JAAS

PAPER

View Article Online
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Cite this: DOI: 10.1039/d5ja00416k

Observations on sample size for lead isotopic analysis of ancient copper alloys

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Received 28th October 2025
Accepted 20th February 2026

DOI: 10.1039/d5ja00416k

rsc.li/jaas

Provenance studies of ancient copper alloys typically involve a combined approach using trace element and lead (Pb) isotopic analysis. While minimum sample masses for elemental analysis have been previously discussed in literature, these have rarely been considered for isotopic analysis. In the context of increasingly small samples employed in archaeometallurgical studies, this paper evaluates the effect of low sample mass for Pb isotopic analysis of different copper alloy and Pb standards. The Pb isotope ratio results obtained using multi-collector ICP-mass spectrometry (MC-ICP-MS) show excellent long-term stability and reproducibility for standards, ensuring comparability of data over time. However, some variability is observed in Pb isotope ratios obtained for different sample aliquots taken from individual samples and standards. This observed variability, often strongly exceeding the accepted precision for MC-ICP-MS Pb isotopic analysis, relates to low sample masses and is further exacerbated for low-lead alloys. These results suggest the existence of micro-scale heterogeneity in the Pb isotope ratios of some copper alloys, which can lead to (strongly) divergent results when taking very small samples – a problem which cannot be recognized *a priori* nor *a posteriori* without fully independent replicate analyses (*i.e.* based on another sample aliquot). In the context of archaeological research and the analysis of museum-curated objects, however, repeated sampling of ancient copper alloys is usually impossible. Thus, these results outline the necessity for sample masses of > 20–30 mg for the Pb isotopic analysis of copper alloys to prevent incompatible datasets: smaller samples may not be representative, even if their isotopic analysis is feasible.

Introduction

The analysis of copper alloys in archaeology has a long history, going back to the eighteenth century.[1] Analytical instrumentation has changed significantly, enabling the precise and accurate determination of major, minor and trace elements as well as a range of isotope ratios, and new methodologies continue to develop. A key driver for the adoption of new techniques across archaeological and heritage science is a desire to work with the smallest possible samples, especially in the context of rare museum-curated objects. These advances have been necessary to enable the study of substantial metal assemblages without their complete consumption in the process.

However, the nature of ancient metals has not changed since we started studying them, and their often-heterogeneous nature was recognised many decades ago already by various researchers.[2–5] Most researchers converged on a recommended minimal sample mass of *ca.* 30–50 mg to obtain a representative elemental composition for copper alloys, across a variety of analytical techniques. From the perspective of analytical chemistry today, it is of course possible to obtain accurate and precise elemental data for much smaller samples, whether through solution-based ICP-OES (ICP-optical emission spectrometry) and ICP-MS (ICP-mass spectrometry) methods for dissolved material or directly (*i.e.* without dissolution) when using LA (laser ablation) sampling combined with such instrumentation, or through NAA (neutron activation analysis). Nonetheless, sample representativeness remains an essential consideration,[6,7] and recent work by the authors of this paper has consistently favoured the use of these minimal sample masses.[8,9] At the same time, many recent publications on ancient copper alloy analysis do not explicitly state sample mass.

As far as we are aware, the effect of sample size has only been considered relevant in the context of elemental analysis, but not for Pb isotopic analysis of copper alloys (yet see examples of isotopic heterogeneity assessed in other materials[10,11]). Indeed, while lead concentrations may vary throughout an object due to its limited solubility in copper, Pb isotope ratios are expected to be homogeneous. Given that sufficiently large samples are commonly taken for combined elemental and Pb isotopic analysis, this assumption is usually not questioned. A recent

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study using portable laser ablation sampling and subsequent Pb isolation and solution MC-ICP-MS analysis suggested that very small samples (*ca.* 50–250 μg) may be adequate to measure Pb isotope ratios in silver, at higher precision than obtained through *in situ* nsLA-MC-ICP-MS.[12] For low-lead alloys, however, an increased risk of external Pb contamination to the sample should be considered for increasingly low sample masses.

With regards to copper alloy analysis, instances of LA-MC-ICP-MS use for Pb isotopic analysis are relatively rare (yet see examples[13–18]), but increasingly small sample masses have been reported for solution-based Pb isotopic analysis using MC-ICP-MS. For example, sample masses reported for the analysis of Egyptian and Nubian metals by one research group[19–21] are mostly below 5 mg and rarely exceed 10 mg. Similarly, researchers[22] recently adopted a sample size of *ca.* 2 mg for the analysis of Eastern Zhou bronzes. As an example, the latter paper specifically reported that "for lead isotope analysis, only a small amount of sample is required and it is not necessary to touch the metal body of the sample. For bronzes to which lead has been intentionally added, a few surface corrosion powders may be representative of the lead isotopic signature of the artifact (Ponting *et al.*, 2003;[23] Weeks *et al.*, 2009 [24])†. Even for metal artifacts with low lead content, especially copper-based artifacts, the lead content is much higher than the lead content in the soil. Thus, the source of lead in patina or corrosion is still predominantly from the object itself, unless the surrounding environment is contaminated with lead similar to industrial impacts, which would have been nearly impossible in ancient times (Cui and Wu, 2008 [25]). Moreover, some simulation experiments show that the lead isotopic composition of corrosion rinds (within experimental error) is similar to that of the metallic matrix of bronze, and that corrosion rinds could be used to investigate the provenance of ancient bronzes without compromising the integrity of the artifacts to the greatest extent possible in this way (Snoek *et al.*, 1999;[26] Wei *et al.*, 2006 [27])".

In the context of a research project reexamining samples held in the British Museum's Department of Scientific Research archive, the authors have been revisiting a wide range of ancient Egyptian copper alloys (previously analysed[28] using Atomic Absorption Spectroscopy [AAS] and ICP-OES) to determine their Pb isotope ratios, and where sufficient sample is available re-measure their trace element composition (selected preliminary results published[29]). The results of this project are beyond the scope of this paper. However, some discrepancies were noted for small samples, instigating a more structured investigation into the potential effect of small sample sizes. To this end, isotopic analysis has been conducted for varying sample masses across a group of 10 different CHARM standards[30–33] over six analytical batches, resulting in a total of 65 Pb isotope ratio measurements. While these standards, the elemental composition and microstructures of which were designed to closely match those of ancient copper alloys for XRF calibration, are not designed to be used as isotopic standards (and their Pb isotope ratios have not been reported previously), there is no reason to assume lead isotopic heterogeneity within them *a priori*.

As a background to the results obtained for these CHARM standards, we report on the reproducibility of Pb isotope measurements for copper alloy samples obtained within and across analytical batches by the authors of this paper over the past 10 years. Based on these results, some important considerations are outlined for the sampling of copper alloy artefacts for Pb isotopic analysis, not previously reported in literature.

Materials and methods

CHARM standards held at the KU Leuven Department of Earth and Environmental Sciences were sampled in the first stage of this research, while a second group of CHARM standards held at the British Museum Department of Scientific Research were sampled subsequently. The selection comprises different copper alloys (arsenical copper, tin bronze, leaded tin bronze, brass, leaded brass and gunmetal), as well as two lead standards. The standards were sampled using two different methods: on the one hand, metallic samples were taken using a clean 1.5 mm drill bit (RS PRO HSS Twist Drill Bit); on the other hand, acid-impregnated cotton swabs were swept across the metal surfaces.

For the first sampling method, drill samples ranging between a few mg to over 100 mg were taken from three to four individual locations on each standard (five for 85X ANTH). Each sample was analysed in a separate analytical batch (batches labeled A, C, D, E and R for Leuven standards; batches labeled BM and R for British Museum standards). Four drill samples were sub-sampled to assess homogeneity within drillings taken from a single location (BM-46/47, BM-49/50, BM-52/53 and BM-55/56).

For the second sampling method, cotton swabs impregnated in either dilute (1 M) nitric (HNO_3) or hydrochloric (HCl) acid were used, sampling each of the Leuven standards at two locations (processed in batches labeled C and D), in addition to the drill samples. The latter method has been described for the Pb isotopic analysis of lead coins[34] and was previously employed for the analysis of lead ore[35] and lead glazes[36] (equally using acetic acid[37]).

Each of the drill samples was then dissolved following a high-temperature acid digestion procedure‡ and (for some samples) an aliquot taken for ICP-OES analysis,[38] followed by chromatographic isolation of lead (using Pb-SPEC resin: Triskem International, France).[39] Samples were extracted from the cotton swabs by stirring in dilute (1 M) HNO_3, followed by chromatographic isolation of lead.[34] Lead concentrations of the isolate were determined using Q-ICP-MS and solutions for MC-ICP-MS measurement prepared at 150 μg per L Pb, with 30 μg per L Tl (NIST SRM 997) as internal standard for mass bias correction (instrumental settings described by Rademakers *et al.* (2020)[38] and references therein). Procedural blank Pb

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† It should be noted that the remarks by Ponting *et al.* (2003)[23] regard the analysis of silver coins, not copper alloys. The sample amounts taken by Weeks *et al.* (2009)[24] are all *ca.* 30 mg, distinguishing clearly between corroded and metallic samples.

‡ The two lead standards (83X PR8 and 85X ANTH) were directly dissolved in dilute nitric acid with important residue formation, particularly for the larger sample masses, leading to lower analytical recovery by ICP-OES. This may reflect formation of Pb-oxide at the surface.

Table 1 Pb isotope ratios measured for MBH-CRM-CR32-PB110 copper alloy standard

Date	Sample number	Sample mass (g)	Pb after isolation (μg L^{-1})	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb	2SD ^{206}Pb/^{204}Pb	2SD ^{207}Pb/^{204}Pb	2SD ^{208}Pb/^{204}Pb	2SD ^{207}Pb/^{206}Pb	2SD ^{208}Pb/^{206}Pb
Apr-16	FA-55	0.0422	39 500	17.389	15.548	37.206	0.8942	2.1396	0.007	0.007	0.018	0.0001	0.0004
Apr-16	FA-56	0.0814	58 100	17.396	15.550	37.218	0.8939	2.1394	0.008	0.007	0.019	0.0001	0.0004
Apr-16	FA-57	0.1095	54 300	17.386	15.547	37.202	0.8942	2.1398	0.007	0.007	0.017	0.0001	0.0004
Jun-16	J-33	0.0655	193 000	17.389	15.547	37.205	0.8941	2.1396	0.012	0.010	0.026	0.0002	0.0005
Oct-16	FO-32	0.0909	86 400	17.392	15.549	37.211	0.8940	2.1396	0.006	0.006	0.018	0.0001	0.0004
Dec-16	FE-7	0.0911	94 900	17.391	15.548	37.207	0.8940	2.1395	0.006	0.005	0.013	0.0001	0.0003
Jan-17	K-27	0.0741	26 900	17.392	15.548	37.208	0.8940	2.1394	0.004	0.005	0.012	0.0001	0.0003
Jan-17	K-28	0.0738	68 700	17.393	15.549	37.212	0.8940	2.1395	0.008	0.007	0.018	0.0001	0.0003
Feb-20	D-16	0.0371	63 300	17.390	15.546	37.205	0.8940	2.1394	0.007	0.007	0.016	0.0001	0.0003
Feb-20	E-24	0.0157	37 300	17.402	15.548	37.222	0.8935	2.1390	0.006	0.006	0.014	0.0001	0.0002
Oct-21	PB 110 (2021)	0.0757	212 000	17.382	15.541	37.189	0.8941	2.1396	0.012	0.010	0.025	0.0002	0.0003
Oct-22	PB 110 (2022)	0.0349	14 100	17.387	15.546	37.202	0.8941	2.1397	0.004	0.004	0.010	0.0001	0.0002
Oct-23	BM69	0.0415	105 000	17.386	15.545	37.200	0.8941	2.1397	0.007	0.006	0.016	0.0001	0.0003
Aug-24	R-65	0.0926	39 700	17.388	15.546	37.204	0.8940	2.1395	0.018	0.017	0.046	0.0003	0.0009
Oct-25	PB 110	0.0905	49 000	17.392	15.549	37.211	0.8940	2.1396	0.005	0.005	0.013	0.0001	0.0003

concentrations were negligible compared to sample Pb concentrations (<0.1–0.01%).

In the course of analytical work conducted by the authors on ancient copper alloys, the bronze standard MBH-CRM-CR32-PB110 has been routinely analysed as a lab-internal QA/QC standard for ICP-OES analysis,[38] and its Pb isotope ratios have been measured occasionally between 2016 and 2025. These results are presented here for the first time (this standard has no certified Pb isotope ratio values, and we are not aware of previously published Pb isotope ratio values).

In the presentation of the Pb isotope ratio data (Tables 1 and 2) we include here, for the first time, a column specifying the amount of "Pb after isolation (μg L^{-1})". This refers to the lead concentration in the solution after chromatographic isolation, measured using Q-ICP-MS. This metric has not been reported previously and served exclusively to prepare adequate dilutions for MC-ICP-MS measurement. However, it is reported here as it offers the best handle to assess "absolute lead recovery" during sample processing, even though it was not designed for this purpose. We emphasise that the analyses reported on in this column were not selected to systematically represent different sample masses and the results were never intended for direct comparisons between them. Indeed, beyond the dominant effect of sample mass and lead concentration, variations in the amount of chromatographic resin in the extraction column as well as variations in the final sample solution volume (usually between 1.5 and 2 mL) influence the reported concentrations. Indeed, in our existing protocol, the post-column isolate solution volume was never considered critical (as the exact isolate lead concentrations are determined using Q-ICP-MS for subsequent dilution to 150 µg per L Pb) and was added using disposable pipettes, rather than accurately measured and standardised. As the volume is unknown, it is not possible to determine the "absolute lead recovery" as mass, or the "relative lead recovery" as percentage relative to the lead loaded onto the column. Furthermore, not all samples were analysed by ICP-OES, for which *ca.* 37.5% of the sample digest is removed prior to Pb isolation (indicated in Table 2). Thus, the concentrations reported in this column must be assessed and compared with care: orders of magnitude are most instructive in this regard.

We have, however, compared the "Pb after isolation" to the calculated maximum absolute Pb recovery for the samples (based on reported Pb concentrations, sample mass and a 2 mL isolate solution volume). As Fig. 1 shows, the absolute Pb recoveries after isolation agree well with the corresponding expected values in order of magnitude, yet taper off at high concentrations (observed in particular for the pure lead standards and high-lead copper alloys). This is likely due to column saturation, whereby only a few % of the lead is retained when loading lead-rich solutions§. However, significantly lower recovery is observed for a few samples (*e.g.* A-16 and A-20), while relatively higher recovery is noted for others (*e.g.* B-56 and B-57). These are discussed further in the results section below.

As this research project focused specifically on determining Pb isotope ratios for the CHARM standards, elemental analysis was excluded initially (batches A, C, E). For batches D, R and BM, however, ICP-OES analysis was conducted. The results of ICP-OES analysis of different standards reported in the SI were obtained following the protocol outlined by the authors.[38]

Results

Long-term stability of lab measurements

Between 2015 and 2025, we prepared 35 analytical batches of *ca.* 32 copper alloy samples for Pb isotopic analysis. 20 NIST SRM 981 lead standard measurements were included within each run as part of the sample-standard bracketing procedure (intended for external correction of the bias introduced by instrumental mass discrimination), for which results are summarised in Fig. 2. These graphs show the average and 2SD for NIST standard measurements within each batch, illustrating long-term stability across different analytical batches, with tolerable variation reflecting experimental uncertainty.

This long-term stability is further demonstrated by the consistent results obtained for samples re-measured over time. The Pb isotope ratios of the MBH-CRM-CR32-PB110 copper alloy standard, not previously reported, have been measured 15 times, with results provided in Table 1 and Fig. 3. Here too, relative differences between ratios generally do not exceed 0.1% (this value is commonly considered adequate for provenance research of ancient metals based on Pb isotopic analysis, accounting for comparisons to legacy datasets[41,42]). FA-56 (measured in the same batch as FA-55 and FA-57: April 2016 (B)) differs slightly and E-24 (measured February 2020) is the biggest "outlier". The latter represents the smallest sample (*ca.* 16 mg) of this standard for which Pb isotopic analysis was conducted.

In addition to Pb isotopic analysis, elemental analysis has been conducted regularly for the MBH-CRM-CR32-PB110 copper alloy standard over time. On the one hand, fresh samples of varying mass have been processed as within-run standard, for which results are included in the upper part of Table S.1 (SI). On the other hand, a 'master solution' (labeled 'PB110a') made in 2016 has been re-measured over time too, as summarised in the lower part of Table S.1. In both cases, element recoveries typically average between *ca.* 85 and 100% (except for phosphorus and sulphur), with overall analytical totals between 95 and 100 wt%.

Pb isotopic analysis of CHARM standards

The results of Pb isotopic analysis for the different CHARM standards are presented in Table 2 and illustrated in Fig. 3.

Drill samples. For the KU Leuven CHARM standards, four drill samples from four individual sampling locations were dissolved for analysis (five for 85X ANTH). For the BM CHARM standards, four drill samples from three individual sampling locations were dissolved, whereby the drill sample from the first

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§ In the standard protocol described by De Muynck *et al.*,[39] only c. 15 µg lead is loaded, resulting in complete recovery. When using lead-rich solutions, however, the loaded mass can be over 100 times higher, resulting in relative recovery of only a few % of the total lead mass in the sample solution as the resin gets saturated.

Table 2 Pb isotope ratios measured for CHARM standards

Standard	Analysis number	Sample type	Sample mass (g)	Pb after isolation (μg L^{-1})	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	2SD $^{206}Pb/^{204}Pb$	2SD $^{207}Pb/^{204}Pb$	2SD $^{208}Pb/^{204}Pb$	2SD $^{207}Pb/^{206}Pb$	2SD $^{208}Pb/^{206}Pb$
32X SN6	A-17	**Std. drill**	**0.0043**	**2300**	**17.361**	**15.556**	**37.214**	**0.89602**	**2.14354**	**0.004**	**0.005**	**0.011**	**0.00010**	**0.00022**
Tin bronze	C-1	**Std. drill**	**0.0151**	**86 300**	**17.361**	**15.556**	**37.216**	**0.89599**	**2.14350**	**0.007**	**0.007**	**0.017**	**0.00011**	**0.00028**
(1.56 wt% Pb)	D-17	**Std. drill**	**0.0115**	**[a]35 300**	**17.361**	**15.554**	**37.210**	**0.89592**	**2.14336**	**0.006**	**0.006**	**0.013**	**0.00011**	**0.00024**
	R-59	**Std. drill**	**0.0566**	**[a]44 900**	**17.359**	**15.553**	**37.207**	**0.89598**	**2.14338**	**0.017**	**0.016**	**0.041**	**0.00019**	**0.00073**
	C-9	HNO_3 swab		12 300	17.362	15.552	37.210	0.89574	2.14315	0.013	0.012	0.029	0.00014	0.00036
	D-25	HNO_3 swab		22 700	17.364	15.553	37.212	0.89573	2.14313	0.009	0.008	0.020	0.00011	0.00026
	C-15	HCl swab		4000	17.373	15.555	37.225	0.89535	2.14268	0.007	0.007	0.017	0.00013	0.00031
	D-31	HCl swab		2600	17.372	15.554	37.222	0.89539	2.14266	0.009	0.008	0.022	0.00014	0.00029
31X 7835–8	A-18	**Std. drill**	**0.0069**	**23 600**	**17.864**	**15.592**	**37.751**	**0.87281**	**2.11332**	**0.007**	**0.006**	**0.016**	**0.00010**	**0.00021**
Brass	C-2	**Std. drill**	**0.0162**	**110 000**	**17.724**	**15.583**	**37.633**	**0.87923**	**2.12325**	**0.010**	**0.009**	**0.021**	**0.00012**	**0.00032**
(3.15 wt% Pb)	D-18	**Std. drill**	**0.0092**	**[a]47 600**	**17.629**	**15.574**	**37.510**	**0.88343**	**2.12769**	**0.007**	**0.007**	**0.016**	**0.00011**	**0.00024**
	R-60	**Std. drill**	**0.0750**	**[a]65 400**	**17.614**	**15.574**	**37.494**	**0.88412**	**2.12854**	**0.016**	**0.016**	**0.041**	**0.00024**	**0.00077**
	C-8	HNO_3 swab		15 800	17.611	15.571	37.486	0.88412	2.12851	0.010	0.009	0.022	0.00014	0.00032
	D-24	HNO_3 swab		24 600	17.611	15.569	37.484	0.88411	2.12847	0.009	0.008	0.020	0.00011	0.00024
	C-14	HCl swab		3400	18.139	15.646	38.240	0.86256	2.10812	0.009	0.008	0.021	0.00012	0.00028
	D-30	HCl swab		1600	17.612	15.570	37.485	0.88406	2.12843	0.010	0.009	0.022	0.00012	0.00028
31X B26	A-20	**Std. drill**	**0.0060**	**250**	**18.619**	**15.664**	**38.714**	**0.84128**	**2.07927**	**0.008**	**0.007**	**0.017**	**0.00011**	**0.00029**
Brass	C-3	**Std. drill**	**0.0078**	**56 100**	**17.992**	**15.613**	**37.989**	**0.86782**	**2.11153**	**0.009**	**0.008**	**0.020**	**0.00011**	**0.00030**
(0.95 wt% Pb)	D-19	**Std. drill**	**0.0064**	**[a]14 900**	**17.604**	**15.570**	**37.484**	**0.88446**	**2.12928**	**0.005**	**0.005**	**0.013**	**0.00009**	**0.00021**
	R-61	**Std. drill**	**0.0662**	**[a]45 200**	**17.604**	**15.568**	**37.479**	**0.88437**	**2.12912**	**0.013**	**0.013**	**0.035**	**0.00021**	**0.00085**
	C-7	HNO_3 swab		14 600	17.608	15.570	37.487	0.88426	2.12907	0.010	0.009	0.021	0.00011	0.00030
	D-23	HNO_3 swab		48 900	17.604	15.569	37.481	0.88442	2.12919	0.007	0.006	0.014	0.00011	0.00026
	C-13	HCl swab		4300	17.633	15.574	37.521	0.88324	2.12788	0.009	0.008	0.020	0.00011	0.00027
	D-29	HCl swab		2900	17.605	15.568	37.482	0.88433	2.12905	0.010	0.008	0.021	0.00011	0.00026
32X LB15	A-16	**Std. drill**	**0.0004**	**730**	**17.610**	**15.572**	**37.488**	**0.88425**	**2.12873**	**0.008**	**0.007**	**0.017**	**0.00011**	**0.00020**
Leaded bronze	C-4	**Std. drill**	**0.0182**	**83 600**	**17.670**	**15.579**	**37.553**	**0.88170**	**2.12527**	**0.008**	**0.007**	**0.017**	**0.00012**	**0.00031**
(21.42 wt% Pb)	D-20	**Std. drill**	**0.0164**	**[a]51 400**	**17.669**	**15.578**	**37.549**	**0.88169**	**2.12518**	**0.007**	**0.006**	**0.014**	**0.00008**	**0.00019**
	R-62	**Std. drill**	**0.1146**	**[a]49 600**	**17.667**	**15.576**	**37.544**	**0.88166**	**2.12516**	**0.012**	**0.013**	**0.034**	**0.00019**	**0.00079**
	C-10	HNO_3 swab		65 000	17.664	15.573	37.536	0.88166	2.12507	0.010	0.009	0.022	0.00013	0.00030
	D-26	HNO_3 swab		114 000	17.662	15.572	37.532	0.88165	2.12493	0.010	0.009	0.022	0.00014	0.00031
	C-16	HCl swab		14 800	17.667	15.576	37.542	0.88167	2.12505	0.011	0.009	0.022	0.00012	0.00035
	D-32	HCl swab		12 100	17.664	15.575	37.540	0.88172	2.12515	0.008	0.009	0.023	0.00011	0.00026
83X PR8	C-5	**Std. drill**	**0.0039**	**77 500**	**17.503**	**15.561**	**37.366**	**0.88905**	**2.13495**	**0.008**	**0.007**	**0.017**	**0.00011**	**0.00028**
Lead	D-21	**Std. drill**	**0.0118**	**[a]155 000**	**17.500**	**15.558**	**37.358**	**0.88902**	**2.13467**	**0.006**	**0.005**	**0.013**	**0.00010**	**0.00021**
	E-26	**Std. drill**	**0.0063**	**61 200**	**17.501**	**15.558**	**37.361**	**0.88902**	**2.13479**	**0.007**	**0.007**	**0.017**	**0.00012**	**0.00023**
	R-63	**Std. drill**	**0.0694**	**[a]46 200**	**17.505**	**15.562**	**37.375**	**0.88900**	**2.13501**	**0.013**	**0.012**	**0.035**	**0.00021**	**0.00079**

Table 2 (*Contd.*)

Standard	Analysis number	Sample type	Sample mass (g)	Pb after isolation (μg L^{-1})	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb	2SD ^{206}Pb/^{204}Pb	2SD ^{207}Pb/^{204}Pb	2SD ^{208}Pb/^{204}Pb	2SD ^{207}Pb/^{206}Pb	2SD ^{208}Pb/^{206}Pb
	C-11	HNO$_3$ swab		103 000	18.405	15.654	38.524	0.85053	2.09314	0.016	0.014	0.035	0.00018	0.00037
	D-27	HNO$_3$ swab		29 800	17.497	15.557	37.354	0.88910	2.13487	0.009	0.007	0.018	0.00012	0.00025
	C-17	HCl swab		19 500	17.501	15.559	37.362	0.88905	2.13485	0.008	0.007	0.018	0.00014	0.00032
	D-33	HCl swab		21 400	17.500	15.558	37.359	0.88902	2.13482	0.009	0.008	0.018	0.00013	0.00029
85X ANTH Lead	A-19	**Std. drill**	**0.0011**	**12 600**	**17.419**	**15.540**	**37.241**	**0.89213**	**2.13792**	**0.016**	**0.015**	**0.038**	**0.00018**	**0.00040**
	C-6	**Std. drill**	**0.0048**	**60 600**	**17.429**	**15.553**	**37.271**	**0.89237**	**2.13841**	**0.008**	**0.007**	**0.018**	**0.00010**	**0.00028**
	D-22	**Std. drill**	**0.0091**	**^{a}212 000**	**17.432**	**15.552**	**37.267**	**0.89213**	**2.13786**	**0.006**	**0.005**	**0.014**	**0.00010**	**0.00022**
	E-27	**Std. drill**	**0.0076**	**86 900**	**17.423**	**15.547**	**37.253**	**0.89233**	**2.13815**	**0.010**	**0.009**	**0.021**	**0.00013**	**0.00025**
	R-64	**Std. drill**	**0.0676**	**47 500**	**17.429**	**15.553**	**37.269**	**0.89239**	**2.13845**	**0.012**	**0.013**	**0.035**	0.00022	0.00088
	C-12	HNO$_3$ swab		11 800	17.429	15.553	37.269	0.89240	2.13838	0.007	0.007	0.015	0.00011	0.00027
	D-28	HNO$_3$ swab		32 900	17.425	15.550	37.260	0.89234	2.13825	0.010	0.009	0.021	0.00012	0.00027
	C-18	HCl swab		7900	17.429	15.553	37.268	0.89237	2.13835	0.008	0.007	0.017	0.00011	0.00025
	D-34	HCl swab		8100	17.425	15.549	37.259	0.89232	2.13825	0.010	0.009	0.020	0.00010	0.00023
36X CUAS3 A Arsenical copper (<0.0001 wt% Pb)	BM-46	**Std. drill**	**0.0721**	**^{a}390**	**17.929**	**15.602**	**37.917**	**0.87020**	**2.11480**	**0.007**	**0.006**	**0.016**	**0.00010**	**0.00032**
	BM-47	**Std. drill**	**0.0194**	**170**	**17.882**	**15.597**	**37.873**	**0.87219**	**2.11793**	**0.005**	**0.005**	**0.014**	**0.00020**	**0.00040**
	BM-48	**Std. drill**	**0.0681**	**^{a}270**	**17.862**	**15.674**	**37.945**	**0.87750**	**2.12437**	**0.009**	**0.011**	**0.024**	**0.00024**	**0.00041**
	R-55	**Std. drill**	**0.0621**	**^{a}200**	**17.885**	**15.593**	**37.822**	**0.87177**	**2.11464**	**0.014**	**0.013**	**0.036**	**0.00019**	**0.00067**
33X GM20 A Gunmetal (0.106 wt% Pb)	BM-49	**Std. drill**	**0.0185**	**^{a}3600**	**18.236**	**15.626**	**38.062**	**0.85687**	**2.08718**	**0.005**	**0.005**	**0.013**	**0.00012**	**0.00030**
	BM-50	**Std. drill**	**0.0071**	**^{a}1700**	**18.239**	**15.624**	**38.063**	**0.85666**	**2.08695**	**0.004**	**0.004**	**0.011**	**0.00010**	**0.00029**
	BM-51	**Std. drill**	**0.0148**	**^{a}4100**	**18.238**	**15.625**	**38.061**	**0.85672**	**2.08695**	**0.006**	**0.005**	**0.015**	**0.00010**	**0.00028**
	R-57	**Std. drill**	**0.0837**	**^{a}7600**	**18.238**	**15.627**	**38.068**	**0.85684**	**2.08735**	**0.012**	**0.013**	**0.032**	**0.00021**	**0.00074**
32X LB17 A Leaded bronze (9.83 wt% Pb)	BM-52	**Std. drill**	**0.0584**	**^{a}59 300**	**17.610**	**15.572**	**37.511**	**0.88425**	**2.13008**	**0.004**	**0.003**	**0.009**	**0.00007**	**0.00020**
	BM-53	**Std. drill**	**0.0057**	**^{a}66 000**	**17.617**	**15.568**	**37.509**	**0.88368**	**2.12915**	**0.005**	**0.005**	**0.014**	**0.00010**	**0.00032**
	BM-54	**Std. drill**	**0.0559**	**^{a}50 300**	**17.602**	**15.570**	**37.501**	**0.88457**	**2.13049**	**0.005**	**0.005**	**0.013**	**0.00010**	**0.00030**
	R-58	**Std. drill**	**0.0945**	**^{a}36 000**	**17.600**	**15.569**	**37.496**	**0.88456**	**2.13043**	**0.013**	**0.012**	**0.034**	**0.00021**	**0.00071**
32X SN5 A Tin bronze (0.259 wt% Pb)	BM-55	**Std. drill**	**0.0486**	**^{a}34 700**	**17.689**	**15.581**	**37.577**	**0.88085**	**2.12435**	**0.006**	**0.006**	**0.015**	**0.00011**	**0.00030**
	BM-56	**Std. drill**	**0.0011**	**^{a}10 300**	**18.702**	**15.678**	**38.778**	**0.83828**	**2.07343**	**0.005**	**0.005**	**0.013**	**0.00010**	**0.00029**
	BM-57	**Std. drill**	**0.0179**	**^{a}51 300**	**18.684**	**15.676**	**38.755**	**0.83898**	**2.07425**	**0.007**	**0.006**	**0.016**	**0.00010**	**0.00030**
	R-56	**Std. drill**	**0.0381**	**^{a}24 000**	**17.689**	**15.582**	**37.578**	**0.88086**	**2.12437**	**0.012**	**0.012**	**0.032**	**0.00021**	**0.00083**

[a] Aliquot of sample solution taken for ICP-OES analysis.

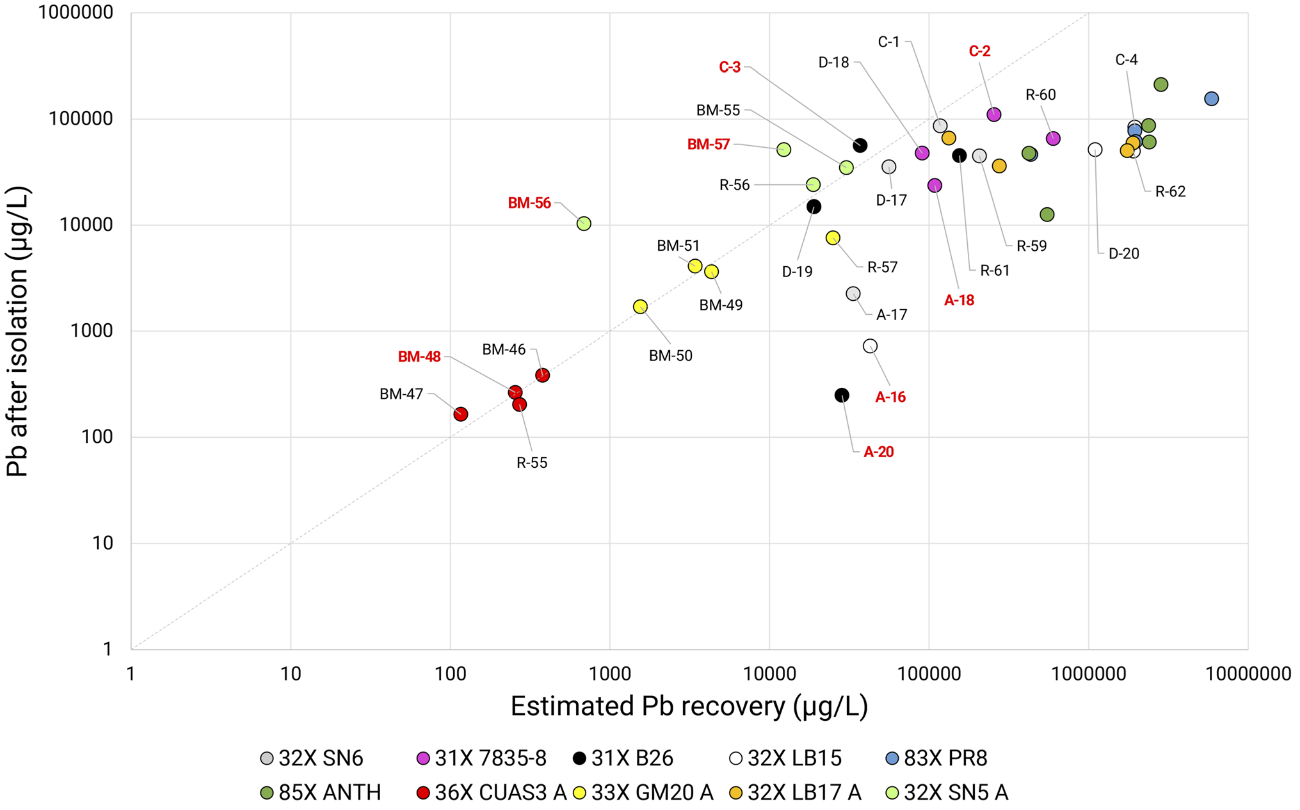

Fig. 1 Comparison of the measured "Pb after isolation" *vs.* "Estimated lead recovery" for drill samples (*cf.* descriptions in main text "Materials and methods"). Samples highlighted in bold red have significantly divergent Pb isotope ratios.

location was sub-divided (BM-46/47, BM-49/50, BM-52/53 and BM-55/56) and the two sub-samples dissolved separately.

For most standards, the measured Pb isotope ratios for each of the drilled samples are identical within experimental error. This is the case for 32X SN6, 83X PR8, 85X ANTH, 33X GM20 A, 32X LB17 A and MBH-CRM-CR32-PB110 (*cf.* previous section). These results highlight the strong reproducibility of our analyses, and stability of results across different analytical batches processed over several years.

However, discrepancy can be noted between drilled samples for five standards. As a first example, 32X LB15 (21.42 wt% Pb) can be considered. While the Pb isotope ratios for three of the drill samples are identical, sample A-16's ratios to ^{204}Pb differ by up to 0.33%. A-16 is the smallest sample taken for 32X LB15, weighing 0.4 mg only. The absolute lead recovery after isolation is *ca.* 730 µg L^{-1}, sufficient for precise measurement. While lower in absolute recovery, its "relative Pb recovery" (compared to maximum estimated Pb recover) is like that of the other 32X LB15 samples (*cf.* Fig. 1).

As a second example, 36X CUAS3 A is highlighted. Here, minor differences can be observed between each of the four measurements. The best agreement exists for BM-47 and R-55, although a relative difference of > 0.1% is noted for ^{208}Pb/^{204}Pb. A more significant dispersion is noted in BM-46, particularly in terms of its ^{206}Pb/^{204}Pb ratio which differs by 0.26% from that of BM-47 – sub-sampled from the same drill sample. Finally, a large dispersion exists for BM-48, with ^{207}Pb/^{204}Pb differing by almost 0.5% from the value for BM-47. It can be noted here that, despite the extremely low concentration of lead in this standard (<1 µg g^{-1}), sufficient lead was extracted during isolation for normal measurement at 150 µg L^{-1} (*i.e.* solutions from *ca.* 170 µg L^{-1} for BM-47 to almost 400 µg L^{-1} for BM-46) – with c. 100% relative lead recovery during the isolation phase (*cf.* Fig. 1). These results thus indicate potential heterogeneity in Pb isotope ratios for copper alloys with extremely low lead concentrations.

32X SN5 A provides a third important example. The measured Pb isotope ratios for this tin bronze, with 0.259 wt% lead, split into two very distinct clusters. Indeed, those for BM-55 and R-56 (measured in two different analytical batches) are identical within analytical error, as are those for BM-56 and BM-57 (measured in the same analytical batch). However, the difference between these two clusters is *ca.* 0.6% in terms of ^{207}Pb/^{204}Pb, *ca.* 3.2% in terms of ^{208}Pb/^{204}Pb and *ca.* 5.7% in terms of ^{206}Pb/^{204}Pb – a huge discrepancy. Again, variability is observed between two fractions taken from the same drill sample (*i.e.* BM-55 and BM-56). The difference in Pb isotope ratios is thus not so much related to sampling location but rather seems to correlate to sample mass: BM-56 and BM-57 represent the smallest samples (<20 mg), while BM-55 and R-56 represent the largest samples (>30 mg). Notably, the lead concentration measured in all four samples (*cf.* ICP-OES results in SI) is consistent with the reference values, and absolute lead recovery is high for all samples (over 10 mg L^{-1} even for sample BM-56, at only 1.1 mg). Interestingly, relative lead recovery appears "too high" for BM-56 and BM-57 (*cf.* Fig. 1).

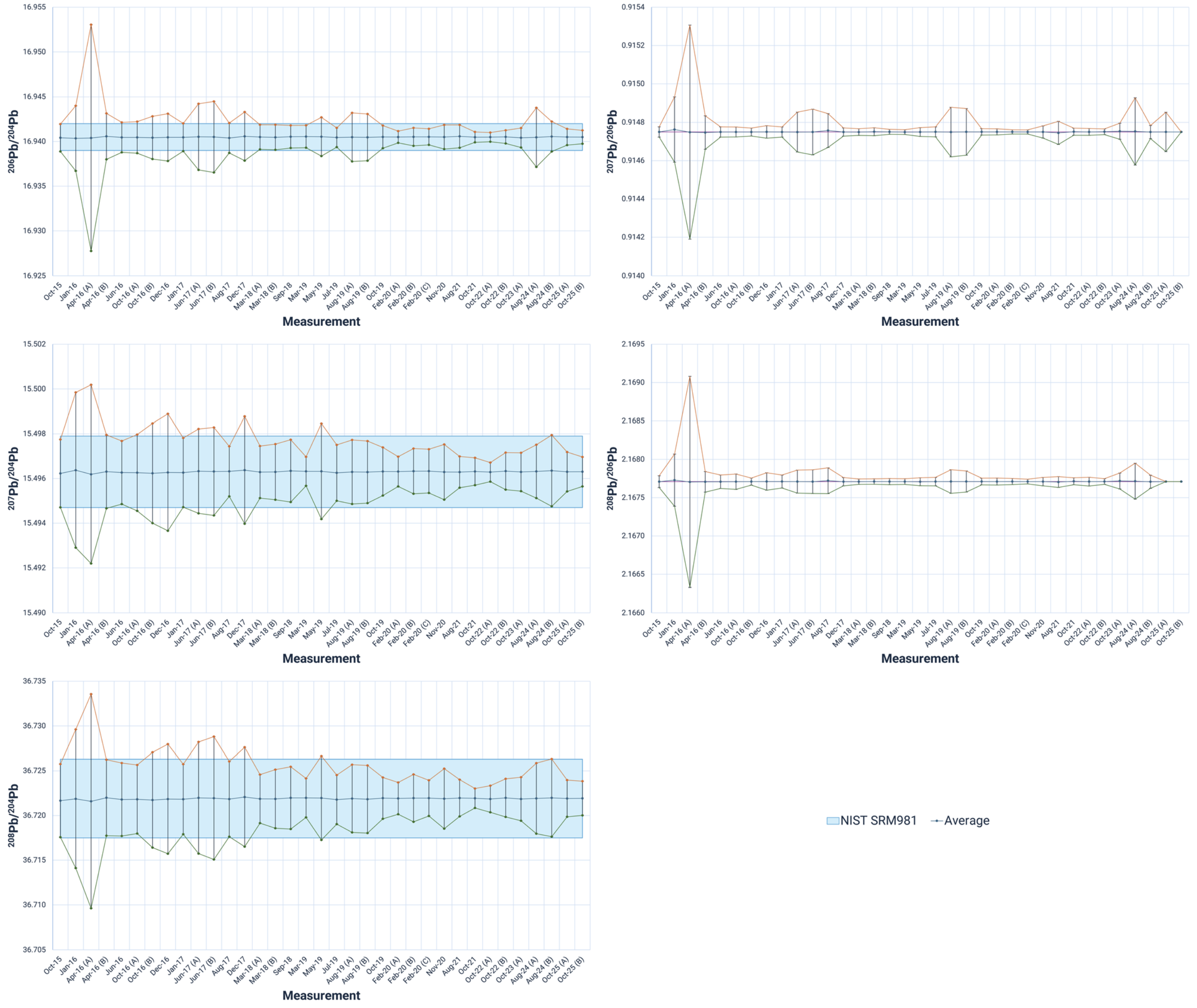

Fig. 2 Long-term replicate measurements of NIST SRM 981 used as a bracketing standard for Pb isotopic analysis. Reference values[40] in light blue, ranges show average and 2SD for 20 standard measurements within each batch. Bias is < 0.010‰ on all ratios, and usually < 0.005‰.

As a final example, the two brass standards (31X 7835-8 and 31X B26) are highlighted. For both, significant Pb isotope ratio variability is observed between samples. While D-18 and R-60 are consistent (across different analytical batches), the other two values (A-18 and C-2) are very different for 31X 7835-8 (yet lead recovery is similar: *cf.* Fig. 1). Similarly, D-19 and R-61 are consistent, while A-20 and C-3 differ by up to almost 6% in their ratios to ^{204}Pb. This is not an effect of inter-batch variations, as consistent results across these four batches are obtained for other standards. Rather, there appears to be significant heterogeneity w.r.t. Pb isotope ratios for these two brass standards. While the sample masses for D-19 and A-20 are identical, their Pb isotope ratios differ significantly – as did the absolute lead recovery (*ca.* 15 mg L^{-1} for D-19 as opposed to only *ca.* 250 µg L^{-1} for A-20, *cf.* Fig. 1). Interestingly, relative lead recovery for C-3 is c. 100% (*cf.* Fig. 1), yet its Pb isotope ratios still deviate strongly (>2% in ^{206}Pb/^{204}Pb). This likely reflects heterogeneity of these standards in terms of their lead distribution at the scale represented by drill samples of a few mg but equally points to possible heterogeneity in Pb isotope ratios. If "large samples" (>30 mg) are taken as the reference value (R-60 and R-61, respectively), it appears that small samples (<10–20 mg) sometimes diverge, but sometimes not (D-18 and D-19, respectively).

For the lead standards, variability in the absolute lead recovery is notable, which is not always proportional to the dissolved sample mass. As noted above, this is partly due to variations in column resin mass and solution volume, and the prior removal of aliquots for ICP-OES analysis (and for sample E-26 only half of the sample solution was loaded onto the column for isolation). Indeed, the calculated concentrations of lead in the solutions prior to isolation typically exceed the column capacity. The perfect alignment of reported results for these lead standards illustrates that resin (over)saturation on the column does not cause notable fractionation.

Acid swab samples. For the acid swabs, no direct measurement of sample mass is possible. As such, it is instructive to

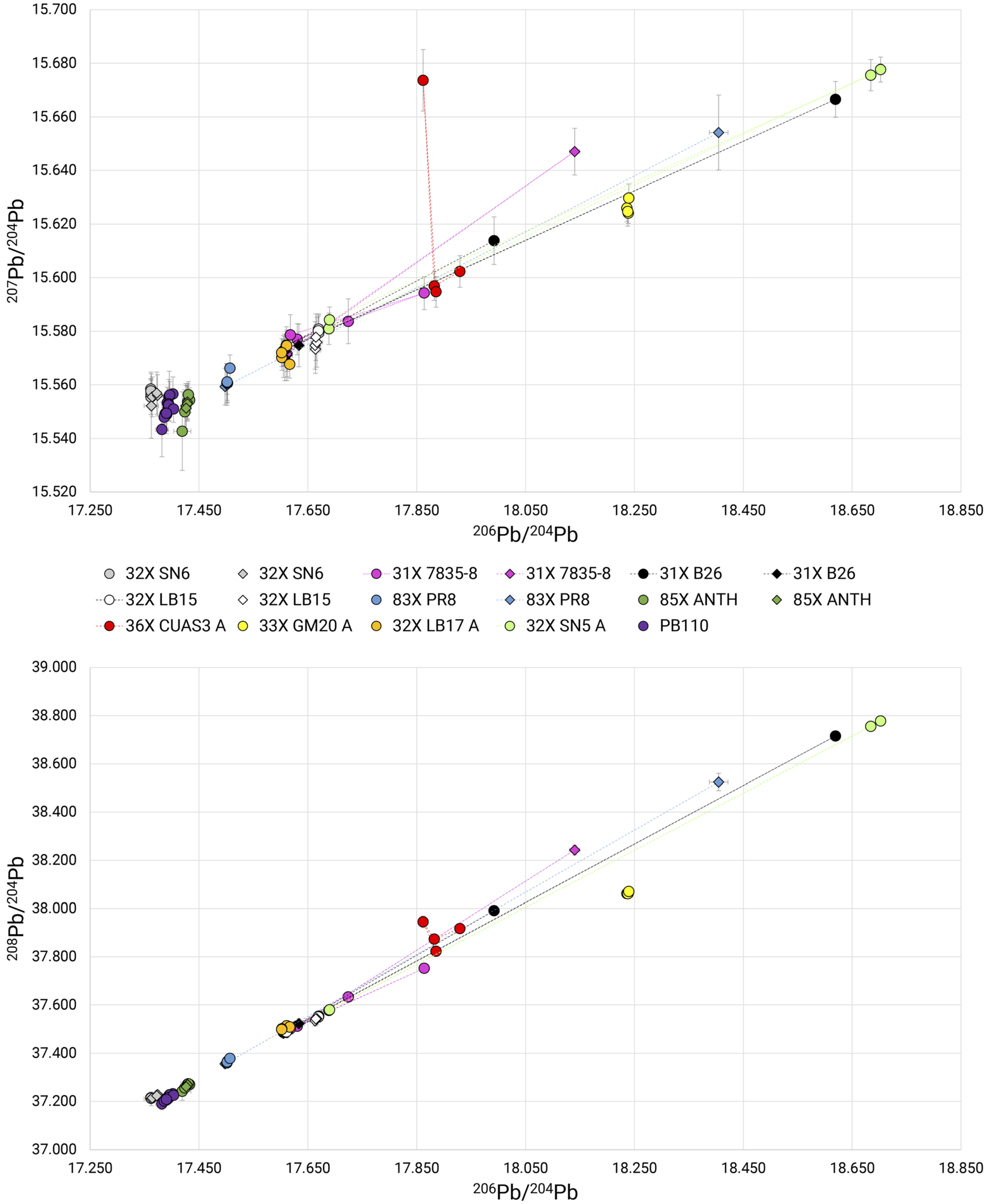

Fig. 3 Pb isotope ratios measured for the different standards. Round symbols reflect drill samples, while diamond symbols reflect swab samples (*cf.* Table 2). Dashed lines highlight strong discrepancies between measurements of the same standard. Close-up plots for selected standards are provided in the SI.

compare the absolute lead recovery (*i.e.* "Pb after isolation") for acid swabs and drill samples of each standard: this is generally higher in the drill samples (ignoring the smallest sample masses), and often several times higher (*e.g.* 32X SN6 and 31X 7835-8). This is not surprising, as higher metal mass is removed by drilling. Overall, all acid swabs recovered sufficient lead for precise measurement (all > 1 mg L^{-1}).

Across the different copper alloy and lead standards, the results for both HNO_3 and HCl acid swabs are identical to those obtained for the drill samples (within experimental error), with only few exceptions. Notably, the swab technique has not been tested for the low-lead standards 36X CUAS3 A or the (apparently) isotopically divergent standard 32X SN5 A.

The Pb isotope ratio variability observed between drill samples of the two brass standards (31X 7835-8 and 31X B26) is equally observed in their acid swab samples. However, both HNO_3 swabs and one HCl swab (D-29) for 31X B26 give similar results to those obtained for D-19 and the largest sample (R-61). For 31X 7835-8, the Pb isotope ratio results based on both HNO_3 swabs and one HCl swab (D-30) are very similar to those of the largest sample (R-60). The remaining HCl swabs differ significantly (>0.1% for at least one ratio to ^{204}Pb) for both standards, resulting in overall higher ratios to ^{204}Pb (like the smaller drill samples).

Beyond the brass, there is a notable discrepancy in one of the HNO_3 swabs for lead standard 83X PR8, despite high absolute lead recovery. This is surprising and has not been observed in previous swabs of pure lead.[34]

Case study for early Egyptian copper alloys

As a final dataset, results are presented for five Early Dynastic copper alloy objects from the British Museum collection in Table 3. These were first sampled within the framework of one of the largest studies of early Egyptian copper alloy compositions[28] (and analysed using AAS and ICP-OES). The residual samples of this analytical campaign, kept at the British Museum Department of Scientific Research, were analysed by the authors to evaluate their Pb isotopic composition. The results presented here (measured as part of analytical batch A, *cf.* above) are part of a much larger dataset, the archaeological interpretation of which is beyond the scope of this paper.

A selection of these same objects was re-sampled for lead isotopic analysis using MC-ICP-MS in 2019 by Jiří Kmošek, Yulia V. Kochergina and Martin Odler, as part of an external examination request (EER). As part of the EER agreement, the results of such examinations may be made publicly available by the British Museum five years after being received (*in casu*, February 2020), regardless of whether they have been published elsewhere. However, we have anonymised the object numbers here to ensure Kmošek and colleagues can publish their interpretation of this data first.

Comparison of the data in Table 3 reveals two important results. Firstly, the data obtained for objects 1 and 2 are identical within experimental error (*i.e.* the difference is < 0.1% in all ratios). This suggests good comparability between the data obtained in different labs, despite differences in analytical protocols (*e.g.*, Kmošek *et al.*[19] normalise their ratios to NIST certificate values (TIMS data) rather than to Galer and Abouchami[40] values (TIMS data), which differ by up to 0.03%). Secondly, however, for objects 3, 4 and 5, significant discrepancy is noted for all Pb isotope ratios – from *ca.* 0.4% in object 3 to over 7% in object 4. Such differences are enormous and would imply very different interpretations regarding the material provenance for these objects.

Following the analysis of residual samples (analytical batch A, Table 3) and the results described above, it was decided to resample object 3 in 2025, in consultation with curatorial staff of the British Museum Department of Egypt and Sudan, to eliminate possible inter-lab variability underlying the observed discrepancies and underpin future sampling protocols. A new drill sample was obtained from the existing drill hole (previously sampled by Cowell[28] and Kmošek *et al.*) and subdivided into three aliquots of varying weight (2.5 mg, 8 mg and 67.8 mg) before digestion and processing as described above. The measured Pb isotope ratios are presented in Table 3 (analytical batch B). The results for B-1, B-2 and B-3 (all for object 3) align perfectly with those reported by Kmošek *et al.* (within experimental error) and clearly illustrate the reproducibility of the method and comparability between labs. Notably, the absolute lead recovery for the three samples is higher than that for A-7 (1.1 mg sample).

Indeed, the absolute lead recovery in our study is highest for objects 1 and 2, and lower for the others – with the lowest recovery for object 4. This coincides with differences in lead content (highest in objects 1 and 2) as well as the available residual sample mass for these objects. Nonetheless, absolute lead recovery was sufficient for accurate and precise measurement in each case, and without the existence of replicate measurements by Kmošek and colleagues, there would be no reason to suspect these results might be "wrong". If the data by Kmošek *et al.* indeed can be taken as reference values for "large samples", which our replicate analysis (samples B-1, B-2 and B-3) confirms, this small dataset illustrates the same pattern observed for the standards: small samples may not recover a representative amount of lead compared to larger ones, especially when lead concentration within the copper alloy is relatively low.

Discussion

The replicate analysis of archaeological objects is only rarely undertaken, which represents a widespread and largely unavoidable challenge in archaeological research (*e.g.* Farahani[43] and references therein on replication and reproducibility, or Bayliss and Marshall[44] on radiocarbon reproducibility). This is typically compensated for by the development of standard practices monitoring the repeatability and accuracy of analytical methodologies using QA/QC standards and procedures. Sampling procedures are part and parcel of such standard practices, designed to minimise potential issues related to sample heterogeneity and contamination. In the context of archaeometallurgical research, and "provenance analysis" in particular, standard practices have been largely

Table 3 Results of Pb isotopic analysis of five Early Dynastic Egyptian copper alloys in the British museum collection

Object	Analysis	Sample mass (g)	Pb content[a] (wt%)	Pb after isolation (μg L^{-1})	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	2SD $^{206}Pb/^{204}Pb$	2SD $^{207}Pb/^{204}Pb$	2SD $^{208}Pb/^{204}Pb$	2SD $^{207}Pb/^{206}Pb$	2SD $^{208}Pb/^{206}Pb$
1	Kmošek *et al.*	*ca.* 0.0300			18.810	15.700	38.963	0.83400	2.07200					
	This study (sample A-21)	0.0057	1.5	3500	18.812	15.702	38.975	0.83464	2.07179	0.002	0.002	0.005	0.00003	0.00013
2	Kmošek *et al.*	*ca.* 0.0300			19.245	15.704	39.230	0.81600	2.03900					
	This study (sample A-18)	0.0055	1.2	15 900	19.255	15.709	39.255	0.81587	2.03874	0.002	0.002	0.006	0.00004	0.00014
3	Kmošek *et al.*	*ca.* 0.0300			19.375	15.663	39.113	0.80800	2.01900					
	This study (sample A-7)	0.0011	0.42	1300	19.302	15.651	39.025	0.81085	2.02183	0.002	0.002	0.006	0.00004	0.00014
	This study (A-7, solution remeasured in other batch)	0.0011	0.42	1300	19.299	15.652	39.024	0.81101	2.02204	0.002	0.002	0.005	0.00003	0.00011
	This study (sample B-1)	0.0025	0.42	3700	19.382	15.655	39.101	0.80772	2.01743	0.003	0.003	0.008	0.00005	0.00018
	This study (sample B-2)	0.0080	0.42	8600	19.383	15.655	39.101	0.80768	2.01734	0.003	0.003	0.007	0.00005	0.00016
	This study (sample B-3)	0.0678	0.42	51 900	19.383	15.656	39.103	0.80767	2.01736	0.003	0.002	0.007	0.00005	0.00015
4	Kmošek *et al.*	*ca.* 0.0300			20.363	15.723	39.723	0.77200	1.95100					
	This study (sample A-23)	0.0004	0.02	210	18.905	15.669	38.836	0.82881	2.05430	0.003	0.003	0.007	0.00005	0.00014
5	Kmošek *et al.*	*ca.* 0.0300			19.136	15.641	38.819	0.81700	2.02900					
	This study (sample A-5)	0.0054	0.07	1230	17.997	15.572	37.739	0.86528	2.09696	0.002	0.002	0.005	0.00004	0.00014
	This study (A-5, solution remeasured in other batch)	0.0054	0.07	1230	17.995	15.573	37.738	0.86544	2.09716	0.002	0.002	0.005	0.00004	0.00011

[a] Pb contents reported after Cowell.[28]

driven by considerations related to elemental analysis, with lead isotopic analysis working well for the same samples if sufficient lead is recovered. As analytical instrumentation improved, "sufficient lead" has become less of a concern, enabling the measurement of increasingly small samples. Issues of sample heterogeneity with respect to isotope ratios have been rarely addressed, yet exceptions exist (*e.g.* for copper ore specimens[45] or for tin ingots[46]). Overall, however, sample heterogeneity is considered to be irrelevant when determining the lead isotopic composition of copper alloys.[47]

The data presented in this study show, however, that problems may arise for increasingly small samples of copper alloys. These problems appear not to be related to the analytical methodology as such – Pb isotope ratios for internal and external standards are reproducible within and between analytical batches. When considering the CHARM standards, "correct results" (obtained for samples > 30 mg) are indeed reproducible. Conversely, many of the "wrong results" (*i.e.*, diverging from the "correct results", sometimes obtained for samples of smaller mass) are equally reproducible across analytical batches, indicating they may represent an underlying characteristic of the material being analysed rather than simply a "wrong measurement". Notably, our observations are not limited to standard reference materials but are equally observed for a small selection of re-sampled ancient copper alloys.

Various factors may underlie the occurrence of "wrong results", but the most important one appears to be low absolute lead recovery from the sample during isolation. This reflects the loading of low lead content from the sample onto the column, due either to low lead content in the alloy, low sample mass or a combination thereof. However, it is difficult to identify a cut-off value at which absolute lead recovery is too low to obtain "correct" or rather "representative results". For example, absolute lead recoveries are similar (and in the same order of magnitude as for other samples) for the four samples taken of 32X SN5 A, yet divergent Pb isotope ratios were obtained. Similarly, no discrepancies were noted for 32X SN6 despite divergent sample mass, although 31X 7835-8 and 31X B26 display highly variable Pb isotope ratios for different sample masses (and sometimes divergent absolute lead recovery for the same sample mass). This shows sample mass is not an absolute indicator for all copper alloys. Yet sample mass can affect even highly leaded bronzes, such as 32X LB15, even if in most cases no discrepancy is noted (even for swabs). In this case (sample A-20), very low sample mass apparently led to very low relative lead recovery (possibly by the haphazard exclusion of immiscible lead globules in A-20). Nonetheless, other factors beyond sample mass appear to be at play.

The results obtained for brass standards suggest that significant variability in lead concentration exists throughout these alloys, which results in strong sensitivity to how much lead is included in very small samples. Furthermore, it shows that the Pb isotope ratios for lead in different phases within these alloys may differ (as perhaps for lead in leaded bronze). This suggests that if comparisons between different brass alloys are to be made, these should all be for sufficiently large samples. Even if the results obtained for small samples, including acid swabs, sometimes correspond to the largest samples, significant variability is observed between such samples.

We thus conclude that two overall effects are likely to cause the observed variation. On the one hand, there may be heterogeneity in the Pb isotopic composition within alloys, especially for those materials containing extremely low lead concentrations (*e.g.* 36X CUAS3 A). While sufficiently large samples should compensate this effect, commonly acceptable masses in archaeological research (*e.g.* BM-48 at *ca.* 70 mg) may not be able to do so for extremely lead-poor alloys. On the other hand, there may be an effect of lead heterogeneity at the micro-scale for more lead-rich samples as well. This is where low sample mass comes into play (*e.g.* 32X SN5 A, 32X LB15 and the swab samples). It appears that this effect is more pronounced for certain alloy types, with high zinc content possibly causing particular problems. This goes against the common paradigm of lead isotopic homogeneity within copper alloys, suggesting sample size does matter for Pb isotope ratio determination as much as for elemental analysis.

Crucially, no clear external indicator appears available to signal when "wrong results" might be obtained¶ – only replicate sampling and analysis can reveal potential heterogeneity. However, the theoretically ideal scenario of sampling multiple object locations will almost always be impossible in archaeological case studies, particularly when analysing museum collections where sampling is usually restricted to a single location due to curatorial considerations. Given that sub-sampling of a single (drill) sample lowers the average lead recovery per sub-sample and thereby increases the likelihood of divergent results (as observed in our dataset), we do not believe this approach resolves the problem. Indeed, the results obtained for larger and smaller samples appear to reflect different material properties, and their averaging as part of such a sampling strategy would not necessarily produce meaningful isotope ratios. While the analysis of sub-samples could flag potential problems, constraints on budget and instrument availability within archaeological research projects will often impede multiplying the number of analyses for each sampled object.

Based on these observations, and the reality of archaeological/heritage sampling considerations, we would thus recommend that a minimum (single) sample mass of > 20 mg (and ideally > 30 mg) is adopted for solution-based Pb isotopic analysis of ancient copper alloys, and that absolute lead recovery be monitored and reported. For the latter, however, it is difficult to establish a firm minimum value based on our results (divergent Pb isotope ratios have been observed for samples with lower relative lead recovery, but not consistently so, and equally where relative lead recovery is close to 100%: *cf.* Fig. 1). While overall good agreement is observed between acid swab (regardless of acid type) and (large) drill samples, issues of lead heterogeneity observed for small drill samples in selected

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¶ Samples of a few mg may yield identical results, especially for copper alloys with higher lead concentrations, but our results do not allow us to predict cases where they might diverge (significantly).

standards are equally reflected in some of the swabs. As such, we would recommend against acid swab sampling for alloys with low lead, and by extension for any ancient copper alloy. As widely established in copper alloy studies,[47] trace element composition provides essential complementary data towards any interpretation of metal provenance, and sampling for combined trace element and Pb isotopic analysis should thus be encouraged at all times. The common adoption of minimum sample weights thus represents the most robust guarantee for inter-study results comparability.

In a previous study, researchers[48] noted poor agreement for Pb isotope ratios obtained using LA-MC-ICP-MS for low-lead copper (compared to solution-based analysis of the same objects), suggesting that erroneous mass bias corrections for non-matrix matched standards are the cause (see also comments by Stos-Gale and Gale[42]). Based on the results presented here, however, we would suggest that such difficulties may be compounded (or overruled) by the effects described above for small sample sizes. Indeed, typical sample masses analysed when using laser ablation for sampling are on the μg scale. While elemental analysis of copper alloys using LA-ICP-MS presents specific challenges (especially for heterogeneously distributed elements such as lead[49,50]), we would suggest that laser ablation sampling is not always appropriate for Pb isotopic analysis of copper alloys as the corresponding sample size may not provide representative results. Although effects of heterogeneity might be overcome to some degree by repeated LA sampling at different locations for a single object, the averaging of such results would still represent a tiny sample mass compared to those described in this paper, and likely not overcome the effects observed here.

Finally, the results obtained for the Early Dynastic objects underscore the validity of these considerations for archaeological case studies and should encourage a critical and perhaps sobering evaluation of published data. Where Pb isotope ratio data has been reported for very small samples of ancient copper alloys, and particularly those with low lead concentrations, the results may strongly diverge from those obtained for larger sample masses. Inferences of metal provenance for these copper alloys, based on comparisons to data obtained for larger samples of copper alloys (and ore), may need to be disregarded as their representativeness cannot be assessed.

Conclusion

This paper has assessed the effect of sample size on the measurement of Pb isotope ratios for copper alloys in the context of archaeological research. It has presented the results of replicate sampling and MC-ICP-MS isotopic analysis of 11 different standards, whose Pb isotope ratios were not previously reported in literature. The results demonstrate excellent repeatability of the protocol, underlining the comparability of Pb isotopic measurements acquired over time. However, the results illustrate potential problems when processing copper alloy samples of < 20 mg, especially when the alloy's lead concentration is low. Significant dispersion is observed between samples taken from the same copper alloy in some cases, which indicates some degree of heterogeneity on the micro-scale. This effect is equally observed for a small selection of archaeological copper alloys. We suggest that the only way to compensate for this, in a context where replicate sampling is usually impossible, is to adhere to a minimum sample mass of 20–30 mg, as smaller masses can lead to non-representative results despite successful measurement, with no external means of validation available. We urge other researchers to explicitly report sample mass and lead recovery when publishing Pb isotopic data, to ensure compatibility between datasets, and to critically evaluate the sampling protocols of existing studies.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included in the main text and as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5ja00416k.

Acknowledgements

We would like to thank the British Museum Department of Egypt and Sudan for their support in re-sampling the Early Dynastic copper alloy object, in particular Rebecca Whiting, Aurélia Masson-Berghoff, Marie Vandenbeusch and Evan York. This was made possible thanks to the financial support of the British Museum Research Fund. We also thank Ana Franjić for her help in sampling some of the KU Leuven CHARM standards. We are very grateful to Kris Latruwe for performing the MC-ICP-MS measurements reported in this study. FV acknowledges the Flemish Research Foundation (FWO-Vlaanderen) for providing the funding for the acquisition of MC-ICP-MS instrumentation (ZW15-02-G0H6216N).

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