

## Article

# Trends in Colouring Blue Glass in Central Europe in Relation to Changes in Chemical Composition of Glass from the Middle Ages to Modern Age

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**Abstract:** The study deals with the development of the chemical composition of blue glass from the 13th to the 19th century in the region of Bohemia (Central Europe). Nearly 100 glass samples (colourless, greenish, and blue) were evaluated by an XRF method to distinguish the colouring components of blue glass. As early as in the 13th century, blue glass based on ash containing colouring ions of Co and Cu was produced here. To achieve the blue colour of glass, a copper-rich raw material was most likely applied. This information significantly complements the existing knowledge about glass colouring in the Middle Ages, as the glass of later periods was typically coloured with raw materials containing cobalt.

**Keywords:** blue glass; smalt; Bohemia; Europe; Middle Ages; Renaissance; modern age; chemical composition; ash; potash; cobalt; copper; XRF



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## 1. Introduction

The production of blue glass has enjoyed a long tradition since the Late Bronze Age and is related to areas such as Egypt or Mesopotamia [1,2]. In Europe, the occurrence of small glassware objects started to increase significantly in the 6th–5th century BC with blue beads frequently appearing in this production [3].

Venclová et al. [4] describes one of the most important sites of its kind, a La Tène glass processing workshop in Europe (Němčice locality). A large part of the finds uncovered there (more than 2000 pieces) consisted of blue glass objects. Their coloration is associated with the use of cobalt (mostly in hundreds of ppm) and copper (in thousands of ppm). Several samples also show greater amounts of antimony and manganese. This corresponds well with the work [5].

Another work [1] maps the use of cobalt-based colourants in glass during the 1st millennium AD. The authors state that, in the period between the middle of the 4th century and the beginning of the 6th century, a change occurred in the type of the cobalt raw material applied (this is mainly true for the Eastern Mediterranean area). In the Western Mediterranean, this trend was less pronounced and continuous recycling of old glass shards is suggested for this period, as confirmed by analyses of the window glass found in Gothic cathedrals. While fragments of blue tesserae were used as a colorant in the 12th century glass, sources of cobalt coming from Central Europe are assumed to be the colourants applied in the 13th century glass.

Similar conclusions were drawn by Biron and Beauchoux [6], e.g., for the so-called Mosan enamels from the area between the rivers Rhine and Meuse dating from the 12th century to the beginning of the 13th century. Glass of the 12th century is that of a sodium natron type following the tradition of Roman glass production and the composition here therefore differs from the common medieval production of potassium glass in Central and

Western Europe [7]. Authors Biron and Beauchoux [6] also consider the use of tesserae shards in the production of blue enamels. This suggestion is based on a comparison of the composition of blue enamels and blue tesserae coming from the period of the 2nd–4th century. As already mentioned before, the change in the chemical composition of enamels is associated with as late as the beginning of the 13th century.

Changes in the cobalt raw materials used in Western Europe at the end of the 12th century are related to the extraction of cobalt raw materials in Central Europe and the source of cobalt is associated with a high zinc content and the presence of indium [1]. Gratuze [8] further specifies cobalt systems for individual periods as follows: (a) the end of the 12th century—end of the 15th century: Co–Zn–Pb–In–Fe, (b) around 1500: Co–Ni–Mo–Fe, (c) early 16th century—3rd century: Co–As–Ni–Bi–W–Mo–U–Fe and (d) 19th century: Co–Ni (less As); the first three groups relate to the area of the so-called Ore Mountains.

Raw materials related to cobalt in glass are also addressed in the work [5] listing the following types: (1) cobalt raw material containing Cu, Mn, Sb—used until the 12th century and raw material sources traced to the Middle East, (2) cobalt associated with Zn, Pb, and In (related to the Ore Mountains)—raw material used in 13th–15th century, and (3) cobalt raw material with Ni admixture used in the 15th century.

In the literature, we may also encounter texts evaluating the use of blue colouring agents over time and in the context of a particular material. Here, we can name cobalt colourants used in glass production during the 1st millennium [1], French glass from 13th–18th century [9], cobalt applied as a glass colourant used from 1800 BC to the 19th century AD [10], cobalt-blue decorated ceramics from Spain from the 15th–18th century [11] and review “Cobalt and associated impurities in blue (and green) glass, glaze and enamel” [12] and several others. Although many works refer to cobalt ore resources in the Central Europe/Ore Mountains area, samples representing the area have not been examined yet.

The presented work provides the results of analyses of blue glass from Central Europe (particularly from the Czech Republic) originating from an extensive period, and thus bringing new findings that complement the current state of knowledge. The development in the use of raw materials in Czech glass is studied from two perspectives. One is the evaluation of the development of the basic composition of ordinary greenish or colourless glass, and the other aspect is the use of colouring agents to provide a blue colour.

## 2. Brief Overview of Development of Glass Chemical Composition Focusing on Central Europe

A major turning point in the history of glassmaking is represented by the period of the so-called Carolinian Empire, when significant changes occurred in the raw materials applied. Ash as an alkaline raw material replaced original natron used so far (a deposit with a high sodium content). For the regions of Central and North-western Europe, these were mainly ashes of local plants—beech, oak, fern, etc. [7,13]. According to the alkalis with major representation, glass is then referred to as potassium–calcium glass. Producing this glass only required mixing a quartz raw material and ash in a suitable ratio. However, the chemical composition of ashes applied is highly variable [14–19] and depends on a host of parameters, such as the subsoil where resource plants grow, what plant parts are processed into ash (trunk, branches, bark, leaves), as well as the type of the plants given (beech, oak, fern, etc.; [17,20]). Another substantial criterion for the glassmaking is the actual age of the ash applied (the effect of ash storage), because the properties of ash change over time by gradually “gaining” air humidity, thus changing the phase composition and most likely even its weight [17]. The CaO/K<sub>2</sub>O (or opposite) ratio is frequently discussed in the literature [7,17] in relation to the raw materials used, especially with respect to ashes. Beech ash, which is expected to be used in medieval glassmaking (listed in Theophilus, Heraclius, later Agricola; [21]), has a higher CaO content compared to K<sub>2</sub>O in the case of ash produced from tree trunks (CaO/K<sub>2</sub>O  $\approx$  12; [7]). For ashes from parts such as branches, leaves or bark, the CaO/K<sub>2</sub>O ratio is known to be even higher (CaO/K<sub>2</sub>O up to 16; [7]), while fern, another raw material, shows a K<sub>2</sub>O content above that of CaO while often

accompanied with high contents of  $P_2O_5$  (2–12%) and  $MgO$  [16,20,22]. It is the magnesium and phosphorus content that proved to be key in the study of medieval European glass [19], when it was possible to distinguish individual areas—NW France, the Rhine and Central Europe. Contents of  $P_2O_5$  over 2% were found in the glass from NW France and the Rhineland compared to the content not exceeding 2% in the glass from Central Europe. Higher phosphorus contents correlate with the use of fern ash, for example in France, see [19,21,23].

A description of glass production in the Middle Ages and the proportion of raw materials (two parts of beech ash from a tree trunk and one part of sand) is provided in *Schedula Diversarum Artium* (1100–1120) by Theophilus Presbyter [7,19].

The work in [19] evaluating European glass from the 12th–15th centuries also pointed out the changes occurring within this period, specifically to the increasing content of  $SiO_2$  and  $CaO$ . The “transition” period in glass production technology is dated to the 1st half of the 15th century. Steppuhn [24] describes the course of the 15th century as the age when the glass centres located north of the Alps achieved their independence from the centres of the Mediterranean. The author also describes it as the period of changes in the raw materials applied. Müller [25] reports the same period as a turning point, when the growth of potassium glass products starts replacing sodium glass in the region of Eastern Austria and Hungary. The work [26] mentions the raw material, technological and artistic independence of Bohemia and dates it even to the 14th century.

So-called HLLA (high lime low alkali; [13]) glass appearing in Europe, specifically in the Rhineland, is also related to the period discussed above. Wedepohl [7] associates changes in the composition of German glass with the period of 1300–1400 and refers to the new type of glass as wood ash-lime glass (with  $CaO/K_2O$  ratio up to 3.4). As a raw material, the use of ash is assumed, specifically that coming from lower quality wood, respectively such parts as branches, bark, etc. This trend corresponds to controlled logging in related regions [7].

Johannes Mathesius mentions the production of glass in the 16th century in his *Mining Postil* (Sarepta oder Bergpostill; [27]). It describes German glassworks using sand and crushed quartz as a quartz raw material. Another component was ash, and the work lists a wide list of its sources: oak, maple, beech, fir, pine and willow. In addition to these two primary components, the additions of salt, glass shards, fern ash and tartar were also described. Regarding the production technology, a certain method of re-melting raw materials or rather frit was depicted there. Typically, the mixture of sand, ash and salt was poured into the furnace and mixed/shuffled. When it started sintering, it was put into water (the process was repeated twice) and then melted. Based on this text, it is obvious that the medieval technology of remelting frit was also utilised in a later period.

The work of Velde et al. [23] discusses potash-based glass (ash extract) as a new type of glass occurring in Belgium and the Netherlands from the late 16th century to the beginning of the 17th century. Similarly, Wedepohl [7] states that this type of glass appeared at the end of the 17th century. However, the glass suffered from a lack of calcium. Glass batches solely based on potash, saltpetre and sand without a stabilizing component ( $CaCO_3$ ) were also noted in the Czech context [28].

Another important milestone in the glassmaking history of Central Europe is the second half of the 17th century. Crystal glass started to be produced, more powerful glass furnaces appeared, and production in the region of Bohemia was influenced by stimuli from abroad—especially from the Netherlands [29]. Basic three groups of glass of Central Europe related to new raw materials at the end of the 17th century are defined by Kunicki-Goldfinger [30], namely chalk glass and two types of glass with a lower calcium content—early crystal glass ( $CaO$  with approximately 0.8% and higher content of  $B_2O_3$ ) and crystal glass ( $CaO$  2–6%). All three glass types already contained arsenic.

According to [29,31], the glass batch for crystal glass consists of: quartz, chalk, saltpetre, arsenic, borax, tartar and minium. In comparison, the batch for cheaper chalk glass contains sand, chalk, potash and, to a lesser extent, additions of arsenic, burel and minium.

Limited variability may be seen in the batches within each group with certain minor additive components missing occasionally.

A well-preserved recipe book from the 1st half of the 19th century by glassmaker Jan Křtitel Eisner (Bohemia) presents more than 300 recipes to produce both colourless and coloured glass. Even during this period, the production of chalk glass was not a forgotten practice in Bohemia, and the recipe book lists several melting variations, which are based on the basic composition mentioned above; sometimes supplemented with Glauber's salt. There are also described several versions of crystal glass, some without the addition of lead raw material [32]. In many recipes presented, saltpetre is mixed with cheaper potash. Recipes for blue glass contain sand, potash, limestone, saltpetre, arsenic, less frequently also burel and borax (some recipes contain no stabilizing component—limestone). Cobalt-based raw materials are listed in two forms: in the form of smalt or so-called Kobold (in several recipes, the use of both forms is indicated at the same time). Even from this recipe book, it is clear that glassmakers undoubtedly responded to demand and produced items of varying quality depending on the requirements of the market.

### 3. Site, Materials and Methods

The samples (Figure 1) to be examined were acquired by methods of non-destructive archaeology—a field survey and a site probe. The samples come from the locations of former glassworks as documented in local chronicles, for instance. To establish proper dating of the finds, written local sources (from the time of individual glasswork operation) were used or alternatively the ceramic objects uncovered at the given site were employed as an aid in determining the dating of the samples examined. An overview of the samples studied, their dating and of individual sites is presented in Table S1.



**Figure 1.** Selection of examples of blue fragments and glassworking waste. The fragments are organized chronologically.

In order to be able to identify colouring components of blue glass, it is also necessary to evaluate the glass that was normally produced in the glassworks without raw colouring agents. For this reason, the sets of blue glass to be examined were also complemented by colourless and greenish glass samples.

An XRF analysis was performed with an ARL 9400 XP sequential WD-XRF spectrometer. The spectrometer was equipped with a Rh anode and a window X-ray tube type 4GN and fitted with a 75 mm Be window. All peak intensity data was collected in vacuum by WinXRF software. The generator settings and collimator-crystal-detector combinations were optimised for 79 measured elements with the analysis time of 6 s per element; there are presented significant elements in Table S1 with content higher than 50 ppm. The obtained data was assessed by the software Uniquant 4. The powders analysed (indicators related to glass production, layers from melting pots, and glass fragments ground in an agate mortar) were pressed into boric acid pellets without any binding agent and covered with 4 µm of a supporting polypropylene (PP) film. To validate the entire analytical procedure, the reference standard (Corning Glass D) was also measured.

## 4. Results

### 4.1. Glass of the High/Late Middle Ages (13th–15th Century)

The very first archaeologically documented glassworks in Bohemia date back to the 13th century [33] and there is also direct evidence of contemporary blue glass production in the form of its residual layers found on the inner surface of the crucibles (Table S1).

Chemical composition of the Czech medieval glass evaluated in this work (Table S1, Figure 2) is that of potassium–calcium with SiO<sub>2</sub> contents mostly up to 60 wt %.

Based on the presence of MgO (ca. 2.8%), P<sub>2</sub>O<sub>5</sub> (1.1%), BaO (0.3%) and SrO (0.12%), it can be stated that ash was applied in the production of this glass. Even in such a small set examined, there is variability in composition: in case of oldest colourless glass (No. 5 and 6), the SiO<sub>2</sub> content is up to about 55%, while in the glass produced later than in the 14th–15th century, this content is close to 60% and there is a decrease in the amounts of alkalis and P<sub>2</sub>O<sub>5</sub>. For most glass, the CaO/K<sub>2</sub>O ratio was  $\geq 1$ , but the set examined contained even objects with a ratio of less than 1 (No. 14, 15). The composition is not unusual in the Bohemian region from where we can name, for example, the finds from Prague dated to the 2nd half of the 14th century—the 1st half of the 15th century [34] with values of K<sub>2</sub>O as high as 24.1% and the ratio of CaO/K<sub>2</sub>O reaching 0.6—the composition being comparable to the finds from Most [35] or Opava [36]. These glass finds are also characteristic of a lower P<sub>2</sub>O<sub>5</sub> content (often up to 1%). Here, the addition of a potassium raw material is considered quite likely as is described later.

Comparing the glass of blue and colourless or greenish shades, we have concluded that similar types of glass batches containing ash were used, to which a colouring raw agent was added.

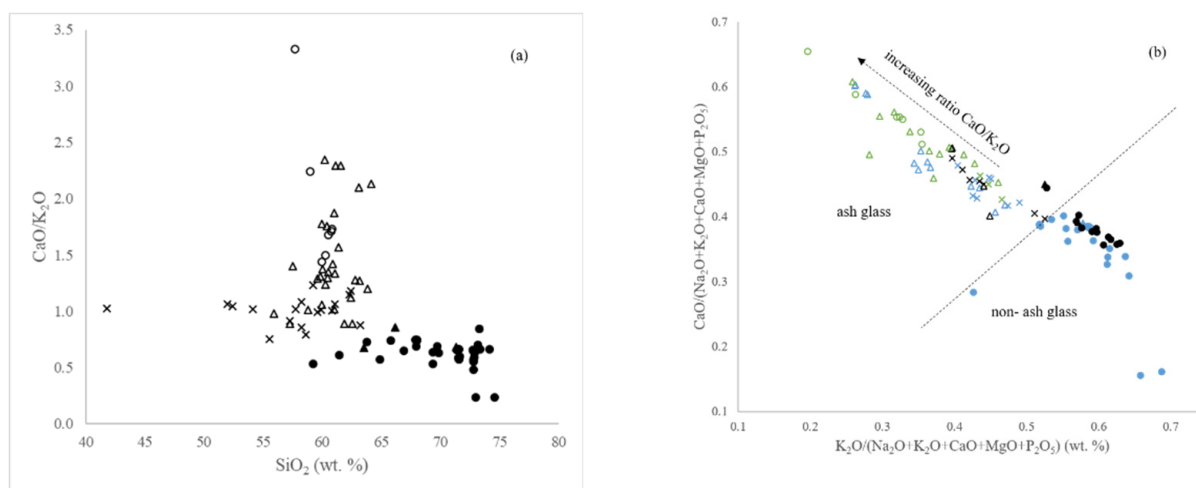
Ash as a raw material has a relatively rich chemical composition and it can also introduce components that can be attributed to colouring agents (as their admixtures). Beech ash, for instance, contains hundredths of a percent of NiO, CuO and ZnO, and tenths to units of a percent in case of Fe<sub>2</sub>O<sub>3</sub> or MnO [20]. Fe<sub>2</sub>O<sub>3</sub> contents in the analysed samples can also be affected by the transfer of iron from the material of melting pots.

The most interesting specimen in the set of the finds from the 2nd half of the 13th century is a crucible from Svor with a dark blue layer of glass (Figure 3, Table S1, No. 1).

The analysis revealed that the glass used is of an ash potassium calcium type with a relatively high content of CoO (2.27%) and Fe<sub>2</sub>O<sub>3</sub> (7.08%). Also, its value for ZnO (3.9%) exceeds the values found in other blue glass objects, where ZnO was represented only in tenths of a percent. However, in the case of intentionally colourless glass, ZnO reaches only hundredths of a percent, so Zn can be considered as another indicator of added colouring raw material. Another element clearly introduced by a colouring agent is copper (detected in all blue medieval glass samples). Compared to the other medieval blue glass objects in the set, 0.1% of SnO<sub>2</sub> was recorded in the sample from Svor, and even 3% of PbO and 0.27%



of  $\text{In}_2\text{O}_3$ . This glass corresponds to the Co–Zn–Pb–In–Fe colouring raw material described in the literature [5,8] and specified above. However, the authors do not include copper in this group, whose content in Bohemian glass is obviously associated with an introduced raw material (found in glass of blue colour in tenths of %, while for uncoloured glass the maximum value of CuO is 0.02%).



**Figure 2.** (a) Plot of  $\text{CaO}/\text{K}_2\text{O}$  against  $\text{SiO}_2$  for potassium–calcium glass, ash and non-ash glass (full symbols). The graph shows an increasing trend in the values of  $\text{CaO}/\text{K}_2\text{O}$  in ash glasses and a general increase in  $\text{SiO}_2$  over time. (b) Dependence of selected silicate network modifiers. The samples are differentiated by colours—green, blue and colourless (the colourless samples are represented by black colour/black symbols). Symbols:  $\times$ —medieval ash glass,  $\Delta$ —early modern ash/Renaissance glass,  $\circ$ —modern age ash glass,  $\blacktriangle$ —early modern/Renaissance non-ash glass,  $\bullet$ —modern age non-ash glass. Details concerning the samples are provided in the supplementary file, Table S1.



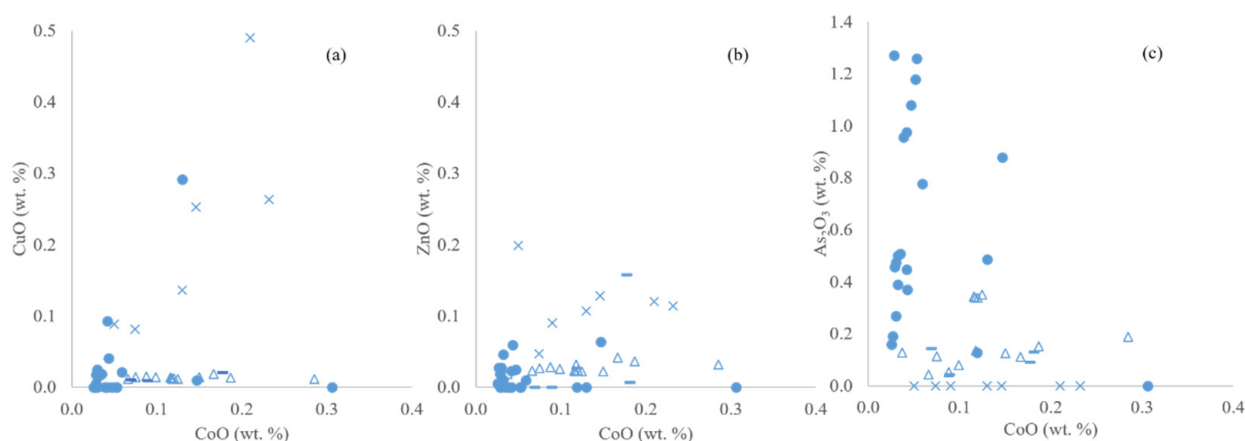
**Figure 3.** Crucible from Svor with dark blue glass layer.

From the macroscopic evaluation of the crucible (Figure 3), it is evident that there is a relatively thick layer of metal under the glass layer. Analysis (XRF) showed that Cu (53%) and Pb (24%) are predominantly present, but it also revealed up to 2% of Sn and Sb and smaller amounts, in tenths of a percent, of Mn, Fe, Co, Ni, Zn, As, and In. Bismuth, which is associated with raw materials of the 16th century was detected in the amount of 870 ppm.

Another metal relic (a ball with a diameter of about 1 mm) was found in a layer of blue glass in a melting pot in a sample from Jilmová (Table S1). It was found [33] that Cu (80%) was predominantly present in the metal. Pb was detected to a lesser extent (16%) and Sb was identified in the value of 2%. Mere units of a percent were found for Co, Ni, Zn, As, Ag and Sn, i.e., showing a relatively similar representation of these elements. It can be assumed that these metal relics represent the raw material that was used to colour the glass blue.

Blue glass was applied quite frequently in Czech medieval glassmaking to create decors (in the form of smelted fibres or small prunts). Hejdová et al. [37] mentions the use of cobalt in combination with copper (other elements were not analysed) for the creation of decors. Another analysis into blue decors of glass objects found in Prague (Czech Republic) was the subject of the work [34] examining blue glass containing colouring elements in the combination of Co–Cu–Zn–Pb, just as the glass samples evaluated in this work.

From the information above, it is clear that blue medieval glass found in Bohemia, besides cobalt ions, also contains blue colouring copper ions (Table S1 and Figure 4a) and accompanying elements such as Fe, Zn (Figure 4b), Sn and Pb. The iron contents found are difficult to discuss, as this element can be introduced by both quartz raw materials and ash.



**Figure 4.** Oxides associated with the colour of blue glass; CoO, CuO as colouring agents and ZnO, As<sub>2</sub>O<sub>3</sub> as examples of accompanying oxides. (a) CuO plotted against CoO for blue glass from different historical periods; higher CuO contents are clearly visible in medieval glass samples and less frequent in later glasses (18th–19th century), (b) ZnO plotted against CoO, higher zinc contents again recorded in medieval glasses. Contents of CuO and ZnO are rather constant in early modern/Renaissance blue glass; CuO  $\approx$  0.01 wt % and ZnO  $\approx$  0.03 wt %, (c) plotting of As<sub>2</sub>O<sub>3</sub> against CoO; the presence of As<sub>2</sub>O<sub>3</sub> is confirmed in the glass from the 16th century or younger. The cobalt contents of the glass from the 18th–19th century are lower compared to the glass from earlier periods. According to higher values of As<sub>2</sub>O<sub>3</sub>, it is possible to deduce probable additions of arsenic to the glass batch. Symbols: x—medieval glass, Δ—early modern/Renaissance glass, ●—glass of 18th–19th century and —glass of 2nd half of 19th century. Details concerning the samples are provided in the supplementary file, Table S1.

Based on our results, we can add information concerning glass colouring in the European region pointing also raw materials other than cobalt. Owing to the high content of copper in the glass evaluated and the relics of metal found, copper seems to be the key element in determining the raw material applied. Similar conclusions concerning the use of colouring raw materials associated with the production of metals are presented by

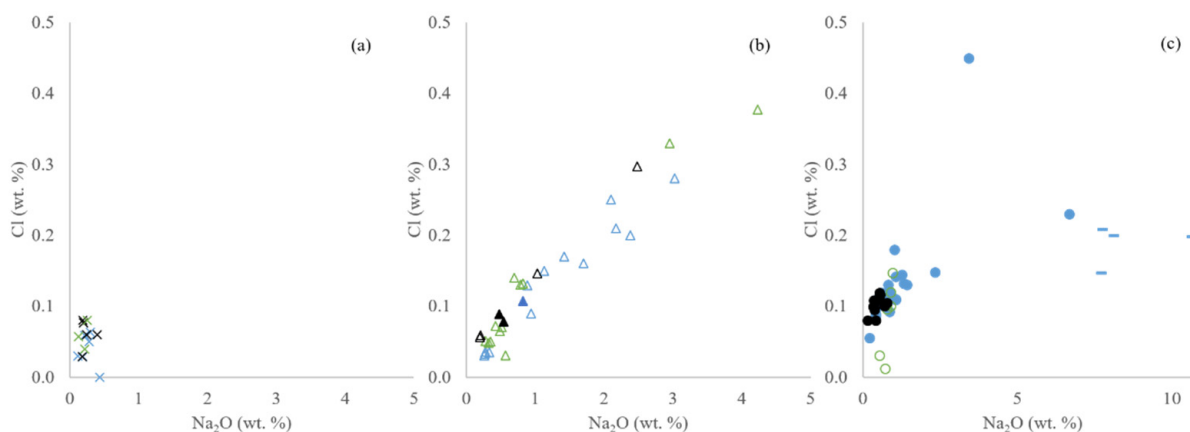
Wedepohl et al. [38]. His work identified brass as a likely blue colouring raw material of the glass finds dating to the 12th century.

#### 4.2. Early Modern Glass I (16th–17th Century)

During the 2nd half of the 17th century, Transalpine glassmaking separated itself from the Italian influence. The popularity but also unavailability of cut rock crystal vessels in Central Europe is reflected in the glass industry and its efforts to imitate this material [29]. Glassmakers experimented extensively with raw materials, and the turning point arrived with the emergence of Baroque crystal potassium glass. Gradually, this type of glass even overshadowed, at that time highly demanded, Venetian glass.

According to [39], crystal glass was produced in just a few glassworks in Central Europe in the 1670s, namely in Bohemia and Brandenburg. Containing saltpetre, crystal glass was relatively expensive, and its production was often supplemented by a cheaper variant—chalk glass based on potash [29,31].

The data presented in Table S1 show evident differences in the composition of glass of the Renaissance period being more pronounced when compared to the group of medieval glass. It is possible to distinguish two distinctive types of glass within the colourless glass group—glass based on ash and glass based on a chemically purer potassium raw material (No. 49, 50). Samples 49 and 50 exhibit lower contents of  $\text{MgO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SrO}$ , while  $\text{ZnO}$ ,  $\text{BaO}$  and  $\text{PbO}$  were below the detection limit. In contrast, higher values were detected for  $\text{SiO}_2$  (Figure 2) while  $\text{As}_2\text{O}_3$  emerged as a new compositional compound (up to 0.5%). This means that no ash was used in the production of these samples, but the substance applied was either potash or another potassium raw material (or their combination). Comparison with the results of the work [30] show that the glass investigated is of the chalk rather than crystal type. Signifying the change in composition, higher  $\text{Na}_2\text{O}$  contents were newly detected in the glass objects from the Krompach glassworks (up to 5%), indicating the addition of salt (chlorine content is also increased in the glass objects of that period; see Figure 5b).



**Figure 5.** Amounts of Cl compared to  $\text{Na}_2\text{O}$ , differentiation according to dating: (a) medieval glass (b) early modern glass I/Renaissance and (c) glass of 18th–19th century. Figure (a) clearly demonstrates that no NaCl was added to the medieval glass. Additions of NaCl to the glass batch during 16th–17th century can be inferred from Figure (b). Finally, NaCl additions were abandoned in younger glasses (as seen in Figure (c)). The glass dated to the 2nd half of 19th century does not correspond to the dependence of Cl– $\text{Na}_2\text{O}$  and Figure (c) indicates the usage of a sodium raw material other than NaCl. Symbols: ×—medieval ash glass, Δ—early modern/Renaissance ash glass, ▲—early modern/Renaissance non-ash glass, ○—ash glass of 18th–19th century ●—non-ash glass of 18th–19th century and —glass of 2nd half of 19th century. Samples differentiated by colours—green, blue and colourless (the colourless samples are represented by black colour/black symbols). Details concerning the samples are provided in the supplementary file, Table S1.



Furthermore, it is evident that glassmakers continued the tradition of glass production using ash (which applies to all greenish samples and most of the blue samples). In the group of green glass, sample 42 deviates from others with a higher content of MgO (3.13%), P<sub>2</sub>O<sub>5</sub> (1.66%), SrO (0.12%) and BaO (0.4%), and a significantly differing ratio of CaO/K<sub>2</sub>O  $\approx$  1.9 compared to the ratio of about 1.3 in other samples of the group. An interesting finding is the content of arsenic identified in some green glass objects, which probably suggests the recycling of shards containing As<sub>2</sub>O<sub>3</sub> rather than a deliberate addition (in the case of glass from the Krompach glassworks, arsenic was found in neither colourless nor green glass).

In the case of blue glass, a significant change in composition occurred compared to medieval glass (Figure 4). As and Bi are newly represented in all evaluated blue samples. In samples from Krompach, molybdenum appears in several instances, in one sample even antimony occurs. It can be assumed that the glassmakers started to use colouring raw materials in the form of zaffer or smalt. Blue colouring zaffer (ground and calcinated ore containing cobalt, sometimes combined with sand) was prepared in 1520 by Peter Weydenhammer and the discovery of smalt is attributed to Christopher Schürer around 1540 [40,41].

The finds from the Rejdice glassworks confirm the use of smalt in Czech glassworks of this period (Table S1, No. 51–53). Glass/smalt displays a high K<sub>2</sub>O content. Other represented components, being also characteristic of smalt, are: CoO, Fe<sub>2</sub>O<sub>3</sub>, NiO, CuO, As<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>, occasionally MoO<sub>3</sub> and U<sub>3</sub>O<sub>8</sub> [41]. Apart from molybdenum and uranium, all these components are represented in the blue glass of this period.

After comparing the blue, green and colourless glass from the Krompach glassworks, no significant differences were detected in the composition of individual types (except No. 27 discussed below), apart from the colouring components, the glass batches were also similar, meaning ash based.

Certain variability was found in blue glass samples from the Okrouhlá site. Blue samples No. 32–35 are similar to each other (as well as sample No. 27 from Krompach), and generally they differ from all the other glass finds of the set from Okrouhlá. Especially the CaO/K<sub>2</sub>O ratio is relatively high (approximately 2%), compared to the value of approximately 1.2 for ordinary green and colourless glass based on ash. Compared to other samples, SrO contents are the highest reaching up to 0.19%. It can be assumed that ash from lower quality wood was used for melting this glass as also stated by Wedepohl [7]. However, the samples cannot be classified as the HLLA type, as they do not meet the CaO/(CaO + K<sub>2</sub>O) ratio criterion being greater than 0.75 [19]. An atypically blue sample is No. 31 (with P<sub>2</sub>O<sub>5</sub> up to 2.5%) while sample 36 showed the content of P<sub>2</sub>O<sub>5</sub> of just 0.11%, and rather low contents of MgO (0.18%), BaO (0.06%) and SrO (0.007%). With the ratio of CaO/K<sub>2</sub>O at 0.68, the analysis indicates the use of a potassium raw material other than ash.

#### 4.3. Early Modern Glass II, Modern Age Glass (18th–19th Century Period)

The set of analysed glass coming from this period (Table S1) again includes colourless, greenish and blue glass (Figure 2b). In the case of colourless glass, ash-based glass was not detected. SiO<sub>2</sub> contents are relatively high (over 70%; Figure 2) and CaO/K<sub>2</sub>O ratio is about 0.6 with arsenic being added into the glass (average content at 1% of As<sub>2</sub>O<sub>3</sub>). Compared to ash glass, of course, the values of MgO are low (0.1%) as well as those of P<sub>2</sub>O<sub>5</sub> (0.07%) and SrO (0.02%); BaO was not detected by the method applied. Also, low contents of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were identified, which may indicate a purer source of SiO<sub>2</sub>, but these lower contents may also be caused by the absence of ash in the glass batch. PbO was not present to a greater extent in any of the glass samples, and according to [30] the glass can be described as the chalk type.

Within the group of colourless glass specimens, it was possible to visually distinguish three samples with a light touch of grey colour (samples No. 91–93 from Nová Huť glassworks). Their composition is relatively consistent and, when compared to colourless glass (see above), slightly higher As<sub>2</sub>O<sub>3</sub> contents were found (1.4% vs. 1%). In addition, PbO (in hundredths of %) and SnO<sub>2</sub> were detected (in hundreds of ppm). Although

according to the literature [30], it is not typical crystal glass, we know from Hais [31] that a certain type of crystal glass used to be produced in the region—a glass sample from this location was analysed containing 5–6% of  $B_2O_3$  and 8.6% of  $PbO$  [31,42].

Glass that is typically of a greenish colour represents a more common type and is still based on ash with the content of about 60% of  $SiO_2$ . No greater differences were recorded compared to older glasses (e.g., from Okrouhlá location). A specific group of glass is represented by dark green-brown glass (No. 60 and 61), where a higher  $Al_2O_3$  content was detected (almost 5%). As for later glass described in the literature [28], several possible additive substances are discussed, for example, the additions of feldspar, which could explain the amount of  $Al_2O_3$ . The  $CaO/K_2O$  ratio was also higher  $\sim 2$  for the two samples (Figure 2). Increased contents of  $MnO$ ,  $TiO_2$  and  $Fe_2O_3$  were identified contrasting with the contents typical of common greenish ash glass. From the data, it is obvious that inferior raw materials were used to produce glass of lower quality.

Blue glass composition corresponds to that of colourless glass (ash was not used as a potassium raw material). Although three samples show higher  $P_2O_5$  contents (up to 1.26%), other elements characteristic of tree ash such as barium, strontium and magnesium are not present in their usual amounts.  $CaO/K_2O$  ratio was detected at  $\sim 0.5$ – $0.7$ ; only for samples 71 and 79, the ratio value was 0.2, which was surprisingly low (see Figure 2b). Differences were identified in the intensity of coloration among the glass finds examined and that even within one locality—some glass specimens are blue-grey while others are purple blue. Hais [43] primarily links the expansion of blue glass with the 1st half of the 19th century. Raw materials appearing in contemporary recipes also introduce Mn, U and Cr to the glass batch.

This is evident in the analyses of the set examined (Table S1). Glassmakers obviously worked with a combination of colouring agents. Increased contents of Ni, Cu, Mn can be seen, and cobalt is present in all glass objects and especially in those of an intense blue colour, reaching up to tenths of a percent of  $CoO$ . The content of  $As_2O_3$  is around 1% for some samples (Figure 4c). Sample 79 is somewhat atypical containing oxides of tin, chromium and uranium (up to 0.5%).

For the blue glass from the 2nd half of the 19th century, higher additions of a sodium raw material are noticeable, see Figure 5c (while also displaying a decrease in  $K_2O$ ). Even in these youngest glass samples, cobalt was again found to be a colouring component (Figure 4c). However, bismuth is missing, and nickel is represented less. Arsenic contents are about 0.1% of  $As_2O_3$ , which corresponds to the literature [28] and information about its less frequent use in later periods.

## 5. Discussion on the Development of Chemical Composition

Potassium ash can be clearly identified as a key raw material in Czech glassmaking. Ash-based glass was melted as early as in the Middle Ages. Ash is used in glass production, and later widely utilised in potash production. Ash-based glass objects were found, for example, in early modern waste pits at the Prague Castle [44], so evidently, it was the usual composition of glass in this period. The popularity of the use of ash decreases during the period under review as it is still a raw material of lower quality. However, even in modern times, glass with ash was melted (namely for greener objects of lower quality). The use of ash in the glass batch is not completely unusual in the modern age, relevant data can also be found in the literature [45,46].

As mentioned in the introduction, Wedepohl [7,38] widely devoted to studying ash glass in Europe and describes the oldest type as that with the ratio of  $CaO/K_2O \approx 1$  (wood-ash glass)—the value of the ratio increases for later types. While glass of the 13th century evaluated in this work corresponds to the glass of the wood-ash type, younger glass has a different content. For the ash glass of the 14th–15th century, greater variability in composition was observed (given the number of samples). The value of the  $CaO/K_2O$  ratio is about 1, however, glass objects with values lower than 1 are also common, see Table S1 (Figure 2a). In early modern glass/Renaissance, the value tends to rise above 1 (in case of

blue glass, the values of the ratio even exceeded 2; see Figure 2b). This increasing trend was already noted in our previous work [20]. CaO/K<sub>2</sub>O values of up to 1.7 were found in modern glass from the turn of the 18th and 19th century, but only with respect to lower quality greenish glass. No type of glass with a significantly higher CaO/K<sub>2</sub>O ratio, such as HLLA in neighbouring Germany, was recorded in the research presented. Occurrence of this glass type in the Czech environment is rather rare (archive of the author's analyses).

As mentioned earlier, the values of the CaO/K<sub>2</sub>O ratio for tree ash usually reach above 1. Laboratory experiments [17,20] suggest that in case of the glass with a CaO/K<sub>2</sub>O ratio lower than 1, it was necessary to add another potassium raw material to a two-component batch (quartz raw material, ash) and the addition of potash is also considered (the use of tartar is documented for the 16th century; [27]). Fern ash is also an option, although ferns frequently contain larger amounts of phosphorus, but this element is usually not measured in glass in higher amount.

It is rather difficult to point to specific raw materials, respectively ash in the glass batch based on the analyses of final glass products, mainly due to the variability of ashes [16] and the possibility of recycling/addition of glass shards during glass melting. As Smedley and Jackson [15] rightly point out, this factor is often overlooked, although it can have a significant effect on the final composition of glass. In addition, it is possible to assume the use of several different kinds of ash at once, which further complicates the situation. Therefore, the general designation of glass only as an ash type without specifying the type of the ash used is implemented, for example, in the work [30] and the authors of this article agree with this conclusion.

The literature [47] mentions a limited source of high-quality wood used to obtain ash to produce ordinary glass or potash in Bohemia. Zuman [47] specifically states, that, in 1637, the master of glassworks in Krompach (northern Bohemia) was allowed to collect only old, fallen wood and was not allowed to collect high quality "standing/live" wood. There are also mentions of the use of fir ash in the records. Problems leading to the reduction of logging by glassworks in the 17th century are mentioned by Woitsch [48]. Only stumps, branches, shrubs and rot-infested wood could continue to be used for potash production. The quality of ash for potash production deteriorated over time as "forest" ash was replaced by ash from glassworks, businesses and households. However, better quality timber was still commonly burned in remote mountain areas [48].

The whole text shows that in the glassworks of the 17th century and perhaps even before, not just ash from high quality wood (logs) was used, but also the ash from second-grade wood, which characteristically has higher CaO contents compared to those of K<sub>2</sub>O [7,10,49]. However, the glass evaluated does not display more significant increases in CaO and CaO/K<sub>2</sub>O ratio (compared to German glass). Therefore, it is possible to infer possible additions of potash (and possibly other potassium raw materials), which could compensate for the low potassium content. Although the use of potash is mentioned in the texts no sooner than at the end of the 17th century, objects indicating additions of potassium raw materials are represented in finds from earlier periods as well, e.g., in the work of Müller [25] describing such finds coming from the turn of the 13th–14th century and, more abundantly, from the 16th century (in the area of neighbouring southern Germany). Moreover, Hamburg and Lübeck are referred in the literature [48] as the centres of potash trade as early as in the end of the 14th century. Locally, the oldest reports of potash production in Bohemian glassworks concern Prague and the year of 1575 [28].

Potash-based glass without the addition of ash is represented in the finds from the Okrouhlá site (turn of the 16th–17th century), and, of course, also those from the Baroque Rollhütte and Nová huť glassworks. Compared to conventional ash glass, glass without the addition of ash has much lower values of MgO (up to about 0.3%), P<sub>2</sub>O<sub>5</sub> (up to about 0.1%), SrO (up to about 0.03%) and BaO was mostly below the limit of detection (limit of potash glass with max. 0.3% of P<sub>2</sub>O<sub>5</sub> was reported by Stern and Gerber [18]). Stern and Gerber [18] further discuss the content of P<sub>2</sub>O<sub>5</sub> as an important factor when the values in

glass exceed 1% (they also accept a wider limit of around 1%) indicating the glass of ash type as already discussed.

In the case of glass without ash addition, it is somewhat difficult to determine what potassium raw material was introduced. The predominant raw material applied was potash, however, batches based on the combination of potash with the addition of saltpetre were also used, and tartar mentioned by some of contemporary recipes cannot be neglected either [28,31]. From recipe books of that time, a trend is clear, when higher-quality crystal glass based on saltpetre started to be produced combining saltpetre with borax and tartar. However, the popularity of cheaper batches based on sand, potash, limestone, supplemented with a refining agent (potassium saltpetre, arsenic oxide) and melting accelerators (salt/NaCl, borax) was still evident as late as in the 1st half of the 19th century [50].

We do not assume that this text provides a final overview of the development of Czech, let or even Central European, glassmaking. There were several glassworks in Bohemia, which certainly kept their recipes secret, and a uniform recipe for the given period certainly did not exist, which was also partly caused by available raw material sources and actual possibilities of their purchase or import. However, certain trends in the composition of glass are evident and that is why this work may be beneficial to further research studies addressing this issue.

## 6. Conclusions

The results of this study show that the predominant type of glass melted in Bohemia since the Middle Ages has been potassium–calcium glass. From the Middle Ages to the Modern Age, ash-based glass was produced in this region. However, in the Modern Age, it was clearly only used for lower quality goods. The text presented describes in its introductory section certain milestones seen in the compositional changes of glass, which are studied throughout the whole of Europe, the 15th century being one of them. Based on the analyses, it is clear that even in the Bohemian region this period (perhaps even earlier) was accompanied by certain changes. In the case of glass, a change in the ratio occurred concerning most of the oxides (e.g., an increase in SiO<sub>2</sub> content). The period of the early modern age is often associated with the production of a new type of glass—chalk type, but more importantly, a clear transition can be seen in the raw colouring agents applied in blue glass. Cobalt raw materials started to be used, replacing the raw materials with the majority of copper. It is the latest finding regarding the copper raw materials that seems crucial as it specifies the currently available information on colouring of not just blue medieval glass, particularly in the region of Central Europe.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/min11091001/s1>, Table S1: Composition of samples, determined by XRF (wt %); samples No. 3–6 taken from [33], No. 8–11 from [51] and No. 16–18 from [52]. n.d.—not detected

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