Ex novo development of lead glassmaking in early Umayyad Spain

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This study investigates glass finds from the Iberian Peninsula as a proxy for identifying the mechanisms underlying technological transformations and innovation in the wake of the Arab conquest in the seventh and eighth centuries CE. High-resolution laser ablation inductively coupled plasma mass spectrometry data combined with lead isotope analyses of a precisely dated (mid-eighth century to 818 CE) glass assemblage from the Rabad of Šaqunda in Cordoba, capital of Umayyad Spain, enabled us to trace the origins of an Iberian glassmaking industry and to unambiguously link it to the exploitation of local raw materials. The analytical data reveal increased recycling, some isolated imports of Islamic plant ash glasses from Mesopotamia, and, most notably, the development of a new type of glassmaking technology that resorted to the use of lead slag from silver and lead mining and processing in the region around Cordoba. The production of this type of lead glass from Šaqunda was short-lived and was subsequently refined by introducing additional fluxing agents. The technological innovation of Islamic glassmaking in Spain evidently drew inspiration from adjacent high-temperature technologies. The revival of glass and the development of a local glassmaking tradition was indirectly related to the wider processes of Islamization, such as the introduction of glazed ceramics that are compositionally related to the lead glasses from Šaqunda.

lead glass | lead isotopes | technological innovation | recycling

The processes of innovation and transfer of skills are fundamental concerns in the study of past technologies (1, 2). The advent of ancient technologies and the adoption of new ones are often explained by analogy to evolutionary theory (3–5). Mutation of technological traditions and innovation are often recognized during major transitional periods and cross-cultural contacts as a result of complex sociohistorical scenarios (3). Thus, the transformation of ancient technologies into medieval technologies may be seen as a direct consequence of wider geoeconomic and social processes leading to what would become the medieval world system. The principal changes in the primary production of glass during the early Middle Ages was the introduction of plant ash to replace mineral soda as the fluxing agent, along with the concurrent decentralization and multiplication of primary glassmaking installations that operated on a significantly smaller scale (6). This transition took place simultaneously in Carolingian Europe and the Islamic Mediterranean and may be related to the formation of cultural identities.

Investigations into the transformation of ancient glassmaking have focused on the eastern Mediterranean, on Egypt and the Levant, because of the region's long history of primary glass production (7–10). The supply of glass to the central and western Mediterranean regions relied on imports from the east, and from the late antique period onward increasingly on the recycling of Roman glass (11, 12). Relatively little is known about medieval and early Islamic glassmaking in the Iberian Peninsula (13–17). The earliest archaeological evidence of the primary production of new plant ash glasses in Iberia dates to the turn of the first millennium CE (13). In contrast, Arab sources attribute the invention of glassmaking in al-Andalus to the beginning of the ninth century CE (18). Essential for understanding the changes in the Iberian glass industry and economy in the wake of the Arab conquest is the characterization of glasses from the transitional period in the eighth and ninth centuries, when the Iberian Peninsula became fully integrated into the Umayyad Empire that maintained close cultural, commercial, and technological links with both the Islamic Near East and Christian Europe. The glass finds recovered from Šaqunda, an old suburb (Rabad) of Cordoba, date to this precise chronological window.

Cordoba had been chosen as the seat of government soon after the Arab conquest of Hispania in 711 CE, and it became the capital of the newly independent Umayyad Emirate in 756 CE. The Umayyad Amir 'Abd al-Rahman I (731 to 788 CE) expanded and embellished his new capital city, first and foremost with the construction of the Great Mosque and the Alcazar (19). Spurred by rapid population growth, the urban area expanded to the south bank of the Guadalquivir river to the Rabad of Šaqunda. Šaqunda was created ex novo around the middle of the eighth century with no pre-Islamic occupation, and hence no residual material, and it was literally razed to the ground a mere 70 years later in connection with a popular uprising in 818 CE (19). A ban of building in this part of the city imposed by the

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Significance

The Islamic conquest of the Mediterranean has long been associated with fundamental geopolitical and economic transformations that sundered the medieval world from antiquity. An eighth- to ninth-century glass assemblage from Cordoba provides new insights into the processes of technological innovation, adaptation, and dissemination contingent on the specific historical environment. Its compositional characteristics reveal the mechanisms underlying the development of a new glassmaking tradition that, based on lead isotope analyses, can be attributed to a local production, using raw materials from nearby ore deposits. Our study illustrates that the second half of the eighth century and the ninth century was a period of considerable technological development in al-Andalus, triggered by a rupture in glass supplies from the eastern Mediterranean.

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Amir al-Hakam I (770–822 CE) remained in effect until modern times; thus, excavations begun in 2001 unearthed an early Islamic suburb almost untouched by later developments (19). The finds from Šaqunda represent the earliest substantial glass assemblage from Islamic Iberia, providing a glimpse into the circulation and consumption of glass between the middle of the eighth century and the first quarter of the ninth century CE, along with the innovation of a new lead glassmaking recipe.

To explore questions of supply and to unravel the phenomena of transmission and innovation, we conducted high-resolution analyses of major, minor, and trace elements as well as lead isotopic compositions of the glass finds retrieved during three excavation campaigns at Šaqunda in 2001, 2002, and 2005. The fact that an excavated area of 22,000 m^2 yielded fragments of only 78 different glass objects illustrates the relative scarcity of vitreous materials, especially compared with Roman and Visigothic times. The glass from Šaqunda also differs from earlier assemblages in terms of functionality and typology. Whereas large open tableware constitutes the bulk of Visigothic assemblages (11), these are largely absent in Šaqunda, being replaced by closed forms, such as unguentaria, bottles, and beakers (*SI Appendix*, Fig. S1). A surprisingly large number of glass bangles ($n = 9$) was recovered, making them the oldest Islamic glass bracelets known in al-Andalus (20, 21). Thus, the formal repertoire of the Islamic glass assemblage from Šaqunda represents a clear departure from earlier traditions in the Iberian Peninsula.

Results

Compositional Characteristics. Our sampling strategy included all identifiable objects to capture the early Islamic glass assemblage in its entirety. Compositionally, the assemblage from Šaqunda encompasses a mix of natron-type and some soda-rich plant ash glasses, as well as high-lead samples (Fig. 1*A*). The bulk of the assemblage (n = 48) adheres to the ancient natron glass recipe, and virtually all of these samples show elevated levels of transition metals, clearly indicating a significant contribution of recycled material (Dataset S1). The glasses nonetheless can be attributed to distinct natron-type glass groups, depending on the proportion of primary glasses in the recycled material (Fig. 1*B*). One subset of natron glass has high titanium, zirconium, and manganese concentrations that are consistent with a glass type known as Foy 2.2, a recycled variant of the Egyptian Foy 2 family (22). Another subpopulation is closely related to Levantine glass that contains lower heavy element levels (22, 23).

Three samples stand out due to their high titanium and zirconium levels, indicative of an Egyptian provenance (23). One of these samples is a silver-stained (luster) fragment with characteristics similar to Egypt 2 but with a lower lime concentration (10, 25) (Dataset S1; MIR 051). The overall group structure of the natron glasses demonstrates on the one hand extensive recycling of older glass groups and on the other hand the importation of early Islamic natron-type glasses from Egypt. However, this import appears to relate only to isolated, finished objects and not to the trade of raw glass en masse. In contrast, raw glass chunks indicative of bulk imports and regional secondary working have been recovered from numerous late antique and Visigothic Iberian sites (11, 26).

Three of the six soda-rich plant ash glasses of the Šaqunda assemblage date to the eighth or early ninth century CE, making them the oldest plant ash glasses so far identified in al-Andalus. The plant ash glasses are highly variable in terms of both the plant ash component and the silica source (Fig. 1*C*), severely limiting the historical and archaeological interpretation. However, what we can say is that the three early samples match contemporaneous Mesopotamian glasses, specifically glass from Samarra and/or al-Raqqa. This illustrates the medieval long-distance exchange of glass objects from Mesopotamia. The three 10th-century plant ash samples have very different compositional signatures, characterized by elevated silica-related elements such as alumina, titanium, and zirconium (Dataset S1), that are consistent with early Islamic plant ash glasses produced in the Iberian Peninsula (27).

The most significant experimental result was the identification of a large number of high-lead glasses ($n = 15$) at Šaqunda with a very homogeneous composition. Of a distinct dark-yellow or greenish-yellow color, these glasses contain mostly lead and silica, with significant levels of alumina and lime as well as some iron and potash, with all other elements usually <1% (Dataset S1). Different types of high-lead glasses appeared in the 9th to 10th century CE across Europe and the Islamic world, including lead silica glasses in the strict sense consisting of very high lead (PbO $\geq$ 60%) and silica as the main constituents, as well as potash lead (several variants) and soda ash lead glasses with lower lead oxide contents (PbO typically between ~20% and 60%) and considerable amounts of alkali and alkaline earth elements (14, 27–32). Even though the Šaqunda samples appear to be related to Islamic lead silica glasses (except one fragment), they have slightly lower lead and higher alkali and alkaline earth concentrations (Fig. 2*A*). Compared with Islamic soda ash lead glasses from the Iberian Peninsula, the Šaqunda samples have somewhat higher lime and potash contents but lower overall alkali concentrations as a consequence of the substantially lower soda content.

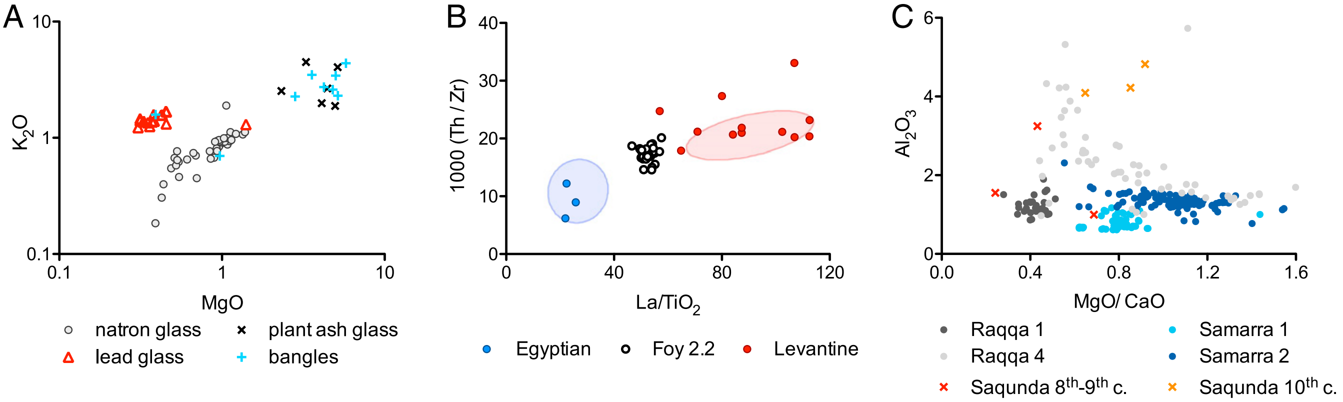

Fig. 1. LA-ICP-MS data of all analyzed glasses from Šaqunda (*A*), natron-type subgroups (*B*), and plant ash (*C*) samples. Data points represent individual samples; ellipses in *B* represent 95% confidence intervals of Levantine (9) and Egyptian (10) reference groups. Plant ash glasses in *C* are compared with data from Raqqa (7) and Samarra (24).

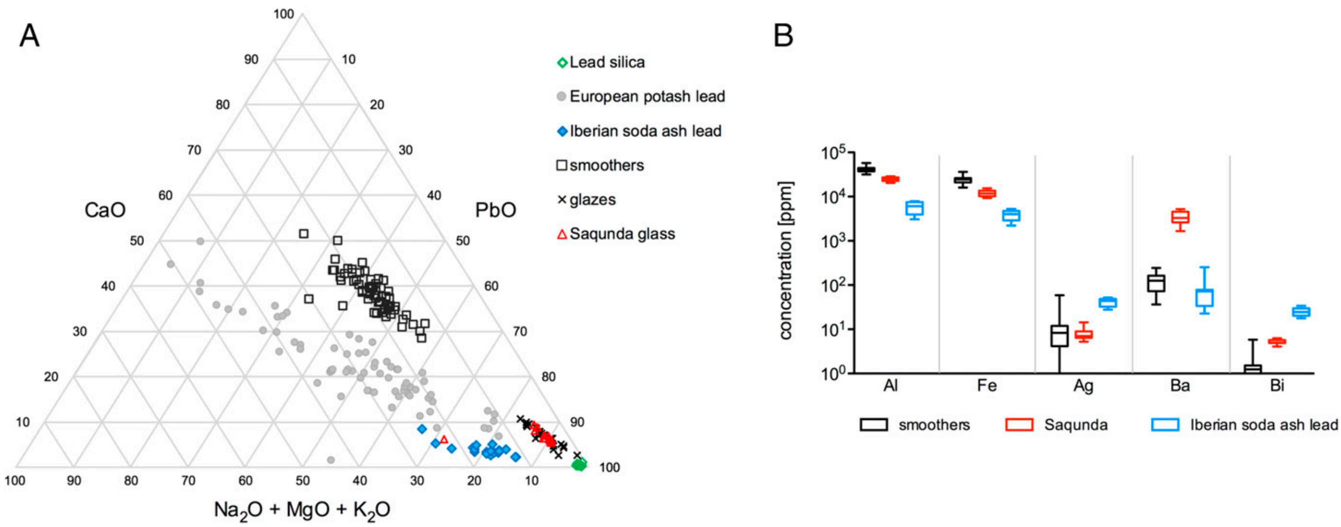

Fig. 2. LA-ICP-MS data of high-lead glasses from Šaqunda compared with published data of different types of high-lead glasses and glazes. (*A*) Lead oxide levels compared with the alkali and alkaline earth concentrations reveal different production traditions. (*B*) Elements associated with the silica (Al, Fe) and lead component (Ag, Ba, Bi) reflect different raw materials. Data sources: smoothers, (29); Iberian soda ash lead glasses, (14, 27, 33); central European potash lead glasses, (31, 34–37); Islamic lead silica glasses, (38); ceramic glazes from Cordoba, (39).

To date, no other glass finds with comparable characteristics have been identified in the Iberian Peninsula, the wider Islamic world, or central Europe; however, the lead glass from Šaqunda shares compositional features with monochrome and bichrome lead glazes from Cordoba dating to the second half of the ninth century (39). In fact, archaeological remains from Pechina (Almería), the earliest glazed-ware workshop in al-Andalus dating to the second half of the ninth century, revealed the use of prefused ground lead glass as the glazing mixture that was applied to the ceramic surface to obtain a transparent lead glaze (40). This suggests a technological and material link between the production of Andalusian lead glass and lead glazes, whereby the tradition of lead glass production precedes the Islamic glazing technologies by roughly half a century. No lead-glazed ceramic is known from the Visigothic or early Islamic periods in the Iberian Peninsula before the second half of the ninth century (40, 41).

The high-lead glasses from Šaqunda form a dense cluster, and it can be assumed that they have a common origin. They are not the simple mixture of quartz and lead oxide that is thought to underlie Islamic high-lead silica glasses from the Near East, nor do they represent a typical Andalusian soda ash lead glass, as they do not contain sufficient soda. Furthermore, they are comparatively rich in alumina, iron, antimony, and barium (Fig. 2*B* and Dataset S1). In this respect, the high-lead glasses from Šaqunda show similarities with high-lead smoothers that emerge from the archaeological record in the ninth century CE. These smoothers have been found in France and numerous medieval sites across Europe from the British Isles to Russia and have been shown to represent a mixture of slag from silver mining in Melle (France) and a component contributing soda, potash, and alumina (28, 29). No such additional element was introduced to the high-lead glasses from Šaqunda, as they do not contain significant amounts of alkali and alkaline earth elements.

Data on lead slag from various medieval European sites show a high compositional variability that depends on the primary ore, the addition of secondary reactants (total charge), and the stage of the smelting process at which the slag was extracted (42–44). The major and minor element compositions of the lead glass from Šaqunda are well within the compositional range of published data for lead slags (42–44). The presence of high barium and low silver levels in the Šaqunda samples corroborates the use of lead slag (Fig. 2*B*). Barite is associated with the lead ore and dissolves in the slag during the smelting process, while the metal phase absorbs most of the silver (43). The separation of the metallic lead phase during smelting thus gave rise to a lead slag rich in barium and silicates but low in silver that could then be used for glassmaking.

In contrast to these findings, one exceptional sample from Šaqunda is made of soda ash lead glass, a type of glass that has been identified only in the Iberian Peninsula, mainly in 10th-century contexts (27). The main ingredients of this type of glass are lead, silica, and soda-rich plant ash containing high soda, moderate magnesia and potash, and relatively low lime concentrations (Fig. 2*A*). Compared with the high-lead glasses, it has significantly lower alumina, iron, and barium levels but is enriched in chlorine, silver, tin, and bismuth (Dataset S1; MIR 066). This combination of characteristics suggests the use of litharge from silver cupellation, the separation of silver from argentiferous lead instead of the use of lead slag.

Lead Isotopes. In the past, Roman lead-glazed ceramics have been linked to the use of recycled litharge from the silver mines in southern Spain (45). Silver mining in the southern Iberian Peninsula intensified in the early Islamic period, possibly due to rising demands generated by a new monetary system (46–48). Given the mining activities in the region around Cordoba during both the Roman and Islamic periods (49), we hypothesized that the lead raw material used in the production of the high-lead glasses from Šaqunda was locally sourced, indicative of the emergence of a local glass production. The use of waste products (slag, litharge) from ancient mining activities for glassmaking cannot be excluded but seems unlikely. While copper and lead recycling was a common practice during the early caliphal period in al-Andalus (50), silver and lead mining was firmly established in the early Islamic period. For example, Islamic lighting devices and 8th- to 10th-century silver coins were found in some of the galleries of the mines of Los Pedroches (49). The primary production of glass was certainly a new development, as there is no archaeological or analytical evidence of glassmaking in the Iberian Peninsula before the Islamic conquest.

To test our model that the lead in the glass from Šaqunda was derived from a specific mining district in al-Andalus, the lead isotopic signatures of five glass samples were determined (*SI Appendix*, Table S1) and compared with the isotopic composition of ore deposits in the Iberian Peninsula, especially those from the Pyrite Belt in the southwest (51) and from areas in the central Iberian zone, such as the Alcudia Valley, the Ossa Morena zone, Los Pedroches, and Linares (52, 53) (Fig. 3). The lead glasses from Šaqunda have very homogeneous lead isotope ratios within the limit of analytical error, implying a common source of lead. Despite the small number of samples and the difficulties in affiliating a lead isotopic signature to a specific mining district, the lead component can be undoubtedly identified as Andalusian (Fig. 4). After evaluating the isotopic data from the Iberian Peninsula, only ore samples from the mining district of Linares La Carolina (Jaén) and Los Pedroches, located just northeast and north of Cordoba, were identified as a close isotopic match (Fig. 3). In particular, the samples from the Morras de Cuzna mines in Villanueva del Duque (Los Pedroches) have lead isotope ratios consistent with those of the Šaqunda glass (53). A few samples from the Alcudia Valley also have compatible isotopic signatures, but the overlap is only marginal. Lead from these areas was also used for 10th-century metallic objects from Madīnat al-Zahrā', ~7.5 km west of Cordoba (50). The isotopic signatures from the Los Pedroches and Linares mines cannot be separated, and thus it is impossible to assign the lead glasses from Šaqunda to one or the other. The major difference is that Linares was exploited for its lead ores, whereas the Villanueva del Duque mines in Los Pedroches north of Cordoba were mined for silver (49, 50). There is substantial archaeological and textual evidence of silver mining in the early Islamic period, possibly in connection with the establishment of a new silver-based monetary system (54). The extent of lead mining is less clear due to extensive recycling of metallic lead (50). Therefore, we believe it more likely that lead slag generated during silver processing was used for the production of the high-lead glass from Šaqunda, although the use of byproducts of lead mining cannot be excluded.

Discussion

Historical sources attribute the invention of a new type of glassmaking in al-Andalus to the ninth century CE. According to an 11th-century text by Ibn Ḥayyān, for instance, Abū l-Qāsim 'Abbās b. Firnās (809 to 887 CE) was the first to "extract glass out of stone (الحجارة)" (ref. 55, p. 148). What the term الحجارة designates is not entirely clear and may indeed refer to a somewhat unusual ingredient. What is certain from the Šaqunda assemblage is that Abū l-Qāsim 'Abbās b. Firnās cannot have been responsible for the development of lead glass recipes. Our analytical and isotopic data demonstrate that this unusual type of glass was produced in al-Andalus in the first quarter of the ninth century, possibly as early as the second half of the eighth century, when Ibn Firnās was but an infant. This is shortly after the Abbasid uprising in the east and after Umayyad al-Andalus had become an independent emirate.

The compositional makeup of the glass assemblage of Šaqunda illustrates the demise of glass supplies from the eastern Mediterranean, the concurrent increase in recycling practices, and eventually the innovation of a new glassmaking recipe based on the use of lead waste (slag) from silver and lead mining. Following the shortage of fresh glass imports in the seventh and eighth centuries, when only few glass objects from the Near East and Egypt found their way to the Iberian Peninsula, local craftsmen apparently started experimenting with lead slag that forms a glassy mass during the smelting process. The glass tends to be strongly colored (dark amber and bottle green) and probably poses some challenges during its transformation into artifacts. This may explain why the production of this type of slag glass was short-lived. No other glass objects of the same composition have been identified elsewhere, with the exception of lead glazes from the Emiral period (c. 850 to 875 CE) (39, 40). Our results from Šaqunda thus show that the innovations in glassmaking predate the introduction of translucent lead-glazed ceramics in Iberia in the second half of the ninth century (39–41, 56) by more than half a century.

The ninth century seems to have been an exceptionally creative period in the development of local technological traditions.

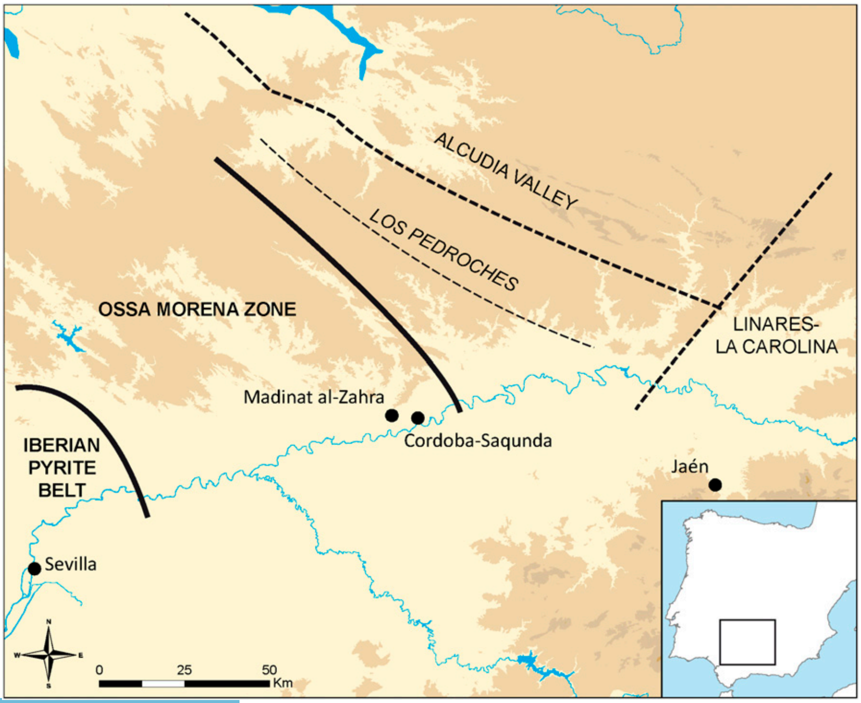

Fig. 3. Areas of historic lead and silver mining districts north of Cordoba (Šaqunda) with matching lead isotope fingerprints.

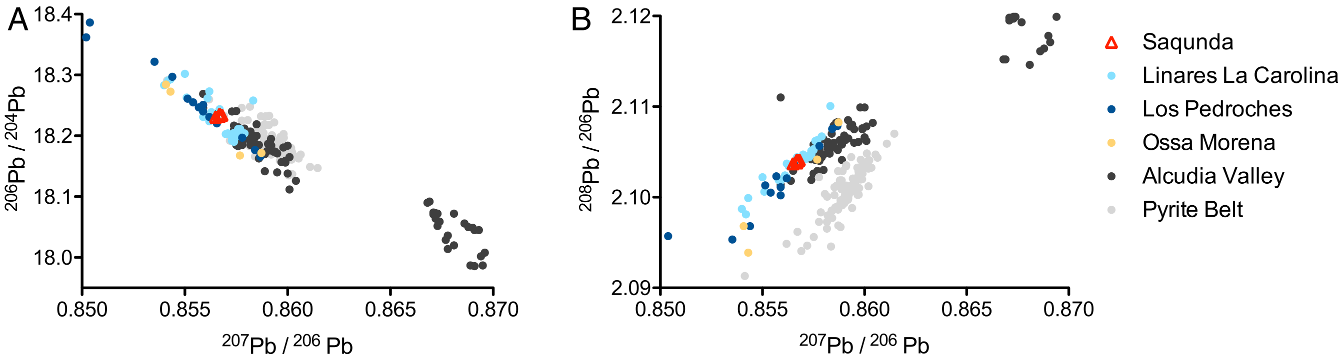

Fig. 4. Lead isotope ratios of the analyzed glasses from Šaqunda and relevant ore deposits in the south of the Iberian Peninsula. Note that the Šaqunda data closely match the deposits from Los Pedroches and Linares La Carolina (*A*), whereas the Iberian Pyrite Belt and the majority of samples from the Alcudia Valley clearly deviate (*B*). Data sources for comparative data of ore deposits: refs. 51–53, http://oxalid.arch.ox.ac.uk/. Note that some data points lie outside of the axis limits.

The high-lead glasses from Šaqunda appear to be among the earliest examples of lead glass produced anywhere in Europe and the Islamic world. The new glass manufacturing technique derived from a waste product of metallurgical processes was subsequently refined by using litharge rather than slag as starting material and the addition of some alkali to the batch. The use of litharge offers a cleaner option and enables the production of nearly colorless glass (MIR 066). The discovery of considerable quantities of soda ash lead glass from Cordoba (14) is a good indication that the production center of this type of glass is likewise in this region, and that the high-lead glasses from the Rabad of Šaqunda may have been a direct precursor of the soda ash lead glassmaking tradition.

In parallel to these developments, another type of glass appears in the archaeological record of al-Andalus. The eighth- to ninth-century plant ash glasses from Šaqunda are the earliest Islamic soda-rich plant ash glasses identified in the Iberian Peninsula to date. These plant ash glasses correspond to Mesopotamian compositional groups, confirming that Islamic plant ash glassmaking was still not firmly established anywhere else in the Islamic world. Historical sources inform us of the presence of merchants from Egypt and Khurasan in Cordoba in the 10th century (57); thus, the import of Mesopotamian plant ash glasses is not unexpected.

The earliest analytical evidence of potentially Iberian plant ash glass production dates to the 10th century (27, 58). It is noteworthy that there are four plant ash glasses dated to the eighth to ninth century among the samples from Cordoba (14); however, without any trace element data and more details about the archaeological context and dating of the samples, the attribution of these glasses remains uncertain. The first mention of a glass workshop is in relation to 11th-century Sevilla, and during the Taifa period, Málaga, Murcia, and Almería were known as glassmaking centers (59). The shift toward Islamic soda ash glassmaking varies according to the geographical region. While there is evidence for a certain degree of continuity in plant ash glassmaking technologies between pre-Islamic and Abbasid Mesopotamia, the first soda ash glass in the Levant dates to the end of the eighth century, and in Egypt this change appears not to have occurred before the 10th century (9, 10, 60). It seems unlikely that soda-rich plant ash glassmaking was introduced to the western Mediterranean before it was established in the Levant and Egypt. Therefore, our present results strongly suggest that the production of lead glass preceded the production of plant ash glasses in al-Andalus. The manufacture of lead glass is technologically less challenging than that of alkali silica glass, because high-lead glass softens and melts at lower temperatures. This means that a more homogeneous melt can be achieved, and that the material can be worked in furnaces that reach lower temperatures.

The cultural and technological connection between the eastern and western Islamic worlds is manifest in the trade of finished objects, as well as the movement of technological and artistic ideas. Accordingly, a chronological delay is usually apparent in the adoption of forms and decorative techniques in al-Andalus and the Maghreb compared with oriental prototypes (6). By the 10th century, the glassmaking tradition was well established in the Iberian Peninsula. Soda ash lead glasses as well as Iberian plant ash glasses have been identified among the glass assemblages from 10th- to 12th-century Vascos (27), from 11th- to 13th-century Murcia (61), and from the Christian territories in the north of Spain in Gauzón (33).

The quantity and quality of glass finds in the Iberian Peninsula have had highs and lows. The development of a local glassmaking tradition was indirectly related to the wider processes of Islamization and may have been conditioned by the geopolitical transformations from a single, universal caliphate under the Umayyads of Damascus to its partial fragmentation after the Abbasid revolution in 750 CE and the establishment of the three competing caliphates (Abbasid, Fatimid, and Umayyad) in the 10th century. The compositional data of the glass finds from Šaqunda can be viewed as an indicator of the wider social and cultural transformations in relation to manufacturing traditions and exchange systems. There is no conclusive evidence for a technological transfer from the eastern Mediterranean to al-Andalus before the 9th or 10th century; instead, the eighth- to ninth-century glass assemblage from Šaqunda reflects the transformation of the glass industry from a centralized production and distribution model to a decentralized system of multiple primary production locations, using new raw materials and new manufacturing technologies. The invention or innovation of lead glass may have been a fortuitous side effect of silver mining and processing, the proliferation of which coincided with the adoption of a monometallic silver-based monetary system (46–48, 54).

The simple transformation of lead slag into glass objects as reflected by the glass finds from Šaqunda represents the first stage of a lengthy trajectory toward the development of a local glass industry. There evidently followed a period of adaptation during which the working properties of the lead-rich material were improved by introducing a fluxing agent and using litharge instead of slag. This suggests a close connection between metallurgy and glass production in early Islamic al-Andalus. The well-documented glass workshops from Murcia at Puxmarina and Belluga that were active in the 12th century seem to have combined primary and secondary workshops for the entire production cycle from the raw materials to the finished products, including possibly even the processing of lead (62). Evidence from the 9th- and 10th-century ceramics workshop at Pechina (Almería) and San Nicolás (Murcia) also suggests close interactions between the production of glass and glazes (40, 56, 63). Thus, the advent of lead glasses in Šaqunda signals the technological, economic, and cultural emancipation of early Umayyad Iberia.

Materials and Methods

A total of 78 individual glass artifacts (69 vessels and 9 bangles) were recovered during the excavations by the Gerencia Municipal de Urbanismo de Córdoba in 2001, 2002, and 2005. Only reliable stratigraphic contexts have been considered, and sampling was not selective, to minimize potential bias. All the glass fragments in each context were separated and typologically assessed. A single sample of each object was taken to capture the entire population of the glass finds from Šaqunda. None of the glass vessels are intentionally colored, and decorations are rare and limited to applied threads. One exception is an unusual stained glass (luster) fragment of a beaker decorated with vegetal motifs and an inscription in austere Kufic that support an eastern Mediterranean provenance of this object (25). The glass bracelets have diverse colors (yellow, dark blue, opaque black, or colorless) and shapes, including twisted with circular or rectangular cross-sections, ribbed, and plain with circular cross-sections.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry. The chemical compositions of the glasses were determined following a standard laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) protocol (64). The mounted and polished cross-sections were analyzed using a Resonetics UV laser microprobe (193-nm excimer laser coupled with a Thermo Fisher Scientific Element XR ICP-MS system) at IRAMAT-CEB (Orléans, France), operating at 5 mJ with 10-Hz frequency and a typical spot size of 100 μm. A preablation time of 15 s was followed by 30 s of analysis. The signal intensities were converted into quantitative results based on an internal standard (^{28}Si) and a suite of international standards (National Institute of Standards and Technology [NIST] SRM610; Corning B, C, and D). Accuracy and precision were monitored by intermittent analysis of reference glasses (NIST SRM612; Corning A, B, D) (*SI Appendix*, Table S2).

Lead Isotopes. Lead isotope analyses were conducted at the Bureau de recherches géologiques et minières (French Geological Survey, Isotope Laboratory) in Orléans, France. Small fragments of glass were dissolved with HF at 120 °C in a Teflon container. The solutions were dried and then dissolved with 1 M HBr. The Pb was then purified with AG 1X-8 ion-exchange resin using HBr and HCl acids. After evaporation, the residue was recollected with HNO_3 and dried again. Blanks for the overall procedure were <100 pg and negligible relative to the amount of sample analyzed. Measurements of the lead isotope ratios (^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb) were obtained on static mode on a multicollector Finnigan MAT262 thermal ionization mass spectrometer. Samples and standards were loaded on a zone-refined rhenium filament that had been previously outgassed. Silica gel was used as an emission stabilizer. Approximately 150 ng of Pb was loaded with H_3PO_4 onto each filament. The Pb isotopic ratios were corrected for a mass bias of 0.13% per atomic mass unit as determined by repeated measurements of the NIST NBS982 standard. The individual error in all ratios was often better than 0.01% ($2\sigma_m$), while external reproducibility (2σ) was 0.06% for the ^{206}Pb/^{204}Pb ratio, 0.07% for the ^{207}Pb/^{204}Pb ratio, and 0.09% for the ^{208}Pb/^{204}Pb ratio.

Data Availability. The complete lead isotope data are provided in *SI Appendix*, Table S1, and all LA-ICP-MS data are provided in Dataset S1.

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