

## ORIGIN OF SULPHATE EFFLORESCENCE FROM SANDSTONE OF THE BOHEMIAN CRETACEOUS BASIN

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### ABSTRACT

Sandstone PLAs in Bohemian Cretaceous Basin offer number of outcrops with typical effect of the salt weathering (surface disturbance, salt efflorescence, incrustation, honeycombs etc.). Formation of surface salt efflorescence is common weathering phenomenon. An origin of the efflorescence in the nature is difficult and depends on physical-chemical conditions of the system interacting with water and atmosphere. Sandstone matrix on recent atmospheric conditions is reactive with various either atmospheric or other solutions (air humidity, rainwater or groundwater) with growing of sulphate efflorescence enriched aluminium.

**KEYWORDS:** aluminium, atmosphere, efflorescence, groundwater, isotopes, salt weathering, sandstone, sulphates

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### INTRODUCTION

Not only bizarre rock forms (macro-forms) could be admired in sandstone rock cities but also many unusual forms of micro- or mezzo-relief. E.g. pitted sandstone weathering caused probably by salt-acting represents one of forms of typical selected weathering (Young, 1987). The salts form white, grey or black efflorescence growing on rock surface. The efflorescence is composed of small crystals and they may influence both weathering and disintegration of the rocks on behalf on recent atmospheric conditions. Efflorescence appears to be common phenomenon accompanying chemical weathering. Distribution of these phenomena depends on atmospheric pollution and climatic conditions and presence of pore solutions in sandstone.

### STRUCTURE OF THESIS

The presented thesis comprises 11 chapters, with 26 figures and 12 tables in the text. Chapter 1 (Introduction) compiles the concept of weathering and previous study of salt crystallization, it also informs about the main goals of the thesis. Chapter 2 (*Sampling and sample processing*) describes field works and used methods. Chapter 3 (*Geology and importance of Bohemian Cretaceous Basin*) is focused on description of the main geographical and geological setting of the studied localities. Chapter 4 (*Mineralogy and chemistry of salt efflorescence*) provides an information about composition of the

studied samples. Chapter 5 (*Origin of elements in salt efflorescence*) compares probable source of salts based on atmospheric sources and rock sources. Chapter 6 (*Different salt growth and morphology of selected salt efflorescence*) includes results devoted to the laboratory study of several efflorescence. Chapter 7 (*Conclusions*) evaluates the main outcomes from the study of salt efflorescence on the sandstone. Chapter 8 (*Summary*) summarizes the new information. Chapter 9 (*Literature*) consists of alphabetical list of references used in the thesis. Chapter 10 (*CV and papers*) comprises of curriculum vitae and author's papers. Chapter 11 (*Supplements*) is subdivided into 7 tables with some results of different methods using in this thesis.

### METHODS AND RESULTS

Mineralogical composition of the efflorescence from different sandstones rock-city areas situated on Bohemian territory is similar as proved by previous research dealing with efflorescence mineralogy (about 160 samples from all sandstone rock-city areas in Bohemian Cretaceous Basin – BCB). Gypsum has been found at all samples accompanied with some other sulphates namely bisulphates – the alums. These salts contain sulphate anions and aluminium and potassium or ammoniac cations (with regard to alum type); the transitive alum species may contain beside aluminium both last cations together. Alums with ammoniac cations occur on sandstones from rock-

cities located around “black triangle”, a territory with most polluted atmosphere in Middle Europe extending on N and NW margin of Bohemia. Syngenite, the alum containing no aluminium but calcium and potassium cations was identified at samples from Český Ráj rock-city, the rock-city lying furthestmost to “black triangle”; potassium and calcium forms were rather detected in efflorescence.

Isotopic composition of both sulphur and oxygen from efflorescence samples has been indicated atmospheric origin predominantly (Schweigstillová et al., in print, b). Infrared spectrometry proved presence of organic matter in sampled efflorescence which derives from decay and mouldering of herbal or animal tissues in soil. Some of them may originate from combustion processes (HULIS – Graber and Rudich, 2006).

Chemical reactions inside pore-system of sandstones depend on several phenomena - a composition of matrix, chemical composition of precipitation and chemical composition of groundwater (vadose or soil water) infiltrating system by capillarity action. All mentioned phenomena are highly influenced by anthropogenic pollutions in atmosphere. Previous researchers worked with hypothesis of calcite distributed at matrix as a primary source for origin of gypsum crystals. But no calcite was found by X-ray diffraction of clay matrix from some sandstones of BCB (- 63  $\mu\text{m}$  fraction).

Presented research was focused on finding whether rainfall or other atmospheric water may be a source of salts forming efflorescence. Precipitation in term of 2000 – 2006 have been divided in three groups in line with data from Czech hydrometeorology institute (CHMI), namely 1 – lower polluted rainfalls in south a southwest Bohemia, 2 – acid rainfalls with high sulphate content in north Bohemia and 3 – rainfalls with higher content of pollutants in Prague and its surrounding and in north a northwest Bohemia. A sole origin of calcium and sulphates was indicated by correlation coefficient ( $R^2 = 0.67$ ) and higher correlation coefficient were determined also for ammonium, magnesium, sulphate and nitrous ions ( $R^2 =$  about 0.5). Spontaneous crystallization of the gypsum was proved by simple evaporation of rainfall waters. Gypsum was only rarely accompanied with other salts e.g. by syngenite and boussingaultite.

Saturation indexes of selected mineral phases were determined by help of USGS PHREQC modelling software, vers. 2.61 using phreeqc.dat a mineql.dat databases (Parkhurst and Appelo, 2001) and with average values of solute ions under 8 °C determined in year of 2000-2006 (types 1 – 3). Saturation indexes have been calculated before and after simulated evaporation. pH of the solutions was successively lowered to pH under 1 by method of successive evaporation of the water in residual drop. An evaporating solution becomes oversaturated with gypsum and anhydrite in a last phase (positive values

of saturation indexes). Such conclusion corresponds with monomineral gypsum crusts found in city environment (Soukupová et al., 2002). Gypsum was found as a most preferred phase especially under acid and dusty environment represented by type 3 (Schweigstillová and Hradil, 2007). Alums become during evaporation more preferred mineral phase than alunite owing to dropping pH to very low values whereas indexes of saturation remain negative.

Aluminium is deficit element in rainfall water, and just its low concentrations are not sufficed to an origin of alums. Even rainfalls have relatively high pH, the aluminium has ability to be liberated from kaolinite already on  $\text{pH} < 5$  (e.g. Wieland and Stumm, 1992). Very low pH presupposed by modelling program is able to dissolve clay minerals from sandstone matrix being on normal conditions relatively stable (Hradil and Hostomský, 1999). XRD analyses have proved clay minerals as only aluminium rich mineral phase presented in Turonian sandstones. Values of feldspars as possible alternative source of aluminium are very low, they were found just in two samples.

Sandstone matrix was experimentally leached in 0.5 M  $\text{H}_2\text{SO}_4$  solution for the duration of 2, 4, 6 and 10 days and quantity of the liberated  $\text{Al}^{3+}$  (determined by atomic absorbing spectrometry) was sufficient to origin of alums. It verified the hypothesis anticipating the possible liberation of  $\text{Al}^{3+}$  ions which are necessary for an origin of alums from clay minerals of the sandstone matrix under conditions of highly acid environment.

Groundwater is supposed to be other possible source of aluminium and sulphates. They can move through sandstone pore system whether by capillarity action (Novák et al., 2007) or simply flowing through (Přikryl et al., 2007). Four water samples from two localities in Český Ráj area – Klokoč and Besedice Rocks – were analysed to determine a chemical composition of soil water and water leaching through unsaturated sandstone zone (vadose water). The samples were taken in March 2008. Experiments dealt with two sample types:

- (a) a soil water – a water leaching from soil base with thickness about several tens cm, flowing on sandstone surface beneath soil base to catchment's plane where dropped into collecting vessel (K2).
- (b) a surface water leaching through a sandstone or flowing on its surface (K3, B2 and B3).

Following mineral phases were identified by XRD analyses after simple evaporation of the taken samples: alum (excluding B3 sample), gypsum and only for B3 sample bassanite, boussingaultite as well as ettringite. pH values of all samples were almost identical (with average pH 4), but this value is lower than pH of the rainfalls. There are also considerable differences not only between chemical compositions of both water samples one another but also compare to

rainfall water. Water from not saturated zone has proved higher aluminium content (Schweigstilllová et al., in print, a). Similar results on higher aluminium concentrations in surface water were received during research in České Švýcarsko sandstone area (Patzelt 2007).

An experimental crystallization of sulphates from saturated solutions proved more destructive effects on alum crystallization compare to gypsum. Experiments indicated a preferring crystallization of gypsum inside pores and on sandstone surface (heterogeneous crystallization) compare to preferring more destructive crystallization of alums "under" surface (homogeneous crystallization). Microscopic observations (SEM/EDX) have confirmed the experimental indications (Schweigstilllová et al., 2005). Both alums and gypsum occur in salt efflorescence, the gypsum crystallize on surface of sandstone or inside its pores (efflorescence) while alums penetrate the pore system of the rock (subflorescence). Theoretical reaction model predicts clay minerals as a possible source of aluminium. The experiments have verified the ability of clay minerals in the rock matrix to be substituted by alums as result of reaction with leaching solutions of a low pH.

## CONCLUSIONS

Obtained research results proved that the presence of calcium salts in salt crusts growing on sandstones in BCB does not need indicate a reaction of acid water with calcite. Also origin of other alums – potassium and ammoniac and origin of syngenite is not conditioned with particular contribution of these elements, their contents in a rainfall is sufficient. On contrary the aluminium content in the rainfall water is not sufficient for an origin of alums in the crusts and the clay minerals in the sandstone matrix have been determined as a source of its additional contribution.

Sandstones (especially their clay matrix) are reactive with various either atmospheric or other solutions (air humidity, rainwater or groundwater) with growing efflorescence. Recent Mid-European atmosphere is enriched with  $\text{SO}_4^{2-}$  ions and local atmospheric water has lower pH than in surrounding territories. These conditions on the Czech territory are favourable to crystallization of sulphates or bisulphates (so-called alums) having aluminium in their crystalline lattice (e.g. Ševelová et al., 1998). Aluminium is probably liberated from soil or rock aluminosilicates through reactions with acid atmospheric solutions. Contribution of the aluminium has been confirmed by heighten concentrations in vadose water.

The research has clarified connections between mineralogy of the salt crusts, rock composition and pollution of the atmosphere. It also partly describes possible mechanisms of the element transport on surface and subsurface zone of the rock with regard on the origin of the salt crusts and the way of their crystallization.

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## MECHANISMUS VZNIKU SÍRANOVÝCH VÝKVĚTŮ NA PÍSKOVČÍCH ČESKÉ KŘÍDOVÉ PÁNVE

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### ABSTRAKT:

Chráněné krajinné oblasti pískovců České křídové pánve nabízejí dostatečné množství výchozů s typickými projevy solného zvětřávání (povrchové narušení, solné výkvěty, inkrustace, voštinovitý reliéf a pod.). Vznik solných výkvětů na povrchu kamene je v prostředí zvětřávání běžným jevem. Stanovení zdrojů solí a proces jejich formování je v přírodě komplikovaný a týká se fyzikálně-chemických podmínek systému, který je v kontaktu s vodou a atmosférou. Základní hmota pískovců, které se nacházejí v současných atmosférických podmínkách, reaguje s různými síranovými roztoky (vzdušná vlhkost, srážková a podzemní voda) za vzniku síranových výkvětů obohacených hliníkem.