

The XRD measurements allow us to identify the mineral phases that are present in the ceramic pastes; the composition of the samples is quantified with a full-pattern matching of the diffractograms. Three types of minerals are identified in all samples: i) major phases that are relevant for the elaboration process (i.e., they appear after annealing at high temperatures): diopside, gehlenite, kalsilite and cristobalite; ii) minor phases that also appear (or are altered) by the application of high temperatures: forsterite-fayalite, mullite and hematite; iii) phases that are present in the pastes but do not play any significant role in the elaboration process: illite, calcite, K-feldspars, plagioclase and quartz.

An inspection of the XRD data from 18th-century jars with a well-established manufacture location suggests that the presence and relative amount of the mineral phases in the pastes is linked to the provenance of the objects. To further assess this point, we have performed a principal component analysis (PCA) of the XRD data. The intensities of the main XRD peaks from the major mineral phases in the pastes have been taken as variables for the analysis. The PCA reveals that pharmacy jars crafted in different geographical locations tend to cluster in a score plot of the first and second principal components, PC₁ and PC₂. This confirms that relevant information about the origin of the objects is gained from the XRD measurements.

To illustrate the ability of powder diffraction and subsequent PCA to determine the provenance of pottery objects, we have applied the method to investigate a series of 18th-century pharmacy jars of unknown origin from an old pharmacy at Barbadillo del Mercado, in Burgos, Spain, owned by a private collector. Our XRD data and subsequent PCA reveal that all the samples investigated were crafted in Villafeliche, Zaragoza, an important center of pottery and gunpowder fabrication during the 17th, 18th and 19th centuries. Our results are in excellent agreement with those obtained independently by authentication experts, which confirms the usefulness of powder diffraction for the study and authentication of pottery art objects.

Keywords: x-ray_diffraction, ceramics

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Difficulties in identification of copper-based pigments in objects of art

Petr Bezdička,^a Silvie Švarcová,^b Zdeňka Petrová,^a Alicja Rafalska-Łasocha,^c Wiesław Łasocha,^c David Hradil,^a ^a*Institute of Inorganic Chemistry of the ASCR, v.v.i., ALMA Laboratory, č.p. 1001, 250 68 Husinec-Řež, (Czech Republic).* ^b*Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4, 170 22 Praha 7, (Czech Republic).* ^c*Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, (Poland).* E-mail: petr@iic.cas.cz

Material identification and the description of painting techniques by modern analytical and/or micro-analytical methods should be integrated into the artistic or art-historic evaluation of the fine art. Correct identification of pigments and all other components found in colour layers of objects of art is relevant for searching the origin, preparation pathways and for specification of their degradation including colour changes. The success of that identification depends on the nature of materials and the correct choice of analytical methods. There are many materials used in objects of art which indisputable identification is possible only on the basis of phase analysis. Copper salts, existing in a wide range of chemical and/or structural varieties, can be a good example. They were used for centuries as blue or green pigments [1].

In the presented study we will focus on two main groups of Cu pigments having close chemical composition: 1) copper carbonates (malachite, azurite), 2) copper acetates (neutral and basic verdigris).

When looking into literature, there are indications for the existence

of several phases with the different ratio between copper, acetate and hydroxyl within one molecule. On contrary, looking into the databases of crystal structures, only the structure of neutral copper acetate is well described. Basic copper acetate was described by Masciocchi *et al* [2] on the basis of structure solution from powder data. The authors stated the difficulties in preparing crystals of good quality and therefore the structure has not been solved completely. Some peculiarities in the location of acetate groups persisted.

On the basis of literature data and historical recipes for preparing various variants of verdigris we tried to prepare model compounds to put the light into this complicated system of copper acetates. In the majority of cases the results of our model syntheses showed that only complicated mixture of phases came up giving very complicated X-ray powder pattern that could not be attributed to a single phase. As the best result, we came back to the synthesis of the simplest copper acetate phases that are probably the only which could be prepared in the pure form. We re-examined the synthetic procedure of the basic copper acetate. We succeeded in obtaining crystals of good quality to solve the structure completely, describing the positions of all atoms correctly.

Analysing a large number of real samples by X-ray powder micro-diffraction (μ -XRD) we found that copper carbonates are much more stable and retain their crystal structure for centuries. On the contrary, copper acetates that are originally well crystalline undergo degradation to be amorphous. Their identification is then either very complicated, or almost impossible by means of μ -XRD. There are only very few cases of positive identification of verdigris in the real samples of objects of art because of its readily degradation leading mostly to amorphous products.

[1] S. Švarcová, D. Hradil, J. Hradilová, E. Kočí, P. Bezdička *Anal. Bioanal. Chem.* **2009**, 395, 2037-2050. [2] N. Masciocchi, E. Corradi, A. Sironi, G. Moretti, G. Minelli, P. Porta, *J. Solid State Chem.* **1997**, 131, 252-262.

Keywords: X-ray powder diffraction, micro-diffraction, copper-based pigments

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Determination of the metallurgical properties of six ferrous Japanese arrow tips through time of flight neutron diffraction

Elisa Barzagli,^a Francesco Grazzi,^a Antonella Scherillo,^{a,b} Francesco Civita,^c Marco Zoppi^a. ^a*Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, Sesto Fiorentino (Italy).* ^b*Science and Technology Facility Council, ISIS Neutron Source, Didcot (UK).* ^c*Museo Stibbert, Firenze (Italy).* E-mail: elisa.barzagli@fi.isc.cnr.it

The phase composition of six ferrous Japanese arrows of the Edo period (17th-19th century) has been determined through Time of Flight Neutron Diffraction (ToF-ND).

ToF-ND has been applied on all the samples by using the INES diffractometer at the ISIS pulsed neutron source in UK [1]. The measurements have been performed on the average gauge volume of all the samples in order to determine the quantitative distribution of the metal and non metal phases. The data have been processed by using the GSAS code in order to perform Rietveld refinement of all the diffractograms. The cementite to ferrite ratio has been used in order to quantify the carbon content. The comparative analysis of the phase distribution among the samples permitted to identify peculiar characteristics related to the type of arrow. The carbon content, the fayalite amount, the presence of wuestite and troilite have been exploited to gain knowledge about the quality of the material and smelting and smithing methods. The shape of the ferrite peak has also been studied in order to semiquantitatively determine the texture level, the strain level and the domain size of the grains of each of the

samples which are important parameters to gain knowledge about the technological level of the Japanese weaponsmiths. A comparison with the typical characteristics of Japanese swords and helmets is also presented, showing that the quality of the metal composing the arrows is intermediate between the one used for swords (very high quality) and the one used for armour pieces (low quality).



Fig.1 Picture of the six arrows measured through neutron diffraction.

[1] F. Grazzi, M. Celli, S. Siano, and M. Zoppi, *Nuovo Cimento C* **2007**, *30*, 59.

Keywords: japanese arrows, neutron diffraction, quantitative analysis.

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Importance of X-Ray Analyses in Slag Studies at Clintonville, New York, USA

Meghan R. Guild, Dori J. Farthing, *Department of Geological Sciences, State University of New York at Geneseo, (USA)*. E-mail: mrg1@geneseo.edu

X-ray diffraction and x-ray fluorescence analyses of historical iron slags from Clintonville, NY, USA help describe the slags and provide insight to the uniformity and efficiency of the techniques used at the Clintonville Forge in the 1840s. Over 70 samples of slag, byproducts of the smelting process, were collected then divided based on macroscopic morphological characteristics. Samples were then analyzed with powder x-ray diffraction (XRD) in order to identify the mineral constituents within the slag. The wide range of morphologies does not govern mineralogical assemblages in Clintonville samples, as originally hypothesized. Modal abundances do, however, vary for some morphological groups. Clintonville slag commonly contains fayalite and magnetite, with minor occurrences of wüstite, forsterite, and glass. Although these phases are common in iron slag, the XRD is quintessential for definitive identification. This is especially important when these phases make up the fine-grained ground mass. Analyses using x-ray fluorescence spectroscopy (XRF) indicate chemical homogeneity for major oxides and trace elements throughout the morphological groups of slag. Consistent mineralogies and chemistries amongst slags reflect uniformity in the smelting processes at the forge. X-ray data further indicate that the Clintonville process was not efficient. Pure iron prills are nearly ubiquitous in the slags. Ore and cinders from this site have a total iron oxide content (FeO_x) ranging from 80-88 weight percent. Clintonville slag samples contained between 56 and 68 weight percent FeO_x . The smelting processes utilized at Clintonville consolidated only 12-20% of the iron into the final product.

Keywords: slag, fayalite, archaeometry

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The fluorescence life time of ruby at high pressures and temperatures

Johannes D. Bauer, Lkhamsuren Bayarjargal and Björn Winkler, *Institut für Geowissenschaften, Abteilung Kristallographie, Goethe-Universität Frankfurt am Main, Frankfurt (Germany)*. E-mail: J.Bauer@kristall.uni-frankfurt.de

The pressure determination in diamond anvil cell (DAC) experiments at high pressure and temperature (high- p,T) based on the ruby fluorescence method [1] is not straightforward, as both, pressure and temperature, have a significant influence on the frequency of the ruby fluorescence [2]. Here we suggest an alternative approach based on fluorescence life time measurements.

Fluorescence life time (FLT) thermometry is an established method at ambient pressure, where the ruby FLT decreases by three orders of magnitude between 300 and 900 K [3]. Up to now, only few reports concerning the pressure dependence of the FLT have been published. At 295 K the ruby FLT linearly increases between ambient pressure and 40 GPa by one order of magnitude [4].

Here we present the first study of the FLT of ruby at high- p,T . The FLT was measured in an externally and laser heated DAC. The fluorescence was excited by a ns pulse of a Nd:YAG laser at 532 nm. At constant temperatures the FLT increases linearly with pressure in the pressure range studied (< 30 GPa). At constant pressure the FLT decreases linearly with temperature. Our experiments show that FLT measurements may provide a reliable method for the determination of temperatures in a DAC at high pressure. A significant advantage will be, that FLT measurements on doped samples will unambiguously give bulk temperatures.

[1] K. Mao, J. Xu, P.M. Bell, *J. Geophys. Res. B:Solid Earth*, **1986**, *91(B5)*, 4673–4676. [2] A.F. Goncharov, J.M. Zaug, J.C. Crowhurst, E. Gregoryanz, **2005**, *Journal of Applied Physics*, *97(9)*, 094917. [3] K.T.V. Grattan, Z.Y. Zhang. *Fiber Optic Fluorescence Thermometry*. Chapman & Hall, **1995**. [4] Y. Sato-Sorensen, *High-Pressure Research in Mineral Physics*, **1987**, *39*, 53–59.

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Energy-domain SR ^{57}Fe -Mössbauer spectrometer for high-pressure mineral physics

Naohisa Hirao,^a Yasuo Ohishi,^a Takahiro Matsuoka,^a Takaya Mitsui,^b Eiji Ohtani,^c *^aJapan Synchrotron Radiation Research Institute (JASRI), Sayo, Hyogo 679-5198, (Japan)*. *^bJapan Atomic Energy Agency (JAEA), Sayo, Hyogo 679-5148, (Japan)*. *^cInstitute of Mineralogy, Petrology and Economic Geology, Graduate School of Science, Tohoku University, Sendai 980-8578, (Japan)*. E-mail: hirao@spring8.or.jp

Iron is the most abundant element in the Earth. The multiple electronic configurations of iron (valence and spin state) give rise to complex physical and chemical properties of the Earth's mantle, resulting in the influence on the structure, dynamics, and evolution of the Earth's interior. The spin-state crossover and the valence state in $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ silicate perovskite and post-perovskite, the most abundant mineral (~ 75 wt.%) in the lower mantle and the lowermost mantle, respectively, are essential for modeling the Earth's lower mantle. The degree to which the spin and valence states of iron in the