# Medieval Glassworks and the Glass Production in North-Western Bohemia

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## 1. Introduction

The aim of the present work is the characterization of a set of findings coming from medieval glasshouses situated in "Krušné Hory" mountains, northern-west Bohemia. The first glasswork is situated in Jilmová- the oldest glasswork in this region. Ceramic artifacts discovered in the course of archaeological investigations indicate that the glass was produced here since the second half of $13^{th}$ century AD [1]. Archaeological investigations in Jilmová have supplied us with many production indicators that have been classified macroscopically by the archaeologists. These indicators (frits, glass masses and vitreous working waste) are important for scientific analysis in order to characterize and classify them throwing new light on the glassmaking technology in the medieval age. Still no glass fragments of the finally artifacts from these glassworks were discovered for the present. Second group of samples comes from pre-industrial glasswork Moldava dated to the beginning of $15^{th}$ century AD. This excavation yielded a large number of fragments of glass vessels of different decorations and colours. The colourless fragments of window panes are represented here too. Both mentioned glasshouses were constructed in wooded houseless landscape. Glassmen probably used raw material for the batch and for the firing from the neighbouring landscape. In the course of archaeological excavation relicts of three different large furnaces were discovered in each of these two regions. The largest furnace served for glass melting. The others were probably auxiliary furnaces. Their true function is not yet known.

The samples were examined visually at first, and then the physico-chemical methods (SEM/EDS, XRD, and XRF) were applied. Results of our analyses should clarify on relationships among glass samples from Jilmová and Moldava regions and the glass from elsewhere in Europe. The aim is also to compare the archaeological classification based on macroscopic observation and stratigraphic position, with the physico-chemical classification of the examined finds.

## 2. Experimental

### 2.1. Materials

Eighty-eight finds belonging to different stages of the glass production cycle at Jilmová site have been classified as non-vitreous production waste, frits, droplets and glassy layers on the inner surface of melting pots. The glasses are variously coloured (green, yellow-green, yellow, blue-green). The frits appear externally as pale brown effusive materials, similar to skims and waste. Internally as pale green vitreous materials. Final products fragments were found only in site of Moldava. Most of the analyzed samples are made of a transparent colourless glass or slightly coloured one in various hues from green to yellow.

### 2.2. Physico- chemical measurements

To investigate processes of deterioration some glasses from the site Moldava have been analyzed using surface and microscopic techniques like optical microscopy, SEM/EDS and infrared microspectroscopy. The powder X-ray diffraction (XRD) was used for a phase identification. For SEM/EDS suitable areas for analysis were selected and than grinded. The weathered layer was removed and the original glass was stripped. Major and trace elements determination was carried out by scanning electron microscope coupled with an energy-dispersive X-ray analyzer (Hitachi S-4700). This method was completed with X- ray fluorescence (XRF) data.

## 3. Results and discussion

### 3.1. Corrosion

As a result of environmental conditions, the samples are covered by a thin corrosion layer, some having rainbow colours. The glasses were observed with optical microscope and SEM. It was found that the surface is not smooth containing many caves and holes, as shown in Fig.1. The reason for the iridescence of the glasses' surface is that surface layers have different optical properties (different refractive index). The composition of glasses' surface determined by EDS is (in wt%): 90.6- 69.9 $SiO_2$; 9.97- 2.74 $Al_2O_3$; 6.55- 0.1 $Fe_2O_3$; 9.75-1.19 $CaO$; 2.33- 0.63 $MgO$; 5.74- 0.41 $K_2O$; 1.66- 0 $Na_2O$. The corrosion and the weathering of glasses are described in many works [3, 4]. Alkalies are washed out from glass surface and then they react with environmental medium, creating incompact crust of sulphates and carbonates. These phenomena damage irremediably the physical and optical properties of glass. Univalent K-sulphates were confirmed by infrared microspectroscopy in our case. By this method mostly nitrates, aluminosilicates and a little carbonates were found, so we can assume some reactions with soil rather than with atmosphere. No mineralogical phases were found by powder x-ray diffraction.

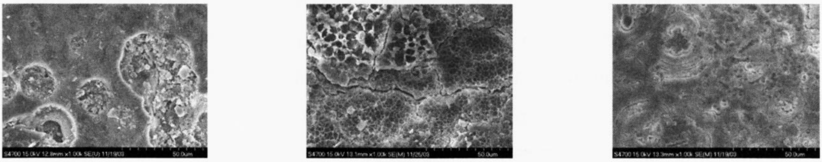

Figure 1. SEM images of glasses' surface.

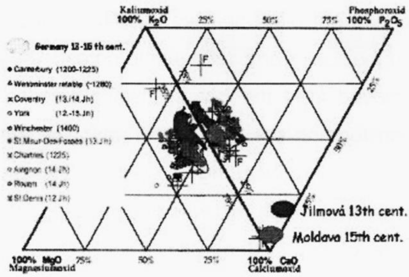


Figure 2. Diagram comparing the composition of 12$^{th}$ to 15$^{th}$ century woodash glasses from Jilmová and Moldava with those from Germany, France and England [5].

**3.2. Chemical composition and origin of minor elements in glasses**

The composition of the residual glass layers adhering to the inner surface of the melting pots are particularly interesting because it may give evidence for the in site production of glass articles. The quantity of the dissolved elements and the thickness of the contaminated layer are mainly a function of the composition of the pots, of the time of contact and of the viscosity (hence, of the temperature) of the melt. The composition of the glass findings is reported in Fig.2. As expected, the major components are restricted to the following oxides: MgO, $K_2O$, CaO and $P_2O_5$. The analyzed samples can be classified as potassium-lime-silica wood glasses, no other types of glass were identified.

Analysis of one sample from Jilmová, (the glass layer from crucible) and blue decorations of cup suggest that the blue coloration was achieved using a copper oxide. Presents of iron may also have played a role in this coloration. After all, some differences were obtained by comparison of our glass composition with the glass composition produced in other areas in Europe. Lower contents of $P_2O_5$ were found in glasses from Jilmová, a little more was in glasses from Moldava. We can envisage of using different raw materials, first of all about the different composition of ash. Transparent glass is produced of siliceous sand or quartz and alkali medium. The elements clearly representing impurities in these materials are Ti, Mn, Fe, Rb and Sr. In order to deduce their origin, we have analyzed ashes of beech wood and grains of quartz. The elements Mn, Rb, and Sr are only related to ashes; their concentrations vary in different plant species [2]. The ashes are rich in content of Ca, K, Mg and P. When the ash is precipitated into potash, the insoluble Mg, Ca and Sr compounds are removed from the product, while it still contains Rb, an alkali metal similar to K which forming soluble compounds. The presence of Rb and Sr can be used to deduce the manufacturing procedure. Glasses' samples contained Sr and rich in Mg, indicate that rough ash was directly used for the glass production. The melting temperature of the system $SiO_2$-CaO-$K_2O$ [5] is about 1250°C and glasshouses making such glass melt were using a two-step process. We can deduce it from finds of the frit lumps, in which pseudowollastonite (a product of thermal CaO reaction from the ash with $SiO_2$) was determined by XRD having the chemical composition comparable to the glasses. The second and the third smaller furnaces were probably employed to make these frits.

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