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PALYGORSKITE IN CAVES AND KARSTS: A REVIEW

PALIGORSKIT V JAMAH IN KRASU: PREGLED

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Pavel Bosák & Nadja Zupan Hajna: Palygorskite in caves and karsts: a review

Palygorskite is fibrous mineral representing the transitional phase between chain silicates and layer silicates with modulated phyllosilicate structure. Although often found in carbonate environments, it forms quite uncommon constituent of cave fills. Palygorskite occurs in cave fills in two forms: (1) allogenic palygorskite which in arid and semiarid conditions can represents substantial constituent of cave fills, often associated with smectite, gypsum, calcite and halite; it is airborne or transported by surface run-off to caves from desert soils and paleosoils, calcretes, dolocretes and related deposits in cave surroundings. (2) Authigenic palygorskite occurs as *in situ* precipitate in cave fills from percolating water solutions and/or transformation of smectite and kaolinite in dry evaporative conditions and suitable geochemical composition of solutions. In carbonate hostrocks palygorskite fills fissures and faults and often it is found in cave walls. It occurs commonly as part of the “mountain leather” as a result of hydrothermal and/or weathering processes or represents a product of *in situ* chemical precipitation from percolating meteoric solutions with suitable pH a redox conditions and chemical composition.

Key words: palygorskite, caves, karst.

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Pavel Bosák & Nadja Zupan Hajna: Paligorskit v jamah in krasu: pregled

Paligorskit je vlaknat mineral, ki je prehodna fazo med inosilikati in listastimi silikati z modulirano strukturo filosilikata. Čeprav je pogost v karbonatnih okoljih, je precej neobičajna sestavina jamskih sedimentov. Paligorskit se v jamah pojavlja v dveh oblikah: (1) kot alogeni paligorskit, ki je v sušnih in polsuhih razmerah lahko znaten sestavni del jamskih sedimentov, pogosto povezanih z montmorillonitom, sadro, kalcitom in halitom; v teh primerih gre za eolski nanos ali pa za transport v jame s površinskim transportom iz puščavskih tal in paleotal, kalkret, dolokret in podobnih sedimentov; (2) kot avtogeni paligorskit se pojavlja v jamah kot »in situ« oborina iz prenikajočih raztopin in/ali z obarjanjem med transformacijo montmorillonita in kaolinita v jamskih sedimentih v suhih razmerah izhlapevanja in primerno geokemično sestavo raztopin. V karbonatnih kamninah paligorskit zapolnjujejo razpoke in prelome in ga pogosto najdemo na jamskih stenah.

Običajno se pojavlja kot del “gorskega usnja”, ki je posledica hidrotermalnih in/ali procesov preperevanja. Lahko pa nastane tudi zaradi in situ kemičnega obarjanja iz prenikajočih meteornih raztopin z ustreznim pH, redoks potencialom in kemično sestavo.

Ključne besede: paligorskit, jame, kras.

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INTRODUCTION

Hill and Forti (1997) summarized palygorskite occurrence known at that time in caves. They stated that it represents quite uncommon mineral there. They listed several palygorskite-bearing sites described from Botswana (Gcwihaba Cave), Japan, Namibia (Leeurantegrot), New Zealand (Broken Hill, Oyster, and Luckie Strike), South Africa, United Arab Emirates (Kahf Wadi Gulam), United States (Carlsbad Cavern, Lechuguilla Cave, New Mexico; Pend Oreille mining district, northwestern Washington), and Venezuela (Cueva Las Úrsulas). They mentioned a general study of Broughton (1972) as a good source of information. After the summary of Hill and Forti (1997), palygorskite was newly described in some other caves. The location of caves in which palygorskite was reported are summarized on Figure 1.

Because of palygorskite rarity in cave fills we present the review here.

Fig. 1: Location of caves with reported palygorskite: 1. – 2. Southern Africa region (1. Botswana: Gcwihaba Cave, 2. Namibia: Luurante Cave, Rössing Cave, Tinkas Cave), 3. Japan (Ootakine Cave, Tateishi Syonyudo Cave), 4. – 5. New Zealand (4. North Island: caves Broken Hill, Oyster, Luckie Strike, Waitomo; 5. South Island: Riwaka), 6. United Arab Emirates (Kahf Wadi Gulam; Wadi Haqil), 7. – 8. Saudi Arabia (7. Coast: Hibashi lava tube; 8. Desert: Sulb Plateau, B31, Friendly, Surprise and Murubbeh caves, Jabal Al Qarah Caves), 9. – 11. United States (9. New Mexico Guadelupe: Carlsbad Cavern, Lechuguilla Cave; 10. South Dakota´s Wind Cave; 11. Washington: Pend Oreille), 12. Canada (Kootenay Cave), 13. Venezuela (Cueva Las Úrsulas), 14. Spain (Mallorca Island).

GENESIS OF THE MINERAL

Palygorskite belongs to the palygorskite-sepiolite mineral group, which includes several varieties enriched in some elements (e.g., Al, Mn, Fe, Na, K, Ni; Melka & Šťastný 2014). It represents the transitional phase between chain silicates and layer silicates with chain bond of Si–O tetrahedrons, usually Mn-rich, dioctahedral with monoclinic and orthorhombic structural modifications. Although the mineral has fibrous character, it can be assumed as silicate with 2:1 layer modulated phyllosilicate structure (Guggenheim & Krekeler 2011; Melka & Šťastný 2014; Fig. 2). Relationship between palygorskite and biological (biomineralization) activity was also proposed (see Cuevas *et al.* 2011). The synonymous mineral name – attapulgite – often appearing in older studies, is still commonly used in industry (Guggenheim & Krekeler 2011, p. 7).

Palygorskite is commonly found in carbonate environments (see summary and references in Post & Crawford 2007; Singer & Galan 2011; Kaplan *et al.* 2013; Lacinska *et al.* 2014) and as alteration products of ore veins or serpentinites or at fissures of different rock types (Melka & Šťastný 2014). The Al- and Si-bearing carbonate-alkaline environment is conductive to palygorskite neomorphism (e.g., Jones & Galan 1988; Bloodworth & Prior 1993; Hobbs *et al.* 2002). A general genetic model for palygorskite/sepiolite origin is based on the interac-

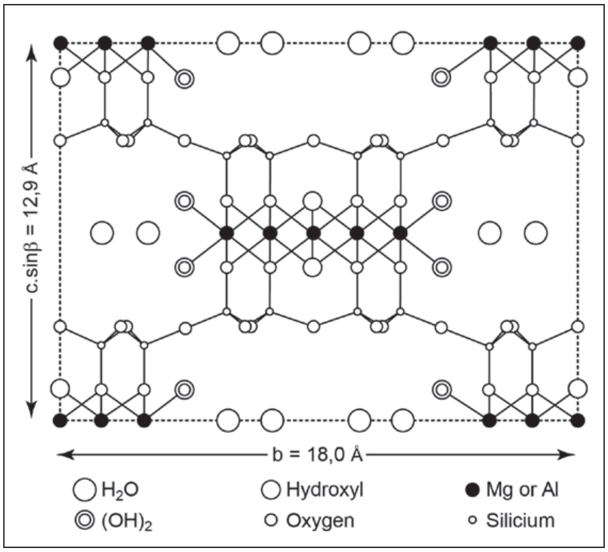

Fig. 2: Palygorskite structure (M. Šťastný, original).

tion between Si- and Mg-bearing solutions (e.g., Jones & Conko 2011), in an environment with high pH and high salinity, and on the activity of Al in solution or the presence of reactive Al-bearing phases in the case of palygorskite (Ferrell 2011). Palygorskite is therefore common neomorphic (pedogenic) mineral in arid soils and paleosoils (Jenkins 1976; Elprince *et al.* 1979; Singer 1979; Mackenzie *et al.* 1984; Mashhady *et al.* 1980; Shadfan & Mashhady 1985; Shadfan *et al.* 1985; Aiban 2006, 2007; Gunatilaka 1989; El-Sayed *et al.* 1991; Aqrawi 1993; Hojati & Khademi 2011; Yalçin & Bozkaya 2011). Therefore, it is commonly associated with dolomite and gypsum, in regions with less than 300 mm mean annual rainfall (Paquet & Millot 1973). Palygorskite directly crystallizes in duricrusts (calcareous soils, calcretes, caliches, dolocretes; Callen 1984, Maizels 1988; Karakaş & Kadir 1998; El-Sayed 2001; Kadir & Eren 2008; Macklin *et al.* 2012; Kadir *et al.* 2010, 2014; Kaplan *et al.* 2013) often within fluvial/alluvial sequences and in ancient sabkhas enclosing ophiolitic rock fragments (Clarke & Walker 1977; Maizels 1988; El-Sayed 2001; Macklin *et al.* 2012; Lacinska *et al.* 2014). Most of palygorskite/sepiolite deposits are thus detected in depositional settings with evaporative regime in arid/semiarid climatic conditions (fluvial to lacustrine systems, including playas, alluvial fans, brackish to hypersaline environments, including sabkhas; for review see Galán & Pozo 2011). Palygorskite is transformed into smectite in wetter conditions (e.g., Paquet & Millot 1973; Heine 1988; Heine & Völkel 2010).

Palygorskite precipitation in joints in carbonate host-rocks is often associated with *in situ* neomorphism directly from percolation of subsurface meteoric water charged with soluble constituents sourced from the breakdown (weathering, dissolution) of minerals from e.g., soil profiles overlying carbonate host-rocks (Soong 1992; Hansen 2008). Hansen (2008) expected that both palygorskite formation and persistence require alkaline pH, high Mg and Si, and low Al activities. Some palygorskite occurrences are connected with late stages of hydrothermal ore-forming processes (e.g., Dings & Whitebreat 1965) and alterations of Mg-rich host-rocks (like serpentinites, gabbroic rocks, carbonate rocks, clay sediments; Melka & Šťastný 2014).

PALYGORSKITE IN KARST AND CAVES

PALYGORSKITE IN KARST

Prevailing number of occurrences of palygorskite in caves is not related to speleogenesis itself, with cave-filling processes and/or transformation/diagenesis of cave fill. Palygorskite usually fills fractures in carbonate host-rocks (limestones, dolostones and their metamorphosed equivalents) and can thus be easily detected on cave wall where it can even hang out of fissures (e.g., Park & Cannon 1943) in a form of so-called *mountain leather* (e.g., Hunt 1960). We present here some of palygorskite occurrences in host-rocks which appear on cave walls but not related to speleogenesis and/or infilling processes, although we are sure, that the review cannot be exhausting.

Soong (1992) summarized palygorskite occurrences in ***New Zealand*** described before 1992; most of them are associated with joints and faults in limestones. He also identified palygorskite at Canaan, Thomson Hill (direct neomorphism from meteoric waters that percolate through soils above marbles), and Riwaka (percolation of subsurface meteoric water through narrow passages and cavities in weathered dolomitic marbles) in northwest Nelson, South Island. Hansen (2008) studied the Latest Oligocene to earliest Miocene aged Otorohanga Limestone formation of the Te Kuiti Group. A distinctive leathery palygorskite occurs commonly as a chemical precipitate also in joints. Palygorskite is formed *in situ*, i.e., it is not washed into joint fill as allogenic material.

Palygorskite has been reported by Park and Cannon (1943), Halliday (1963), Dings and Whitebreat (1965), and Frost (1971) in the caves of the Pend Oreille mining district, northwestern Washington (***USA***), developed in Metaline metamorphosed limestone (Middle Cambrian). Palygorskite occurs as leathery deposits filling fractures and hangs from the roof and sides of the cave in dangling masses, and in many places it is wet and shiny. Park and Cannon (1943) and Dings and Whitebreat (1965) stated that palygorskite is commonly present in many of the caves where it fills fractures and hangs from the roofs and sides in dangling bodies resembling soiled and frayed rags or a wet and torn newspaper. Palygorskite is of hypogene origin formed at a late stage after most of the sulfides and coarse carbonates were developed.

In ***Venezuela***, Urbani (1975a, b, 1996) described palygorskite from Cueva Las Úrsulas developed along a joint in quartz-mica-albite-schists as 1 mm thick leathery sheets and crusts on the walls and fractures. The sheets are light brown but also reddish due to iron-oxide staining. They are flexible and associated with minor amounts of calcite.

In the Yucatan Peninsula (***Mexico***) palygorskite is found in high contents in different localities and was used by the ancient Mayas to prepare especially the Maya blue pigment (a composite of organic and inorganic constituents, primarily indigo dyes derived from the leaves of añil *Indigofera suffruticosa* plants combined with palygorskite; Sanchez del Rio *et al.* 2011). Palygorskite can be a constituent of Tertiary lacustrine deposits (Sanchez del Rio *et al.* 2009).

Sepiolite and palygorskite are reported by Imai and Otsuka (1984) from the Ogano and Hanezuru mines in the southern part of the Ashio Mts. (Kuzuu District 80 km north of Tokyo, ***Japan***) as the fill of faults in Paleozoic and Mesozoic limestones and dolostones. Other occurrences of palygorskite related to fill of fractures, fault and other tectonic structures and found in caves are reported from some caves in former ***Czechoslovakia*** and ***Czech Republic*** by Cílek (1984; plates in mud, fallen from fissure fillings in marbles), Morávek (1998; from fissures, in places protruding to small cavities, i.e., macroporosity in the Vitošov limestone Quarry in Moravia), Drbal (2007) and Krejča (2008) from the Chýnovská Cave in Proterozic marbles in the association with boxwork selectively corroded from fissure fillings in marbles. Crusts and layers of fibrous aggregates in fissures in dolomites of the Bleiberg Pb-Zn deposit (***Austria***) was mentioned by Velebil (2005) and by Jeršek *et al*. (2006) from nearby Mežica Pb-Zn deposit (***Slovenia***). Rečnik (2013) described palygorskite as a few centimeters large cloth-like assemblies in fissures of silica-rich intraclastic dolosparite in the Idrija mercury mine (***Slovenia***). Lauritzen (2006) mentioned palygorskite from ***Western Spitsbergen*** in G18 Dobbeltgrotta (Paleozoic marbles) in small veins. Cílek (2012, pers. com.) discovered probably hydrothermal palygorskite in tectonically crushed zone with calcite at the Dolný vrch Plateau (Slovak Karst, ***Slovakia***).

PALYGORSKITE IN CAVES

In the ***USA***, palygorskite was identified in South Dakota´s Wind Cave by Bern (2004). Authigenic palygorskite is abundant in clay fill of caves of the Guadalupe Mountains, New Mexico (e.g., Davies 1964a, b; DuChene 1986; Hill 1987; Cunningham *et al.* 1995; Polyak & Güven 1996, 2000; Polyak 1998). Hill (1987) described waxy, colorful (blue, blue-green, pure-white and lavender) clay, and less waxy, soapy-feeling, colorful (gray-green, pink, brick-red and brown) clay fills sponge-work pockets in the limestone or underlies clastic sediment. The waxy clay usually occurs as veins, pods, or stringers within the soapy-feeling clay, with a sharp color differentiation displayed by the two clay types. The clay deposits have dried, compacted, and cracked so that they are now sloughing out of the spongework and are piling up as talus debris on the cave floor. Clays are composed of 10 Å variety of halloysite (former endellite), smectite and palygorskite. Palygorskite was converted to hydrated halloysite and alunite in green clays (Polyak and Güven 1996). Palygorskite is associated with smectite, illite, and kaolinite in the <2-μm fraction of these deposits according to Polyak & Güven (2000): the TEM micrographs show fibers of palygorskite radiating from oval-shaped smectite aggregates; the SEM images show palygorskite fibers disseminated in the clay-rich matrix of the laminated silt, and sometimes concentrated along quartz grain surfaces. They concluded that palygorskite is not a clay constituent of the carbonate bedrock, therefore it formed in a carbonate-alkaline environment produced by drip waters that saturated the silt and clay deposits, or by detrital grains of calcite and dolomite occurring in the laminated silt. The $^{40}Ar/^{39}Ar$ dating of alunite from these sediments ranged from 11.3 Ma for caves located at the higher elevations to 3.9 Ma for the Carlsbad Cavern at lower elevation (Polyak *et al*. 1998).

In ***Canada***, Horne (2005, p. 60) reported that "*the first known find, in a Canadian cave, of the mineral attapulgite is in a Kootenay Cave*". Bates *et al.* (2008) related chlorite and palygorskite in siltstones from the Middle to Upper Triassic paleocavity fill at the sub-Watrous unconformity to (semi-)arid environment either through transformation of smectite or by neoformation in Al-rich soils and/or shallow water.

In ***New Zealand***, Laird and Donald (1961) and especially Lowry (1964) described in detail palygorskite from in the Free Attic Passage, Broken Hill Cave, and other caves in the Te Kuiti District (Oyster Cave, Luckie Strike and a cave on the property of Mr. Axel Juno). Lowry (1964 , p. 917) connected the palygorskite with

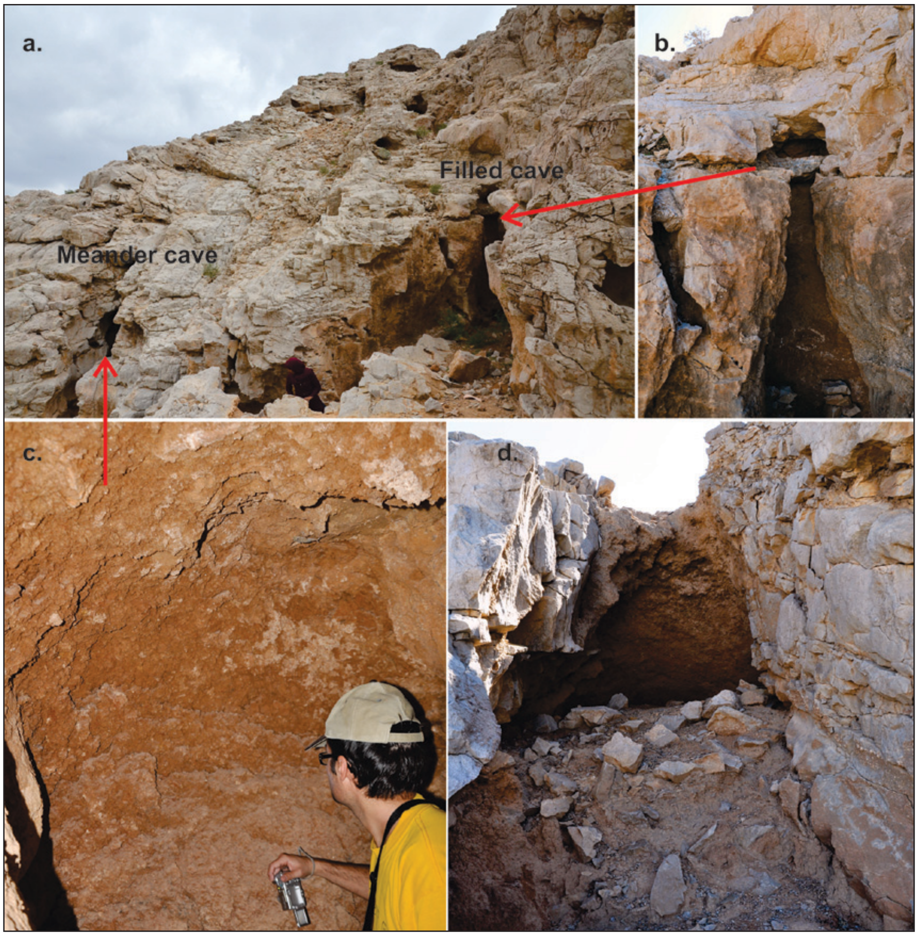

Fig. 3: Unroofed caves filled by palygorskite bearing sediments on the slopes of Wadi Haqil (Musandam Mountains; Ras Al-Khaimah Emirate). a. locations of cave entrances and unroofed caves; b. with sediments filled cave from where are samples No. 1 (bottom), 2 (middle), 3 (top); c. brown fill in Meander cave with location of sample No. 6.; d. unroofed cave on the slope of the hill with location of sample No. 5 (grey sediment mixed with scree) (Photo: N. Zupan Hajna).

former flooding of the cave by the water: "*it was probably at that time that the joints* (in the host-rock) *became filled with palygorskite*". The presence of palygorskite ($(Mg, Al)_2Si_4O_{10}(OH).4H_2O$) in Broken Hill caves was confirmed recently by Onac and Forti (2011). Soong (1992) identified palygorskite at Canaan, Thomson Hill, and Riwaka in northwest Nelson, South Island. It is suggested that the clay mineral neoforms directly from subsurface meteoric water that percolates through the soil profiles overlying marble at Canaan and Thomson Hill, and through narrow passages and cavities in weathered dolomitic marble at Riwaka. Hansen (2008) studied Oligocene-Miocene Otorohanga Limestone Formation (Te Kuiti Group). A distinctive leathery clay mineral – palygorskite – occurs commonly as an *in situ* chemical precipitate both in joints and caves as an infill. Caves act as natural sediment traps for siliceous materials, the fills being enriched in clay minerals, including palygorskite. Waitomo Disctrict Council (2009) mentioned the presence of important speleothems (calcite pearls and palygorskite) in the Waitomo Headwaters (Cave) System giving any details. Hill and Forti (1997) mentioned more study of Kermode (1969) and of anonymous author (1964) on palygorskite in caves of New Zealand.

Kashima (1987, 1993) mentioned palygorskite in ***Japan*** from the Ootakine Cave in limestones (Fukushima Province) giving unfortunately no further details. Hill and Forti (1997) mentioned more study of the Cave Research Group (1983) from the Tateishi Syonyudo Cave.

In ***United Arab Emirates***, palygorskite was observed in the caves of Kahf Wadi Gulam inside of mud cracks on the cave floor at ca 200 m a. s. l. Borreguero and Jeannin (1990) interpreted that palygorskite was related to activity of brackish waters during an ancient stage in cave development when sea level was higher and the cave was subjected to an ingression of sea water. Zupan Hajna *et al.* (2013, 2016a, b) described palygorskite-rich cave fill from small caves of ancient hypogene origin from the entrance of the Wadi Haqil (Musandam Mountains; Ras Al-Khaimah Emirate). Caves are situated close to the surface and they are partly or completely unroofed (Fig. 3a, b, d). Various types of calcite and gypsum crystals and flowstones are present together with allochthonous clastic sediments (Fig. 3c). According to the XRD, samples (for location see Fig. 3b,

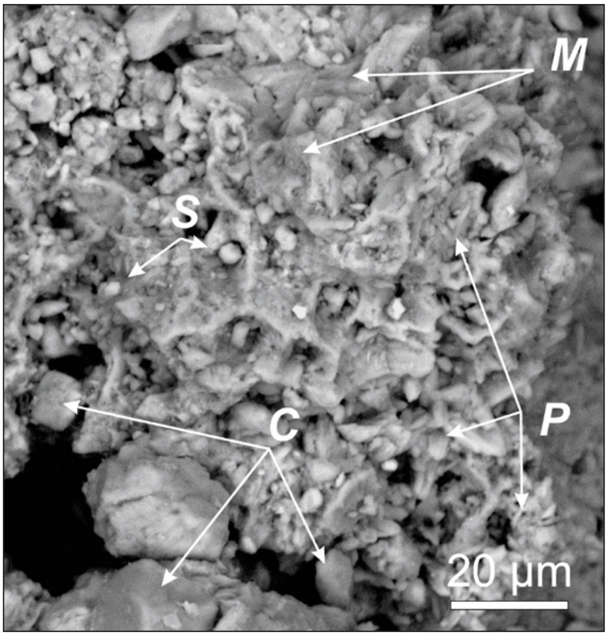

Fig. 4: Scanning electron microscope images of aggregates of mutually inter-grown palygorskite fibers (P) accompanied with grains of other clay minerals (M), minute calcite rhombohedra (C) and rare iron sulfide grains (S), Wadi Haqil, United Arab Emirates (Photo: R. Skála).

c) contain quartz, gypsum, smectite, kaolinite, calcite, and palygorskite (10 wt. % to 26 wt. %; Fig. 4), some of them Fe-dominant chlorite, illite, feldspars and goethite. Higher palygorskite content is typical for samples of grey color (samples Nos. 1; Fig. 5) while the lowest content was identified in brown sample (No. 6; Fig. 5).

Calcite dominates in most samples; smectite prevails in clay fraction (Skála *et al.* 2011; Fig. 5).

Palygorskite empirical formulae between $(Mg_{1.09}Al_{0.89}Fe_{0.02})(Si_{3.99}Al_{0.01})O_{10}(OH)_{0.90}\bullet 4.11H_2O$ and $(Mg_{1.36}Al_{0.61}Fe_{0.02})(Si_{3.90}Al_{0.10})O_{10}(OH)_{0.54}\bullet 4.29H_2O$ were calculated (Zupan Hajna *et al.* 2016c). Cave sediments represent palygorskite-bearing weathering products and desert soils re-deposited from the cave surroundings by slope processes, wind and/or surface runoff. Fine-grained quartz fraction is probably airborne. Gypsum and calcite are the precipitates (crusts and/or cements), although gypsum can also be re-deposited from omnipresent gypsum-cemented surface sediments. High kaolinite content and negligible feldspar content may indicate (1) high degree of weathering of original source-rocks, and/or (2) re-deposition of older weathering crusts, coming at least partly from ultrabasic (mafic) magmatites (Zupan Hajna *et al.* 2016c). The marine transgression-related model proposed by Borreguero and Jeannin (1990) and the *in situ* palygorskite neomorphism within the cave fill due to brackish water is unlikely here with the respect to geomorphic evolution of the area. Palygorskite *in situ* precipitation in mud cracks can be rather related to smectite or kaolinite transformation in dry evaporative condition and activity of Mg- or Al-rich solutions (dripwater) in this broader region.

In ***Saudi Arabia***, Forti *et al.* (2004) and Pint *et al.* (2005) described palygorskite from Ghar Al Hibashi lava tube as snow-white soft tufts of densely interlaced thin elongated vitreous fibres on a burned jaw of an animal. Pint and Pint (2005) and Forti *et al.* (2008) found rather common palygorskite in the desert caves in Saudi Arabia (As Sulb Plateau, B31, Friendly, Surprise and Murubbeh caves). It occurs as light milky white cotton tuffs consisting of elongated and banded fibres, sometimes as acicular

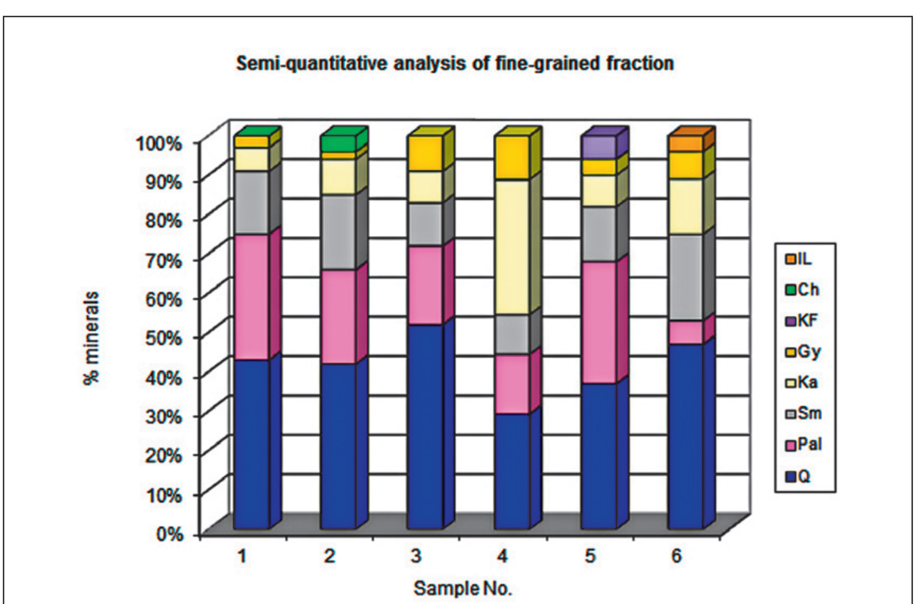

Fig. 5: Semi-quantitative analysis of fine-grained fractions from cave sediments from Wadi Haqil, Ras Al-Khaimah. Legend: 1. grey sediment, 2. laminated sediment, 3. red sediment, 4. yellow sediment, 5. grey sediment with gypsum crystals; 6. cemented brown sediment; Q – quartz, Pal – palygorskite, Sm – smectite, Ka – kaolinite, Gy – gypsum, KF – potassium feldspar, Ch – chlorite, IL – illite (from data in Skála et al. 2011).

milky white crystals on walls of the small voids among the halite crystals. It is associated with gypsum. They expected that palygorskite developed inside natural caves. The Jabal Al Qarah Caves of the Hofuf Area contain wind-blow dust and speleothems (Hussain *et al.* 2006); palygorskite and Mg-rich smectite dominate among clay minerals. The origin of those clay minerals was related to the deposition in the ephemeral saline lake or saline flood plain. Hussain *et al.* (2006) reported common occurrence of palygorskite in soils in the studied region and the whole Arabian Peninsula (see also Jenkins 1976; Mackenzie *et al.* 1984).

In ***Southern Africa region***, Martini (1993) summarized the occurrences of number of minerals in caves of Botswana and Namibia. In *Botswana*, Martini (1996) described palygorskite from the Gcwihaba Cave. In *Namibia*, Heine (1988) and Heine and Völkel (2010) mentioned high proportion of palygorskite (35 to 65 %) in airborne cave fill in the Rössing Cave (late Quaternary) and in the Tinkas Cave (Little Ice Age). It is associated usually with smectite, illite, kaolinite and mixed-layer clay minerals. In the Rössing Cave, palygorskite is associated with at least three noticeable climatic fluctuations on a time-scale around 2 ka occurred during which more humid conditions were replaced by more arid (and more windy) ones and vice versa in a period between ca 34 and 27 ka. Martini (1993) reported whitish powdery palygorskite associated with minerals of smectite group, halite and gypsum from the Luurante Cave. It resulted from the transformation of residual kaolinic clay by Mg-rich solutions concentrated by evaporation.

Eolian origin of palygorskite (component of dust deposits) found in karst sediments is reported from Mallorca Island (***Spain***) by Fiol *et al.* (2005), nevertheless the mineral has not been detected in Late Pleistocene to Recent cave fill.

GENETIC MECHANISMS OF PALYGORSKITE IN CAVES AND KARSTS

Hill and Forti (1997) summarized the origin of palygorskite in caves from different sources. Palygorskite is related to different processes within caves: (i) to the weathering of the cave walls which contain quartz, plagioclase, muscovite, and calcite (Cueva Las Úrsulas; Urbani, 1975a, b; 1997); (ii) to the transformation of smectite to palygorskite under dry conditions and to 10 Å variety of halloysite (former endellite) in acidic conditions, which can further transform into halloysite by drying (Davies 1964a, b; Hill 1987; Hill & Forti 1997); (iii) to the transformation of residual kaolinitic clay by magnesium-rich solutions concentrated by evaporation (Leeurantegrot; Irish *et al.* 1991; Leevante Cave; Martini 1993); (iv) to an ingression of sea water into the cave (Kahf Wadi Gulam; Borrequero & Jeannin 1990), or (v) to the hydrothermal (hypogenic) processes (the Pend Oreille; Frost 1971).

We summarize, that palygorskite in cave fills is always connected with dry (arid, semiarid, evaporitic) conditions both of external and cave climates. Two forms can be distinguished: (1) allogenic palygorskite can represent substantial constituent of cave fills in places. It is commonly associated with smectite, gypsum, calcite and halite. It is airborne or transported by surface run-off to caves from desertic soils and paleosoils, calcretes, dolocretes and related deposits in cave vicinity; and (2) authigenic palygorskite occurs as *in situ* precipitates in cave fills from water solutions percolating through carbonate host-rocks and overlying soils or weathering profiles and/or transformation of smectite and kaolinite in cave fills in evaporative conditions and with suitable geochemical composition of solutions (especially Mg-rich).

In carbonate host-rocks (limestones, dolostones and their metamorphosed equivalents) it fills fissures and faults and usually occurs in a form of "mountain leather". It is result of hydrothermal and/or weathering processes or represents a product of *in situ* chemical precipitation from percolating meteoric solutions with suitable pH a redox conditions and chemical composition.

CONCLUSIONS

Palygorskite is fibrous mineral representing the transitional phase between chain silicates and layer silicates with modulated 2:1 layer phyllosilicate structure. The carbonate-alkaline environment containing alumina and silica is conductive to palygorskite neomorphism, which is based on the interaction between Si- and Mg-bearing solutions in an environment with high pH and high salinity, and on the activity of Al in solution or the presence of reactive Al-bearing phases (e.g., Jones & Conko 2011; Ferrell 2011). Therefore palygorskite represents common neomorphic (pedogenic) mineral in arid soils and paleosoils often associated with dolomite and gypsum (calcareous soils, calcretes, caliches, dolocretes, gypcretes) or halite, in regions with low mean annual rainfall. Most of palygorskite/sepiolite deposits are thus detected in depositional settings with evaporative regime in arid/semiarid climatic conditions (fluvial to lacustrine systems, including playas, alluvial fans, brackish to hypersaline environments, including sabkhas; for a review see Galán & Singer 2011).

Although often found in carbonate environments, palygorskite forms quite uncommon constituent of cave fills. Palygorskite occurs in cave fills in two forms: (1) as allogenic palygorskite in arid and semiarid conditions can represents substantial portion of cave fills, often associated with smectite, gypsum, calcite and halite; it is airborne or transported by surface run-off to caves from desertic soils and paleosoils, calcretes, dolocretes and related deposits, and (2) as authigenic palygorskite occurs as *in situ* precipitates in cave fills from percolating solutions and/or transformation of smectite and kaolinite in cave fills in dry evaporative conditions and with suitable geochemical composition of solutions.

In carbonate host-rocks (limestones, dolostones and their metamorphosed equivalents) it fills fissures and faults and is often found in cave walls. It occurs usually in a form of "mountain leather" as a result of hydrothermal and/or weathering processes or represents a product of *in situ* chemical precipitation from percolating meteoric solutions with suitable pH a redox conditions and chemical composition.

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