Supplementary information

Limitations in using the Cu isotopic composition of minerals from ancient copper mines for archaeometric purposes

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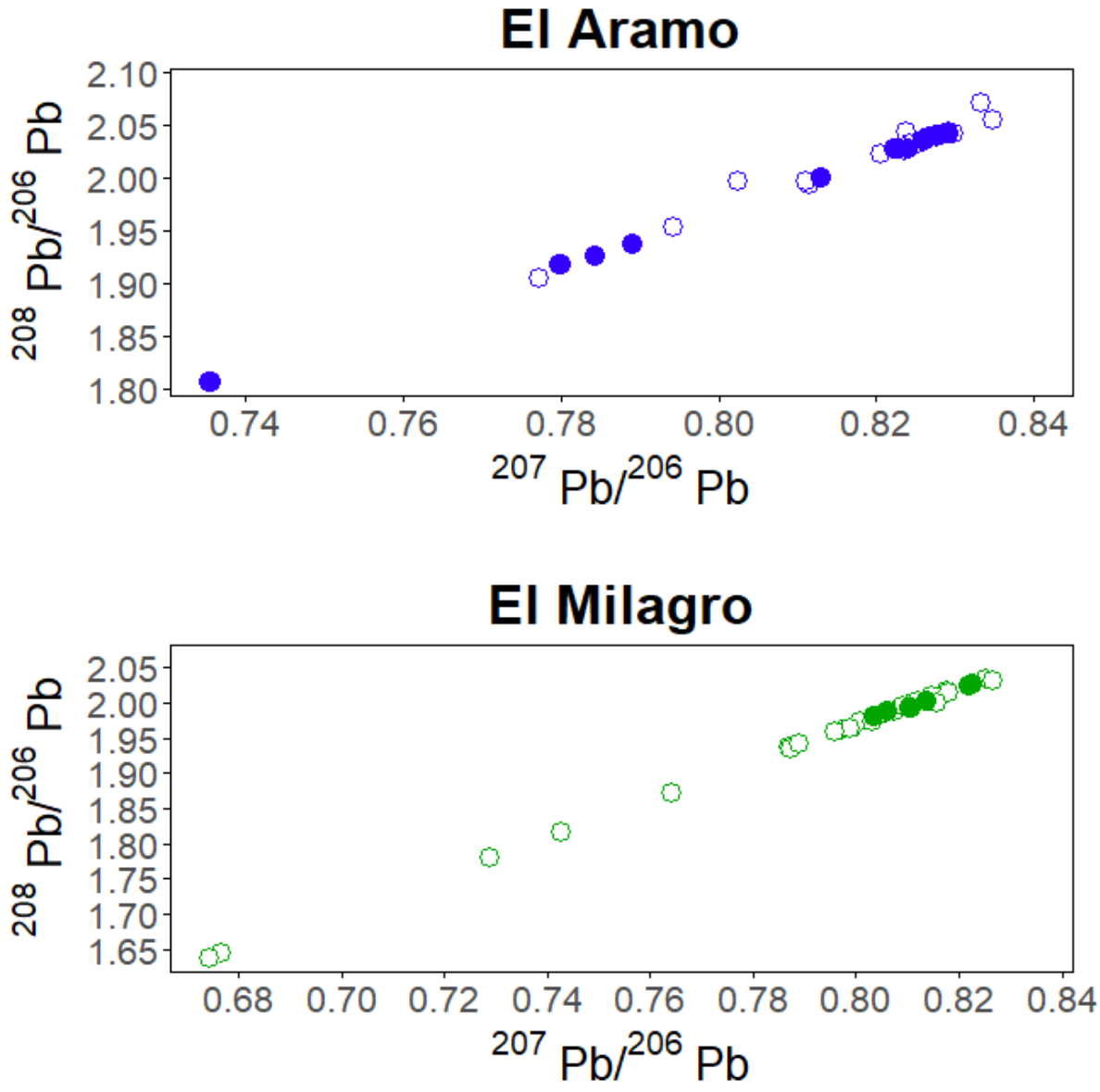
Figures S1-S4

Tables S1-S3

Figure S1. New data for lead isotope ratios for the three mines studied (shaded symbols) in comparison with previously published data[18-20] (open symbols).



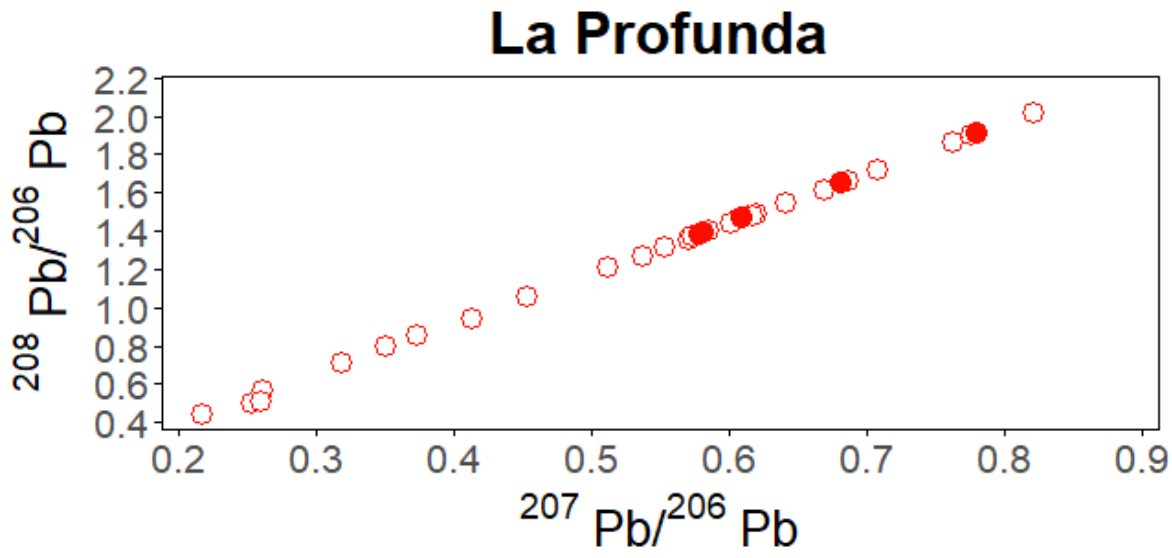


Figure S2. Cu isotope ratio data obtained for the certified reference materials BHVO 2 (δ^{65}Cu= 0.15 ± 0.08 ‰) and BIR 1 (δ^{65}Cu= 0.09 ± 0.08 ‰). Dots represent the experimental values, the solid line represents the average reported value[1] and the dashed lines represents the reported value ± SD.

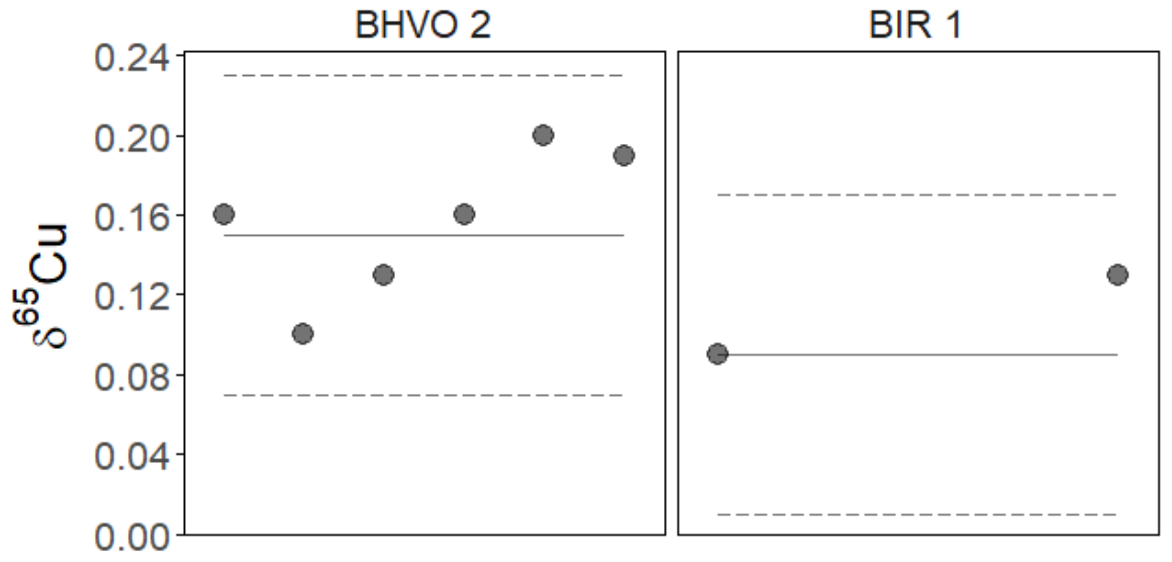


Figure S3. Quality control data based on analysis of the in-house copper standard ($\delta^{65}Cu$ reference value = 0.22 ± 0.07 ‰ (2 SD), horizontal line) on 6 different measurement days (using different markers for each day).

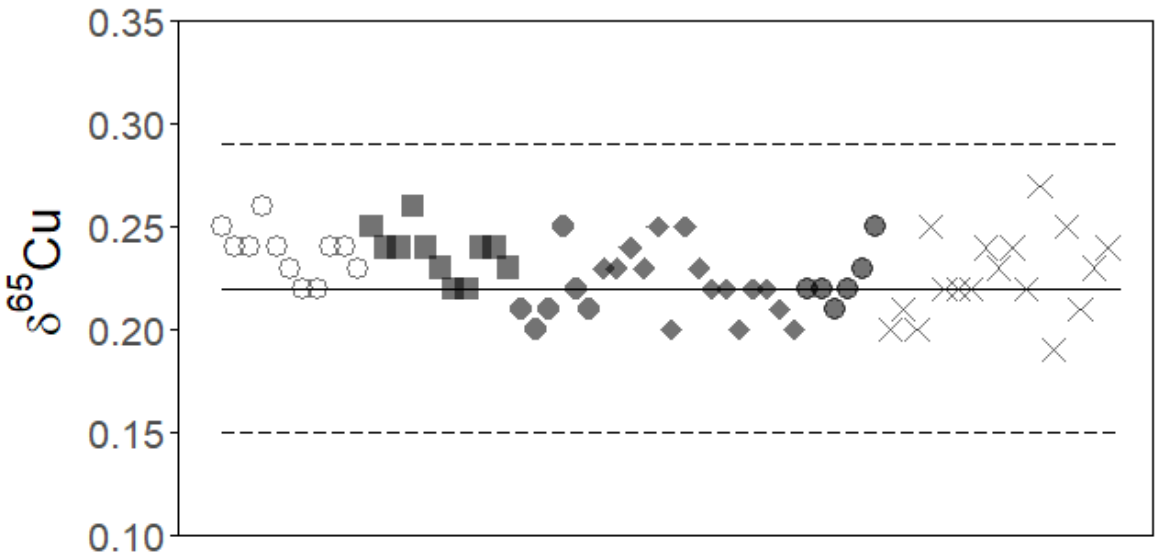


Table S1. Instrument settings and data acquisition parameters for the Neptune MC-ICP-MS units.

Neptune MC-ICP-MS	
RF Power (W)	1200
Guard electrode	Connected
Ar flow rates(L min^{-1})	Plasma gas: 15 Auxiliary gas: 0.80 Nebulizer gas: 1.050
Sample uptake rate (µL min^{-1})	100
Acquisition mode	Static
Number of blocks	1
Number of cycles	50
Integration time	4.194
Cup configurations	L4 L2 C H2 H4 ^{63}Cu ^{65}Cu ^{67}Zn ^{69}Ga ^{71}Ga L3 L2 L1 C H1 H2 H3 ^{202}Hg ^{203}Tl ^{204}Pb ^{205}Tl ^{206}Pb ^{207}Pb ^{208}Pb

Table S2. Pb isotopic composition of the measured samples. Data are expressed as the mean isotope ratio and 2 times the standard deviation (2SD) calculated from 3 measurement replicates. (a), (b) and (c) correspond to sub-samples.

Mine/Site	Sample ID	$^{208}Pb/^{206}Pb$	2SD	$^{207}Pb/^{206}Pb$	2SD	$^{206}Pb/^{204}Pb$	2SD
El Aramo/inner part	AI 01 (a)	1.8066	0.0003	0.7354	0.0001	21.4826	0.0093
	AI 01 (b)	1.8067	0.0003	0.7354	0.0001	21.4810	0.0093
	AI 01 (c)	1.8072	0.0002	0.7356	0.0002	21.4788	0.0092
	AI 02 (a)	2.0353	0.0003	0.8260	0.0002	18.9699	0.0084
	AI 02 (b)	2.0352	0.0003	0.8260	0.0002	18.9658	0.0084
	AI 02 (c)	2.0357	0.0003	0.8262	0.0002	18.9651	0.0085
	AI 03 (a)	1.9172	0.0004	0.7780	0.0001	20.0921	0.0089
	AI 03 (b)	1.9171	0.0004	0.7799	0.0001	20.0874	0.0089
	AI 03 (c)	1.9170	0.0003	0.7799	0.0001	20.0954	0.0090
	AI 04 (a)	1.9372	0.0004	0.7891	0.0001	20.0017	0.0086
	AI 04 (b)	1.9372	0.0004	0.7891	0.0002	20.0001	0.0086
	AI 04 (c)	1.9372	0.0004	0.7891	0.0002	20.0003	0.0085
	AI 05 (a)	1.9995	0.0004	0.8130	0.0001	19.3623	0.0083
	AI 05 (b)	1.9995	0.0003	0.8130	0.0001	19.3628	0.0082
	AI 05 (c)	1.9995	0.0003	0.8130	0.0002	19.3630	0.0081
	AI 06 (a)	2.0411	0.0004	0.8291	0.0002	18.9620	0.0082
	AI 06 (b)	2.0411	0.0004	0.8291	0.0001	18.9606	0.0081
	AI 06 (c)	2.0411	0.0004	0.8291	0.0002	18.9608	0.0080
	AI 07 (a)	2.0274	0.0004	0.8224	0.0001	19.1250	0.0083
	AI 07 (b)	2.0275	0.0004	0.8225	0.0002	19.1255	0.0084

	AI 07 (c)	2.0275	0.0004	0.8224	0.0002	19.1258	0.0081
	AI 08 (a)	1.9251	0.0004	0.7844	0.0001	20.1411	0.0087
	AI 08 (b)	1.9252	0.0003	0.7844	0.0001	20.1406	0.0087
	AI 08 (c)	1.9252	0.0004	0.7844	0.0002	20.1400	0.0086
	AI 09 (a)	2.0276	0.0004	0.8241	0.0002	19.0914	0.0082
	AI 09 (b)	2.0276	0.0004	0.8241	0.0002	19.0907	0.0081
	AI 09 (c)	2.0276	0.0004	0.8241	0.0001	19.0913	0.0083
	AI 10 (a)	1.9909	0.0004	0.8078	0.0002	19.4428	0.0089
	AI 10 (b)	1.9907	0.0004	0.8078	0.0001	19.4348	0.0084
	AI 10 (c)	1.9908	0.0004	0.8078	0.0002	19.4387	0.0086
	AI 11 (a)	2.0410	0.0003	0.8276	0.0002	18.9993	0.0082
	AI 11 (b)	2.0409	0.0004	0.8276	0.0001	19.0000	0.0085
	AI 11 (c)	2.0410	0.0004	0.8276	0.0002	18.9998	0.0083
El Milagro/dump	MD 01 (a)	2.0244	0.0004	0.8219	0.0002	18.5747	0.0085
	MD 01 (b)	2.0244	0.0004	0.8219	0.0002	18.5773	0.0085
	MD 01 (c)	2.0243	0.0004	0.8218	0.0001	18.5775	0.0084
	MD 02 (a)	2.0277	0.0004	0.8227	0.0001	18.9748	0.0082
	MD 02 (b)	2.0277	0.0003	0.8226	0.0002	18.9781	0.0083
	MD 02 (c)	2.0276	0.0004	0.8226	0.0002	18.9729	0.0083
	MD 03 (a)	2.0089	0.0004	0.8092	0.0001	18.1898	0.0084
	MD 03 (b)	2.0091	0.0004	0.8093	0.0001	18.2069	0.0078
	MD 03 (c)	2.0090	0.0005	0.8093	0.0001	18.2144	0.0088
	MD 04 (a)	2.0316	0.0005	0.8198	0.0001	19.5262	0.0074

	MD 04 (b)	2.0310	0.0004	0.8197	0.0001	19.5317	0.0075
	MD 04 (c)	2.0296	0.0004	0.8192	0.0001	19.5329	0.0079
	MD 05 (a)	2.0209	0.0004	0.8149	0.0002	19.7002	0.0083
	MD 05 (b)	2.0207	0.0004	0.8148	0.0002	19.7100	0.0089
	MD 05 (c)	2.0207	0.0004	0.8149	0.0002	19.7080	0.0088
	MD 06 (a)	2.0113	0.0004	0.8098	0.0001	19..5229	0.0096
	MD 06 (b)	2.0117	0.0005	0.8099	0.0001	19.5218	0.0090
	MD 06 (c)	2.0116	0.0004	0.8099	0.0001	19.5090	0.0094
	MD 07 (a)	2.0184	0.0004	0.8127	0.0001	19.3398	0.0083
	MD 07 (b)	2.0182	0.0005	0.8126	0.0001	19.3405	0.0079
	MD 07 (c)	2.0181	0.0005	0.8126	0.0001	19.3405	0.0080
La Profunda/dump	PD 01 (a)	1.4676	0.0004	0.6085	0.0001	26.3387	0.0116
	PD 01 (b)	1.4674	0.0004	0.6084	0.0001	26.3404	0.0115
	PD 01 (c)	1.4680	0.0005	0.6086	0.0001	26.3304	0.0158
	PD 02 (a)	1.9080	0.0004	0.7797	0.0001	20.2423	0.0087
	PD 02 (b)	1.9080	0.0004	0.7797	0.0001	20.2434	0.0087
	PD 02 (c)	1.9080	0.0005	0.7797	0.0001	20.2433	0.0088
	PD 03 (a)	1.3880	0.0003	0.5814	0.0001	27.8593	0.0120
	PD 03 (b)	1.3880	0.0003	0.5813	0.0001	27.8614	0.0122
	PD 03 (c)	1.3880	0.0003	0.5813	0.0001	27.8581	0.0121
La Profunda/inner part	PI 01 (a)	1.3812	0.0003	0.5780	0.0001	28.0003	0.0121
	PI 01 (b)	1.3812	0.0003	0.5780	0.0001	27.9991	0.0103
	PI 01 (c)	1.3813	0.0003	0.5780	0.0001	27.9975	0.0105

PI 02 (a)	1.6490	0.0003	0.6804	0.0001	23.4332	0.0108
PI 02 (b)	1.6492	0.0003	0.6804	0.0001	23.4316	0.0102
PI 02 (c)	1.6493	0.0003	0.6805	0.0001	23.4292	0.0105

Table S3: Cu isotope ratio for the measured samples. Data are expressed as the mean δ^{65}Cu value (‰) and 2 times the standard deviation (2SD) calculated from 3 measurement replicates. (a), (b) and (c) correspond to sub-samples.

Mine/Site	**Sample ID**	**δ^{65}Cu (‰)**	**2SD**
El Aramo/Inner Part	AI 01 (a)	-0.142	0.019
	AI 01 (b)	-0.072	0.016
	AI 01 (c)	-0.015	0.009
	AI 02 (a)	0.902	0.006
	AI 02 (b)	0.610	0.035
	AI 02 (c)	0.950	0.031
	AI 03 (a)	-0.173	0.017
	AI 03 (b)	-0.363	0.011
	AI 03 (c)	-0.989	0.014
	AI 04 (a)	-0.531	0.023
	AI 04 (b)	-0.004	0.091
	AI 04 (c)	-0.157	0.035
	AI 05 (a)	-0.398	0.017
	AI 05 (b)	-0.952	0.017
	AI 05 (c)	-1.472	0.034
	AI 06 (a)	0.347	0.062
	AI 06 (b)	-0.698	0.008
	AI 06 (c)	-0.209	0.019
	AI 07 (a)	-0.782	0.011

	AI 07 (b)	-1.165	0.039
	AI 07 (c)	-0.968	0.050
	AI 08 (a)	0.600	0.036
	AI 08 (b)	0.594	0.031
	AI 08 (c)	0.380	0.060
	AI 09 (a)	0.778	0.021
	AI 09 (b)	0.808	0.001
	AI 09 (c)	1.020	0.013
	AI 10 (a)	0.329	0.012
	AI 10 (b)	0.399	0.009
	AI 10 (c)	0.386	0.019
	AI 11 (a)	-0.584	0.005
	AI 11 (b)	-0.634	0.029
	AI 11 (c)	-0.765	0.034
El Milagro/dump	MD 01 (a)	-0.345	0.021
	MD 01 (b)	-0.315	0.011
	MD 01 (c)	-0.515	0.010
	MD 02 (a)	-0.215	0.011
	MD 02 (b)	-0.040	0.023
	MD 02 (c)	-0.346	0.016
	MD 03 (a)	2.103	0.016
	MD 03 (b)	1.628	0.002
	MD 03 (c)	1.983	0.026
	MD 04 (a)	0.158	0.016
	MD 04 (b)	-0.079	0.024

	MD 04 (c)	-0.382	0.019
	MD 05 (a)	-1.640	0.026
	MD 05 (b)	-1.504	0.005
	MD 05 (c)	-1.308	0.021
	MD 06 (a)	0.245	0.002
	MD 06 (b)	0.260	0.013
	MD 06 (c)	0.468	0.021
	MD 07 (a)	1.020	0.011
	MD 07 (b)	1.370	0.012
	MD 07 (c)	0.638	0.021
La Profunda/dump	PD 01 (a)	2.167	0.020
	PD 01 (b)	1.986	0.090
	PD 01 (c)	2.089	0.057
	PD 02 (a)	0.878	0.020
	PD 02 (b)	0.967	0.015
	PD 02 (c)	0.573	0.059
	PD 03 (a)	1.115	0.007
	PD 03 (b)	1.395	0.014
	PD 03 (c)	1.194	0.008
La Profunda/inner part	PI 01 (a)	-0.618	0.023
	PI 01 (b)	-0.498	0.045
	PI 01 (c)	-0.616	0.017
	PI 02 (a)	-1.045	0.033
	PI 02 (b)	-0.629	0.040
	PI 02 (c)	-0.834	0.048

El Aramo/inner part (intra-variability)	IV 01 (a)	-0.358	0.025
	IV 01 (b)	-0.321	0.013
	IV 01 (c)	-0.177	0.021
	IV 02 (a)	-0.371	0.030
	IV 02 (b)	-0.643	0.027
	IV 02 (c)	-0.475	0.024
	IV 03 (a)	-1.248	0.023
	IV 03 (b)	-1.292	0.013
	IV 03 (c)	-1.723	0.036
	IV 04 (a)	-0.970	0.021
	IV 04 (b)	-1.021	0.022
	IV 04 (c)	-1.084	0.009
	IV 05 (a)	-1.374	0.010
	IV 05 (b)	-1.156	0.023
	IV 05 (c)	-1.296	0.002
	IV 06 (a)	-0.736	0.012
	IV 06 (b)	-0.375	0.005
	IV 06 (c)	-0.635	0.013
	IV 07 (a)	-1.381	0.015
	IV 07 (b)	-1.171	0.019
	IV 07 (c)	-1.140	0.020
	IV 08 (a)	-0.991	0.010
	IV 08 (b)	-1.331	0.006
	IV 08 (c)	-1.314	0.027

IV 09 (a)	-0.338	0.008
IV 09 (b)	-0.501	0.018
IV 09 (c)	-0.331	0.022
IV 10 (a)	-0.831	0.010
IV 10 (b)	-0.703	0.020
IV 10 (c)	-0.565	0.013
IV 11 (a)	-0.621	0.010
IV 11 (b)	-0.944	0.026
IV 11 (c)	-1.060	0.011
IV 12 (a)	-0.517	0.026
IV 12 (b)	-0.567	0.016
IV 12 (c)	-0.400	0.017
IV 13 (a)	-0.755	0.007
IV 13 (b)	-0.163	0.010
IV 13 (c)	-0.126	0.007

References

1. H. Jeong, K. Ra and J. Y. Choi, *Geostandards and Geoanalytical Research*, 2021, **45**, 551-563.