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POROSITY CHANGES INDUCED BY SALT WEATHERING OF SANDSTONES, BOHEMIAN CRETACEOUS BASIN, CZECH REPUBLIC

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ABSTRACT
Different types of rock crusts and the underlying unweathered sandstone were sampled in the Bohemian Cretaceous Basin, Czech Republic. Structure and mineral composition of the samples were studied using optical microscopy, scanning electron microscopy with EDAX, and X-ray diffraction. Pore parameters were determined using mercury intrusion porosimetry/ helium pycnometry. Principal salts identified in the rock crusts and in the efflorescences are gypsum and alums. Two types of rock crusts were distinguished on morphological basis:
1. patterned rock crusts with a variety of weathering forms (honeycombs, wandkarren), and
2. armoured rock crusts with a relatively smooth, hardened layer.
Patterned rock crusts on medium- to coarse-grained quartzose sandstones show an increase in the size of macropores relative to unweathered sandstone, which mostly implies an increase in total effective porosity. This is explained by the subflorescent growth of salt crystals, the force of which leads to the loss of contact among grains, pore widening, and granular disintegration.
Armoured rock crusts on fine-grained clayey sandstone show a reduced volume and size of macropores, as these are filled with clay mineral aggregates and gypsum crystals. A prominent increase in the volume of micropores is due to secondary porosity in kaolinite and corrosion of feldspar grains. Insufficient passability of macropores in the armoured layer for pore waters shifts the evaporation front deeper into the rock. This results in contour scaling as the main process of rock-surface degradation, as opposed to granular disintegration on patterned rock crusts.

KEYWORDS: porosity, sandstone, rock crust, salt weathering, case hardening, honeycombs

INTRODUCTION

Pore spaces in coarse detrital rocks function as dominant pathways for fluid migration and transport of solutes. In the early stage of rock evolution, they convey diagenetic/hydrothermal fluids, which are responsible for the distribution of cement in sandstone bodies in a sedimentary basin. With the continued uplift of the basin fill, introduction of cooler, oxidized meteoric waters may induce changes in cement distribution, hence also pore space rearrangement. After exhumation to the earth surface, and even shortly before, the rock becomes exposed to various atmospheric effects (physical, chemical, biological) including the water cycle of precipitation – saturation – evaporation. The effects of diagenetic changes (notably the cement distribution) become accentuated during the weathering process.

Evaporation of pore waters on the rock surface, and shallow under the surface, has the largest impact on the formation of rock crusts and small-scale landforms in sandstone landscapes. The two processes in operation, *salt weathering* and *case hardening*, have been first described by Beyer (1912) in the Sächsische Schweiz in Saxony. Beyer recognized the role of pore waters in the formation of salt efflorescences and rock crusts, and identified alum salts ("Alaun") as the principal mineral contributing to sandstone deterioration. He also noted the presence of superficial crusts "sintered" by gypsum, and speculated that these crusts prevent pore waters from penetrating to the rock surface.

Despite the evidence brought about by Beyer, processes responsible for the origin of cavernous and pitted surfaces on sandstone outcrops have become a subject to a wide discussion until 1970s when convincing experimental work has been carried out (Evans, 1970; Goudie et al., 1970) and the effect of saline solutions has been acknowledged.

In inland settings, salt weathering is typically associated with surface crusting (Robinson and

Williams, 1987). An association of salt weathering with surface crusting represents a basic condition to produce well-defined honeycomb pits and tafoni. The strengthened layer on sandstone surface is reinforced by precipitation of substances (iron, silica, salts) contained in the pore waters. Generally accepted models (cf. Turkington and Paradise, 2005) presume that the process of surface crusting proceeds simultaneously with the process of rock weakening in a shallow subsurface. Breaching of the strengthened layer would allow local evaporation of pore waters, which is otherwise prevented/retarded by the crust. Destructive effect caused by the growth of salt subflorescences concentrates to the deepest parts of the honeycomb pits. Salt efflorescences, on the other hand, concentrate to the periphery of the honeycomb pits. Their destructive effect is considerably smaller and, in fact, may turn into a constructive one. In case of a missing hardened surface, the distribution of honeycomb pits on the sandstone surface is generally controlled by primary sedimentary structures of the rock, i.e., by the presence of clay laminae or grain-size contrasts. The pits are arranged in lines parallel to bedding planes or cross-bedding foreset laminae, or tend to follow bioturbation patterns. On the surfaces of massive, homogeneous sandstones, very initial forms of honeycombs are distributed irregularly; during the subsequent phases of development, random patterns turn into ordered ones. Shapes and typical distances of the pits depend, e.g., on grain size, inclination of the surface and insolation (Mikuláš, 2001).

An important role of salt weathering in honeycomb formation is accepted for sandstone outcrops lying within the reach of wave splash and salt spray at seashores (e.g., Mustoe, 1982, 2010; Pye and Mottershead, 1995; McBride and Picard, 2004), even though such process is only rarely accompanied by surface crusting.

Data from mercury intrusion porosimetry serve as a good indicator of changes in the pore space in detrital sedimentary rocks (Gregg and Sing, 1982). They reflect many aspects related to sedimentary and diagenetic processes (grain packing, sedimentary texture and cementation) as well as to rock disintegration and weathering. As yet, their use has been mostly limited to the conservation of historical buildings and monuments (Rossi-Doria, 1983), e.g., for the distinguishing of rock provenance (Fitzner and Snethlage, 1982; Šrámek, 2009). Siedel (2010) combined porosity measurements of sandstone building blocks from the Zittau area with analyses of salt subflorescences. He concluded that sandstone partly impregnated with iron oxyhydroxides is more vulnerable to granular disintegration and cavernous weathering because of its enhanced microporosity.

Sandstones which underwent the same diagenetic history generally show similar patterns in pore size distribution. Using a set of samples from the Bohemian Cretaceous Basin, Šrámek et al. (1992) demonstrated that building sandstones from a specific area share common porosity characteristics, notably the total pore volume *vs.* median ratio, and differ from those in other areas. Differences in pore size distribution among sandstones from the same area, or even from the same site, should be therefore largely a function of the different styles of weathering and their intensity. This assumption was tested by Přikryl et al. (2007) who studied pore-size distributions in sandstone samples affected by salt weathering from natural outcrops in the Bohemian Switzerland area, Bohemian Cretaceous Basin.

In order to determine the validity of such approach over a wider geographic area and a variety of products of salt weathering/case hardening, we studied pore-size distributions in different sandstone types in the Bohemian Cretaceous Basin and compared them with those in the overlying superficial layers affected by weathering. Special attention was given to: 1, changes in pore-size distribution in the zone of honeycomb pit formation, 2, changes in pore-size distribution in armoured surface crusts bearing no honeycomb pits.

GEOLOGICAL AND GEOGRAPHICAL SETTING

The Bohemian Cretaceous Basin (BCB) extends from Saxony, Germany, towards ESE across most of the Czech Republic. Fluvial, lacustrine and estuarine sediments were deposited in the Early and Mid Cenomanian (from ca. 98 Ma). From the Late Cenomanian onwards, the basin was flooded by a shallow epicontinental sea lying between the boreal ocean in the NW and the deep-water Tethyan basin in the SE. The youngest preserved sediments are Santonian in age (ca. 85 Ma). Detrital material for Cenomanian sediments was derived from multiple elevations in the crystalline basement. In the Turonian and Coniacian, however, with the tectonic uplift of blocks beyond the northern basin margin, most of the material was transported to the basin from the granite-dominated West Sudetic and East Sudetic islands in the north (Skoček and Valečka, 1983). Partly overlapping wedge-shaped packages of coarse detrital sediments of shallow marine origin, max. 150–350 m thick, extend from the northern basin margin towards the basin axis (Uličný et al., 2009). Internal arrangement of the sandstone bodies shows upwards-coarsening (i.e., upwards-shallowing) cycles of several orders of magnitude (metres to tens of metres in thickness) separated by flooding surfaces. A typical cycle consists of bioturbated fine-grained clayey sandstone, passing upwards to horizontally stratified or cross-bedded medium- to coarse-grained sandstone (Adamovič, 1994). Most of the cycles are topped by conglomerate beds.

Sandstones of the BCB are composed almost exclusively of quartz, with less than 5 vol. % feldspar grains and mica flakes. Accessory heavy minerals (<1 vol. %) are mostly represented by tourmaline, zircon and rutile, although staurolite, garnet or anatase are also present in elevated amounts near source areas in the Cenomanian sediments (Skoček and Valečka, 1983).

The most common clay mineral in the fine-grained clayey sandstones is kaolinite. Its content rarely exceeds 10 vol. %. In strongly bioturbated intervals, clay minerals are concentrated to wall linings of tunnels formed by the activity of in-fauna, or to the passive fill of burrows. They are also present in occasional smears and laminae generated by bottom currents. Secondary clay minerals are produced by disintegration of feldspar grains during diagenesis.

Five regions dominated by sandstone can be distinguished within the BCB (from W to E): Bohemian-Saxonian Switzerland (Lower to Upper Turonian), the Lužické hory/Zittauergebirge Mts. (Middle Turonian to Coniacian), the Ralská pahorkatina including the Kokořín area (Middle to Upper Turonian), the Bohemian Paradise (Upper Turonian to Coniacian) and the Broumov area extending to the Góry Stołowe in Poland (Middle Turonian to Coniacian). Lowland regions have warm or moderately warm climate with average annual temperatures of 7–8 °C and annual precipitations of less than 700 mm (Ralská pahorkatina, Bohemian Paradise). Others are rather cold (e.g., 6 °C in Góry Stołowe – max. altitude of 919 m), with annual precipitations between 700 and 1100 mm (Góry Stołowe, Lužické hory Mts.). Temperature inversions are common in narrow gorges. Bases of cliffs are shaded by tree vegetation, thus preserving higher moisture content compared to bare, dry cliff tops.

Formation of large-scale landforms is generally controlled by tectonic deformations, such as tilting of blocks and low-angle folding. Valley courses follow zones of intensive fracturing, and “rock cities” commonly form in areas with orthogonal jointing. Valley profiles show recessive steps and notches at the level of cycle boundaries, which implies that lower parts of cliff faces are mostly composed of fine-grained sandstone types. High variability of small-scale weathering forms is supported by differences in sedimentary textures and structures, by the variable intensities of sandstone cementation and types of cement, and by the favourable humid temperate climate (Adamovič et al., 2006, 2010).

METHODS

Rock samples were taken from each site to represent all weathering products: unweathered sandstone, sandstone with salt subflorescences, rock crust, and salt efflorescences. Polished thin sections of rocks and polished cross sections of the rock surface were made for petrographic study. These were studied using the Olympus BX51 polarizing optical microscope. Scanning electron microscopy (SEM) was applied to rock surfaces and surfaces of freshly broken rock crusts using the Cameca SX 100 electron microprobe (secondary electrons), or in combination with energy-dispersive X-ray spectra (EDX) using Tescan Vega 3 scanning electron microscope at the Institute of Geology AS CR in Prague. Selected samples of salt efflorescences were cast in a polyester resin, and polished cross-sections were created. They were studied at the Institute of Rock Structure and Mechanics AS CR in Prague, using the Leica polarizing microscope with Leica DC 200 camera in reflected light, and in scanning electron microscope with energy dispersive X-ray microanalysis (SEM/EDX; Quanta 450, EDAX).

Mineral phases of subflorescences and some efflorescences were identified using X-ray diffraction (XRD) on the Philips X’pert X-ray diffractometer at Institute of Geology AS CR in Prague (analyst J. Dobrovolný). Mineral phases of most efflorescences were identified using a PANalytical X´Pert PRO diffractometer at Institute of Inorganic Chemistry AS CR in Prague-Řež in a transmission mode.

Skeletal densities (densities of solid phase) were determined by means of helium pycnometry at Institute of Chemical Process Fundamentals AS CR in Prague, using the Accupyc 1330 Micrometrics helium pycnometer (analyst H. Šnajdaufová), with 5 cycles of purging, equlibration rate of 0.58 Pa/s = 0.005 psig/min.). Statistical evaluation provides accuracy down to 0.001 g/cm^3. Measurements of the total intrusion volume, median and average pore radii and bulk density of the samples were performed at the same institute using a high-pressure mercury Micrometrics AutoPore III porosimeter (analyst H. Šnajdaufová). This instrument allows high-pressure mercury intrusion of up to 400 MPa (corresponding to pore radii of 1.5 nm).

DESCRIPTIONS OF SAMPLING SITES

The sampling sites were selected after a careful field examination in order to cover the different types of sandstone (grain size and silt/clay content, sedimentary structures). Quartzose sandstones (quartz over 95 vol. %) and clayey sandstones (clay proportion over 5 vol. %) were identified. Sampling was performed on surfaces of rather uniform inclination (80–85°) at similar heights above the cliff base (0.5–2.0 m) as it has been proved by previous observations that these factors strongly influence the processes on sandstone surfaces (cf. Mikuláš, 2001).

Of the eight sampling sites (Figs. 1 and 2), five lie in the Ralská pahorkatina region in north-central Bohemia: in the Kokořín area (Dobřeň 1 and 2, Planý důl, Kobylka) and the Doksy area (Hradčany). All of them belong to the Jizera Formation (Middle to Upper Turonian). Two sites, Rohliny and Záborčí, lie in the Bohemian Paradise region in NE Bohemia, in the Teplice Formation of the BCB (Upper Turonian to Coniacian). The site of Černuc lies in central Bohemia and the sandstone represents the Peruc-Korycany Formation (Upper Cenomanian). Within the BCB, the sites belong rather to warm or moderately warm sandstone regions with annual precipitations of less than 700 mm. The outcrops lie in forested areas with

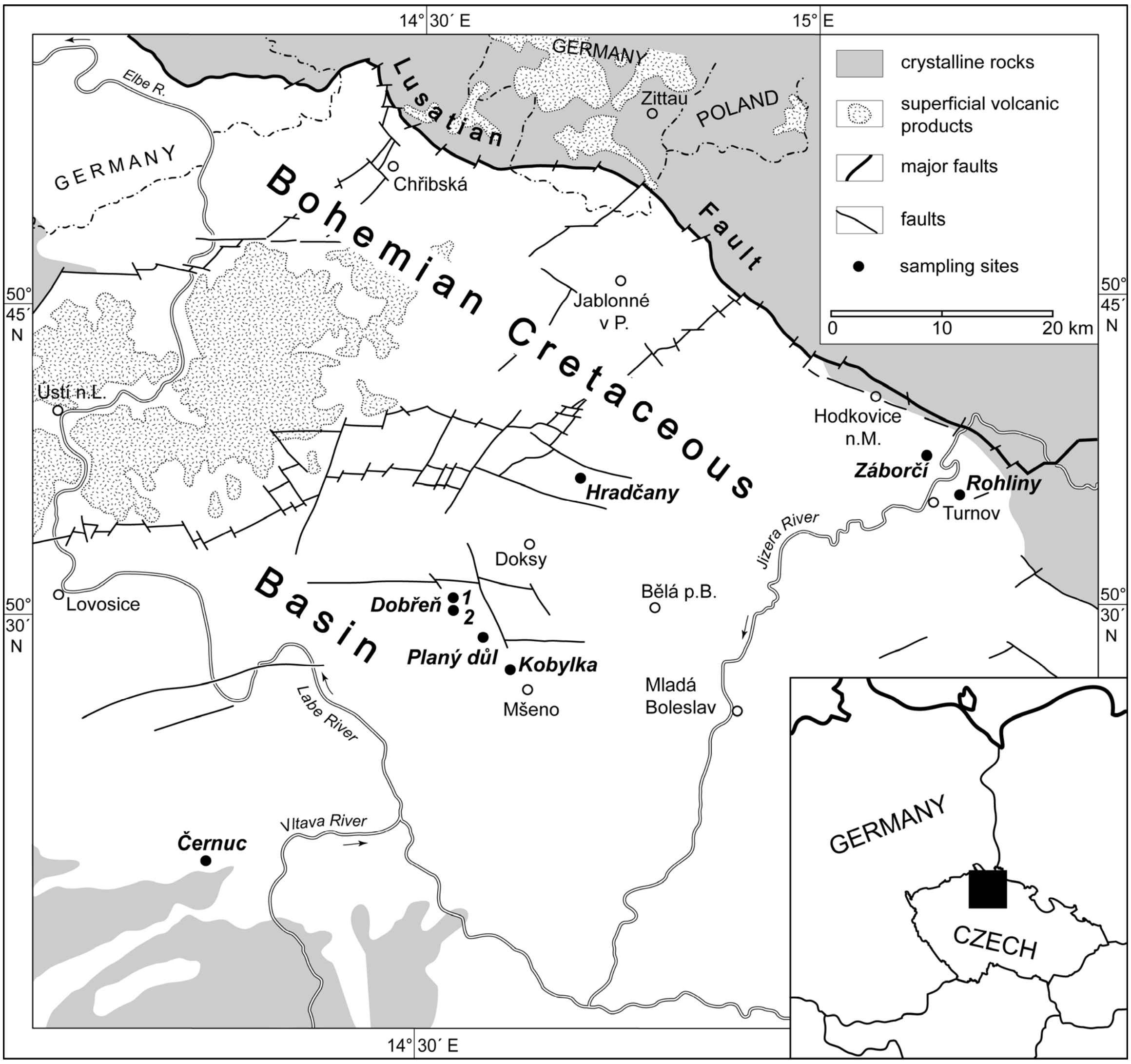

Fig. 1 A simplified geological map of the central and northern part of the Bohemian Cretaceous Basin showing the positions of the studied sites.

the exception of Černuc, which is an old quarry face sparsely shaded by vegetation.

DOBŘEŇ 1

Grey, coarse-grained, horizontally stratified quartzose sandstones on a N-facing cliff; cliff face inclined N at 85°. A dense network of arcuate honeycomb pits, mutually interconnected, extending 15 cm deep beneath rock-crust surface. Spherical pits are formed at places where the rock crust has fallen off. Cliff base 358 m a.s.l., 4 m above the bottom of a dry gorge.

Sst: sandstone 0.5 m above cliff base; PRC: rock crust with honeycombs 2 m above cliff base; S: salt efflorescences under a rock-shelter 1 m above cliff base

DOBŘEŇ 2

Yellowish, medium-grained, horizontally stratified quartzose sandstones with admixture of coarse grains and granules on a N-facing cliff; cliff face inclined S at 85°. Individual large arcuate honeycomb pits developed beneath a locally developed armouring 1 cm thick, with tortoise-shell cracks. Shallow spherical pits are formed elsewhere. Cliff base 373 m a.s.l., 2 m above the bottom of a dry gorge.

Sst: sandstone 0.5 m above cliff base; PRC, ARC: rock crust with lighter armouring 2 m above cliff base; S: salt efflorescences from a notch 0.5 m above cliff base

PLANÝ DŮL

Yellow, coarse-grained, bioturbated quartzose sandstones on a ESE-facing cliff; cliff face inclined WNW at 86°. A dense network of arcuate honeycomb pits extending 15 cm deep beneath rock-crust surface. Cliff base 298 m a.s.l., 28 m above the bottom of a dry valley.

Sst: sandstone 1 m above cliff base, depth 20 cm; PRC: rock crust with honeycombs 2 m above cliff base; S: white salt efflorescences 1–1.4 m above cliff base

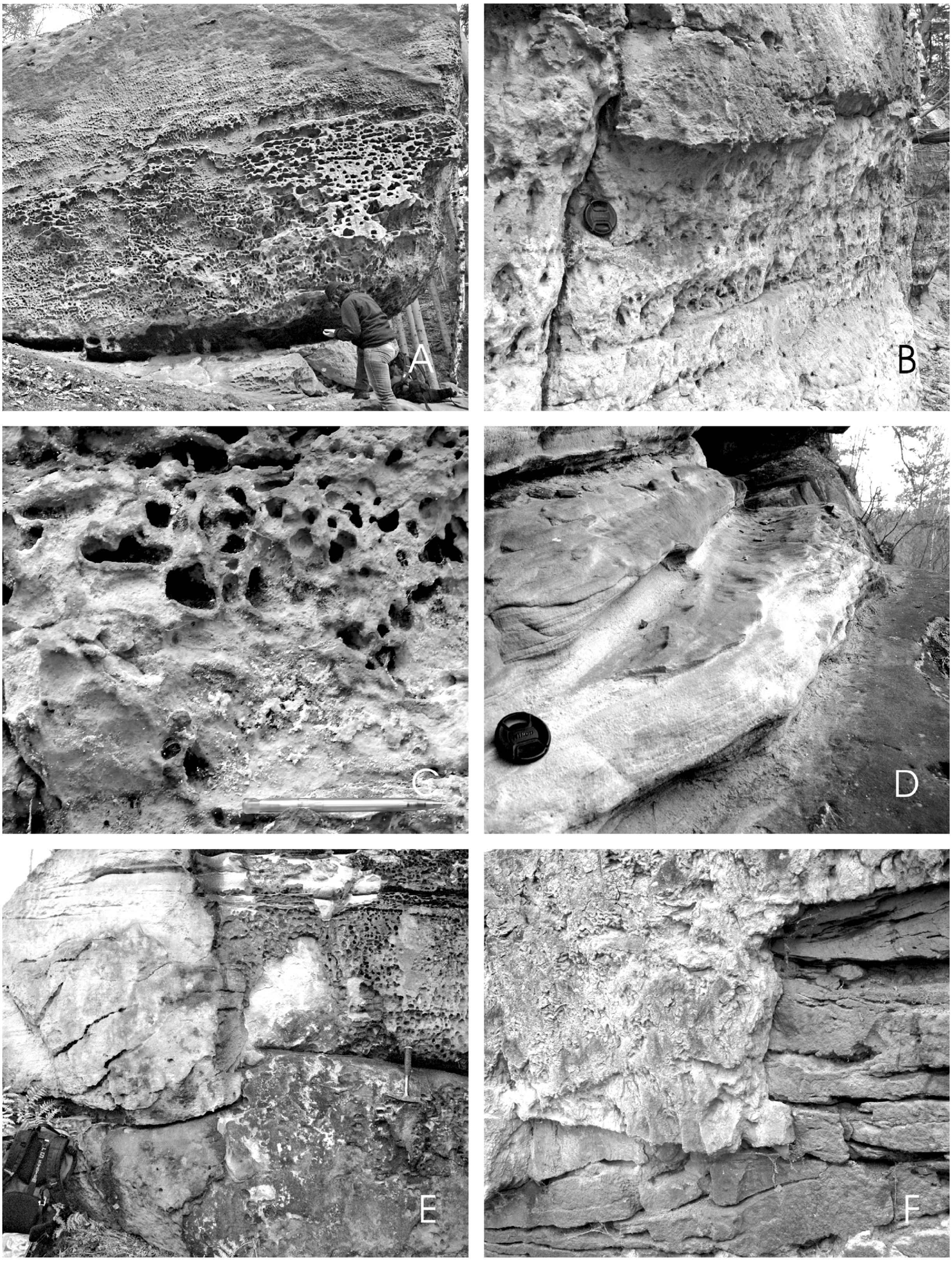

Fig. 2 The character of rock crusts at the individual sites studied. A. Deep honeycomb weathering in coarse-grained sandstone at Dobřeň 1. The rock crust becomes progressively destructed to the left. B. An armoured rock crust obscuring primary sedimentary structures (top) at Kobylka. Where the armouring is absent, the underlying fine-grained sandstone bears gypsum efflorescences (middle). C. Partly destructed gypsum-kaolinite armouring on a rock crust at Hradčany, with efflorescences of potassium alum on the fine-grained clayey sandstone below. Note the thick armouring on honeycomb lips. D. An armoured rock crust with kaolinite on a prominent bedding plane in fine-grained sandstone at Rohliny. E. Medium-grained sandstone at Záborčí with a tortoise-shell armoured rock crust (left) and partly destructed honeycombs. F. A thick kaolinite-rich armoured rock crust (left) with irregular wandkarren at Černuc. Photo width 70 cm.

Table 1 A review of the sites sampled within this study, with a summary of minerals identified at each site by optical microscopy (*), X-ray diffraction (**) and scanning electron microscopy with EDX (***).
Material: Sst – sound sandstone, RC – rock crust, ARC – armoured rock crust (a harder surface part of the rock crust), PRC – patterned rock crust (honeycombed), S – salt efflorescences and other surface coatings
Mineral composition: B – brushite, C – calcite, F – detrital feldspar (Or orthoclase, Mi microcline, Plg plagioclase), G – gypsum, Gl – glauconite, Goe – goethite, H – halloysite, K – kaolinite, KA – K-alum, KNA – potassium-ammonium alum, M – montmorillonite, Mi – mica, Py – pyrite, Q – detrital quartz, T – tschermigite

Sampling site	Coordinates WGS84	Sample No.	Material	Mineral composition
Dobřeň 1	50.47836°N	23	Sst	Q*
	14.54833°E	22	PRC	Q*, F-Mi**
Ralská pahorkatina, Kokořín area		24	S	G**, KA**
Dobřeň 2	50.47799°N	27	Sst	Q*
	14.54904°E	26A	PRC	Q*, F-Or**, Goe*
(Ralská pahorkatina,		26B	ARC	Q*, F-Mi**, F-Plg**
Kokořín area)		28	S	G**, KNA**, phosphate***
Planý důl	50.47136°N	5	Sst	Q*, clay min.*
	14.60079°E	6	PRC	Q*, G**, clay min.***
(Ralská pahorkatina, Kokořín area)		7	S	G**, KNA**
Kobylka	50.45481°N	15	Sst	Q*, clay min.*
	14.61906°E	11	RC	Q*, G**, KA**, T**
(Ralská pahorkatina,		14	ARC	Q*, G**, B**, M**, H**
Kokořín area)		13	S	G**, KA***
Hradčany	50.61213°N	81	Sst	Q*, Gl*
	14.70521°E	49	PRC	Q*, G**, K**
(Ralská pahorkatina,		80	ARC	Q*, G**, K**
Doksy area)		51	S	G**, KA**
Rohliny	50.60693°N	37	Sst	Q*, Gl*
	15.19700°E	36	ARC	Q*, G*, clay min.***
(Bohemian Paradise, Turnov area)		38	S	G**, KNA**, K**
Záborčí	50.63274°N	47	Sst	Q*
	15.17474°E	45B	PRC 1	Q*, F-Or**
(Bohemian Paradise, Turnov area)		45A	PRC 2	Q*, G**, B**, C**, clay min.*
		44	ARC	Q*, G*
		46	S	G**, KNA**
Černuc	50.30075°N	79	Sst	Q*, Mi*
	14.23519°E	78	ARC	Q*, F-Mi**, K**, Mi**, clinochlore in the rusty layer**, Py***
(central Bohemia, Velvary area)				

KOBYLKA

Yellow, fine-grained, bioturbated clayey sandstones on a WSW-facing cliff; cliff face inclined ENE at 82°. A flat armouring with fine sculptation on the surface, hiding primary sedimentary structures. Small spherical honeycomb pits surrounded by white salt efflorescences are developed at places where the armouring has been destructed. Cliff base 339 m a.s.l., 9 m above the bottom of a dry gorge.

Sst: sandstone 0.5 m above cliff base; ARC: 0.5 m above cliff base; S: salt efflorescences above a notch 0.6 m above cliff base

HRADČANY

Yellow, fine-grained clayey sandstones, horizontally stratified with vertical burrows, on an E-facing cliff; cliff face inclined W at 82°. A flat but perforated armouring 3–10 mm thick is locally present, hiding primary sedimentary structures, and often preserved in the interiors of tafoni and older-generation honeycomb pits. Younger-generation spherical honeycomb pits of variable size and patches of white salt efflorescences are developed where the armouring has been destructed. Cliff base 319 m a.s.l., 16 m above the bottom of a dry gorge and 51 m above a stream (600 m to the N).

Sst: 0.5 m above cliff base; PRC, ARC, S: 1.5 m above cliff base

ROHLINY

Yellow, fine-grained, thinly bedded quartzose sandstones with primary stratification dipping S at 13° (clinoforms) on a ESE-facing cliff; cliff face inclined ESE at 78°, passing to a shallow rock-shelter. Armoured rock crusts ca. 15 mm thick are locally developed on strata-parallel ledges. Small spherical honeycomb pits are rare, salt efflorescences concentrate to the interior of the rock-shelter. Cliff base 393 m a.s.l., 70 m above the valley bottom with a small stream.

Sst: sandstone 0.5 m above cliff base; ARC: armoured rock crust from top surface of a ledge1 m above cliff base; S: salt efflorescences from a rock-shelter 1 m above cliff base

ZÁBORČÍ

Grey, medium-grained quartzose sandstones with horizontal stratification on a WSW-facing cliff; cliff face inclined ENE at 78–89°. The rock crust (sample PRC 1, depth 5–7 cm) is light grey, ca. 10 cm thick, with a network of spherical to arcuate honeycomb pits arranged in lines parallel to bedding. Walls and bottoms of honeycombs are lined by a somewhat darker (rusty) layer down to the depth of 3–5 mm (sample PRC 2). This layer does not seem to function as armouring; instead, it shows some degree of degradation. Elsewhere, the surface of the rock crust is flat, with honeycomb pits restricted to cracks arranged in a tortoise-shell pattern. Salt efflorescences are present at places where the rock crust has fallen off, at the best protected (the most overhanging) sites of the face. Cliff base 426 m a.s.l., 27 m above the bottom of a dry valley.

Sst, PRC: sandstone and the overlying rock crust 2 m above cliff base; S: 1 m above cliff base

ČERNUC

Light yellowish, fine-grained quartzose sandstone with horizontal stratification and large-scale cross bedding on a SW-facing quarry face, inclined SW at 88°. It bears fine vertical rillenkarren in places but no honeycombs. Armoured rock crust 2–4 cm thick is slightly darker, with irregular wandkarren and small pits, totally obscuring primary sedimentary structures. A 1-mm rusty layer of clayey appearance is present on the surface of the armoured rock crust. Exposure base 201 m a.s.l.

Sst, ARC: 1 m above the base of a quarry face

ROCK CRUSTS

The term “rock crust” is herein reserved for a surface layer of sandstone, usually 2–15 cm thick, which occurs almost exclusively on surfaces protected from a direct rainfall – i.e., on subvertical, vertical and overhanging rock surfaces or inside rock shelters. The exact limits of the rock crusts are difficult to define in the field, both in the direction parallel to and perpendicular to the cliff face. The effects of salt weathering *vs.* case hardening are of variable intensity, both geographically and within the outcrop scale. In the sandstones of the BCB, rock crusts often bear small-scale weathering forms, most notably honeycombs and wandkarren, and may be associated with the formation of tafoni. Elsewhere in the basin, however, honeycomb formation is very limited, and the cliffs rather show signs of surface crusting (e.g., Góry Stołowe Mts. in Poland).

Due to the coalescence of individual honeycomb pits, the outer parts of the rock crust are irregularly but unavoidably detached and destructed, thereby becoming a part of scree accumulations at the foot of the cliff face. The evaporation front usually changes in time; the change is typically connected with the recess of the rock surface. An uneven distribution of moisture along a cliff face, controlled by various intrinsic factors (lithology, fracturing) and extrinsic factors (height above the soil cover, shading), implies different rates of rock surface recess. As a result, different stages of rock crust development can be usually observed on each outcrop. Second-generation (less frequently third- or fourth-generation) rock crusts are a common phenomenon.

The presence of honeycombs does not necessarily imply the presence of a rock crust. Especially on weakly litihfied sandstones or on fresh outcrops (younger than ca. 200 years; cf. Mikuláš, 2009), initial honeycombing can occur without any discernible hardening anywhere on the surface.

Some rock crusts in the BCB are notable for their hardened, “armoured” superficial layers. The contrastingly sharp morphologies and reduced porosities of these layers motivated the present authors to propose the term *armoured rock crust* (ARC) for the portions of the rock crust where continuous armouring is present. Armoured layers on medium-to coarse-grained quartzose sandstones are typically a few millimetres thick and mostly lighter than the underlying sandstone, unless iron and manganese minerals are involved, and sometimes bear a tortoise-shell pattern of shallow cracks (Dobřeň 2, Záborčí). Armoured layers on fine-grained clayey sandstones are thicker (1–3 cm), often contrasting in their greyish colour with the yellow sandstone underneath. Thick armoured rock crusts obscure primary sedimentary structures; their surfaces are smooth even in outcrops where bioturbation structures or cross bedding are otherwise highlighted by the action of salt weathering. Rock crusts with discontinuous or no armouring, bearing small weathering forms like honeycombs or wandkarren, are herein called *patterned rock crusts* (PRC) as a counterpart to ARC.

Figure 3 illustrates the contrasting features of PRC and ARC observed on medium- to coarse-grained quartzose sandstones (A) and those on fine-

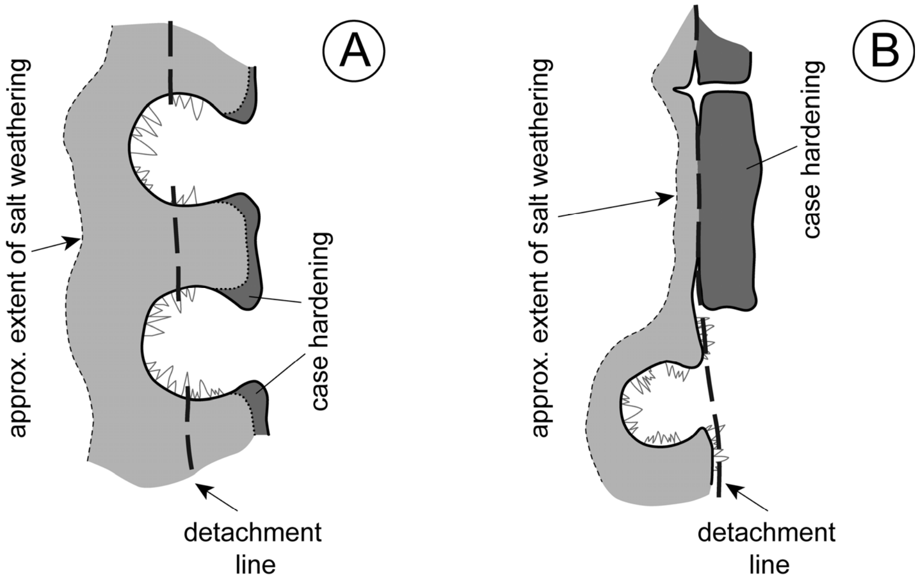

Fig. 3 Schematic drawings showing the character of rock crusts (ARC, PRC) formed on different substrates. A. Medium- to coarse-grained quartzose sandstone. B. Fine-grained clayey sandstone.

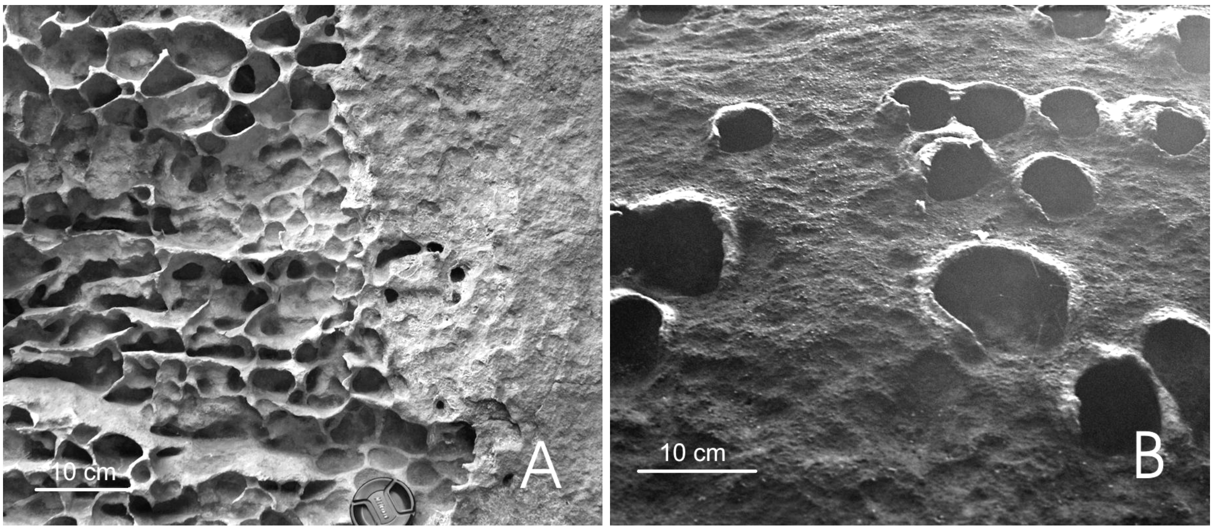

Fig. 4 Examples of complex relationships between patterned rock crusts (PRC) and armoured rock crusts (ARC). A. A sharp transition between PRC (left) and ARC (right) on a vertical cliff face. The boundary probably follows the limit of a former sandstone block on the right, later destructed. ARC developed on a fissure protected from rapid evaporation and remained unchanged after the rockfall. Unprotected left part of the cliff face gave rise to an "ordinary", honeycombed rock crust. Rozumov, Klokočské skály Cliffs, 600 m SE of the Rohliny site, Bohemian Paradise. B. A "transitional" PRC/ARC type. The surface started to develop as a honeycombed one; subsequently, the growth of the pits ceased and the whole surface became "armoured" including the interior of the pits. "Pod Pětichlapkou", Klokočské skály Cliffs, 1700 m SE of the Rohliny site, Bohemian Paradise area, from Adamovič et al. (2006).

grained clayey sandstones (B). Figure 4 shows examples of sharp boundaries between non-hardened and hardened sandstone surface at particular stages of the weathering cycle.

X-RAY DIFFRACTION

Minerals of the rock crusts in the BCB were primarily identified using XRD, which provides an unequivocal identification of mineral phases. The low sensitivity of the method, however, necessitated

Table 2 A summary of results from mercury intrusion porosimetry. Values of total effective porosity were calculated from skeletal density obtained from helium pycnometry and bulk density obtained from mercury intrusion porosimetry. The micropore/macropore diameter transitions equal to the least-frequency pore diameters in the differential pore size distribution diagrams, and are therefore sample-specific.

Material: Sst – sound sandstone, PRC – patterned rock crust (PRC 1 inner crust, PRC 2 outer crust), ARC – armoured rock crust

Sampling site	Sample No.	Material	Total intrusion volume (ml g^{-1})	Macropore/ micropore diameter transition (nm)	Proportion of micropores (% of total intrusion volume)	Median pore diameter (nm)	Total effective porosity (%)
Dobřeň 1	23	Sst	0.144	4000	2.6	43140	23
coarse-grained	22	PRC	0.136	4800	3.8	46070	26
Dobřeň 2	27	Sst	0.114	5200	4.3	45330	26
medium-	26A	PRC	0.118	4200	7.1	52220	24
grained	26B	ARC	0.097	5400	7.8	43690	23
Planý důl	5	Sst	0.090	4400	6.7	56750	19
coarse-grained	6	PRC	0.098	5300	5.0	56930	22
Kobylka	15	Sst	0.147	5400	6.9	28270	27
fine-grained	14	ARC	0.099	4300	17.6	24730	24
Hradčany	81	Sst	0.124	5000	4.3	31770	21
fine-grained	80	ARC	0.112	4800	14.3	23130	20
Rohliny	37	Sst	0.167	4200	4.4	27750	32
fine-grained	36	ARC	0.138	5500	5.9	20490	27
Záborčí	47	Sst	0.136	5200	7.6	30150	27
medium-	45B	PRC 1	0.123	4100	9.2	23120	22
grained	45A	PRC 2	0.113	4500	6.4	21420	25
Černuc	79	Sst	0.181	4200	3.3	25020	31
fine-grained	78	ARC	0.176	4200	7.1	23520	28

a combination with optical microscopy and SEM, especially in the case of subflorescences (Table 1). Principal minerals of rock crusts in the studied region are gypsum ($CaSO_4 \cdot 2H_2O$) and locally developed goethite (αFeOOH), but various water-soluble salts were also encountered in subflorescences: potassium alum [$KAl(SO_4)_2 \cdot 12H_2O$], tschermigite [$NH_4Al(SO_4)_2 \cdot 12H_2O$] and brushite ($CaHPO_4 \cdot 2H_2O$).

Salt efflorescences from all sites contain gypsum. Alums were commonly identified, being represented by potassium alum at Dobřeň 1 and Hradčany and by potassium-ammonium alum [$(K, NH_4)Al(SO_4)_2 \cdot 12H_2O$] at Dobřeň 2, Planý důl, Rohliny and Záborčí.

Armoured layers on medium- to coarse-grained sandstones were found to be sintered by gypsum with a contribution of brushite (Kobylka) or a thin coating of brushite (Rohliny – a site 200 m away from the described one). Gypsum was also found to be the main constituent of armoured rock crusts on fine-grained sandstones, being accompanied by clay minerals. Kaolinite (Hradčany, Černuc), montmorillonite and halloysite (Kobylka) were identified.

OPTICAL MICROSCOPY AND SEM

Photomicrographs of the minerals and salts identified using the optical microscope and SEM are shown in Figure 5.

Gypsum is the main mineral in pore spaces identified by optical microscopy and SEM. It forms either individual large crystals growing between quartz grains (max. length 0.2 mm), or crystal aggregates filling voids. Gypsum crystals typically grow with their *c*-axes perpendicular to grain surfaces. Good examples were found in rock crusts both on fine-grained sandstones (Hradčany, Rohliny) and on medium-grained quartzose sandstones (Kobylka, Záborčí). Small gypsum crystals 20 μm in length were also found dispersed in spongy clay matrix in SEM images from Planý důl (Fig. 5F).

Clay minerals form linings of quartz grains in many fine-grained clayey sandstones. Their content increases within the rock crust where they tend to form aggreagetes completely filling the voids. A sudden increase in thein proportion within a ca. 1 mm thick layer on the rock surface is also visible in medium- to coarse-grained quartzose sandstones. Clay linings on quartz grains and clay mineral aggregates are common substrates for the growth of gypsum crystals.

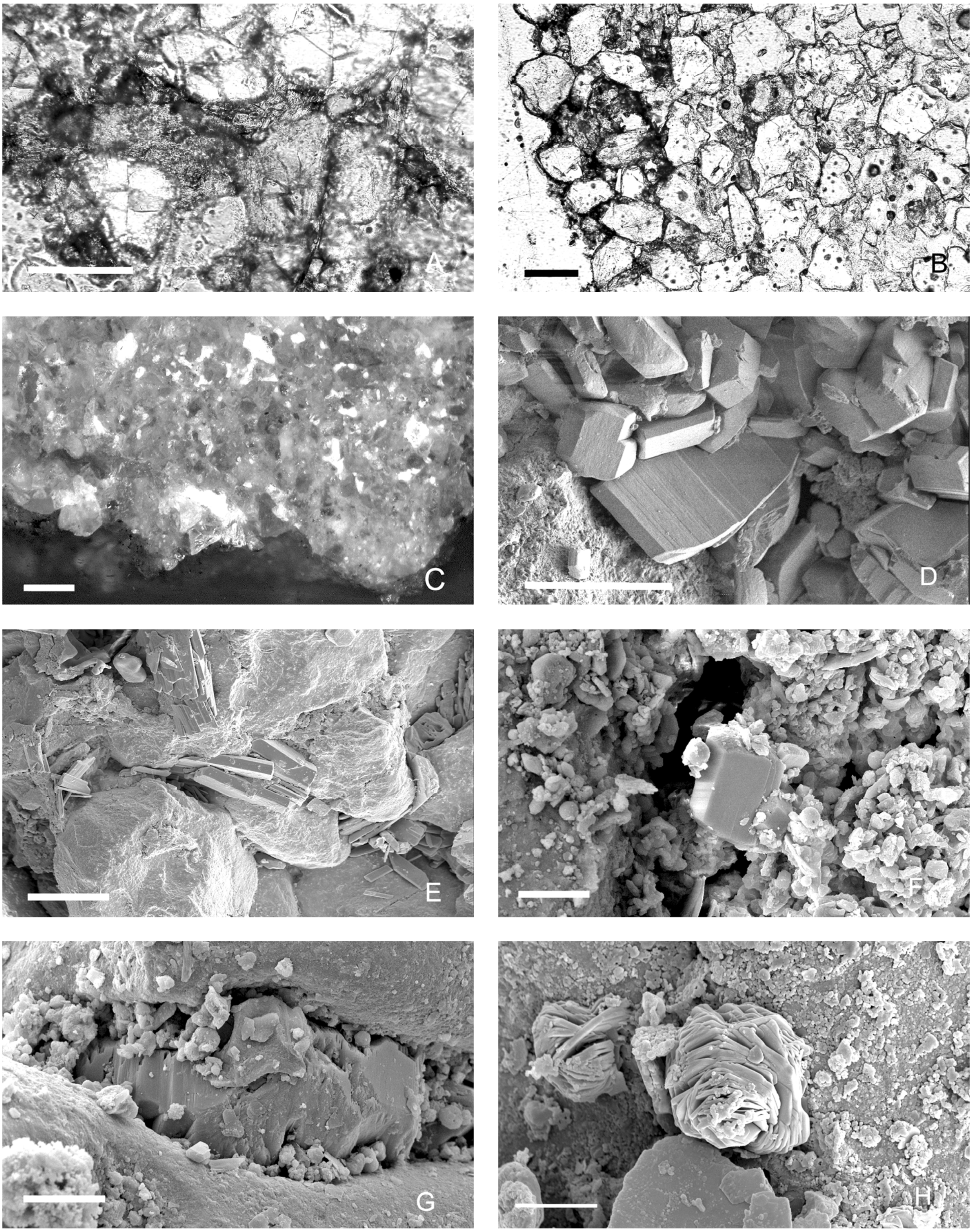

Fig. 5 Photomicrographs from the optical microscope (OM) and scanning electron microscope (SEM) with products of salt weathering in sandstones of the Bohemian Cretaceous Basin. A. Gypsum crystals filling voids in an armoured rock crust at Záborčí, Sample 44, OM, plane-polarized light, scale bar 200 μm. B. Clay minerals filling voids near the surface (left) of a honeycombed rock crust at Záborčí, Sample 45, OM, plane-polarized light, scale bar 200 μm. C. Gypsum subflorescences in medium-grained sandstone, 400 m SE of Rohliny, OM, reflected light, scale bar 1 mm. D. Gypsum crystals on the surface of medium-grained sandstone, 300 m SE of Záborčí, SEM, scale bar 100 μm. E. Gypsum crystals on the surface of a honeycombed rock crust at Záborčí, Sample 45, SEM, scale bar 100 μm. F. A gypsum crystal surrounded by clay minerals on a honeycombed rock crust at Planý důl, Sample 6, SEM, scale bar 20 μm. G. Gypsum filling of a contact between quartz grains at Planý důl, Sample 6, SEM, scale bar 20 μm. H. Aggregate of phosphate mineral on the surface of an armoured rock crust at Dobřeň 2, Sample 26B, SEM, scale bar 10 μm.

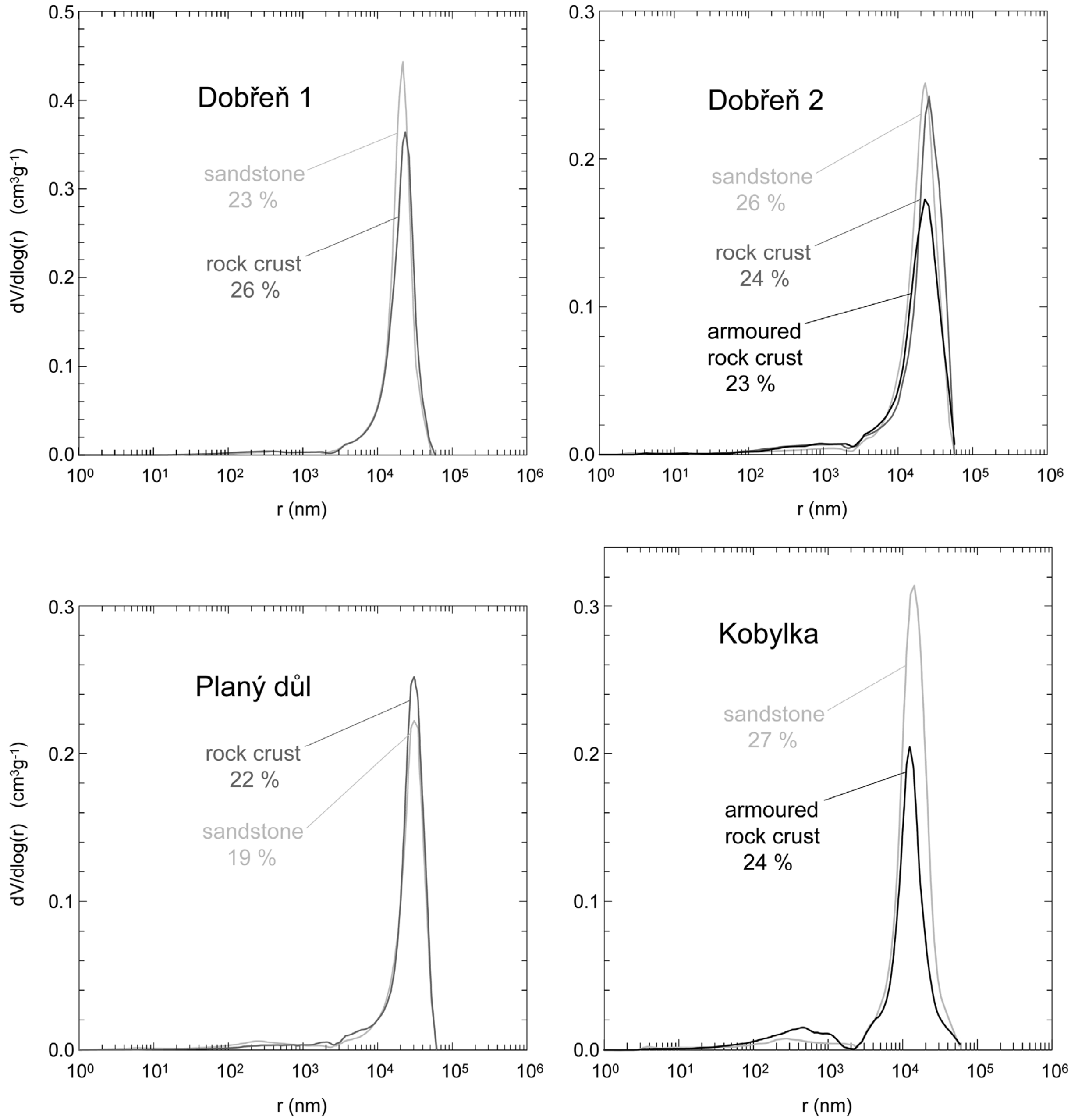

Fig. 6 Diagrams of differential pore-size distribution in sandstones and rock crusts from the Ralská pahorkatina, Kokořín area. Total effective porosities in per cent are given for each sample.

SEM revealed the presence of thin (~100 µm), amorphous-looking coatings of potassium alum with desiccation cracks in several samples from the rock surface (Planý důl, Kobylka, Záborčí). These coatings tend to flood, partly or completely, columnar gypsum crystals on the rock surface and often contain pollen grains and other impurities trapped by atmospheric deposition. Cubic pyrite crystals identified at Černuc by SEM typically overgrow detrital grains of altered K-feldspar.

RESULTS OF POROSIMETRY STUDIES

Results of porosity measurements are shown in Table 2 and Figures 6 and 7.

Patterned rock crusts on medium- to coarse-grained sandstones in the Kokořín area show, relative to unweathered sandstone, an increase in the size of macropores, which is manifested by a shift of the median pore diameter towards higher values. This may be either due to the creation of new interconnections among pores, or due to the

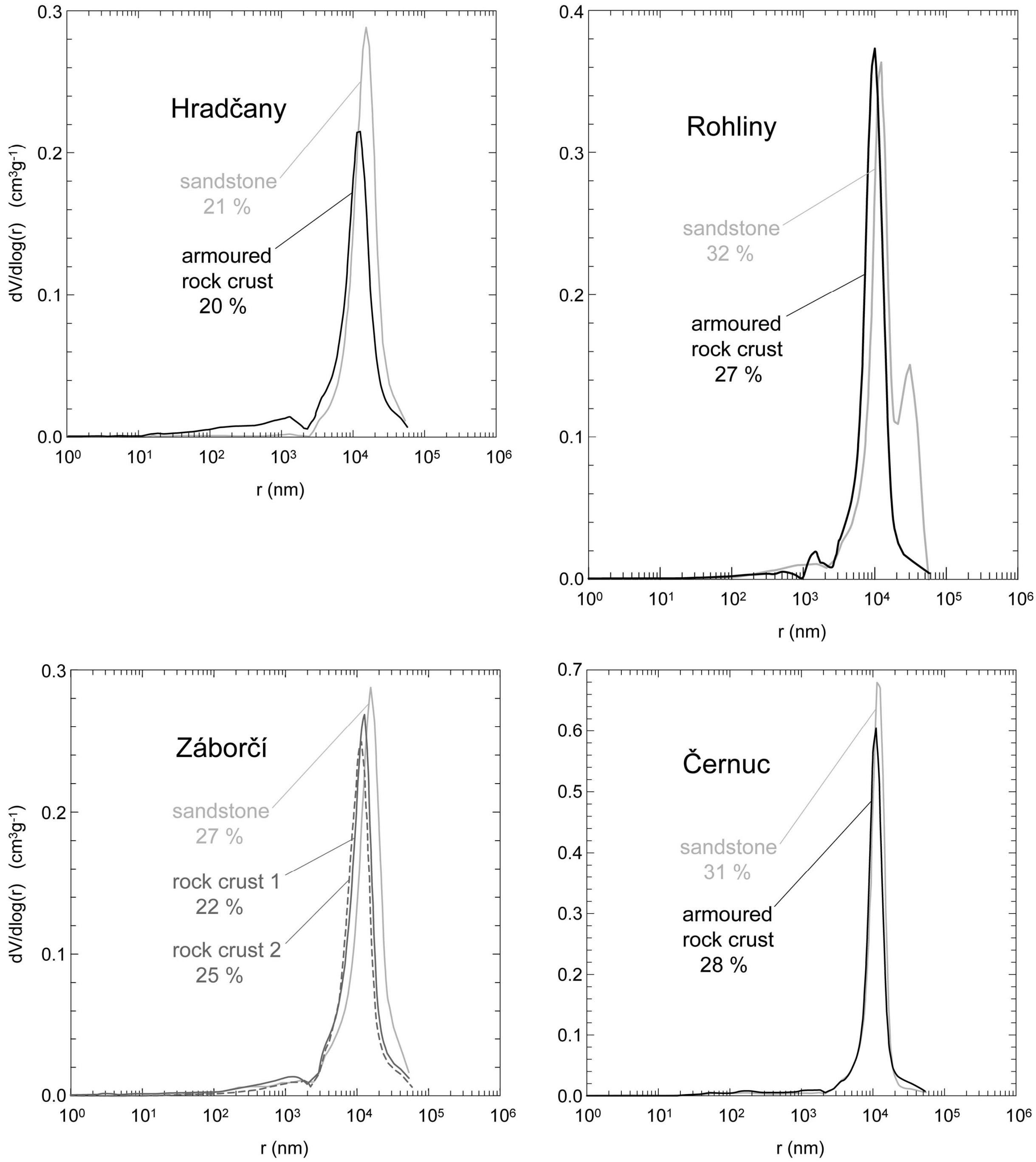

Fig. 7 Diagrams of differential pore-size distribution in sandstones and rock crusts from the Ralská pahorkatina, Doksy area (Hradčany), from the Bohemian Paradise (Rohliny, Záborčí), and from central Bohemia (Černuc). Total effective porosities in per cent are given for each sample.

detachment of closely packed grains. Although the volume of macropores in the rock crusts may relatively decrease, the increase in their size usually results in an increase in total effective porosity. At the Záborčí site in the Bohemian Paradise, on the contrary, a prominent decrease in the proportion of macropores was encountered, resulting in a reduction in total effective porosity (from 27 % to 22 %) in the inner part of the rock crust (PRC 1). Microscopic observations revealed a tighter grain packing in this region, with frequent linear contacts between grains (Fig. 8). In the walls and bottoms of the honeycomb pits (PRC 2), however, this trend becomes reversed: the proportion of macropores increases and so does the total porosity. The very low median pore diameter in honeycomb walls at Záborčí results from partial filling of large pores with clay minerals, gypsum, brushite and calcite (Table 1 and Fig. 5A, E).

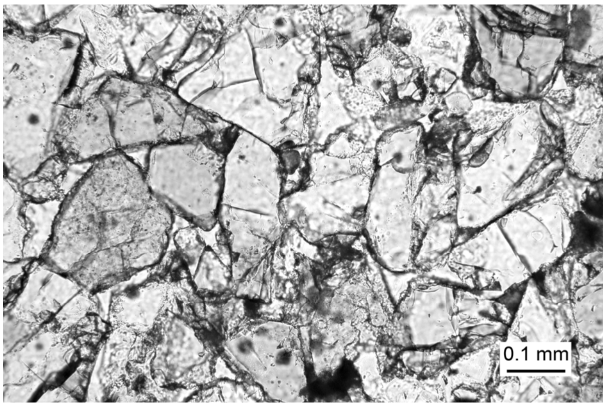

Fig. 8 A photo from optical microscope showing a tight packing of sand grains in the inner part of the patterned rock crust at the Záborčí site, Sample 45B. Plane-polarized light.

Porosity changes in an armoured rock crust at Dobřeň 2, relative to unweathered sandstone, can be characterized by a decrease in the volume of macropores, a decrease in their size and a reduction of total effective porosity. No massive crystallization of salts was found in the armoured layer, so this reduction must be ascribed to the tight packing of sand grains with mostly linear contacts, similarly as in rock crust PRC 1 at Záborčí.

In fine-grained sandstones, armoured rock crusts share many common porosity characteristics. Total effective porosities in such crusts are always lower compared to the relatively sound sandstone below: they are reduced from 27 % to 24 % at Kobylka, from 21 % to 20 % at Hradčany, from 32 % to 27 % at Rohliny, and from 31 % to 28 % at Černuc. This reduction is associated with prominent shifts of the median pore diameter towards lower values (see Table 2). Notable is the almost disappearance of pores >40 μm in diameter at Rohliny. As indicated by microscopic observations and XRD analyses, these changes can be most readily explained by partial sealing of large pores by clay minerals and by the growth of gypsum crystals. The reduction of macropores is partly compensated by a prominent increase in the volume of micropores, which was encountered at all four sites (Table 2, Figs. 6–7). At Hradčany, for example, the proportion of micropores in the total intrusion volume increased by the factor of 3. As the populations of macropores and micropores are always well separated, such an increase cannot be explained by a reduction of effective pore radii of the macropores. SEM observations suggest that it rather reflects microporosity in clay mineral aggregates whose proportion rapidly increases in the topmost few millimetres of sandstone outcrops. Microfracturing of detrital grains induced by the growth of gypsum crystals cannot be excluded; however, no convincing examples were found on SEM images (cf. Figs. 5A, E, G). Some of the microfractures may also represent desiccation cracks in thin coatings of potassium alum observed by SEM.

DISCUSSION

Mineral phases of salt efflorescences identified by the present authors on sandstones in the central part of the BCB generally correspond with those reported from this region by previous authors (Breiter, 1976; Cílek et al., 1998; Soukupová et al., 2002; Schweigstillová et al., 2009). Brushite, which has been reported from Ralská pahorkatina as a rare phase by Cílek and Melka (2000), was found also at Záborčí in the Bohemian Paradise as a common constituent of salt subflorescences together with gypsum. On the other hand, syngenite [$K_2Ca(SO_4)_2{\cdot}H2O$] found at several sites in the Ralská pahorkatina and the Bohemian Paradise (Schweigstillová et al., 2009) was not encountered by the present study. Neither was confirmed the presence of alunogen [$Al_2(SO_4)_3{\cdot}16H_2O$] or alunite [$KAl_3(SO_4)_2(OH)_6$], which seem to be much more common in the NW part of the BCB (Lentschig-Sommer, 1960, 1961; Williams and Robinson, 1998; Přikryl et al., 2007). However, gypsum and alums (Beyer, 1912) are clearly the most common mineral phases in all regions of the BCB, while gypsum, clay minerals and cristobalite dominate the coarse-grained sandstones and conglomerates of the Polish Carpathians (Alexandrowicz and Pawlikowski, 1982).

The exact mechanism of action of saline fluids producing sandstone disintegration can be manifold: 1, an increase in intergranular pressure due to salt crystal growth, resulting in crack widening and loss of contact between grains (Hume, 1925; Winkler and Singer, 1972; Goudie and Viles, 1997), 2. an increase in intergranular pressure due to salt hydration (Winkler, 1975), 3. enhanced dissolution of detrital quartz and clay matrix by saline fluids (Young, 1987; Young et al., 2009), 4. reaction with expandable minerals in sandstone matrix (Pye and Mottershead, 1995). The prevailing mechanism may vary depending on sandstone lithology and climate (cf. Turkington and Paradise, 2005), although steady flow rates and high rates of evaporation seem to be critical for honeycomb and tafoni formation (cf. the comparison of Turkington, 1998).

Beyer (1912) proposed that crystallization of salts is a process producing the greatest effect on near-surface sandstone deterioration. Alum salts have been demonstrated the most destructive in sandstone weathering experiments, especially at the presence of gypsum (Williams and Robinson, 1998; Robinson and Williams, 2000). In the study area, the presence of gypsum and water-soluble sulphates or phosphates in amounts detectable by XRD was proved in most sandstones showing honeycomb weathering, and gypsum crystals were often observed to completely fill the pore spaces, although in certain areas of the rock crust only. Effects of salt hydration/dehydration should not be overestimated in our case because sandstone outcrops in forested areas are not exposed to large swings in moisture content, especially within the reach of soil humidity. An increase in the size of macropores, which was observed in sandstones within the patterned rock crusts, should be therefore attributed to the growth of salt and gypsum crystals and the resulting granular disintegration. The same conclusion was made by Přikryl et al. (2007) who found a positive correlation between bulk porosity and the concentration of water-soluble salts in rock crusts in the NW part of the BCB.

No opal coatings were found on the studied samples, and etching traces on quartz grains were observed only rarely (Záborčí). It can be, however, presumed that some silica was released from clay matrix and feldspar grains, which show frequent signs of corrosion. The presence of opal coatings and impregnations on the surface of sandstone outcrops has been reported from the NW part of the BCB by Cílek and Langrová (1994) and by Přikryl et al. (2007). In the central part of the basin, however, any substantial silica redistribution seems to be prevented by relatively lower precipitation and a higher evaporation rate of precipitation in the recharge area. Other factors, like a lower ionic strength of the fluids, may be also involved.

At the site of Záborčí, the changes in pore-size distribution described above as characteristic for patterned rock crusts are limited to a layer reaching 3 to 5 mm beneath the walls and bottoms of honeycomb pits. Changes in pore spaces deeper in the rock (down to 7 cm) rather parallel those observed in the armoured layers on medium- to coarse-grained sandstones elsewhere (Dobřeň 2 site), and are manifested by tight grain packing in thin sections at the absence of gypsum or salt subflorescences. This situation can be explained by repeated, periodical freezing of water in the near-surface layer, which would result in a temporary forced crystallization of the dissolved salts in the rock interior immediately beyond the frozen fringe (e.g., Williams and Robinson, 2001). Such recurrent process would eventually lead to re-orientation of grains and their tighter packing in a relatively narrow zone defined by the freezing front. The observed concentration of clay minerals to the topmost 1 mm beneath the surface of medium- to coarse-grained sandstones (Fig. 5B) may be also an effect of frost weathering. In fact, it cannot be excluded that tighter grain packing and clay mineral concentration, presumably induced by frost action, are the main causes of the growth of salt subflorescences in the BCB, since reduction in pore size provides a larger surface area for evaporation and, at the same time, reduces the flow rate of pore waters, thereby promoting supersaturation deeper under the surface (cf. Rodriguez-Navarro and Doehne, 1999).

Little attention has been given by previous authors to salt weathering of fine-grained clayey sandstones in the BCB, possibly due to their poor exposure in the classical area of the Bohemian/Saxonian Switzerland in the NW part of the BCB and their infrequent use as building stone. Yet, the armoured layers several centimetres thick (Figs. 2B, C, F; Fig. 4) formed on this sandstone type are the most eye-catching examples of salt weathering/case hardening in the field. Reduction of macropores and the prominent increase in micropores are a rule, probably reflecting a combined process of growth of salt crystals and volumetric changes of clay minerals at contact with the saline fluids. The new observations are in general agreement with the degradation processes of clay-rich sandstones described by Warke and Smith (2000) from an urban environment in Northern Ireland: the zone of sandstone alteration, measured by the contents of calcium and sulphates, has been found to extend to a depth of 60 mm, and swelling and secondary microporosity of clays has been suggested as a factor augmenting the destructive effect of salt crystallization.

Our field observations documented various stages of destruction of armoured layers, similar to the process of contour scaling by Smith and McGreevy (1988). With the continued crystal growth and reduction of macropores penetrable for water in the armoured layer, pore waters and capillary waters restrict their circulation to the underlying sandstone. This implies a shift of the evaporation front deeper into the rock and the absence of salt efflorescences and honeycomb pits on the armoured rock surface. Then, the armoured layer becomes separated from the underlying rock crust by a thin fissure parallel to the rock surface. This separation itself should be explained rather by different volumetric response of the armoured layer to temperature changes than by salt weathering. A subsequent evaporation of saline pore waters within the fissure results in salt precipitation and finally in gravity-induced detachment of separate segments of the armoured layer.

New information on the distribution of secondary minerals and porosity in rock crusts can be matched with the present knowledge of factors influencing the origin of pitted/cavernous surfaces (cf. Mikuláš, 2001, 2007). Besides "pure" patterned rock crusts (PRC) and "pure" armoured rock crusts (ARC), a variety of transitional forms can be observed in the field (Fig. 4). Further, it is beyond any doubt that PRC and ARC may form next to each other regardless of the homogeneous sandstone lithology. A succession of events may result in the formation of several generations of rock crusts, combining PRC and ARC types, or formed by PRC laterally passing into ARC. For new, fresh sandstone surfaces, such as those formed by rockfall, the course towards the development of PRC *vs.* ARC is decided about within the first few centuries or even decades (cf. Mikuláš, 2009). If no honeycomb pits develop within this relatively short interval, a smooth rock crust will probably form and will almost irrevocably evolve into an ARC. In contrast, surfaces with early-formed pits tend to be conserved for a very long time, evolving into a specific distribution of destructive elements (evaporation front, growth of salt subflorescences, frost) reaching deeper into the rock. In rocks with homogeneous lithologies, the primary origin of honeycomb pits is controlled by the influx of pore waters, composition of solutes, and evaporation. For a given site, these factors are affected by local vegetation or configuration of instable blocks. Short-term climatic oscillations may also play a role. Such factors are usually difficult to decipher in the geological record available on sandstone cliffs or in their close vicinity (scree slopes or talus accumulations). As the controlling factors can be only rarely traced back to the past, the patterns of the resulting weathering forms may give an impression of random origin.

CONCLUSION

The presented differentiation between patterned and armoured rock crusts on natural sandstone surfaces in the BCB seems to be fully justified by differences in the pore-size distribution, mineral redistribution and the resulting weathering forms. Samples of PRC taken from the walls and the deepest parts of honeycomb pits, although having a more compact appearance than the unweathered sandstone below, show an increase in the size of macropores. In most cases, this increase implies a higher total porosity. Microscopic observations confirmed the presence of salt subflorescences in this zone, and suggest that this increase in pore size is due to the crystallization force of salts (notably gypsum) and the consequent loss of contact between grains. Dissolution of silica and hydration force of salts are believed to play a minor role in this process. Nevertheless, the common corrosion of feldspar grains and clay minerals in the matrix could have provided free silica and alumina for the secondary salts, notably potassium alum. A zone of tighter grain packing and pore-size reduction found in medium-grained sandstone just beyond honeycomb pits (depth 5 to 7 cm) could have originated by grain reorientation during repeated freezing of pore waters.

At macro-scale, the observed changes in pore spaces in the PRC contribute to the preservation and further evolution of topographically fixed cavernosity. An increase in pore size and pore connectivity in a near-surface zone is a factor which not only supports the influx of saline fluids from the rock massif but also enhances, at a favourable exposure of the cliff face, evaporation of these fluids near the rock surface. Such process leads to further salt crystallization and pore enlargement. In this respect, pore spaces function as a memory record of the weathering forms at a given place on the cliff face, and keep on generating the same forms unless the supply of saline fluids from the rock massif gets altered or depleted.

Tighter packing of grains in ARC on medium- to coarse-grained sandstones and concentration of clay minerals near their surface are rather a result of frost action. Although gypsum is present in some of the ARC, salt crystallization does not seem to be necessary for their formation. The reduced volume and size of macropores in the ARC are compatible with the abundant presence of clay mineral aggregates and gypsum crystals in these pores. Secondary porosity in kaolinite and the observed corrosion of feldspar grains are responsible for the prominent increase in the volume of micropores relative to that in unweathered sandstone. The mechanism of clay concentration into a several centimetres thick surface layer is a subject to discussion, and should be seen either in frost action or in chemical re-distribution of alumina and silica in the weathering zone, or a combination of both.

The relatively small volume of macropores in the ARC does not allow fluid transport from the rock massif to the surface, and the evaporation front is shifted deeper. Crystallization of salts at a certain depth eventually leads to the destruction of the armoured layer, similar to contour scaling in arid environments. This is the principal difference from PRC where the evaporation front lies at, or near, the rock surface and allows a variety of weathering forms to develop.

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