

# Phosphate: a neglected argument in studies of ancient glass technology

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Received: 24 July 2016 / Accepted: 9 December 2016 / Published online: 19 January 2017  
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**Abstract** The phosphate content of ancient alkali-glass has been tested as an indicator for biogenic ash, used in glass production. The living tissue of plants and vertebrates accumulates phosphate that remains in native ash as a main component (1 to over 10 wt%) forming together with biologically essential element oxides a complex chemical fingerprint that characterises any glass made with it. If, instead of native plant ash its alkali extract is used, soluble oxides are concentrated in the extract whilst insoluble oxides get depleted, leading to a different elemental fingerprint of the glass. Geogenic raw-materials for glass production like quartz-rich sand, evaporitic natron, or limestone are virtually phosphate free (below detection limit up to  $\approx 0.15$  wt%). Several collections of ancient glass stemming from different archaeological excavations, regions and times have been analysed by instrumental methods (WD-XFA, ED-XFA, thermal techniques), i.e. flat- and hollow K–Ca glass dated 1699/1714 N = 340, Na–Ca glass 13th/14th cy N = 94, Na–Ca glass 7th/9th cy N = 110, and alkali-Ca glass La Tène N = 395. Although the phosphate content of native alkali plant ash gets diluted with quartz sand by a factor of roughly two in glass production, it remains a main component of the product glass. Wood-ash glass contains 1–3 wt% phosphate, whilst glass manufactured from halophyte ash contains around 0.2–1 wt%. When processed wood-ash is used, the phosphate content in glass sinks below 1 wt%, the depletion factor

amounting to roughly 8–15. Glass made from evaporitic soda displays phosphate contents below 0.2 wt% in the cases examined. The phosphate content of ancient alkali glass thus indicates whether virtually phosphate-free evaporitic soda has been used as a flux, or native ash of halophyte plants. Ternary melting diagrams reveal at least three groups of alkali glass: Naturally coloured forest glass displays a broad distributional pattern with minimum melting temperatures ranging from 1200 to  $\geq 1450$  °C, colourless potash-extract glass from 900 to  $\approx 1200$  °C, and the typical, tight cluster of Roman sodium-calcium glass ranges from 800 to  $\approx 900$  °C. The wide-spread sodium-lime glass made with native halophytic ash, contains besides Na<sub>2</sub>O as the chemical main component always some K<sub>2</sub>O, and melting temperatures range from 800 to  $\approx 1000$  °C.

**Keywords** Chemical fingerprint of ancient glass · Fingerprint of biogenic and geogenic raw materials · Fingerprint of native and processed plant ash for making alkali glass

## 1 Introduction

The first Roman glass was chemically investigated by M. H. Klapproth at the end of the 18th century, and published 1801 (Bezborodov 1975, 35). But essential chemical elements had yet to be detected, sodium and potassium in 1807, calcium in 1808, silicon in 1824, and analytical chemistry had to be established during the 19th century. Listings amount to 640 analysed ancient alkali glasses around 1970 (Bezborodov 1975, 151), but due to extensive application of efficient instrumental analysis during the past 50 years thousands of glass analyses are available

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Editorial handling: E. Gnos.

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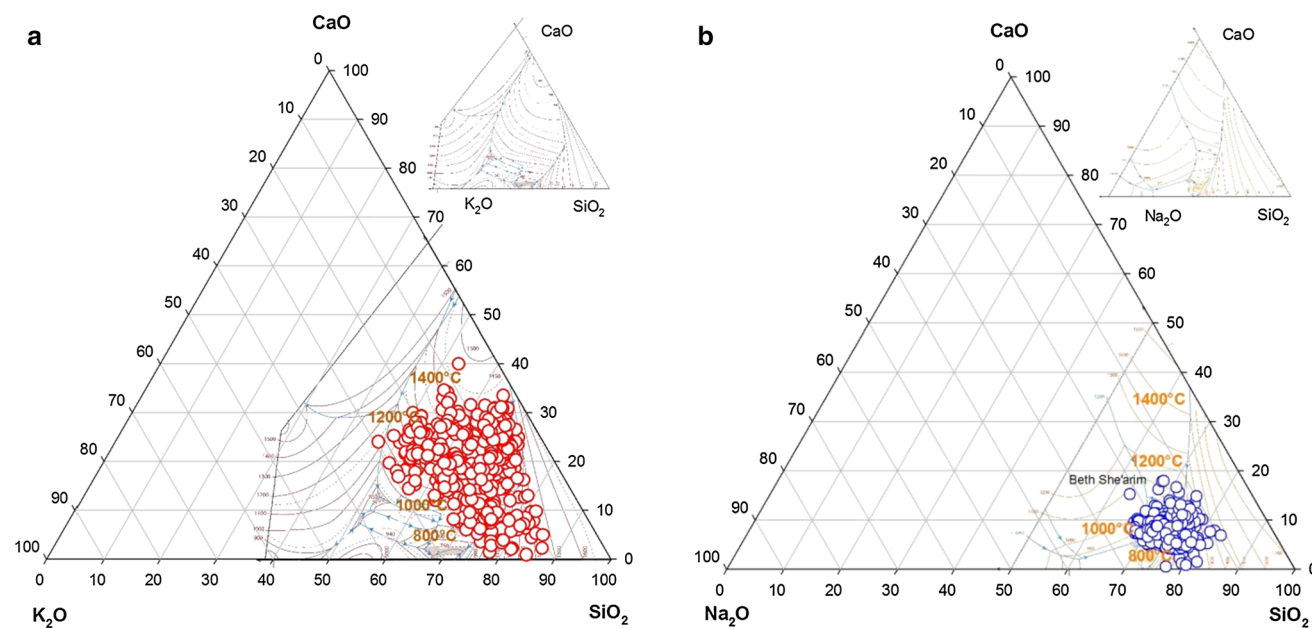
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today (e.g. Brill 1999), although many are incomplete lacking main components like silica ( $\text{SiO}_2$ , indicated by difference to 100% only), or phosphate ( $\text{P}_2\text{O}_5$ ).

Alkali-lime glass is the product of a fairly sophisticated technical process (Frank 1982). The chemical composition of glass with its compositional variation may give arguments as to the character and provenance of applied raw materials, their mixing proportions, and to technological details of glass production. Chemical character and identity of the educts for glass making—network former, network modifier and stabiliser—are, however, much less investigated and far less known than the product glass.

- Geogenic network formers are crushed and ground quartz crystals ( $\text{SiO}_2$ ), quartzite pebbles, sandstones or natural sands consisting of either quartz grains or silica-rich grains. They often include silt or fine conglomeratic fractions, but only sands containing preferably over 90 wt% quartz are suitable for the production of alkali-calcium glass. Minor impurities of alkali feldspar ( $\text{K,Na})(\text{AlSi}_3\text{O}_8)$  or its alteration products like kaolinite,  $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ , are not adverse, in contrast to mafic minerals that have a colouring effect on product glass. Suitable quartz-rich educts are for example Triassic sandstones in Europe and the Near East. Because of the high melting point of quartz ( $\geq 1700^\circ\text{C}$ ) a flux/network modifier is needed to produce glass as manufactured since roughly 3.5 millennia.

- Network modifiers are either geogenic evaporitic sodium carbonate minerals like natron (= soda)  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  or trona,  $\text{Na}_3(\text{CO}_3)\text{HCO}_3 \cdot 2\text{H}_2\text{O}$ , or else biogenic potassium-rich ashes (containing e.g. kalici-nite  $\text{KHCO}_3$ ) of terrestrial plants or rather their wood (not leaves), or complex sodium-rich ashes of halophile plants from coastal-marine areas or deserts. Alkali carbonates are soluble in water and do hence not exist on the Earth's surface under moderate climatic conditions. They act as network modifiers and are able to reduce the melting temperature of quartz sand from  $\geq 1700^\circ\text{C}$  down to  $\approx 750^\circ\text{C}$  (see e.g. Wedepohl 2003). Relatively abundant chemical data on plant ash have been collected since Wolff (1871) had published the first compilation. Besides phosphate and potassium oxide, most plant (and all vertebrate) ashes contain also lime (Allaby 2012) that acts as stabiliser in glass production.
- Because geogenic evaporitic natron or trona and pure quartz are virtually free from Ca-carbonate, a stabiliser has to be introduced as a third component when pure educts are used in producing Na–Ca glass. Limestone ( $\text{CaCO}_3$ ) is practically free of phosphate, relatively abundant and hence easily available. Quartz-rich marine sands may contain fragmented mollusc shells, consisting of phosphate-free calcite or aragonite, both chemically  $\text{CaCO}_3$ .



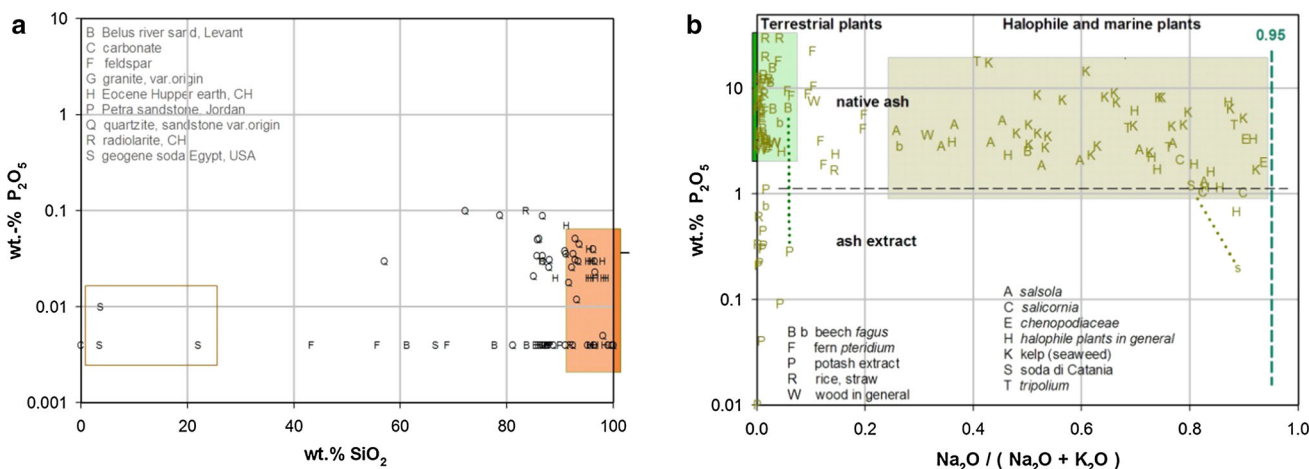
**Fig. 1** Ancient alkali glass. Essential components totalling to 85–95 wt%. Analyses from Bezborodov (1975), Brill (1999), Geilmann and Jenemann (1953), Geilmann (1955) and Wedepohl (1993, 1998, 2003). Inserted melting diagrams after Morey et al. (1930) and Shahid and Glasser (1971). **a** K–Ca glass *red circles*,

**b** Na–Ca glass *blue circles*,  $N = 760$ . Analyses from Barrera and Velde (1989), Maus and Jenisch (1999) and Gerber and Stern (2012). **b** Na–Ca glass *blue circles*,  $N = 560$ . Analyses from Arletti et al. (2010), Foster and Jackson (2009, 2010), Verità (1985, 1995) and Wolf et al. (2005)

The large quantity of analysed glass giving quantified data on a dozen chemical main and minor oxides and estimated 20 possibly significant trace elements calls for a deliberate strategy of evaluation and validation. I propose here a set of criteria specifying the general character of educts for making glass with a general distinction of geogenic from biogenic nature (Fig. 1), and introducing the phosphate content of educts and glass (Fig. 2) as a so far neglected specific argument, (Fig. 3).

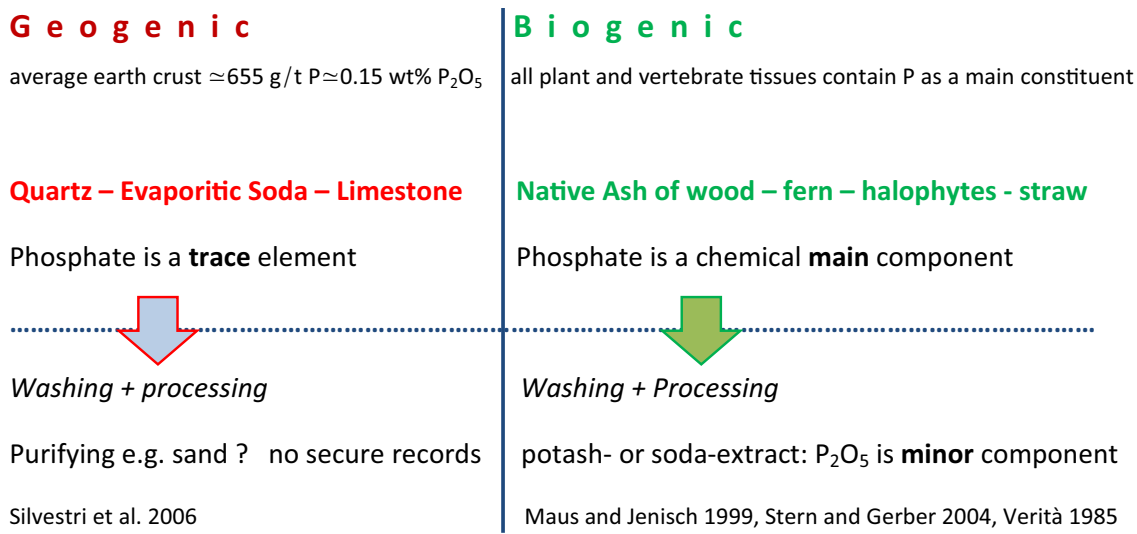
## 2 Educds for the production of alkali-lime glass and their influence on melting temperature

Geochemical data on the average composition of the Earth's crust indicate  $\approx 655$  g/t (ppm) phosphorus  $\approx 0.15$  wt%  $P_2O_5$  (Rudnick and Gao 2003); Phosphorus is hence a trace element in geogenic educts for making glass like the network former quartz that is virtually free of it (below detection limit of most analytical techniques). The same



**Fig. 2** Educds/raw materials for making alkali glass. Analyses in general: Ref. Brill (1999); Maus and Jenisch (1999); Wedepohl (2003). **a** Geogenic educts N = 102. Analyses from Brems et al. (2012), Brill (1999), Burkhardt (2016, unpublished, see acknowledgement), de Quervain and Friedlaender (1942), de Quervain

and Jenny (1956), Gerber and Stern (2012), (Niggli et al. (1930) and Silvestri et al. (2006); **b** Biogenic educts N = 127. Analyses from Barkoudah and Henderson (2006), Cilová and Woitsch (2012), Stern and Gerber (2004), Gerber and Stern (2012), Tite et al. (2006), Verità (1985), Wolf et al. (2005) and Wolff (1871)



Trace element <LoD up to  $\approx 0.2$  wt%, Main chemical component  $>2-100$  wt%, Minor component  $0.2-2$  wt% (by convention)

**Fig. 3** Overview over geogenic and biogenic raw materials for ancient glass making. Phosphate in ancient glass indicates whether biogenic native plant ash, plant ash extract or geogenic soda were used as network modifiers

holds for geogenic network modifiers like evaporitic soda or the stabiliser limestone or lime, CaO. Native biogenic educts for making glass, in contrast, contain phosphate as a chemical main component that enters the product glass made with it. As will be pointed out later is the phosphate content also an indicator for man-made improvements of biogenic native network modifiers like wood ash or halophyte ash for producing either potassium-calcium glass or sodium-calcium glass.

The main, essential oxides of potassium- and sodium glass, plotted in their respective ternary diagrams, display a conspicuous difference: K–Ca glass occupies a vast compositional field (Fig. 1a), Na–Ca glass (Fig. 1b) a narrow one. The melting diagrams of Morey et al. 1930 (K–Ca–Si) and the diagram of Shahid and Glasser (1971, Na–Ca–Si) fitted into their according diagrams give important insights: The narrow compositional field of ancient sodium-calcium glass ( $N = 560$ ) plots between  $\approx 800$  and  $\approx 1000$  °C on, or close to, the eutectic minimum. This has a large impact on energy consumption, on constant glass quality and on simple kiln construction without stoking devices. The heat necessary is comparable with the one of firing clay.

The large compositional field of K–Ca glass (Fig. 1a,  $N = 730$ ) indicates higher general melting temperatures of  $\approx 900^\circ$  to  $\geq 1400$  °C, without matching eutectic minima. The consequences are small-sized but sophisticated kilns with suitable stoking devices, refractory furnace linings and melting pots, a huge energy consumption and an uncontrollable product quality, see Eramo (2005) for kiln construction and refractory materials.

These observations explain, why antique glass production relied on sodium glass rather than on potassium glass although K-rich ash from kitchen furnaces was available easily—but obviously avoided when making glass. The ternary  $\text{SiO}_2$ – $\text{Na}_2\text{O}$ – $\text{CaO}$  plot makes also clear why the famous giant glass slab (8–9 tons) excavated at Beth-She’arim failed. Due to a high lime content the necessary melting temperature of  $\approx 1100$  °C was considerably higher than the usual 800 to  $\approx 1000$  °C (Freestone and Gorin-Rosen 1999).

Geogenic educts for making glass like quartz-rich sands as a network former or evaporitic natron as a network modifier are presented in Fig. 2a. The scarce complete literature data all display low phosphate contents, in accordance with the low average content of silica. Only quartz rich rocks with silica  $>90$  wt% are of interest as sands for making glass (orange box). Evaporitic, natural geogenic natron is specifically rare on the Earth surface (e.g. Wadi Natrun in northern Egypt). Complete analyses of evaporitic soda are scarce if not missing at all (Gülai et al. 1986; Lake Owens Mining 2009; Shortland 2004; Shortland et al. 2011; Wenigwieser 1992).

Biogenic educts for making glass like native plant ashes are documented in a phosphate versus alkali diagram wt%

**Fig. 4** Case Study I. Pre-industrial K–Ca glass from Swiss Jura and German Black Forest. *Left column* glass hut Court Chaluet, operational 1699–1714 (Gerber and Stern 2012,  $N = 220$ ) **a** Phosphate vs Alkali-index. **c** Phosphate vs main components indicating the effect of ash-processing (*arrows* different slope of soluble  $\text{K}_2\text{O}$  and less soluble oxides of Mg, Al, Ca, Fe). **e** Ternary diagram with chemical main components  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ , CaO and melting diagram after Morey et al. (1930) displaying naturally coloured wood-ash glass made from native wood-ash (*red crosses*) and colourless potash extract glass (*red circles*). **g** Same diagram with *average* glass compositions from glass-hut Court Chaluet (**e**) and Black Forest (**b**), wood-ash glass vs potash extract glass. *Right column* Black Forest, selected glass fragments from 37 glass huts of the 12th to 18th century. Data from Maus and Jenisch (1999),  $N = 102$ . **b** Phosphate vs Alkali-index. **d** Phosphate vs main components, caption same as from **c**. **f** Ternary diagram, captions same as from **e**. **h** Phosphate vs estimated year of production (naturally coloured forest glass and colourless potash extract glass). Potash extract glass is present since earliest documented huts and is present also as coloured window glass (ca. 1300 AD) in Freiburg i.B. cathedral (Brill 1999, *large red circles*)

$\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$  in Fig. 2b. Native ashes from terrestrial plants (left green box) contain 3–20 wt% phosphate. Terrestrial, K-preferring plants avoid Na, whereas marine, coastal or desert halophile plants (right green box) are rather Na-tolerating than Na preferring and all take up (as known so far) some potassium. Halophyte ash containing over 0.95  $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$  does obviously not exist.

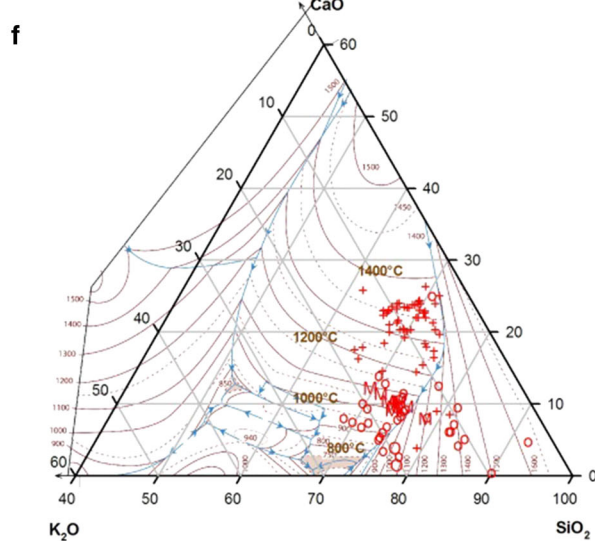
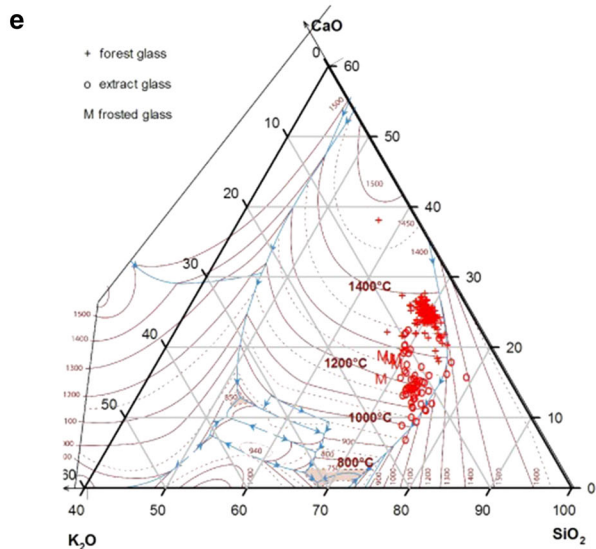
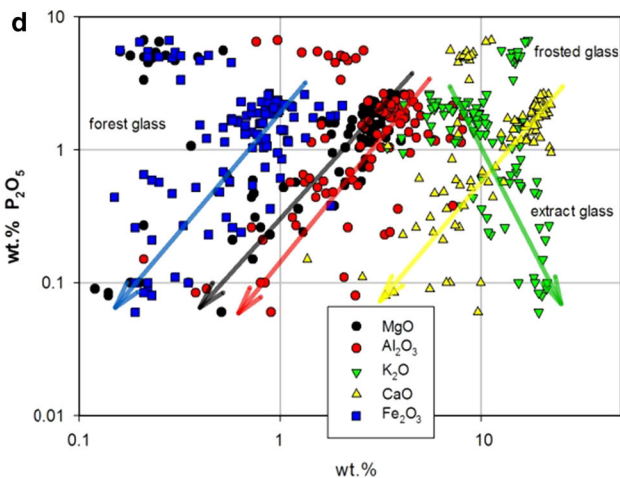
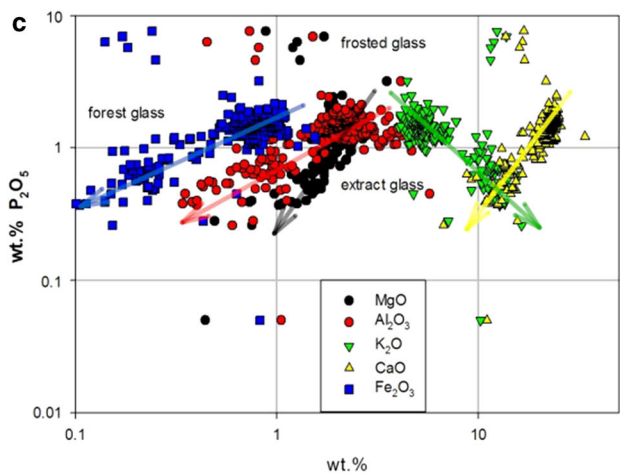
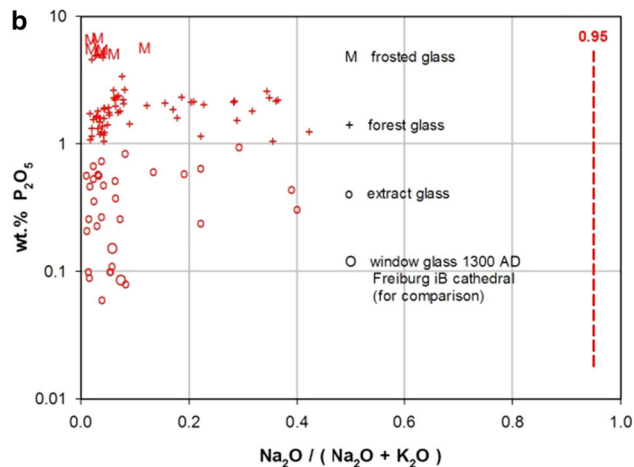
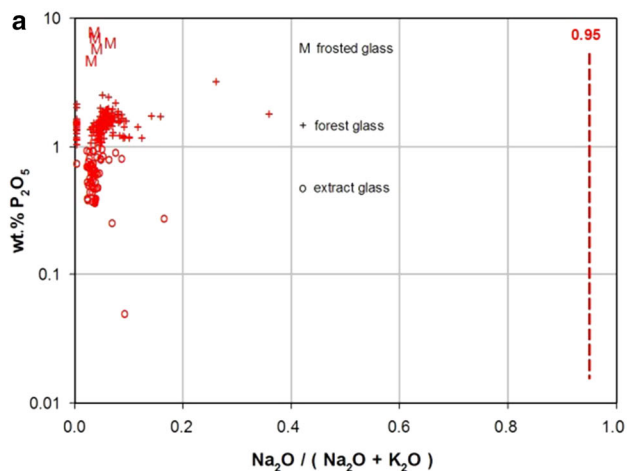
The resulting large compositional variation of halophyte ash versus the low compositional variation of ancient sodium-calcium glass (Fig. 1) implies either an efficient selection of sodium-rich halophile plants or plant *parts* for obtaining soda, or else relying on evaporitic soda that is virtually free from potassium- and phosphorus-oxide (yellow-lined box in Fig. 2a).

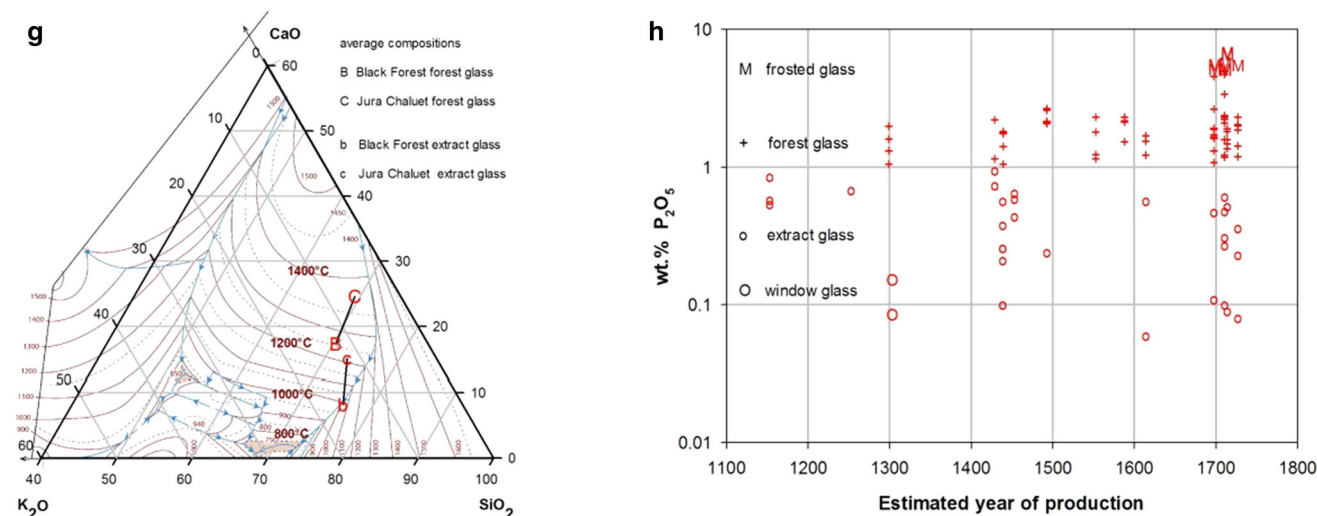
Plant- and vertebrate ashes do not only contain much phosphate but also bear biologically essential oxides like  $\text{MgO}$ ,  $(\text{Al}_2\text{O}_3)$ , CaO, MnO or  $\text{Fe}_2\text{O}_3$  that may influence the glass quality (Allaby 2014). As a consequence, native plant ashes have been processed and improved by washing and separating soluble from less soluble components, as indicated by green dotted tie lines in Fig. 2b. The procedure was possibly common practice since medieval times when producing K–Ca glass, or even since antiquity in case of Na–Ca glass, but is not thoroughly discussed so far in literature. An overview over the impact of phosphate in geogenic and biogenic educts in ancient glass making gives Fig. 3.

### 3 Case studies

#### 3.1 Case study I. Pre-industrial K–Ca glass from Swiss Jura and German Black Forest

Own analyses of K–Ca glass from the Swiss Jura are visualised as graphs in Fig. 4a, c, e, g; literature data of K–





◀ Fig. 4 continued

Ca glass from the Black Forest, Germany, are visualised in Fig. 4b, d, f–h. Analogue graphs display identical scalings and symbol colours.

In 2001 the Archaeological Service of Bern, Switzerland asked us for cooperation in an on-going excavation project at the site of a historical glass hut, operational from 1699 until 1714 in the Swiss Jura mountains near Court-Chaluët. Some 340 excavated specimens of glass, ceramics and refractory material have been analysed in 2002/03 by WD-XFA (9 main components, 10 trace elements) in the Geochemical Laboratories of Basel University (Stern and Gerber 2004; Gerber and Stern 2012), and many hundreds followed from other excavations in or near Switzerland (case studies II–IV).

The a-prioristic question of the colleagues was whether the shards of glass excavated by thousands next to the glass hut were cullet brought from abroad for recycling, or debris of the production site. The relatively small chemical variation, the absence of sodium glass, and the similarity between glass fragments and glass rests sticking on broken melting pots and on blowing pipes suggested local production, but not recycling. The data set revealed, however, unexpected information, too. Stern and Gerber (2002, 2004) displayed the existence of two different glass types: (1) a large, high-phosphate (1–3 wt%)-Mg–Al–Ca–Fe group representing naturally coloured, common forest glass with a yellowish to greenish tint produced at a high estimated (and experimentally proven) melting temperature of  $\approx 1250$  to  $1450$  °C (red crosses) in Fig. 4e and a smaller, colourless low-phosphate-Mg–Al–Ca–Fe group displaying a melting temperature between  $\approx 1100$  and  $1250$  °C (red circles).

Forest glass is obviously made of *native* wood ash as a network modifier/flux, whereas colourless glass is made from potash *extract*. In the meantime laboratory

experiments with local raw-materials had been carried out, i.e. Eocene, silica-rich sands, called “Hupper Earth”, ashes of local native beech- and pine wood, and potash made from native ash. All educts were analysed chemically (some also mineralogically by means of XRD), and also the product glass, manufactured in the laboratory was analysed.

The chemical composition of native ash and potash extract differs strongly (Fig. 4c, d) as is indicated by arrows: soluble components like alkalis are extracted and concentrated, whereas less soluble oxides of Mg, Al, Si, P, Ca, Mn, Fe remain in the residual fraction, i.e. are depleted by a factor of 8–15 in the potash fraction. The extraction process serves two aims: K<sub>2</sub>O is accumulated to 85–95 wt%, whilst colouring components like MgO, MnO, Fe<sub>2</sub>O<sub>3</sub> are reduced together with P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub> and CaO. The production of colourless glass is hence facilitated without applying decolourising agents. The experimental studies were extended later to bracken and cereals (Stern and Gerber 2009; Stern 2010). A final synthesis giving also an in-depth statistical validation was published 2012 (Gerber and Stern), a congress contributions followed (Gerber 2014). The importance of processing and improving plant ash for producing glass has hitherto not found its way into recent text books.

The few cases of frosted glass with exceptionally high P<sub>2</sub>O<sub>5</sub>, high CaO but low MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> may indicate that potash extract in combination with bone ash has been used for obtaining opaque high-phosphate/low-iron K–Ca glass.

Maus and Jenisch (1999) published analyses of alkali-lime glass fragments, collected at 37 abandoned glass huts, operational from the  $\approx 12$ th/13th to the 19th century in the Black Forest (Germany), an innovative research that was published at a remote place and remained unnoticed for

years, right column. Maus reports colourless potash glass made from wood ash extract, and naturally coloured forest glass made from native wood ash. His data have been visualised and are presented on Fig. 4b, d, f–h. Phosphate content and proposed years of production reveal that phosphate-depleted ( $P_2O_5 < 1.0$  wt%) is present since the  $\cong$ 12th/13th century (Fig. 4h). The highly innovative research of Maus and Jenisch (1999) went unnoticed in English printed media, see e.g. Henderson (2013).

The large compilation of glass analyses published by Brill (1999) contains many K–Ca analyses of medieval European window glass. Two are low-phosphate analyses from Freiburg Cathedral, Germany (Konstanz window dated  $\approx$  1300 AD, XI #5124, #5126), that support the findings of Maus and Jenisch (1999) on early K–Ca potash extract glass (Fig. 4f, h).

The CaO-content of beech wood reflects, in contrast to  $SiO_2$ , the nature of soil where the tree is growing on. One may hence predict that glass made from local raw materials reflects the regional lime content of calcareous soil (Jura) or siliceous, low-lime soil (Black Forest). Indeed is the average glass composition different and so is the minimal melting temperature (Fig. 4g, lowest left triangle). CaO in average forest glass from Court Chaluet (C, N = 105) amounts to 25% CaO  $\approx$  MP  $\geq$  1370 °C which is considerably higher than in average glass from the Black Forest (B, N = 52) 15%  $\approx$  MP  $\geq$  1250 °C; a similar trend holds for colourless potash extract glass, i.e. from the Jura glass hut (c, N = 52) 25%  $\approx$  MP  $\geq$  1200 °C versus Black Forest (b, N = 31) 8%  $\approx$  MP  $\geq$  1000 °C.

Whether ash extraction was also performed in case of herbaceous plants like fern or halophytes has seldom been a topic of archaeometrical research so far (Verità 1985; Stern and Gerber 2009; Cilová and Woitsch 2012). Verità (1985) mentions “Soda di Catania” that was processed in Murano since 1450 in order to produce colourless and transparent high-quality “cristallo” (see Fig. 2b, green dotted tie-line). The halophyte species used for making *Soda di Catania* extract has unfortunately not been reported.

### 3.2 Case study II: Medieval Na–Ca glass. Serravalle Castle, CH-Ticino and Venice Lagoon, Italy

Own analyses of Na–Ca glass from Serravalle are visualised as graphs in Fig. 5a, c; analyses of literature data from Venetia in Fig. 5b, d. Same scalings and symbol colours for analogue graphs.

A set of flat and hollow glass (N = 94) from archaeological excavations carried out 2002/07 by Silvana Bezzola and Werner Meyer at Serravalle Castle in Ticino, Switzerland was analysed by energy-dispersive X-ray fluorescence

analysis (ED-XFA, Spectro X-Lab 2000) in the Basel Geochemical Laboratory by A. Burkhardt. His data report had been forwarded to the responsible archaeologists in 2004, but no results have been published yet. The castle was first mentioned 1224, and destroyed 1402. The excavated glass hence dates from the 13th/14th century and consists of sodium-lime glass, displaying a phosphate content typical for biogenic ash ( $P_2O_5 > 0.2$  wt%; Fig. 5a). Two groups with comparable phosphate, but different alkali index were found, 0.4 to 0.7 and 0.75 to 0.9  $Na_2O/(Na_2O + K_2O)$ . The latter group is similar to Venetian flat- and hollow- glass of the 13th/16th century (Fig. 5b), as reported by Brill (1999) and Verità (1985). Low phosphate ( $< 0.2$  wt%) glass as is typical for glass made from processed ash of halophytic plant ash (Fig. 5b, large blue circles, see Verità (1985)) was not encountered. All analysed specimens displayed an alkali index below 0.95; typical high  $Na_2O/low P_2O_5$  (crosses in Fig. 5b) are not present. Extract glass, as was produced in Venice since the middle of the 15th century (Verità 1985) is not present in the 14th century Serravalle data set. Three specimens represent altered, sodium-depleted glass and are chemical outliers.

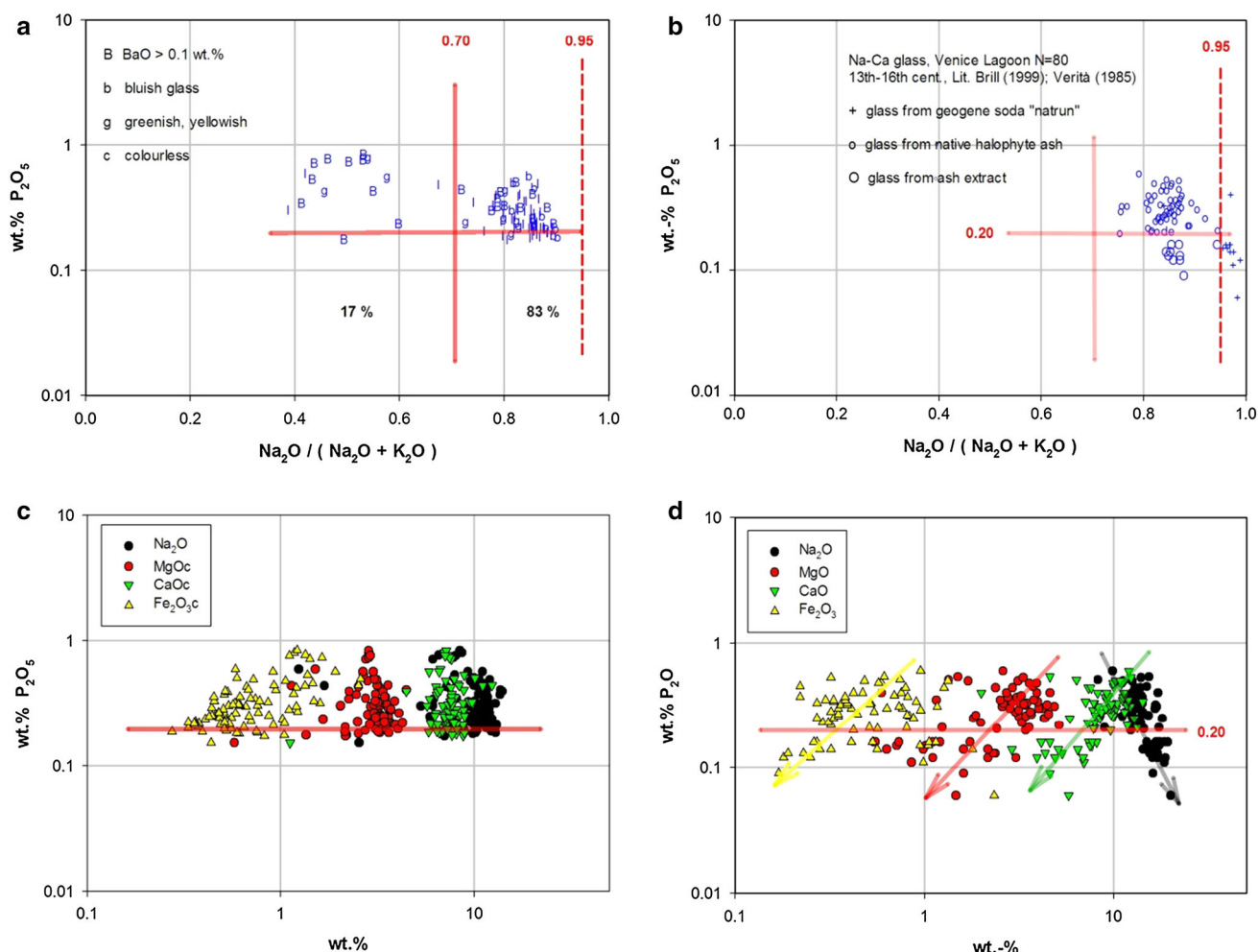
The small group (left in Fig. 5a, isolated points) displays somewhat higher phosphate and  $K_2O$  contents and concerns mostly brownish–greenish fragments containing 0.04–0.2 wt% BaO, N = 12. It has no counterpart among contemporary Venetian published analyses, as it seems. All 10 blue specimens contain elevated CoO and CuO between 0.04 and 0.3 wt%, whilst  $Sb_2O_3$  is always below detection limit.

Contemporary Venetian glass (Fig. 5b, d) displays two different clusters, a large one with elevated  $P_2O_5$  and lower  $Na_2O$ , and a small one with low  $P_2O_5$ , MgO and lime but high  $Na_2O$ —and represents *probably* soda glass made from *extracted* halophyte ash, e.g. from *extracted soda di Catania*, as described by Verità (1985). The extraction process provokes a reduction of less soluble oxides like magnesia, lime and iron as indicated by arrows in Fig. 5d.

The medieval flat- and hollow glass from Serravalle and contemporary glass of Venetian origin were both produced with a biogenic native flux containing medium phosphate and some potassium oxide, suggesting the use of imported halophyte ash, but not of evaporitic low-phosphate/low-potassium soda, type “Wadi Natrun”. The presence of  $K_2O$  in certain halophyte ashes, and hence in glass made with it, prevents the use of a ternary plot with combined chemical and physical data (melting diagram Na–Ca–Si).

### 3.3 Case Study III: Early medieval and late Roman Na–Ca window glass

Own analyses of early medieval Na–Ca glass are visualised as graphs in Fig. 6a, c, e; literature data of Roman Na–Ca



**Fig. 5** Case Study II. Serravalle Castle, CH-Ticino and Venice Lagoon, Italy. *Left column* Serravalle, excavations by W. Meyer and S. Bezzola, mainly 14th century N = 95. Analyses by A. Burckhardt, ED-XFA Geochem. Lab. Univ. Basel, unpublished. **a** The large group represents 83% of the total consisting of elevated phosphate/sodium glass (*right*), and a small group (17%) consisting of high phosphate/low sodium glass (*left*). High sodium glass (index >0.95) as is typical for glass produced from geogenic soda is not present. **c** The large group represents probably glass made from native halophyte ash, P<sub>2</sub>O<sub>5</sub> >0.20 wt%. *Right column* Venice Lagoon, 13th/16th century

(Brill 1999; Verità 1985; N = 80). **b** Glass from Venice Lagoon consists of at least three compositional groups. One (*small blue circles*) represents according to a tentative interpretation Na–Ca glass made from native ash of halophile plants, one (*large blue circles*) consists of Na–Ca glass made from soda extract, one small group (*blue crosses*) might represent soda glass produced with geogenic soda, type “Wadi Natrun”. **d** displays glass containing >0.20 wt% P<sub>2</sub>O<sub>5</sub>, where highly soluble oxides like Na<sub>2</sub>O are enriched, whilst less soluble ones are depleted as represent by *arrows*. This preliminary interpretation needs verification by experimental research

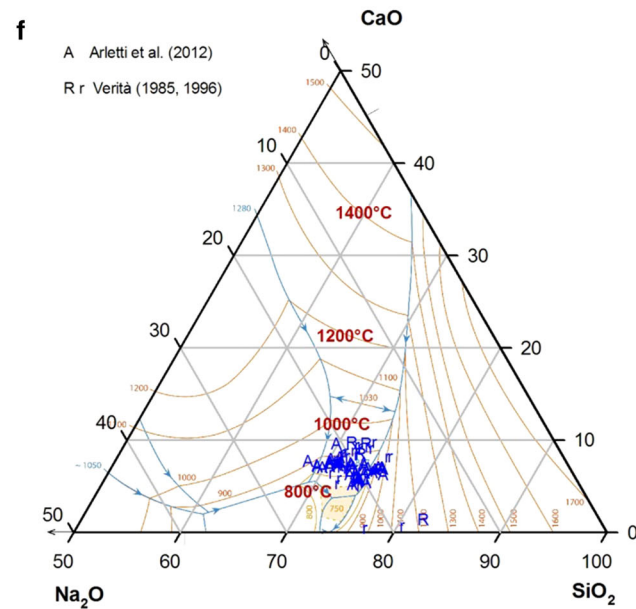
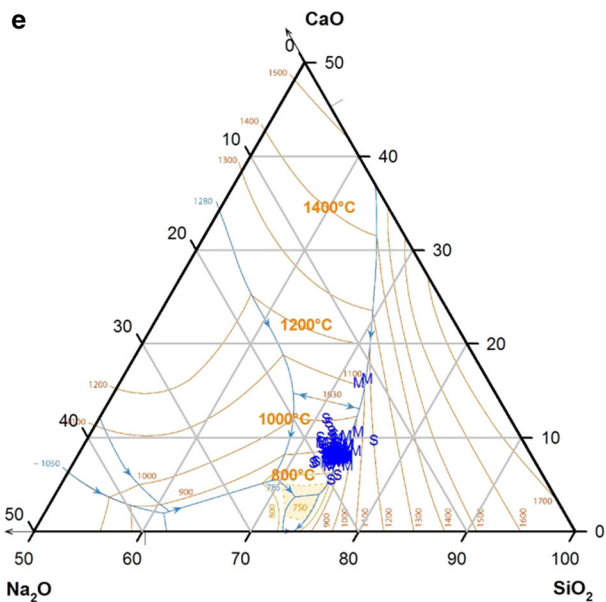
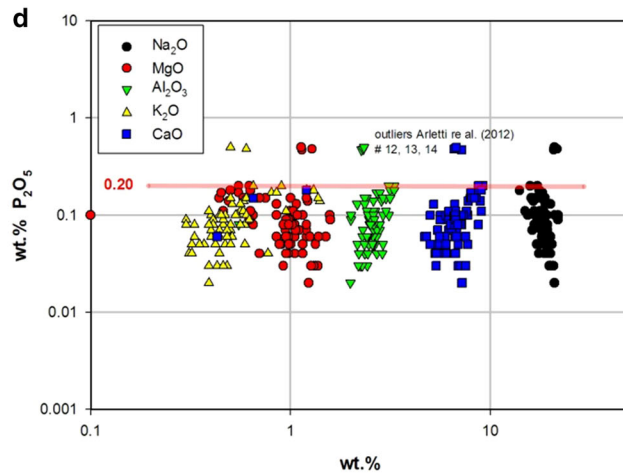
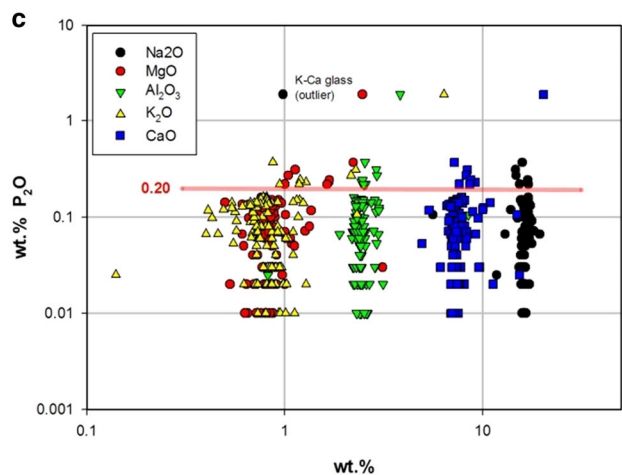
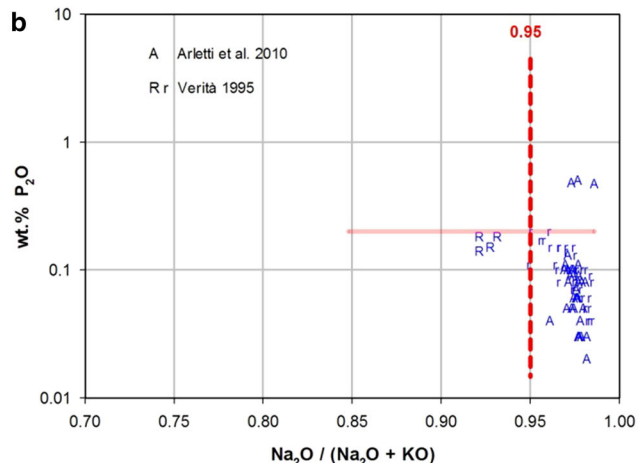
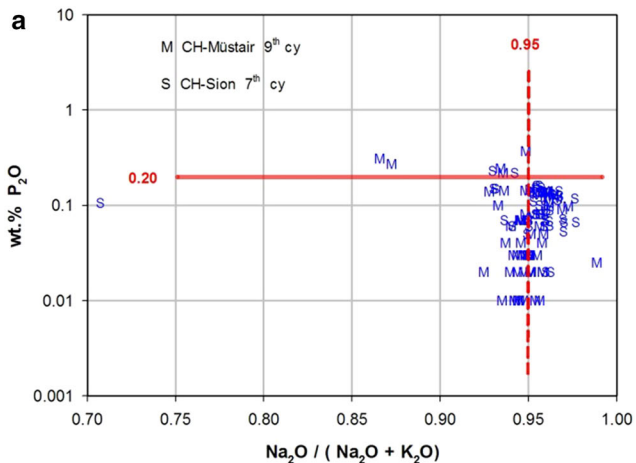
glass are visualised as graphs in Fig. 6b, d, f. Same scalings and symbol colours for analogue graphs.

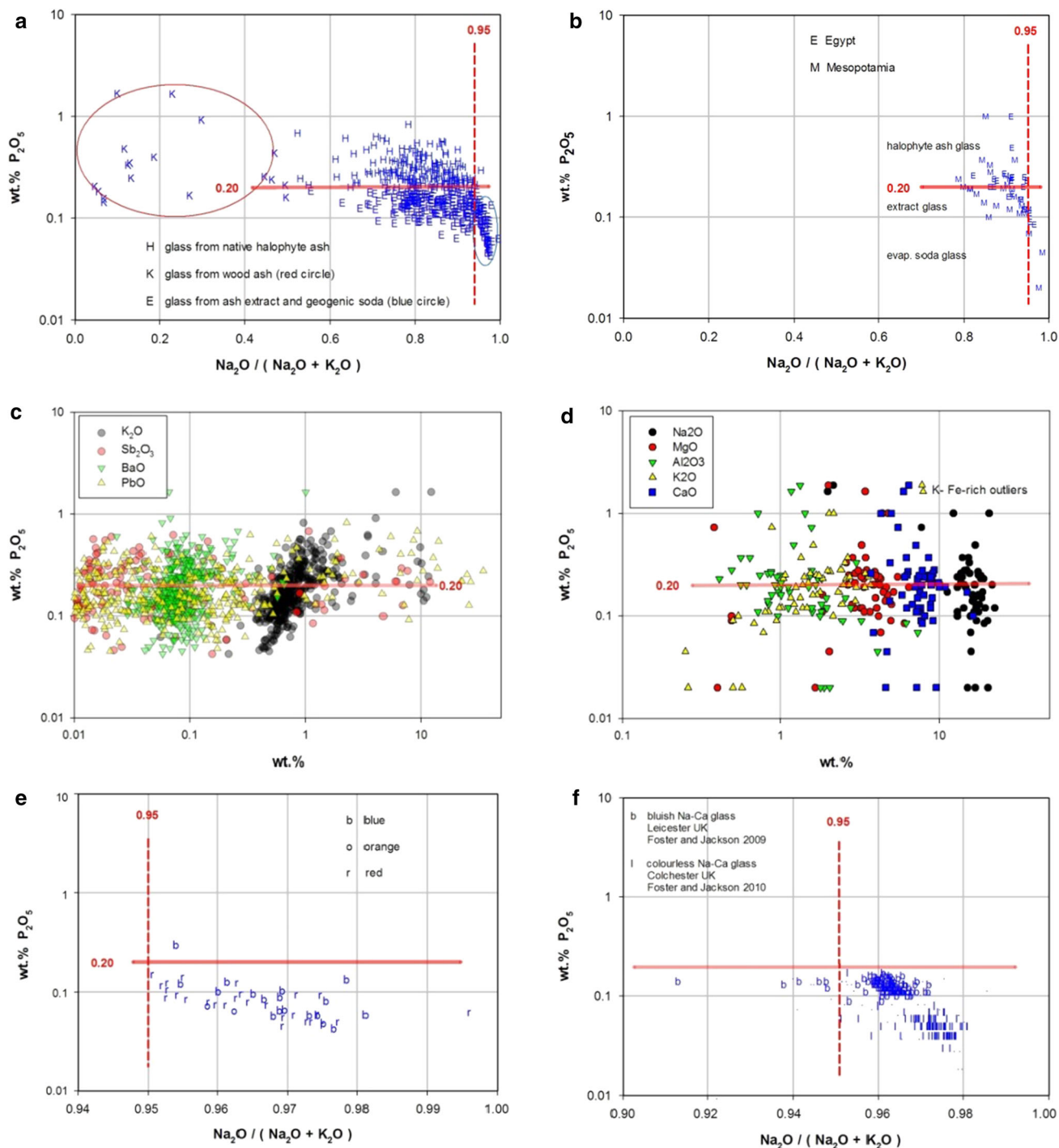
120 specimens of flat glass from Sion CH-Valais 7th century, and from Müstair monastery, CH-Grisons, 9th century, (Wolf et al. 2005; Wolf and Kessler 2015; Wolf et al. 2015) were analysed 2002/03 by means of WD-XFA covering 12 main- and minor components + 11 trace elements at Basel Geochemical Laboratories.

The two groups are chemically similar consisting of low-phosphate/high sodium glass with a majority of  $S \approx 0.95$  Na<sub>2</sub>O/(Na<sub>2</sub>O + K<sub>2</sub>O) (Fig. 6a; blue letters for Müstair and Sion). The chemical variation of S is relatively small as is typical for sodium-calcium glass manufactured

**Fig. 6** Case Study III. Early medieval and late-Roman Na–Ca flat glass. *Left column* CH-Sion 7th, and CH-Müstair 9th century. WD-XFA Basel. N = 120. Analyses: Ref. Wolf et al. (2005). **a** Most analysed glasses contain <0.20 phosphate together with around or over 0.95 Na<sub>2</sub>O/(Na<sub>2</sub>O + K<sub>2</sub>O) indicating possibly the use of geogenic soda. **c** Phosphate vs main oxides. **e** Ternary chemical diagram with inserted physical/melting data, probable melting temperature between 850 and 1000 °C. *Right column* Italian peninsula. Analyses: Data from Arletti et al. (2010) and Verità (1995), N = 80. **b** Phosphate vs alkali-index. All but 7 analyses display an index >0.95 together with P<sub>2</sub>O<sub>5</sub> <0.20 representing Na–Ca glass, probably made from geogenic soda. **d** Phosphate vs main oxides. **f** Ternary chemical diagram with inserted physical/melting data, probable melting temperature between 850 and 1000 °C

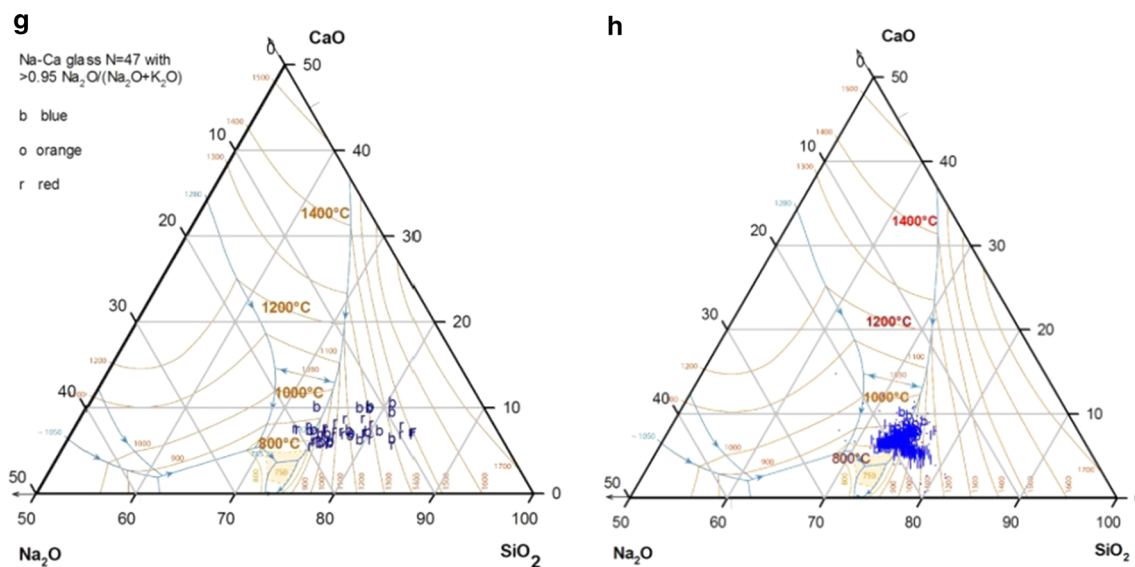






**Fig. 7** Case Study IV, La Tène alkali-Ca glass. Tarodunum/D-Zarten and antiquity. *Left column* celtic Tarodunum/D-Zarten. Analyses by A. Burckhardt, ED-XFA Geochem. Lab. Univ. Basel (Wagner 2006; Burckhardt and Steuer 2006). **a** Phosphate vs alkali-index of 395 glass fragments. Roughly 5% consist of high phosphate high  $K_2O$ -glass (K, left circle), 10% represent low phosphate low  $K_2O$  specimens. **c**. Main oxides vs phosphate. **e**. Phosphate vs alkali-index of 47 high sodium glasses (index  $>0.95$ ). **g** Ternary chemical diagram with inserted physical/melting data. Part displays a melting temperature probably over  $1000\text{ }^\circ\text{C}$ . *Right column* Egypt, Mesopotamia. Analyses from Brill (1999) and Shortland and Tite (2000),  $N = 50$ . **b**. Phosphate vs alkali-

index. Most glasses from Egypt and Mesopotamia were probably made with native ash ( $P_2O_5 > 0.20$ ) and ash extract ( $P_2O_5 < 0.20$ ), and roughly 10%, mostly Mesopotamian specimens represent probably geogenic soda glass. **d** Phosphate vs main oxides. **f** Late Roman vessel glass. Analyses: Ref. Foster and Jackson (2009, 2010),  $N = 220$ . Most blue flat glasses contain between 0.09 and 0.20 wt%  $P_2O_5$ ; all colourless contain less than 0.08 wt% phosphate and over 0.95  $Na_2O/(Na_2O + K_2O)$  and may represent hence geogenic soda glass, type Wadi Natrun. These tentative attributions need experimental verification. **h** Ternary chemical diagram with inserted physical/melting data. Probable melting temperature between  $\approx 850$  and  $\approx 950\text{ }^\circ\text{C}$



◀ Fig. 7 continued

from evaporitic, virtually potassium-free soda, type “Wadi Natrun” and quite different from halophytic extract glass (Fig. 5b). The estimated melting temperature is close to 900 °C (Fig. 6e, f).  $K_2O$  is slightly lower in S than in M, where one part may consist of halophyte extract glass rather than geogenic soda. All specimens but one represent sodium-calcium glass, one is a chemical outlier representing a high-phosphate potassium-calcium glass (# M-002). One low alkali/high lime + alumina specimen (SE-5) has been omitted in Fig. 6f.

Roman window glass (N = 80) reported from the Italian peninsula (A Arletti et al. 2010; R, r Verità 1985, 1995) is quasi-identical (Fig. 6b, f). The Alkali-index differs clearly from native halophytic ash.

### 3.4 Case Study IV: Celtic complex glass and Na–Ca glass from antiquity

Own analyses of Celtic Alkali-Ca glass are visualised as graphs in Fig. 7a, c, e, g; literature data of Na–Ca glass from antiquity as graphs in Fig. 7b, d, f, h. Same scalings and symbol colours for analogue graphs.

The archaeological excavation of a glass workshop in the oppidum of Tarodunum, Zarten, in Southern Baden, Germany, produced a rich complex of mainly coloured glass fragments that were studied and published in the framework of a PhD thesis by Wagner (2006), and partially published in Burkhardt and Steuer (2006). 395 glass fragments have been analysed by A. Burkhardt 2003/04 at the Basel Geochemical laboratories by means of non-destructive ED-XFA with a Spectro X-Lab 2000 spectrometer.

Alkali-lime glass displaying moderate phosphate (0.2–0.7 wt%) and mixed alkali (0.6–0.95  $Na_2O/$

( $Na_2O + K_2O$ ) is with 80% by far the largest group. It contains both alkali oxides (sodium > potassium) as chemical main components and does not stem from ashes of local terrestrial plants like beech, pine or fern. But it is similar to certain halophile plant ashes of arid areas of the Levant *and* to kelp (seaweed) of the Atlantic and the North-Sea coasts, see Fig. 2b (code A, K, H). Na–Ca glass containing  $PbO$  as a major chemical component forms a group representing 4.5% of the total, whereas K- and P-rich/Na-poor glass forms another group of 4.5% (code K, left circle in Fig. 7a). It consists merely of blue raw glass and was possibly made with wood-ash as is found in kitchens where log wood is burnt for cooking—or in glass huts where log wood served as fuel.

A large group of 11% (N = 47) of all analyses consists of low-phosphate/high Na–Ca glass (Fig. 7e) resembling colourless late Roman glass from Colchester UK (Fig. 7f). The ternary diagram displays only for Na–Ca glass meaningful readings ranging from  $\approx 800$  to 1150 °C (Fig. 7g); alkali glass containing much  $K_2O$  cannot be plotted adequately in a ternary Na–Ca–Si melting diagram.

Published analyses of ancient sodium glass with phosphate as a minor constituent (0.1–0.2 wt%) displays either an alkali index below 0.95 like early Mesopotamian glass, or above 0.95 like naturally coloured glass e.g. from Leicester and Mancetter UK (Foster and Jackson 2009, 2010; Fig. 7f, h). This glass was according to the authors manufactured in Great Britain in late Roman time, but probably produced with imported raw-glass from the Near East. The actual data from Tarodunum ask for comparison, but do not (yet) enable firm conclusions.

Potassium-free glass with an alkali-index over 0.95 (Fig. 7e, f) may represent soda glass made from geogenic,

evaporitic soda, type Wadi Natrun. It fits the inner centre of the ternary diagram Fig. 7h, plotting close to the eutectic minimum melting temperature, ranging from  $\approx 800$  to  $\approx 900$  °C.

#### 4 Discussion

The large set of analytical data to be evaluated needs specific visualisations; two different presentations have been selected. One diagram shows phosphate versus the alkali-index  $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ , the other combines three essential oxides in alkali glass (Si–Ca–K or Si–Ca–Na) with their respective melting diagrams after Morey et al. (1930) and Shahid and Glasser (1971) (Fig. 1). The oxide sum of ternary diagrams amounts to  $\approx 85$  and  $\approx 95\%$  in K–Ca glass, and  $\approx 89$  to  $\approx 96\%$  in Na–Ca glass. The remaining constituents are oxides of Mg, Al, P, Mn, Fe + possibly colourising salts of e.g. Cu or Co or decolourising oxides of e.g. As, Mn or Sb.

Figure 8 displays visualised analyses of medieval K–Ca glass made from native and processed ash in graphs a and b; visualised analyses of different plant organs/parts and different plant species in graphs c and d; visualised analyses of cereal straw ashes and from different plant parts (chaff, stalks/leaves, grains) in graphs e and f.

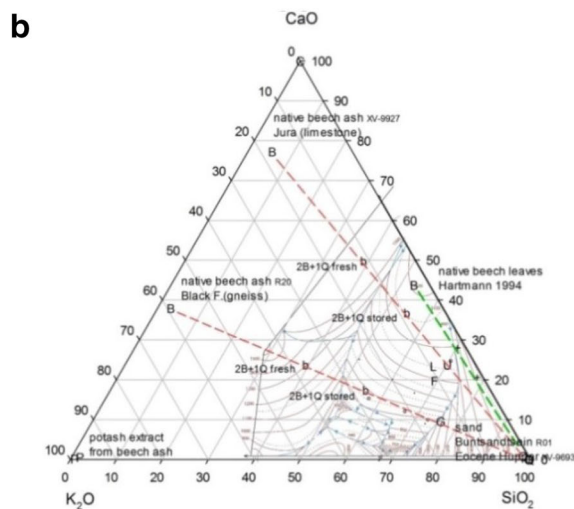
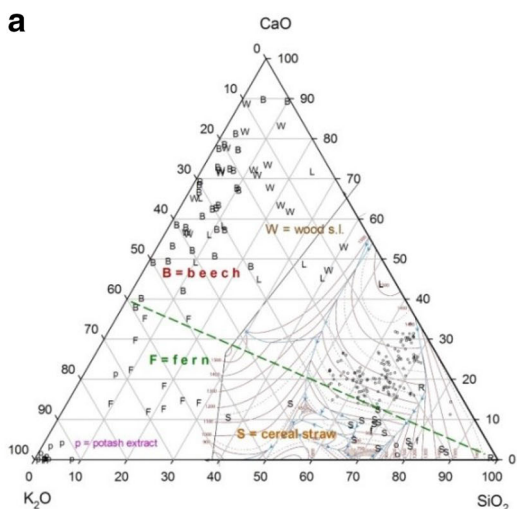
The chemical diversity of plants (Allaby 2014) and their ashes as used as network modifier in glass production is influenced by fundamentally different factors i.e. by plant species (e.g. *fagus sylvatica*/beech versus *pteridium aquilinum*/fern (Fig. 8a), by plant tissue (wood versus leaf; Fig. 8c, d) and by elemental availability (lime-rich versus silica-rich soil (Fig. 8b), boxes with numerical data). The Ca-content of beech wood changes by a factor of  $>2$  in function of substratum (Fig. 8a, d), the Si-content remains practically constant in spite of a drastic difference of silica content of gneiss from Black Forest versus limestone from Jura.  $\text{SiO}_2$  is accumulated in leaves, CaO in wood (Fig. 8c, d). Fern and cereals contain little lime but may concentrate silica to a high level (Fig. 8a, e): ash analyses of rice chaff display over 95 wt%  $\text{SiO}_2$  mineralising as cristobalite,  $\text{SiO}_2$ , (Stern and Gerber 2009; Fig. 8e). The different parts of cereal straw (Fig. 8f, yellow band) indicate that many mixtures of stalks and chaff are close to eutectic melting temperatures around 800 °C and may form an entirely biogenic “one-educt”-glass. It has been produced at laboratory scale in the Basel Geochemical Labs. A patent procedure (Stern 2008) by Basel University proved that so far nowhere a “straw glass” has been invented; glass and building materials made from one component—ash of cereal straw—are of commercial interest, but were never realised in the past—at least not at large scale.

**Fig. 8** Igniting wood and leaves: chemical diversity of plant ash as network modifier. Analyses: Ref. see under Fig. 1. **a** Ternary diagram with chemical and physical/thermal data of medieval K–Ca glass represented as points (*right area*) and wood ash to the left (*B* beech, *L* beech leaves, *W* wood in general; *F* fern, *R* rice, *S* wheat straw). The composition of beech ash (trunk) is dominated by a varying lime content. Fern and cereal ash contains less lime, cereal ash much silica. **b** Same diagram with selected beech wood ash from calcareous habitat (CH-Jura, *upper B*) and silicate habitat (D-Black Forest, *lower B*), both connected by a red tie-line with the projection point of network former quartz (*right corner*). Calculated intermediate mixing proportions of ash and quartz are indicated with **b**. The four boxes represent calculated glass compositions, based upon Theophilus’ recipe “two parts ash + one part sand” assuming fresh ash (*left two boxes*) and stores ash (*right two boxes*). **c** The silica content of ashes from trunk and leaves of different plant species (17 pairs, data from Wolff (1871)). **d** The lime content of trunk vs leaves from the same species. **e** Mixtures of selected plant ashes and quartz, connected with tie-lines. According to ash composition and mixing proportions of ash and quartz different melting temperatures result (calculated compositions): high-lime/native beech ash ( $\approx 1400$  °C), low lime beech ash or beech ash extract ( $\approx 1200$  °C), ash of native fern ( $\approx 900$  °C), ash of native wheat straw ( $\approx 800$  °C). Ash of native wood and ash extract differ by their respective CaO- and  $\text{P}_2\text{O}_5$ -contents (not shown in this diagram). **f** Individual parts of one and the same plant, e.g. winter wheat (*triticum aestivum*), contain nearly the same lime, but a strongly differing silica and  $\text{K}_2\text{O}$ -content. By blending ignited chaff and stalks of one and the same plant, melting temperatures varying from  $\approx 800$  to 1700 °C are possible

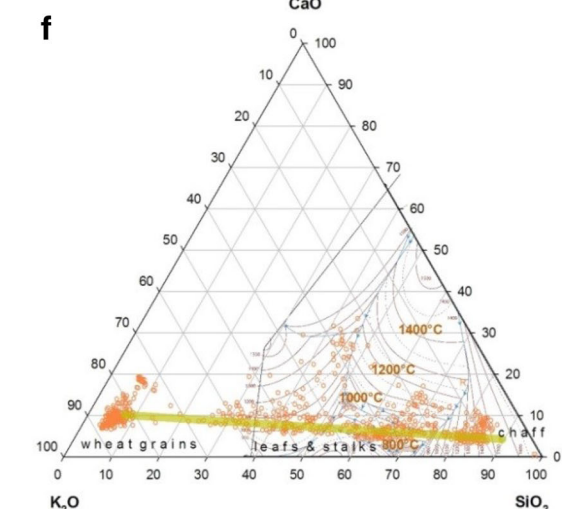
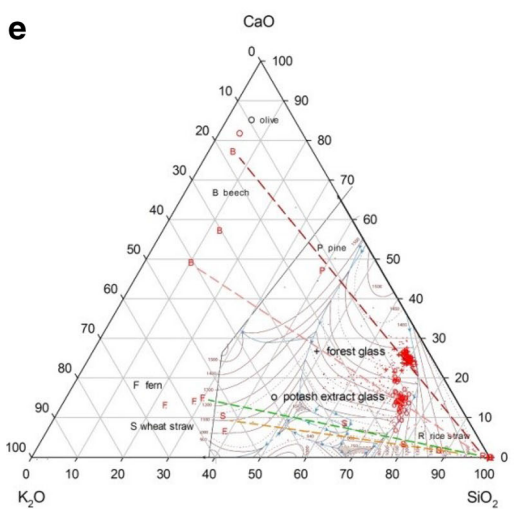
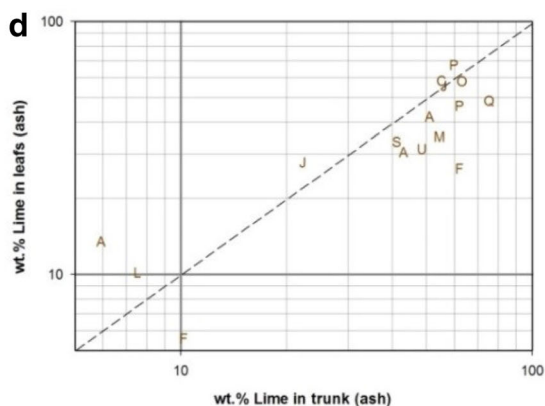
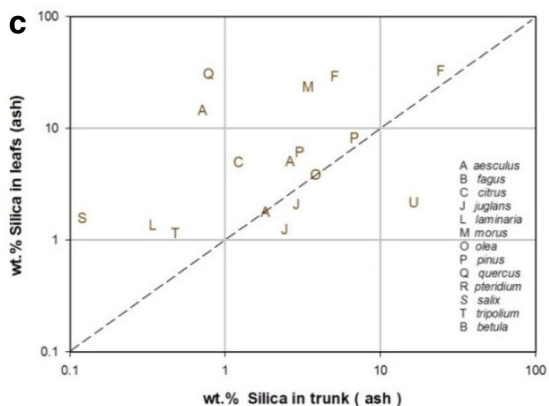
#### 4.1 K–Ca glass

Case study I demonstrates that ancient K–Ca glass made with native plant ash as the network modifier displays a complex and varying chemical composition, its melting temperature varies accordingly from 1250 to over 1400 °C (Fig. 4). These high production temperatures have consequences at different levels: kilns have to be lined with refractory ceramics (Eramo 2005) and specific stoking devices. The kilns were small, the energy consumption was high, but comparative technological studies on e.g. Levantine versus medieval European kilns do not exist as it seems. Potash extraction is not discussed in recent text books like Wedepohl (2003) and Henderson (2013) and was probably not common in medieval Britain, in contrast to Central Europe since the 12th/13th century (Barrera and Velde 1989; Maus and Jenisch 1999; Brill 1999; e.g. XI # 5124 (blue), # 5126 (ruby) from Freiburg Cathedral, Germany, Konstanz window ca 1300 AD).

Potash extract from native ash serves two aims: (1) the resulting glass is nearly colourless without applying decolourising agents, and (2) the minimum melting temperature is lower, ranging from  $\approx 900$  to 1100 °C. Besides custom and habit may colourless transparent glass display a distinct quality of its own when it comes to the production of bright and vivid coloured glass for church windows. Although potash extraction was common practice for



2B+1Q Jura nat	2B+1Q R20 nat	2B+1Q Jura sto	2B+1Q R20 sto
SiO <sub>2</sub> 35.41	SiO <sub>2</sub> 33.39	SiO <sub>2</sub> 50.76	SiO <sub>2</sub> 48.92
Al <sub>2</sub> O <sub>3</sub> 1.54	Al <sub>2</sub> O <sub>3</sub> 0.58	Al <sub>2</sub> O <sub>3</sub> 1.81	Al <sub>2</sub> O <sub>3</sub> 0.8
Fe <sub>2</sub> O <sub>3</sub> 0.29	Fe <sub>2</sub> O <sub>3</sub> 0.25	Fe <sub>2</sub> O <sub>3</sub> 0.25	Fe <sub>2</sub> O <sub>3</sub> 0.28
MnO 0.12	MnO 1.83	MnO 0.09	MnO 1.38
MgO 3.79	MgO 9.44	MgO 2.84	MgO 7.23
CaO 45.41	CaO 20.19	CaO 34.07	CaO 15.35
Na <sub>2</sub> O 0.15	Na <sub>2</sub> O 0.03	Na <sub>2</sub> O 0.11	Na <sub>2</sub> O 0.04
K <sub>2</sub> O 10.26	K <sub>2</sub> O 31.34	K <sub>2</sub> O 7.74	K <sub>2</sub> O 23.76
P <sub>2</sub> O <sub>5</sub> 2.19	P <sub>2</sub> O <sub>5</sub> 1.82	P <sub>2</sub> O <sub>5</sub> 1.64	P <sub>2</sub> O <sub>5</sub> 1.38
99.16	98.87	99.31	99.14



making soap is its application for producing K–Ca glass hitherto not mentioned or discussed in all relevant text books on ancient glass.

Theophilus Presbyters report on making wood ash glass ( $\cong 1115$  AD, Brepohl 2013) describes the procedure of igniting logs of beech-wood. His recipe recommends to carefully blend two parts of beech ash with one part of sand. When *fresh*, water- and carbonate-free ash is applied, a unrealistic glass composition of  $\cong 35$  wt% silica results (left two boxes). When *stored* and recarbonated ash is applied (right two boxes), a reasonable composition with  $\cong 50$  wt% silica results.

Theophilus' report does not mention potash extraction, but he does not write of fern ash either—that is and remains a common topic in scientific articles on medieval K–Ca glass (Jackson and Smedley 2004, 2008; Smedley and Jackson 2006). Fern ash contains little lime and displays hence a specifically low CaO/K<sub>2</sub>O ratio, and high phosphate content. A glass produced with native ash of fern or bracken would display the same chemical fingerprint. But analyses of medieval K–Ca glass do not fit this pattern (Brill 1999).

Experiments have shown that K–Ca glass can be made from native ash of one single plant species like wheat (Stern 2010) when waste straw of chaff and stalks is blended. The resulting glass melts at a low temperature between 800 and 1100 °C, but its low CaO/K<sub>2</sub>O ratio combined with high phosphate is not encountered in analyses of ancient glass—a useful concept obviously needs not be realised in fact, neither today nor in the past (Fig. 8f), lowest right triangle with unpublished WDXF-analyses of wheat straw at Basel Geochemical Labs (unpublished analyses by I. Hildermann).

#### 4.2 Na–Ca glass

Case studies II and III deal with medieval Na–Ca glass. Its chemical composition is remarkably constant and corresponds with a eutectic melting minimum of the system Na<sub>2</sub>O–SiO<sub>2</sub>–CaO (Fig. 1). The resulting low production and working temperature of  $\approx 800$  to  $\approx 1100$  °C is similar to clay firing when ceramics are manufactured. The kiln might be large and suitable for producing large glass slabs of up to 8 tons or over like the one excavated at Beth She'arim in today Israel.

Because geogenic evaporitic soda was (and is) available every year on the shore of Wadi Natrun and neighbouring ponds in Northern Egypt one might expect that early sodium glass was originally produced with geogenic soda as a network modifier (Fig. 7a). Geogenic natrun, quartz-rich sand and limestone are free of phosphate and potassium also, but early sodium-calcium glass from 2nd and 1st millennium AD Eastern Mediterranean seems to generally

contain phosphate and potassium oxide. It was hence produced merely with a biogenic, native halophyte ash as network modifier/flux (Fig. 7d).

Pliny the Elder's report (1st century AD) on glass invention in the Near East writes of specific raw materials for making glass, i.e. sand from the mouth of “river” Belus flowing into the Mediterranean Sea, and of lumps of nitrum that was cargo on board of a commercial trader. Pliny attributed the miraculous event of fluid glass to the sand, as did most of his readers until today (Freestone 2008; Rasmussen 2012; Shortland et al. 2006). However, Belus sands are remarkably heterogeneous in composition (Brill 1999) with a highly varying CaO/SiO<sub>2</sub>-ratio that is not reported in antique sodium glass. And for what reason would traders have nitrum as cargo on board if not for selling it as a raw material for producing sodium glass? Whether the mentioned lumps of nitrum originated from evaporitic soda or from processed halophyte ash, is neither known nor even discussed so far.

In contrast to early Mesopotamian and Egyptian Na–Ca glass contains Roman sodium glass neither phosphate nor potassium oxide, and was hence produced with geogenic evaporitic soda as a network modifier, and not with extract from native halophyte ash, because the latter would still contain some K<sub>2</sub>O (Figs. 2b, 7f).

### 5 Concluding observations

The production of glass might be understood as a man-made metamorphism where selected crystalline raw materials are transformed by melting into a homogeneous glass as an entirely new raw-product with distinct characteristics for manufacturing hollow- and flat-glass. The melting temperature depends on composition and mixing proportions of the selected educts, and selection principles are basically a matter of experience as long as the chemistry of educts and product is not known. Today, chemical analyses permit to better understand the ancient technology of glass production (Freestone 2005).

Although sodium-calcium glass may consist of only three oxides, SiO<sub>2</sub> as a network former, Na<sub>2</sub>O as a network modifier and CaO as stabiliser, contains ancient Na-glass many more oxides, due to the complexity of most natural raw materials. Certain main constituents like volatiles (CO<sub>2</sub>, H<sub>2</sub>O) disappear during glass production, but the remaining complex composition including MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, CaO, MnO, Fe<sub>2</sub>O<sub>3</sub> as minor or major components enters glass and defines its chemical fingerprint. Ancient glass analyses are available by thousands today, but the used raw materials are much less known. The diversity of native ashes used in glass making remained hitherto largely unconsidered, e.g. the chemical difference

of log wood versus leaf or bark of a certain plant, like *fagus sylvatica* (Fig. 8). It is not by accident that Theophilus writes explicitly of beech log-wood, that has to be ignited in a clean workshop, and not of twigs or leaves for making glass. Another important but seldom discussed topic are processing techniques improving the quality of raw materials for producing glass (Fig. 3). Using e.g. ash extract instead of native plant ash facilitates clear and colourless glass essential not only for making “cristallo” but also for manufacturing vividly coloured hollow- and flat glass (Stern 2015).

Because the network former quartz is principally the same in K–Ca glass and in Na–Ca glass, the large variational difference between the two glass types (Fig. 1) has to be attributed to the network modifiers being of biogenic origin, or in case of sodium glass also of geogenic nature (evaporitic soda, type Wadi Natrun), see Fig. 3. One chemical constituent, phosphate, defines the attribution: geogenic educts are virtually free of it, biogenic native ash as network modifier contains it as a main component, whereas ash extract is P<sub>2</sub>O<sub>5</sub>-depleted. It follows that:

1. The network modifier of ancient potassium-glass is of biogenic origin and contains P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O as chemical main components (among others that are essential in plant metabolism), when native ash of terrestrial plants is used.
2. The network modifier of ancient sodium-glass is either of geogenic evaporitic origin (type Wadi Natrun) being virtually free of P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O, or it stems from biogenic native sodium-rich ash of halophile plants containing both oxides (among other elements essential in plant metabolism).
3. When native biogenic ash is processed by washing, K-carbonates and Na-carbonates are accumulated in the eluate by a factor of 8–15, whilst less soluble oxides of Mg, Al, Si, P, Ca, Mn, Fe remain in the residue and do not enter the product glass.
4. High-phosphate potassium glass is produced with native ash of terrestrial plants, whilst phosphate-free potassium glass represents potash-extract glass. Phosphate-free sodium glass stems either from geogenic evaporitic soda or from processed halophyte ash; the two types are distinguished by means of their K<sub>2</sub>O-content: evaporitic soda is virtually potassium-free, native and processed halophyte-ashes contain it both as a chemical minor or major component. Further investigations are needed.

**Acknowledgements** The author is indebted to Intra-muros funding 2000/2008 by the Archäometriefonds of Basel University, and has to thank Yvonne Gerber and Heinz Hürlimann for support and assistance, Andreas Burkhardt for contributing analytical data and reports and Micro-EDXAnalyses (Xray Analytics Switzerland AG Ltd,

Zürich SkyRay 4500H 2016) of a banded sandstone from Petra/Jordan, Atelier Guido Köhler Binningen for constructing scalable melting diagrams, Christian Körner Basel University for references and oral communication on plant metabolism, Edwin Gnos Muséum d’Histoire naturelle Genève, Leander Franz (referee, Basel University) and Sophie Wolf (referee, Vitromusé Fribourg) for critical reading and useful suggestions.

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