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GEOCHEMICAL STUDY OF PRECIPITATES IN THE ARCHITECTURAL SURFACES FROM BERN, SWITZERLAND

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ABSTRACT

This geochemical study aims to resolve genesis of precipitation spots on the walls on the Nydeggbrücke in Bern, Switzerland. The bridge is composed of Jurassic limestone and dolomites and coated on both sides with Miocene flysch sandstone. As a result of infiltration of aqueous solutions derived directly from the road embankment into the sandstone, sulfate encrustation on the walls of sandstone has been formed.

The study of these precipitates using optical and electron microscopy clearly shows dominant sulfate phases are gypsum (calcium sulfate), mirabilite (sodium hydrated sulfate) and polyhalite (potassium, calcium and magnesium sulfate). Impurities of Ni, Cu, Zn and Pb was encountered by ICP-MS analysis. Identified polymetallic mineralization is associated with the infrastructure of the bridge and the accumulation of pollution from vehicular traffic. This is also confirmed by sulfur and oxygen stable isotope analyses of sulfates.

Keywords: precipitates, sulfate, geochemistry, pollution, microscopy, isotope analysis.

1. INTRODUCTION

Switzerland is a country located in the central part of Western Europe, surrounded by the Alps Mountains and bordering with France, Italy Austria, Liechtenstein and Germany. The capital city, Bern, is located in the southern part of Switzerland Plateau at the Aare river (Fig.1). The city was founded in 1191 by Duke Berthold V von Zähringen. The main attraction of Bern is the medieval old town, rebuilt after a fire in 1405. Due to the location of the promontory created by the waters of the river, the old town is surrounded by water from three sides. In the eastern part of the promontory is located the Nydegg bridge (Nydeggbrücke) – built in 1843 in the form of stone arches (Emch 2012). As building materials were used the Jurassic limestone and dolomite, whereas for decoration of the bridge walls were used the Miocene Ostermundigen sandstones (Jabeydoff 2003; Demoulin et al. 2014). The Ostermundigen quarries, located near Bern were active since the XV century (Storemyr 2012). Contemporary on the walls of these bridge patches of mineral precipitates are formed. The precipitates have form of concentric circles along the original laminae of the sandstone.

The Bern region is located in temperate climate zone, characterized by an average temperature of -1.2ºC and 17.3ºC for January and July, respectively. The major source of pollution in Bern area is vehicular traffic emission and operating in the city the pharmaceutical companies, micro-mechanical, optical and IT industry (materials of the Polish Embasy in Bern, 2014).

In this paper, we decipher the nature of encrustations formation on the decoration walls of the Nydegg bridge by geochemical study of the mineral precipitates, including both optical and electron microscopy with stable isotope analysis.

2. METHODS

Encrustations samples were taken in 2014 from the decorative walls of the Nydegg bridge, which then were subjected to petrological analysis. The precipitates were initially examined using a polarizing optical microscope Leica DM 2500P in transmitted and reflected light. Subsequently, these samples were subjected to microprobe analysis using a scanning electron microscope Hitachi SU6600 with an EDS attachment in low vacuum conditions, by the 15 kV (standard) beam energy. Then they were tested for chemical and composition by the use of the ICP method. Finally isotope mass spectrometric analyses of sulfur and oxygen in SO_4 ions extracted from the precipitate in form of $BaSO_4$ were conducted on a dual inlet and triple collector mass spectrometer with precision of ±0.1‰.

Microscope analyses have been carried out in the Department of Geology and Lithosphere Protection, chemical composition was examined using ICM-MS technique in the Department of Soil Science and Soil Protection, the Faculty of Earth Sciences and Spatial Management while the isotopic studies have been done in Mass Spectrometry Laboratory in the Institute of Physics. All of these analyses were performed in the laboratories at the Maria Curie-Skłodowska University in Lublin, Poland.

3. RESULTS

The visible encrustations in sockeds form highlight the layering of flysch sandstone plates. They create mineral accumulations along laminae of higher permeability (Fig. 1) contributing to the loosening of the plates in walls.

Figure 1: Panorama of old Bern with the Aare river and Nydeggbrücke bridge with precipitates.

The sandstone plates are located in direct contact with permeable carbonate rocks. These rocks being the building backbone of the bridge have been subjected to karst processes and become strongly cavernous, which is visible around the pool, located in the walls of the bridge in the area of the Nydeggkirche. There is a connection between the embankment of the road and the sandstone plates, which make possible to transport polluted road solutions.

Microscopy observations of the encrustations material reveal needle of mirabilite together with gypsum and polyhalite tablets crystals developed in radial and polysynthetic forms (Fig. 2). These aggregates are well visible in the image of backscattered electrons obtained by electron microscopy (Fig. 3). Multi-point analyses showed the presence of sodium, magnesium, and calcium sulfates (Fig. 4). Electron microprobe analysis also indicated the presence of carbonates. Chemical analysis showed little impurities of metals such as iron (0.22 wt%), nickel (32.3 ppm), zinc (26.1 ppm), lead (21.7 ppm), chromium (37.2 ppm) and copper (2.17 ppm).

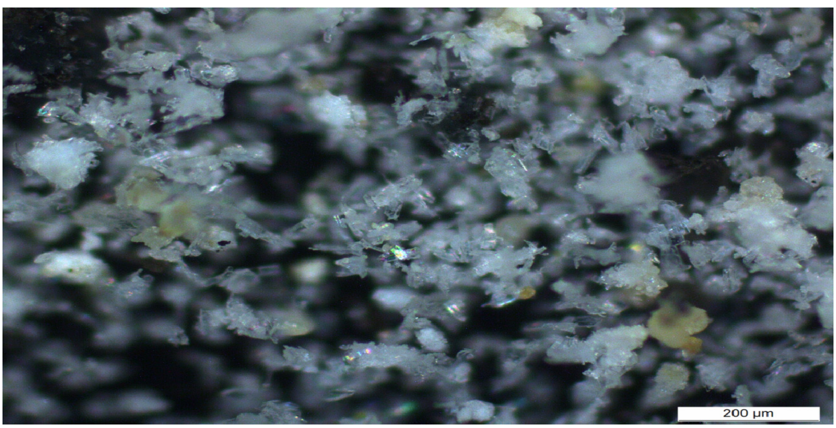

Figure 2: Mirabilite macrophotographs (Refected light 1N).

The sulfur isotope analysis of $BaSO_4$ derived from a precipitate sample give $\delta^{34}S$ =+18.3‰ , the result of SO_4 oxygen, $\delta^{18}O$ = + 8.0‰.

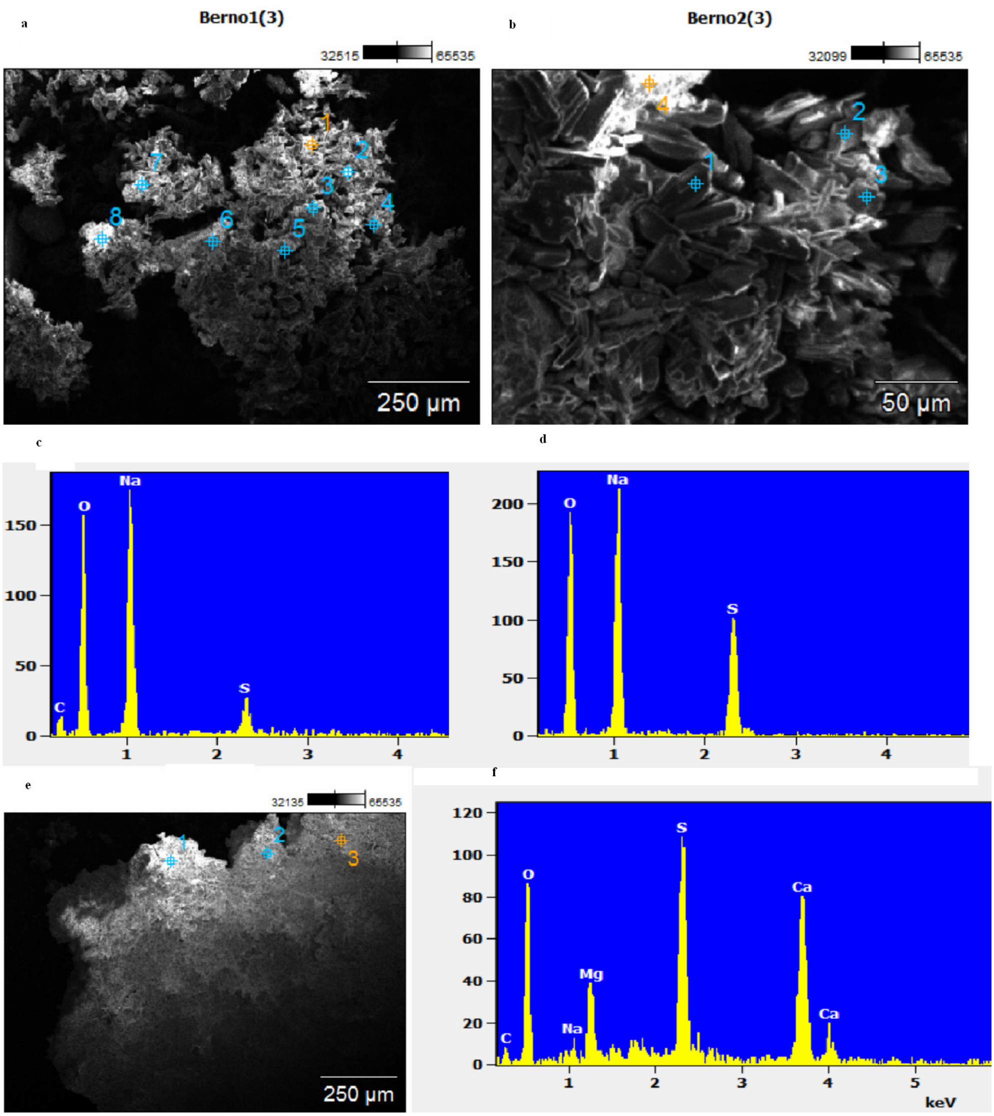

Figure 3: BSE microphotographs of mirabilite (a,b,c,d) and gipsum (e,f) with EDS spectra.

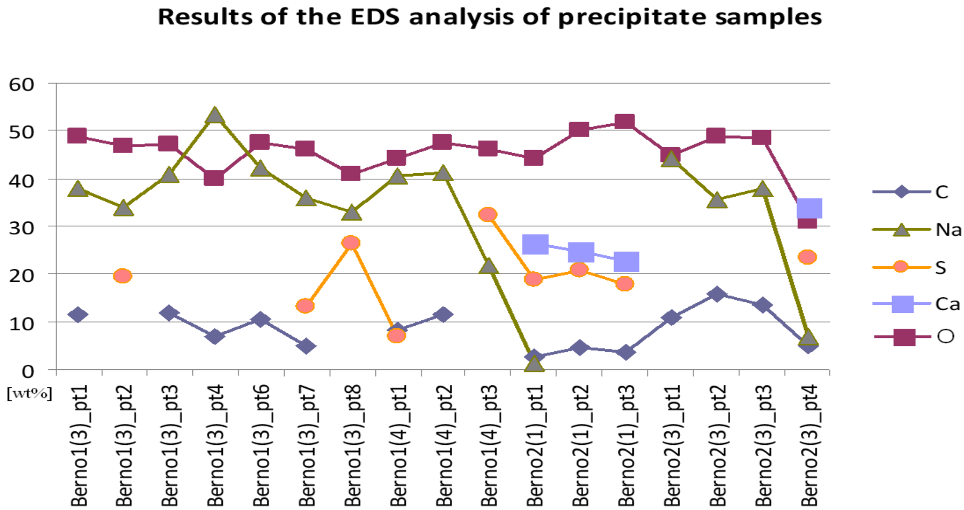

Figure 4: Contents of selected elements, obtained by SEM-EDS microanalysis.

4. DISCUSSION

Encrustation samples from the Nydeggbrücke examined by ICP MS clearly indicate the origin associated with the pollution emitted by vehicles and industrial sites. At present, the traffic on the bridge is limited by the protection zone. On the bridge, an electric infrastructure is present, which can be another source of metals such as Cu and Ni. Presumably some of these pollutants could come from the older accumulations, deposited in caverns and voids of the limestone rock, when the traffic was unlimited. Gradually, they are released by leaching with migrating solutions. Calcium and sodium ions can be associated with the leaching process from the flysch sandstones. Calcium is also present in limestone and sodium is present in salt dispersed during the winter time.

The extracted sulfates from the encrustations have isotope signature which can be interpreted as originated by mixing of sulfate from burning fuels and leached Jurassic marine sulfates from the rock of the building material. $\delta^{18}O$ value is somewhat lower than Jurassic evaporites, which attain in average +14‰ according to Claypool et al. (1980). It should be noted that similar values were found in Zechstein anhydrites in Western Poland, with mean values ranging from +9 to +11‰ (Peryt et al. 2010). Also Badenian evaporates from Carpathian Foredeep have similar values, ranging from +11.3 to +13.3‰ (Cendóna at al. 2004). Therefore the SO_4 ion present in encrustations has considerably lower $\delta^{18}O$ value than it could be leached from the building material of the bridge, both limestones/dolomites and flysch sandstones.

On the other hand, SO_4 in atmospheric precipitations has $\delta^{18}O$ depending on $\delta^{18}O$ of precipitation water, which for Bern is varying from -3 to -15‰ (Schürch et al. 2003). If winter combustion of fuels is considered, then at such low $\delta^{18}O$ of precipitation water, sulfates formed may attain delta values considerably below +10‰ (Krouse and Grinenko, 1991).

The observed $\delta^{34}S$ value in SO_4 of the encrustations (+18.3‰) is similar or somewhat lower than observed in Jurassic evaporites (Claypool et al.1980). On the other hand, sulfur in fuels (coals and oils) may vary in large range, but predominantly about +5‰. Therefore there is no contradiction against our interpretation of the sulfur sources. In flysh sedimentary pyrite is often present. This may be oxidized and form also various secoundary sulfates having lower sulfate isotopic signature than the sulfates precipitate from Jurassic waters.

5. CONCLUSIONS

1. The observed encrustations generally occur in various places on the surface of the Nydeggbrücke decorative sandstone plates. Analyzed precipitates were formed by the migration of polluted rainwater through the voids of the bridge rocks. Crystallization of sulfates is probably associated with the oxidation of sulfur present in fuels by atmospheric O_2 and precipitation water.
2. The polymetallic impurities come from the bridge construction, electrical infrastructure on the bridge and emission from vehicular traffic. The presence of contaminants associated with emissions is a typical urban problem of harmful automobile exhaust, which today suffer most of European cities.
3. Understanding of encrustation formation leads to conclusion that they may be stopped by better sealing the upper part of the bridge construction.

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