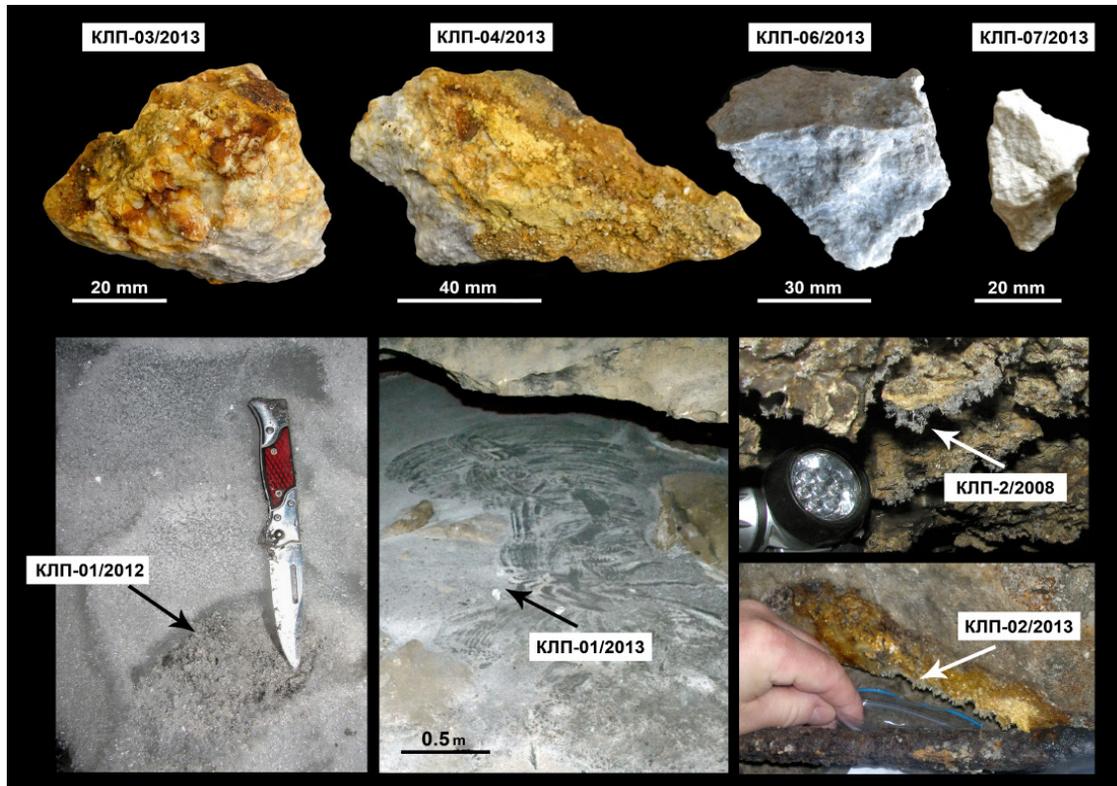


Figure 2. Primary evaporites – gypsum and gypsum-anhydrite rock (top row) and secondary sulphate mineral formations (cryogenic gypsum powder, gypsum, mirabilite “fluff” and modern gypsum crystals) of Kungur cave (bottom row).

rocks of evaporite strata) and their redeposition with the formation of the newly formed sulfate minerals – gypsum, mirabilite, bled, jarosite.

One can see typical samples of primary sedimentary evaporites and the newly formed sulfate minerals that authors studied in the Kungur cave in Fig. 2.

The sulfur isotopic composition of sulfate (gypsum, anhydrite, mirabilite) of Kungur cave is shown in Table 1. The isotopic composition of sulfur of Kungur cave sulfates shown in Fig. 1.

The host rocks (gypsum and anhydrite), selected in the Diamond and the Coliseum grottoes have the isotope composition of of $\delta^{34}\text{S} +10.09\text{‰}$ to $+12.32\text{‰}$, which corresponds to a typical Lower Permian marine evaporites composition [26]. Authors didn't find significant changes in the isotopic composition of sulfur between sulfates of bedrock and secondary deposits formed by freezing out of solutions (cryogenic fine-grained “flour” in the caves of the Diamond and the Coliseum) and relative to the equilibrium crystallization of water infiltration (gypsum crystals from the Colosseum grotto). This is

consistent with the data about a slight sulfur isotope fractionation during crystallization from aqueous solutions [22]. Authors observed the lighter structure ($\delta^{34}\text{S} + 8.62\text{‰}$) for the needle-like crystals of mirabilite and gypsum from the Diamond grotto.

Enrichment of mirabilite relative to gypsum with light isotope of sulfur was also mentioned for the Canadian cave Kastlegard [19]. Authors assume that this phenomenon is connected with the crystallization feature of these units from the capillary solutions, where one can find anaerobic conditions conducive to the development of sulfate-reducing bacteria.

Kinderlinsk Cave: estimated sulfuric acid corrosion

Kinderlinsk Cave (Republic of Bashkortostan, Gafuriysky District) is located within the West-Ural outer zone of folding, incorporated in the west wing of Tashastinsk syncline, in the limestones of Famennian stage of Upper Devonian (D₄fm) [27], which in the cave area is represented by the layered bituminous gray and dark gray limestones with chert layers.

Table 1. Isotopic composition of sulphate sulfur in the samples from the Kungur cave.

Number sample	Year of sample selection	Location	Description, mineral composition	$\delta^{34}\text{S} \text{ ‰, CDT}$
The host rocks $^{ir}_{10}\text{P}_{1k}^{ir}$ (gypsum and anhydrite)				
КЛП-2/2012	2012	Diamond Grotto	Gypsum	+10.09
КЛП-03/2013	2013	Colosseum Grotto	Gypsum	+11.87
КЛП-04/2013	2013	Colosseum Grotto	Gypsum	+12.26
КЛП-06/2013	2013	Colosseum Grotto	Gypsum and anhydrite rock	+11.37
КЛП-07/2013	2013	Colosseum Grotto	White gypsum rim around the block of gypsum-anhydrite rock Secondary sulfate deposits	+12.32
КЛП-1/2012	2012	Diamond Grotto	Black cryogenic flour (soot pollution?)	+9.40 +9.57
КЛП-01/2013	2013	Cross Grotto	White cryogenic flour	+10.32
КЛП-2/2008 (ПОЛ-2)	2008	Polar Grotto	White needle fluffy formations of mirabilite with an admixture of gypsum on the roof of the grotto	+8.62
КЛП-02/2013	2013	Colosseum Grotto	The newly-formed modern gypsum crystals on a retaining wall	+10.97

Note: NBS-123 standard was used in the measurement. Measurement error in the series is equal to 0.27 ‰ CDT.

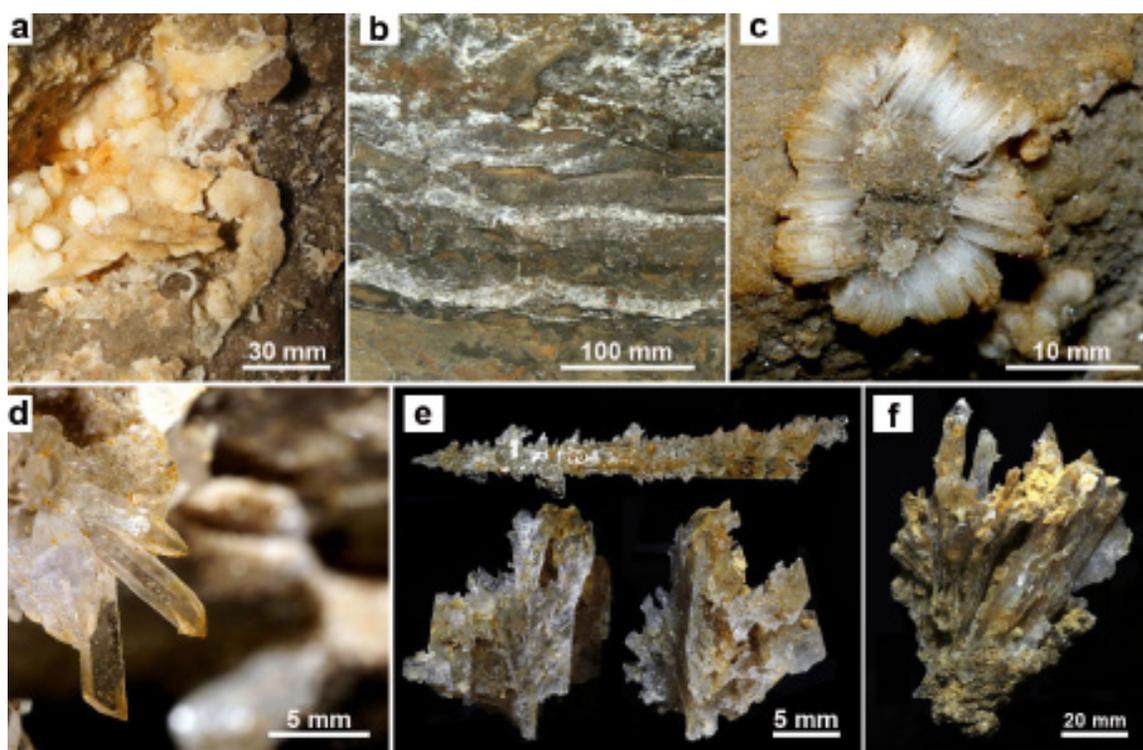


Figure 3. Different types of secondary gypsum deposits the Kinderlinsk cave. a – the fine-grained gypsum crusts; b – cracks on the interlayers; c – fibrous aggregates «stone flower» (antholites); d – an elongated prismatic crystals; e – polycrystalline aggregates growing in the surface layer; f – large crystal growths inside loams.

The Kinderlinsk cave is characterized by an abnormally wide, compared to the other known calcareous caves of the Urals, spread of gypsum deposits, although upon stratigraphic cuts of surrounding and overlying rocks there are no known sulphate deposits. Most gypsum-bearing areas are confined to dry intensively ventilated cavities. Typical forms of gypsum in Kinderlinsk cave is shown in Fig. 3. These are crystal-grained crusts on the walls (up to several centimeters), gypsum cracks filler, fibrous crystal aggregates (“stone flower” or antholites) tabular and elongated prismatic crystals (grown presumably in subaqueous conditions), and different morphologically complex crystalline aggregates inside loams. A feature of the majority of deposits (bark, antholites, clay aggregates) is their formation from the capillary water at the evaporation barrier.

The isotopic composition of sulfur in gypsum samples collected in 2012–2013, is shown in Table 2 and Fig. 1. They are characterized by a light isotopic composition of sulfur, which is usual for sulfur which has passed through a bacterial sulfate reduction (medium negative “shift” is about $\delta^{34}\text{S} -30 \text{ ‰}$).

Discussion of the results and a literature review

Comparing the obtained results with the literature data on sulfur isotopes in the secondary gypsum of various karst carbonate caves (table. 3) shows that gypsum from the Kinderlinsk cave is quite close to gypsum as a “classic” cavities of sulfuric acid speleogenesis: Krauskhülle in the Austrian Alps (according to

Puchelt and the Blum (1989) – quote from [17]), caves of the Chern Valley in Romania [18], Frasassi in central Italy [16], and to the gypsum produced by the oxidation of sulfides in the host rocks for caves having mainly epigenous origin – such as Kastlegard in Canada [19] and Buco della Rana-Pisatela in Italy [20]. Thus, it is possible to eliminate the imposition of gypsum in the Kinderlinsk cave with direct participation of the marine sulfates that have a heavier isotope composition of sulfur.

Kinderlinsk cave is embedded in organogenic bituminous limestones. Such limestones have higher sulfur content. The presence of sulfur in the sulfide form in the host rocks is not directly confirmed, but extensive development of ferrugination and goethite finds in a cave [5] indicate the possibility of existence of diagenetic pyrite in the form of inclusions in the sediment. However, the most probable source is organically bound sulfur contained in the bitumen material, which oxidizes in oxygen conditions to sulfates with participation of sulfur-oxidizing (thionic) bacteria. Microbial sulfur oxidation process itself causes a slight fractionation of sulfur isotopes [24], so the composition of the gypsum formed inherits the composition of the starting material. However, organically bound sulfur in bitumen is usually reduced (i.e. passed through the sulphate reduction at the stage of diagenesis), so it is also characterized by a lighter isotope composition of [32], what could explain the formation of gypsum with a light isotope composition of sulfur.

Table 2. Isotopic composition of sulfur in the samples of recycled gypsum from the Kinderlinsk cave.

Number sample	Year of sample selection	Description, mineral composition	$\delta^{34}\text{S}$ ‰ CDT
K-2/2012	2012	Gypsum antholites	-22.31
K-3/2012	2012	Gypsum crusts	-23.25
K-4/2012	2012	Gypsum antholites	-23.03
K-5/2012	2012	Gypsum – crack filler	-23.51
K-13/2012	2012	Brown gypsum crusts	-22.22
K-21/2012	2012	Gypsum crusts	-19.64
K-22/2012	2012	White gypsum growths	-17.28
K-5/2013	2013	Gypsum crusts	-13.85
K-7/2013	2013	Gypsum	-16.49
K-8/2013	2013	Gypsum antholites	-15.288

Note: NBS-123 standard was used in the measurement. Measurement error in the series is equal to 0.27 ‰ CDT.

Table 3. The isotopic composition of sulfur in secondary sulfates from different caves of carbonate karst (according to published data).

Object	$\delta^{34}\text{S}$, ‰ CDT	Laying of cavities	The source of sulfate prospected by authors	Reference
Cave Ogof near Daren Cilau, South Wales, United Kingdom				
Gypsum crystals	-30,3 -31,6 -33,3	carboniferous limestone	Diagenetic pyrite oxidation	Bottrell, 1991 [28]
Gypsum crust	-26,3			
Brujas Cave, Argentina				
Gypsum bubbles	+5,4	Jurassic limestones	The oxidation of pyrite in the Jurassic limestone and redeposition from the the overlying Jurassic-Triassic evaporites. Marine evaporites in the section $\delta^{34}\text{S} + 16,6$ ‰ CDT	Sancho e.a., 2004 [29]
Gypsum crust	+5,8 +9,7 +9,6			
Corkscrew Cave, Arizona, USA				
Gypsum crust substitutions	-8,1	Carbonate breccia collapses, Lower Carboniferous rocks	Oxidation of deep warm sulphide water (SAS)	Onac e.a., 2007 [30]
Gypsum flowers (antholites)	-8,7			
Barite crust	-10,2 -9,3 -9,0			
Cerna Valley, Romania (8 caves)				
Gypsum (crust, antholites) tamarugit-NaAl – NaAl(SO ₄) ₂ ·6H ₂ O (Antholites), alunite and aluminum (aggregates)	Fist group avg. -25 Second group avg. +17 Third Group avg. -7	Marly limestones of the Lower Cretaceous	Active hydrothermal SAS-caves with the release of steam, enriched with H ₂ S. Estimated source of H ₂ S are evaporites below (bacterial reduction of hydrogen sulfide and methane as an electron donor). To explain the heavy composition of sulfur in one of the groups sulfate reduction is expected during the an excess of electron donors (methane) and shortage of sulfate ions in solution	Onac e.a., 2011 [18]
Kraushöhle Cave, Austria				
Gypsum (crystals, crust)	From -15,8 to -23,1	Lower Jurassic limestones	Oxidation of sulphide waters (SAS). The source of hydrogen sulfide are gypsum-bearing rocks of Upper Permian age located below in the section	Puchelt and Blum (1989), quote by Plan e.a., 2012 [17]
Cave Provalata, Macedonia				
Gypsum	-2,1 -2,2	Cambrian marbles	Oxidation of sulphide waters (SAS). Hydrogen sulfide source – coal deposits, where inclusions of pyrite, organic sulfur, gypsum are known.	Temovski e.a., 2013 [31]
Cave Castleguard, Canada				
Gypsum (crust, antholites) Mirabilite	From +14,2 to +22,6 +7,8	Middle Cambrian limestones	The oxidation of pyrite in the host rocks ($\delta^{34}\text{S} + 15,5$ ‰) and redeposition from the evaporites (anhydrite, $\delta^{34}\text{S} + 15,5$ ‰)	Yonge, Krouse, 1987 [19]
The cave system Buco della Rana-Pisatela, Italy				
Gypsum (crust, antholites)	From -29,5 to -33,2	At the contact between Eocene basalts and Eocene-Oligocene marls and kalkarenite	Diagenetic pyrite oxidation from the host rocks	Tisato e. a., 2012 [20]
Frasassi cave system, Italy				
Fine-grained gypsum Gypsum crystals	From -7,82 to -24,24 From -7,53 to -22,52	The limestones of Jurassic age	Currently active SAS-cave, the oxidation of sulphide waters. The source of hydrogen sulfide are evaporites located below in the Upper Triassic section	Galdenzi, Maruoka, 2003 [16]

One can assume that the sulfuric acid corrosion plays a role in the genesis of cavities of the Kinderlinsk cave. Earlier we noted [33] that the existing set of characteristic morphological elements (pressure domes and niches, cascades of isometric upward-fireplace mines, plenty of «blind» upward strokes, rock «bridges» and «suspensions», the elements of the coarse labyrinths), with a weak development of surface supply karst forms above it, gives grounds for assuming the inception of cavities by a model of hypogenic (artesian) speleogenesis in the conditions of the rising water exchange on the model of A. B. Klimchuk [12]. At the occurrence of oxygen or oxygen water in the system activity of sulfur-oxidizing bacteria has begun, which could help to maintain the dissolving ability of water in closed from the direct inflow of exogenous soil carbon dioxide conditions.

Conclusion

On the example of caves of sulfate (Kungur, Perm region) and carbonate karst (Kinderlinsk, Bashkortostan) authors show the features of the formation of the isotopic composition of sulfur in the secondary sulphate deposits.

In the first case (Kungur cave), host rocks (gypsum and anhydrite) had isotope composition of $\delta^{34}\text{S}$ from +10.09 ‰ to +12.32 ‰, which is typical for the Lower Permian marine evaporites. The system [host rocks => infiltration of water => secondary sulfate deposits] did not show any noticeable changes in the isotopic composition, which is consistent with the literature data on the insignificant fractionating upon crystallization from aqueous solutions [22]. Authors observed a slightly lighter structure ($\delta^{34}\text{S} + 8.62$ ‰) for mirabilite from the grotto Diamond, which could be due to the partial sulphate reduction in capillary solutions.

In the second case (Kinderlinsk cave) there was a lighter isotope composition of sulfur in the secondary gypsum deposits ($\delta^{34}\text{S}$ from -23.25 ‰ to -13.85 ‰). This composition is typical for bacterial reduction of sulfur compounds and eliminates the deposition of gypsum with the direct participation of marine origin sulfates (heavy isotopic composition). The most likely source is organically bound sulfur contained in the bituminous material in the host rocks, which oxidizes in oxygen conditions to sulfates with participation of sulfur-oxidizing (thionic) bacteria. Earlier we noted [33] that Kinderlinsk cave has a set of morphological elements characteristic to the hypogenic (artesian) speleogenesis by the model of A. B. Klimchuk [12]. At this stage, the sulfuric acid corrosion could play a role in the formation of cavities while maintaining dissolving power of water in closed from the direct inflow of exogenous soil carbon dioxide conditions.

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