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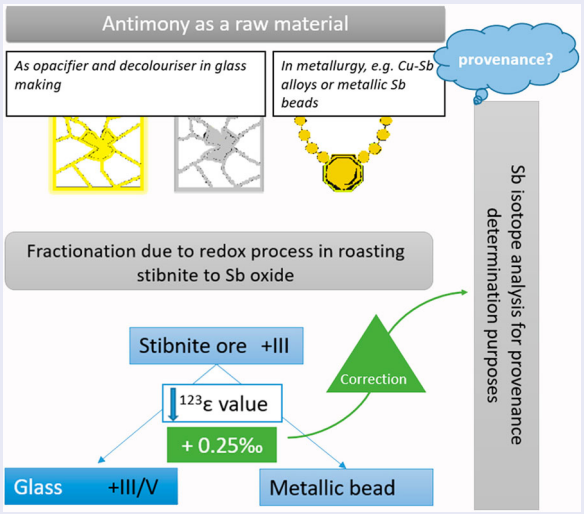
# Antimony as a raw material in ancient metal and glass making: provenancing Georgian LBA metallic Sb by isotope analysis

Sarah Dillis[a], Alicia Van Ham-Meert [a,b], Peter Leeming[c], Andrew Shortland[d], Gela Gobejishvili[e], Mikheil Abramishvili[e] and Patrick Degryse[a,f]

[a]Earth and Environmental Science, Centre for Archaeological Science, KU Leuven, Heverlee, Belgium; [b]Analytical, Environmental and GeoChemistry, VUB, Brussels, Belgium; [c]University of Exeter, Exeter, UK; [d]Cranfield Forensic Institute, Cranfield University, Defence Academy of the United Kingdom, Swindon, UK; [e]Georgian National Museum, Tbilisi, Georgia; [f]Department of Archaeological Sciences, Faculty of Archaeology, Leiden University, Leiden, Netherlands

**ABSTRACT**

Sb was frequently used as a raw material, both in ancient glass-making (as an opacifier and decolouriser) and metallurgy (either as an alloying element or as a pure metal). Despite this ubiquity, antimony production has only occasionally been studied and questions concerning its provenance are still not satisfactorily answered. This study evaluates the suitability of Sb isotope analysis for provenance determination purposes, as experiments under lab conditions have revealed fractionation occurring during redox processes in oxidising stibnites and in making opacified glasses. The results of this paper help to evaluate the possible influence of the pyrotechnological processes on the antimony isotope composition of glass artefacts. This paper focuses on the Caucasus as case study by applying mineralogical, geochemical and isotopic analysis to Georgian ores (mainly from the Racha-Lechkumi district) and Late Bronze Age (LBA; 15th–10th century BCE) metallic Sb objects found at the sites of Brili and Chalpiragorebi.

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## Introduction

### *Sb in the archaeometallurgical record*

Finds of antimony in the archaeological record show a long history of use. First, in metallurgy, Sb appears mostly as antimonial copper (see Figure 1). In the southern Levant, Cu-based metals with variable levels of As and/or Sb, ranging in content between 1 and 20%, and traces of Ag, Bi and Ni, appear during the Chalcolithic period (5500–3300 BCE) (Shalev and Northover 1993; Carmi, Epstein, and Segal 1995; Hauptmann and Gambaschidze 2001; Golden 2014). In Central Italy, these kind of Cu-As-Sb alloys also appear from the early or mid-4th millennium BCE (Chalcolithic period) at various sites (Dolfini 2010). The objects, archaeologically assigned to the Rinaldone culture, are similar in composition to the Levantine Sb-rich alloys with 1–20% Sb and/or As and traces of Ag, Bi & Ni (De Marinis 2006; Grazzi et al. 2012; Petitti, Persiani, and Pallecchi 2012). In the region of the

**CONTACT** Sarah Dillis Sarah.dillis@kuleuven.be Earth and Environmental Science, Centre for Archaeological Science, KU Leuven, Celestijnenlaan 200E, B-3001 Heverlee, Belgium

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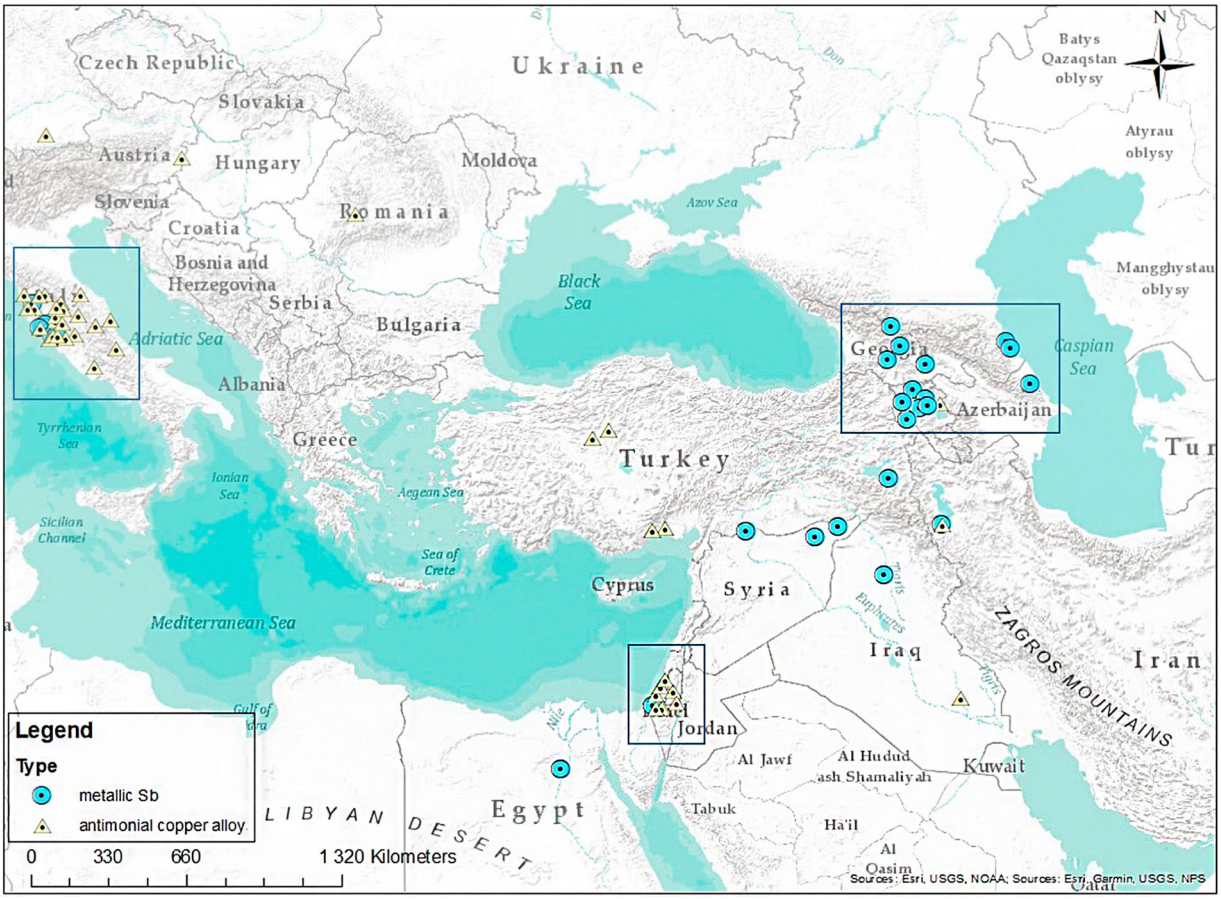


**Figure 1.** Dispersal of Sb-rich alloys and Sb metallic objects during the Chalcolithic period, Early Bronze Age (EBA), Middle Bronze Age (MBA), Late Bronze Age (LBA) and Early Iron Age (EIA).

Caucasus, at the end of the Early Bronze Age (EBA; 3300–2100 BCE) or definitely from the Middle Bronze Age (MBA; 2100–1550 BCE) onwards, Cu-Sb alloys with 1–20% Sb and sometimes with a similarly high As content are found (Hauptmann and Gambaschidze 2001). They are mainly assigned to the Caucasian cultures of Bedeni (2500–2200 BCE), Sachkhere (2600–2000 BCE) and Trialeti (2000–1700 BCE) (Chernykh 1992) and characterised by traces of S (Pike 2002). In this aspect they differ from the previously mentioned Chalcolithic Levantine and Italian Sb-rich alloys. During the LBA (1500–1150 BCE) the use of Sb-rich alloys became even more widespread in the Caucasian region, especially in the northern Koban area (Pike 2002). New complex alloys such as Cu-Sb-Pb and Pb-Sb are also found (Meliksetian and Pernicka 2003). At Hasanlu, Iran, Sb-rich alloys have been discovered, securely dated to Iron II or Hasanlu IVB (around 800 BCE) (Fleming, Nash, and Swann 2011).

In the case of metallic Sb objects, the same region in Central Italy during the Chalcolithic period is of interest (see Figure 1). At the sites of Ponte San Pietro (Tombs 21 and 22) (Dolfini 2014) , Selvicciola (Tombs 21, 23, and 35) (Grazzi et al. 2012; Petitti, Persiani, and Pallecchi 2012), Grotta del Fontino (Zanini 2002) and Montebradoni (Cambi and Cremascoli 1957) multiple Sb beads and buttons have been found. These pieces of evidence combined with the finds of antimonial copper consistently indicate that the working of antimony began in this region during the Early Chalcolithic period (Pallecchi, Pecchioli, and Tocci 2002; Dolfini 2010). In Mesopotamia, Sb objects are reported from the 3rd millennium BCE (e.g. at Tello, Tell Leilan, Jerablus Tahtani) (Shortland 2002; Moorey 1999), and later from the 1st millennium BCE in Egypt at Lahun (Petrie 1891), in Anatolia at Yoncatepe (Belli and Konyar 2001), and in Iran at Hasanlu (Fleming, Nash, and Swann 2011). In the Caucasus, metallic Sb objects are abundant. Their first use-age is identified in the middle of the 3rd millennium BCE, becomes even more prominent during the 2nd millennium and runs far into the LBA and Early Iron Age (EIA; 1200–1000 BCE). Examples are known from sites in Armenia, e.g. at the MBA and LBA levels of the Lchashen and Artik settlements, and in burial contexts at Metsamor (LBA–EIA) (Meliksetian and Pernicka 2003), Redkin Lager (LBA) (Lindsay and Smith 2006), Chesmanis (LBA–EIA), Chambarak (ninth century BCE) (Tite 2002; Meliksetian et al. 2011), Bjini (EIA–MIA) (Meliksetian et al. 2011), in Georgia in burial contexts at Brili, Treli, Kvasatali, Tsaghvli, Chalpiragorebi, Kvatskhelebi, etc. dating between the 16thand 12th centuries BCE (Hauptmann and Gambaschidze 2001), and in Dagestan small Sb

ornaments were also cast in the Kayakent–Khorochoi culture (2nd millennium BCE) at Mamai-Koutan, Korochoi (Burial 2) and Kayakent (Burial 16) (Chernykh 1992). Interestingly, there is archaeological evidence for Sb mining in the Racha–Lechkumi area (Georgia) at the Sagebi and Zopkhito mines, possibly from the 19th century BCE but definitely from the 17th century onwards (Chernykh 1992).

### *Sb as opacifier and decolouriser in glass production*

Sb was not only used in metallurgy, but was also widely used in glass production, either as an opacifier (Sb content usually >1%) in coloured glass from the LBA onwards, or as decolouriser (around 0.5% Sb) from the Hellenistic period (fourth century BCE) onwards.

As far as opacifying agents are concerned, the early history of glass mainly sees the use of calcium and lead antimonates for the production of opaque white ($Ca_2Sb_2O_7$ or $CaSb_2O_6$) and yellow ($Pb_2Sb_2O_7$) glasses. A process of making a precursor is proposed for the LBA Egyptian yellow glasses (Shortland 2002). Apart from calcium and lead antimonate, which have been found to be the predominant opacifiers used in the LBA glasses, sodium antimonite crystals (brizziite, $NaSbO_3$) have been reported associated with lead antimonate and calcium antimonate as the white opacifier used in the Iron Age glasses from Hasanlu (Stapleton 2011). These Sb-based opacifiers continued to be used in the Roman world (Shortland 2012). Similarily to the LBA yellow glasses, it was suggested that roasted stibnite (i.e. antimony oxide), rather than calcium antimonate, was added to Roman colourless and blue glass to make these glasses opaque white and opaque blue (Freestone and Stapleton 2015). For the Roman yellow and green opaque glasses antimonial litharge or a precursor lead-antimony-silicate ("anime") was proposed as the antimony source added to the soda-lime-silica glasses (Mass, Wypyski, and Stone 2002; Freestone and Stapleton 2015). These antimonates are not only present in the earliest glasses, Sb opacified-coloured glass is also by far the most common glass used, accounting for at least 90% by weight (Shortland 2012).

Since small amounts of $Fe_2O_3$ are usually unintentionally present as impurities in the sand raw material which results in a green–blue tint of the glass, a decolouriser is needed to obtain colourless glass. The colour can be neutralised by the addition of Mn or Sb by the oxidation of the $Fe^{2+}$ to the practically colourless or weak yellowish $Fe^{3+}$ (Sayre 1963; Schreurs and Brill 1984). Antimony levels in sand are typically at the ppm (or sub-ppm) level (Brems 2012; Brems and Degryse 2014), and greater concentrations in glass indicate the deliberate addition of an antimony-bearing ingredient (Freestone and Stapleton 2015). The technology of use and provenance of the raw materials of antimonates are therefore vital to the understanding of the history of glass.

## Objectives

Despite the long-term and widespread use of antimony, many questions remain concerning its origin. What is the primary origin of the Sb raw materials used? How was this Sb distributed, by processes of trade, exchange or tribute? What was the nature of its adoption in several technological processes?

For the Levantine antimonial copper alloys, an ore of the tetrahedrite-tennantite solid solution (s.s.) (in roughly equal proportions) with accessory nickel minerals is suggested by Tadmor et al. (1995). Depositis with such a signature in the Caucasus are likely sources (Tadmor et al. 1995). One likely origin of the antimony used as an opacifier in ancient glass making throughout the Near East also lies in the Caucasus (Shortland 2002). Hence, this paper aims at provenancing the Sb raw materials used in the early Caucasian Sb metallurgy industry, and investigate possible links to glass making. Metallic Sb beads from the Racha-Lechkumi region (Georgia) are investigated using mineralogical, geochemical and isotopic techniques to have a better understanding of the technology and provenance of the Sb raw materials used in the Caucasian LBA–EIA metal production.

The second objective of this paper is to evaluate the potential for provenancing of high Sb content materials (>10 wt%) using Sb isotopic analysis. To use isotopes or trace elements for provenancing purposes the signature (i.e. isotope ratio, trace element composition) has to stay unaltered between the source and the product, or change in a predictable way. In the case of isotope ratios one possible source of changes is fractionation. Fractionation encompasses all the ways the isotopic ratio can change during processing. During most steps of ancient metallurgy and glass working heat is applied, which can be accompanied by partial evaporation and/or oxidation of some elements, which in turn can induce fractionation. This has been studied in detail for Cu (Asael et al. 2007; Mathur et al. 2009), Cd (Wombacher et al. 2003), Sn (Berger et al. 2018), Ni (Ratié et al. 2016) and Zn (Mattielli et al. 2009) where fractionation occurs and must be accounted for, and for Pb, where fractionation is within the experimental error of the analysis tools used and much smaller than the natural variation within one ore field, hence not influencing provenance issues (Cui, Wu, and Huang 2011). In other metals, such as Fe, the metal phase did not indicate any isotope fractionation relative to the starting material during smelting. Sb fractionation has not yet been studied in archaeological context, and very little in chemical-geological studies. Therefore, three fractionation experiments have been set up to test the hypotheses whether fractionation

takes place due to a change in oxidation state during digestion of the samples in laboratory study (hypothesis 1) and whether fractionation occurs in redox reactions during pyrotechnological processing in ancient metallurgy and glass making (hypothesis 2). Only thereafter Sb isotope ratio analysis comparing ores to early metals and glass can be performed.

## Materials and methods

### *Archaeological & geological context*

A collection of Sb-rich ores ($n = 90$) from various regions across the world was analysed with XRD and ICP-OES ($n = 42$) to obtain mineralogical and chemical characteristics. Furthermore, under the auspices of the Georgian National Museum in Tbilisi, 27 samples of Sb-rich materials were obtained for mineralogical, geochemical and isotopic analysis: 9 ores from the Racha-Lechkumi region of which 8 stibnites and 1 tetrahedrite-tennantite s.s., and 18 metallic Sb objects from the LBA cemeteries of Brili and Chalpirogrebi. The list of samples studied can be found in Appendix I.

The Zemo (Upper) Racha ridge, situated in the district of Racha-Lechkumi in the Republic of Georgia, is rich in mineral deposits. Geologically, the Racha-Lechkumi region is centred in an area of Jurassic rocks. It occurs as a narrow slate belt that follows the general WNW-strike of the Greater Caucasus. The slates are distinguished by anomalously high concentrations of As, Sb, Cu, Zn and Au, likely defining a broad region of hydrothermal alteration. In addition, narrow horizons of diagenetic pyrite are also present and this early pyrite is enriched in As, Au and Sb, which could be a source for some of the younger epigenetic metal enrichments (Kekelia et al. 2008). The Sb deposits of Sagebi (W–Sb–Au), Kairobi (Mo–Sb), Sanartskhia (Sb–Au), Kvardzakehti (Sb–Au), Zopkhito (Au–Sb) and to the west, the Guli Sb deposit, are situated in this district (https://www.mindat.org/min-3782.html, last visited on 20/06/2018).

The region also contains a dense concentration of prehistoric sites associated with early metallurgy. About a hundred locations have been discovered at which copper, as well as antimony and arsenic ores were worked (Chernykh 1992). There are also several major deposits of antimony which were exploited in prehistoric times, including: Gona, Zopkhito and Sagebi (Inanishvili, Maisuradze, and Gobejishvili 2010). During the 10–12th of September 2016 an expedition was carried out by P. Leeming and the Georgian National Museum (GNM) to collect some of this Rachan material. During the expedition the site "Chkornali 1" was visited (N 42° 49′ 21.6″; E 43° 32′ 51.5″; 2429 m elevation). Although the mine itself is flooded, three samples were collected from spoil between 5 and 15 m from the entrance. The source of the samples is shown in Figure 2. "Georgia 1" was collected close to the Zopkhito Sb-deposit, where traces of antimony smelting have been found near the ore body (Chernykh 1992). Samples Georgia 2–5 also come from ancient mines (sloping galleries and pit faces) in this part of the Racha-Lechkumi district.

Fifteen beads found at the site of Brili, excavated from Grave 32 (11 beads studied), Grave 33 (1 bead) and Grave 1 (3 beads studied) were analysed. The

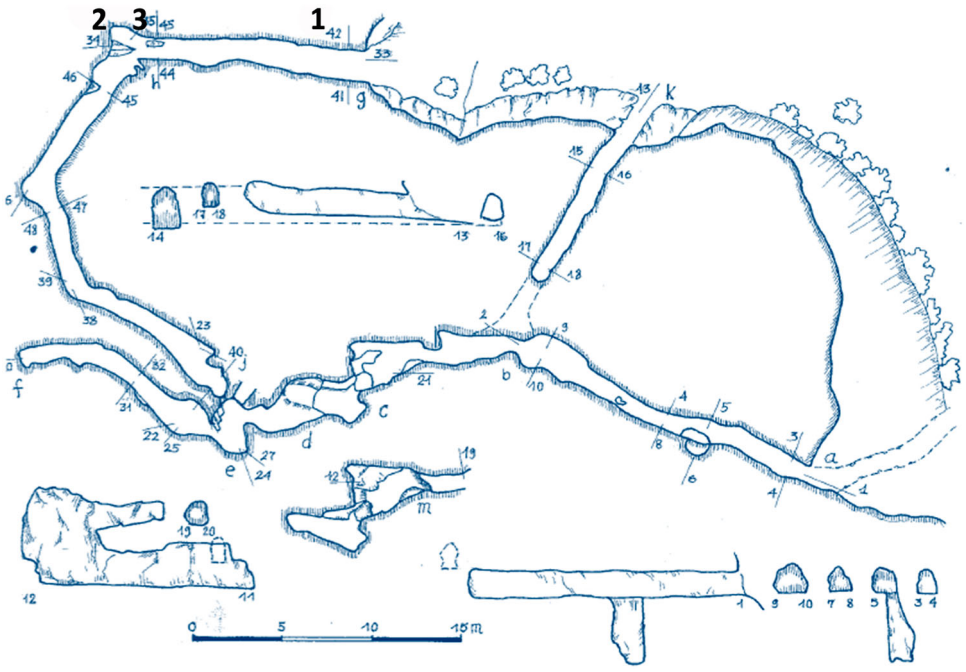


**Figure 2.** Plan of the mine showing sampling points 1–3, which, respectively are samples Georgia 2, 3 and 4 (after Maisuradze and Gobejishvili 2001 ).

beads of Grave 32 are part of three different necklaces (see Appendix I): necklaces A and B are bi-lobed beads consisting of two spherical bodies that share a common flat bottom (typical grave goods in the tombs of Brili, Nuli and Kvasatali (Shida Kartli)) (Hauptmann and Gambaschidze 2001); necklace C is tri-lobed, consisting of three spherical bodies.

Brili is a multi-period cemetery in the region of Racha-Lechkumi, situated to the west of the area of Gona. The site was excavated in nine seasons between 1939–1961 under the leadership of Germane Gobejishvili (Gobejishvili 1977, 1952). Even though the cemetery has not been completely excavated, more than 200 graves have been opened. Local communities used the cemetery intermittently as a burial ground for about 2000 years from the early 2nd millennium BCE (MBA) to the fourth century CE. They are characterised by a diversity of belief systems and mortuary practices – earthen pit graves, stone cists, and cremation platforms (Sagona 2017). The site is only dated by relative chronologies and is being analysed burial by burial with thus far limited publication (e.g. Pantskhava, Maisuradze, and Gobejishvili 1939). This lack of absolute dating is common in the Bronze Age of Georgia as a whole, where programmes of $^{14}C$ dating are still in their infancy.

From the Chalpiragorebi cemetery in Tbilisi, in use during multiple periods, spanning the 2nd and 1st millennium BCE, 5 beads from five different graves were analysed: "CHPG 1" from Grave 15 belongs to a composite spacer-plate necklace of over 80 beads, of which an axe-head shaped bead (like a so-called Central Transcaucasian battle axe) was analysed; "CHPG 2" from Grave 75 is a flattened truncated bicone or lozenge bead; "CHPG 4" are broken fragments from a necklace found in Grave 3; the accession numbers of the two other samples "CHPG 5" and "CHPG 6" are currently being investigated and the site is being prepared for full publication by one of the authors, M. Abramishvili. Unfortunately, not much contextual information in English has been published so far.

## Fractionation experiments

The outline of the fractionation experiments can be found in Table 1.

### Fractionation experiment 1

Originally, Sb isotope analysis of low Sb content materials was developed by Lobo et al. (2012) isolating Sb using a combination of cation exchange chromatography with Dowex resin and anion exchange chromatography using Amberlite resin (Lobo et al. 2012, 2013, 2014; Degryse et al. 2015). This procedure was altered for high Sb content materials due to the creation of viscous gels instead of clear solutions when preparing such samples. The first fractionation experiment (see Table 1) starts off with a stibnite "China 3" from the ore collection (F1). The crushed ore was heated at 400°C in order to obtain $Sb_2O_3$. Then this roasted stibnite (F2) was heated with C at 500°C during 4 h to $Sb_2O_4$ (F3a). This was repeated with the same conditions for complete oxidation of the ore to $Sb_2O_5$ (F3b). A frit composed of $SiO_2$-$Na_2O$-CaO (74.5:18:7.5), which is close to average composition of Roman glass and at a eutectic point in the ternary phase diagram was created by heating the raw materials at 1200°C for 4 h (F4). The $Sb_2O_5$ (95:5) was added to this frit and fired at 800°C for 4 h (F6a). Samples F1–4 were digested according to Procedure 2: the samples were weighed to 0.1 g after which 1.5 ml 12 M HCl was added. The beakers were closed and placed on the hotplate overnight followed by evaporation at 80°C on a hotplate. Then *Aqua Regia* (AR) was added, 0.8 ml 14 M $HNO_3$ with 2.4 ml 12 M HCl. The beakers were closed and heated again overnight at 90°C before they were opened to evaporate. Samples F5 and F6a were digested by the same procedure, with the additional step of adding 3 ml of 22 M HF with 2 ml of 14 M $HNO_3$ after evaporating the *Aqua Regia*. The closed beakers were heated for two hours before they were opened to evaporate. Finally, 10 ml of 0.14 M HF was added to samples F1–F6a to redissolve the samples for Sb isolation before MC-ICP-MS analysis.

### Fractionation experiment 2

The same experiment outline (Table 1) as in fractionation experiment 1 was followed, except for the adding of Sb. This time $Sb_2S_3$ (F1) was added to the base glass (F4) and heated first at 800°C, then at 1200°C for twice 4 h (F6b). In this fractionation experiment Procedure 3,

**Table 1.** Fractionation experiment outline. Stibnite "China 3" was selected. The crushed ore was heated at 400°C in order to obtain $Sb_2O_3$. Then the roasted stibnite was heated with C at 500°C during 4 h. This was repeated with the same conditions for complete oxidation of the ore to $Sb_2O_5$. (F1–F3b were analysed by XRD). A frit composed of $SiO_2$-$Na_2O$-CaO (74.5:18:7.5), which is close to average composition of Roman glass and at a eutectic point in the ternary phase diagram is created by heating the raw materials at 1200°C for 4 h. Either a frit of $Sb_2O_5$ (95:5) is added and fired at 800°C for 4 h (F6a) or $Sb_2S_3$ is added to the base glass and heated first at 800°C, then at 1200°C for twice 4 h (F6b).

| | F1/L1 | F2/L2 | F3a | F3b | F4 | F5/L5 | F6a/L6a | F6b/L6b |
|---|---|---|---|---|---|---|---|---|
| Raw material | Stibnite | Roasted stibnite | Oxidised stibnite | Oxidised stibnite | Raw materials glass | Glass frit | Opacified Sb glass by adding $Sb_2O_5$ | Opacified Sb glass by adding $Sb_2S_3$ |
| T | | 400°C | 500°C | 500°C | | 1200°C | 800°C | 800–1200°C |
| T | | 12–16 h | 4 h | 4 h | | 4 h | 4 h | 4–4 h |

offering total digestion for elemental analysis, was used. To closely monitor any change in oxidation state during the digestion procedure, every step of Procedure 3 was sampled. Firstly, all samples were weighed to 50–70 mg in Savillex beakers to which 10 ml of *AR* was added (2.5 ml of 14 M $HNO_3$ + 7.5 ml of 12 M HCl). The samples were heated overnight at 120°C. Then, two times 1 ml and one time 2 ml was taken out (=4 ml in total) to respectively use for titration, ICP-OES analysis and Sb isotope analysis. The remaining 6 ml was evaporated at 150°C. 10 ml 22 M HF was added and heated overnight at the same temperature. Again, 4 ml was taken out for the analysis as described above. The remaining 6 ml was evaporated at 150°C and brought into solution again with 7 ml of 3% $HNO_3$.

In this experiment stibnite "China 3" (F1) and an additional ore "Georgia 6" were digested with two different procedures in order to evaluate the influence between digestion procedures on the Sb isotopic composition. Procedure 1 (Lobo et al. 2012) and Procedure 3 were chosen. Procedure 1 goes as follows: a mixture of 4: 1: 1 $HNO_3$: $H_2O_2$: HF was made (4 ml 14 M $HNO_3$ + 1 ml 10 M $H_2O_2$ + 1 ml 22 M HF), of which 1.5 ml was added to the samples and evaporated at 40°C. Then 2.5 ml of *AR* was added. The beakers were closed and put on the hotplate to heat overnight at 90°C. Afterwards, the beakers were opened and evaporated at the same temperature. The residue was redissolved in 10 ml of 0.14 M HF.

### Fractionation experiment 3

This fractionation experiment copies the outline of experiment 1 (F1–F6a). A glass opacified by the adding of $Sb_2S_3$, as in experiment 2, was created as well (F6b). These samples (F1–F6a/b) were digested with Procedure 2, as described for experiment 1. Around 65 mg was taken from each samples, except for F3, of which 36 mg remained.

Additionally, these samples were also digested with Procedure 1, as described for experiment 2, and here labelled as L1 (stibnite) and L2 (roasted stibnite). The glass samples (L5 and L6a/b) had an additional addition of a mixture of 3 ml 22M HF and 2 ml 14M $HNO_3$.

## Methods

### XRD

The ores were crushed in an agate mortar and placed on the XRD holder using silica gel. Powders were measured using a Phillips PW1830 diffractometer with a Bragg/Brentano θ–2θ setup and Cu Kα radiation at 45 kV and 30 mA. Angles from 5 to 75° 2θ were scanned with a step size of 0.02° 2θ and 1s per step. ConvX software was used for file conversion, mineral identification was performed using DiffracPlus (EVA).

### SEM-EDS/ESEM

A Hitachi 3500U Environmental Scanning Electron Microsocope (ESEM) at Cranfield University was used to obtain the major and minor element chemical composition of 10 jewellery samples, mainly beads found at the sites of Brili and Chalpiragorebi and 8 ores obtained in the Racha-Lechkumi region. The samples were mounted on carbon-coated stubs and analysed with 20 kV accelerating voltage, an intensity of 89 μA, 30s live time and 10 mm working distance. The Octane Plus EDS detector (EDAX – AMTETEK Inc.) was used with a standardless approach. The measured intensities have been quantified using eZAF Smart Quant Results. Raw data were corrected with ZAF correction procedure to process for matrix effect. Multiple spots were analysed to calculate a mean value. The samples are given as elements with some exception presented as oxides. The results are presented with oxygen content included to indicate the corrosion condition of the metal.

### ICP-OES

The major and minor elemental compositions of the ore collection samples were obtained by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analyses with a Varian 720-ES instrument (simultaneous ICP-OES with axially viewed plasma). Firstly, 42 ore samples were qualitatively analysed (only partial dissolution). Since they were similar in their major and minor elemental composition, subsequently only 19 ore samples were quantitatively analysed. These 19 ore samples are discussed in the paper. 70 mg of ore was powdered. The powdered samples were subjected to digestion in Teflon beakers. Procedure 3 was used to dissolve the samples (4 ml AR, 3 ml HF, 3 ml $HNO_3$). The digest was transferred into a larger tube (15 ml), and diluted to 8 ml using 1M $HNO_3$. 5 ml of the 8 ml solution was transferred back into Teflon beakers to be used for Sb isotope analysis (see below), while the remaining 3 ml was retained for chemical analysis by ICP-OES.

Exact instrumental setup can be found in Brems et al. (2012). The operating conditions and instrumental parameters are summarised in Table 2.

### MC-ICP-MS

Samples were weighed (around 50 mg, or less in case of a small sample) in Savillex beakers and digested according to Procedure 3 (4 ml AR, 3 ml HF), and eventually diluted in 3% $HNO_3$ for Sb concentration check and isotope ratio measurement.

The concentration of Sb in the solutions was determined using a PerkinElmer SCIEX Elan 5000 ICP–MS instrument. An internal standard (Ru) was used to correct for matrix effects, signal drift and instrument instability, and Sb stock was used to calibrate. Sb isotope ratios were determined using a Thermo Scientific

**Table 2.** ICP-OES instrumental settings.

| Parameters VARIAN 720-ES: conditions used by all lines | |
|---|---|
| Power kW | 1.30 |
| Plasma flow L/min | 15.0 |
| Auxiliary flow L/min | 1.50 |
| Nebulizer flow L/min | 0.75 |
| Replicate read time (s) | 3.00 |
| Instrumental stabilisation delay (s) | 15 |
| Sample introduction settings | |
| Sample uptake delay (s) | 60 |
| Pump rate (rpm) | 15 |
| Rinse time (s) | 5 |
| Standards | |
| Standards | quantitative |
| % slope deviation | 10 |
| No of standards | 15 |
| Correlation coefficient | 0.995000 |
| Curve type | Quadratic & linear |

**Table 3.** Operating conditions for the Faraday cups and data acquisition.

| Thermo Scientific Neptune multi-collector ICP-mass spectrometer | | | |
|---|---|---|---|
| Cup configuration | | | |
| L2 | C | H2 | H3 |
| $^{113}$In | $^{115}$In | $^{121}$Sb | $^{123}$Sb |
| Data acquisition parameters | | | |
| Number of blocks | 7 | | |
| Number of cycles per block | 5 | | |
| Integration time (s) | 4 | | |

Neptune multi-collector inductively coupled plasma – mass spectrometer (MC–ICP–MS), equipped with a micro-flow PFA-50 Teflon nebulizer and a double spray chamber, consisting of a cyclonic and a Scott-type sub-unit for sample introduction, and running in static multi-collection mode, at the University of Ghent (Belgium). It was operated with a constant flow of 3% $HNO_3$ at 100. The ion signal intensities of $^{121}$Sb and $^{123}$Sb were detected simultaneously by multiple Faraday cups (see Table 3 for operating conditions) using $^{113}$In and $^{115}$In for the correction of the instrumental mass discrimination.

Revised Russell's law using Indium (In) as internal standard was chosen as method of correction for instrumental mass discrimination (Baxter et al. 2006), as it was shown by Lobo et al. (2013) that the latter method leads to improved precision and is reproducible, in contrast to the sample-standard bracketing method. Sb isotopic results are reported in $^{123}\varepsilon$ units. These ε values express the isotopic composition of Sb as a relative difference or deviation with respect to an in-house standard (SPC Science), measured in a standard-sample-standard bracketing sequence with a 1000 ppb Sb standard solution and 150 ppb In as an internal standard (Lobo et al. 2012, 2013, 2014).

## Results

### *Fractionation experiments*

Figure 3 shows the results of the three fractionation experiments combined. A shift in isotopic composition of the different phases in the experiments is revealed,

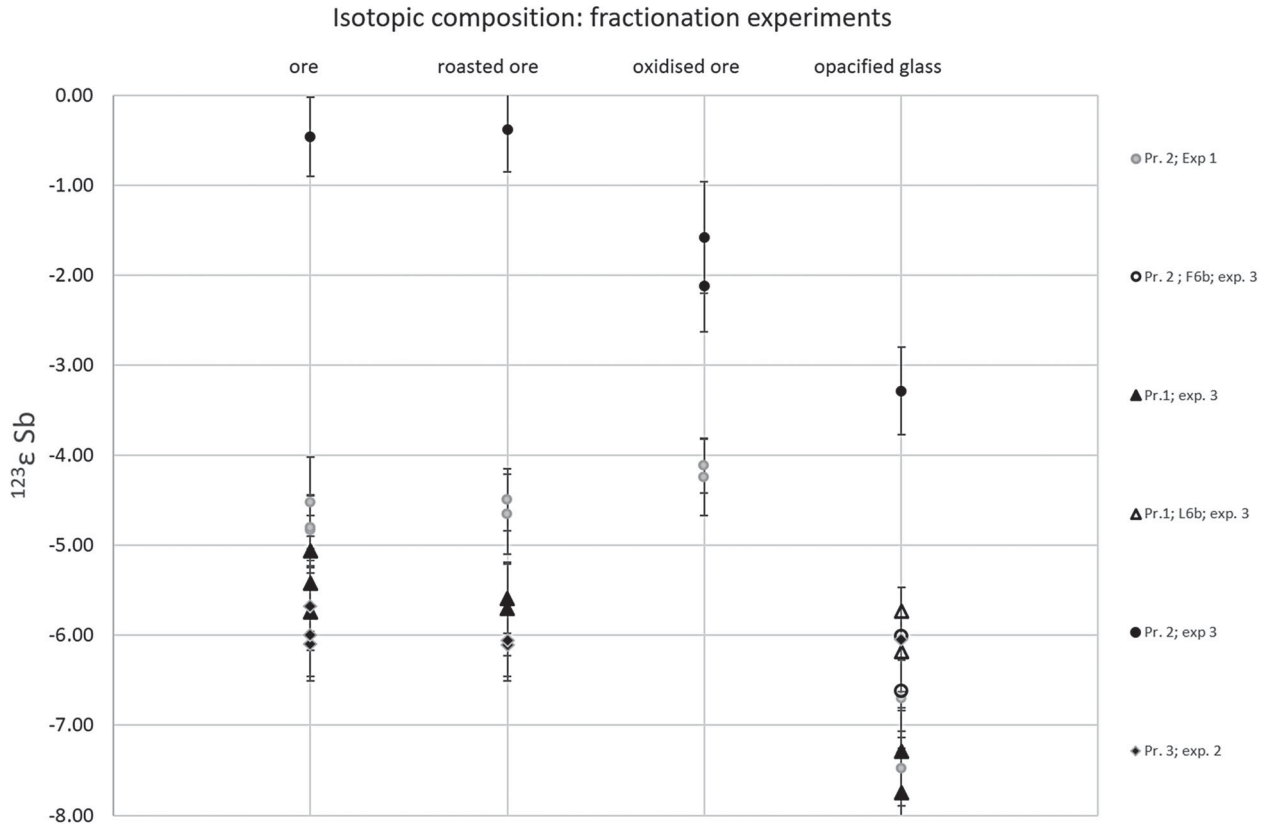


**Figure 3.** Overview of the Sb isotopic composition of the fractionation experiments. Procedure 1 is denoted with triangles, Procedure 2 with dots and Procedure 3 with diamonds. Experiment 1 is denoted in black colour, experiment 2 in pink and experiment 3 in red (if opacified by $Sb_2O_5$; F/L6a) and green (if opacified by $Sb_2S_3/Sb_2O_3$; F/L6b).

except for the samples digested with Procedure 3 in experiment 2. The newly produced opacified glass of experiment 1 has a Sb isotope ratio which is around 3.0 $^{123}\varepsilon$ units lower than the unprocessed ore. No significant change occurs between the unprocessed (F1) [$Sb_2S_3$] and roasted stibnite (F2) [$Sb_2O_3$]. After partial oxidation (F3a) [$Sb_2O_4$] the isotopic values drop around 1.5 $^{123}\varepsilon$. After adding the oxidised Sb (F3b) to the glass (F4), an opacified glass (F6a) is obtained. Its isotopic composition is again another 1.5–2.5 $^{123}\varepsilon$ lower compared to the previous step. The same trend can be observed in both procedures (1 & 2) used in experiment 3, i.e. no shift occurs between the ore (F/L1) and the roasted ore (F/L2), but does occur between the oxidised ore (F/L3) and the opacified glasses (F/L6a/b). The shift is however larger for the samples digested with Procedure 2, i.e. between around 1.5 and 3.0 $^{123}\varepsilon$ value, while for the samples digested with Procedure 1 the shift ranges between barely a difference (0.0) and 2.2 $^{123}\varepsilon$. For the opacified glasses it is noted that more negative Sb isotopic values are found in the glasses opacified with the Sb oxide (F/L6a) in comparison to the glasses opacified with stibnite (F/L6b).

As can be seen in Figure 4, no fractionation between the different technological steps is observed in experiment 2. Neither is any significant fractionation occurring between the different steps of the digestion procedure (Procedure 3), nor when using HCl as first step. Figure 5 shows a discrepancy in $^{123}\varepsilon$ Sb values between this Procedure 3 and Procedure 1. Samples digested with Procedure 3 have more negative values compared to samples digested with Procedure 1. A difference of 1.15 $^{123}\varepsilon$ is noted for "Georgia 6" and 1.97 $^{123}\varepsilon$ for "China 3." Since both samples were run without the isolation preparation, there is no impact at all possible of an eventual on column fractionation. Likewise in experiment 3, the samples digested with Procedure 1 have a more negative Sb isotopic value than the ones digested with Procedure 2.

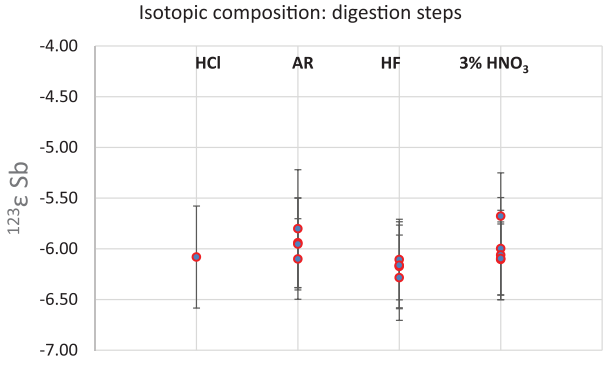


**Figure 4.** Isotopic composition of "China 3" (ore) during different digestion steps in experiment 2.

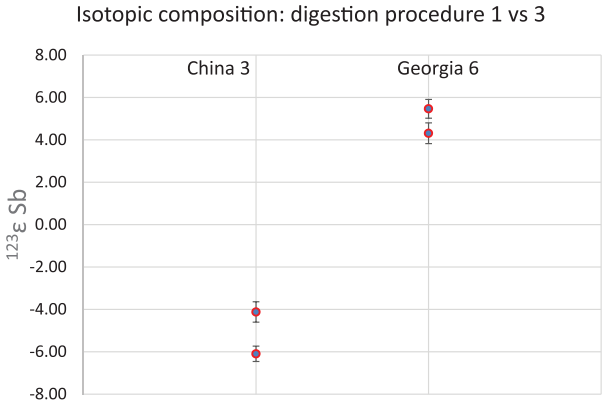


**Figure 5.** Isotopic composition of the final digestion phase of Procedure 1 and Procedure 3 for the ore samples "China 3" and "Georgia 6."

## Ore collection

### XRD and ICP-OES results

A summary of the results are shown in Tables 4 and 5. Data can be found in Appendix I (XRD) and Appendix II (elemental composition). Table 4 shows that the sulfide, stibnite [$Sb_2S_3$], was identified the most. The two other most common minerals identified in the collection were tetrahedrite-tennantite s.s. [$(Cu,Fe)_{12}Sb_4S_{13}$] and boulangerite [$Pb_5Sb_4S_{11}$]. Geochemical analysis shows that these stibnites contain on average c. 75% Sb and c. 27% of S, indicating these stibnites occur without any significant content in any other major element. In only a few cases were As, Fe, Pb and Zn detected. Therefore, when used in ancient processes, stibnite would not influence in a major way an artefact's composition other than for its Sb content. The tetrahedrite-tennantite s.s. has a different S – Sb ratio and an association with As, Fe, Zn and mainly Cu can be seen. In the case of the use of boulangerite, Pb is present in significant amounts (see Table 5).

### Sb isotope analysis

The Sb isotope composition of stibnites in the ore collection ($n = 63$, including remeasured ores) could be determined with a good repeatability (internal precision; the variation arising when all efforts are made to keep conditions constant by using the same method on the identical test items in the same laboratory by the same operator using the same equipment within short intervals of time) of 0.48 $^{123}\varepsilon$ (2RSD), comparable to precisions reported in literature (e.g. similar to the

**Table 4.** Minerals identified by XRD.

| Mineral | *N* = 90 | Associated minerals |
|---|---|---|
| Stibnite ($Sb_2S_3$) | 64 | Stibiconite, berthierite, chalcopyrite, galena, sphalerite |
| Tetrahedrite-tennantite s.s. ($(Cu,Fe)_{12}Sb_4S_{13}$) | 4 | Galena, pyrite, sphalerite, chalcopyrite |
| Boulangerite [$Pb_5Sb_4S_{11}$] | 4 | Falkmanite, galena, sphalerite |
| Other Sb-rich minerals | 18 | |

**Table 5.** Average major and minor elements identified by ICP–OES.

| Stibnite ($n = 16$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Major (mean–median) (%) | | | Traces (in few cases) (max) (%) | | | | Gangue material (in few cases) (max) (%) | | |
| **Sb** | **S** | **Total** | **As** | **Fe** | **Pb** | **Zn** | **Al** | **Ca** | **K** |
| 67.89 ± 16.88 | 25.13 ± 5.8 | 93.70 ± 47 | | | | | | | |
| 74.0 | 27.1 | 101 | 0.699 | 0.536 | 0.518 | 0.149 | 2.06 | 1.69 | 0.101 |
| Tetrahedrite-tennantite s.s. ($n = 1$) | | | | | | | | | |
| Major (%) | | | | | | Traces (%) | Gangue material (%) | | Total (%) |
| **As** | **Cu** | **Fe** | **Sb** | **S** | **Zn** | **Bi** | **Ca** | **Mg** | |
| 8.69 | 39.1 | 2.33 | 14.5 | 24.8 | 3.95 | 0.139 | 0.491 | 0.275 | 94.4 |
| Boulangerite ($n = 1$) | | | | | | | | | |
| Major (%) | | | Traces (%) | | Gangue material (%) | | Total (%) | | |
| **Pb** | **Sb** | **S** | **As** | **Fe** | **Ca** | **Mg** | **Mn** | | |
| 6.49 | 25.4 | 5.60 | 1.00 | 0.647 | 0.509 | 0.287 | 0.107 | 40.2 | |

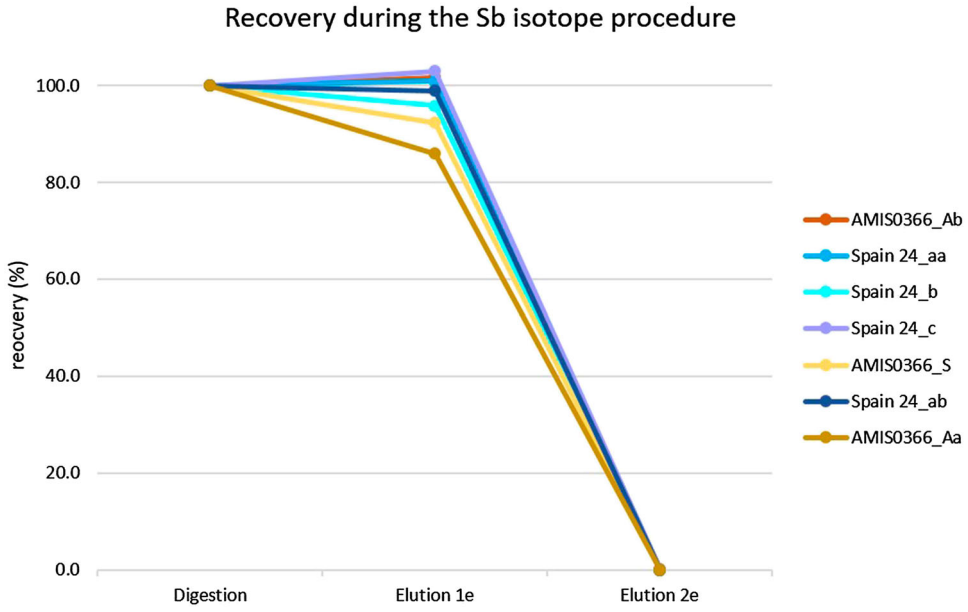


**Figure 6.** Sb recovery after digestion, of the elution after the cation isolation (1st elution) and of the elution after the anion isolation (2nd elution). AMIS0366 is a standard, Spain 24 is a stibnite ore.

reported 0.4 $^{123}\varepsilon$ by Lobo et al. (2012)). However, the reproducibility (obtained on replicates during the same run of the instrument) for high Sb materials (>10 wt% Sb) was bad, replicate measurements on stibnites yielding a difference of up to 5 $^{123}\varepsilon$ units. In practice, comparing values in the same batch was possible, but comparing between batches proved unreliable. Therefore, for high Sb content samples the preparation procedure for isotope measurements had to be redeveloped. Recoveries were checked in elution profiles, which is the process of extracting one material from another by running a solvent, called an "eluent", through loaded ion-exchange resins in columns to remove captured ions. After the solvent molecules displace the analyte (i.e. the isolation), the analyte can be carried out of the column for analysis.

A major loss of Sb was observed in elution profiles, especially after the second isolation step (see "elution 2e" in Figure 6). This loss can be ascribed to Sb that is retained in the resin on the column. Since geochemical analysis showed that not many associated elements are to be expected, chromatography was entirely eliminated from the preparation procedure of the high-Sb archaeolgocial samples and from fractionation experiment 2, and high Sb content solutions were directly loaded for isotopic measurements.

## *Metallic Sb samples of the Racha – Lechkumi area*

### *SEM-EDS and EPMA results*

Six metal beads from the Brili site were analysed. Five beads were identified as metallic Sb and one ("Bead 1") as a Cu–Sn alloy (see Appendix II). On average the metallic Sb beads contain 69.0 wt% Sb. However, less corroded zones and original cores reveal that the original Sb content was much higher, e.g. 86.9 wt% in "bead 56". For Bead 1 an increase of Sn towards the outer zones due to the phenomenon of decuprification is observed (Figueiredo et al. 2010; Oudbashi, Hasanpour, and Davami 2016). Three metal samples from Chalpiragorebi were measured. SEM analysis reveal that they are made of metallic Sb, with contents up to 95.0 wt%, e.g. the metallic core in "CHPG 11". Cu is

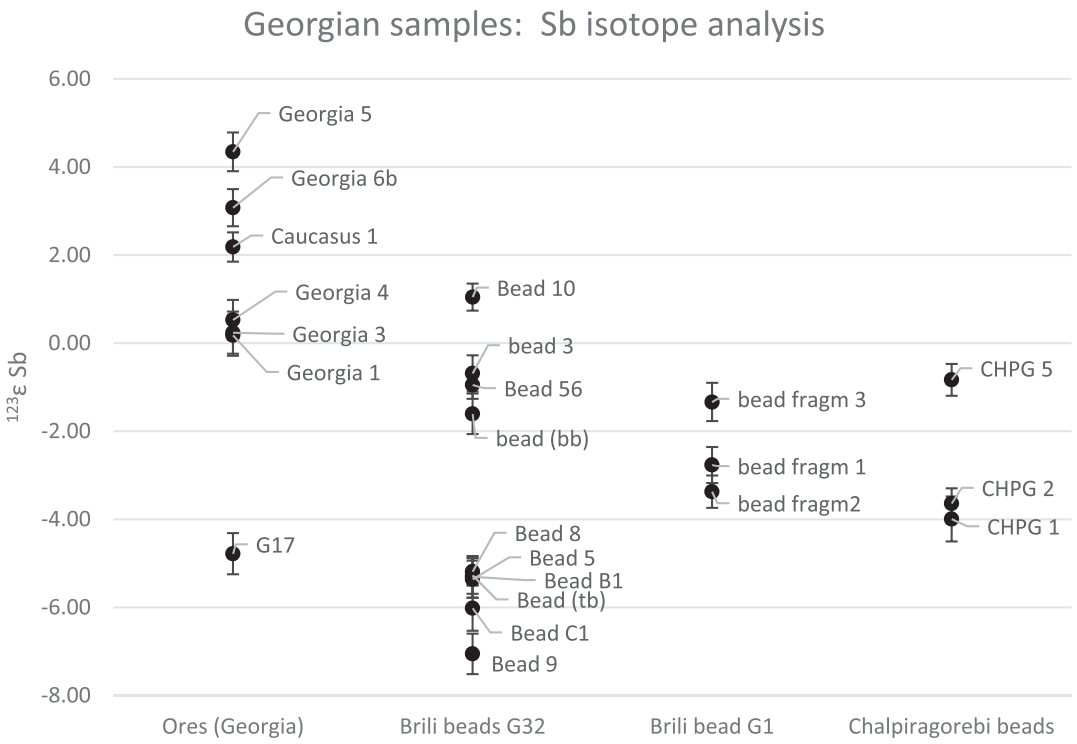


**Figure 7.** Sb isotopic data of Georgian stibnites and Sb-rich jewellery.

attested only in the Brili beads, as 4 out of 5 samples yielded a Cu content of at least 1.00 wt%, and one even has almost 6 wt% Cu.

### *Sb isotope analysis*

Sb isotope analysis has been carried out on the Georgian ore and metallic Sb samples in two runs. Data are listed in Appendix III. Figure 7 shows the isotopic ratios for the samples analysed. Six of the Georgian ores plot above the 0.00 $^{123}\varepsilon$ value, while only one has a negative value ("G17"). On the contrary, all archaeological samples plot below the 0.00 $^{123}\varepsilon$ value except for Bead 10 (G32), which has a positive value.

## Discussion

### *Fractionation during analysis (hypothesis 1)*

In Procedure 3 no shift in isotopic composition is observed. This can be explained by the fact that Sb is already present as Sb (+V) in the ore digests (as shown by titration) through the use of *AR* as strong oxidising agent in the digestion procedure. In this case, the digestion causes the transition in oxidation state, changing the Sb isotope composition of the original, roasted and oxidised ore. The risk of inducing fractionation in the digestion procedure is thus real (hypothesis 1).

### *Fractionation during pyrotechnological processes (hypothesis 2)*

Our experiments revealed that fractionation does occur in making Sb opacified glass, altering the Sb isotopic ratio to a lighter isotopic composition and hence more negative values.

Fractionation is known to happen in the transition of oxidation state (cfr. parallel to the redox reactions suggested by Ratié et al. (2016) for Ni isotopes) from +III to +V, which occurs when roasted stibnite (F2) is oxidised to $Sb_2O_4$ (F3a) or $Sb_2O_5$ (F3b) to add as antimony source to the glass batch, or which occurs when $Sb_2S_3$/$Sb_2O_3$(+III) is added to the glass batch to form $Ca_2Sb_2O_{6/7}$ (+V). It is put forward here that the more Sb (+III) is present in the final glass, the closer the Sb isotopic value will be to the roasted and/or unprocessed ore. The more Sb (+V) is present, the more negative the Sb isotopic ratio will be due to fractionation.

First, in the process of roasting stibnite no difference in Sb isotopic ratio is seen (<SD) (Table 6) between unprocessed and roasted ore, thus no fractionation occurs in this procedure. In oxidised ore, no significant shift (i.e. around SD) is observed when $Sb_2O_3$ is obtained, but a difference of 1.39 $^{123}\varepsilon$ is seen when $Sb_2O_4$ is obtained, due to the mixed valence in the latter. The opposite trends (i.e. higher Sb isotope ratio compared to the roasted ore) for the oxidised ores [$Sb_2O_4$, cervantite] in Procedure 2 of experiment 1 can be explained by the uncontrolled parameters in this experiment (see Figure 3), such as oxygen fugacity or partial pressure during heating in the oven. Hence, the ratio of $Sb^{3+}$/$Sb^{5+}$ in these cervantites will vary, and oxidised ores with more Sb(+III) still present will have a Sb isotopic ratio closer to the roasted ore. If more Sb (+V) will be present, then the Sb isotopic

**Table 6.** Average $^{123}\varepsilon$ value of the stibnites and roasted ores for the different digestion procedures in the different experiments.

| | Stibnite | Roasted | Stibnite – roasted | Oxidised | Stibnite – oxidised | Opacified | Glass | Stibnite – glass | Oxide – glass |
|---|---|---|---|---|---|---|---|---|---|
| Exp 1/Pr. 2 | −0.46 | −0.38 | −0.08 | −1.85 | 1.39 | Sb oxide | −3.29 | 2.83 | 1.44 |
| Exp 2/Pr. 3 | −5.92 | −6.08 | 0.16 | | | stibnite | −6.05 | 0.13 | |
| Exp 3/Pr. 2 | −4.68 | −4.57 | −0.11 | −4.18 | −0.5 | Sb oxide | −7.01 | 2.33 | 2.83 |
| Exp 3/Pr. 2 | −4.68 | −4.57 | −0.11 | −4.18 | −0.5 | stibnite | −6.31 | 1.63 | 2.13 |
| Exp 3/Pr. 1 | −5.41 | −5.65 | 0.24 | | | Sb oxide | −7.52 | 2.11 | |
| Exp 3/Pr. 1 | −5.41 | −5.65 | 0.24 | | | stibnite | −5.96 | 0.55 | |

ratio will be more negative and hence closer to the isotopic composition of the opacified glasses.

Finally, in the process of making an opacified glass, and thus theoretically going completely to a + V valence, differentiation is seen among the different digestion procedures. While for Procedure 3 no fractionation seems to occur (0.13 $^{123}\varepsilon$ value <SD), Procedure 2 shows that fractionation from a stibnite to a Sb oxide opacified glass gives a shift in Sb isotopic value of around 2.5 $^{123}\varepsilon$ value. Interestingly, a lower shift is observed when stibnite was used directly in the opacification process (1.63 $^{123}\varepsilon$). For Procedure 1, a shift from stibnite to the Sb oxide opacified glass of 2.11 $^{123}\varepsilon$ is noted, whereas for the glass opacified with the stibnite this is only 0.55 $^{123}\varepsilon$ value. In this case, it seems that not all Sb (+III) was oxidised to Sb (+V) during the in-situ opacification process. Hence, the oxidation state of the Sb in the glass matrix stays mainly the same as the Sb source. These findings are in line with the observations made by Lahlil et al. (2008), who states that if Sb (+III) is the predominant species in the glass matrix and if it is known that the glass has been made under conditions below 1200°C, the sources of Sb potentially used are compounds of the type $Sb_2O_3$ or $Sb_2S_3$ (Lahlil et al. 2008). From our experiments it can be concluded that the transition in oxidation stage from +III to +V during the technological process of using stibnite in glass making leads to a drop in the Sb isotopic ratio of c. 2.5 $^{123}\varepsilon$. This fractionation factor (0.25‰) can be used to interpret any further Sb isotopic data from archaeological data.

Therefore, the assumption that there is a direct relationship between mineral raw minerals and the artefacts, so that the geological signature is not transformed physically or chemically during the manufacturing process (Ixer 1999), is not fulfilled. The goal of using Sb isotopic compositions for the determination of provenance can only be aimed for when Sb stays as Sb (+III) (e.g. Lobo et al. 2012) or when a fractionation factor is taken into account. Moreover, since this fractionation happens during technological processing, and since we can control the digestion procedures used in measuring Sb isotopes, this method can be of use with regard to technological issues in antiquity. Since different technological processes can determine whether Sb enters the glass batch in Sb(+III) or as Sb (+V), it might give us some insight in the production of antimonates. Previous study by Degryse et al. (2015) (Figure 8) suggested that the Sb used in LBA glass making has a distinct source from later Sb used in Greco-Roman times as a decoulouriser, and that the LBA glass has a signature similar only to remains of early Sb metallurgy, developed in the Caucasus. Metallic or mineral Sb was used to opacify glass, and factories in Mesopotamia and Egypt seem to have used the same source of the material (Degryse et al. 2015). It can indeed be observed (see the red line on Figure 8) that the LBA glass has a negative Sb isotopic composition, while the Roman glasses show higher Sb isotopic compositions. Since fractionation is occurring in the oxidising phase, this difference in isotopic composition can no longer only be explained by a different Sb source, but also by a different technological process.

Using the principle of Occam's razor, a schematic overview for the mass-dependent Sb fractionation as partially deduced experimentally is presented in Figure 9. Since the most straightforward procedure to make metallic Sb starts with roasting stibnite (+III to +III/+V) and consequently reducing it in closed moulds, the same fractionation factor for metallic Sb beads is proposed, as it would induce redox reactions as well. However, the oxidation state of the metallic beads remains difficult to predict. The roasting of the stibnite renders either $Sb_2O_3$ (+III) or $Sb_2O_4$ (+III/+V). While a oxidation state of a metal is always (0), this is not necessarily the case when we are dealing with artefacts that are not a full 100% metallic Sb. In that case, reducing might turn it (partially) into +III and/or Sb(0).

### *Case study: provenancing the metallic Sb beads*

The elemental composition of the ores analysed, leads us to conclude that the use of stibnite in ancient industries would not contribute many elements to the end product other than Sb and S. Based on their ubiquity in ore deposits, only the tetrahedrite-tennantite s.s. and boulangerite are likely other ore minerals to be used. When a tetrahedrite-tennantite s.s. is used, the presence of As, Fe, Zn and mainly Cu as accompanying elements is expected. In the case of boulangerite, Pb would be a significant associated element. Given the interesting geological and archaeological background of the Caucasus, such patterns were investigated in the composition of the metallic Sb samples. A first indication for the use of a different antimony source and/or technology can be suggested: in the Brili beads the

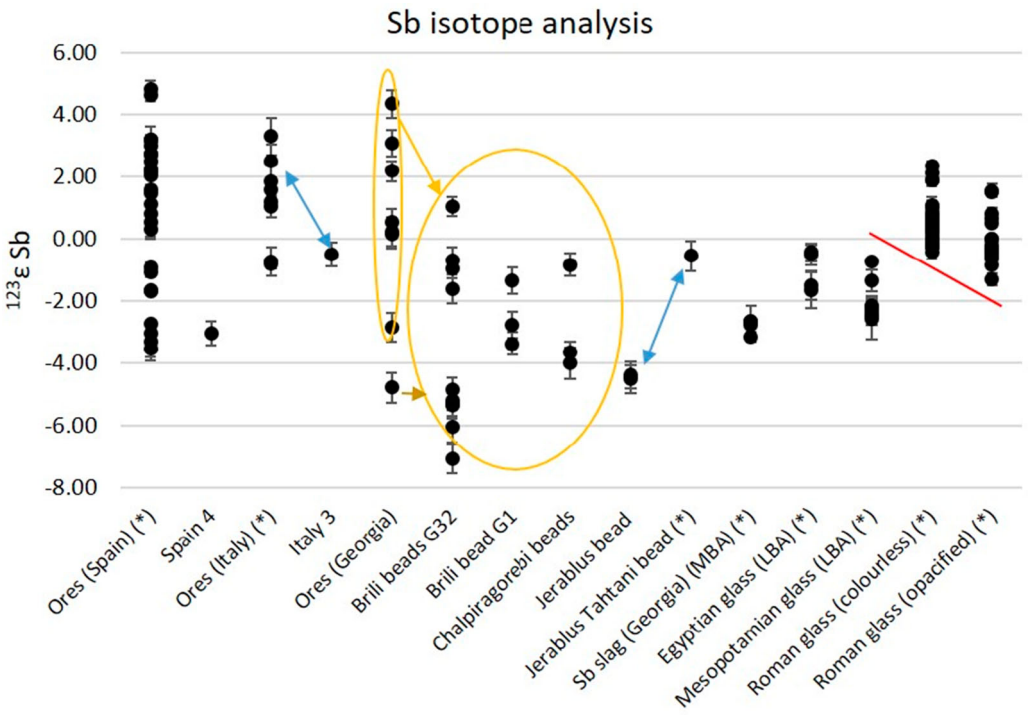


**Figure 8.** Blue arrows point out the difference between the 123ε values obtained for Spain 4, Italy 3 and the Jerablus bead and the values obtained for these identical samples by Lobo et al. (2012); orange shapes show the correction with the fractionation factor between the unprocessed ores of the Racha region and the metallic beads of Brili and Chalpiragorebi, and the red line indicates the observation made by Degryse et al. (2015) that the Egyptian and Mesopotamian glasses have a lower value than the Roman glasses. *Data obtained from Degryse et al. (2015).

association of Sb and Cu hints at the use of tetrahedrite-tennantite s.s. ore, whereas the lack of associated elements for the Chalpiragorebi beads suggests stibnite instead.

Using the scheme for fractionation correction and in view of the uniqueness of the Caucasian deposits and the strong archaeological tie between these ores and the very existence of Sb metallurgy, it is suggested that the metallic Sb beads of Brili and Chalpiragorebi

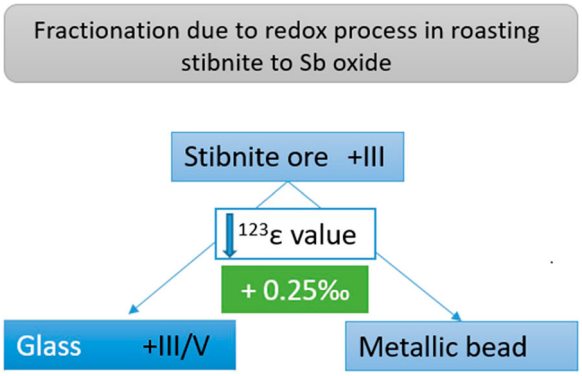


**Figure 9.** Fractionation happening between the raw material on the one hand and the pyrotechnological end product on the other hand. This change in oxidation state during the process of roasting the stibnite (+III) to a Sb oxide (+V) leads to a lighter Sb isotope composition (decreasing $^{123}\varepsilon$ value). This fractionation can be accounted for when making archaeological interpretations by correcting with 0.05–0.25‰ for opacified glass.

are consistent with the local Sb sources of the Racha-Lechkumi region.

In light of the redox processes and fractionation, the negative value for "G17" is interesting (Figure 7). "G17" was originally labelled as ore, found in grave 17 on the site of Brili. However, its XRD shows an amorphous phase and an unattributable antimony peak (Sb, $Sb_2O_3$, $Sb_2S_3$ …). Chemically, "G17" contains 57.6 wt% Sb, 2.5 wt% Fe, and 1.3 wt% As. Therefore, it is most likely evidence of the smelting practice, considering the amorphous phase and the high amounts of Sb, Fe and As. In that case, the negative isotopic value for "G17" can also be explained by the fractionation occurring in the redox process during the metallurgical processing, which seems to follow the same pattern seen in the glass making process. An alternative explanation, based on the redox process, to understand the negative value is that the ore got oxidised under burial circumstances similarly to the valentinite beads at Selvicciola (Italy). Pallecchi, Pecchioli, and Tocci (2002) consider the valentinite nature of the beads as the result of postdepositional processes (oxidation of Sb) due to their small size.

However, the experiments showed that the digestion Procedure 3 also causes a shift of +III to +V in the stibnites. Since these samples have been digested with this procedure, it should be expected that the stibnites have shifted in oxidation state and hence give Sb isotopic values that are 0.25‰ lower than if they would still

be in their original state +III. It remains unclear whether the still highly positive values of the Rachan ores mean that no redox reactions have occurred during digestion or if/whether the metallic beads were affected by this digestion procedure.

## Conclusion

Sb as a raw material was frequently used, both as an opacifier and decolouriser in ancient glasses, as well as an alloying element or in its metallic phase in metal production. Despite this ubiquity, antimony production has only rarely been studied (for medieval times and later, see Siebenschock 1996) and questions concerning its provenance and origin remain unanswered.

While this paper has presented evidence from a relatively limited number of specific laboratory experiments, the results have general significance for the interpretation of Sb isotope compositions as a whole. Firstly, the experiments revealed significant fractionation of stable Sb isotopes during the conversion of stibnite ($Sb^{+III}$) into Sb oxide ($Sb^{+V}$). The range of fractionation appears to be around $^{123}\Delta$ Sb = 0.25‰. Since the induced isotopic shifts can be explained by redox processes, these isotopes can be largely corrected for and being used as a fingerprint with the relation to the source of the element. Hence, for provenancing purposes, fractionation can be taken into account and corrected for when looking for a consistent match with a source, as the Caucasian case study has demonstrated. Secondly, Sb isotopes can be used to differentiate between natural and anthropogenic sources, potentially revealing information about ancient antimony smelting and production techniques. This includes fractionation during technological processing. These results also highlight the potential value of the method to distinguish different technological processes in ancient pyroindustries. Extended fractionation experiments in future research should evaluate the influence of fractionation on Sb-rich metal artefacts (reduction) to model this potential shift quantitatively. Future research should link these results with archaeometallurgical and ancient glass making processes, and look into the Caucasus. This region is of interest, especially the Racha-Lechkumi district in Georgia. Elemental and isotopic data of LBA metallic Sb objects and stibnites from this region were obtained. They suggested that both stibnite and tetrahedrite-tennantite s.s. could have been used as a raw material. Based on the fractionation scheme the Sb isotopic data of the archaeological artefacts are consistent with the local Sb sources. Unfortunately, the digestion procedure used complicates the picture and more research is needed on the link between fractionation and reducing antimony before confident claims about provenance of the metallic Sb jewellery found can be made.

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## Notes on contributors

*Sarah Dillis* is a Ph.D. student at the KU Leuven (Belgium) working on the raw material antimony, in ancient times, focussing on provenance determination of this raw material used in vitreous and metal making by the application of Sb isotope analysis.

*Alicia van Ham-Meert*, having completed an M.Sc. in chemical and materials engineering and in archaeological science, her main doctoral research has focused on non-invasive chemical and isotopic analysis (KU Leuven). Now within the Timber project she focuses on Sr isotopic analysis for tracing medieval timber trade.

*Peter Leeming* is a graduate from the Department of Archaeology and honorary research fellow at the University of Exeter (UK). He has been working in several projects in conjunction with the National Museum of Georgia.

*Andrew Shortland* is professor leading the Cranfield Forensic Institute (UK). His expertise is the identification and interpretation of material culture from the ancient and historical worlds. He is particularly involved in the analysis of glass, glaze and ceramics of a wide range of dates.

*Gela Gobejishvili* is an anthropologist and archaeologist, and the curator of the Brili archive (Georgian National Museum).

*Mikheil Abramishvili* has been the director of the Tbilisi Archaeological Museum (now part of the Georgian National Museum) for the last 20 years. His research interests comprise the development of ancient metallurgy, trade relations and religious beliefs in the Old World.

*Patrick Degryse* is full professor in the division Geology at the KU Leuven (Belgium) and part-time professor in the faculty of Archaeology at Leiden University (the Netherlands). His main research efforts focus on the history and use of mineral resources in ancient ceramic, glass, metal and building materials production, developing geochemical techniques for characterisation and provenancing.

## ORCID

*Alicia Van Ham-Meert* http://orcid.org/0000-0001-6796-3141

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**Dillis, Sarah; van Ham-Meert, Alicia; Leeming, Peter; Shortland, Andrew J.; Gobejishvili, Gela ...**

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