The samples are mainly of ancient Egyptian, with some comparative samples from the Near Eastern regions. The analysis yielded interesting results; a marked difference in pattern of elemental composition from one king's reign to another was observed; use of different mineral as colorant was confirmed; a tendency to increase the amount of lead toward the end of the dynastic period was attested, and so on. The above results clearly indicates that procurement of ingredient minerals for the production of ancient vitreous materials changed over the course of time. From the analysis result, we are now able to draw a possible map of ancient trade network for the viterous materials, especially during the middle of the New Kingdom period. The interdisciplinary collaboration between science and archaeology is now able to offer some historical interpretations which had not been possible before.

Keywords: archaeology, ancient Egypt, synchrotron

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Salt corrosion of lead-based pigments: Laboratory experiments and analysis of ancient frescoes

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Salts are one of the most dangerous degradation agents of wall paintings. Salts cause not only mechanical changes by crystallization pressure, but also chemical and mineralogical alteration of colour layer. Although they were not recommended for using in wall paintings, lead-based pigments (lead white, masicot, red lead) were used since antiquity due to their bright colours. Interactions of selected pigments (lead white, masicot, red lead) with different salt solutions were performed within long-term laboratory experiments. We used salts which are part of the environment (Na_2SO_4, $MgSO_4$, $CaSO_4$, NaCl, $NaNO_3$, $Ca(NO_3)_2$, Na_2CO_3, urea) and salts which can be applied on fresco by restorer during fresco cleaning ($NaHCO_3$, $(NH_4)_2CO_3$, NH_4HCO_3). The phase analyses of reaction products were carried out using X-ray powder diffractometer. These analyses allowed us to conclude that minium has tendency to darken irrespective to the character of salt due to the formation of plattnerite. Massicot also reacts irrespective to the character of salt to form hydrocerussite which then transforms to cerrusite. By contrast lead white reacts with suphates to form sussanite, with NaCl to form laurionate. Markedly damaged 11th century frescoes from the small church of St. George in Kostolany pod Tribecom are probably the oldest preserved wall paintings in Slovakia. Samples taken from the dark brown parts of the wall paintings were analysed using X-ray powder microdiffraction. Microdiffraction revealed the presence of several different lead phases: hydrocerussite, cerussite, plattnerite and lead magnesium carbonate. The results of laboratory experiments allowed us to clarify presence of the lead phases as degradation products of red lead. The project was supported by GA AV CR KJB400320602.

Keywords: pigments, microdiffraction, corrosion

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Structural investigations of archaeological hybrid materials

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Organic-inorganic hybrid materials have emerged in various archaeological contexts, long before they captured one's interest owing to their mechanical, thermal, electronic, optical or catalytic properties, and their potential commercial applications. Many examples of hybrid organic-inorganic materials are described in old texts[1]: African patinas[2], body-care oils, mummification[3], tattooing, easel paintings (e.g. acetates, resinates), cosmetics or pharmaceutical products. Some hybrid materials are also found to form after degradation with time (e.g. in reaction with organic binders such as lead soaps[4] in lead paints, bio-mineralised textile fibres and bones, ...). Several examples are discussed. The search for stable dyes, resisting heat and moisture in murals, artefacts and clothing, led artists and craftsmen to substitute vegetal colours with artificial hybrids. Lacquer pigments were developed in Europe in the Greek-Roman periods and the Middle Ages. They consist of plant colouring matter and animal extracts, fixed on an inert mineral host. A blue pigment, formed by heating a mixture of a fibre clay and indigofera leaves, was extensively used in Mesoamerica (300-1500 AD), on frescoes, potteries, sculptures and ritual objects. These materials may be considered as the first artificial organic-inorganic hybrids, associating properties of the mineral substrate (chemical resistance, thermal and mechanical stability) and the colour of the organic dye[5]. The understanding of such complexes and the implementation of the relevant chemical and physical methods (synthesis, characterisation and modelling) lead to the description of historical hybrid materials in their archaeological contexts (use and properties). The open archaeological question is to identify the know-how of the ancient societies, by reproducing the conditions of synthesis and past practices, while monitoring the properties of the materials, their durability and their behaviour. Crystal structure solving of these archaeological composite materials and understanding the nature of the interactions between the guest molecule and its matrix are thus essential.

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CIF and a new DDL − What it can do; How it is done

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