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Production, mixing and provenance of Late Bronze Age mixed alkali glasses from northern Italy: an isotopic approach

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ABSTRACT

Late Bronze Age glass in Mesopotamia, Egypt and Greece was made from silica and plant ashes. Around 1200 BC in Europe a new glass type appears of a mixed alkali composition. Although the highest concentration of this glass is found at Frattesina in the Veneto, northern Italy there is no absolute proof that it was fused there from raw materials. A variety of possible alkali raw materials have been suggested but there is still no certainty about its identity. The chemical compositions of these mixed alkali glasses are characterised by a series of mixing lines which suggest that raw materials or glasses were mixed. To address these issues we present here the first set of radiogenic isotope ($^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$) results for highly coloured samples of 11th century BC raw and waste glass from Frattesina together with new isotopic results for northern Italian silica and plant samples. Although a relatively small number, the isotopic results suggest that primary production of mixed alkali glass occurred in northern Italy. Moreover, it can be suggested that two of the samples were made from a mixture of different glasses, with contrasting isotopic signatures, one probably deriving from northern Italy and the other from a non-local source. This indicates that there were two production centres for mixed-alkali glass. We have shown that Frattesina glasses were made using isotopically distinct raw materials from those used to make the slightly earlier Late Bronze Age Mesopotamian and Egyptian plant ash glasses. Even though we have tested a small number of samples the isotopic results nevertheless provide significant new evidence for these mixed-alkali glasses being the first European glasses.

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1. Introduction

Scientific and archaeological research provides evidence for the production of plant ash soda-lime glasses during the Late Bronze Age partly under the auspices of palatial economic and ritual systems in both Mesopotamia and Egypt (Rehren and Pusch, 2005; Degryse et al., 2010a,b; Henderson et al., 2010; Smirniou and Rehren, 2011; Henderson, 2013, 131–132, 167–175). Around 1200 BC the palatial Bronze Age economies in Mesopotamia, Egypt, Turkey and Greece collapsed and it is shortly after this- and probably as a result of this-that a new compositional type of glass appeared in Europe characterised by mixed-alkalis (Henderson, 1988a; Brill, 1992; Santopadre and Verità, 2000; Angelini et al., 2004). It is also characterised by low levels of magnesia and calcium oxide and a small proportion of silica crystals and has been termed 'low magnesia-high potassium' glass (LMHK) (Henderson, 1988b). Compared to many plant ash glasses found in Mesopotamia, European mixed alkali glasses exhibit minimal weathering and this may partly be due to the 'mixed-alkali effect'. This 'effect' is known to improve the durability of glass especially when the soda level is around 12% and the potassium level around 3% (Hench and Clark, 1978, 95). Nevertheless, many Late Bronze Age mixed alkali glasses contain close to equal proportions of sodium and potassium oxides so the 'mixed alkali effect' may not be the only reason that they are durable.

Here we present new chemical analyses of mixed alkali raw and waste glass samples from Frattesina, Fratta Polesine in the Po valley, northern Italy. We also present the first set of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ results for LMHK glasses and compare these with isotopic results for sands and ashed plants from the Po valley and

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other sands from Italy. Only five samples have been subjected to isotopic analysis because this is all that was available for the research project due to the large sample size involved (c. 4 cm^3)- all are for unworked glass rather than formed artefacts. These have been used to investigate the provenance of Frattesina glass and the identity of the alkali and a calcium-rich raw materials used to make it. The isotopic data has also been used to investigate whether glasses or raw materials have been mixed, whether the raw materials used to make mixed-alkali glass could possibly have derived from the Middle East and whether a single or multiple primary production centres were involved in the manufacture of LMHK.

2. The appearance and development of mixed-alkali glasses

Middle Bronze Age faience and glassy faience from the Italian peninsula and elsewhere contain a higher proportion of silica crystals than Late Bronze Age glass. However, all three are united by having a mixed-alkali glassy matrix (Artioli et al., 2008). Unlike in the Middle East and Egypt, the technological development from faience, via glassy faience to glass seems to form a clear progression for these vitreous materials characterised by mixed alkalis. The first high potassium glass, which in other ways is compositionally similar to LMHK, is found in Late Bronze Age and Early Iron Age contexts (Henderson, 1992; Towle et al., 2001).

LMHK and high potassium glasses were used for the manufacture of beads in these periods (c.1200 BC – c. 1000 BC). LMHK glass, the type found at Frattesina, has also been found in Switzerland, Germany, Bohemia, Greece, France, England and Ireland (Henderson, 1988a; b; Towle et al., 2001; Gratuze and Billaud, 2003; Nikita and Henderson, 2006; Venclová et al., 2011). A diagnostic bead type with a spiral wound decoration in a contrasting opaque colour, the *Pfahbauperlen mit spirale* (Haevernick, 1978), found at Frattesina, elsewhere in Europe, at Kaman in central Anatolia (Pers. Comm. Dr. Omura), the Cape Gelidonya shipwreck off the Turkish coast and Beth She'an in Israel (McGovern et al., 1993, 7, Fig 2u; McGovern, 1987, Table 3, BLA-1X2; Spaer, 2001, 106 (133), Fig. 43) is often of an LMHK composition, so it may have been considered as culturally symbolic. Nevertheless, an intense deep blue example with opaque white spiral decoration from a Recent Bronze Age context from Perda'e Accutzai, Sardinia, with typological parallels from Gurob, Egypt, has a plant ash composition (Bellintani and Usai, 2012; Angelini et al., 2012). Similar barrel-shaped beads diagnostic to (slightly earlier) phase II of the Recent Bronze Age of northern Italy (second half of the 13th century BC) but with dark brown matrices also have plant ash compositions with high iron (Angelini et al., 2005, 35, Table 1; Angelini, 2011, 21; Bellintani, in press).

It is significant that the largest concentration of LMHK glass has been found in northern Italy and Switzerland (Henderson, 1988a). It appears that the most easterly occurrence of definite LMHK and high potassium glass is currently Greece (Henderson, 1992; Nikita and Henderson, 2006); other Greek Late Bronze Age glasses tend to be of a plant ash composition (Panagiotaki et al., 2005; Nikita and Henderson, 2006). The distribution and chemical characteristics of LMHK glass therefore suggest strongly that it was fused from raw materials in Europe, but till now this has not been proven unambiguously.

3. Chemical compositions and raw materials

Mixed alkali glasses (LMHK) contain between c. 4%–9% Na_2O, c. 6%–12% K_2O, 0.5%–1.0% MgO, 1.0%–3% Al_2O_3, 1.0%–3.5% CaO and 0.25%–1.5% Fe_2O_3. A contemporary kind of glass characterised by high potassium oxide levels of between c. 15%–18% K_2O shares the other compositional characteristics of LMHK including a small proportion of undissolved silica crystals. The colourants used in LMHK glasses are CuO in turquoise and both Cu_2O and metallic copper in opaque dullish red glass (Brill, 1992; Angelini et al., 2004, 1180–3). Correlated copper and tin oxide levels in a ratio of 9:1 suggests that scrap bronze was used as a source of copper (Brill, 1992; Towle et al., 2001). Cobalt oxide in deep blue glasses associated with elevated Fe, As and Ni, with a strong correlation between cobalt and nickel ($R^2 = +0.754$), could possibly indicate that a mineral like skutterudite ((Co, Ni, $Fe(As)_3$) was used to colour it (Towle et al., 2001, 23–24; Henderson, 2013, 69) although other cobalt sources are possible. White glasses are rendered opaque with silica crystals. There is no evidence that colourless LMHK glasses were decolorised with manganese or antimony oxides: they seem to have been produced by controlling the furnace atmosphere.

The nature of the alkali used is a matter of debate. Brill (1992) suggested three possible alternative sources of alkali. The first (also suggested by Lorenz, 2006) was woody plant ashes in which the levels of soluble calcium and magnesium salts were (partly) reduced by removing them. He considered that Frattesina glasses with lower P_2O_5 levels than found in most plant ash glasses could be evidence that the plant ashes had been leached prior to use, the insoluble alkali salts being precipitated during the process. However, for the samples with a relatively consistent ratios of calcium to phosphorus oxides or calcium oxide to magnesia (Henderson, 2013, Fig. 6.16) dolomitic limestone and plant/wood ashes are possible calcium sources, such as found (at higher levels) in much later glasses (Basso et al., 2008).

The second possible alkali source suggested by Brill was an impure form of natron, with a contamination by potassium salts. The third source, nitrate deposits, are found in efflorescent salts from latrines or manurial soils. These contain salts such as saltpetre (KNO_3) and sodium nitrate ($NaNO_3$). Hartmann et al. (1997) carried out experimental work which they claimed supported the use of wood ash to make LMHK, in this case beech wood. One oxide that might be expected at elevated levels had beech wood ashes been used to make LMHK glasses is manganese oxide but using EPMA this is normally either not detected in LMHK glass or is detected close to its minimum level of detection (0.03%) so this reduces the likelihood that beech ashes were used. In interpreting the chemical analyses of mixed alkali *Pfahbauperlen* glass beads from the Altendorf hoard, Germany Lorenz (2006) suggested that beech ashes or fern ashes or ashed plants of the genus *Salicornia* were combined with a pure source of sand to make them. Angelini et al. (2004) also suggested the use of plant ashes.

If local plants were used to make LMHK glass a possible next step would be to chemically analyse the ashes of any halophytic plants, ferns and beech trees growing near Frattesina. This might make it possible to exclude the use of some. However, a number of factors can impact on the chemical composition of the ashes (Sanderson and Hunter, 1981; Smedley et al., 1998; Jackson et al., 2005, 791; Barkoudah and Henderson, 2006; Henderson, 2013, 315–325), including, potentially, Late Bronze Age fluvio conditions (Arenoso Callipo and Bellintani, 1994). Some halophytic plant ashes have a mixed alkali composition; perhaps they were used for making LMHK in Europe (Tite et al., 2006). Variable melting conditions can also influence what plant ash components are transferred directly into glasses made from them (Rehren, 2008).

The presence of a mixed-alkali vitreous phase in European faience, glassy faience and glass (Henderson, 1988a; Robinson et al., 2004; Angelini et al., 2005) indicates that a similar or the same alkali was used to make all three. Therefore, although not out of the question, if plant ashes had been used to make them, it would be necessary to argue that (e.g. beech) ashes were purified as early as c. 2000 BC.

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