Burnett and Nunziata
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Divergent gunshot residues and characterization of the memory effect in a .22 caliber revolver and pistol

Bryan R. Burnett[1*] and Felice Nunziata[2]

Abstract

Background The forms and compositions of primer gunshot residue (GSR) in shooting cases have been routinely analyzed in many crime labs by scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDS). Gunshot residue studies over the last 30 years have identified a contribution by residual GSR from surfaces within the firearm to GSR (the "memory effect"). In this study, we first focus on the GSR compositional differences between target, bore, and cylinder gap for a .22 caliber revolver which has received little attention in the literature. Secondly, we examine the behavior of elements involved in the residual contribution to GSR for a .22 caliber pistol.

Results The compositions of target, bore, and cylinder gap GSRs from a .22 caliber revolver were determined for 11 discharge series. Breech GSR compositions from a .22 caliber pistol changed in sequential discharges revealing behavior of individual primer and bullet elements. The target GSR forms from some .22 caliber ammunitions were not spherical.

Conclusions For the revolver, GSR compositions from the target, bore, and cylinder gap are divergent. Analysis of the pistol's breech GSRs indicated mixing with the previously deposited GSRs resulting in a sequential contribution or loss of elements and redeposition of the new composition. Aluminum did not contribute to the residual GSR. The GSR composition of a discharge and its contribution to residual GSR on the internal parts of the firearm represents a complex process which likely involves a number of variables including, but not restricted to firearm design, primer composition, pressure and temperature of the discharge gas, and bullet surface composition.

Keywords Gunshot residue, .22 caliber, Revolver, Pistol, Scanning electron microscopy/energy-dispersive X-ray spectroscopy, Memory effect

Background

Zeichner et al. (1991) reported GSR composition from one cartridge firing can be contaminated by elements from previously fired cartridges of different primer compositions. Later studies confirmed GSR from previous firearm discharges contributes to GSR (Gunaratnam and Himberg 1994; Harris 1995; Zeichner et al., 1997a; Henchoz 1999; Wrobel et al. 1998; Henchoz et al. 1999; Lebiedzik 2001; Brożek-Mucha 2007; Brożek-Mucha 2008; Martiny et al. 2008; Mastruko et al. 2009a; Mastruko et al. 2009b; Rijnders et al. 2010; Charles et al. 2011; Charles and Nys 2013; Lebiedzik 2013; Romolo et al. 2018; Donghi et al. 2019; Romanò et al. 2020). This phenomenon has been called the "memory effect" (Rijnders et al. 2010; Charles et al. 2011). Charles and Nys (2013) noted for a .32 caliber pistol as much as a 47% of the GSR composition had elements from previous discharges and for a .22 caliber pistol 40%. None of these previous studies accounted for the potential of inorganic elements

*Correspondence:
Bryan R. Burnett
brburnett73@gmail.com
[1] Meixa Tech, 1624 Debann Road, Cardiff, CA 92007-1102, USA
[2] Mathematics and Physics Department — Università degli Studi della Campania LUIGI VANVITELLI Viale Lincoln No. 5, 81100 Caserta, Italy

associated with gunpowder (Miyauchi et al. 1998; Burnett et al. 2020), a contribution which could be mistaken for residual firearm GSR resulting in the memory effect. Merli et al. (2021) examined the contribution of bullet jacket ablation to GSR by firing heavy-metal-free ammunition in a new pistol.

Different proportions of lead (Pb), antimony (Sb), and barium (Ba) between the muzzle and breech GSR were first reported for a .357 revolver (Burnett 1989). Brożek-Mucha (2008) noted the composition of GSR from the muzzle of a 9mm pistol discharge differed from that collected from the hands and clothing of the shooter (i.e., GSR from the breech of the pistol). However, Rijnders et al. (2010) compared GSR compositions surrounding a 9 mm pistol from four different brands of ammunition finding high correlations between four samples surrounding the pistol for all ammunitions.

The purpose of this paper is to present our preliminary research on the nature of GSR compositional differences, from a revolver between the muzzle, bore, and cylinder gap and pistol breech, to ascertain the persistence and mobilization of residual elements from the firearm interior surfaces (the memory effect). This analysis included the behavior of Pb-associated individual primer and bullet elements that participate in the memory effect phenomenon. Rimfire .22 caliber firearms were selected for this work mainly due to low cost. There were a variety of Pb-based primer compositions between different manufacturers (Andrasko and Maehly 1977; Heye and Guinn 1988) and even different lots from the same manufacturer leading to our selection of ammunitions with Pb as the only heavy metal to provide insight into the behaviors of primer and bullet elements. The latter included bullet clad copper (Cu) and brass (CuZn) and the bullet surface metal, Sb (Zeichner et al., 1997b; Wrobel et al., 1998).

Methods

A used .22 caliber Smith and Wesson (S&W) Model 18 six cartridge revolver was purchased from a gun store. The history of this S&W revolver prior to these tests was unknown. To locate areas of GSR deposition, the revolver was imaged with a high-resolution, high depth of field Pixera 600CL digital camera coupled with a Computar Macro 10× lens.

A .22 caliber Ruger MKII semiautomatic pistol was purchased new. The ammunition used with this pistol was recorded from its first discharge after purchase. There were no unrecorded shots during this study except the likely one or two test discharges at the factory of unknown primer composition.

The ammunitions used in this study had two sources. Vintage .22 caliber ammunitions were purchased on eBay, and gun shows in San Diego. The ages of some of these ammunitions could have been more than 40 years when these experiments occurred. New ammunitions were purchased at a local gun store.

Bullet diameters were measured to hundredth millimeter using a digimatic micrometer. Fifty bullets from each of four unclad and three clad (CuZn and Cu) brands/lots boxes were measured.

Bullets of .22 caliber LR cartridges from CCI, Federal, Peters, Remington, Winchester, Eley, Dynamit Nobel, Imperial, Aguila, and Junior and were separated from their casings by a momentum hammer. Unfired casings were cut with long nose nippers to expose the primer. The half casings with intact primer were imaged with the Pixera digital camera system.

An ETEC Autoscan scanning electron microscope (SEM) was used in these analyses and was equipped with a Kevex Quantum X-ray detector interfaced via a Kevex 4850s to an IXRF Systems 500 for digital image captures and energy-dispersive x-ray spectroscopy (EDS) for element analysis.

The surfaces of .22 caliber bullets from Federal Power-Flite and Remington Golden bullets were removed by razor blade swipe and examined by SEM/EDS. The bullet surfaces of other brands examined in this study were analyzed by SEM to identify bullets with surface Sb.

Unfired primers from Peters Golden Bullet and vintage Federal Power-Flite .22 LR cartridges were examined by SEM/EDS (now not advisable (Burnett et al. 2020)). Discharged casings of Aguila, Imperial, Federal, CCI, Winchester, and Remington were sampled for primer composition. A piece of graphite-impregnated double sticky tape was wrapped around a 3.15 mm D dowel and inserted into the fired casing. The casing sides were dabbed. The tape was unwrapped from the dowel with a forceps and applied to a SEM stub. The elemental compositions of the primer residues adherent to the tapes were identified by EDS.

Prior to the S&W revolver and Ruger pistol discharges, their bores were cleaned by a wire brush followed by a cotton swab soaked with a commercial firearm cleaning fluid (Kleen Bore Gun Conditioner®). Two dry cotton swabs were passed through the bores of each firearm multiple times to collect residual cleaning fluid and loose debris.

To determine suitable .22 caliber ammunitions for the experiments that would address the nature of the memory effect as well as the compositional differences between muzzle and breech or cylinder gap GSRs, more than thirty brands/lots were discharge at rayon fabric cloths at 10 cm and some at 5 cm. Pieces, 1 × 1 cm in size, were cut with a razor blade 1 cm from the bullet hole and mounted on the sticky SEM stubs. Three drops of an electroconductive organic compound (Burnett

2014) were dripped onto the fabric sample and dried and viewed in the SEM.

The surveying in the SEM of these many ammunitions with the revolver showed some .22 caliber brands (e.g., Eley) produced oddly shaped GSR particles that were not used for later analyses.

Scanning electron microscope samplers were constructed by attachment with double sticky tape of a 1.5-mm-thick graphite disk to a standard 13 mm D SEM stub. Graphite-impregnated double sticky tape was attached to the carbon disk (sticky SEM stub).

Additional rayon fabric targets were shot with select ammunitions at 10 cm muzzle-target distance for further study. The bore wipe samples for both the revolver and pistol were collected by a cotton swab passed through the bore of the revolver using a cleaning rod. For the side target, GSR was collected on Canson® velum (backed by masking tape) taped over the cylinder gap of the revolver (Fig. 1) and ejection port (breech sample) of the pistol. These sample surfaces were each dabbed ten times with the sticky SEM stubs.

Four experiment series were performed with the Ruger MKII pistol (Table 1, bottom). Only breech samples were taken using the vellum collection technique (Fig. 1). Series 1 (Federal Power-Flite) and series 2 (CCI) were not sampled for GSR. For series 3, Remington Golden Bullet (primer: PbSbBa; bullet CuZn on Sb/Pb) 7 cartridges were fired and breech sampled from discharges 1, 2, 4, 5, 7, 11, and 12 for EDS analysis. Series 4 consisted of 20 discharges of Aguila .22 caliber cartridges (primer: PbCaSi; bullet clad: Cu on Pb) from which 5 breech samples were collected (samples 4, 8, 12, 16, and 20) for EDS analysis. The Aguila .22 LR ammunition was well suited

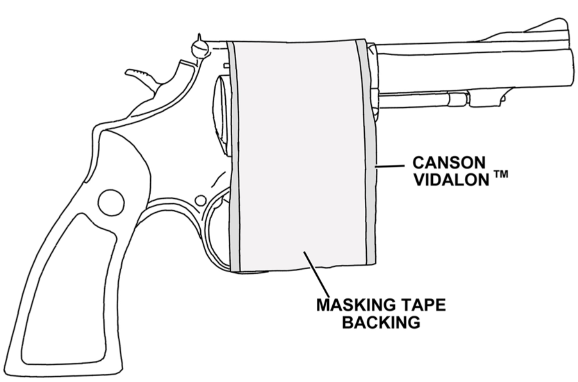

Fig. 1 The Smith and Wesson Model 18 revolver with the attached vellum backed by masking tape draped over its side to intercept cylinder gap GSR, minimizing retrograde muzzle GSR contamination. The exit port of the Ruger MKII pistol was similarly draped for breech GSR collection

for this experiment series because the only detected elements in its primer were Pb, Ca, and Si (likely lead styphnate and calcium silicide, $CaSi_2$), with no Sb layer on its bullet surface.

Only spherical particles, approximately 1 μm in diameter, were sampled by EDS. The beam, in spot mode, was directed at the center of each particle for a 5-s EDS acquire. The number of particles analyzed per sample for the S&W revolver ranged from 93 to 149 ($N = 23$, mean 102). For the Ruger breech GSR samples ($N = 12$), one-hundred particles per sample were analyzed. The peaks for Pb Lα, Sb Lα, Ba Lα, Cu Kα, Zn Kα, Al Kα, and Si Kα were integrated over nine channels (four channels on either side of the central peak line) of 10 eV/channel. The IXRF systems software calculated the elements' weight percentage using IXRF's deconvolution software routine. These data were transferred to ASCII files for computer analyses. A BASIC program is written to sort the particles' compositions into categories which were Pb (no detected Sb or Ba), PbSb, PbBa, and PbSbBa. Association of the bullet surface elements, Cu, and Zn, with these particles were tabulated as separate categories, CuZn and Cu (Zn not detected). For series 6 of the S&W revolver experiment, the X-ray counts per second (CPS) for Cu (without detected Zn) and Zn (without detected Cu) were graphed.

Results

The .22 caliber cartridge primer structure

The .22 caliber primer material covers the base of the cartridge. For many of the .22 cartridges (e.g., Aguila (Fig. 2A), CCI (Fig. 2B), Imperial (Fig. 2C)), the primers were not restricted to the base but extend onto the casing sides. This primer form included CCI, Imperial, Winchester, Federal, and Remington. Intimately associated with these cartridges' cream-colored primer was a green material of unknown function. Eley rimfire primer, restricted to the casing base, was covered by a red wax-like material (Fig. 2D). For the Junior rimfire steel cartridges, primer was restricted to the casing base without the associated green covering material (Fig. 2F).

The .22 caliber bullet

Plots of the .22 caliber bullet diameters for the seven brands/lots are shown in Fig. 3. Fifty bullets were measured per brand. The range of diameters for unclad bullets for the four brands/lots was 5.54 to 5.64 mm (Fig. 3). For the three boxes of clad bullets, the diameter range was 5.60 to 5.67 mm.

Table 1 Number of shots fired and GSR sampling for the S&W Model 18 revolver and Ruger MKII pistol. For the S&W revolver, eleven shooting series and samples were taken as indicated. One spent casing from each brand was sampled to determine the primer composition. The Peters Golden Bullet analysis was performed on unfired primer. A bullet from each ammunition lot was examined in the SEM to determine by EDS the presence of an antimony (Sb) layer (marked with an "X" if present and a "0" if not. Bullets lacking cladding of Cu or CuZn were designated "0." Key: *Fed.* Federal, *Rem.* Remington, *Win.* Winchester, *BW* bore wipe, *T* target, *CG* cylinder gap

	Series	# Fired	Brand	Primer	Bullet Sb layer	Cu/CuZn	Comments
	1	40	Fed. Lightning	PbSbBa	X	0	Final shot BW sample
	2	18	Aguila	PbCaSi	0	Cu	Final shot BW sample
	3	24	Fed. Power-Flite	PbSbBa	X	0	Final shot BW sample/same lot series 5
	4	24	Fed. Lightning	PbBa	0	0	Final shot BW sample/same lot series 6
S&W	5	24	Fed. Power-Flite	PbSbBa	X	0	No GSR samples
Model		2	Peters Golden Bullet	PbCaSi	X	CuZn	Final shot BW & T samples/same lot series 6, 7, & 8
18	6	24	Fed. Lightning	PbBa	0	0	No GSR samples
Revolver		2	Peters Golden Bullet	PbCaSi	X	CuZn	Final shot BW & T samples/same lot series 5, 7, & 8
	7	24	Peters Golden Bullet	Pb	X	CuZn	Final shot BW, T, & CG samples/same lot series 5, 6, & 8
	8	24	Fed. Lightning	PbBa	X	0	No GSR samples
		2	Peters Golden Bullet	PbCaSi	X	CuZn	Final shot BW, T, & CG samples/same lot series 5, 6, & 7
	9	24	Win. Wildcat	PbBa	X	0	No GSR samples/same lot series 10
		2	Rem. Golden Bullet	PbSbBa	X	CuZn	Final shot BW, T, & CG samples/same lot series 10 & 11
	10	24	Win. Wildcat	PbBa	X	0	No GSR samples/same lot series 9
		2	Peters Golden Bullet	PbCaSi	X	CuZn	Final shot BW, T, & CG samples/same lot series 10 & 11
	11	14	Rem. Golden Bullet	PbSbBa	X	CuZn	Final shot BW, T, & CG samples/same lot series 9 & 10
Ruger	1	15	Fed. Power-Flite	PbSbBa	X	0	No GSR samples/same lot S&W series 3
MKII	2	4	CCI	PbBa	X	0	No GSR samples
Pistol	3	12	Rem. Golden Bullet	PbSbBa	X	CuZn	Breech GSR shots 1, 2, 4, 5, 6, 11, and 12
	4	20	Aguila	PbCaSi	0	Cu	Breech GSR shots 4, 8, 12, 16, and 20

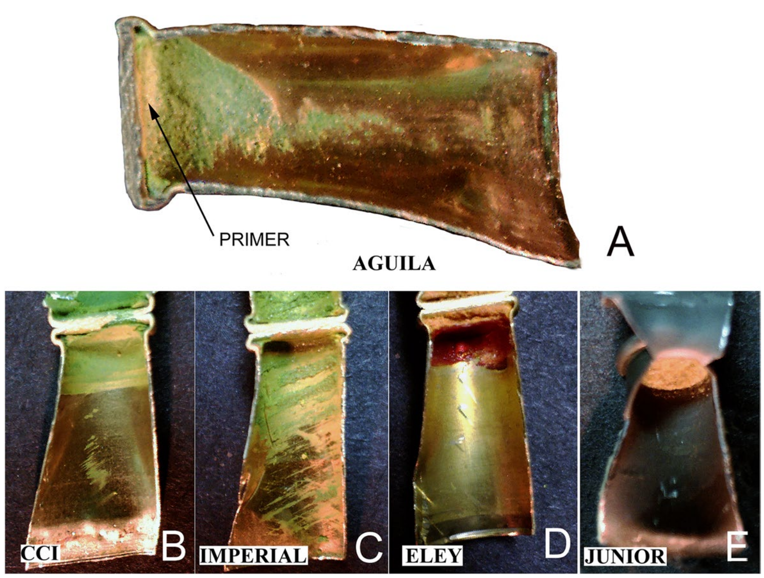

Fig. 2 Unfired longitudinally cut .22 caliber rimfire casings showing primer distribution for five different brands. **A** The Aguila primer was cream colored with green-colored covering material not restricted to the casing base, but extending to the casing sides. The green material associated with the primer has not been identified. **B** and **C** As in A with CCI and Imperial primers. **D** The Eley primer appeared to be overlaid by a wax-like substance. **E** The jJunior primer material was restricted to the steel casing base without the associated green material

The .22 caliber bullet surface

Federal, Winchester, Peters, and Remington .22 bullet surfaces were examined by SEM/EDS showing surface Sb layers were also present under Cu or CuZn claddings. The SEM/EDS analyses of Federal bullets with no cladding (Fig. 4A) and Remington with CuZn cladding (Fig. 3B) had surface layers of Sb or PbSb. The bullets listed in Table 1, "Sb Layer," marked by an "X," and those with no Sb layer, are marked by "0."

The .22 caliber primer compositions

The compositions of .22 caliber cartridge primers (Table 1) varied from manufacturer to manufacturer. Peters Golden Bullet primer (Fig. 5A), as well as Aguila primers (Fig. 5B), in addition to Pb were found to likely have calcium silicide ($CaSi_2$). These primers might also include silica (glass) particles. Vintage Federal Lightning, vintage Federal Power-Flite and recently purchased Remington (head stamp "*REM*") primers were tri-component, PbSbBa (e.g., Fig. 5C). Most .22 caliber brands (CCI, Winchester, some Federal, Eley, Imperial, Junior, and Dynamit Nobel) examined in this study had PbBa-containing primer (e.g., Fig. 5D).

Other more recent Federal .22 caliber cartridges, including other lots of Federal Lightning, had PbBa primer compositions, while some vintage Federal .22 caliber ammunitions had primer compositions of PbSbBa. There have been no other recent studies of .22 caliber primer compositions that the authors are aware.

The form of muzzle GSR particles

Not all .22 caliber ammunitions surveyed produced spherical GSR. The majority of these particles were composed of Pb, except as otherwise noted. A Federal Champion produced not only the typical spherical particles but also irregular fibers (Fig. 6A) perhaps from ablation of the bullet that was not subject to melting. Most of the target .22 caliber GSR observed in the SEM had spherical particles (e.g., Fig. 6B). Imperial produced extremely small (nano) Pb particles (Fig. 6C). Some ammunitions produced relatively large molten particles that splattered on the target (Fig. 6D). Dynamit Nobel Subsonic produced oval particles (Fig. 6E). Federal Power-Flite's GSR from this lot was fibrous, likely crystalline (Fig. 6F). Dynamit Nobel Target had elongated rounded particles as well as oval and spherical particles (Fig. 6G). A discharge with Remington Kleanbore at 5 cm coated the target fibers with irregular and spherical particles (Fig. 6H).

The Smith and Wesson revolver

The S&W revolver cylinder-barrel face is shown in Fig. 7A. The left chamber flare overlaps the right (Fig. 7A at black arrows), and an apparent heavy deposition of GSR is in the left chamber marks of the edge of the casing (at arrow). Residual GSR can be seen in both chambers. The barrel face of the revolver also has a GSR flare (Fig. 7B between arrows), and the

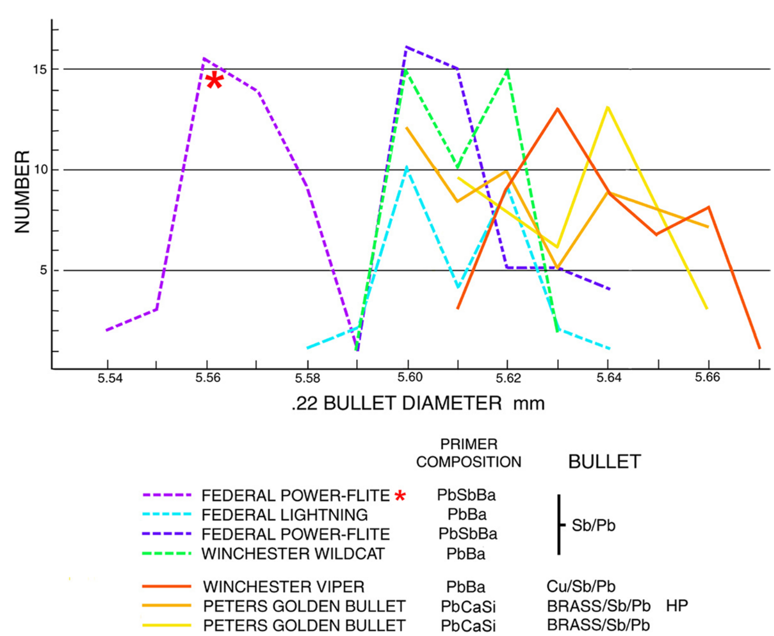

Fig. 3 Graph of the diameters of seven brands of .22 caliber bullets; fifty bullets were measured from each brand. The asterisked Federal Power-Flite bullet diameters are smaller than the other .22 caliber bullets

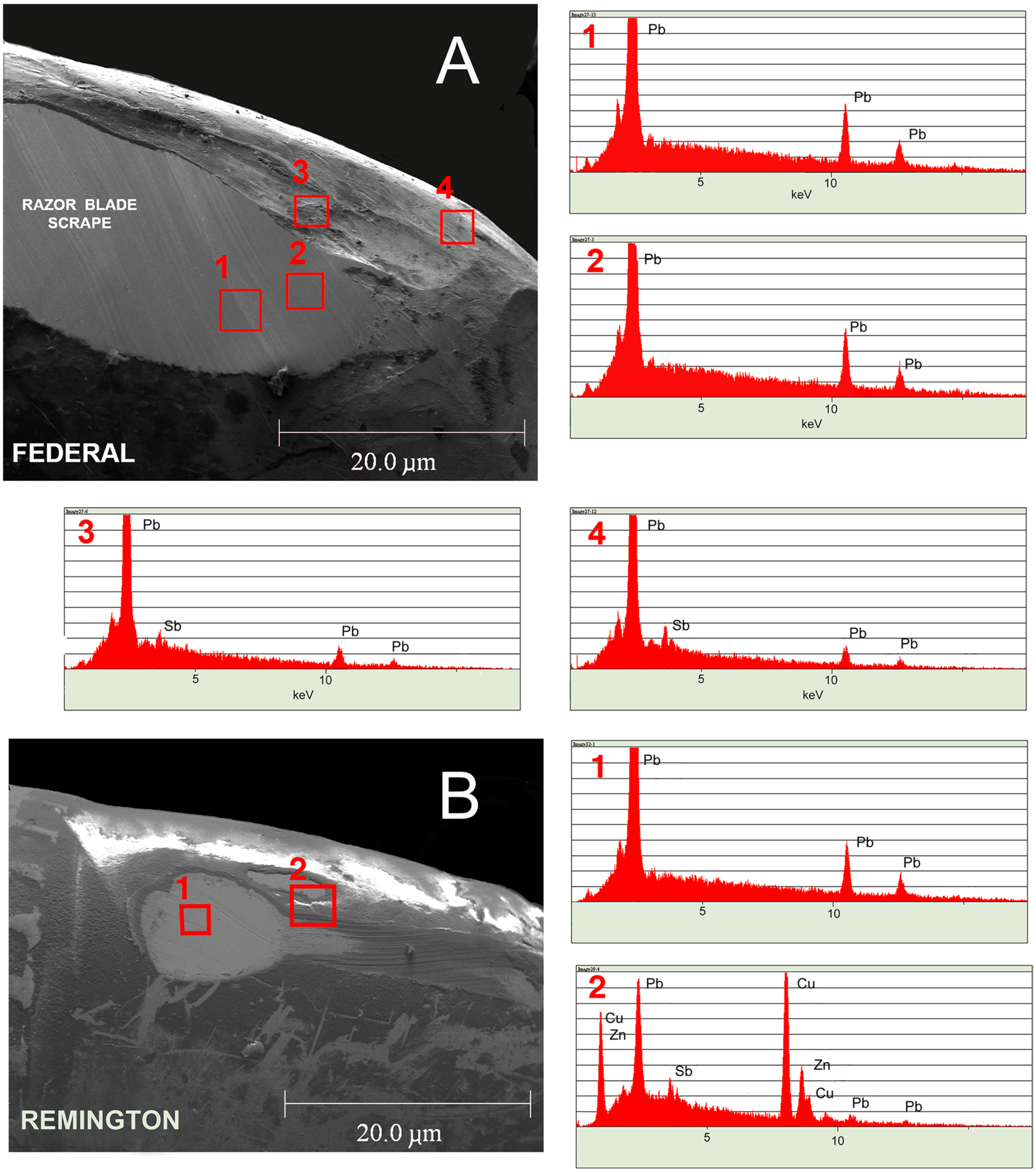

Fig. 4 Antimony surface layers on two .22 caliber bullets. **A** The surface of a Federal Power-Flite bullet that had been scraped by a razor blade; Sb was not detected in areas of EDS samples 1 and 2 from the razor scrape area but was detected in areas of the unscraped bullet (EDS areas 3 and 4). **B** The scraped surface of a Remington Golden Bullet upon which beam rastering (EDS area 1) did not detect Sb; Sb was detected in EDS area 2 on the unscraped surface

accumulation from the barrel face also likely contributed to the GSR from previous discharges to the cylinder gap GSR.

An area in the bore (Fig. 7B) of this revolver has circumferential rugae, which may ablate the passing bullet, possibly generating the fibrous GSR observed in

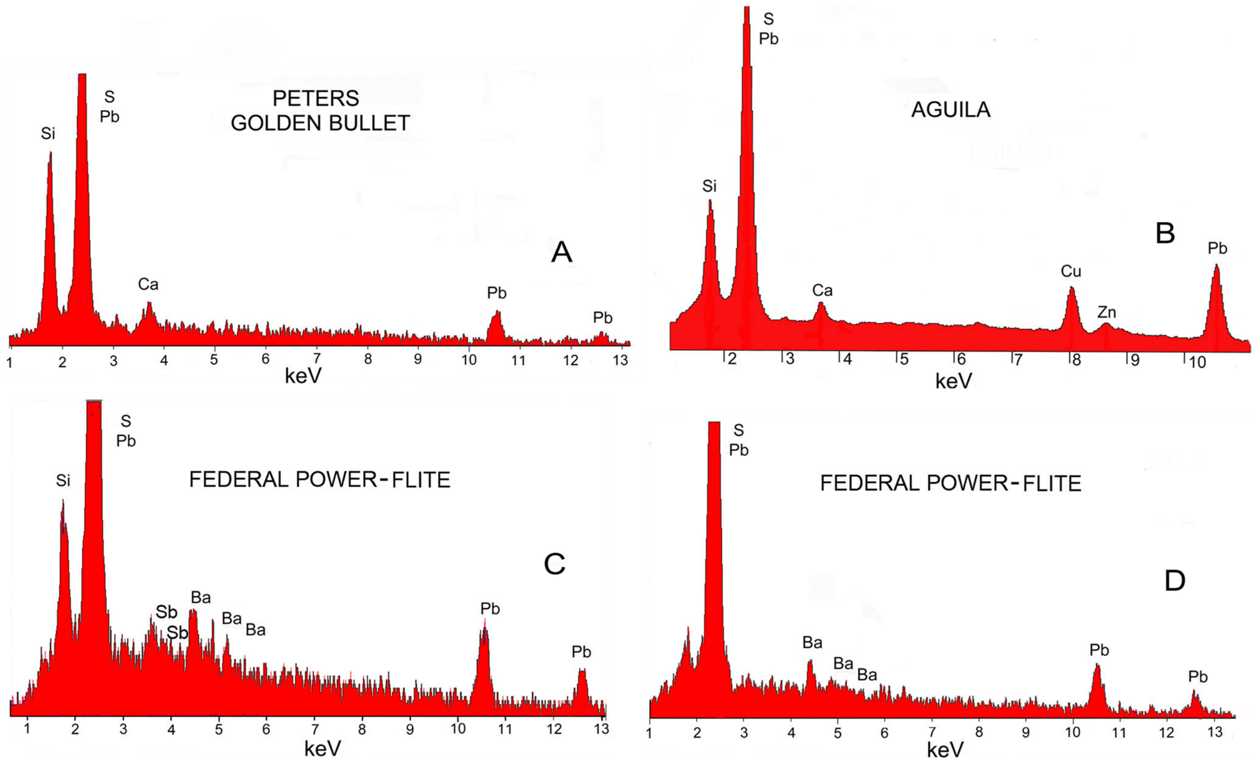

Fig. 5 **A** Spectrum of Peters Golden Bullet unfired lead/calcium silicide ($PbCaSi_2$) primer. **B** Spectrum of Aguila fired lead/calcium silicide ($PbCaSi_2$) primer; the CuZn is from the casing. **C** Spectrum of Federal Power-Flite unfired PbSbBa primer. **D** Spectrum of Federal Power-Flite unfired PbBa primer

one samples (Fig. 6A). Other fibrous GSR (Fig. 5 F and G) appeared to be crystalline and likely formed by a different process.

Target, bore, and cylinder gap GSR from the S&W revolver

The first four series from the S&W revolver (Table 2, samples 1 through 4) were followed by only bore wipes from the final discharges (Fig. 8A). In series 2 (primer PbCaSi), the bullets were Cu clad, and the final shot produced GSR particles had 20% Cu association. Bore wipe samples following the final shots of series 1, 3, and 4 showed no Cu associated with their GSRs. Of these four series, only series 3 had bullets with the Sb layer.

Figure 8B plots of the percentage compositions (Pb, PbSb, PbBa, and PbSbBa) of the five series (Table 2, samples 5, 6, 7, 8, and 10) are shown where the final primer discharge composition was PbCaSi. For series 5 and 6, both the bore wipe and target samples were analyzed. For series 7, 8, and 10, bore wipe, target, and cylinder gap samples were analyzed for the final shot in the series and the resultant GSR percent compositions shown. The bore wipe, target, and cylinder gap GSR compositions for the final discharge PbSbBa primer of series 9 and 11 (Table 2, samples 9 and 11) are shown in Fig. 8C.

Brass (CuZn) and copper (Cu)

The final discharges of series 5 through 11 had bullet CuZn cladding. The percentages of CuZn, Cu, and Zn associated with characteristic and consistent GSR particles are presented as box plots in Fig. 9. Brass detected in the GSR particles was less than 15% in most of the samples (Fig. 9A, left) with two at 21% on the bore and target samples of series 11. The series 7 cylinder gap sample had 78% GSR particles with CuZn association (Fig. 9A left, outlier).

The Cu (Zn not detected) GSR association with the target samples was especially pronounced over the bore and cylinder gap (Fig. 9A, right). Copper also tended to associate with cylinder gap GSR more than bore wipe GSR. In these samples, Cu and Zn showed evidence of segregation, as exemplified by series 6 (Fig. 9B). The Zn alone (Cu not detected) tended to associate with bore GSR (Fig. 9B, left), whereas Cu tended to associate with target GSR particles (Fig. 9B,

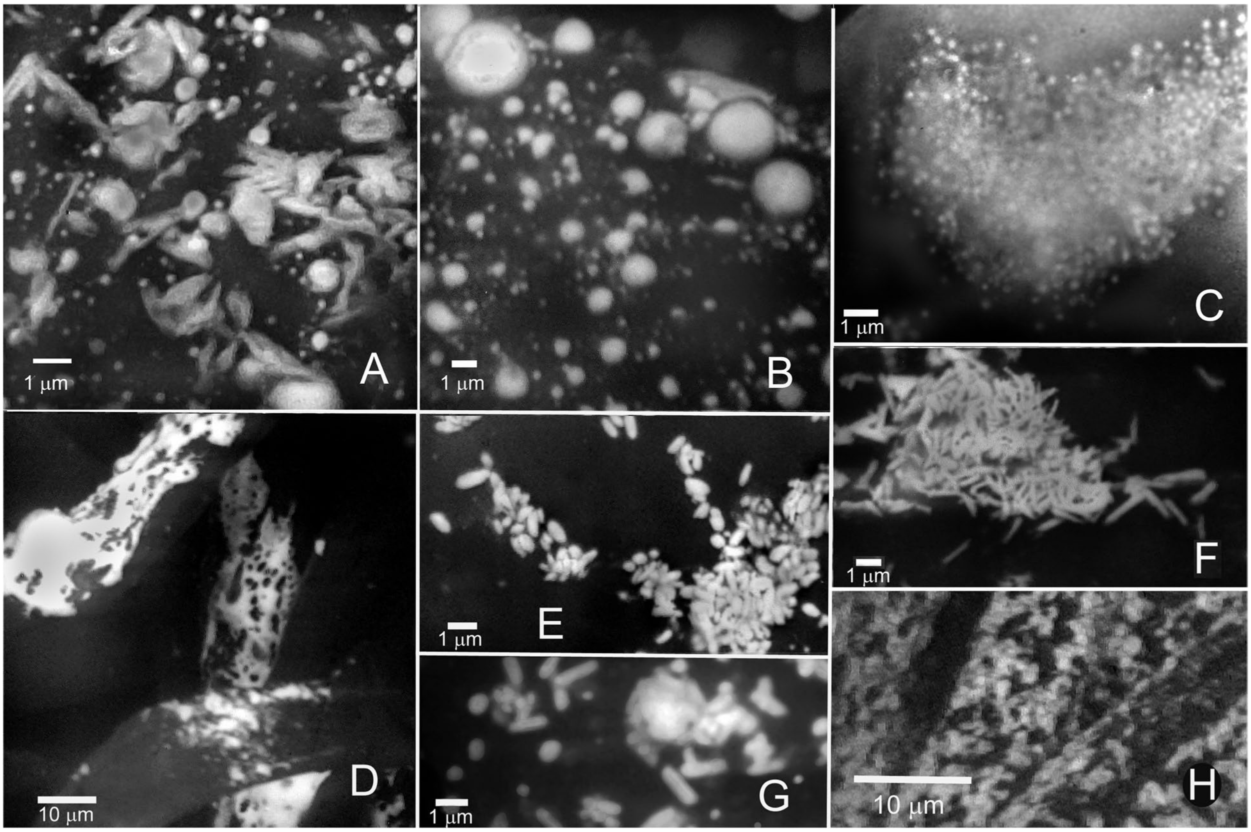

Fig. 6 Backscatter electron images (BSEI) of muzzle GSR particles from the S&W revolver; all the targets were rayon fabric shot at a muzzle to target distance of 10 cm, except H which was 5 cm. The samples were coated with an organic electrostatic compound (Burnett, 2014). Brands and compositions of .22 ammunitions: **A** Federal Champion; Pb. **B** Federal Lightning; some spherical PbSb, rest and fibrous Pb. **C** Imperial; Pb. **D** Federal Power-Flite (Lot 3A-9261); Pb. **E** Dynamit Nobel, subsonic; Pb. **F** Federal Power-Flite (Lot F29HG); Pb. **G** Dynamit Nobel Target; spherical Pb, and fibrous Pb. **H** Remington Hi-Speed Kleanbore; Pb

right). However, Zn-associated particles, without detected Cu, were found associated with GSR particles in all these samples.

Breech GSR from the Ruger pistol

Four different cartridge brands were fired from this pistol after its purchase. The compositions of the primer material and bullet surface for each brand are listed in Table 1 (bottom). Breech GSR samples were evaluated from a number of shots for the Remington and Aguila series. Aguila ammunition was well-suited for this experiment series due to the only detected primer metal which was Pb (with CaSi), while its Cu-clad bullets lacked a Sb layer. This allowed tracking of the behaviors of Ba, Sb, Cu, Zn, Al, and Si over the 20 Aguila discharges which provided insight as to the physical-chemical nature of the memory effect.

The pistol's breech GSR results were graphed based on the percentage composition of the various compositions (e.g., PbSbBa, PbSb) of the GSR populations. Results are presented for characteristic particles (PbSbBa — Fig. 10), consistent particles of PbSb (Fig. 11) and PbBa (Fig. 12), and characteristic and consistent GSR particles containing CuZn (Fig. 13A) Cu without detected Zn (Fig. 13B), Al (Fig. 14A), and Si (Fig. 14B).

Characteristic (PbSbBa)

The sample percent composition for the PbSbBa GSR for the Remington and Aguila ammunition discharges from the Ruger MKII pistol is shown in Fig. 10. The breech release of characteristic GSR of the Remington discharges was variable (7 to 35%) and for the Aguila samples 0 to 6% (Fig. 10). The transition from the characteristic particle generating Remington (shot 12 at 32%)) to the Aguila (shot 4 at 0%) occurred within the intervening three Aguila shots. A small number (6%) of characteristic particles were present in Aguila's sample 8.

Lead-antimony

For the Remington discharges, PbSb gradually increased (Fig. 11) from 1% composition for sample 1 to 14% of the population in shot 12. The previous four CCI shots

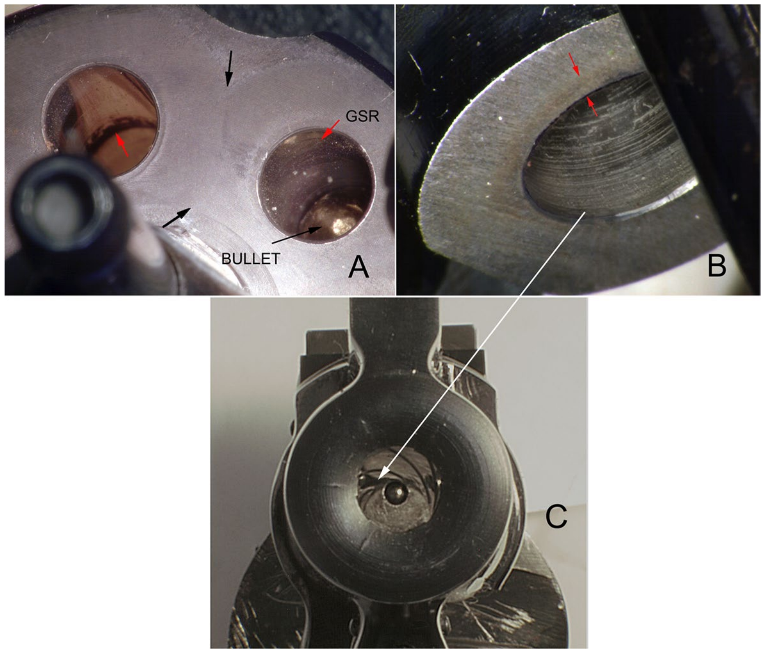

Fig. 7 The Smith and Wesson Model 18 .22 caliber revolver. **A** The cylinder-barrel face showing two chambers; the chamber on the right has the bullet nose of a Remington CuZn-clad bullet. The left chamber with no cartridge has a band that corresponds to the edge of the casing (red arrow). The right chamber shows larger GSR debris as well as discoloration, representing the GSR coating. The cylinder surface has a flare that overlaps the right chamber flare (demarcation at black arrows). **B** The barrel face which shows a band (flare) of discoloration due to a GSR deposit (between arrows) that is heavier than the rest of the face; the revolver's bore has a rough milled surface before the rifling which might abrade the bullet when it passes this area. Gunshot residue deposits probably associated with this rough surface and contribute to the memory effect. **C** The rough area (arrow) within the S&W revolver bore

had PbBa primers. PbSb particles were not detected in Aguila shots 4 and 8 samples but were present in the following samples (shots 12, 16, and 20). The Aguila shot 20 had 22% PbSb was the largest percentage for this particle type.

Lead-barium (PbBa)

Figure 12 shows the percent compositions for the PbBa particles in the breech GSR samples. The PbBa primer CCI discharges, prior to Remington shot, appear to add to PbBa particles in the following Remington shot. The PbSbBa Remington primers appeared to be the PbBa source from shots 5 through 12. Following the final shot of the Remington series, the PbBa composition of the GSR, in the Aguila populations, declined incrementally over the 20 shots, from 23%, for shot 4 to 5%, for shot 20.

Brass (CuZn)

The percent sample composition for particles containing CuZn is shown in Fig. 13A. The Remington .22 bullets were clad with CuZn, the origin of the CuZn found in these GSR samples, although there might have been a small contribution from the casing. The percentage of CuZn-containing particles for the Remington shots varied between samples, from 20 to 50%. For the Aguila shots, the percentage of particles containing CuZn incrementally declined from 37% in shot 4 to 3% in shot 20.

Copper (Cu)

Copper, without detected Zn, was also found in Remington GSR (Fig. 13B). The origin of this Cu was likely from the CuZn cladding of the Remington bullets, since the previous 19 shots of Federal Power-Flite and CCI had unclad bullets. Zinc was also likely present in most of these particles but at an undetectable concentration. The Cu-coated Aguila bullets contributed Cu incrementally from shots 4 to 20 of the breech GSR.

Aluminum (Al)

The percentages of Al-containing particles in the breech GSR samples are shown in Fig. 14A. Remington ammunition produced GSR with variable amounts of Al, ranging from 8 to 63%. The Remington casing GSR did not contain Al. None of the Aguila GSR samples detected Al.

Table 2 Listing of the GSR examinations from the S&W revolver. **A** Series number and type, BW, bore wipe sample; T, target sample; CG, cylinder gap sample. **B** The primer composition, bullet surface composition, and number of shots with that primer and bullet prior to the sample taken after the last shot. **C** Previous shots of that series in B have a different primer and bullet composition than the final shot. **D** The number of GSR particles that were EDS sampled for the final shot of the series

A		B			C			D
Series				Number	Previous		Number	#
#	Type	Primer	Bullet	Shots	Primer	Bullet	Shots	Anal
1	BW	PbSbBa	Pb	40				94
2	BW	Pb	Cu/Pb	18				95
3	BW	PbSbBa	Sb/Pb	24				101
4	BW	PbBa	Pb	24				96
5A	BW	PbCaSi	CuZn/Sb/Pb	2	PbSbBa	Sb/Pb	24	99
5B	T							101
6A	BW	PbCaSi	CuZn/Sb/Pb	2	PbBa	Sb/Pb	24	104
6B	T							93
7A	BW	PbCaSi	CuZn/Sb/Pb	24				96
7B	T							101
7C	CG							105
8A	BW	PbCaSi	CuZn/Sb/Pb	2	PbBa	Sb/Pb	24	111
8B	T							113
8C	CG							100
9A	BW	PbSbBa	CuZn/Sb/Pb	2	PbBa	Sb/Pb	24	113
9B	T							113
9C	CG							98
10A	BW	PbCaSi	CuZn/Sb/Pb	2	PbBa	Sb/Pb	24	100
10B	T							97
10C	CG							149
11A	BW	PbSbBa	CuZn/Sb/Pb	14				126
11B	T							117
11C	CG							114

Silicon (Si)

Silicon levels in the GSR samples are shown in Fig. 14B. Between 28 and 60% of the GSR from the Remington shots contained Si. Between 4 and 8% of the GSR particles from the Aguila shots contained Si. The formation of the GSR particles containing the oxidized calcium silicide may have been in a form not assessed by the analysis parameters, e.g., GSR particles > 1 μm in diameter. In a recent case, GSR was detected on the hands and clothing of the alleged shooter. Of the eight characteristic GSR particles found, seven appeared to have a source of either calcium silicide, in the primer, or perhaps, associated with the gunpowder (Burnett et al. 2020). Seven of these particles were nonspherical and were about the same size of approximately 2 μm (e.g., Fig. 15, BSEI inset).

Discussion

The .22 caliber cartridge

There is variation between manufactures as to primer distribution within the casing. It appears for most manufacturers the primer extends to sides of the casings (e.g., Fig. 2 A, B, C). This may be purposeful to assist the ignition of the gunpowder. All these primers had a green material associated. Other manufacturers confine the primer to the casing base (e.g., Fig. 2 D, E).

For the .22 caliber bullet diameters (Fig. 3), the Cu or CuZn cladding is approximately 0.03 mm thick. These data show that cladding for this limited number of observations was applied to standard-diameter bullets, with no compensation by making the bullets destine for cladding smaller in diameter. The larger diameter of most of the clad bullets could affect not only performance of bullets but also GSR composition over the smaller diameter clad bullets. The smaller diameter of the Federal Power-Flite in Fig. 3 (asterisk), compared to the other .22 caliber bullets, could also cause these bullets to deviate from normal performance, and affect GSR composition, by having less ablation of the bullet surfaces when discharged.

Surface Sb was detected on most of the .22 caliber bullets, but not on bullet surface scrapes (Fig. 4). This was

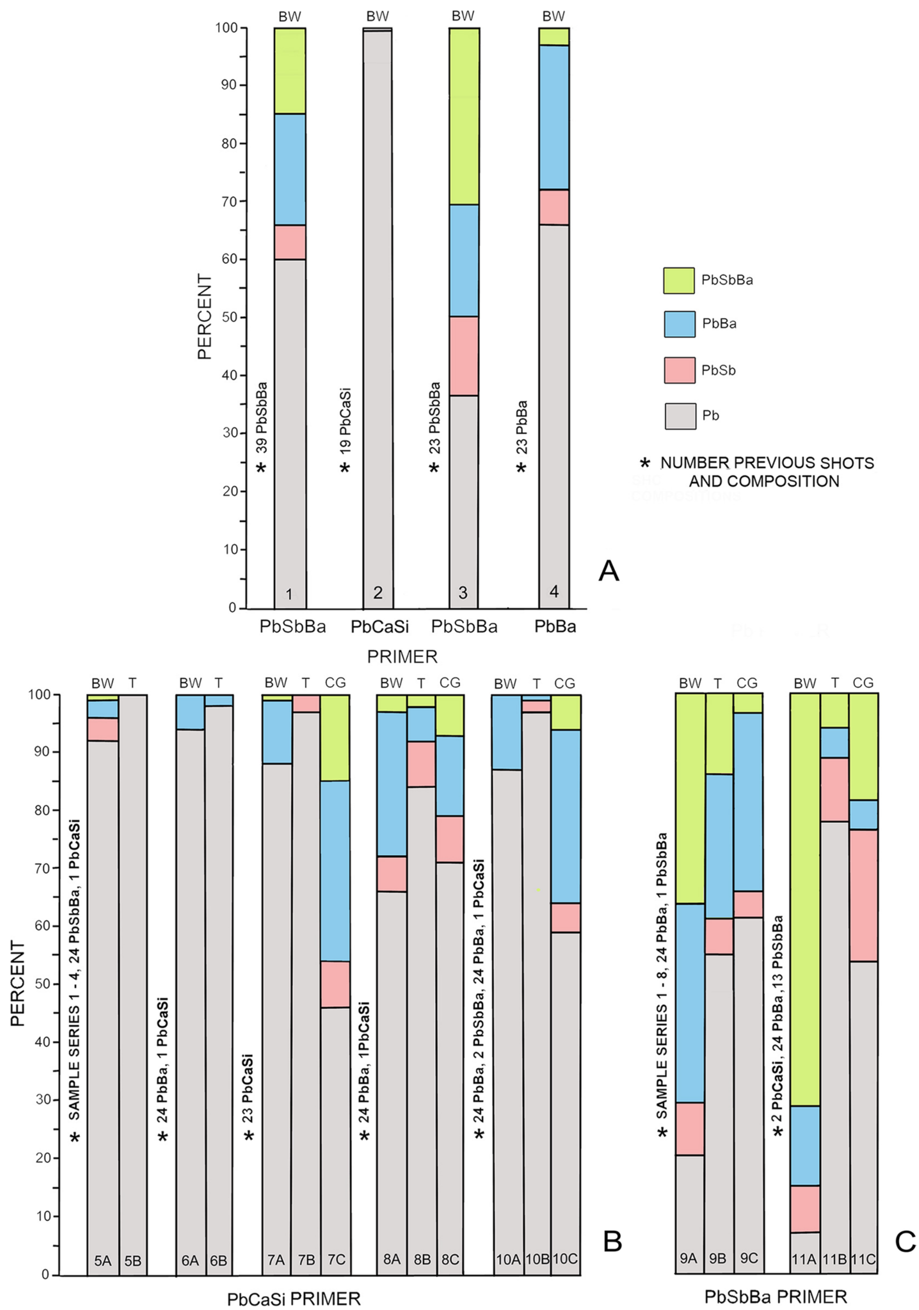

Fig. 8 Gunshot residue examinations for Pb, PbSb, PbBa, and PbSbBa from the S&W revolver; the compositions of the GSR firing PbCaSi and PbSbBa only primered ammunitions. These shots were preceded by 24 or 25 discharges of ammunitions with the same or different primer compositions (Table 2). BW, bore wipe sample; T, target sample; CG, cylinder gap sample. **A** The percent compositions from four bore wipe samples from series 1 through 4 (with different primers) taken after the final shot of each series. **B** The GSR compositions of the final shot with a Pb primer in series 5, 6, 7, 8, and 10; these samples were preceded by 23 to 25 discharges of ammunition of a different primer composition (except series 7) from the previous series. All the final shots that were GSR sampled had CuZn bullet claddings. **C** The two series in which the primer composition of the final shot was PbSbBa. Series 11 was preceded by 13 discharges with the same ammunition

likely because during alloy fusion, where the Sb segregates on thin layers of bullet external surfaces, the contribution of bullet Sb to GSR is limited (Zeichner et al., 1997a).

Heye and Guinn (1988) reported primers of .22 caliber rimfire cartridges for Federal were PbSbBa; Browning, CCI, and Winchester were PbBa; and Remington was Pb only. Andrasko and Maehly (1977)

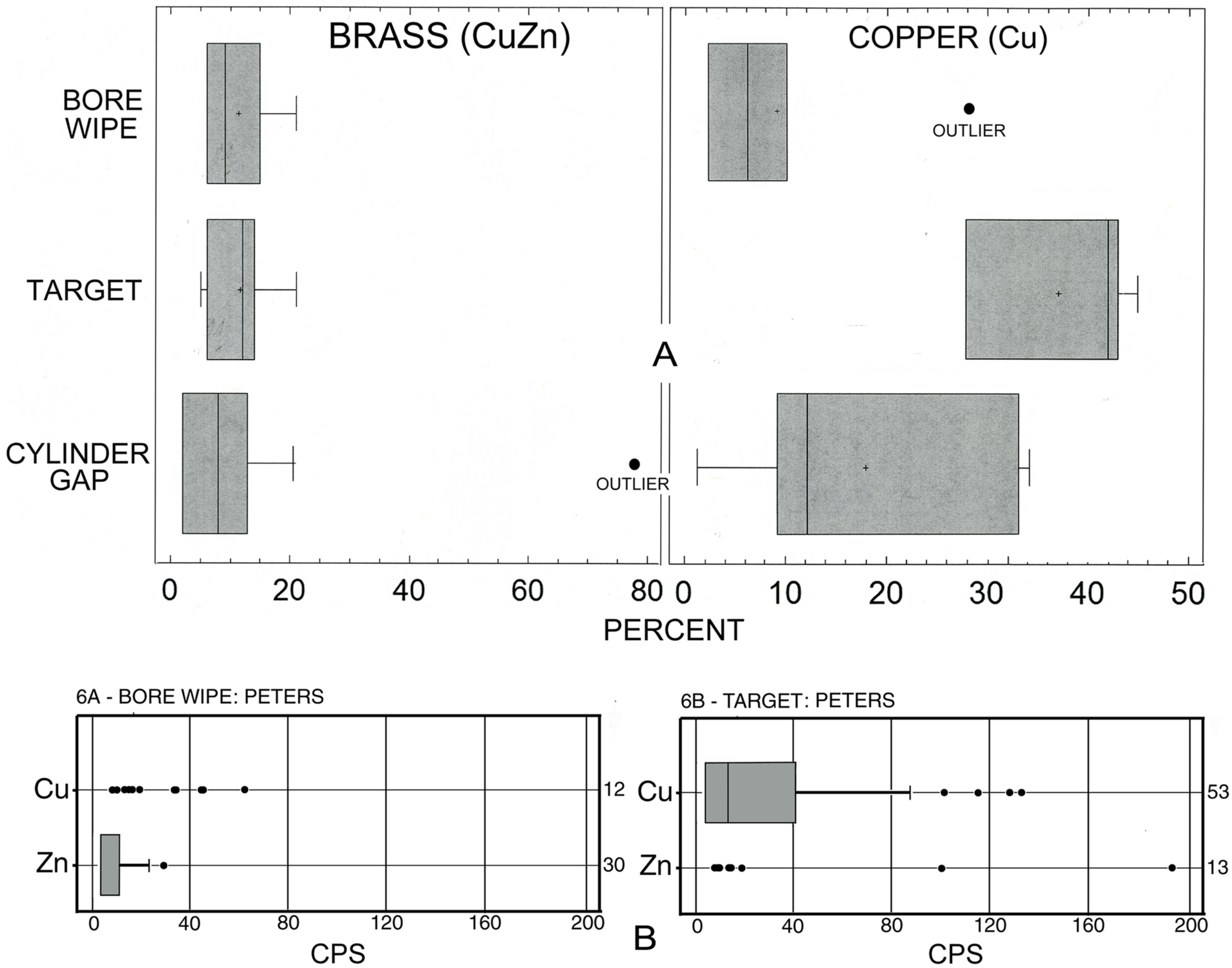

Fig. 9 **A** Box plot GSR compositions of the final discharges from series 5 through 11 (Table 2) from the revolver for CuZn and Cu-associated GSR; the bullets were CuZn clad for these final discharges. Left, the combined percentage CuZn composition of the particles in the samples for these seven samples is similar for the bore wipe, target, and cylinder gap. The cylinder gap data has an extreme outlier. Right, Cu without detected Zn for the combined seven series showed no concordance between the bore wipe, target, and cylinder gap categories. The bore wipe data has an extreme outlier. **B** Box plots of GSR counts per second (CPS) for the final shot of series 6 for Cu and Zn-associated GSR for the bore wipe (right) and target (left) samples; at the right of each graph are the numbers of particles for which each metal was detected. Those particles with Zn did not have detectable Cu and vice versa

reported .22 caliber primers from Winchester and European brands had PbBa; Remington and Peters had PbCaSi. In our survey of over thirty .22 caliber primers, we also found that Remington and Peters (a Remington brand), both with headstamps "U," and Aguila primers were PbCaSi (Figs. 5 A and B). However, Charles et al. (2011) reported that Aguila .22 caliber cartridges had PbBaSi primers. Remington (headstamp *Rem*) and Federal cartridges, manufactured prior to 1991, had PbSbBa primers (e.g., Fig. 5D) (Burnett, 2003). Federal cartridges, manufactured after 1991, had PbBa primer composition (Burnett, 2003), while all other brands we surveyed had PbBa primers, usually with Si, as reported by Heye and Guinn (1988) and Andrasko and Maehly (1977).

A spherical form of muzzle GSR particles was found for most ammunitions we surveyed, although a few were oddly shaped, and some were mixed with fibrous particles (Fig. 6). These latter ammunitions were excluded from our study.

The divergent GSRs of the Smith and Wesson revolver

The first four discharge series from the S&W revolver (Table 2, samples 1 through 4) were followed by only bore wipes from the final discharges, consistent with each primer composition (Fig. 8A).

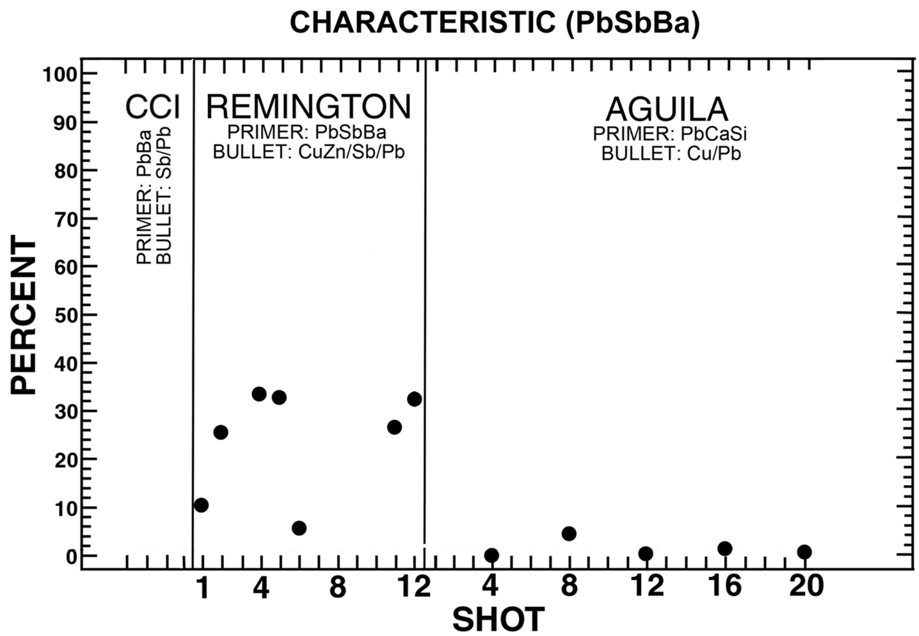

Fig. 10 Graph of characteristic (PbSbBa) GSR percent composition from the Remington primer discharges to the Aguila; there were small, apparent periodic mobilizations, of residual GSR of characteristic GSR in the Aguila breech samples 8 (6 particles) and 16 (1 particle)

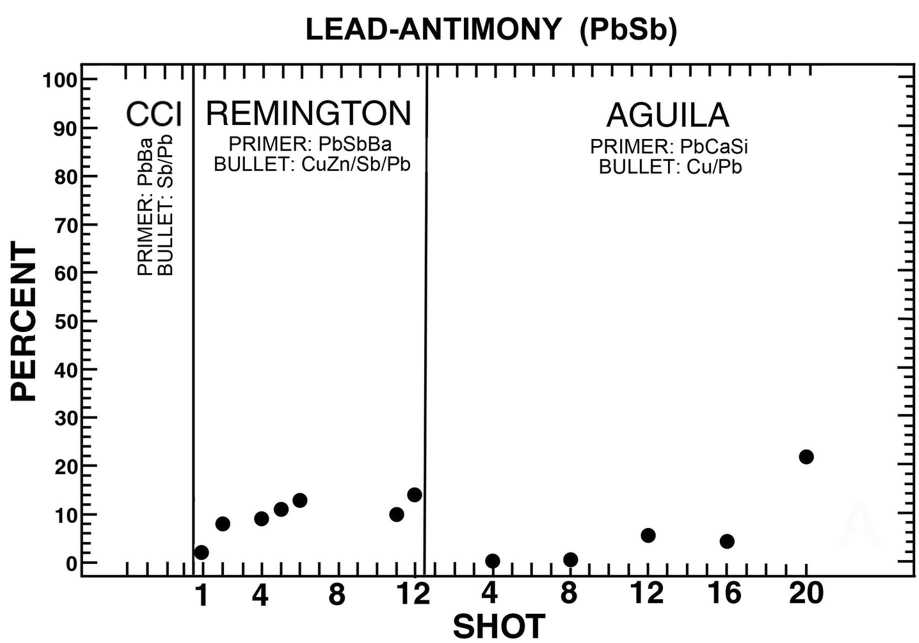

Fig. 11 Graph of breech PbSb in GSR; PbSb composition gradually increased in the Remington series to shot 12. PbSb was not detected in Aguila shots 4 and 8 but was detected in shots 12, 16, and 20. The Aguila shot 20 showed the most PbSb particles for both Remington and Aguila

A disparity between the GSR compositions of the bore, target, and cylinder gap was previously reported for a .357 revolver (Burnett 1989). In our study, GSR composition comparisons for particle types (series 5, 6, 7, 8, and 10; Fig. 8B) showed compositional differences between these samples by the Pb-only-primered cartridges, as was also apparent for series 9 and 11, with PbSbBa-primered cartridge discharges (Fig. 8C). A hypothetical shooting case could attempt to match a revolver target with cylinder gap GSR (i.e., on a shooter's hand). But, as shown,

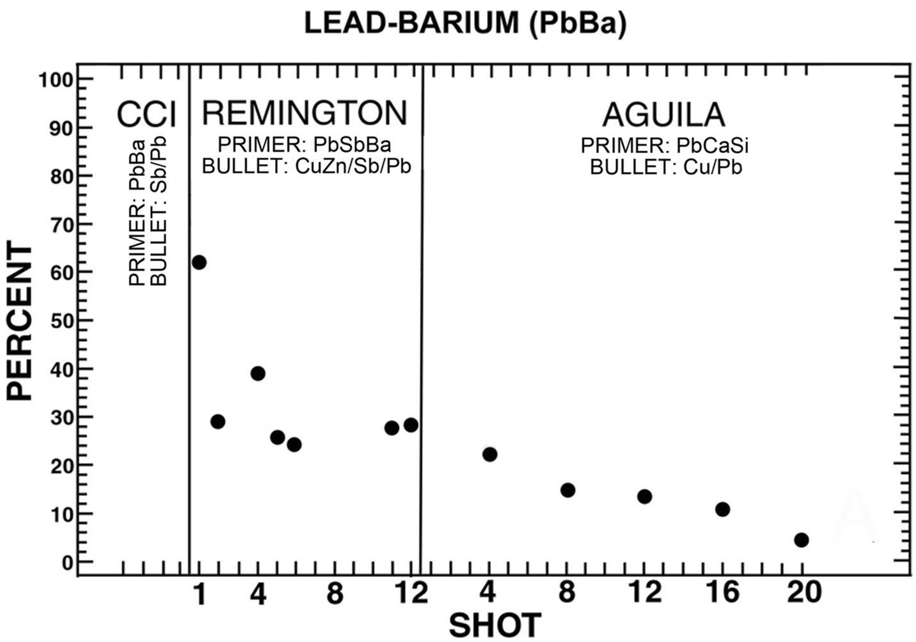

Fig. 12 Graph of breech PbBa in GSR; PbBa particles in the Remington series ranged from 24 to 62% but gradually declined in the Aguila series from shot 4 at 23% to 5% at shot 20

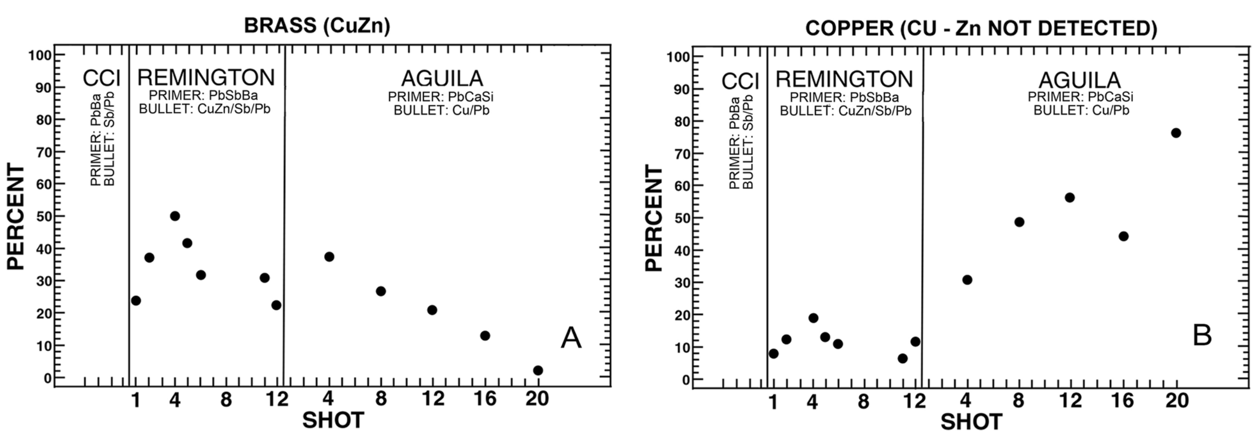

Fig. 13 **A** Graph of percentages of GSR particles with detected brass (CuZn); the Remington bullets were clad with brass. The CuZn-containing particles ranged from 22 to 50% of the population. The Aguila GSR samples showed a gradual decrease in brass-containing particles. **B** Graph of Cu-containting paticles (Zn not detected); the Aguila bullets were clad with copper, and Aguila GSR showed a gradual increase in copper-containing GSR with shots

the assumption that these two GSR sources, from the same discharge, are compositionally the same is not valid. For example, the composition of the target sample 7B compared to the cylinder gap sample 7C (Fig. 8B) showed that even when the previous 23 Pb-only primer discharges occurred, the cylinder gap GSR had PbSbBa, PbSb, and PbBa in quantities not reflected in either the target or bore GSR. For example, the cylinder gap sample had 30% PbBa particles, compared to 0 for the target, and 15% PbSbBa particles, compared to 0 for the target.

The lack of constancy between samples within a series was also exemplified by series 9 (Fig. 8C) with a PbSbBa primer for the final two shots. Prior to these two PbSbBa, primer shots in series 9 were 24 PbBa primer cartridges. The PbSbBa particles were 36% bore, 12% target, and 3% cylinder gap. Series 11, the other PbSbBa primer final shot, also had similar sample discrepancies between the PbSbBa particle categories (Fig. 8C).

For all samples shown in Fig. 8, the target and cylinder gap GSR samples showed greater than 45% Pb,

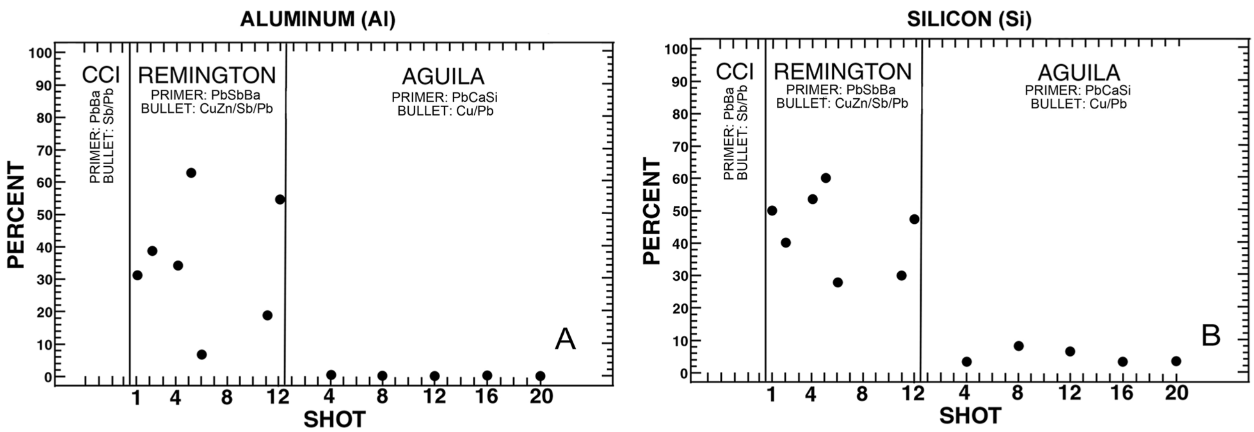

Fig. 14 **A** Graph of Al-containing breech GSR; Al was not observed in the Remington GSR from a discharged casing. Al was not observed in any of the samples from the Aguila series. **B** Graph of Si-containing breech particles; the Remington primer had silica particles as frictionators, which were associated with the breech GSR. The Aguila had a much smaller amount of silicon despite having calcium silicide as a primer component

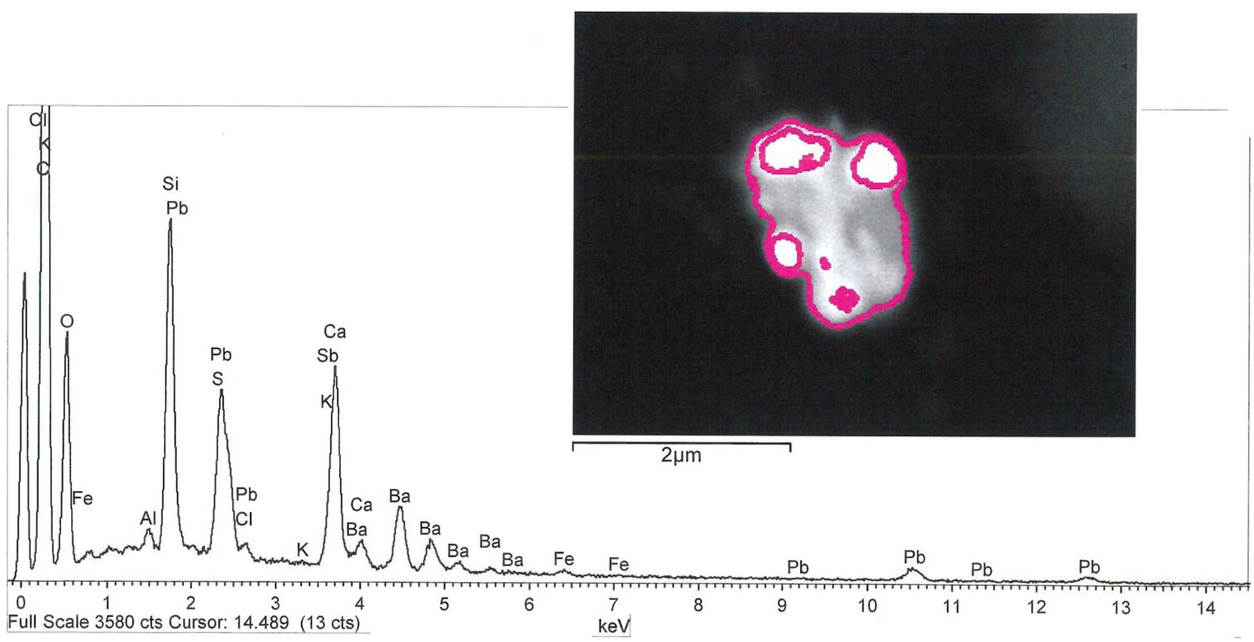

Fig. 15 A PbBa containing particle from a 9mm pistol discharge with major silicon and calcium peaks; six of these particles appeared similar (BSEI inset), and all seven had similar elemental compositions. Trace Sb was identified in this particle, and the others justified the criminalist's characteristic designation. The other six characteristic GSR particles had a similar morphology. The likely presence of calcium silicide in the origin primer might have influenced the GSR form

including series 9 and 11, with the final two shots by primer PbSbBa for these two series (Fig. 8C). The bullet was likely the major Pb contributor to these target and cylinder gap GSR samples.

Characteristic (PbSbBa) and PbSb GSR, in series 8 (Fig. 8B), were found in bore, target, and cylinder gap GSR. There were 77 previous discharges without primer Sb, such that the Sb came from either the bullet's surface or residual GSR within the pistol (the memory effect). The latter suggests that residual GSR persists within the firearm after a large number of discharges.

It was apparent when comparing the bore wipe samples, following the final shots of series 1 through 11 (Fig. 8), that these GSR samples reflect primer composition from the last discharge, with 8A as a notable exception (Fig. 8B). Residual PbBa appeared to contribute to bore sample GSR more than PbSbBa and PbSb. While the discharge histories, prior to samples 6A and 8A, were the same over their previous 25 discharges, the bore compositions differed. However, the revolver chamber histories were not recorded. Since these assessments are based on a small dataset, more work is obviously required.

Rijnders et al. (2010) examined GSR compositions by SEM/EDS from the casing, chamber bore, and four sampling positions around a 9 mm pistol, using four ammunitions with different primer compositions. The pistol was ultrasonically cleaned in isopropanol prior to discharge and GSR sampling of each ammunition. These authors showed a strong correlation between the GSR samples taken around the pistol with the primer compositions. However, the pistol cleaning minimized the contribution of residual GSR to a discharge, thus invalidating their interpretation, considering that for most firearms in shooting cases, residual GSR within a firearm likely plays a major role in the composition of GSR surrounding a discharge (this paper and references cited above).

The breech GSR of the Ruger pistol

The sample percent composition of the PbSbBa GSR for the Remington and Aguila ammunitions discharges, from the Ruger pistol, is shown in Fig. 10. The variable (7 to 35% range) breech release of characteristic GSR for the Remington discharges suggests that the conditions, within the pistol, that create the PbSbBa particles differ from one discharge to another.

For the Aguila samples, the range was 0 to 6% PbSbBa particles (Fig. 10). The transition from the characteristic particle generating Remington (shot 12 at 32%) to the Aguila (shot 4 at 0%) occurred within the intervening three Aguila shots. However, the small number (6%) of characteristic particles, present in Aguila's sample 8, suggests that PbSbBa GSR for the Ruger pistol had marginal or no residual retention, and that PbSbBa formation occurred, with residual GSR mobilization, during a discharge (likely by combining PbSb and PbBa).

Zeichner et al. (1997b) reported for PbBa-primed ammunitions that "only a small percentage ($\leq$ 2%) of the [GSR] particles containing at least Pb and Ba were found to contain a considerable concentration of antimony," for those bullets with an Sb-rich surface layer. Wrobel et al. (1998) stated, "The projectile composition is probably less important than the primer" in GSR, but did not provide supportive data. The PbSb was found to increase for the Aguila GSR pistol breech GSR from 0 (shots 4 and 8), to shot 20, at 22% (Fig. 11). A primer contribution of Sb from the Remington-primered cartridges that had PbSbBa primers (the memory effect) could not have contributed Sb to the Aguila breech samples 4 and 8, due to undetectable Sb. Also the Aguila bullet surface did not have a Sb layer. An explanation for these data is proposed below.

Primer-like PbSbBa and Ba and KS particles were found on gunpowder surfaces (Miyauchi et al. 1998; Burnett et al. 2020). Inorganic elements, associated with gunpowder, could contribute to a GSR sample and be mistaken for a memory effect. However, the decline of Ba from the Ruger pistol for the Aguila series (Fig. 12) indicates, at least for this sample series, no gunpowder input of Ba or PbSbBa.

Our data support an internal GSR reservoir made up of newly deposited GSR components, from the current discharge, combined with GSR components of previous discharges (Fig. 16). With every discharge, sources of metals, primer, possible gunpowder elements, and the bullet are added to remobilize interior surface GSR from previous discharges. As mixing occurs, a portion of the mixed metals and gases is released as breech GSR. Aluminum departs the reservoir immediately, whereas other components, Ba, CuZn, and Cu, are cycled within the reservoir, and with no additional input, these elements gradually decrease in concentration with each discharge.

These data and interpretation are preliminary. Weapon design likely influences the formation mechanism of GSR. It is not known if another pistol with the same design and ammunition history would produce the same breech GSR pattern over the same number of shots. There also can be different bullet surfaces: Pb with a surface layer of Sb with or without Cu or CuZn cladding and Pb without a surface layer of Sb with or without Cu or CuZn cladding.

Different primer compositions have been used both within and between manufacturers for .22 caliber cartridges, all with Pb as a component. For instance, Pb is the only heavy metal in the primer of older Remington (Peters was a Remington brand) rimfire cartridges (head stamp of "U"), whereas after 1989, Remington used the standard centerfire primer composition of PbSbBa (head stamp "*Rem*") for its .22 caliber cartridges (Burnett 2003). Moreover, Charles et al. (2011) reported Aguila .22 caliber rimfire cartridges to have PbBaSi-composed primer cartridges. In the current study, the Aguila .22 caliber rimfire primer was PbCaSi (likely lead styphnate and calcium silicide, $CaSi_2$). Federal changed its .22 caliber rimfire ammunition from PbSbBa to PbBa in 1990 (Burnett 2003). Additional primer composition changes may have occurred in these, and other ammunitions, since.

It has been shown that at least one manufacturer was inconsistent in the type of gunpowder used in the

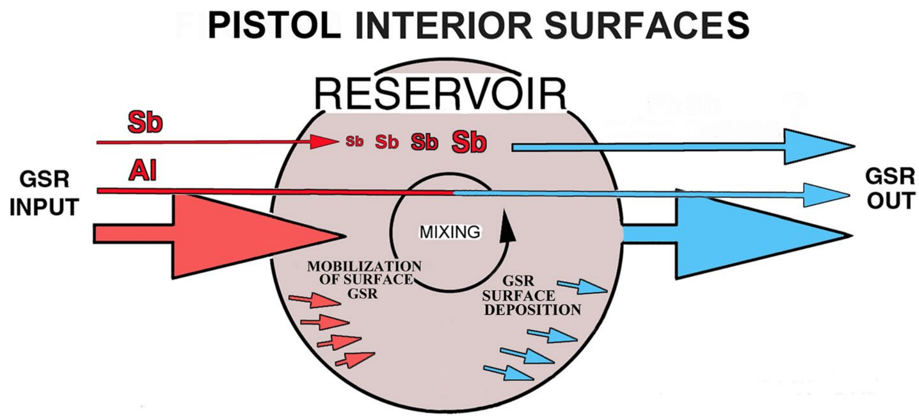

Fig. 16 The GSR reservoir hypothesis for the creation of pistol breech GSR; the behavior of GSR elements in this proposed reservoir is based on observations of the pistol experiment and may differ in other firearms. In this case, PbSb accumulates on the interior surfaces before being released, likely due to reduction of PbBa concentration within the pistol

manufacture of the same caliber and type of cartridge (Burnett et al. 2020). These authors examined the gunpowders from 15 different lots of 9 mm Winchester Silvertip hollow point ammunition and found some, but not all, powder surfaces to have Ba-potassium (Ba K) coatings. Others had associated PbSbBa particles, and 1 of 15 lots had surface calcium silicide particles. Such gunpowder variability might also be found in .22 cartridges, likely affecting GSR form (e.g., Fig. 6) and composition. In author BRB's shooting investigation, firearm examiners from the Los Angeles, CA, USA, area described firearms recovered from shootings as having a "ghetto load" of cartridges, a term applied to gang members' firearms containing a mix of cartridge brands. A firearm discharging a mix of cartridge brands might produce GSR of unique composition.

The Remington .22 bullets examined in this part of the study were clad with CuZn, which was the origin of the CuZn found in these samples (Fig. 12A). Copper, without detected Zn, was also found in the Remington GSR. The origin of this Cu is likely from the CuZn bullet cladding. Zn may have also been present in these particles, undetectable by EDS. The Cu-clad Aguila bullets produced breech GSR that incrementally increased Cu, with subsequent discharges (Fig. 12B).

Aspects of GSR formation

There is no reason to believe there is a difference between centerfire and .22 caliber firearms in the formation of GSR. The breech/cylinder gap and target GSRs in centerfire firearms will have different compositions, regardless of the firearm type. A consideration of the recombination process of the GSRs (current discharge plus residual GSR), in light of the memory effect, must take into account four points:

1. *The mechanical characteristics of the revolver and GSR formation:* The revolver has a gap between the cylinder and the barrel face (the cylinder gap). Leakage of high-pressure gases, after low brisance primer deflagration (Nunziata and Morin 2017), through the cylinder gap, likely more rapidly solidifies its elements, both on revolver surfaces and in the air, rather than the pistol. The molten GSRs in revolvers continue in the barrels, solidifying onto the bore surfaces, and of course, in the air. Depending on the history of ammunitions fired in the revolver, each chamber could generate a different composition of GSR in the bore, on the target, and from the cylinder gap.
2. *The mechanical characteristics of the pistol and GSR formation:* The interior of the semiautomatic pistol is subject to a high pressure and temperature pulse upon its firing, both of which rapidly decline upon the opening of the pistol's ejection port. In a blowback pistol, the bullet advances, and the slide moves backwards, while in a recoil-operated pistol, the slide moves backward in recoil when the projectile is released (Chin 1951). These characteristics likely determine the magnitude of the impulse release of GSR that accompanies these different operations. In both the semiautomatic pistol and revolver with the bore, the GSRs are carried by deflagration gases that can both follow and overcome the projectile (Settles et al. 2005). These different modalities likely result in different regional GSR compositions that participate in retention and accumulation. During the travel of the bullet in the firearm bore, GSR is deposited on the lands and grooves before the passage of the bullet. The bullet/rifling tribological effect will likely affect not only the form and com-

position of GSR within the bore but also that on the bullet (Burnett 2018).

3. *The characteristics of an impact nature between new and previous GSRs:* This phenomenon can be hypothesized to exclude particular tribologic effects between surfaces in mechanical contact, such as bullet coatings, rifled bores, and mechanical surfaces of the weapon. The relative motion of interacting surfaces within the firearm likely manifests in microscopic hotspots of elevated pressure and temperature (microscopic flash temperatures that far exceed the average values found at any time within the firearm), due to their respective asperities (Blok 1963; Bogdanovich and Tkachuk 2006; Vakis et al. 2018).
4. *Fluid dynamics dominates GSR composition:* The movement of compressed gases, and consequent pressure effects, will detach previous GSRs coating the interior of the firearm. This characteristic must be considered fundamental to the composition of the residual GSR. The detachment of previously formed GSRs, from a pistol's interior surfaces, is likely subject to other physical influences. For instance, mechanical detachment is possible, considering time rates and both the thermal and heat transfer requirements for melting. A major disadvantage of hot gases of the combustion products of the gunpowder is the low heat transfer coefficient caused by low density, but most of all, by low thermal conductivity (Engineers Edge 2022). Heat conduction in gases is outlined by the kinetic gas theory in which the thermal conductivity (proportional to the dynamic viscosity) is related to the heat capacity per unit volume, average gas velocity, and the mean free path which increase roughly in proportion with the absolute temperature and pressure (Engineers Edge 2022).

Brass and copper

During bullet motion, the tribologic effects between bullet cladding and rifling barrel contribute to direct transfer of Pb, Cu, CuZn, Zn, and Sb into the GSR. We do not know if the Pb in a GSR particle associated with CuZn or Cu comes from the primer or the bullet surface. Likely, it is both. The Sb content in GSR from .22 caliber bullet appears to be minimally derived from the external layer of a bullet (Zeichner et al., 1997a).

Thermochemical and thermodynamic GSR phenomena

Thermochemical and thermodynamic phenomena of the elemental components of the bullet and the primer should be analyzed with a holistic approach that takes into account the internal surfaces of the weapon to the semisolid/molten elements of the discharge that are mixed. In the process, given the time rates and heat transfer requirements, discharge gas cannot volatize previously deposited GSR and can only contribute to its possible removal from the surfaces, on which they are stored and mix with the primer elements of the last shot while molten. The redeposition of the GSR occurs with "undercooling" (Nunziata and Morin 2017) along with the release of part of the GSR/aerosol mixture which condenses upon cooling.

Our PbSb and PbBa data (Figs. 11 and 12) suggest that residual GSR in the pistol is likely layered, with each layer having homogeneous mixtures of two or more metals. The diffusions of Sb and Ba between these layers are a function of atomic radii (Science Direct 2022). The Ba atomic radius is greater than Sb (Haynes et al., 2016) which means that theoretically (and supported by our data), the PbBa layer overlies PbSb. In addition, PbSb and PbBa are interstitial alloys with chemical affinity (Smith, et al. 2006).

The complexity of the layering phenomenon depends on the impurities and the products of primer deflagration. During primer initiation, elemental contribution is not vinculated by chemical bonds, as the achieved high temperatures determine the dissociation of compounds such that only after recombination, during particle solidification, are there contributions of oxygen (from barium nitrate), carbon, nitrogen, hydrogen (from lead styphnate), sulfur (from antimony sulfide), etc. For example, in Sb_2S_3 oxidation, the reaction with iron that would release elemental Sb ($Sb_2S_3 + 3\ Fe \rightarrow 2\ Sb + 3\ FeS$) should also be evaluated, with all components of various antimony oxides that could be formed.

As there is interdependence between the two alloys, PbBa and PbSb are as follows:

- The tribological effects between barrel and bullet surface and the thickness of the residual GSR deposition layers, the thickness of the alloy layers, and the crushing induced by both the mechanical parts during firing
- The hot gas pressure mechanically contributes to detaching pieces of the residual GSR.

With each discharge of the Aguila, the PbBa layer separately eroded apart from the PbSb layer, and by the final Aguila shot 20, we saw most of the PbBa gone from the residual GSR and the mobilized PbSb.

The behavior of PbBa particles is due to the mechanical proprieties of Pb in PbSbBa and PbSb. Lead has a low Brinell grade. Indeed, when Pb-based semisolid GSRs collide with a steel surface, they adhere to it (Brożek-Mucha 2007; Spathis 2017). The interaction between melted droplets and steel must be considered from the point of view of scale factors, surface roughness, substrate thermal properties, and contact pressure, in addition to the pileup process, including the bulk liquid, capillarity effects at the liquid-solid interface, heat transfer, and solidification (Xue et al. 2007; Du et al. 2014).

Adhesion results from the tendency of the external GSR layer to diffuse into previously deposited GSR. However, this adhesion is not strong, and every shot detaches the accumulated GSR along with melting. A significant contributor to this process is the chemical affinity between Pb and Sb, due to Sb's solid solubility (Bagherian et al. 2016), which might explain the behavior of PbSb (Fig. 11) in this process.

Revolvers and semiautomatic pistols mechanically differ. The processes of GSR formation, with the incorporation of previously deposited GSR, may result in different GSR compositions between these two firearm types, even given the same ammunition history. In addition, the passage of the bullet, which expands minimally on both the groove and land of the rifling barrel, has a tribological process that likely affects the GSR composition from the muzzle. Barrel length will also likely affect target GSR composition. All these phenomena must be considered in the understanding of GSR formation, not only in light of the melting/mobilization points of single elements but also from the point of view of the possible alloys formed and their eutectic points (a eutectic mixture has a lower melting point than that of the individual elements that compose it (Wikipedia 2022)).

The Basu GSR formation model

Based on our findings, the Basu model of GSR formation (Basu 1982) needs to be modified to consider the effect on GSR composition and form by primer compositions other than PbSbBa. Consideration of the heterogeneous nucleation phenomena induced by unburnt and partially burnt gunpowder particles, which act as nucleation and growth centers during the GSR solidification phase, is required (Brożek-Mucha 2007). Basu's model is flawed on several fronts: (1) it is based on a PT curve (Lee et al. 1968) of the high explosives (primer mixture initiation is not a detonation but a low brisance deflagration (Cook 1963; Nunziata and Morin 2017); (2) it overestimates the pressures (Nunziata and Morin 2017); and (3) it underestimates the temperatures generated within a firearm (Nunziata and Morin 2017).

Conclusions

The results described in this article demonstrate that GSR element composition, regardless of source, is governed by not only primer composition but also the GSR coating the interior surfaces of the firearm from previous discharges with different primer compositions (i.e., the memory effect). The variables governing the elemental composition of GSR, and its form (e.g., Fig. 6), require further refinement and perhaps even identification of additional variables governing the resulting compositions of a GSR population. Inorganic particles and gunpowder coatings (Burnett et al. 2020), and possibly, the composition of the gunpowder itself, could also influence the elemental composition of GSR. The design difference between the revolver and pistol likely also influences GSR composition. More research is obviously needed.

Abbreviations

BSEI	Backscatter electron image
CCI	Cascade Cartridge Industries
EDS	Energy-dispersive X-ray spectroscopy (some authors use the abbreviation "EDX")
LR	Long rifle
GSR	Gunshot residue
Characteristic GSR	"Elemental composition is derived from ammunition incorporating primers based on the Sinoxid® formulation that contains lead styphnate (and/or other lead compounds), antimony sulfide, and barium nitrate. Characteristic GSR particles must contain lead, antimony, and barium" (Fojtášek et al. 2021).
SEI	Secondary electron image
SEM	Scanning electron microscopy
S&W	Smith and Wesson

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Authors' contributions
BRB performed the tests, graphics, and some analysis. FN contributed analysis and interpretation and was a major contributor to the manuscript. The authors read and approved the final manuscript.

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Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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