CHEMICAL AND LEAD ISOTOPE CHARACTERISATION OF FIRST WORLD WAR SHRAPNEL BALLS AND BULLETS USED ON THE ALPINE AUSTRIAN–ITALIAN FRONT

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Abstract

Chemical and lead isotope characterisation was carried out on shrapnel balls and bullets dating back to the First World War (WWI). These ammunitions were widely utilised in the Alpine Austrian–Italian front located in the Italian Alps. The investigation has been performed using inductively coupled plasma quadrupole mass spectrometry equipped with an octopole reaction system (ORS-ICP-QMS). The main goal of this work was to identify the elemental and lead isotope composition of raw materials and to discriminate between the military objects analysed. The results of multi-elemental analysis indicate that the shrapnel ball samples consisted of soft Pb or hard Pb with Sb depending on the use, the weapon type and the specific nation. The Italian shrapnel balls were made from hard Pb, as opposed to those of the Austrian–Hungarian samples. Through the investigation of lead isotope ratios, it has been possible to differentiate most of the Italian shrapnel balls from those of Austrian–Hungarian origin. Furthermore, some Italian shrapnel balls had a different lead isotope composition depending on their calibre. The elemental composition and lead isotopic signature of bullets show a clear discrimination between the external jacket and the core in relation to projectile type and nationality. The bullet cores consist of

Pb–Sb alloy regardless of the region of origin. This work allowed us to investigate the potential applications of trace elements and lead isotope analyses to discriminate military artefacts of different origins.

Key words: ICP-MS, trace element, source identification, principal component analysis, forensic science.

Research aims

The aim of this work was to characterise and discriminate between shrapnel balls and bullets dating back to the First World War (WWI) according to their type, use and region of origin. The multi-elementary analysis and lead isotopic composition of these types of samples provide new insights and interesting data on the different raw materials used for the production of these types of munitions used by the Italian and Austrian–Hungarian armies during WWI. The combination of these two analytical techniques to study these types of objects could be a valuable tool for archaeological reconstructions and forensic science.

Introduction

One of the most lethal artillery munitions, extensively used in the European theatre of the First World War (WWI) was the Shrapnel shell (invented by Henry Shrapnel in 1784). This is a type of ogival-headed cylinder grenade with a cavity for the gunpowder charge and a large number of balls that are released on explosion in the air. It was widely utilised in the Austrian–Italian Alpine front that was located in the Italian Alps within the Adamello-Presanella, Ortles-Cevedale and Dolomiti mountain groups, on glacial and periglacial areas above 3,000 metres.

A Shrapnel shell was originally made of cast iron, but gradually its manufacturing materials, as well as its shape and design, were improved thanks to metallurgy innovations from the end of the 19th century.[1] These improvements led to the development of more lethal and effective weapons during WW1 (the Great War) (1914–1918). Despite these technical developments, during the Great War, shrapnel projectiles made previously and with different shapes and materials were also used, given the difficulty of weapon production. Iron shrapnel dating back to 1875, steel shrapnel produced during the first years of the 20th century, and grenade shrapnel from 1917 onwards, were all used during WWI (Figure 1).
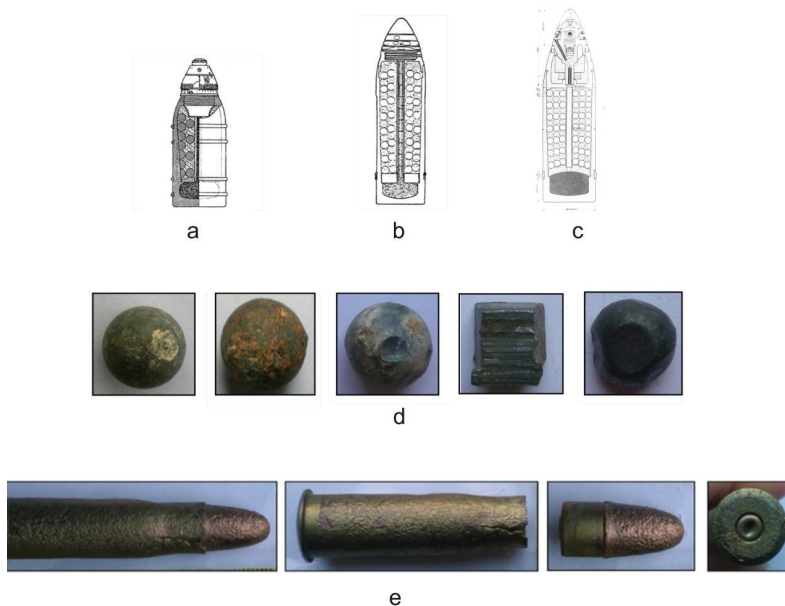
Fig. 1 Some examples of Shrapnels used during WWI: a) Iron shrapnel dated back to 1875, b) steel shrapnel produced in the first years of the 20th century, c) grenade shrapnel from 20thcentury (Marcuzzo, 2003); d) pictures of some shrapnel ball samples analyzed (samples 12, 23, 53, 62, 69); e) pictures of different parts of bullet sample 39.

The differences among these kinds of projectiles refer to the type, the number and the weight of the balls, for example, a 75 mm shrapnel projectile contained between 100 and 300 balls, each weighing between 10 and 16 g.[2] These balls were made of Fe or Pb, and sometimes of hardened Pb (Pb and Sb alloy). They could differ, depending on the nation: in some French shrapnel projectiles, brass balls were also found.[3] The exchange of weapons and war materials, including shrapnel shells, was frequent between cobelligerent nations. This was further complicated by the fact that large quantities of weapons and munitions captured from the enemy were widely used to exploit all the available raw materials and to rectify any chronic lack of munitions.

The application of analytical methods for the characterisation of historical objects of this type, and the determination of their source or geographical origin are appropriate in the context of archaeological recovery. Italian Law no. 78/2001,[4] defines the status of cultural heritage for Great War finds, and museum conservation could help with historical and geographical interpretation.

Several studies using elemental fingerprinting methods (major, minor and trace elements) on a huge variety of samples have provided very valuable information. In addition to elemental concentrations, recent studies have relied upon the subtle

differences in the Pb isotopic abundance present in the samples or objects investigated, in order to characterise a particular material and to use the value for provenance studies. Lead is one of the few elements for which the isotopic composition varies according to the place of origin. In fact, three of the four stable isotopes, ^{206}Pb (24%), ^{207}Pb (23%) and ^{208}Pb (52%), are formed as end products of the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. The ^{204}Pb isotope is the only primordial stable isotope with a constant abundance on earth over time.[5] The isotopic composition of these elements in geological materials and the relative abundance of the different Pb isotopes depend on the relative concentration of the elements involved and the time during which they were together in the material.[6] Therefore, the isotopic composition of Pb in the investigated samples will reflect the isotopic composition of its origin and thus it will vary according to the original composition of the ore body. Moreover, Pb isotopes are apparently not fractionated by industrial usage.[7]

In archeometry, these methods are used to determine the provenance of an archaeological object or the source of a material to characterise its transportation history.[8] These methods are also used both in forensic science to provide useful information in crime and firearms investigations[9] and in environmental research to determine sources of pollution.[10] These fingerprinting methods are most often based on the use of inductively coupled plasma mass spectrometry (ICP-MS). Tamura[11] has demonstrated that the lead isotope ratio measured by using a quadrupole ICP-MS was useful for a practical analysis of bullet samples in forensic science. The introduction of mass spectrometric measurement of the lead isotope ratios of ancient lead artefacts or bullets (and shotgun pellets) has revolutionised the study and characterisation of metals and the discrimination of their origin. Several studies have shown that a combination of chemical and lead isotope analysis is a powerful tool for this purpose. Although ICP-MS analyses do not achieve the precision and the accuracy of isotope ratio determinations obtained using thermal ionisation mass spectrometry (TIMS), several advantageous features make the use of ICP-MS a suitable alternative: fast sample throughput, low sample analysis cost, instrument robustness and simplified sample preparation.[12] The multi-elemental capability, the sensitivity, and the dynamic range of ICP-MS make this instrument the ideal technique for trace element and isotope analysis of bullets, cartridge cases and Pb artillery shots.[13]

In this study, shrapnel balls dating back to WWI from the Austrian–Italian Alpine front were analysed by ICP-MS, equipped with an octopole reaction system (ORS-ICP-QMS), to determine the chemical composition (major, minor and trace elements) and lead isotope ratios. These samples have both known (Italian, Austrian–Hungarian) and unknown origins. Furthermore, investigations have also been conducted on some types of bullets of known origin for different arms (rifles and side arms), dating back to WWI that were used on the Austrian–Italian Alpine front.

The main goal of this work was to identify the elemental and lead isotopic composition of the raw materials and to discriminate among the analysed war objects.

Materials and methods

A total of 13 shrapnel balls and 15 bullet samples provided by the Italian War History Museum of Rovereto (Trento, Italy) and 28 shrapnel ball samples collected by the authors and other experts on the Italian and Austrian–Hungarian front were analysed (Figure1).

Three shrapnel balls from seven types of selected projectiles, dating from WWI with different origins (Italian or Austrian–Hungarian) were taken, making a total of 21 shrapnel balls of known origin (sample codes 51–71, Table 1). The types of selected projectiles were three shrapnel projectiles originating from 1875, two steel shrapnels dating back to the beginning of the 20th century and Italian shrapnel and Austrian grenade shrapnel originating from 1917. Twenty undated shrapnel balls of unknown national origin (sample codes 1, 3–5 and 12–27, Table 1) were also analysed. Moreover, 15 bullets (Table 2) for different models and types of firearm used by the Italian and Austrian–Hungarian armies during WWI were also investigated.

Table 1 Description of the shrapnel ball samples.

Sample Code	Description	Origin
1, 3-5, 12-14 *	Shrapnel ball	Unknown, Marmolada Glacier (BL)
15-27 **	Shrapnel ball	Unknown, Trentino Alto Adige
51, 52, 53 *	Shrapnel ball for shrapnel projectile, caliber 75 mm. Dated back to1875	Italian
54, 55, 56 *	Shrapnel ball for shrapnel projectile, caliber 120 mm. Dated back to 1875	Italian
57, 58, 59 *	Shrapnel ball for shrapnel projectile, caliber 75 mm. Dated back to beginning of the 20th century. Reproduction of drawings at end of the 19th century.	Italian
60, 61, 62 *	Shrapnel ball for shrapnel projectile Pancani, caliber 105 mm Dated back to 1917	Italian
63, 64, 65 *	Shrapnel ball for shrapnel projectile, caliber 150 mm Dated back to1875	Austrian
66, 67, 68 *	Shrapnel ball for shrapnel projectile, caliber 75 mm. Dated back to beginning of the 20th century. Reproduction of drawings at end of the 19th century.	Austrian
69, 70, 71 *	Shrapnel ball for shrapnel projectile, caliber 100mm M15 Brisant Granate. Dated back to 1917. German production.	Austrian

*Shrapnel balls collected on Italian and Austro-Hungarian Alpine front.
**Samples provided by Italian War Historical Museum of Rovereto (Trento, Italy).

Table 2 Description of the bullet samples.

Sample Code	Description	Origin	Year	Average size (mm)
29[**]	Cartridge 8 mm Mannlicher (Mannlicher M95 rifle). Lead bullet with nickel-plated steel external jacket and brass case.	Austrian	1888	8.15 * 50.3
31[**]	Bullet for 8 mm Mannlicher cartridge. Lead bullet with nickel-plated steel external jacket.	Austrian	1888	Caliber 8.15
32, 33[**]	Cartridge 6.5 mm Carcano (Mannlicher - Carcano M91 rifle). Lead bullet with cupronickel external jacket and brass case.	Italian	1895	6.75 * 52.3
34, 35[**]	Cartridge rifle, with case and bullet	Italian		6.75 * 52.3
36[**]	Cartridge 6.5 mm Carcano (Mannlicher - Carcano M91 rifle). Lead bullet with cupronickel external jacket and brass case.	Italian	1895	6.75 * 52.3
38-40[**]	Cartridge 10.4 mm (Vetterli rifle). Lead bullet with brass external jacket and case.	Italian	1870	10.75 * 47.4
42[**]	Cartridge 8 mm Mannlicher (Mannlicher M95 rifle). Lead bullet with nickel-plated steel external jacket and brass case.	Austrian	1888	8.15 * 50.3
47[**]	Cartridge 10.4 mm Glisenti (Glisenti revolver). Armoured brass bullet with brass case.	Italian		
48, 49[**]	Cartridge 9 mm Glisenti (Glisenti revolver model 1910). Armoured brass bullet with brass case.	Italian		8.96 * 19
50[**]	Cartridge 9 mm Steyr gun (model 1911). Lead bullet with steel external jacket and brass case.	Austrian	1911	9.00 * 22.9

** Samples provided by Italian War Historical Museum of Rovereto (Trento, Italy).

Sample preparation

The selected samples, made of metallic materials, were characterised by a heterogeneous oxidised surface layer with different encrustations. The samples were mechanically cleaned using brushes, spatulas and scalpels in order to remove any surface contamination due to soil, organic components and corrosion products to sample the original material. Particularly adherent surface encrustations were removed using deionised water to limit any damage to the samples. Each sample was cleaned with ethanol to remove all organic materials and then dried.

Three representative subsamples were taken from each sample using a battery-powered drill, with a 1 or 2 mm stainless steel bit (decontaminated in an ultrasonic cleaning bath for 5 minutes). In this way, a mixture of fine powder and shavings was obtained for each sample.

A double sampling was performed for bullets with different compositions between the central core and the jacket. The inner core (a) and the external jacket (b) were treated individually for both elemental and isotopic analysis (Figure 1).

To determine the elemental composition and isotope ratios, about 100 to 200 mg of pulverised sample was digested by using a closed digestion procedure in about 15 ml of supra pure HNO_3 (65%; Merck KGaA, Darmstadt, Germany) and ultra pure water (obtained by coupling a Purelab-Option with a Purelab-Ultra system from ELGA-Vivendi Water Systems, Bucks, UK), until complete crystallisation of the sample. The resulting solutions were diluted to 50 ml (by weight) in clean polypropylene centrifuge tubes. The samples were kept frozen at -20 °C until analysis. Sample preparation was performed in a Class 100 Clean Room Laboratory in order to reduce any possible sample contamination.

Analytical method

Major elements (Pb, Sb, Fe, Ni, Cu, Zn), trace elements (Li, Be, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Tl, Pb, Bi, U) and Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) were determined by quadrupole ICP-MS, equipped with an octopole reaction system, Agilent 7500cx (Agilent Technologies, Yokogawa Analytical Systems, Tokyo, Japan), with a quartz double pass spray chamber, thermostated to 2 °C, and fitted with a concentric low flow (< 500 µl min^{-1}) nebuliser (Elemental Scientific Inc, Omaha).

The quantification of major and trace elements was made by external calibration, using solutions prepared gravimetrically from more concentrated certified standard solutions, containing the analytes of interest at a concentration range from 0.97 µg/L to 1083 µg/L. The standard for trace elements was ICUS 2012 (Ultra Scientific, USA – inorganic custom standard, 30 analytes, 10 µg/mL, in water with dilute HNO_3, 5%). A second series of standards has been made for Sn, Ti and Cs, which are not present in the ICUS 2012. The internal standard used was Xenon (129), which is present as an impurity in the argon of the instrument and not present in the samples (as it is a gas) to monitor instrumental sensitivity drift during the analytical run.

Several reagent blanks for each kind of sample were processed to calculate the instrumental detection limit (3x SD of the blank). Data collected from each analysis were corrected for the blank digestion value and the specific dilution factor. Seven shrapnel ball samples were used to check the reproducibility of the method in the absence of a certified material of a similar composition to the samples analysed. Three subsamples were taken, at different points of the sample, and were analysed separately. The average concentration has been calculated for each element, and the mean relative standard deviation (RSD%) was found to be < 15%, except for Li, Mg, Ni, Se, Mo, Sn, Sb where the RSD was between 15 and 20%.

Before quantitative analysis, a semi-quantitative determination of the metals present was performed using a 23-element 90 µg/L multi-element standard. This was done to obtain a clearer idea of the elements present and the order of magnitude of their concentrations, to optimise the method, choose the standards for calibration and to dilute the digests sufficiently to remain in the linearity of the instrument. This preliminary analysis showed that the original material of the samples was quite heterogeneous. Based on this semi-quantitative analysis, aliquots of the principal solutions were diluted 1:10000 to quantify all the important elements in one analytical run, making full use of the linearity of the ICP-MS instrumentation.

A sample of SRM 981 common lead isotopic standard (NIST, Gaithersburg, MD, USA) was dissolved in cold 1:1 (v/v) diluted HNO_3 (65%), which was diluted to give a concentration of 50 mgL^{-1}. This was then diluted to a total lead concentration of 10 µg L^{-1} to be used as a mass bias correction solution for isotope ratio analysis. This in turn was used as a bracketing standard for every four samples to check the mass bias of the isotopic analysis. Each measurement is the average of six replicates. The calculated RSD was < 0.5%. For isotope ratio analysis, each solution was diluted in order to obtain a solution with a lead content of < 10µg L^{-1} for the ICP-MS measurement to ensure that all measurements were carried out in the pulse-counting detection mode.

Elaboration of results

The experimental data were elaborated by using multivariate statistical analysis. Principal component analysis (PCA) and hierarchical clustering analysis (HCA) were applied to the dataset (major, minor and trace element concentrations as well as lead isotope ratios) to evaluate the different characteristics of the samples. This analysis was performed by using the software package Statistica (StatSoft Inc., Tulsa, OK, USA) and UNISTAT (UK).

Results and discussion

In this section we discuss the chemical analysis of shrapnel balls and of bullets as well as discuss the results of lead isotope analysis.

Shrapnel balls – chemical analysis

The results of the elemental analyses of the shrapnel ball samples are presented in Table 3.

Lead was the major component of most of the shrapnel ball samples, with a mean concentration of 92.95% and a range between 83.87% and 96.95% (samples 24–27 were excluded). These lead samples were either very pure soft Pb, or Pb hardened with Sb. The content of this element varied from a minimum of 0.15% to a maximum of 12.60% and had a mean value of 3.82%. The soft Pb might have consisted of very pure virgin Pb, or moderately pure recycled Pb, as shown by the chemical composition of the sample, or a mixture of both types. It can contain from less than 1 ppm (0.0001%) to about 1500 ppm (0.15%) of Sb naturally depending on the ore. On the other hand, hard Pb is an industrial alloy with Sb levels between 0.4% and 12%, depending on the type and the function of the weapon.[14]
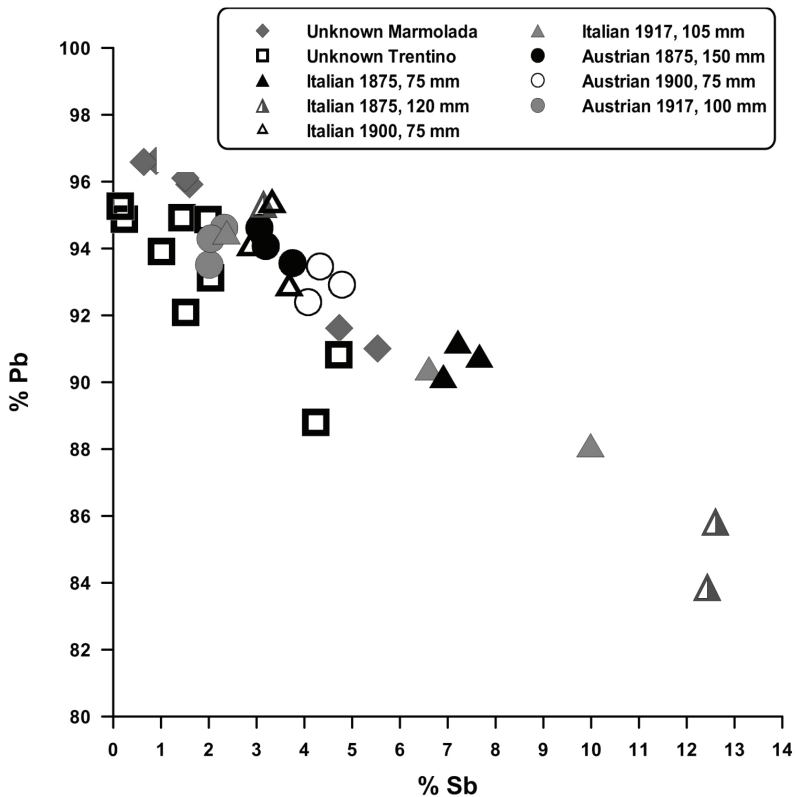

Fig. 2 Scatterplot % Pb vs. % Sb in shrapnel balls samples, without samples with high Fe % (24-27).

In Figure 2, the percentages of Pb and Sb in the analysed samples are compared. The samples have different compositions, depending on their origin, the time of use and the type of projectile. Sb varied from a minimum of about 2% to a maximum of 5% in the Austrian–Hungarian samples and between about 3% and 13% in the Italian samples, showing that Italian shrapnel balls of 1875 (75 mm and 120 mm) and 1917 (105 mm) contained hardened Pb with Sb levels higher than the Austrian–Hungarian samples. The Pb and Sb concentrations were less variable in the Austrian–Hungarian samples, although they had different ages. Furthermore, the Italian samples had different levels of these two elements even between balls retrieved from the same shrapnel projectile. The three Italian balls (57–59) from a 75 mm calibre shell manufactured in 1900 showed similar concentrations to Austrian–Hungarian samples as did samples 54 (120 mm, 1875) and 61 (105 mm, 1917). With the exception of these samples, our results support those reported by Marcuzzo that higher values of Sb were found in Italian shrapnel balls. All the samples of unknown origin had values of Sb that varied but remained lower than 6%. Some samples collected on the Marmolada Glacier had the highest values (average 95%) for Pb (3–5, 12, 14). Most of the Trentino samples of unknown origin had a Pb and Sb composition very similar to Austrian–Hungarian shrapnel balls of 1917.

Some samples (24–27), collected in Trentino Alto Adige, were composed of Fe with a range of 90–97% and an average of 94%. They contained significant traces of V (average of 1.2 mg/g), Mg and Ba (mean values of 4.1 and 8.8 mg/g respectively). References by Marcuzzo confirm the possible use of cast iron or other alloys of Fe for the production of shrapnel.[15]

In order to evaluate the similarities or differences in composition of the analysed samples, PCA was applied on a data set of 41 samples with 26 variables (Li, Be, Mg, Al, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Tl, Pb, Bi, U). Before applying the PCA, standardisation of the variables was performed. Fe, Co and Se were found to be insignificant, as there were too many values below the detection limit (Table 3). The first two PCs covered 59% of the total variance. In the score plot (Figure 3), PC1 and PC2 show a clear distinction between samples of different origins.
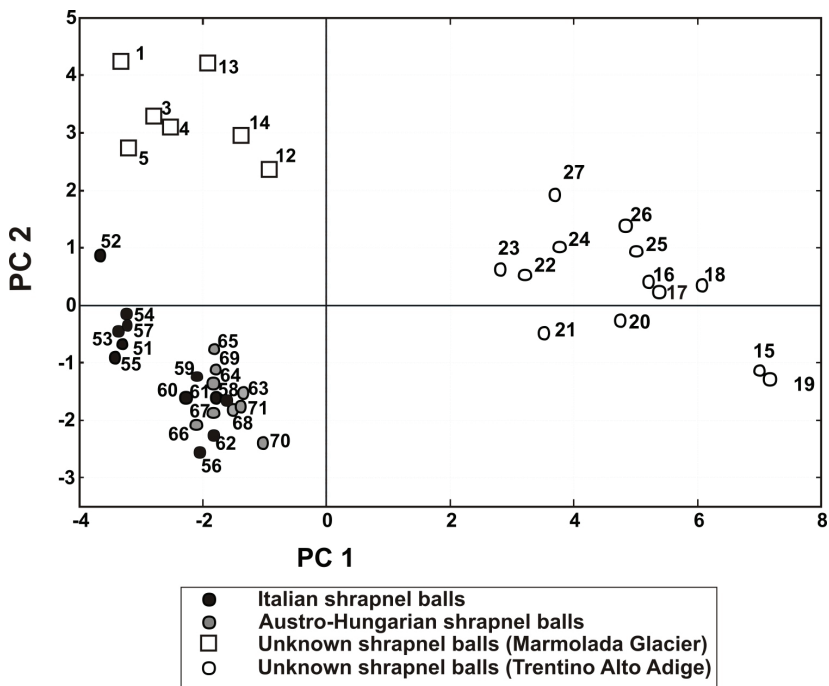
Fig. 3 Score plot of the shrapnel ball samples on the PC1 (46% of explained variance) vs PC2 (13% of explained variance).

PC1 explained 46% of the dataset variance and separated the samples of Trentino origin from the others as highlighted by their high positive scores on the first principal component. They had high positive scores on the first principal component. All the Austrian–Hungarian samples had negative scores on PC1 and PC2 and they were clustered with the Italian samples of different ages and types (56, 58–59, 60–62). The other Italian samples were distinctive and had a higher negative weight on PC1 (all samples from 1875, except sample 56, and sample 57 from 1900). Sample 52 had a slightly higher score on PC2. The shrapnel balls from Marmolada had a negative score on PC1 and a positive score on PC2, representing two subgroups (1, 3–5 and 12–14).

The loading plot of variables (Figure 4) on PC1 and PC2 shows that Sb and Pb had negative scores on PC1 and PC2. They marked all Austrian–Hungarian samples and Italian samples (56, 58–59, 60–62). Some Italian balls (51–55 and 57) were characterised by Tl, Mo, Ag, Bi, Mn with high negative scores on PC1. Li, Ga, Sr, Cd, Ba, Al and Zn were the dominant elements in the positive sector of PC1 and these discriminated the samples from Trentino. V, Be and Cr on PC1 select samples from Trentino with high Fe levels (24–27). Bi, Mn, Ni, As and Cu on PC2 characterised the samples from the Marmolada Glacier.
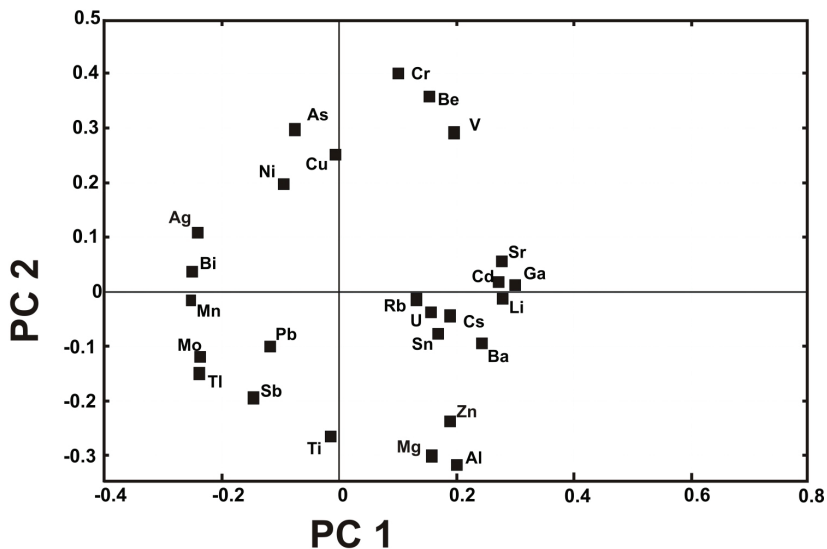
Fig. 4 Loading plot of the variables on the first and the second Principal Component.

This type of data processing confirmed that the Austrian–Hungarian samples had a homogeneous composition, unlike the Italian samples. For these latter shrapnel balls, it was assumed that a mix of raw materials had been used.

Lead isotope analysis

The isotope abundance measurements are reported in Table 4. The reported isotopic ratios considered were $^{208/207}Pb$ and $^{206/207}Pb$. Samples (24–27), with high levels of Fe, were not considered as they contained little lead. About 86% of the source discrimination power was due to the ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes.[16] Since the ratios of lead isotopes did not change during metallurgical processes or chemical reactions, the origin of the metal could be defined uniquely, except where mixing of metals from different provenances occurred.[17] Often, during the First World War, material recovered from the battlefield or war booty was fused and used as a source of metals. The determination of the origin of a specific object was therefore complicated by recycling and re-melting of metals.

In Figure 5, we report the experimental data relative to $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ isotopic ratios of the lead-based shrapnel balls. In accordance with the multi-elemental analysis, the samples of Austrian–Hungarian origin had a very narrow range of the lead isotope values ($^{208/207}Pb$ of 2.456–2.477 and $^{206/207}Pb$ of 1.171–1.193). The samples dating back to 1900 and 1917 possibly originated from similar mining sites, but were different from those dating back to 1875. There was evidence for higher Pb isotopic variability ($^{208/207}Pb$ 2.429–2.472; $^{206/207}Pb$ 1.152–1.188) looking at the Italian samples according to the year and the type of weapon.
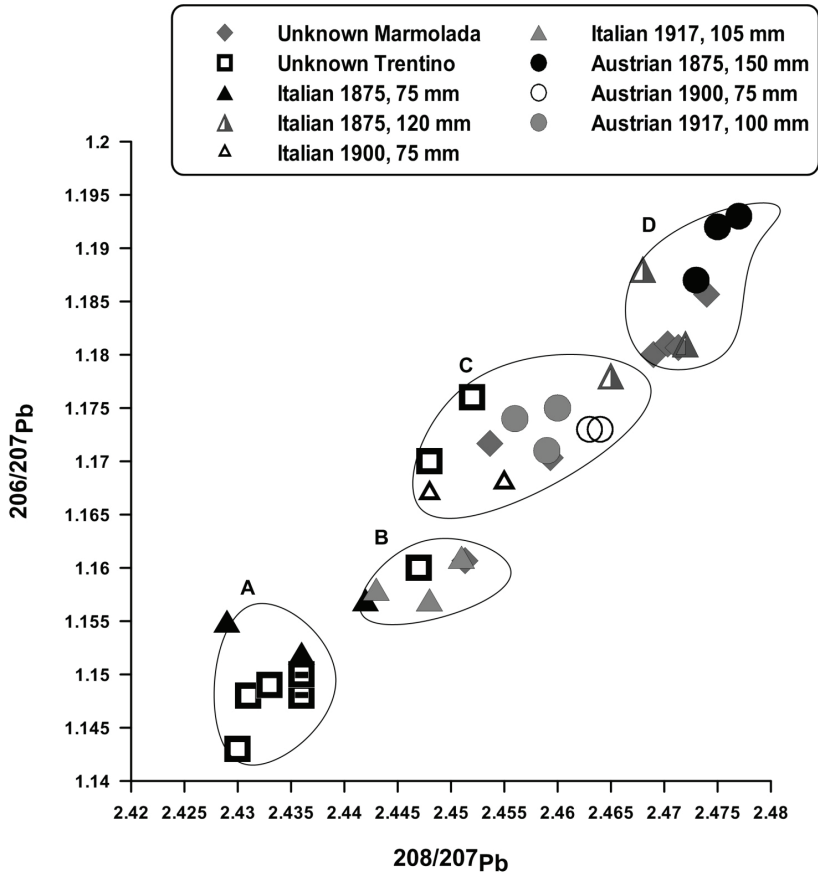
Fig. 5 Lead isotope abundance ratio values 208/207Pb vs 206/207Pb for lead shrapnel ball samples.

Cluster analysis of the lead isotope ratio data was carried out for grouping the samples according to the similarity in the data using Ward's method as agglomerative clustering and Euclidean distances as a similarity measure.[18] Four different groups were found, nominated as A, B, C and D. Group A consisted of two Italian shrapnel balls (51 and 53), belonging to a 75 mm calibre projectile, dating back to 1875. A further five samples from Trentino Alto Adige (15–20) had comparable lead isotopic ratios, which could identify their Italian origin from an 1875 projectile. The PCA showed different characteristics compared to the shrapnels of unknown origin considering the variables Li, Ga, Sr, Cd and Ba. Group B consisted of four samples of Italian origin (sample 52, taken from a 75 mm calibre projectile from 1875; 60–62 from a 105 mm calibre projectile) and two samples of unknown origin, one recovered from the

Marmolada Glacier (14) and one from Trentino Alto Adige (23). Based on Pb isotopic data, these shrapnel balls had an Italian origin, but this data are not confirmed by the results obtained by PCA. The most heterogeneous group was C, which was composed of Italian shrapnel balls from 75 mm calibre projectiles, dating back to 1900 (57–59) and 120 mm projectiles from 1875 (56); Austrian–Hungarian samples for 75 mm calibre projectiles from 1900 and 100 mm projectiles from 1917. This cluster was also confirmed by the PCA. The large variability in the Pb isotopic composition of the Italian samples suggested a possible use of recycled Pb by the Italian armies from captured ammunition. This group also included several samples of unknown origin (4 and 5 from the Marmolada Glacier, and 22 and 21 from the Trentino Alto Adige region), for which attribution of origin was not clear. Italian shrapnel balls for 120 mm calibre projectiles dating back to 1875 (54, 55) belonged to group D, together with three samples of unknown origin (1, 3 and 12). Their Pb isotope ratios were very similar to sample 55 ($^{208/207}$Pb 2.472; $^{206/207}$Pb 1.181). We assumed a probable Italian origin for these samples, although they were distinct from elements with a high positive score on PC2 (As, Ni and Cu). Associated with this group were the Austrian–Hungarian 150 mm calibre balls from 1875 (63-65) and sample 13 found on the Marmolada Glacier. The Austrian–Hungarian origin of this sample was confirmed by macroscopic analysis.

Chemical analysis of bullets

Table 5 reports the elemental concentrations of the core (a) and external jacketing (b) of the investigated bullets.

The inner core of the projectiles consisted of soft Pb or lead hardened with Sb. The Pb average value was 96.21% and varied from 94.74% to 98.50%, and an average Sb content of 0.43%.

Only Austrian–Hungarian bullet cores from 8 mm Mannlicher cartridges (29a, 31a, 42a) and a 9 mm Steyr cartridge (50a) had an Sb concentration > 1%. Even though they had a very similar composition to Italian samples, bullets of Austrian–Hungarian origin had a Pb–Sb alloy core. Italian bullets had soft Pb cores and higher Ni (mean of 0.13%), Cu (mean of 0.38%) and Mo (mean of 0.52 mg/g) concentrations.

Moreover, Italian and Austrian–Hungarian pistol bullet cores were characterised by higher contents of As (mean of 0.59 mg/g), Ag (mean of 2.50 mg/g), Bi (mean of 0.80 mg/g) and Rb (mean of 0.71 mg/g) compared to the cores of rifle bullets.

The external jacket composition varied in relation to the type of projectile and to the specific nation.

Fe was the most abundant element in the Austrian–Hungarian projectiles (29b, 31b, 42b and 50b), with a range of 55.7–100% and an average of 84%. Sample 39b (Italian 10.4 mm cartridge for a Vetterli rifle) was the only one with a Pb jacket. The Italian external jacket of Mannlicher-Carcano M91 rifle bullets (32b, 33b) had high contents of Cu (about 85–100%) and Ni (about 14–18%) but low levels of Zn. They

consisted of cupro-nickel (copper-nickel) (a Cu-Ni-Zn alloy), as reported by Mötz.[19] Instead, the data showed a different composition for Vetterli rifle bullets and Glisenti revolver bullet jackets (38b, 40b–49b). They had a Cu mean concentration of 70% and Zn about 33%. These types of weapons had a bullet with a brass jacket.

Lead isotope analysis

Pb isotope ratio measurements were performed on the core and on the external jackets of the projectiles. The results are presented in Table 6.

Bullet core samples had $^{208/207}$Pb values from 2.434 to 2.456 and $^{206/207}$Pb from 1.143 to 1.171. These observed variations of the core samples did not allow for accurate determination of weapon type or specific nationality. During WWI, weapons and ammunition taken from the enemy troops were often used or were fused to produce other war objects, including cartridges.[20] The use of recycled raw materials seems to have been valid, especially for the core of the projectiles. This was confirmed both by historic information[21] and by macroscopic observation of the structure of the projectiles investigated. The external jacket, which represented the most important part of a bullet, had different technical characteristics and a different chemical composition depending on the type of weapon but also on the country of production. It was principally made of higher-quality materials using non-recycled metal from definite sources. The external jacketing of Italian and Austrian–Hungarian samples were well discriminated, based on their Pb isotope ratio values. Independently of the weapon type, the jackets of the Austrian–Hungarian samples 29b, 31b (bullet for Mannlicher M95 rifle) and 50b (bullet for 9 mm Steyr pistol) had similar Pb isotopic ratios ($^{208/207}$ Pb 2.425–2.432; $^{206/207}$ Pb 1.145–1.149).

For samples 32–35, 47 and 48, analogous value are observed ($^{208/207}$ Pb 2.444–2.454; $^{206/207}$ Pb 1.158–1.164). These samples belonged to Italian bullets for 6.5 mm Carcano rifles (Mannlicher-Carcano M91) and 9 mm Glisenti cartridges (Glisenti revolver model 1910) respectively.

The two samples, 40b and 38b, are bullets for an Italian Vetterli rifle of 10.4 mm calibre. They have different Pb isotopic ratios ($^{208/207}$ Pb 2.466–2.472; $^{206/207}$ Pb 1.179–1.18) compared to the external jacket of the other Italian bullets. The Pb from a different mineral deposit or recycled material was probably used.

Conclusion

This article presented the results of chemical and lead isotope characterisation of shrapnel balls and some bullet types dating back to WWI that were used on the Austrian–Italian Alpine front. The work reported here allowed us to investigate the potential applications of trace elements and lead isotope analyses to discriminate war objects with different origins. The use of an ICP-MS instrument has the advantage of obtaining a large amount of information without a complex pre-treatment of the sample.

The possibility to create a classified data set according to the specific weapon models, the nation of origin, and date of manufacturing of shrapnel balls, allowed us to obtain reliable results. The survey also provided interesting information on the chemical composition and the raw materials used during WWI.

The First World War munitions analysed were mainly made from Pb-Sb alloys, Fe alloys and Cu alloys with variable concentrations of Ni and Zn. The shrapnel ball samples consisted of soft Pb or Pb hardened with Sb depending on the use, the weapon type and the specific nation. The Italian shrapnel balls were made from hard Pb unlike the Austrian–Hungarian samples. Moreover, the Austrian–Hungarian shrapnel balls had a homogeneous chemical composition. Most of the Italian shrapnel balls dating back to 1875 had a different composition compared to other Italian samples and Austrian–Hungarian shrapnel balls.

Lead isotope analysis allowed a separation between Italian samples from 1875 for 75 mm and 120 mm calibre. Italian shrapnel balls dating back to 1900 (calibre 75 mm) and 1917 (calibre 105 mm) also had distinct lead isotope compositions. The Austrian–Hungarian shrapnel balls show a narrow range of variation of lead isotope ratios. The 1900 Austrian–Hungarian shrapnel balls (75 mm calibre) and 1917 (100 mm calibre) probably had the same Pb source. However, the use of recycled material for ammunition production changed the natural variation of isotope abundance ratios. Recycled material was probably used for the production of some Italian shrapnel balls. For this reason, the characterisation of samples of unknown origin (of the Marmolada Glacier and Trentino Alto Adige) can be difficult in some cases. Both analytical methods used showed a clear discrimination of the external jacket of the analysed bullets, which represented the most important part of a bullet, in relation to projectile type and specific nation. The bullet cores consisted of Pb-Sb alloy regardless of the region of origin. This could indicate the use of preferably recycled material for the bullet cores.

This work allowed us to investigate for the first time along the Alpine front the potential applications of trace elements and lead isotope analyses to differentiate between military artefacts of different origins. This could largely benefit future reconstruction of WWI military fighting making it possible to determine the effective role played in the battle by each combatant force and the correspondence between literature and field data on the real deployment of soldiers

Acknowledgements

Table 3 Concentration of determined elements in investigated shrapnel balls samples (major elements expressed as a %, minor and trace elements as mg/g); method detection limit (d.l*) (mg/g) for Be = 0.008; Al = 0.31; V = 0.003; Cr = 0.028; Mn = 0.023; Fe = 0.223; Co = 0.010; Se = 0.342; Tl = 0.002.

Sample Code	Li (mg/g)	Be (mg/g)	Mg (mg/g)	Al (mg/g)	Ti (mg/g)	V (mg/g)	Cr (mg/g)	Mn (mg/g)	Fe (%)	Co (mg/g)	Ni (%)	Cu (%)	Zn (%)	Ga (mg/g)
1	0.04	1.17	2.09	-	0.9	0.44	2.12	0.55	< d.l.	< d.l.	0.29	0.19	0.07	0.01
3	0.02	1.02	1.73	-	0.7	0.38	1.87	0.48	< d.l.	< d.l.	0.25	0.09	0.07	-
4	0.01	0.99	1.92	-,	0.7	0.37	1.84	0.46	< d.l.	< d.l.	0.26	0.14	0.08	-
5	-	0.96	2.56	-	0.71	0.36	1.76	0.45	< d.l.	< d.l.	0.25	0.08	0.08	-
12	0.18	0.31	2.01	2.36	1.44	0.63	0.44	0.98	< d.l.	< d.l.	0.41	0.37	0.19	0.48
13	0.13	0.26	2.32	1.62	1.33	0.56	0.40	0.88	< d.l.	< d.l.	0.44	0.49	0.19	0.44
14	0.12	0.24	1.95	1.79	1.26	0.52	0.37	0.81	< d.l.	< d.l.	0.39	0.54	0.37	0.40
15	0.79	0.75	6.55	18.39	1.35	0.53	0.86	< d.l.	< d.l.	< d.l.	0.09	0.15	0.64	2.11
16	0.75	0.7	4.24	13.38	1.29	0.49	0.81	< d.l.	< d.l.	< d.l.	0.07	0.14	0.45	1.80
17	0.73	0.7	5.12	13.41	1.23	0.49	0.77	< d.l.	< d.l.	< d.l.	0.06	0.14	0.45	1.74
18	0.84	0.78	4.22	15.03	1.34	0.53	0.87	< d.l.	< d.l.	< d.l.	0.07	0.15	0.49	1.96
19	0.83	0.79	11.68	14.95	1.34	0.56	0.91	< d.l.	< d.l.	< d.l.	0.06	0.17	0.60	1.88
20	0.58	0.56	4.80	12.58	1	0.39	0.64	< d.l.	< d.l.	< d.l.	0.06	0.12	0.42	1.55
21	0.56	0.52	2.69	10.67	0.94	0.36	0.62	< d.l.	< d.l.	< d.l.	0.04	0.12	1.10	1.43
22	0.58	0.55	3.72	10.44	0.99	0.39	0.62	< d.l.	< d.l.	< d.l.	0.04	0.10	0.37	1.42
23	0.57	0.53	3.17	8.93	0.95	0.37	0.60	< d.l.	< d.l.	< d.l.	0.03	0.10	0.32	1.25
24	0.52	0.49	4.52	11.75	1.79	1.03	0.85	< d.l.	96.64	< d.l.	0.06	0.19	0.36	1.39
25	0.63	0.59	4.32	13.96	2.21	1.5	1.11	< d.l.	95.11	< d.l.	0.07	0.16	0.44	1.57
26	0.58	0.55	4.13	12.39	1.58	1.47	1.04	< d.l.	95.86	< d.l.	0.07	0.12	0.45	1.73
27	0.54	0.52	3.58	9.57	0.91	1.04	0.87	< d.l.	89.83	< d.l.	0.16	0.17	0.34	1.33
51	0.14	< d.l.	1.63	< d.l.	1.80	< d.l.	< d.l.	0.66	< d.l.	< d.l.	0.29	0.13	0.10	0.03
52	0.12	< d.l.	2.14	< d.l.	1.40	< d.l.	< d.l.	0.52	< d.l.	< d.l.	1.83	0.09	0.09	0.03

Table 3 continued

Sample Code	Li (mg/g)	Be (mg/g)	Mg (mg/g)	Al (mg/g)	Ti (mg/g)	V (mg/g)	Cr (mg/g)	Mn (mg/g)	Fe (%)	Co (mg/g)	Ni (%)	Cu (%)	Zn (%)	Ga (mg/g)
53	0.13	< d.l.	1.84	0.45	1.67	< d.l.	< d.l.	0.58	< d.l.	< d.l.	0.30	0.13	0.10	0.03
54	0.12	< d.l.	2.42	0.45	1.58	< d.l.	< d.l.	0.56	< d.l.	< d.l.	0.26	0.11	0.08	0.03
55	0.1	< d.l	2.69	0.5	1.44	0.01	< d.l.	0.52	< d.l.	< d.l.	0.26	0.10	0.11	0.04
56	0.13	< d.l	4.72	11.35	1.62	0.01	< d.l.	0.66	< d.l.	< d.l.	0.12	0.12	0.42	0.25
57	0.12	< d.l.	2.44	< d.l.	1.58	0.01	< d.l.	0.52	< d.l.	< d.l.	0.14	0.13	0.09	0.04
58	0.14	0.03	4.48	11.15	1.5	0.01	< d.l.	0.66	< d.l.	< d.l.	0.08	0.16	0.38	0.25
59	0.10	< d.l	4.29	9.81	1.29	0.01	< d.l.	0.52	< d.l.	< d.l.	0.06	0.14	0.33	0.23
60	0.11	< d.l	4.38	8.1	1.45	0.01	< d.l.	0.58	< d.l.	< d.l.	0.12	0.10	0.34	0.23
61	0.10	< d.l.	4.63	10.38	1.39	< d.l.	< d.l.	0.55	< d.l.	< d.l.	0.06	0.10	0.36	0.23
62	0.11	< d.l	5.77	9.77	1.50	0.03	< d.l.	0.64	< d.l.	< d.l.	0.04	0.11	0.38	0.24
63	0.11	< d.l.	4.25	12.57	1.61	0.003	0.09	0.59	< d.l.	< d.l.	0.04	0.16	0.41	0.35
64	0.12	< d.l	4.56	12	1.54	0.01	0.03	0.59	< d.l.	< d.l.	0.05	0.16	0.44	0.26
65	0.12	0.02	3.88	10.05	1.41	0.01	< d.l.	0.56	< d.l.	< d.l.	0.03	0.16	0.34	0.22
66	0.11	< d.l	4.51	11.8	1.46	0.01	< d.l.	0.58	< d.l.	< d.l.	0.03	0.12	0.38	0.25
67	0.11	< d.l.	3.82	10.34	1.44	0.01	< d.l.	0.58	< d.l.	< d.l.	0.03	0.11	0.37	0.27
68	0.09	< d.l.	3.96	12.44	1.32	0.01	< d.l.	0.52	< d.l.	< d.l.	0.03	0.11	0.38	0.29
69	0.11	< d.l	3.37	8.79	1.50	0.02	< d.l.	0.59	< d.l.	< d.l.	0.03	0.18	0.33	0.23
70	0.11	< d.l	6.61	15.97	1.43	0.01	< d.l.	0.59	< d.l.	< d.l.	0.03	0.14	0.45	0.27
71	0.11	< d.l.	4.33	11.19	1.60	0.003	< d.l.	0.66	< d.l.	< d.l.	0.04	0.16	0.39	0.26

Table 3 continued

Sample Code	As (mg/g)	Se (mg/g)	Rb (mg/g)	Sr (mg/g)	Mo (mg/g)	Ag (mg/g)	Cd (mg/g)	Sn (mg/g)	Sb (%)	Cs (mg/g)	Ba (mg/g)	Tl (mg/g)	Pb (%)	Bi (mg/g)	U (mg/g)
1	7.39	2.07	0.67	0.02	2.17	0.61	0.33	1.41	5.53	-	5.99	0.31	91.00	0.82	0.13
3	3.03	1.83	0.58	-	1.87	0.55	0.28	-	1.59	0.19	5.33	0.29	95.91	0.72	0.10
4	2.26	1.79	0.57	-	1.80	0.53	0.26	-	0.90	0.18	5.32	0.30	96.61	0.67	0.10
5	2.09	1.64	0.55	-	1.74	0.49	0.26	0.05	1.51	0.17	4.98	0.30	96.10	0.65	0.10
12	2.93	<d.l.	0.75	0.52	-	0.95	-	0.08	0.57	0.24	0.77	<d.l.	96.95	0.22	0.15
13	12.49	<d.l.	0.68	0.47	0.01	0.93	-	1.50	4.73	0.21	0.86	<d.l.	91.61	0.19	0.11
14	3.65	<d.l.	0.64	0.47	0.001	0.84	0.07	0.42	0.64	0.20	0.64	<d.l.	96.58	0.33	0.10
15	2.04	<d.l.	0.79	0.90	0.20	0.01	0.86	11.64	4.24	0.31	12.69	<d.l.	88.79	0.02	0.16
16	1.67	<d.l.	0.74	0.81	0.21	0.01	0.80	3.62	0.24	0.26	10.58	<d.l.	94.87	0.02	0.15
17	1.60	<d.l.	0.71	0.81	0.15	0.02	0.78	0.68	0.15	0.34	9.95	<d.l.	95.26	0.01	0.14
18	1.83	<d.l.	0.80	0.88	0.20	0.01	0.88	2.00	1.01	0.28	11.21	<d.l.	93.90	0.03	0.18
19	1.76	<d.l.	0.83	0.93	0.18	0.03	0.91	6.65	1.52	0.32	10.88	<d.l.	92.08	0.02	0.17
20	1.35	<d.l.	0.59	0.67	0.11	0.01	0.64	7.21	2.04	0.22	9.19	<d.l.	93.12	0.14	0.24
21	1.15	<d.l.	0.54	0.61	0.11	0.03	0.60	2.31	4.73	0.18	8.27	<d.l.	90.82	0.18	0.11
22	2.02	<d.l.	0.57	0.64	0.07	0.01	0.63	0.09	1.44	0.19	8.22	<d.l.	94.91	0.09	0.12
23	1.12	<d.l.	0.56	0.61	0.09	0.01	0.61	0.06	1.99	0.18	7.21	<d.l.	94.86	0.02	0.11
24	1.45	<d.l.	0.52	0.59	0.07	0.001	0.57	0.09	0.03	0.16	8.16	<d.l.	-	0.0004	0.10
25	1.69	<d.l.	0.61	0.70	0.09	0.003	0.68	0.14	0.03	0.19	9.08	<d.l.	0.27	0.002	0.12
26	1.62	<d.l.	0.57	0.69	0.07	0.01	0.66	0.03	0.03	0.18	10.35	<d.l.	-	0.005	0.12
27	1.38	<d.l.	0.52	0.58	0.07	0.01	0.57	0.07	0.03	0.21	7.44	<d.l.	6.53	0.001	0.11
51	2.51	<d.l.	0.66	0.03	1.77	0.55	0.19	0.04	7.66	0.21	0.09	0.26	90.79	0.48	0.13
52	2.05	<d.l.	0.50	0.03	1.37	0.42	0.16	0.01	6.91	0.15	0.1	0.22	90.18	0.37	0.10
53	2.53	<d.l.	0.60	0.03	1.62	0.50	0.19	0.03	7.21	0.19	0.16	0.24	91.21	0.44	0.12

Table 3 continued

Sample Code	As (mg/g)	Se (mg/g)	Rb (mg/g)	Sr (mg/g)	Mo (mg/g)	Ag (mg/g)	Cd (mg/g)	Sn (mg/g)	Sb (%)	Cs (mg/g)	Ba (mg/g)	Tl (mg/g)	Pb (%)	Bi (mg/g)	U (mg/g)
54	2.54	< d.l.	0.55	0.04	1.47	0.47	0.18	0.03	3.14	0.17	0.07	0.22	95.33	0.45	0.11
55	2.59	< d.l.	0.52	0.04	1.39	0.45	0.17	0.06	12.6	0.16	0.43	0.23	85.83	0.39	0.10
56	2.22	< d.l.	0.61	0.15	1.63	0.51	0.20	0.31	12.43	0.19	5.84	0.24	83.87	0.45	0.12
57	2.09	< d.l.	0.56	0.03	1.48	0.47	0.18	0.18	3.33	0.17	0.16	0.26	95.30	0.48	0.11
58	1.76	< d.l.	0.58	0.20	1.47	0.49	0.22	0.36	3.68	0.19	5.51	0.25	92.81	0.50	0.11
59	1.39	< d.l.	0.47	0.13	1.23	0.40	0.16	0.41	2.87	0.14	5.06	0.23	94.02	0.46	0.09
60	1.44	< d.l.	0.52	0.12	1.38	0.43	0.18	0.06	6.6	0.16	5.15	0.21	90.42	0.40	0.10
61	1.37	< d.l.	0.50	0.13	1.35	0.42	0.16	0.03	2.37	0.15	5.07	0.23	94.48	0.39	0.10
62	1.44	< d.l.	0.55	0.16	1.45	0.47	0.19	0.07	9.99	0.17	5.10	0.23	88.12	0.43	0.13
63	3.60	< d.l.	0.55	0.14	1.55	0.51	0.18	0.28	3.19	0.17	6.42	0.32	94.07	0.46	0.17
64	3.70	< d.l.	0.55	0.13	1.47	0.50	0.18	0.06	3.75	0.17	5.83	0.25	93.56	0.41	0.11
65	3.33	< d.l.	0.53	0.15	1.35	0.49	0.19	0.03	3.06	0.17	4.81	0.23	94.61	0.37	0.13
66	1.49	< d.l.	0.53	0.13	1.42	0.45	0.18	0.06	4.78	0.17	5.61	0.25	92.92	0.37	0.11
67	1.39	< d.l.	0.52	0.14	1.36	0.43	0.17	0.04	4.33	0.16	5.96	0.23	93.46	0.35	0.10
68	1.37	< d.l.	0.48	0.14	1.24	0.39	0.16	0.03	4.08	0.15	6.97	0.24	92.39	0.32	0.09
69	1.40	< d.l.	0.55	0.18	1.42	0.49	0.19	0.84	2.32	0.17	4.73	0.24	94.61	0.40	0.11
70	1.11	< d.l.	0.53	0.16	1.37	0.45	0.19	2.80	2.01	0.16	6.10	0.23	93.52	0.42	0.10
71	1.50	< d.l.	0.56	0.16	1.43	0.47	0.18	1.68	2.04	0.17	5.67	0.24	94.29	0.40	0.11

*<d.l. means element present below the method detection limit, calculated from the instrumental LOD by treating the value as a sample result.

Table 5 Concentration of determined elements in investigated bullet samples (major elements expressed as a %, minor and trace elements as mg/g). The bullet cores are labelled with letter "a" and the jackets with "b"; method detection limit (d.l*) (mg/g) for Be = 0.008; Mg = 0.142 ; Al = 0.31; V = 0.003; Cr = 0.003; Mn = 0.028; Fe = 0.023; Co = 0.223; Cu = 0.010; Se = 0.342; Tl = 0.002.

Sample code	Li (mg/g)	Be (mg/g)	Mg (mg/g)	Al (mg/g)	Ti (mg/g)	V (mg/g)	Cr (mg/g)	Mn (mg/g)	Fe (%)	Co (mg/g)	Ni (%)	Cu (%)	Zn (%)	Ga (mg/g)
29a	0.58	0.55	3.34	10.68	1.01	0.39	0.65	<d.l.	<d.l.	<d.l.	0.03	0.10	0.37	1.38
31a	0.58	0.54	3.96	9.75	1.06	0.38	0.63	<d.l.	<d.l.	<d.l.	0.04	0.10	0.36	1.39
32a	0.46	0.44	3.29	11.24	0.78	0.3	0.51	<d.l.	<d.l.	<d.l.	0.03	0.09	0.32	1.18
33a	0.67	0.64	4.13	15.4	1.2	0.45	0.75	<d.l.	<d.l.	<d.l.	0.18	1.03	0.43	1.44
34a	0.51	0.49	4.17	13.14	0.92	0.34	0.56	<d.l.	<d.l.	<d.l.	0.18	0.97	0.39	1.39
35a	0.50	0.48	2.94	11.31	0.92	0.33	0.56	<d.l.	<d.l.	<d.l.	0.12	0.56	0.46	1.10
36a	0.61	0.57	4.11	16.11	1.03	0.41	0.70	<d.l.	<d.l.	<d.l.	0.05	0.26	0.48	1.69
38a	0.58	0.57	4.09	11.38	1.03	0.4	0.65	<d.l.	<d.l.	<d.l.	0.03	0.12	0.37	1.48
39a	0.49	0.47	4.85	13.6	0.93	0.33	0.56	<d.l.	<d.l.	<d.l.	0.03	0.10	0.39	1.33
40a	0.47	0.45	3.66	11.2	0.78	0.32	0.57	<d.l.	<d.l.	<d.l.	0.03	0.34	0.47	1.37
42a	0.46	0.43	3.11	10.82	0.76	0.30	0.53	<d.l.	<d.l.	<d.l.	0.02	0.10	0.33	1.23
47a	0.15	0.01	1.57	<d.l.	1.61	0.01	<d.l.	0.61	<d.l.	<d.l.	0.24	0.13	0.10	0.04
48a	0.17	<d.l.	2.49	<d.l.	1.92	0.01	<d.l.	0.7	<d.l.	<d.l.	0.25	0.15	0.13	0.04
49a	0.20	0.01	3.48	<d.l.	2.41	0.01	<d.l.	0.9	<d.l.	<d.l.	0.34	0.20	0.15	0.06
50a	0.16	0.02	1.70	<d.l.	1.56	<d.l.	<d.l.	0.59	<d.l.	<d.l.	0.23	0.20	0.09	0.04
29b	0.08	0.34	<d.l.	12.5	0.05	0.16	0.94	<d.l.	71.43	<d.l.	0.10	0.16	0.34	0.63
31b	0.04	0.35	<d.l.	14.53	0.07	0.16	1.00	<d.l.	55.69	<d.l.	0.08	0.16	0.36	0.65
32b	0.06	0.27	<d.l.	8.55	0.03	0.14	0.68	<d.l.	<d.l.	<d.l.	14.77	85.92	0.24	0.44
33b	0.03	0.33	<d.l.	17.85	0.1	0.15	0.92	<d.l.	<d.l.	0.2	17.99	102.31	0.50	0.68
34b	0.04	0.27	<d.l.	10.86	0.04	0.12	0.72	<d.l.	<d.l.	0.62	16.11	94.43	0.28	0.51
35b	0.03	0.26	<d.l.	15.24	0.04	0.12	0.70	<d.l.	<d.l.	1.78	14.44	85.25	0.39	0.53
36b	0.04	0.33	<d.l.	19.19	0.11	0.14	0.90	<d.l.	<d.l.	0.32	14.69	85.33	0.54	0.68
38b	0.03	0.29	<d.l.	12.84	0.02	0.13	0.76	<d.l.	<d.l.	<d.l.	0.08	74.27	33.21	0.54

Table 5 continued

Sample code	Li (mg/g)	Be (mg/g)	Mg (mg/g)	Al (mg/g)	Ti (mg/g)	V (mg/g)	Cr (mg/g)	Mn (mg/g)	Fe (%)	Co (mg/g)	Ni (%)	Cu (%)	Zn (%)	Ga (mg/g)
39b	0.04	0.32	<d.l.	12.91	0.05	0.14	0.84	<d.l.	<d.l.	<d.l.	0.26	0.18	0.33	0.59
40b	0.02	0.31	<d.l.	10.58	0.01	0.14	0.84	<d.l.	<d.l.	<d.l.	0.04	68.75	36.32	0.54
42b	0.03	0.37	<d.l.	12.24	0.11	0.16	0.99	<d.l.	107.81	<d.l.	0.05	0.49	0.34	0.67
47b	0.03	0.26	<d.l.	9.41	0.08	0.13	0.72	<d.l.	<d.l.	<d.l.	0.04	67.33	34.88	0.52
48b	0.02	0.25	<d.l.	10.79	0.002	0.11	0.68	<d.l.	<d.l.	<d.l.	0.03	70.50	26.48	0.46
49b	0.03	0.28	<d.l.	13.7	0.06	0.13	0.77	<d.l.	<d.l.	<d.l.	0.04	70.00	33.36	0.59
50b	0.02	0.3	<d.l.	14.15	0.04	0.13	0.87	<d.l.	99.39	<d.l.	0.26	0.18	0.36	0.65

Sample code	As (mg/g)	Se (mg/g)	Rb (mg/g)	Sr (mg/g)	Mo (mg/g)	Ag (mg/g)	Cd (mg/g)	Sn (mg/g)	Sb (%)	Cs (mg/g)	Ba (mg/g)	Tl (mg/g)	Pb (%)	Bi (mg/g)	U (mg/g)
29a	1.11	<d.l.	0.58	0.66	0.04	0.01	0.65	0.03	1.51	0.18	7.95	<d.l.	94.99	0.14	0.12
31a	1.08	<d.l.	0.57	0.64	0.06	0.01	0.63	0.03	1.54	0.18	7.99	<d.l.	95.06	0.14	0.11
32a	0.80	<d.l.	0.46	0.55	0.08	0.0001	0.50	0.03	0.03	0.14	6.91	<d.l.	96.75	0.07	0.09
33a	1.18	<d.l.	0.67	0.73	0.06	0.01	0.72	0.04	0.03	0.20	8.18	<d.l.	94.74	0.09	0.14
34a	0.92	<d.l.	0.51	0.61	0.02	0.001	0.56	0.02	0.03	0.16	8.15	<d.l.	95.22	0.09	0.12
35a	0.89	<d.l.	0.50	0.54	0.03	0.001	0.55	0.02	0.03	0.15	6.17	<d.l.	96.03	0.98	0.10
36a	1.20	<d.l.	0.60	0.69	0.01	0.01	0.67	0.06	0.04	0.18	9.72	<d.l.	95.37	0.09	0.12
38a	1.05	<d.l.	0.58	0.66	0.01	0.01	0.65	0.04	0.03	0.18	8.42	<d.l.	96.25	0.01	0.12
39a	0.86	<d.l.	0.49	0.56	0.01	0.01	0.53	0.03	0.02	0.15	7.86	<d.l.	96.21	0.02	0.10
40a	0.83	<d.l.	0.47	0.55	0.02	0.01	0.50	0.03	0.03	0.15	7.97	<d.l.	96.18	0.06	0.13
42a	0.88	<d.l.	0.46	0.52	0.01	0.01	0.50	0.11	1.53	0.14	7.3	<d.l.	95.26	0.35	0.09
47a	2.17	<d.l.	0.62	0.03	1.70	0.51	0.21	0.04	0.003	0.21	<d.l.	0.24	98.50	0.52	0.12
48a	2.47	<d.l.	0.72	0.05	1.92	0.60	0.26	0.08	0.001	0.23	0.02	0.26	98.21	0.58	0.14
49a	3.23	<d.l.	0.91	0.06	2.42	0.75	0.31	0.05	0.01	0.30	0.46	0.3	97.54	1.53	0.18
50a	2.13	<d.l.	0.59	0.06	1.53	0.51	0.20	0.18	1.61	0.24	0.32	0.26	96.80	0.55	0.11

Table 5 continued

29b	<d.l.	1.70	0.70	0.11	1.82	0.51	0.17	0.15	0.55	0.39	6.02	<d.l.	24.79	0.07	0.13
31b	<d.l.	1.67	0.73	0.11	1.88	0.51	0.16	0.11	0.79	0.24	6.39	<d.l.	40.04	0.08	0.13
32b	<d.l.	1.00	0.53	0.08	1.36	0.41	0.13	0.02	0.02	0.35	4.07	<d.l.	<d.l.	0.01	0.09
33b	<d.l.	1.26	0.68	0.11	1.78	0.50	0.14	0.04	0.03	0.22	8.03	<d.l.	<d.l.	0.01	0.13
34b	<d.l.	0.99	0.56	0.08	1.43	0.40	0.11	0.04	0.02	0.17	5.20	<d.l.	<d.l.	0.01	0.10
35b	<d.l.	0.92	0.55	0.11	1.40	0.40	0.12	0.04	0.02	0.22	6.01	<d.l.	<d.l.	0.01	0.10
36b	<d.l.	1.19	0.69	0.10	1.79	0.50	0.34	0.09	0.03	0.21	7.62	<d.l.	<d.l.	0.01	0.12
38b	<d.l.	1.06	0.59	0.08	1.49	0.53	0.25	0.35	0.02	0.24	5.73	<d.l.	<d.l.	0.06	0.10
39b	<d.l.	1.18	0.65	0.10	1.67	0.48	0.13	0.08	0.03	0.20	5.66	<d.l.	96.68	0.03	0.12
40b	<d.l.	1.05	0.66	0.08	1.66	0.59	0.28	0.02	0.03	0.2	4.68	<d.l.	<d.l.	0.24	0.12
42b	<d.l.	1.53	0.76	0.11	1.91	0.54	0.15	0.04	0.09	0.24	6.25	<d.l.	<d.l.	0.01	0.13
47b	<d.l.	0.91	0.55	0.08	1.40	0.40	0.26	0.03	0.02	0.17	5.22	<d.l.	<d.l.	0.01	0.1
48b	<d.l.	0.87	0.54	0.08	1.33	0.40	0.88	0.04	0.02	0.18	4.14	<d.l.	0.89	0.01	0.1
49b	<d.l.	0.98	0.59	0.10	1.52	0.45	0.47	0.08	0.02	0.18	6.68	<d.l.	<d.l.	0.01	0.11
50b	<d.l.	1.04	0.62	0.10	1.55	0.43	0.12	0.08	0.24	0.19	8	<d.l.	<d.l.	0.03	0.11

*<d.l. means element present below the method detection limit, calculated from the instrumental LOD by treating the value as a sample result.

Table 6 Lead isotope abundance ratios of the bullet samples. The bullet cores are labelled with letter "a" and the jackets with "b".

SAMPLE CODE															
	29a	31a	32a	33a	34a	35a	36a	38a	39a	40a	42a	47a	48a	49a	50a
$^{208/207}$Pb	2.441	2.435	2.440	2.452	2.446	2.438	2.453	2.434	2.444	2.448	2.446	2.454	2.456	2.439	2.447
$^{206/207}$Pb	1.151	1.146	1.152	1.164	1.157	1.156	1.166	1.143	1.150	1.153	1.155	1.171	1.163	1.157	1.156
	29b	31b	32b	33b	34b	35b	36b	38b	39b	40b	42b	47b	48b	49b	50b
$^{208/207}$Pb	2.429	2.425	2.450	2.454	2.451	2.444	2.583	2.472	2.446	2.466	2.462	2.449	2.447	2.445	2.432
$^{206/207}$Pb	1.149	1.145	1.164	1.164	1.158	1.163	1.170	1.179	1.153	1.180	1.175	1.163	1.160	1.170	1.149

Endnotes

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