XRS has long been discussed in an important but somewhat limited context, specifically, as a bulk-sensitive alternative to x-ray absorption spectroscopies. However, continuing developments in both experimental apparatus and theoretical methods are steadily opening up new opportunities which are special to the large momentum transfers q which can be accessed in XRS. In this presentation, we will survey a few such recent studies. These will include applications for basic spectroscopy (He gas), environmental and renewable energy (N_2 gas and $LiTiO_x$), exotic chemical bonding ($C_2B_{10}H_{12}$), and f-electron physics (CeO_2 and UO_2).

Keywords: inelastic x-ray scattering, X-ray Raman scattering, electron energy loss spectroscopy

MS.94.4

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X-ray Raman of water in the condensed phases

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In-situ measurement of the x-ray Raman spectra on the oxygen K-edge of several forms of ordered and disordered ice will be reported. It is shown there is a significant difference in the absorption profile in the near-edge and post-edge region between crystalline and amorphous ices. Comparisons between observed and theoretical spectra are made. Difficulties in the first-principles calculation of core level absorption spectra will be discussed.

Keywords: X-ray raman, a ray absorption spectroscopy, ice

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High-resolution X-ray Raman scattering and the study of ices under high pressure

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High-resolution x-ray Raman scattering (XRS) of oxygen K-edge in various forms of ices have drawn a great deal of interest recently. The double differential cross section can be shown to provide the same information as that obtained by x-ray absorption spectroscopy (XAS) when the momentum transfer is small enough that the dipole approximation is valid. For low-Z elements whose inner shells are in the soft x-ray region, XRS possesses unique advantages compared to XAS due to its inherent bulk sensitivity and good penetration depth, and is especially valuable for studies under extreme thermodynamic conditions such as high pressure. At a total energy resolution of ~300 meV at 9.89keV, studies on ices III, II, IX, VI and VII at various pressure and temperature conditions indicate that the technique provides clear spectral sensitivity to both short- and long-range structural changes of the H_2O frame work. Our studies, for example, have revealed that a diminishing intensity of the pre-edge feature provides a clear signature of proton ordering in the H_2O frame work [1]. The technique, when coupled with optical Raman and x-ray diffraction, provides also a powerful tool for understanding the chemistry in the disassociation of H_2O induced by the incident x-rays under certain (P, T) conditions [2,3]. Details of these studies will be presented and discussed.

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Keywords: hydrogen bonds, electronic structure, X-ray inelastic scattering

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Nanostructure of ancient Damascus blades

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Legends tell how Damascene blades exhibiting extraordinary properties had been manufactured following secret recipes. During the last decades more sophisticated metallurgical methods have revealed details of the microstructure of this crucible (or wootz) steel. There are indications that impurities and unconventional thermo-mechanical treatments might have an essential influence on the typical Damast pattern. Using scanning and high-resolution transmission electron microscopy, X-ray diffraction as well as micro- and nanohardness measurements we have analysed specimens of two genuine Damascus sabres, which date back to the 17th century. They were kindly left to us by the Historic Museum Berne. Significant new details of the microstructure that have been revealed during our study are nanowires of cementite Fe_3C [1-2] as well as carbon nanotubes ([3] and present work). Moreover, Fe_7C_3 has been detected which is known as catalyst for hydrocarbon synthesis and which eventually converts to Fe_3C [4]. Since carbon nanotubes have become known as forming catalytically from natural fibres [5], this sheds a new light on early reports on the addition of leaves to the crucible [6].

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Keywords: archaeometallurgy, nanophase systems, high-resolution electron microscopy

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Scientific contribution to archaeology: Fingerprinting the ancient Egyptian objects

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Since 1999, scientists and an archaeologist have been working side by side to seek the ancient trade network. Our goal of research is to establish the regional variability of glass and faience in ancient Near East by using the high energy SR-XRF and other methods.

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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Keywords: hydride compounds, archaeological materials, diffraction

MS.96.1

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

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