


RESEARCH ARTICLE

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Modeling of Bohemian and Moravian glass recipes from Gothic to Baroque periods

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Abstract

The Bohemian historical glasses have been neglected and have not been in focus of Archaeometric studies so far. Potassium-calcium wood ash glasses, produced in Bohemia and Moravia, from the beginning of the 14th century to the first half of the 18th century, are chemically different from the glasses produced in the same period in Western Europe. There are no written sources for glass batch recipes for Gothic (14th–1st half of 16th c.) and Renaissance (16th–17th c.) glass, while there are only few for the Baroque (end of 17th–18th c.) glass recipes. Systematically investigating the chemical composition and typology of archaeological glasses, we have chosen to reconstruct the glass recipes of potassium-calcium glasses from the three periods. In this study, the glass recipes (the ratio of the raw materials) were calculated based on the chemical composition of the historical glasses studied by X-Ray Fluorescence (XRF) and Scanning Electron Microscopy/Energy Dispersive System (SEM/EDS). The composition of the authentic natural raw materials was studied by XRF and X-Ray Diffraction (XRD): sand or quartz pebbles, beech ash and potash, limestone, NaCl, and As_2O_3 . Model glasses confirmed our presumption of gradual development in the Bohemian glass batch recipes, which used very simple raw materials ratios.

Keywords: Archaeometry, Historical glass, Glass recipes, X-ray spectroscopy, Chemical composition of glass

Introduction

Bohemian glass has played a significant role in European glass production and trade since the beginning of its systematic manufacturing. Therefore, the knowledge about its production technology is not only important to the area of the current Czech Republic but it exceeds the borders to other parts of Central and Western Europe.

Contrary to that, there is not much knowledge about the technology of glass production in historical Bohemia to be found in current research. A few experiments aimed at the reconstruction of Bohemian glass technology were carried out in the past, focusing solely on Gothic glass [1–4]. Only one of them tried to use historically authentic raw materials [1]. This general lack of knowledge and experiments led us to this paper.

For the context of this work, the term “potash” will be used for the extract from wood ash (from German “*Pot- tasche*”, English equivalent of “pearl ash” [5, 6]). The Si-K-Ca glasses in the text will be called “potassium-calcium” glasses because the term “potash glass” would indicate the use of wood ash extract in their production, which is not always true.

Historical development of Bohemian potassium-calcium glass

Potassium-calcium glass was made in Bohemia until the end of the 18th/middle of the 19th century. The change in technology is evident from the chemical analyses of archaeological glasses (see Table 1).

The oldest glasses (Early Gothic glasses from the third quarter of the 13th century) found in Bohemia were made by melting of two main ingredients – sand/quartz and wood ash [7, 8]. However, it is not completely clear whether those glasses were made in Bohemia or imported from other production areas (e.g. Germany). These early gothic glasses have a very low content of SiO_2

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Table 1 Chemical composition of characteristic types of Bohemian and Moravian historical glasses [wt %]

Location	Bohušov	Veselí nad Moravou	Opava	Chrudim	Praha	Brno	Chrudim	Chrudim	Olomouc
Date	1275–1350	14th–15th centuries			1550–1625	16th–17th centuries		17th–18th centuries	1st half of the 18th century
Reference	[9]	[31]	[32]	[33]	[34]	[10]	[33]	[33]	[10]
SiO ₂	38.1	60.6	60.8	58.0	60.3	61.3	60.7	74.8	75.7
Al ₂ O ₃	1.4	–	0.7	1.5	1.9	2.0	1.5	0.2	0.2
Na ₂ O	0.3	–	0.3	0.2	0.9	1.1	0.2	0.9	0.3
K ₂ O	17.6	21.3	22.4	19.9	16.3	13.8	13.7	13.4	13.9
CaO	31.9	12.4	11.4	15.4	16.3	16.8	17.2	9.6	8.2
MgO	2.5	3.1	2.6	2.5	2.4	2.0	2.2	0.2	0.1
SO ₃	0.3	0.5	0.5	0.3	0.1	0.2	0.2	0.2	0.2
P ₂ O ₅	3.0	1.2	0.7	1.0	0.8	0.8	1.0	0.1	<0.1
Cl	0.1	–	–	0.1	0.2	0.3	0.2	0.2	0.1
TiO ₂	0.1	–	–	–	0.2	–	–	–	–
Fe ₂ O ₃	2.5	0.2	0.3	0.3	0.2	0.2	0.5	0.1	<0.1
MnO	2.3	0.2	0.3	0.9	0.2	0.6	1.0	0.1	<0.1
As ₂ O ₃	–	–	–	–	–	–	–	0.3	1.1
CaO/K ₂ O	1.8	0.6	0.5	0.8	1.0	1.2	1.3	0.7	0.6

(around 40 wt %) and high content of alkalis (around 50 wt %) [9] (see Table 1). The CaO/K₂O ratio is generally higher than 1.5 [10]. This number is roughly the same as the ratio of those oxides in beech ash and this fact points to the use of this particular alkali-bearing material for Bohemian glassmaking. In other types of ashes, those ratios are different (4.3 for spruce ash [1], 4.3 for oak [11], 4.5 for birch [12], or less than 0.3 for bracken [6]).

Historical written sources (bookkeeping records, contracts, or general mentions of glass or glassworks) date back the systematic production of glass in Bohemia (e.g. melting of glass from a batch, not re-melting of glass ingots) between the end of the 13th century and the beginning of the 14th century [13, 14]. Chemical compositions of Bohemian Gothic glasses from the beginning of the 14th century to the 1st half of the 16th century show higher levels of K₂O than earlier glasses and, consequently, a change of the CaO/K₂O ratio in favor of K₂O (generally lower than 0.6–0.8, see Table 1). It seems very probable that potash (leachate from beech ash rich in K₂CO₃) was used as a substitution for a part of the wood ash because it is impossible to get the right composition without an additional source of K₂O [1, 10, 12]. This is a surprising finding because there is no direct source proving the use of beech ash potash in Central Europe before the 17th century. In southern Europe however, the purification of halophytic plant ashes was a common process in the 14th century [15, 16]. Due to the higher amount

of iron, the favorable Fe/Mn equilibrium in the beech ash, and the reducing atmosphere in the furnace, Gothic glasses were colored green. This and the location of glass workshops in the woody areas resulted in the term “forest glass”.

At the beginning of the Renaissance era (from the second half of the 16th century until the end of the 17th century), the European market was dominated by Venetian soda glass made with halophytic plant ash as a flux–common glass (*Vetro commune*) with a green tint, *Vitrum blanchum* with a slightly grey tint, and colorless *Cristallo* [17]. Glassmakers in Central Europe had the ambition to develop a similar glass using local materials and they began experimenting with procedures and materials that would eventually lead to colorless glass [13]. The Bohemian glassmakers were limited by the properties of potassium-based glass that is more viscous and solidifies significantly faster than sodium glass [18]. Their focus was therefore on making the glass as clear and colorless as possible (but due to the use of beech ash, light green tint remains) [13]. The Bohemian Renaissance glass is a modification of the Gothic recipe. Glass was still made from sand/quartz, beech ash, and potash but the chemical composition suggests a high probability for the addition of calcium. Limestone or chalk was used as a substitution for a part of potash and ash [5, 10]. As a result, the ratio of CaO/K₂O changed to around 1–1.2 (Table 1). At the turn of the 16th and 17th centuries, glassmakers also

began to use small amounts of NaCl as a refining agent [as stated in 10, 19, 20], manifesting as a higher content of Na₂O (between 1 and 1.5 wt %) together with chlorine (Cl) presence in the chemical composition of archaeological glasses. The use of common salt in glass probably began in the 13th century [21], although it is not stated until 1556 by Agricola [5, 22]. This addition is further supported by the higher amount of Cl (0.1–0.5 wt %) in these glasses, in contrast with earlier glasses where Cl is lower than 0.1 wt %. Lowering the amount of beech ash and probably also by using carefully selected raw materials with fewer impurities helped to partially eliminate the green color from the glass. Some sources mention the use of MnO₂ in the form of *pyrolusite* for intentional decoloring of glass, but chemical analyses of Bohemian Renaissance glasses do not support such a procedure [10]. The content of Mn does not increase significantly and corresponds with the amount introduced to the glass by beech ash. Another type of locally produced Renaissance glass is calcium-potassium glass, commonly used for objects decorated with painting, engraving, or *filigrana* (white glass threads inside clear glass). It was probably produced using a similar recipe as the Gothic glass, only with lower amounts of potash (K₂O only up to 10 wt %, CaO around 13 wt %). The assumed addition of NaCl to its glass batch was up to 3–5 wt %, resulting in the Na₂O concentration in the glass up to 3 wt %. The *filigrana* glass is commonly found in Moravia or Austria [23, 24].

After the second half of the 17th century, a wide range of glass types was produced in Bohemia—both colorless and intentionally colored. The typical and widely known Bohemian Baroque glass is the so-called *Bohemian crystal* that was produced for the whole 18th century. The term “Bohemian crystal glass” signifies the compositional type of specific potassium-calcium unleaded glass with the optical qualities of crystal glass [10]. It is also the trade label of historical and modern glass. In the context of chemical composition and production technology, it is a colorless glass with the amount of SiO₂ around 70 wt % and the CaO/K₂O ratio around 0.7 (see Table 1). The Bohemian crystal glass was made from sand, purified potash (multiply leached potash with only a trace amount of impurities), limestone (or lime), and a small amount of arsenic (III) oxide (0.3–1.2 wt %). Unlike English crystal glass [25], Bohemian crystal does not contain any intentionally added lead [10]. Traces of PbO are occasionally detected, probably resulting from sand or quartz. Raw wood ash was not used anymore, only high-quality purified and calcined potash. The rest of the raw materials were also carefully selected to have minimal content of impurities that would tint the glass. The first mention of adding As₂O₃ to glass is by Johannes Kunckel in his *Ars Vitruviana Experimentalis* in 1679 [5, 26]. Historical

sources suggest around 3.8 kg As₂O₃ to 100 kg of sand [5, 27]. As₂O₃ acts as a refining agent and it also helps with glass decoloring [16].

Apart from *crystal glass*, so-called *chalk glass* was also produced. This term is used to describe a type of potassium-calcium colorless glass made from potash with the addition of limestone (chalk) that had already appeared in the Renaissance era [10]. The borderline between the *crystal* and *chalk* glasses is very unclear and they can be distinguished only by chemical analysis. It is believed that *chalk* glass was made from lesser-quality raw materials, the use of chalk instead of limestone and omitting As₂O₃ addition is possible [28]. *Chalk* glass would therefore not reach the same optical qualities as *crystal* glass [13]. It would be cheaper to make and used as ordinary glassware [10, 29].

In different types of Bohemian Baroque glass, potash was sometimes substituted with saltpeter (KNO₃) or potassium bitartrate (with the main component being KC₄H₅O₆) [19, 20]. Later, at the turn of the 18th and 19th centuries, there is evidence that borax (Na₂B₄O₇·12H₂O) was sometimes used as a glass-forming material [19, 30].

Raw materials for historical glassmaking

Wood ash

In Central and Western Europe, glass was made from wood ash that acts as a flux and provides high quantities of potassium and calcium [7]. Pliny mentions the use of oak ash [5], but later, Theophilus and Heraclius [34] state the use of beech ash as the only alkali-bearing material. Beech ash is also mentioned by Biringuccio in 1540 [35], Agricola in 1556 [27], or Mathesius between 1552 and 1562 [5]. For the Bohemian region, beech (*Fagus sylvatica*, the chemical composition in Table 2) is the most probable source of wood ash [5, 34] since it was the most common type of tree in this region [5]. Generally, beech ash has the CaO/K₂O ratio around 1.5–2.5 and there is always P₂O₅ present in various amounts [1, 7, 10]. The composition of beech ashes from different European locations can be seen in Table 2. It is visible, that the composition varies in between locations. These differences can be explained by the effect of the soil composition, the season of collecting the wood, and the conditions of preparing and collecting the ash [36]. Mostly, the ratio between CaO and K₂O remains around 2. The use of other types of K-Ca ashes (mainly spruce, bracken, or oak) is also possible in some smaller glassworks [5]. Those types of wood ashes were mainly used in western parts of Europe and on the British Isles [36–38].

It is important to note that to successfully calculate the batch recipe and theoretical glass composition, the calculations must be made with data acknowledging that many of the elements in the ash are in the form of

Table 2 Chemical composition of beech ash from different European and Czech locations

Location	Havlíčkův Brod, CR	Moldava, CR	Orlické mountains, CR ^a	Germany	UK ^a	Switzerland
Reference	This paper	[4]	[1]	[12]	[40]	[12]
SiO ₂	1.9	9.5	9.3	23.4	15.6	29.1
Al ₂ O ₃	0.6	2.5	2.7	10.3	0.8	7.5
CaO	35.0	29.1	46.3	34.9	33.2	33.2
K ₂ O	14.8	16.4	23.8	12.4	20.1	11.1
Na ₂ O	0.1	0.3	0.2	0.9	0.4	0.5
MgO	6.3	5.0	7.4	4.7	7.4	8.7
MnO	2.7	2.0	1.7	2.8	6.7	0.2
Fe ₂ O ₃	0.4	1.5	2.2	3.5	0.7	3.7
P ₂ O ₅	2.6	6.3	3.3	3.5	13.8	4.7
TiO ₂	0.04	–	0.4	0.5	0.1	0.5
BaO	0.4	0.4	0.6	0.2	–	–
SO ₃	1.5	3.0	1.7	1.6	1.2	0.6
Cl	0.06	–	0.1	–	–	–
Rb ₂ O	0.04	–	0.02	–	–	–
SrO	0.1	–	0.2	–	–	–
CO ₂	33.5	24.0	no data	16.4	no data	16.1
CaO/K ₂ O	2.4	1.8	1.9	2.8	1.7	2.9

^a These data are only for oxides, without acknowledging the amount of the carbonates

carbonates, as seen also in [39]. When calculating the batch with oxide forms only, great errors occur due to different molecular weight and therefore different weight percentages.

Refined wood ash, potash

It seems that the systematic replacement of wood ash with potash started as early as in the 14th century, i.e. much earlier than it was mentioned in historical texts (first by Neri in 1612) [5]. Potash (see Fig. 1) was produced by mixing the beech ash with hot water, the mixture was then filtered, and the leachate boiled in metal pots or barrels to get solid potash [5, 41]. To make colorless or crystal glasses, it was necessary to refine (purify) the potash to minimize any coloring agents present. The purifying process could be repeated multiple times to provide a product of high quality [5, 20]. Later, potash was additionally also calcined at temperatures up to

800 °C. Calcination removes organic remains (main carbon) that can affect the melting process (red-ox equilibrium in the glass melt) and thus the final color of the glass [5]. The issue of potash refining and calcination remains to be fully investigated.

Potash production process (from any type of wood ash) removes the insoluble compounds such as calcium and phosphorous salts. Therefore, glasses produced with potash will have a significantly lower amount of P₂O₅ and CaO. This fact can be used to distinguish glasses made with only wood ash and those using potash, as in [6].

Alternative sources of potassium were also used—in the Renaissance era, it was saltpeter (KNO₃) which also acts as a refining agent in the glass melt. The use of saltpeter is mentioned by Neri in 1612 or Mathesius [5]. Saltpeter was both produced in Bohemia or imported [19]. There are also sources about the use of potassium bitartrate (called “tartaro” in Venice)—Neri in 1612 or Kunckel in

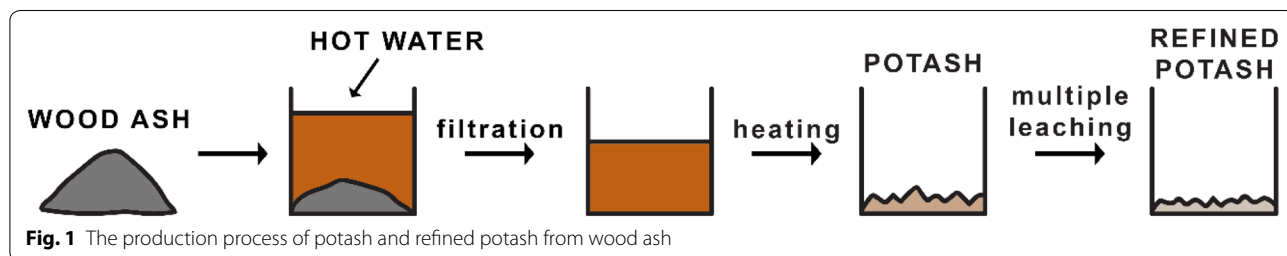


Fig. 1 The production process of potash and refined potash from wood ash

1679. They suggest that this component was very pure but also very expensive, so the use was limited [5].

Calcium-bearing materials

Materials used in Bohemia to introduce calcium into the glass melt were either crushed limestone, chalk, or lime (either slaked lime— $\text{Ca}(\text{OH})_2$ or CaO) [5, 19].

Glass-forming materials

The main sources of SiO_2 were natural quartz, quartz pebbles, or sand. Stone quartz and pebbles had to be ground to smaller size particles to ensure successful melting. Pieces suitable for glassmaking were baked in a small furnace for several days and then rapidly cooled in water. The cooling led to the cracking of bigger pieces of quartz and it also made the quartz softer and easier to grind into particles of the desired size. Only particles smaller than 1 mm were used for glassmaking [5]. The procedure of grinding the quartz was very difficult and therefore it is more likely that suitable sands or softer sandstone were later used for the production [19, 36].

The first aim of this research was to reconstruct the recipes and make model glasses for three types of historical Bohemian glasses (Gothic, Renaissance, and Baroque *Bohemian crystal*) based on the analyses of archaeological glasses, mainly from Chrudim [42]. The second aim was to confirm the validity of calculations by experimental melting of the model glasses, which were analyzed by X-Ray Fluorescence to compare their chemical compositions with the archaeological finds.

Experimental part

The experiment to find and validate the recipes used in Bohemian historical glassmaking consisted of several steps. Firstly, the suitable raw materials were chosen and analyzed by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). When choosing which materials to use, we mainly focused on those mentioned in historical sources—e.g. Theophilus, Agricola. Those analyses were used as the base for recipe calculation. As mentioned before, no historical sources regarding Bohemian glass recipes exist. Therefore, the calculations were made purely by fitting the theoretical chemical composition of model glass to the historical glasses, all the time focusing on simple weight ratios of the raw materials. Only after successful calculations, the model glasses were melted. The last step was to analyze the finished glasses by XRF and comparing them with their historical counterparts. The model glasses prepared for this study were also used to study the historical melting process and physical properties which will be discussed elsewhere.

Analytical methods

XRF

The measurement was carried out in the Laboratory of X-Ray Diffractometry and Spectrometry at UCT Prague on the ARL 9400 XP spectrometer (Thermo ARL). The spectrometer was equipped with Rh anode X-Ray tube and fitted with a 50 μm thick Be end-window. Spectral peaks intensity data were obtained in vacuum by WinXRF software at 60 kV. The generator settings-collimator-crystal-detector combinations were optimized for 82 elements with an analysis time of 6 s per element. The measured data were evaluated by the UNIQUANT 4 software with the integrated standard database. The obtained concentrations were normalized to 100%. All samples were crushed into a very fine powder in an agate mortar and pressed into H_3BO_3 tablets without any binding agents. The analysis was performed for the whole area of a sample (diameter of 29 mm) and took 20 min per sample.

XRD

The mineralogical composition of the raw materials was determined by XRD analysis. Samples were measured in the form of very fine powders. The analysis was performed on the X'PertPRO MPD diffractometer (PANalytical) at the Institute of Inorganic Chemistry of the Czech Academy of Sciences. The measurement used $\text{CuK}\alpha$ radiation (40 kV, 30 mA), fast linear detector PIXcel, and reflexive Bragg–Brentano setting. The primary beam was focused by a 10 mm mask and 0.04 rad Soller collimator aperture, the diffracted beam was focused by anti-scattering collimator on 0.5°, 0.04 rad Soller collimator, and Ni beta-filter. The measurement range was 7–90° 2 θ and the time was 800 s per step of 0.013°. The data were evaluated by the HighScore Plus 4.6.1 software, together with the PDF-4+ (2018) Powder Diffraction File database (ICCD—International Centre for Diffraction Data) [43].

Raw materials used for model glass preparation

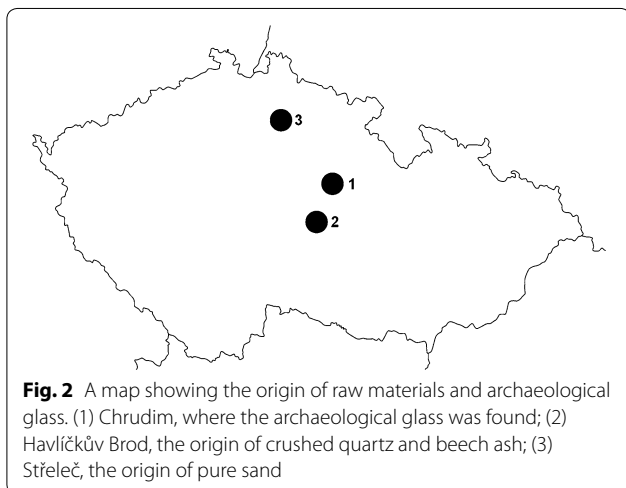
By studying historical sources and the chemical composition of Bohemian archaeological glasses, we put together general recipes to see which raw materials would be necessary to form each type of model glass (Table 3).

To replicate Bohemian historical glasses as closely as possible, we used mainly natural raw materials. When possible, the materials were sourced locally to the presumed area of origin of the archaeological glasses.

The glass-forming raw material used for the model glasses was either natural crushed quartz (for Gothic and Renaissance model glasses) or pure sand used in the glassmaking industry (for Baroque model glass). The quartz was handpicked in the Jihlava region and was provided already crushed by the Museum of Vysočina in

Table 3 General recipes necessary for model glasses

	Glass-forming material	Flux		Calcium source	Additives
Gothic	Quartz	Beech ash	Beech ash potash	–	–
Renaissance	Quartz	Beech ash	Beech ash potash	Limestone	NaCl
Baroque	Sand	Industrially produced potash		Limestone	As ₂ O ₃



Havlíčkův Brod. We suppose that with the growing glass production in the 17th century, it was not profitable to grind big pieces of quartz or pebbles and suitable glass-making sands were used in Baroque glassmaking.

Beech ash was chosen as a flux because beech was the most common tree in the Bohemian area throughout history [5, 20] and therefore we assume that its use is the most probable. The beech ash was kindly provided by the Museum of Vysočina in Havlíčkův Brod. The wood was collected in the nearby area (see Fig. 2).

Beech ash potash was prepared under laboratory conditions but according to historical instructions as in [1] and used for Gothic and Renaissance model glasses. We mixed 100 g of beech ash with 1000 ml of hot demineralized water and left the mixture to stand for 2 days. This caused any soluble salt from the ash to dissolve in water. After 2 days the mixture was filtered and the entire process was carried out again with the remaining ash. During this process, the leachate changed color from dark orange-brown to very light orange. After the third filtration, the leachate was completely colorless. We chose this point to stop the leaching and carry on with the process, the same as in [1]. Then the leachates (3000 ml in total) were heated to ca 90 °C and evaporated to get solid raw potash. To



dry the potash completely was quite a difficult task due to its high hygroscopic ability and it took more than 24 h in the dryer at 90 °C. In the end, we obtained potash of cream color (Fig. 3). The weight of potash we obtained from the initial 100 g of beech ash was only 13.5 g.

In the case of Baroque glass, industrially produced pure K₂CO₃ by Sigma-Aldrich was used to imitate highly purified beech ash potash.

Glasses from the Renaissance and Baroque periods require the addition of calcium. The Renaissance glass has a higher content of CaO that could not be supplied by beech ash only, and Baroque glass was made without any ash at all. For supplying CaO into the glasses, we chose a finely ground natural limestone (no data about any specific source location was provided).

In the case of other additives, it was preferable to use commercially available chemicals. NaCl in Renaissance glass was provided by Penta, s.r.o. and As₂O₃, acting as a refining and decolorizing agent for Baroque glass was by Sigma-Aldrich.

Making of the model glasses

From the composition of archaeological glasses, it seems that only one basic recipe was used in the Gothic era. Glassmakers in the Renaissance and Baroque periods modified this recipe and developed new ones. When calculating the batches, it was necessary to manually adjust the values for sulfates (as SO_3) and chlorides (ac Cl) as they decompose and volatilize during melting [16]. We found out that setting the values for SO_3 and Cl at 0.3 wt % each fitted the best the chemical composition of finished glasses.

The calculated recipes were used to prepare about 300 g of each model glass. The model glasses were prepared in an electrical laboratory furnace with an oxidizing atmosphere. Samples were melted at 1400 °C for 4 h in porcelain crucibles (Fig. 4). The temperature was set higher than would be possible in history to save time during melting. This temperature was high enough to melt the glasses without the need for fritting. Due to foaming, the batches were put into the crucibles gradually in

three parts, 15 min apart. The glass was not stirred during the melting because of the high viscosity of the melts. Despite that, the finished glasses were homogenous. Immediately after the melting process, the glass melt was cast on a smooth stainless steel plate, put in the annealing oven at 560 °C for 1 h, and cooled down with the rate 3 °C.min⁻¹. Finished model glasses can be seen in Fig. 5.

Results and discussion

Chemical and phase composition of raw materials used in the experiment

The chemical composition of crushed quartz and pure sand was similar but, as was expected, the natural quartz contained more impurities. The most important difference is the content of iron in the quartz (0.1 wt % in contrast with 0.03 wt % in the sand) and its coloring abilities (together with manganese) in the historical furnaces with reducing atmosphere. This does not cause any problems for Gothic and Renaissance glasses that were unintentionally tinted green. However, quartz with its impurities



would be unsuitable for colorless Baroque glass. It seems highly probable that Baroque glassmakers specifically chose very pure sand.

The particular beech ash we used contained high amounts of CaO (31 wt % as calcite–CaCO₃) and K₂O (17 wt % as K₂CO₃) and their ratio was around 2 (see Table 4 and 5). The amount of P₂O₅ (around 3 wt %) is typical for wood ashes and can be always found in the chemical composition of the finished glass. XRD analysis (see Additional file 1) confirmed that the phosphorus is in the form of hydroxyapatite (Ca₅(PO₄)₃(OH)). The ash also had quite a high content of manganese (up to 2.4 wt %).

According to analyses, experimentally prepared potash contained mostly K₂CO₃ (Table 4). There was 1.2 wt % of SiO₂ as contamination from the ash. In comparison to untreated beech ash, experimentally prepared potash had significantly lower amounts of CaO, MgO, and P₂O₅ (all less than 0.3 wt %), and MnO was not detected at all. This was caused by the inability of the compounds to dissolve in water in the form of carbonates, phosphates,

etc. XRD analysis (Additional file 2) showed that a majority of the potash is formed by K₂CO₃·1.5H₂O and K₄H₂(CO₃)₂·1.5H₂O. Arcanite (K₂SO₄) and also a very small amount of hydroxyapatite was present. The amount of Rb₂O and SrO is very important, as both oxides are present in the beech ash (Rb₂O/SrO ≈ 0.4) but insoluble SrO is removed during the process of making the potash. There was around 0.2 wt % of Rb₂O and no SrO detected in potash by XRF. This fact could be important in further research regarding the historical technological practices and recipes of archaeological glasses. The Rb₂O/SrO ratio could help distinguish between glasses from the early Gothic period made with wood ash only and late Gothic glass, where wood ash was completely replaced by wood ash potash (Rb₂O/SrO ratio increased to 1).

Limestone consisted mainly of CaO (51.5 wt %) in the form of CaCO₃ (see Additional file 3) and contained negligible amounts of MnO (0.3 wt %), SiO₂ (less than 3 wt %), and Al₂O₃ (1.5 wt %). The 0.02 wt % of SrO will alter the chemical composition of finished glass,

Table 4 Chemical composition of raw materials used for model glass preparation (XRF, in wt %)

	Quartz	Pure sand	Beech ash	Laboratory- prepared potash	Industrially prepared potash	Limestone
SiO ₂	98.9	98.7	1.9	1.2	0.02	2.8
Al ₂ O ₃	0.6	1.1	0.6	0.04		1.5
CaO	0.1	0.04	35.0	0.3	0.01	51.5
K ₂ O	0.2	–	14.8	50.1	56.5	0.3
Na ₂ O	0.1	–	0.1	0.8	0.1	–
MgO	0.02	–	6.3	0.08		1.5
MnO	–	–	2.7	–		0.03
Fe ₂ O ₃	0.1	0.03	0.4	–		0.3
P ₂ O ₅	0.02	–	2.6	0.2		0.02
TiO ₂	0.01	0.05	0.04	–		0.05
BaO	–	–	0.4	–		–
SO ₃	–	–	1.5	6.8		–
Cl	–	–	0.06	0.2		<0.01
Rb ₂ O	–	–	0.04	0.1		–
SrO	–	–	0.1	–		0.02
CO ₂	–	0.06	33.5	40.3	43.3	42.0

Table 5 Phase composition of raw materials used for samples' preparation (XRD)

Quartz	Quartz SiO ₂		Albite NaAlSi ₃ O ₈		Orthoclase (K _{0.92} Na _{0.08})(AlSi ₃)O ₈
Beech ash	Fairchildite K ₂ Ca(CO ₃) ₂	Arcanite K ₂ SO ₄	Calcite CaCO ₃	Quartz SiO ₂	Hydroxylapatite, silicious Ca ₁₀ (PO ₄) _{4.92} (SiO ₄) _{1.08} (OH)O _{0.664}
Limestone	Calcite CaCO ₃	Dolomite CaMg(CO ₃) ₂	Muscovite KAl ₂ (Si,Al) ₄ O ₁₀ (OH) ₂		Quartz SiO ₂
Laboratory-prepared potash	K ₂ CO ₃ ·1.5 H ₂ O	K ₄ H ₂ (CO ₃) ₃ ·1.5 H ₂ O	Arcanite K ₂ SO ₄		Hydroxylapatite Ca ₅ (PO ₄) ₃ (OH)

XRD analysis was not performed on pure sand and industrial potash. Sand is considered to be mainly quartz, industrial potash consists of pure K₂CO₃. Diffractograms can be found in the Additional files 1–4

therefore the hypothesis of it being one of the factors pointing at the glass recipe is only valid for glasses with no addition of limestone. Further research on this problem is necessary.

Calculations of glass recipes

Real archaeological glasses have a slightly varied chemical composition due to the use of naturally inhomogeneous raw materials. Therefore, the calculations of model glass batches were made for average chemical compositions of Bohemian glasses typical for the three different periods, according to analyses in Table 1.

A model glass batch for the Gothic glass was mixed from quartz, beech ash, and beech ash potash. To prepare a Gothic model glass of the same average composition as the historical ones, beech ash potash had to be added into the glass batch, otherwise the content of K_2O around 20 wt % could not be reached with the CaO/K_2O ratio being 0.5. The calculations showed that the ratio of the main glass-forming components (sand or quartz) and alkalis was approximately 1:1. Therefore, 100 kg of the alkali component was added to 100 kg of quartz. Alkalis were supplied by beech ash and potash. By comparing the theoretical (calculated) composition of the model glass with the archaeological “average glass” we found out that 50–70 weight parts of ash and 30–50 weight parts of potash seem ideal (see Table 6).

Renaissance glass batches still had the same ratio of quartz and alkali components (1:1) as the Gothic glass but the amount of beech ash potash was lowered in favor of limestone (20 weight parts) and a small amount of NaCl.

The situation with the Baroque “Bohemian crystal” glass is much easier to model. At that time, pure materials were used with as little impurities as possible and therefore we could make the calculations for pure components as well. Lead-free crystal glass with the addition of As_2O_3 typical for Bohemia and Moravia was selected for the calculations. The Baroque glass batch consisted of pure glassmaking sand, industrially produced potash instead of beech ash potash, limestone, and a small addition of As_2O_3 (typically from 0.2 to 3 wt % in the finished glass). The overall ratio between sand and alkalis changed to 2:1.

Chemical composition of model glasses

Gothic glass (beginning of the 14th century–1st half of the 16th century)

The content of SiO_2 in Gothic glasses (both model and historical) is around 60 wt %. The important parameters of Bohemian Gothic glasses are high amounts of K_2O (20 wt %) and CaO (10–13 wt %) and their ratio of 0.5–0.7, which were achieved in the model glass. Very similar to the archaeological samples is also the 0.3 wt % of Fe_2O_3 that, together with the furnace atmosphere and Fe/Mn ratio, causes the typical green color of the Gothic glass. The presence of P_2O_5 around 1 wt % confirms our assumption of wood (beech) ash use. Overall, the chemical compositions of the prepared model Gothic glass (in Table 7) was in a very good agreement with those of the archaeological glasses. Small differences between theoretical and real chemical compositions of the model glass, particularly in the amount of Al_2O_3 , were caused by chemical inhomogeneity of the beech ash and quartz. Both Rb_2O and SrO are present in the Gothic model glass around 0.04 wt % which is contributed by both beech ash and potash.

Renaissance glass (2nd half of the 16th century–3rd quarter of the 17th century)

The content of SiO_2 in historical Renaissance glasses generally fluctuates around 61 wt %. In the model glass, around 62 wt % of SiO_2 was achieved, as well as the correct amounts of K_2O and CaO , which are 14–16 wt % and 17 wt % respectively. The ratio of CaO/K_2O was around 1.2 in both the historical and model glasses. The amount of P_2O_5 (0.9 wt %) in the glass was also identical to the archaeological glasses. Contrary to the calculations, the content of Cl in the model glass was a little lower than expected—only 0.1 wt % (Table 7). The loss of Cl during heating is probably bigger than anticipated due to the high melting temperature, as confirmed by [44, 45]. The amount of Rb_2O in the Renaissance model glass is almost the same as in a Gothic model glass (0.3 wt %) but there is much more SrO present (0.4 wt %). Here, SrO was supplied by beech ash and limestone because no other raw material bears SrO . From our data, it seems that both of these raw materials contribute to the overall amount of SrO in the glass.

Table 6 Weight ratios of raw materials calculated for model glass batches

	Quartz	Sand	Beech ash	Potash	K_2CO_3	Limestone	NaCl	As_2O_3
Gothic	100	–	50	50	–	–	–	–
Renaissance	100	–	50	30	–	20	2,5	–
Baroque	–	100	–	–	30	20	–	1

Table 7 Chemical composition of the model glasses analyzed by XRF (wt %)

	Gothic, calculated	Gothic, model glass	Renaissance, calculated	Renaissance, model glass	Baroque, calculated	Baroque, model glass
SiO ₂	62.9	62.2	62.1	62.6	74.6	74.1
Al ₂ O ₃	0.6	0.6	0.7	0.7	1.1	0.3
CaO	11.1	11.2	17.2	16.2	7.8	8.5
K ₂ O	20.4	20.8	13.9	14.9	15.4	15.8
Na ₂ O	0.3	0.4	1.0	1.3	–	0.2
MgO	2.0	2.1	2.1	1.9	0.2	0.2
MnO	0.8	0.9	0.8	0.8	0.04	0.01
Fe ₂ O ₃	0.2	0.3	0.2	0.3	0.1	0.1
P ₂ O ₅	0.9	1.1	0.9	0.9	–	–
TiO ₂	0.02	0.02	0.02	0.02	0.04	0.03
BaO	0.1	0.2	0.1	0.1	–	–
SO ₃	0.4	0.2	0.4	0.1	–	–
Cl	0.07	–	0.2	0.1	–	–
Rb ₂ O	0.04	0.04	0.03	0.03	–	–
SrO	0.04	0.04	0.04	0.4	–	–
As ₂ O ₃	–	–	–	–	0.8	0.7
CaO/K ₂ O	0.5	0.5	1.2	1.1	0.5	0.5

Baroque glass (3rd quarter of the 17th century–end of the 18th century)

For Baroque model glass, there were some differences between the chemical composition of model glass and archaeological glasses—mainly the amount of SiO₂. In historical glasses, the SiO₂ is present in an amount around 74–75 wt %. For model glasses, only 71.5 wt % was achieved. The opposite difference can be found in the amount of K₂O. In model glasses, 16 wt % K₂O was detected but in archaeological glasses, the amount goes only up to 13–14 wt %. It seems that in the model glasses, the amount of K₂O went higher than expected at the expense of SiO₂. This was quite unexpected and can be caused either by chemical inhomogeneity of the finished glass that was not detected before the analysis or by insufficient melting of sand. This difference is not too massive to disprove the calculated recipe, and the CaO/K₂O ratio is still around 0.5 as in the archaeological glasses.

Very low content of Fe₂O₃ (less than 0.1 wt %) and the absence of P₂O₅ confirms that natural wood ash was no longer used to make this type of glass and only potash leached out from beech ash was used. Correspondingly, the SrO in the model glass was below detection limit. The amount of As₂O₃ is quite variable in archaeological glasses but is on average around 0.2–3.0 wt %. In the model glass, it was detected as 0.7 wt %, which is a little less than calculated. This loss was probably caused by the partial volatilization of As₂O₃.

Conclusions

This study helped to uncover some important aspects of Bohemian historical glassmaking, which is still an unexplored part of historical glassmaking. The potassium-calcium glasses produced in Bohemia and Moravia were different from similar types of glasses made in the rest of Western Europe (chemically, as well as technologically) and cannot be put into one category with those. This fact is very important for the understanding of the glass technology using wood (beech) ash in the areas north from the Alps. Bohemian glass played an important part in the historical European market; therefore, we believe that this work will be a valuable contribution to other studies.

The calculated recipes and prepared model glasses have shown that it is possible to reconstruct the technology for glass that was produced from the 14th to 18th centuries in Bohemia and Moravia. The premise that Bohemian historical glasses were made by following recipes with very simple ratios of raw materials was confirmed. For Gothic glass, it was 1 part of quartz and 1 part of alkalis. The alkalis consisted of beech ash and potash. During the Renaissance era, the glass recipe changed and the addition of limestone and later also NaCl, acting as a refining agent, was used with high probability. The raw materials ratio remained nearly the same; the content of potash was a little diminished. Baroque “Bohemian crystal” glass recipe was completely different. The raw materials ratio changed to 1 part of sand and 0.5 parts of alkalis,

the arsenic oxide was used as a refining and decolorizing agent. Only purified raw materials were used.

Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s40494-020-00459-z>.

Additional file 1. XRD diffractogram of beech ash.

Additional file 2. XRD diffractogram of experimental potash.

Additional file 3. XRD diffractogram of limestone.

Additional file 4. XRD diffractogram of quartz.

Abbreviations

XRF: X-Ray Fluorescence; XRD: X-Ray Diffraction.

Acknowledgements

The authors would like to thank the Vysočina Museum for providing some of the raw materials, the Institute of Archaeology of the CAS, Prague, v.v.i. and Archaia Brno, o.p.s. for allowing us to analyze the chemical composition of archaeological glasses, and Dr. RNDr. Petr Bezdička for the XRD measurement.

Authors' contributions

DR planned and supervised the whole experiment, together with KP they made the calculations. KP prepared the model glasses, prepared all samples for analysis, and wrote the manuscript. SR analyzed all samples on XRF. All authors read and approved the final manuscript.

Funding

This work was supported by the grant of the Czech Science Foundation No. GA 19-05677S: Glass in the Czech Lands from the Gothic to the Baroque, in the Light of Finds from Chrudim and Brno. The importance of regional production in the European context.

Availability of data and materials

All data generated or analyzed during this study are included in this article and its supplementary information files.

Competing interests

The authors declare that they have no competing interests.

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Received: 18 June 2020 Accepted: 28 October 2020

Published online: 17 November 2020

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