

Rare Alkali Elements as Markers of Local Glass Working in Medieval Tolmo de Minateda (Spain)

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Analytical data of Roman and early Islamic glass established several primary glass production groups linked to glassmaking centres in the Levant and in Egypt. In contrast, the activities of secondary glass workshops are largely invisible in the compositional fingerprint of first millennium glass. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of 261 glass finds from the Visigothic settlement of Tolmo de Minateda (Spain) revealed a site-specific contamination pattern

due to secondary glass processing and recycling, namely the enrichment of the glass batch by a unique combination of rare alkali elements (Li, K, Rb, Cs). With a median of 21 ppm, Li is particularly distinctive. Elevated lithium contents (Li > 30 ppm) are also one of the characteristic features of Iberian plant ash glass from the Islamic period. The earliest known examples of this type of glass were found among the ninth-century remains from Tolmo.

Introduction

For most of the first millennium CE, the primary production of glass from its raw materials (sand, alkali) was concentrated in a small number of primary production installations from where the glass was distributed to secondary workshops throughout the Mediterranean and into central and northern Europe.^[1] About ten major compositional groups of Roman and late antique natron-type glasses have by now been identified that can be traced back to different primary productions in the

Levant and in Egypt.^[2–8] Recent work on late antique and early medieval assemblages from Spain has established changing supply patterns of Egyptian and Levantine base glass types, an increase in recycling particularly in the seventh and eighth centuries, and the gradual development of a local primary glassmaking industry.^[9–11] However, the distinction of the output of different secondary workshops that fabricated vessels from raw glass based on compositional features still proves challenging.^[1]

Glass is subject to changes in composition caused by secondary production due to contaminations from fuel ash and/or colouring elements that were incorporated into the batch and the loss of volatile elements at high temperatures or prolonged heat treatments.^[12–19] These phenomena have been increasingly investigated in recent years in order to understand better differential glass working processes and supply chains.^[12–13, 20–26] The study of debris and associated materials from secondary workshops in well-defined contexts promises to reveal local variations and practises.^[27]

The present article addresses issues of glass supply and recycling in early medieval Spain through large-scale trace element profiling, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of early medieval vitreous materials from a secondary production site at El Tolmo de Minateda. El Tolmo is located in the Minateda-Agramón valley on an important artery since at least the Roman period, about 100 km inland from the southeast coast of the Iberian Peninsula (Figure 1). Thanks to the systematic excavations carried out since 1988 under the auspices of the Dirección General de Educación, Ciencia y Cultura, the Junta de Comunidades de Castilla-La Mancha and the University of Alicante, the stratigraphy and urban dynamics at El Tolmo have been clearly documented.^[28] The site is important because it preserves its early medieval urban fabric and material culture, including industrial facilities that were established as part of new urban developments in the seventh century. Visigothic Tolmo de Minateda survived well into the early Islamic period.

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cplu.202200147>



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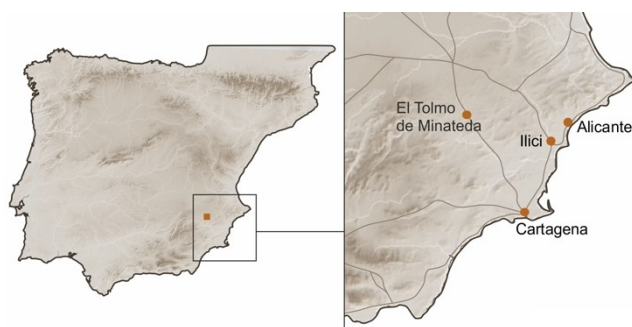


Figure 1. Location of El Tolmo de Minateda showing the Roman road network. © Proyecto Tolmo de Minateda.

It was finally abandoned at the beginning of the tenth century, prior to the establishment of the caliphate of Córdoba.^[29]

Vitreous material makes up a significant component of the archaeological record at El Tolmo de Minateda. The excavations of the last 30 years yielded almost twenty thousand fragments of glass from more than six thousand individual objects, most of which belong to tableware, but include also some lamps, bracelets and production waste (Dataset S1). A considerable amount of glass working debris in the form of moils and chunks, and several glass melting crucibles were recovered, pointing to local secondary glass working activities.^[30–31] In terms of typology, the assemblage from El Tolmo has parallels with other Visigothic sites.^[31] During the earliest phase, bowls with rounded rims predominate that were generally undecorated, but some had applied white thread decorations. From the middle of the eighth century, the typological variability increases, bowls become smaller and less frequent, and new types of objects appear such as beakers, bottles and lamps (article in preparation). The selected material comes from occupation contexts, refuse deposits and abandonment layers with a very well-established chronology based on the stratigraphic sequence.^[28] The sizeable dataset and precise dating of the samples allow us to trace the development of glass working

and to determine the micro-chemical variability in a relatively constrained archaeological context between the early seventh and the turn of the tenth century CE.

The chemical analysis revealed distinctive elemental patterns not previously recorded. There is clear compositional evidence for the contamination of a subgroup of glass as a result of local secondary glass processing. The glass assemblage from El Tolmo de Minateda further shows the use of a surprisingly large number of different types of natron glass from the eastern Mediterranean, some of which predate the early medieval settlement by at least one century. Within the two centuries under consideration, there are no clear changes or breaks in the archaeo-vitreous record of El Tolmo, indicating a degree of continuity in the use and recycling of glass at the site. Furthermore, the site-specific trace element pattern of some of these glasses foreshadows features that are typical of later, early Islamic plant ash glasses from al-Andalus.

Results and Discussion

Of the analysed glass fragments, 253 samples are natron glass with characteristically low MgO and K₂O concentrations (< 1.5 wt% except for Magby, see below), representing seven different base glass groups that originated in the eastern Mediterranean (Figure 2). Five fragments were produced with soda-rich plant ash as the fluxing agent, while three samples are high lead glasses (Dataset S1).

Natron-type glasses

The natron glasses were classified through an iterative process of comparison of the raw data through binary plots (Dataset S1). The different compositional features of the identified glass groups are illustrated by PCA analysis (Figure 2a). All seven natron-type glass categories correspond to well-established primary production groups produced in the Levant and

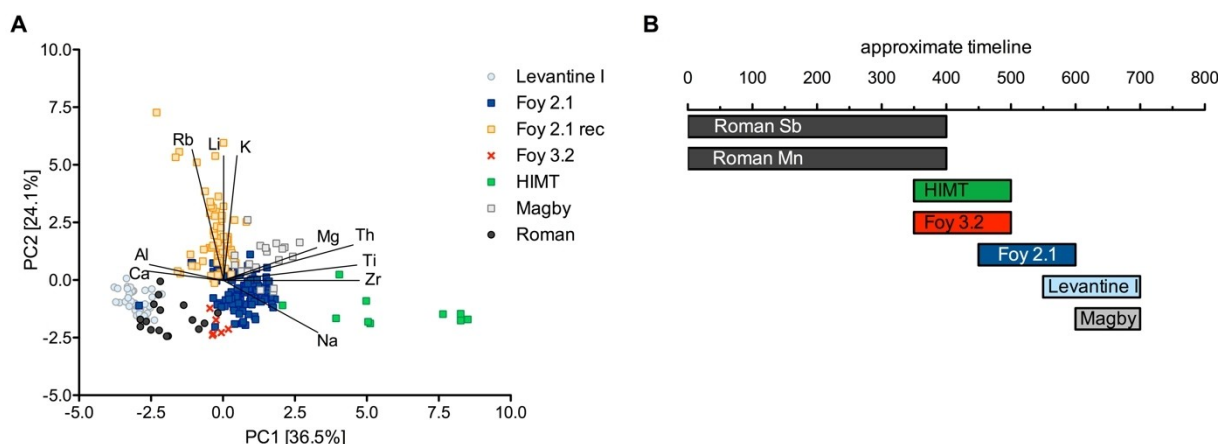


Figure 2. Base glass types identified at El Tolmo de Minateda and their chronological range. (a) Principal component analysis (PCA) of the LA-ICP-MS data of natron type glass divide the dataset into seven different base glass groups. PC1 and PC2 represent about 60% of the overall variance and; (b) approximate chronological span of the different base glasses.^[6]

Egypt.^[6] The groups have different temporal profiles that partly overlap (Figure 2b). The oldest group consisting of 14 samples correspond to Roman glass with moderate aluminium and low titanium levels. They are either Roman Mn or mixed Roman Mn–Sb glass where both manganese and antimony are above the background levels of silica sources (Mn > 250 ppm; Sb > 30 ppm; Dataset S1). Roman Mn- and Roman Sb-decoloured glasses date broadly to the first to fourth centuries CE.^[22–23,32–36] At what point in time the two glass groups were mixed and recycled to obtain a mixed Roman Mn–Sb glass is impossible to tell as this type of glass was very widespread throughout the late antique period especially in the western Mediterranean.^[37–41]

Compositionally intimately related is a group of 33 samples that shows the characteristics of the Levantine I glass associated with the primary glassmaking installations in Apollonia-Arsuf that were active in the sixth and seventh centuries CE.^[3] They have relatively high alumina and lime, coupled with low titanium and zirconium that is consistent with the sand sources on the Levantine coast (Figure 2a). This group shows low levels of additives (colourants & opacifiers), indicating that these glasses have not been extensively recycled (Dataset S1; Figure S1).

A small set of five samples has low alumina and lime, and somewhat higher heavy elements such as titanium and zirconium as well as relatively high soda levels that point to an Egyptian origin. These glasses resemble so-called Foy 3.2 that is typically attributed to the fourth and fifth century CE.^[2,42–45] Not many Foy 3.2 samples have thus far turned up in the archaeological record of Spain. The samples from El Tolmo de Minateda exhibit signs of some recycling in the form of elevated antimony and lead concentrations (Dataset S1; Figure S1). Roughly contemporaneous with Foy 3.2, there is another Egyptian glass group (n=8) characterised by high soda, manganese, iron, titanium (TiO₂ > 0.2 wt %) and zirconium contents consistent with HIMT glass type (high iron, manganese and titanium).^[46] HIMT dominated the archaeological record in the fourth and fifth centuries throughout the Mediterranean as well as central and northern Europe.^[10] Some recycling is evident, but remains limited in the HIMT group.

Although provisionally classified as natron glass, the elevated potassium, magnesium and phosphorus concentrations and the positive correlations between these elements of the group of glass known as Magby (Byzantine high Mg)^[8] can only be explained by an additional plant ash component. The nature of the plant ash additive is uncertain, but judging from the slight negative trend of soda and potash, the ash component may have been fuel ash rather than a soda-rich plant ash from halophytic plants (Dataset S1). In terms of the silica source, the Magby group from El Tolmo (n=20) is variable but tends to have relatively low aluminium and high heavy element contents. It is in this respect closely linked to both Foy 3.2 and Foy 2.1 but not identical (Figure 2a). Its trace element profile points to an Egyptian origin. Magby is dated to the late sixth and seventh centuries CE.^[8–9]

The vast majority of the natron glass from El Tolmo (n = 174 i.e. almost 70%) corresponds to the Egyptian glass group

Foy 2.1 (série 2.1)^[2] that dates to the second half of the fifth and the sixth centuries CE and was widespread throughout the Mediterranean region, including Spain, until well into the seventh century.^[9] Compared to the Levantine and Roman groups, Foy 2.1 has higher soda, magnesium, titanium and zirconium contents (Figure 2a). Foy 2.1 is usually distinguished by elevated manganese concentrations, a deliberate additive that also augmented iron levels (Dataset S1), and it often exhibits signs of recycling.^[20] Particularly antimony and lead concentrations are usually elevated, and this is true also for the glass from El Tolmo (Dataset S1; Figure S1). Whereas the bulk of the Foy 2.1 glasses are virtually identical with respect to silica-related elements, they separate into two distinct sub-categories based on their alkali signatures and their degree of recycling. About 40% of the Foy 2.1 glasses (Foy 2.1 high Li; n = 70) show a 10%–15% dilution effect of the base glass composition, while potassium, lithium and rubidium levels are higher, and K₂O/MgO and K₂O/P₂O₅ ratios are notably different from the more stereotypical Foy 2.1 group (Figure 3). While there are strong positive correlations between K₂O and P₂O₅ and between K₂O and MgO in the Foy 2.1 group, the two elements behave completely independently of one another in the Foy 2.1 high Li glasses. On the contrary, with increasing K₂O concentrations, both P₂O₅ and MgO remain practically unchanged, suggesting very distinct recycling effects for the two Foy 2.1 sub-groups. An elevation in transition metals (Cu, Sn, Sb, Pb) is also more pronounced in the Foy 2.1 high Li sub-type (Dataset S1; Figure S1).

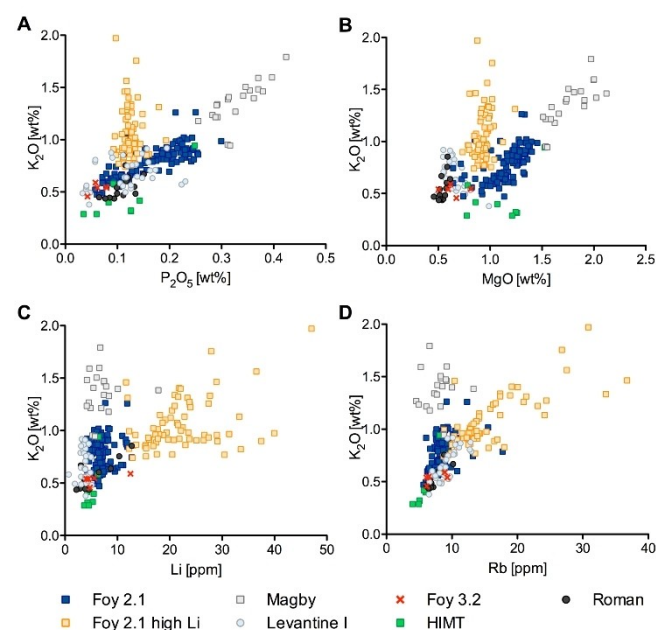


Figure 3. Alkali elements in the different glass groups from Tolmo de Minateda. (a) the enrichment of K₂O independent of P₂O₅ in the Foy 2.1 high Li suggest a different origin of these elements than fuel vapour alone, whereas the two show a positive trend in both Foy 2.1 and Magby glasses; (b) K₂O versus MgO show the same patterns, which argues against simple contamination by fuel ash in the Foy 2.1 high Li samples; (c) K₂O and Li contents underline an unusual enrichment of the Foy 2.1 high Li glass in contrast to the Foy 2.1 and Magby groups; (d) Rb is similarly elevated and positively correlated with K₂O in Foy 2.1 high Li.

The analyses of three crucible fragments show similar trace element patterns. One crucible (TM 263) has a thick layer of glass on the inside (Figure S2) that corresponds closely to the Foy 2.1 high Li glass group, demonstrating that this glass type was worked locally. The contamination through the crucible ceramic is overall minimal, there is only a slight decrease in soda and increase in mineral impurities such as aluminium, titanium, thorium and the lighter REEs compared to the average composition of Foy 2.1 high Li (Figure S3). The main differences are once again the alkali elements K, Li and Rb, which are higher in the crucible glass, and the colourant-related elements (Co, Ni, Cu, Zn, Cd, Sn, Sb, Pb), which are significantly higher in the vessel glass. These compositional tendencies are even more extreme in the other two crucibles, where the crucible walls were covered by only a thin layer of glass which has correspondingly higher contamination levels (Figure S2–3). Taken together, these findings suggest that the crucible ceramic had a direct impact on the contamination of the glass by rare alkali elements.

Plant ash and high Pb glasses

Five samples have high Na₂O, MgO and K₂O (both > 1.5 wt%), as well as P₂O₅ contents characteristic of a soda-rich plant ash signature. They do not form a homogeneous group and have highly variable compositions in terms of both the silica source and the fluxing agent. Their elemental composition largely corresponds to that of an Iberian plant ash glass, which is distinguished by low K₂O to P₂O₅ ratios, elevated lithium contents and relatively high Th/Zr ratios (Figure 4). This new type of Iberian plant ash glass was first identified and defined among the vitreous finds from Ciudad de Vascos close to Toledo.^[47] Except for two specimens (TM 212 & 213), the plant ash glasses show clear signs of recycling as evidenced by the elevated Cu, Sn, Sb and Pb concentrations (Dataset S1).

Three fragments of high lead glass are also consistent with an Iberian production. Specifically, two amber coloured samples (TM 122 & 198) have lead oxide (PbO ~ 50 wt%) and silica

(SiO₂ ~ 35 wt%) as their main constituents, and they have relatively high alumina, lime, barium and antimony concentrations (Dataset S1). Another fragment (TM 180) is a soda-ash lead glass with only moderate levels of lead oxide (20%), significant alkali and alkaline earth elements as well as a remarkably high chlorine level (~ 1.4 wt%).

Glass supply patterns

The evidence for the compositional variability of the glass assemblage from Tolmo de Minateda in relation to the chronology of the primary production groups suggests that the vitreous material predates the establishment of the Visigothic settlement in the seventh century, with the possible exception of Levantine I and Magby glasses. All the other natron-type glass groups were produced earlier, and not as far as we know as late as the seventh century (Figure 2b). The archaeologically earliest glass finds dating to the first half of the seventh century are classified as Egyptian Foy 2.1 and two Magby samples. All late antique natron-type glass categories are represented in the archaeological record of El Tolmo from the second half of the seventh century, and certainly from the first quarter of the eighth century. They were still in circulation in the ninth century CE. None of the early Islamic natron glass groups from the eighth and ninth centuries (Levantine II, Egypt I, Egypt II) have been identified. Based on our data it can therefore be assumed that after the seventh century no new glass supplies reached El Tolmo and that the glass assemblage consists overwhelmingly of recycled/reused material. The degree of recycling varies from group to group. Levantine I glass shows the lowest incidence of recycling, measured in terms of transition metal contents (Figure S1). The Roman and especially the Foy 2.1 high Li glass appear to have been more intensely recycled, and at least some of this recycling occurred locally as demonstrated by the analysis of the crucibles.

Some new Iberian products make an appearance around the middle of the eighth century in the form of lead slag glass that most certainly originated from the area around Córdoba, where we first characterised this specific kind of lead glass in the Rabad of Saqunda.^[11] This slag glass was short-lived and not very common. The two samples (TM 122 & 198) from El Tolmo are the only ones so far attested outside the perimeters of the Umayyad capital of Córdoba. It is likely that not only the primary manufacture of the base glass but also the secondary production of the vessels occurred in or around Córdoba rather than in El Tolmo de Minateda itself. The same probably applies to the single soda-ash lead glass from the second half of the ninth century (TM 180). The closest parallel to the sample from El Tolmo is found in ninth- to tenth-century Baýyāna-Pechina (Almería), where several soda-ash lead glasses with a similar composition have been identified.^[50] The Pechina samples contain similar levels of lead and alkali elements. Lead isotope data point to an origin of the lead component in the southeast of the Iberian Peninsula in the mining districts between Almería and Cartagena.^[6]

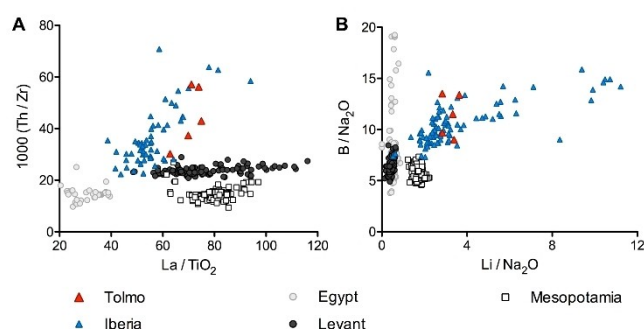


Figure 4. Plant ash glasses from El Tolmo compared to glass reference groups from Iberia, Egypt, the Levant and Mesopotamia. (a) The samples from El Tolmo are consistent with Iberian plant ash glass in terms of the silica source, reflected above all in the relatively high Th/Zr ratios; (b) an Iberian provenance is also suggested by the elevated Li/Na₂O ratios. Data sources:^[17,47–49]

As for the plant ash glass fragments from El Tolmo de Minateda, the analytical evidence indicates an Iberian provenance, making the samples the earliest securely dated and identified Iberian plant ash glasses. It is important to emphasise that the small number and compositional heterogeneity of these plant ash glasses, combined with clear signs of recycling, are suggestive of an early attempt at plant ash glass production that was not yet standardised. Where this 'experimentation' may have occurred is impossible to say based on current evidence. The earliest archaeologically confirmed primary production site of plant ash glass in the Iberian Peninsula are the workshops at Puxmarina in Murcia that date to the twelfth century CE.^[51–54] Analytical data attest to a much earlier production of soda ash glass.^[6,11,47,50] The newly analysed finds from El Tolmo de Minateda date the beginnings of Iberian plant ash glass production as early as the ninth century. To put this into context, this is about a century earlier than the onset of plant ash glass production in Egypt.^[7] Córdoba, from where some of the high lead glass derived, is an unlikely candidate for the manufacture of plant ash glass at such an early date, given the absence of archaeological or analytical evidence. Based on the geographical origin of some of the earliest Iberian plant ash glass finds it can be surmised that the earliest production centres were more likely located somewhere on the south-eastern coast of Spain between Alicante, Murcia and Almería.^[6]

Local secondary working and recycling

Of the 261 glass samples analysed, 29 are associated with secondary glass working activities, the majority of which ($n = 24$) corresponds to the Foy 2.1 high Li compositional group (Dataset S1). The presence of this glass waste proves the local processing and/or recycling of this particular type of glass. The remaining pieces of glass working waste are of the Foy 3.2, HIMT and Roman composition. Secondary glass working and recycling are known to cause significant compositional changes, primarily in relation to the unintentional incorporation of colourants and/or opacifiers, contamination from fuel ash, vapour and the furnace environment, and the potential loss of soda and chlorine due to sustained or repeated heat treatment of the glass.^[12–19]

In the case of Roman glass, the combined presence of manganese and antimony above the impurity levels of the silica source ($Mn < 250$ ppm; $Sb < 30$ ppm) is typically interpreted as the result of mixing and recycling of the two prototypical Roman base glass types.^[37,13,23,41] Accordingly, all Roman glasses from El Tolmo except for two samples (TM 110 & 125) show signs of recycling, which is further substantiated by the elevated colouring elements in these fragments (> 100 ppm). The same applies to the Foy 3.2 samples that all have $Sb > 30$ ppm (Dataset S1; Figure S1). Recycling indicators in the HIMT and Levantine I compositional groups are not as obvious. Only one sample each (TM 057 & TM 188, respectively) displays clear contamination through colouring elements. While the presence of transition metals in otherwise colourless glass can be considered a reliable indicator of recycling, their absence does not necessarily mean that the glass has not been recycled, since the increase in these elements is dependent on the availability of coloured or opacified glass cullet that made its way into the recycling batch.^[55] Some of the Levantine I samples have surprisingly high lime and somewhat elevated potash and phosphorus levels (Fig. 3), which may indicate the contamination of the glass by fuel vapour and the furnace environment.^[12,17,19,23–24,55–56] There is no clear correlation between these elements that would allow firm conclusions. The above observations indicate that the majority of the glass finds from El Tolmo underwent recycling, including the plant ash glasses that have elevated lead levels ($Pb > 1000$ ppm). The typical recycling indicators (contamination with colourants, opacifiers, fuel ash, vapour and/or furnace environment) can be ambiguous, and unfortunately do not usually provide any information about where the recycling took place.

The clearest evidence for extensive local recycling comes from the two Foy 2.1 glass groups. Recycling had very different effects on the composition of the Foy 2.1 compared to the atypical Foy 2.1 high Li group. The latter has higher transition metal concentrations as well as Li, K, Rb and Cs, but lower Mg and P (Figure 5). Foy 2.1 high Li does not exhibit the same positive correlations between K_2O and P_2O_5 and between K_2O and MgO as the Foy 2.1 group. The analytical evidence suggests the admixture of a potassium-, lithium-, rubidium- and caesium-rich additive, one that did not increase the magnesium or phosphorus contents. Hence, contamination caused by fuel ash

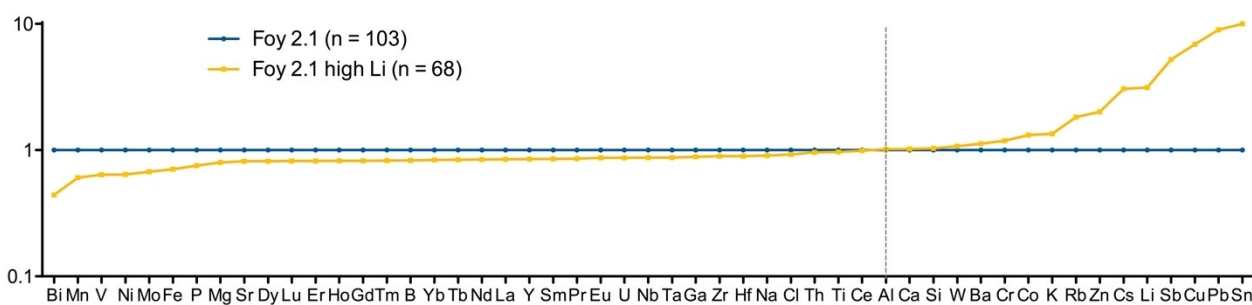


Figure 5. Mean elemental composition profile of the Foy 2.1 high Li group from Tolmo normalised to Foy 2.1 in ascending order. Whereas most mineral impurities are depleted in Foy 2.1 high Li, secondary processing/recycling appears to have introduced colouring and opacifying elements and enriched all alkali elements except soda and magnesia.

and vapour or in fact any other organic material alone cannot explain the increase in potash or the rare alkali contents.

The most likely explanation for the peculiar trace element signature of the Foy 2.1 high Li glasses is that the crucible ceramic had a significant influence on the glass composition. The degree of contamination through the crucible depends on the volume of glass relative to the surface area of the crucible in contact with the glass. The crucibles found at El Tolmo de Minateda, from contexts dating to the second half of the seventh and eighth centuries, have the shape of common kitchenware (Tolmo 1.2.6/T6.2) typical of crucibles of the late Roman and late antique periods, and a relatively small diameter between 15 cm and 22 cm (Figure S2).^[28,57–58] Thus, the surface area of the crucible is relatively large in relation to the volume of glass, which can lead to an increased proportion of molten clay in the glass batch, which in turn may account for the particular features of El Tolmo's Foy 2.1 high Li glass.

On the one hand, we see a 10%–15% dilution effect in the Foy 2.1 high Li for some of the silica-related elements such as Zr, Hf and the REEs compared to the Foy 2.1 category, while the silica contents remain constant (Figure 5). On the other hand, there is a drastic increase of some of the alkalis such as Li, K, Rb and Cs. The glass layers in some of the crucibles exhibit a similar pattern, only more extreme. The exceptions are the REEs that are higher in the crucible fragments, particularly in those that have only a very thin vitrified layer. This difference reflects the differential solubility of the various elements in the glass matrix. The crucible ceramics contain quartz- and potassium-rich feldspar that could be responsible for the dilution effect of some heavy and rare earth elements. Muscovite present in the crucible as minor mineral can be enriched in rare alkalis and may be a source for Li, K, Rb and Cs in the glass layers of the crucibles as well as the glass vessels. The crucible ceramic originates from the Central Iberian Zone around Toledo,^[57] which is known for an enrichment in rare metals including Li, Rb and Cs.^[59] The crucible clay thus appears to have contributed to the K, Rb and Cs levels as evidenced by the depletion of these elements from the crucible interface to the glass surface, which is closest to the composition of the bulk glass (Dataset S1). Lithium behaves differently. The thin glassy layers on the upper walls of the crucibles have exceptionally high lithium contents (>300 ppm), more on the surface than at the boundary between the ceramic body and the glass melt. This suggests that part if not all of the lithium comes from fuel vapour deposited on the upper walls of the crucible. In other words, the thin layer of glass left behind after the crucible has been emptied absorbed large amounts of lithium from the furnace atmosphere. The concurrent low contents of chlorine in this layer indicates that the crucibles were exposed to high temperatures over long periods, which could have caused the accumulation of lithium.

The considerable contamination and unique trace element signature of the vitreous material at El Tolmo de Minateda has not been observed in any other early medieval context. Upon closer inspection, we have now discovered the same phenomenon in some glass samples from contemporaneous Saqunda.^[11] The study of the glass working crucibles and the glass

assemblage from El Tolmo therefore offer specific insights into secondary processing and recycling practices, as well as into long-term changes in the medieval glass industry. Crucibles for secondary glass working are rare in the Roman and Byzantine Levant,^[60] but relatively common in the western Mediterranean during the late antique and early medieval periods.^[61] However, a similar contamination pattern of the associated vitreous material is not known, which makes the crucibles from Tolmo de Minateda unique. There are several explanations for this effect, either the glass volume to surface area was much smaller in the Tolmo crucibles, or the crucibles were made from a very unusual fabric enriched in highly soluble rare alkalis. Alternatively, it is possible that crucibles from other sites were lined with a protective parting layer that may have prevented contamination of the glass melt by the ceramic.^[62]

Conclusion

This study identified unusual trace element contaminations related to local secondary glass working and recycling in Spain during the Visigothic period. It concerns volatile elements such as Li, K, Rb and Cs, but not P, which suggests that these impurities are related to the ceramic of the crucibles on the one hand and to the fuel vapour on the other hand. Contamination by fuel vapour alone cannot explain the behaviour of K, Rb and Cs. Despite systematic recycling evident in practically all of the glasses, the underlying base glass categories still remain distinct. The differences in the effects of recycling suggest that only one of the late antique glass types (Foy 2.1) was processed on site, which gave rise to the Foy 2.1 high Li sub-group. This is supported by the fact that the two Foy 2.1 groups make up almost 70% of the assemblage. None of the other glass types shows the same particular contaminations, despite the presence of typical recycling markers such as enhanced colouring and opacifying elements as well as K₂O and CaO. Since Foy 2.1 largely dates from before the foundation of the early medieval settlement in the seventh century, we can furthermore establish that the glass came to Tolmo in the form of cullet. This reliance on the recycling of old glass suggests that the ancient Mediterranean-wide exchange network of raw glass had been reduced to a regional trade system. Regional supply is also reflected in the absence of post-seventh-century natron-type glass, demonstrating that the supply of glass in al-Andalus became increasingly independent of the traditional glassmaking centres in the eastern Mediterranean. In conclusion, our findings identify rare alkali contamination as an effective region-specific marker of recycling and glass working in first millennium Spain, which could also explain the characteristic lithium concentrations of early Islamic plant ash glasses produced in the southeast of the Iberian Peninsula.

Experimental Section

In total, 265 glass fragments were selected for trace element analysis by LA-ICP-MS, of which 28 samples are glass working debris

including crucibles, moils, drops, semi-fused cullet and chunks. No meaningful data were obtained for four samples due to their poor state of preservation. The 193 nm laser (Resonetics M50E excimer laser) was operated in the spot mode at 5 mJ and a repetition rate of 10 Hz, with a beam diameter of typically 100 μm . The analyses were done using a Thermo Fisher Scientific ELEMENT XR mass spectrometer with a linear dynamic range of twelfth orders of magnitude. The analytical protocol includes a pre-ablation time of 15 seconds and the acquisition of 9 mass scans over 27 seconds in counts/second for 58 elements with an argon/helium glass flow of 1 l/min Ar+0.65 l/min He. The ^{28}Si isotope serves as internal standard, and the data were calibrated using a set of 5 standard reference materials (NIST610, Corning B, C and D and APL1). The average response coefficient (K_i) was thus calculated for each element for a full quantification of the data.^[63]

The layer of glass on the inside of three crucible fragments was repeatedly analysed to trace the changes in contamination levels between the ceramic and glass interface and the glass surface (Dataset S1). To evaluate the LA-ICP-MS data, principal component analysis (PCA) was performed in Matlab on 10 elements (Li, Na, Mg, Al, K, Ca, Ti, Rb, Zr, Th), where PC1 and PC2 account for almost 60% of the overall variability of the dataset.

Acknowledgements

We thank Blanca Gamó and the staff of the Museo de Albacete for their helpful collaboration. We thank María Dolores Sánchez for sharing her expertise, Yasmina Cáceres for her assistance during sample preparation, and C.G. Specht for wading through the manuscript. The reviewers are thanked for their critical reading and constructive feedback that helped improve the paper. This project received funding from the European Research Council under the European Union's Horizon 2020 Research and Innovative Programme (ERC-CoG-2014, grant number 647315 to NS), as well as from the "El contexto como herramienta: escalas de aplicación en los procesos de cambio en la Alta Edad Media (CONTEXT)" PID2019-108192GB-I00 funded by the Ministry of Science and Innovation; "Cerámica y Alimentos. Paleoeconomía de la Alta Edad Media en el sureste peninsular" APOSD/2020/2016 funded by the Regional Government of Valencia and the European Union through the European Development Fund R. The funding organizations had no influence in the study design, data collection and analysis, decision to publish or preparation of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: glass recycling · heritage science · lithium contamination · potassium · Roman glass

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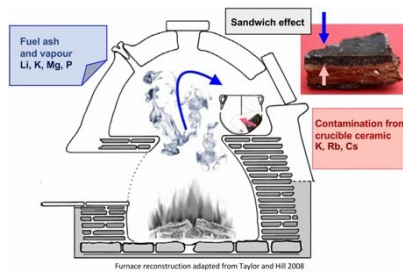
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Manuscript received: March 27, 2022

Revised manuscript received: May 21, 2022

RESEARCH ARTICLE

Rare alkali element contamination of medieval vitreous materials by both the crucible ceramic and fuel vapour are shown in this work. Systematic recycling of old cullet, using crucibles made from clay from the Central Iberian Massif, resulted in unique trace element patterns that can serve as identifiers of Iberian glass processing.



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**Rare Alkali Elements as Markers of
Local Glass Working in Medieval
Tolmo de Minateda (Spain)**

