

Natural pigments as enamel opacifiers on ancient glass: Raman study of lazurite colour decoration on 1st to 2nd century glass vessels from Lubieszewo (Lübsow), Poland

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Glass vessels decorated with colourful designs either by application of pigments or a low melting coloured glass flux were highly estimated by the Germanic population along the Northern and Eastern borders of the Roman Empire in the 1st and 2nd century AD. Despite the fact that a number of splendid examples with depictions of birds, fishes and plants has survived in high ranking tombs of the barbaric elite, investigations either of the glass composition or the decoration technique employed are still quite limited.

In the case of the Lübsow glasses the basic pattern is scratched on the glass body before the coloured glass flux layers carrying the pigments are applied. The presence of lazurite grains as colouring and opacifying agent was confirmed by Raman micro-spectrometry of a pale grey ornament with a more vivid blue colour visible from the back side of the sherds.

The use of Lapis Lazuli as decorative inlay or as pigment for wall paintings in Mesopotamia, Egypt, Greece and the Roman Empire is a well known fact (see e.g. Derakhshani 1999). The as yet earliest evidence for its application in a high temperature process seems to fall into the 13th century with a lazurite rich slip under a cobalt glaze on an Iranian ceramic ewer (Colomban 2003) and the use for blue colours on enamelled transparent glass vessels (Freestone & Stapleton 1998). The observation that lazurite was used as a pigment in a glass flux on vessels from a Roman period context sheds a new light on the development of the manufacturing techniques of enamelled glasses in antiquity.

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The “Mg-sursassite” story

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The high-pressure phase $\text{Mg}_5\text{Al}_5\text{Si}_6\text{O}_{21}(\text{OH})_7$ named MgMgAl-pumpellyite in analogy to the phase MgAl-pumpellyite (Schiffman & Liou 1980) was identified in experiments in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ for the first time (Schreyer *et al.* 1986). Due to its close chemical similarity to pyrope and the high-pressure, low-temperature stability delineated by Fockenberg (1998) up to 10 GPa, this phase was proposed to be an important water reservoir in cold subducting slabs (e.g. Schreyer *et al.* 1991; Fockenberg 1998). Gottschalk *et al.* (2000) found strong evidence that $\text{Mg}_5\text{Al}_5\text{Si}_6\text{O}_{21}(\text{OH})_7$ is isostructural to natural sursassite, $\text{Mn}_4\text{Al}_6\text{Si}_6\text{O}_{22}(\text{OH})_6$. Therefore, they suggested calling this high-pressure phase Mg-sursassite.

Calorimetric and *P-V-T* data for Mg-sursassite have been obtained by Grevel *et al.* (2001). The enthalpy of drop-solution was measured by high-temperature oxide melt calorimetry using lead borate at $T = 700^\circ\text{C}$ as solvent. The resulting values were used to calculate the enthalpy of formation from different thermodynamic data sets; they range from $-13892.2\text{ kJ mol}^{-1}$ to $-13927.9\text{ kJ mol}^{-1}$ (formation from the elements). The heat capacity of the phase has been measured from $T = 50^\circ\text{C}$ to $T = 500^\circ\text{C}$ by differential scanning calorimetry. A Berman & Brown (1985) type four-term equation represents the heat capacity over the entire temperature range to within the experimental uncertainty: $C_p(T) = (1571.104 - 10560.89 \times T^{0.5} - 26217890.0 \times T^{-2} + 1798861000.0 \times T^{-3})\text{ J K}^{-1}\text{ mol}^{-1}$ (T in K).

The *P-V-T* behaviour of Mg-sursassite has been determined under high pressures and high temperatures up to 8 GPa and 800°C using a MAX 80 cubic anvil high-pressure apparatus. By fitting a Birch-Murnaghan EOS to the data, the bulk modulus was determined as $116.0 \pm 1.3\text{ GPa}$, ($K' = 4$), $V_{T,0} = 446.49\text{ \AA}^3 \exp[(0.33 \pm 0.05) \times 10^{-4} + (0.65 \pm 0.85) \times 10^{-8} T\text{ dT}]$, $(\partial K_T / \partial T)_P = -0.011 \pm 0.004\text{ GPa K}^{-1}$. The thermodynamic data obtained are consistent with the phase equilibrium data (Fockenberg 1998) and included into the internally consistent dataset of Grevel (2004); the best agreement was obtained with $\Delta_f H_{298}^0 = -13907.33\text{ kJ mol}^{-1}$, and $S_{298}^0 = 608.39\text{ JK}^{-1}\text{ mol}^{-1}$.

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