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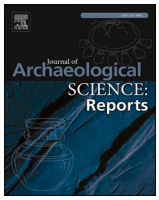

The rise and fall of antimony: Sourcing the "colourless" in Roman glass

P. Degryse [a,b], S.N. Gonzalez [a], F. Vanhaecke [c], S. Dillis [a], A. Van Ham-Meert [a,*]

[a] KU Leuven, Earth and Environmental Sciences, Celestijnenlaan 200E, 3001 Leuven, Belgium
[b] Leiden University, Faculty of Archaeology, Einsteinweg 2, 2333CC Leiden, The Netherlands
[c] Ghent University, Department of Chemistry, Atomic and Mass Spectrometry – A&MS Research Unit, Campus Sterre, Krijgslaan 281 - S12, 9000 Gent, Belgium

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ABSTRACT

Antimony (Sb), a metalloid, is considered a rare occurence in the archaeological record. Though Sb ores are scarce they were utilised over several millennia for a variety of applications from copper alloys to glass and glaze. In particular, they were used for opacifying or decolouring glass and glazes. Amongst Sb minerals, only stibnite can achieve, in a controlled manner, the desired effect as a decolourizer or opacifier. Mass production of Sb-decoloured natron glass seemingly halts close to the time that Dacia is lost to the Roman empire. The use of Sb as an opacifier soon follows suit, with Sn replacing it. In this paper we investigate the possibility that the disappearance of Sb-decoloured glass production is linked to the loss of access to the mines of Dacia. Lead and re-evaluated Sb isotopic analyses show that the most likely sources of stibnite for late Roman Sb-decoloured natron glass are indeed the stibnite mines of Dacia.

1. Introduction

1.1. Antimony in ancient glassmaking

Antimony (Sb) has seen a long history of use from the 5th millennium BCE onwards, first in metallurgy as a natural alloying element in copper alloys, and subsequently and perhaps more importantly in the earliest vitreous material industries in which Sb is used as an opacifier. In white opaque glass, Sb is present under the form of $Ca_2Sb_2O_7$ or $CaSb_2O_6$; in combination with Co and Cu these crystals lead to opaque blue glasses. In opaque yellow glass, colour and opacity are the consequence of the presence of lead antimonate $Pb_2Sb_2O_7$ (Shortland, 2002). Lead antimonate in conjunction with blue colourants yields opaque green glasses. Early glass is considered an elite material. It was mostly used as a substitute for semi-precious stone such as lapis and turquoise. It has been suggested that the earliest yellow glass may have been equivalent in use to gold (Shortland, 2012). This highlights the importance of stibnite in ancient glass making.

From the Hellenistic period onwards, Sb-bearing minerals were added during glass production to obtain translucent, colourless glass (Ignatiadou, 2002). Adding Sb counters the effect of iron and other colour-inducing traces in the raw material batch by reducing them. A full description and explanation of how decolourising elements such as Sb and Mn work is beyond the scope of this paper but can be found elsewhere (Jackson, 2005; Bidegaray et al., 2020). Even glass that was made from very pure sands, which is naturally nearly colourless, can exhibit a high concentration of added antimony. This is thought to be linked to the ability of Sb to render the glass more brilliant (Gliozzo, 2017, Paynter and Jackson, 2019), while it also works as a fining agent (Jackson, 2005). Paynter and Jackson (2019) further show that high-sodium low-calcium glasses in particular (such as the Roman and late antique glass (4th to 8th century CE) produced in Egypt) dissolve Sb leading to decoloured glass, whereas glass with less sodium and more calcium (compositions typically found in glass from the Syro-Palestinian coast) are more prone to form calcium antimonate crystals leading to an opaque glass. They also note that Sb-decoloured glass starts as a luxury, rare product in the Hellenistic period, is ubiquitous in the Roman Imperial period and then disappears from the record in the 4th century CE, presumably due to dwindling Sb-supplies. This of course raises the question of why this was the case and is the subject of the present paper.

In the Mediterranean, during the 4th century CE, the use of Sb in glass making ceases (Jackson, 2005; Paynter and Jackson, 2016 figure 6). Tin (Sn) replaces Sb in opaque glass, and whereas manganese (Mn) and Sb had both been in use to decolour glass, but in different geographical areas (Mn in the Levant and Sb in Egypt) (Gliozzo, 2017; Barfod et al., 2020), Mn is now also used in Egyptian production. Sainsbury (2017) observed this shift in the British glass assemblages and, based on the fact that Sb is a more effective decolourant than Mn,

* Corresponding author.
E-mail address: Alicia.Vanhammeert@kuleuven.be (A. Van Ham-Meert).

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concludes that this shift could not have been a technical choice, but had a different reason. In the case of Egyptian HIMT glass, it has been suggested that Mn was added, to make it more yellow, as a means to distinguish it from the aqua coloured Levantine glasses (Freestone et al., 2018). This paper proposes that the disappearance of Sb as a (de)colourant might have been linked to a diminishing Sb raw material supply.

For glassmaking, stibnite was the only available mineral resource that could provide sufficiently pure Sb to produce the desired opaque strong colours of the earliest glass (Jackson, 2005; Degryse et al., 2020), or to decolour translucent glass without introducing unwanted sources of colour under the form of associated elements. Despite the ubiquitous use of Sb in early (glass) pyrotechnologies, stibnite mining has only rarely been studied. To provenance antimony ores used in ancient materials, several ore types with archaeological relevance have been geologically characterized previously (Dillis et al., 2019) and high-precision Sb isotopic analysis was developed as a method to be able to compare artefacts to ores (Lobo et al., 2012, 2013, 2014, Degryse et al., 2015). Laboratory experiments making opaque glass with known raw materials under controlled conditions, revealed that fractionation of the Sb isotopes occurs in the redox process converting stibnite ore (Sb(III)) to Sb(V) oxide. The range of fractionation appears to be around $^{123}\Delta$ Sb = 0.25 to 0.30 ‰, or up to 3 ε-units (Dillis, 2020, Degryse et al., 2020, Zhai et al., 2021). However, since the induced isotopic shifts can be explained by redox processes, isotopic signatures can possibly be corrected for the corresponding fractionation and still be used as a fingerprint to provenance antimony ore sources, provided the redox processes from raw material to finished product are known. Initial Sb isotopic analysis has shown that the only known match for the isotopic composition of Late Bronze Age Egyptian and Mesopotamian glass vessels are stibnite ores from the Racha-Lechkumi district in the Caucasus (present-day Georgia) (Dillis et al., 2019, Degryse et al., 2020), near the Zopkhito Au-Sb deposits, mined from the 17th century BCE onwards (Chernykh, 1992), just before the start of widespread glass production. This is in line with what was already suggested by Shortland (2002).

Roman to late antique colourless glass vessels and opaque mosaic tesserae showed a different Sb isotopic composition, possibly related to the use of more varied Sb sources, although the common practice of recycling may have mixed the signatures (Degryse et al., 2015). Furthermore, the Sb isotope ratio provides one parameter to study the origins of the decolourant/opacifier in Roman glass only, displaying the usual overlap between sources. Huisman et al. (2009) suggested before, based on variations in Pb and Sb concentration, that multiple sources of Sb were used in natron glass making. Our hypothesis is that one particular source of stibnite, the deposits located in Dacia, were the main source of Sb used for glass decolouring during the late Roman period. This study looks at the Pb isotopic compositions of ores and such glass, to disentangle possible Sb sources.

1.2. Lead sources and lead isotope ratios in colourless glass

In this paragraph, only incidental addition of Pb is considered. In the case of deliberate addition of lead, the lead isotopic composition would be that of the added lead and would not allow to trace the source of antimony. The unintentional introduction of Pb in colourless natron glass can be due to the sand source used (where minerals other than quartz or lime can contain some lead), the mineral matter added to (de) colour the batch, contamination from the clay lining of the tank furnace or the working installations and crucibles, or recycling of cullet and strongly coloured glass. The presence of multiple sources of lead could lead to mixed lead isotopic signatures, the influence of each raw material depending on the concentration of lead in the original material, as well as their relative contribution in the glass. The stibnite sources investigated by Dillis (2020) and analysed for their Pb isotopic composition were variable in lead content (10 s to 1000 s of ppm). Assuming 0.8 wt% Sb in the glass (which is the average value in the samples considered here), this would result in up to 8 ppm Pb in glass resulting from the Sb-source. In glass with 12 to 170 ppm Pb in total, this corresponds to a 4 to 75 % contribution from the Sb source. It is assumed that the Pb isotopic composition of the glass investigated here is a mixture of the lead isotopic signatures of the silica source and stibnite used to produce these colourless glasses, admittedly ignoring the influence of recycling or contamination. The original Pb concentration in sand and ore governs the relative contributions of both materials. Glasses with elevated lead concentrations due to deliberate addition of lead, or indicative of recycling/mixing are not considered in this paper.

2. Re-interpreting Sb-isotopic data

A collection of 30 colourless glass samples were previously analysed for their Sb isotopic composition by Lobo et al. (2013) and Degryse et. al. (2015), and the results are re-interpreted here. These samples originate from 7 different locations (Degryse et al., 2005, Ganio et al., 2012a, 2012b): Kelemantia in Slovenia (1 glass from the 2nd century CE), Oudenburg in Belgium (3 glasses from the 1st–3rd century CE), Embiez in France (5 glasses from the 2nd–3rd century CE), Augusta Pretoria in Italy (4 glasses from the 1st century CE), Potentia also in Italy (3 glasses from 1st to 4th century CE), Sagalassos in Turkey (4 glasses from the 1st–3rd century CE) and Bocholtz in the Netherlands (10 samples from the 2nd–3rd century CE).

Lobo et al. (2013) showed that the Sb isotopic composition (expressed as epsilon values) obtained for colourless glass shows a variation of up to 3 ε-units (i.e. 0.3 ‰). Separated by chronology, 1st c. CE Roman Sb-decoloured glass displays minor variation in Sb isotopic signature, while 3rd-4th c. CE glass is very uniform in its Sb isotope ratio. Ores matching those Sb isotopic signatures are found in Spain, Romania-Slovenia, Germany and the Caucasus for the earlier glass, while the later material matches only Romanian and Spanish stibnite (Lobo et al., 2013, Dillis, 2020). Remarkably, epsilon Sb values higher than 1 can only correspond to the use of Spanish or Romanian sources, while the lowest values (<0 epsilon Sb) can only be attributed to the use of German or Caucasian ores.

3. Materials and methods

For this study, 12 samples of Roman glass decoloured with Sb only and showing no signs of recycling in their trace element profile were selected for Pb isotopic analysis (see Table 1). The methodology was adapted from Rademakers et al. (2020). These glasses originate from 3 different locations (Degryse et al., 2005, Ganio et al., 2012a, 2012b): Embiez in France (4 glasses from the end 2nd – 3rd century CE), Iulia Felix also in Italy (7 glasses from the first half of the 3rd century CE) and Sagalassos in Turkey (3 glasses from the 1st or the 4th – 5th century CE).

Table 1
Description of samples measured in this paper.

sample name	location	type	date	publication
IF-C03	Iulia Felix	cup	1st half 3rd century	Ganio et al.
IF-C11	Iulia Felix	cup	CE	2012
IF-p20	Iulia Felix	plate		
IF-P3	Iulia Felix	plate		
IF-B05	Iulia Felix	bottle		
p23	Iulia Felix	plate		
c17	Iulia Felix	cup		
E258	Embiez	raw glass	end 2nd beginning 3rd CE	
E272	Embiez	raw glass		
gobA	Embiez	cup		
gobB	Embiez	cup		
SA-92-N-330	Sagalassos	cup	4th-5th c. AD	
SA-93-L-143 (A) (2)	Sagalassos	cup	1st c. AD	
SA-92-N-285	Sagalassos	cup	4th-5th c. AD	

Furthermore, results from lead isotopic analysis of Sb-decoloured glasses reported in literature are also incorporated in the study (see Table 2): Meroitic glass (2 glasses, 350 BCE-350 CE, Spedding, 2022), glass from Bocholtz in the Netherlands (10 samples from the 2nd–3rd century CE, Huisman et al., 2009), and Sagalassos in Turkey (2 glasses, Degryse et al., 2005).

4. Results

It needs to be stressed that important assumptions are made in the interpretation of the isotopic composition of the materials studied, in particular with regard to fractionation of the Sb isotopes in the glass making process, and in accepting that the Pb isotopic signature of the glass studied is the result of a binary mixing of Sb ore and Syro-Palestinian or Egyptian silica sources without any other effects of mixing or recycling. We feel confident in making these assumptions as the glass objects/chunks chosen for this analysis have no mixed Mn-Sb contents or other recycling markers (such as elevated concentrations of transition metals).

4.1. Pb isotopic composition (IC) of stibnites of interest

The present research is necessarily limited by the available data. The Pb ICs considered here were obtained from our own work on Sb deposits (Dillis et al., 2019), as well as data present in the IBERLID and GLOBALID databases. There are, however, limitations. On the one hand, not all Sb-bearing ores have been characterised for their Pb IC. It must be noted that some stibnite ores from within the confines of the Roman Empire are not considered, as there is no evidence for their exploitation during the Imperial period. A good example are the Sb-Au deposits of Dùrico-Beirão (Portugal), known to have been exploited for gold during the Roman period, but exploitation for Sb only started in 1858 (Couto et al. 1990). Furthermore, when a Pb IC is available, exact GPS coordinates and lead concentration are often not. Nevertheless, the data presented yield a number of observations useful for provenancing purposes.

Table 2
Other samples considered in this paper with the original publication.

sample name	location	type	date	publication
UC44278.3	Meroe	not specified	Meroitic period	Spedding, 2022
UC44278.5		not specified	Meroitic period	
103	Bocholtz	bowl or plate	2n-3rd century CE	Huisman et al., 2009
104.1		bowl or plate		
105.1		cylindrical bottle		
106		bowl or plate		
107		Globular jug with pinched-in spout		
108		Globular jug with pinched-in spout		
109.1		cylindrical bottle		
110		Globular jug with pinched-in spout		
112		?		
113		cylindrical bottle		
114		cylindrical bottle		
115		cylindrical bottle		
118		bowl or plate		
119		bowl or plate		
120		bowl or plate		
121		bowl or plate		
122		bowl or plate		
13		bowl or plate		
124		bowl or plate		
125		bowl or plate		
126		bowl or plate		
578	Sagalassos	?	350–450 CE	Degryse et al., 2005
579	Sagalassos	?		

The Pb IC of the considered ores are represented in Fig. 1. Information on exact location, values and original publication of the ores are reported in ESI-1. Spanish ores have a wider spread of signatures, as would be expected for various deposits of different ages, and the same is true for Turkish ores. One of the Turkish ores overlaps with a Czech ore in both the $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ plot and the $^{207}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ plot, hence, these deposits cannot be distinguished from each other. The Romanian ores, as well as one Turkish, one Spanish and 2 Slovakian ores are characterised by more radiogenic signatures on both isoplots, with the Romanian ores from the Baia Sprie-Kavnik region forming a tight cluster. The two Slovakian ores plotting in the neighbourhood of the Romanian ores are from neo-volcanic deposits similar (and geographically close) to the Romanian ores, the other come from various types of deposits in Slovakia (Andráš et al., 2010). All but one Georgian (Caucasus) ore form a tight cluster with a less radiogenic signature. It is in fact easy to distinguish the Caucasian ores, proposed as the source of stibnite for late Bronze Age Egyptian glass (Degryse et al., 2020) from Romanian ores, hypothesised as a source for the Sb used to decolour Roman Imperial glass. Most Slovakian ores form a more scattered group, less radiogenic than the Caucasian ores. Portugese ores are even less radiogenic, with finally the German ores as the least radiogenic ones. The scattered nature of many of the ore compositional patterns, makes exact provenancing complicated. However, the sequence of most radiogenic (Romanian ores) to least radiogenic (German ores) is useful for the question at hand.

4.2. Naturally colourless, naturally coloured and Sb-decoloured glass

In Fig. 2, data for different glass samples, including very pure colourless Sagalassos glass (samples 588 and 594, full yellow circles) and Levantine glass chunks: 3 from Bet Eli'ezer (L14.B190/1; L14.B190/4; L14.B190/5) and 3 from Apollonia (6831–10; 6831–11; 6831–12) are plotted (the Pb IC are also reported in Table 3). The Iulia Felix samples which are vessels glass and date to the early 3rd century CE span nearly the whole breadth of Pb ICs, with only L15.B190/1 from Bet Eli'ezer and 6831–10 from Apollonia having less radiogenic signatures. The chunks from the Embiez shipwreck, have nearly identical Pb ICs, whilst the two vessel glasses have more varied compositions. Whilst it is worth noting that chunk glass have a more consistent signature than vessel glass, the sample size is too small to make confident statements on the subject. Both chunks from the Embiez are more radiogenic than the raw glass chunks from Apollonia and Bet Eli'ezer.

The samples from Huisman et al. (2009) correspond, when considering their TiO_2/Al_2O_3 versus Al_2O_3/SiO_2 composition, to a typical Roman-Sb signature (see ESI 3 figure A). The authors noted that there were two main sample types in their dataset, one with very low Pb (<25 ppm) and one with higher lead contents (45–110 ppm Pb), which roughly corresponded to two distinct Pb ICs. However, as shown in ESI 3 figure B, this is not entirely accurate, there is some overlap. When considering the Bocholtz data with the other Pb ICs available from literature, it can be seen that the Bocholtz samples simply span the entirety of the spectrum of compositions.

To make the discussion easier, the samples from Apollonia and Bet Eli'ezer will be plotted together as "levant chunks". The objects from the Iulia Felix and the Embiez shipwreck will also be plotted together. Since the Meroitic chunks fall in the middle of the Pb IC compositions and are of uncertain date, they will not be included in the rest of the discussion. The few samples from Sagalassos fall within the range of the Bocholtz samples and will not be plotted in subsequent graphs. The ores from Rheinland and Portugal have less radiogenic signatures than all of the glass samples. Since the non Sb-decoloured samples have less radiogenic signatures than those containing Sb, the Sb ores should show a more radiogenic Pb IC than the glass samples. Therefore, the Rheinland and Portugese ores will not be included in the subsequent discussion.

In Fig. 3, the Pb ICs of the ores discussed above are plotted with the

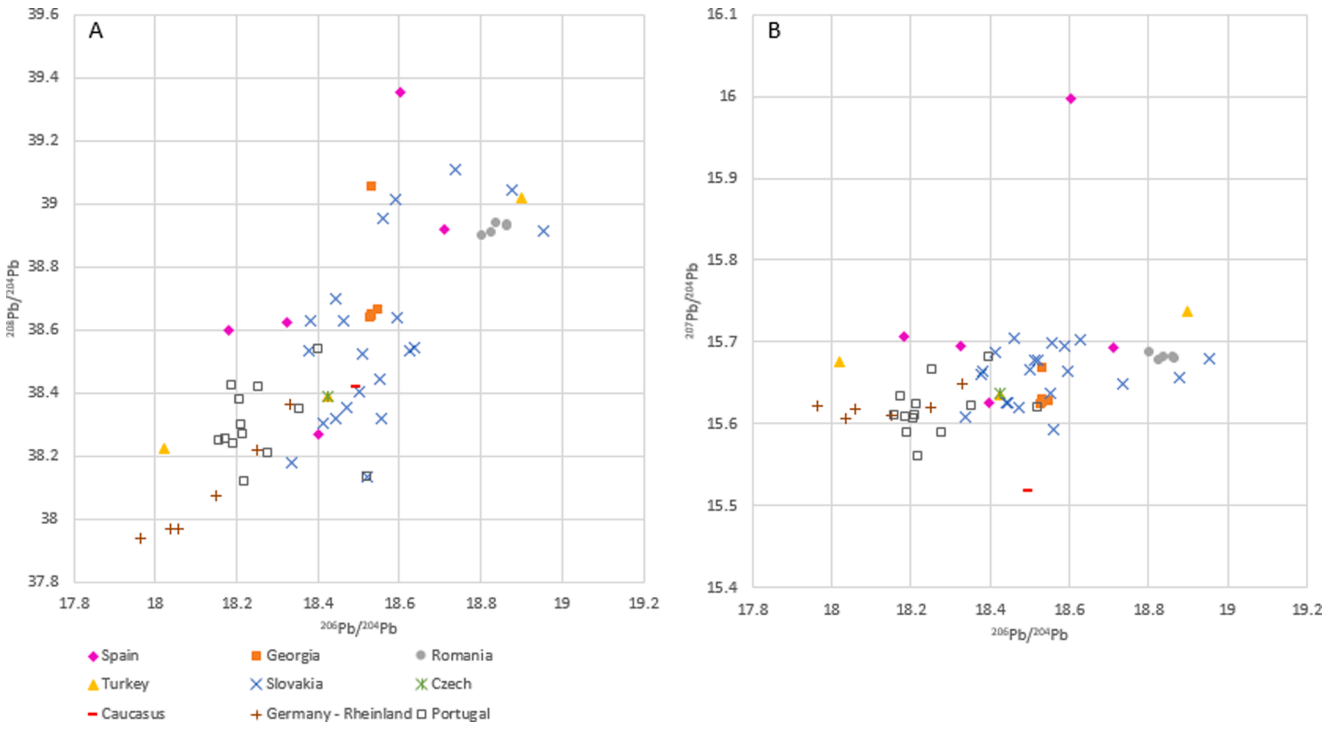

Fig. 1. Pb IC of different ores relevant for the question (Dillis, 2020, Mateus et al., 2006, Neiva et al., 2008, Stos-Gale and Gale 1981, Andráš et al., 2010).

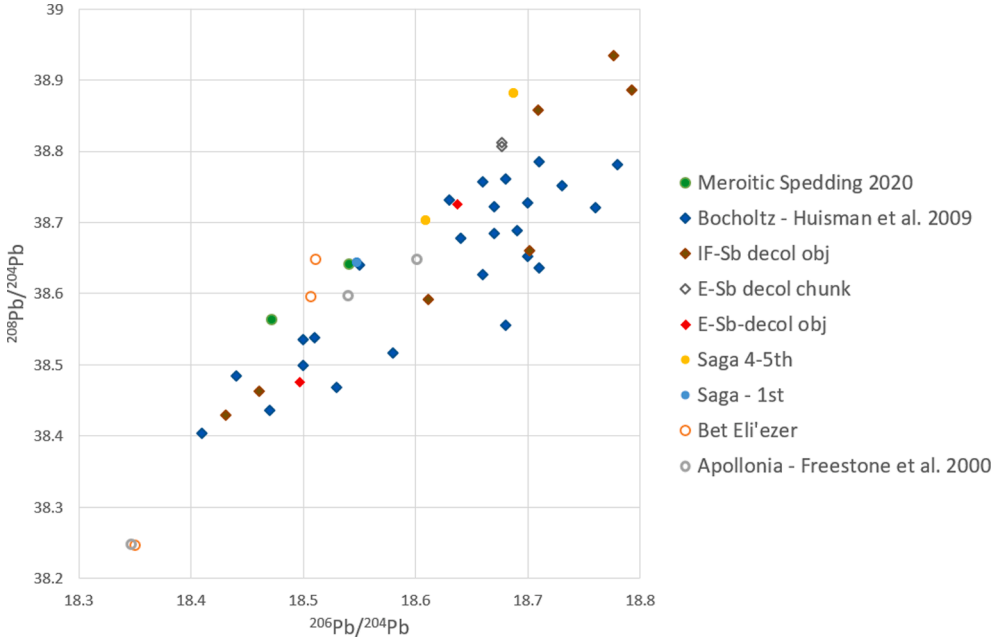

Fig. 2. Lead isotopic compositions of Sb-decoloured glass (diamonds) and glass without decolorant (circles), chunks have open symbols, objects are filled symbols.

Pb ICs of the high-Sb, low-Pb samples, whose Pb IC we expect to be a two-component mixture of lead from the stibnites and lead from the sand. It is noteworthy, that the samples plot on a more or less straight line which could be understood as a mixing line. Since the Sb-decoloured samples have more radiogenic signatures than the non-decoloured end-members (Fig. 2), the Sb ores have to be characterised by radiogenic signatures. Georgian, most Slovakian and most Spanish ores can therefore immediately be disregarded because they are either less radiogenic than all the glass samples (Spanish ores), or lie along the mixing line (for the Georgian, Caucasian and Czech ores). If those ores were the source of stibnite, the mixing trends would look very different. The best candidates are the Romanian ores, the Slovakian ores which correspond to similar deposits (see also Marcoux et al., 2002, Baron et al., 2011) and one Turkish ore. This is in line with the results from Sb isotopic analysis (which suggested Spanish or Romanian ores), and our hypothesis that Dacian ores were used as stibnite source for Sb-decoloured glass during Roman Imperial times.

The geochemical mixing lines with a Pb-isotope ratio on the y-axis and 1/Pb on the x-axis yield a picture which is harder to read (Fig. 4). When considering the left figure with $^{208}Pb/^{204}Pb$, there seem to be three groups of samples, one with a Spanish ore as potential mixing end-member (the mixing line is not drawn, but those samples are above the

Table 3
Pb IC glass samples measured for this paper, the chemical composition is from Monika Ganio's PhD.

Sample no.	Location	MnO (wt%)	Pb (ppm)	Sb_2O_3 (wt%)	value					2SE				
					Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}	Pb^{207}/Pb^{206}	Pb^{208}/Pb^{206}	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}	Pb^{207}/Pb^{206}	Pb^{208}/Pb^{206}
IF-C03	Iulia Felix	0.01	12	1.12	18.431	15.650	38.430	0.849	2.085					
IF-C11	Iulia Felix	0.01	14	1.2	18.461	15.689	38.463	0.850	2.084					
IF-p20	Iulia Felix	0.01	167	1.19	18.709	15.712	38.858	0.840	2.077	0.002	0.002	0.005	0.000	0.000
IF-P3	Iulia Felix	0.01	43	0.98	18.777	15.696	38.934	0.836	2.074	0.002	0.002	0.005	0.000	0.000
IF-B05	Iulia Felix	0.02	15	0.88	18.702	15.685	38.661	0.839	2.067	0.002	0.002	0.004	0.000	0.000
p23	Iulia Felix	0.02	19.78	1.48	18.792	15.701	38.886	0.836	2.069	0.002	0.002	0.002	0.002	0.002
c17	Iulia Felix	0.01	5.37	1.2	18.612	15.690	38.592	0.843	2.074	0.003	0.003	0.003	0.003	0.003
E258	Embiez	0.02	29	1.5	18.677	15.667	38.812	0.839	2.078	0.002	0.002	0.004	0.000	0.000
E272	Embiez	0.01	22	1.36	18.677	15.666	38.806	0.839	2.078	0.002	0.002	0.004	0.000	0.000
gobA	Embiez	0.02	142.07	1.25	18.497	15.639	38.476	0.845	2.080	0.004	0.002	0.005	0.000	0.000
gobB	Embiez	0.02	0.67	0.93	18.638	15.658	38.726	0.840	2.078	0.025	0.025	0.025	0.025	0.025
SA-92-N-330	Sagalassos		61		18.609	15.676	38.703	0.842	2.080					
SA-93-L-143 (A) (2)	Sagalassos				18.548	15.703	38.644	0.847	2.083					
SA-92-N-285	Sagalassos				18.687	15.691	38.881	0.840	2.081					

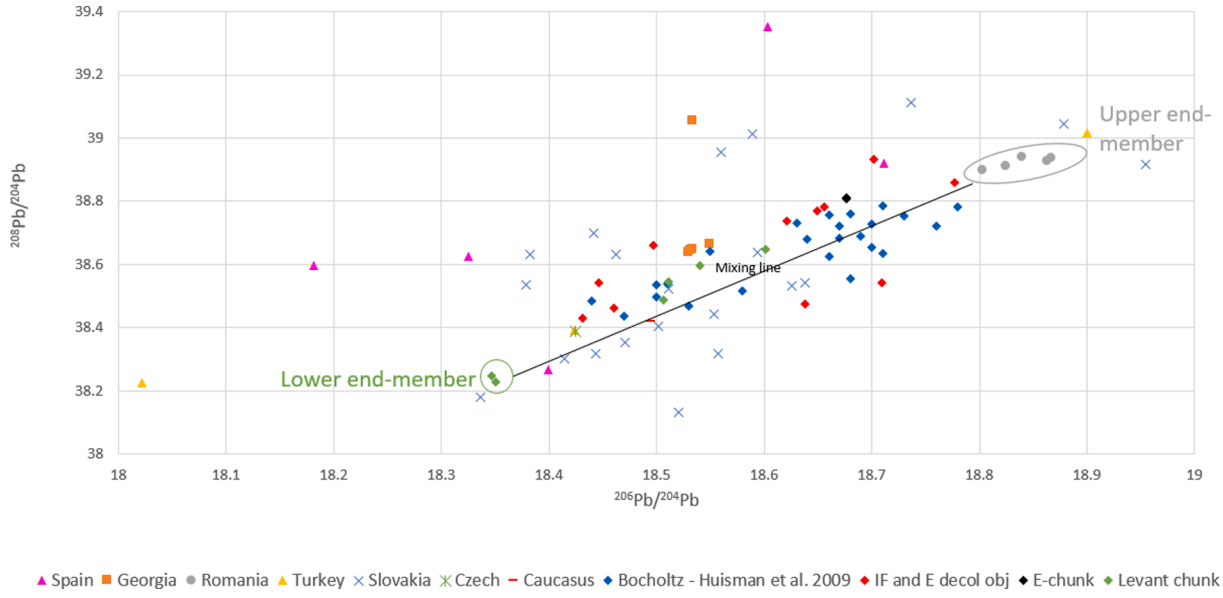

Fig. 3. Pb ICs of relevant ores, Sb-decoloured glass and non-decoloured glass, with a potential mixing line indicated on the graph.

blue mixing lines), one with Romanian ores as potential end-member (blue lines) and one with Georgian ores as potential end-members (green dotted lines). It is interesting to note that the two groups in the Bocholtz samples appear on these graphs, with the higher lead, less radiogenic samples corresponding to potential Georgian ores and the lower lead, more radiogenic samples corresponding potentially to Romanian ores. The sands used for comparison here are based on measurements from Brill on Israeli sands (Brill, 1999). As most Sb-decoloured glasses are thought to be of Egyptian origin, these sands are not the best candidate as value for the silica end-member, neither are the Levantine chunks. Yet, as shown in Fig. 4, they concur with the results from the Sb isotopic analysis. In the next section, results for HIMT glasses are also considered, these are not Sb-decoloured, but are known to be of Egyptian origin and hence provide a good comparison for Egyptian silica sources.

4.3. HIMT glass and its relation to Sb-decoloured glasses

In Fig. 5, HIMT glasses are added as a potential end-member for Egyptian glass. HIMT glass is produced, presumably in Egypt, around the end of the production of Sb-decoloured glass (Freestone et al., 2018). The HIMT samples for which the Pb IC is known, are samples from Wedepohl and Baumann (2000) found in Germany and dated 2nd-4th century CE. Wedepohl and Baumann suggested they might be a local German production, but Freestone et al. (2009) showed that these were actually HIMT, the second set of HIMT glasses are finds from the UK, Carthage and Sinai as published by Freestone et al., 2003.

It is immediately apparent that the HIMT glasses present a scattered pattern with Pb IC values situated around the mixing line, but not on the end-member. In their discussion on the HIMT glasses, Freestone et al., 2009 conclude that the lead concentration in HIMT glasses is variable and increases with the K-content which he attributes to contamination of the sand with clays from the Nile river containing feldspars. This elevated lead content is visible in Fig. 5.b. For the samples with the lower Pb concentrations, the composition is close to what is expected for Levantine sands (Freestone et al., 2009). Since the earlier non-decoloured Egyptian glasses tend to have lower Pb concentrations and are in general made with "cleaner" sands, these are expected, based on

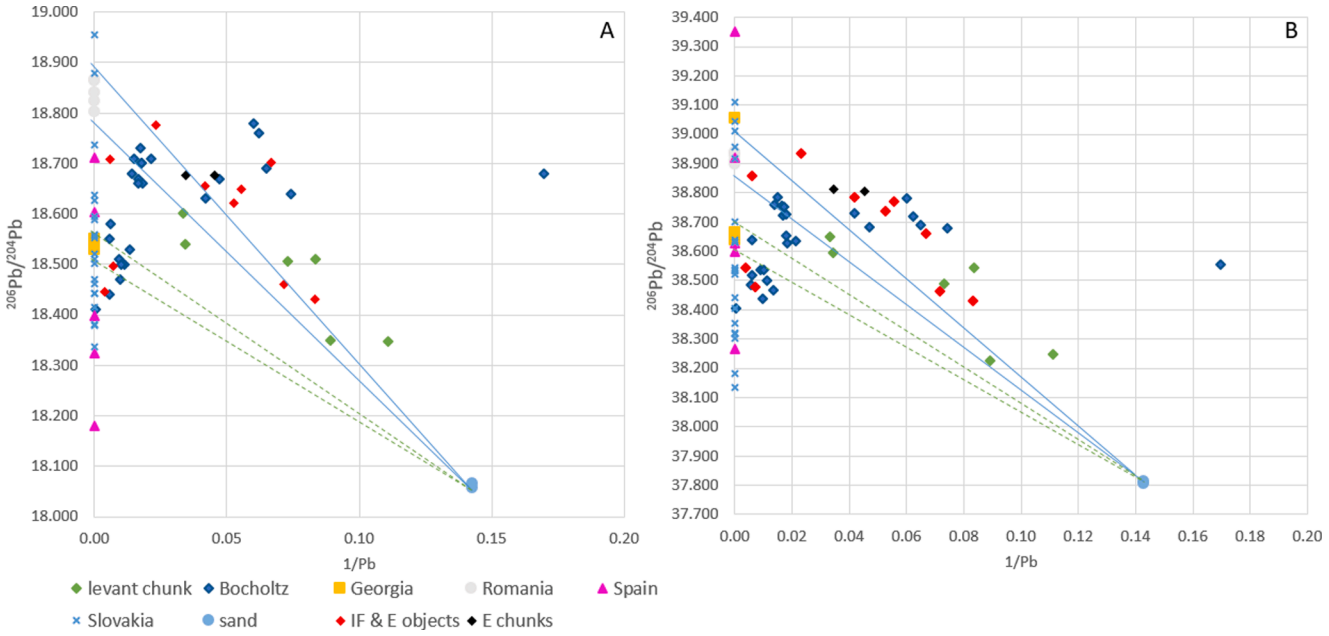

Fig. 4. The full blue mixing lines represent the range of compositions expected for a 2-component mixture of Romanian stibnites and Israeli sands, the green dotted lines are a mixture of Georgian ores and Israeli sands. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

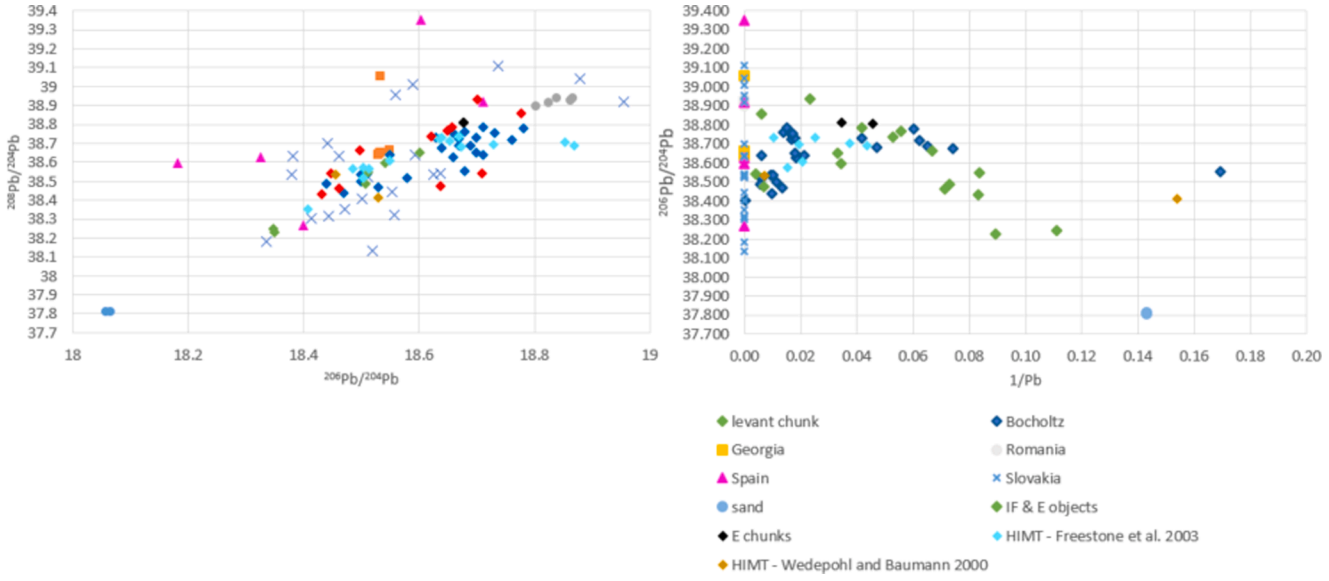

Fig. 5. Pb ICs of Sb-decoloured glass, stibnite ores and HIMT glass (Wedepohl and Baumann, 2000, Freestone et al., 2003.

Freestone's argument, to be close in Pb IC to Levantine material, hence validating our approach in 4.2 to use those sands as end-member.

5. Discussion

Using Pb ICs, the provenance of stibnite used for high-Sb, low-Pb glass is refined. The match between the Romanian stibnites ores as an end-member for one of the mixing lines of lead isotopes in glass, indicates these are at least one probable source of Sb in Roman Imperial glassmaking. We are still missing an appropriate end-member for the silica source, but have used Levantine sands and HIMT glass as a proxy.

The end of the use of Sb for glass decolouring appears to coincide or happen slightly later than the political turmoil in and eventual complete loss (for the Roman Empire) of a territory hosting stibnite mines. The Roman administration in Dacia lasts from 106 to 271 CE and there is evidence for mining in the 2nd and 3rd centuries at *Roșia Montană (Alburnus Maior)*, one of the major sites for gold mining), yet the wooden wax tablets found there are dated between 131 and 167 CE (Baron et al., 2011 and references therein, Green and Smythe, 2021). It is interesting to note that the use of this gold can be traced in Roman coinage by looking at its Sb content as gold and antimony appear together in these deposits. As suggested by Paynter and Jackson (2019) and shown for the gold mines in Dacia (Green and Smythe, 2021), it is likely that access, exploitation and export of stibnite from Dacia was also organized by the Roman authorities. This would explain why, once the Roman authorities leave, the mines close. In particular, the invasions by Vandals and Sarmatians have been suggested as the cause for the closure of the mines at the time (Green and Smythe, 2011).

The potential match with Georgian ores for some of the Bocholtz samples might be a hint for the source of Sb before the exploitation of the Dacian mines. Ores from this region had long been used, particularly in Egypt as a source of Sb for opacifying glass (Dillis et al., 2019).

It could thus be that loss of access to Dacian stibnites meant the end of a technology. It does pose the question, however, as to why other ores in e.g. Spain or Luxembourg were not exploited to a larger extent as an immediate alternative (there is evidence for the exploitation of Luxembourgian mines in the Roman period (Fillela et al. 2009)) or why they did not revert to the use of Georgian ores. This could be linked to the scale of production, necessitating large amounts of stibnite to be mined and transported to Egypt.

6. Conclusion

The Pb isotopic data from this study indicate that Sb-decoloured glass made during Roman Imperial times was fabricated with Sb sources either having originated from the same source or multiple sources with similar Pb isotopic compositions, assuming a binary mixing of Pb from the Sb ore and silica source. Relatively few sources of Sb have a suitable signature to function as an end-member of this mixing line. Most of the later Sb-decoloured glass is uniform in composition and matches well the Sb-Pb isotopic signature of a binary mixing of eastern Mediterranean silica and Romanian stibnite. Interestingly, access to this particular source of raw materials may have been hindered or lost with the loss of the Roman province of Dacia, corresponding in time to the disappearance of Sb-decolouring and opacifying as a technique in glass and glaze manufacturing. One can argue that the loss of access to large enough quantities of stibnite, a trade perhaps controlled by the Roman authorities, determined glass making technology: while the production of decoloured glass continued past the 4th century CE, variations in the boundaries of the Roman realm may have dictated a change in decolourant used.

CRediT authorship contribution statement

P. Degryse: Funding acquisition, Writing – original draft, Conceptualization, Writing – review & editing. **S.N. Gonzalez:** Formal analysis, Writing – review & editing. **F. Vanhaecke:** Funding acquisition, Writing – review & editing. **S. Dillis:** Formal analysis, Writing – review & editing. **A. Van Ham-Meert:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing, Formal analysis, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

ESI 1: Table with Pb IC's of ores considered in this paper.

ESI 2: Table with Pb IC's of glasses considered in this paper.

ESI 3: TiO_2/Al_2O_3 versus Al_2O_3/SiO_2 plot of the Bocholtz samples to determine which glass group they belong to.

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