

# Silver geochemistry and isotope systematics in Ag-rich mine tailings from Namibia

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**Abstract:** In this study, we present a detailed geochemical characterisation and stable isotope systematics of silver (Ag) in a mining waste facility at the Namib Lead & Zinc mine in Namibia (Africa). We examined a series of flotation tailings and ore minerals to address two principal questions: (1) the distribution, chemical form and leachability of Ag, and (2) the local Ag isotopic signature(s) and its variability in relation to Ag speciation in the solid phase, as well as the fate of stable Ag isotopes. Our findings reveal a significant correlation between Ag and Pb concentrations, indicating that galena is the primary Ag carrier. Most importantly, all mild extractions mobilised only a minimal amount of Ag ( $\leq 1$  wt.% of the total amount). This suggests that most Ag is associated with geochemically stable phases, specifically sulphides, which are not subjected to leaching and/or intensive weathering. Unlike other isotope studies, the present research demonstrates a homogeneous Ag isotopic signal in the tailings and individual ore samples with an average  $\delta^{109}\text{Ag}$  value of  $\sim 0\text{‰}$  ( $\pm 0.1$ , 2SD). Therefore, this study provides new knowledge and clearly supports the use of Ag isotopic data to track primary Ag sources globally, not only in Africa.

**Keywords:** critical raw material; extraction; galena; ore; sulphide

Fine-grained tailings resulting from the processing of sulphide ores can be a significant source of environmental contamination. It is suggested that this problem is even more problematic in semi-arid areas due to increased tailings erosion, dust migra-

tion and deposition (Ettler et al. 2025). In addition to being a secondary resource of critical raw materials (Lohmeier et al. 2024a), this type of waste can be hazardous, since it often contains a large proportion of biologically available fractions of toxic

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contaminants (Ettler et al. 2023). Although the environmental impact of silver (Ag) is understudied, the U.S. Environmental Protection Agency (EPA) has identified Ag as a priority pollutant. Its toxicity to microbes, viruses, and potentially higher organisms is well known (Fabrega et al. 2011). On the other hand, the collective knowledge of the fate of Ag in the environment and its potential for mobilisation is incomplete. According to the available literature, waste products from various stages of mining and processing activities do represent the vast majority of anthropogenic Ag released in the environment, mainly soils. Other anthropogenic sources of Ag can be various types of waste associated with specific industrial activities, such as cement, chemical and energy industries, and the application of silver nanoparticles, among others (Purcell & Peters 1998; Padhye et al. 2023). It should also be noted that the average Ag concentration in the upper continental crust is  $\sim 0.05$  ppm (Reimann & Fabian 2022), but it can exceed 1 ppm in mining-affected geosystems (Ash et al. 2014).

This study focuses on the detailed geochemical characterisation of Ag resulting from Ag-rich ore flotation and its stable isotope systematics in a mining

waste facility in Namibia, Africa. For this purpose, a series of flotation tailings was collected from two deep profiles at the Namib Lead & Zinc mine, which is characterised by the extreme aridity of the Namib Desert. We attempted to address the following key questions: (1) what is the distribution, chemical form and leachability of Ag and (2) what is the local Ag isotopic signature, complex variability, and the fate of Ag stable isotopes in relation to Ag speciation in the solid phase?

## MATERIAL AND METHODS

**Study area and mine tailings.** The Namib Lead & Zinc mine is situated in the Rössing Mountain area of the Erongo Region in western Namibia (Figure 1). The Pb-Zn sulphide deposit is hosted within the Karibib Formation of the Swakop Group, Damara Sequence. The host marble contains sulphide-rich beds and is locally Pb- and Zn-rich over a strike extent of  $> 100$  km, with locally anomalous concentrations of copper, tin, indium and fluorine. Granulite facies metamorphic conditions prevail in the area, and mining took place in the upper portions of a remobilised MVT or SEDEX orebody (Basson et al. 2018). The

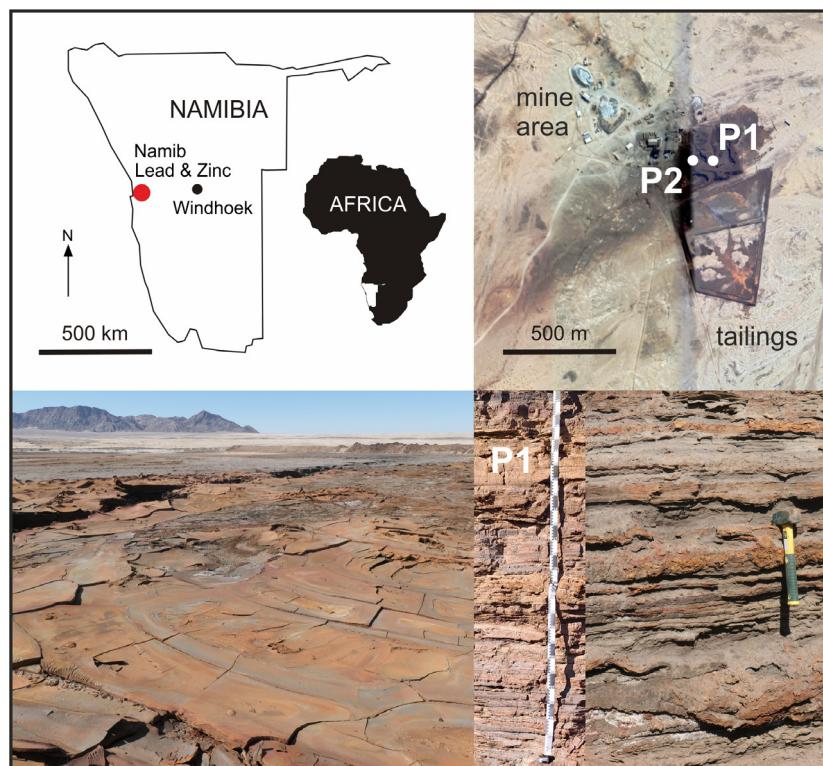


Figure 1. Location of the study area (Namib Lead & Zinc mine) and tailings sampling sites – profiles P1 and P2; details of P1 sections; GPS coordinates – P1: 22.52031S, 14.76158E; P2: 22.51996S, 14.76059E

Namib Lead & Zinc mine operated from 1968 to 1991. Mining and ore processing activities resumed during 2019 and 2020. Currently, the mine is under care and maintenance (Ettler et al. 2025). The site has an extremely arid climate, classified as BWh according to the Köppen-Geiger system, with an average annual precipitation of around 25 mm. However, in some years there is no rainfall at all. The average annual temperature is 18.6 °C. The cold Benguela Current flows along the Namibian coast, resulting in frequent fog extending over 20 km inland. The cyclic wetting by fog at night and subsequent drying during the day plays an important role in the weathering of mining waste (Sracek et al. 2024).

Regarding the sampling process, the tailings were manually collected in 10-cm layers up to a depth of ~ 3 m from two sampling sites of the tailings dam (P1 and P2) (Figure 1). Tailings samples were air-dried, homogenised, and an aliquot of ~ 20 g was finely ground in an agate mill (Retsch planetary mill PM 400, Germany). All the samples were first analysed using a portable X-ray fluorescence spectrometer (pXRF) (Niton XL3 t Gold instrument, Thermo Scientific) to identify tailings with the highest Ag concentrations. Consequently, nine Ag-rich samples from each profile were selected for further use and detailed analysis. To quantify the potential contribution of primary Ag sources in the tailings, selected (contrasting) ore samples (galena, sphalerite, pyrite, pyrrhotite and hematite) were also included in this work.

Solids pH was measured using a 1 : 10 (v/v) ratio of sample and deionised H<sub>2</sub>O (1 h of agitation) with a Handylab pH meter (Schott, Germany). To estimate the approximate abundance of secondary (poorly crystalline) Fe- and Mn-oxides and oxide-associated Ag concentrations, the method of Pansu and Gautheyrou (2006) was applied. This method uses a mixture of 0.2 M ammonium oxalate/oxalic acid (adjusted to a pH of 3) at a waste-to-liquid ratio of 1 : 50 with 4 h of agitation. The labile Ag fractions, specifically the H<sub>2</sub>O-soluble and exchangeable fractions, representing weakly-bound forms of Ag, were determined by extracting the sample with deionised water and 1 M NH<sub>4</sub>NO<sub>3</sub> solution at a waste-to-liquid ratio of 1 : 20 and agitating for 1 h. The following procedure was used to determine the amount of Ag associated with sulphides: a 0.5 g sample was extracted with 5 mL of concentrated H<sub>2</sub>O<sub>2</sub>, heated slowly at 70 °C, accompanied by occasional sample shaking for 2 h. Dilute HNO<sub>3</sub> (5%) was then added to the solution to bring the total volume to 20 mL, after which the mixture was agitated for 1 h.

**Major/trace element concentrations.** Prior to determining Ag/element concentrations and Ag stable isotope ratios, a mass of 0.2 g of sample was completely dissolved in a hot acid mixture in a Multiwave 5000 microwave unit (Anton Paar, Austria) using a combination of hot HNO<sub>3</sub> and HF acids in the ratio of 3/1 in a total volume of ≤ 20 mL (Merck Ultrapure, Germany); the final solution was subsequently transferred to polytetrafluoroethylene (PTFE) beakers (Savillex, USA), evaporated, and redissolved in 2% HNO<sub>3</sub>. The concentrations of Ag, Pb, Zn, Cd, Fe and Mn in the sample digests and individual leachates were determined using a quadrupole-based inductively coupled plasma mass spectrometer (Q-ICP-MS, 8900 Triple Quadrupole, Agilent, USA). The following standard reference materials (SRMs) were used for the quality control (QC): NIST 2710a and 2711a (Montana I/II soil) and NIST 2782 (Industrial Sludge) (Table S1 in Electronic Supplementary Material).

**Determination of Ag isotopic ratios.** Silver was isolated from the sample matrix using a modified two-step chromatography process described by Schönbachler et al. (2007, 2008). Silver recoveries were monitored throughout the entire Ag separation using Q-ICP-MS. The <sup>109</sup>Ag/<sup>107</sup>Ag ratio measurement, reported as δ<sup>109</sup>Ag relative to SRM NIST 978a (Equation 1), was performed using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Neptune Plus, Thermo Scientific, Germany) equipped with a quartz dual spray chamber and a PTFE nebuliser (Elemental Scientific Inc. [ESI], Omaha, NE). Silver separation principles, instrumental and measurement conditions are provided in detail in Vaněk et al. (2023). All reported Ag isotopic data in this study are assigned an estimated error of ± 0.1‰ (2SD). This uncertainty is based on the reproducibility of complete repeat analyses of SRM NIST 2782 (*n* = 8) achieved in our lab (Table S2 in ESM). Therefore, it accounts for different possible sources of error. The isotopic measurements were performed at the Isotope Research Centre of the Faculty of Science at Charles University in Prague.

$$\delta^{109}\text{Ag}(\text{‰}) = \left( \frac{(^{109}\text{Ag} / ^{107}\text{Ag})_{\text{sample}}}{(^{109}\text{Ag} / ^{107}\text{Ag})_{\text{NIST978a}}} - 1 \right) \times 1000 \quad (1)$$

## RESULTS AND DISCUSSION

**Tailings characteristics, trace element and Ag concentrations.** Figure 1 shows that the tailings exhibit rusty-to-red colours and consist of gypsum,

quartz, various types of carbonates, micas, Fe(III)-oxides, sulphides, and associated alteration products (sulphates and oxides) as presented in detail by Lohmeier et al. (2024a) and Ettler et al. (2025). Both tailing's profiles (P1 and P2) had circumneutral pH values (between 6.0 and 7.6) (Table 1). This indicates their ability to buffer the acidity produced by sulphide weathering, which is controlled by dissolution of carbonates. The variable distribution and generally high concentrations of trace/major elements (Zn, Pb, Cd, Ag, Fe and Mn) in the tailings demonstrate the material heterogeneity and suggest significant changes in the ore source feed, as well as the limited efficiency of ore concentrate extraction by flotation (Tables 1 and Table S3 in ESM). Given the average concentrations of Zn ~ 2 wt.%, the results support the findings of Lohmeier et al. (2024a, b), who report anomalous Zn levels of  $\leq$  3 wt.% in the bulk samples from the Namib Lead & Zinc waste dump. The authors emphasise lower efficiency of historical flotation as per sequential techniques, namely the decreased recovery of Zn (sphalerite, ZnS), resulting from the problems with pyrrhotite ( $Fe_{1-x}S$ ) suppression during flotation (Lohmeier et al. 2024a). In the case of Ag, its concentrations ( $\leq$  16 mg/kg) in the tailings correlate well with the Pb concentrations ( $\leq$  5 200 mg/kg) (Table 1), as evidenced by the positive linear relationship between all Ag and Pb data ( $R^2 = 0.96$ ). Consistent with previous studies, galena (PbS) is the primary Ag carrier in hydrothermal Me-Ag ore systems (Ash et al. 2014; Mathur et al. 2018; Vaněk et al. 2023). Accordingly, the concentration of Ag in the galena sample accounted for  $\sim$  260 mg/kg, followed by pyrrhotite and sphalerite with 60 and 40 mg/kg, respectively, representing other Ag-bearing minerals. A similar phenomenon can be observed for Zn and Cd (Table 1), which clearly stems from the preferential accumulation of Cd in ZnS (Robson et al. 2014). In addition to that process, geochemical analogies in the behaviour, fate, or even cycling of Zn and Cd in the environment have been systematically described in the literature (e.g., Vácha et al. 2006; Galušková et al. 2011; Vaněk et al. 2021; Ettler et al. 2023).

**Silver chemical fractionation.** Based on the results of single extractions, it is evident that most of the Ag in the tailings is found in residual phases, primarily sulphides. The sulphide-associated fraction ( $Ag_{S}$ ) accounted for 50–90 wt.% of total Ag fractionation, corresponding to  $\sim$  2–12 mg/kg (Table 1). Combining this Ag data with that of sulfidic Pb (Pb<sub>S</sub>) (Table S4

in ESM) confirms that galena is the key mineral that hosts Ag. However, due to the high levels of Zn in the tailings, the role of sphalerite in the complex process of Ag fixation cannot be omitted. The proportions of labile (weakly-bound) Ag fractions, i.e., those extracted by deionised H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>, were extremely low ( $\leq$  1 wt.%). Interestingly, Ag was released to a higher extent into the water leachate, likely due to the re-adsorption (or re-precipitation) effects of specific Ag species in the nitric solution. Secondary Fe/Mn-oxides seem to be readily extracted with oxalate, resulting in large amounts of Fe and Mn leaching; unlike Ag, of which the amount was always negligible in the oxalate extracts. This finding indicates two phenomena, which should be taken into account: first, extensive pyrite (FeS<sub>2</sub>) weathering, and second, the fact that only a minimal amount of Ag that can be incorporated into the Fe/Mn-oxides (Table 1). Since Mn-oxides are commonly effective at sorption of Ag (Jacobson et al. 2005; Mathur et al. 2018), the mineralogical position of Ag observed in this study supports the hypothesis that the flotation waste is not significantly affected by the Ag-rich sulphide(s) alteration, meaning that most Ag and trace elements (Pb, Zn and Cd) remain incorporated in sulphides. Accordingly, the average Pb concentrations ( $\leq$  5 wt.%) in all leachates (excluding sulphide-associated) imply both geochemical stability of galena and the low potential for Ag release in the long term, when compared to the bulk Pb content. Regarding the Zn mobilisation and the associated degradation of sphalerite, the proportion of Zn found in the non-sulfidic fractions ( $\sim$  20 wt.% of the total Zn), particularly the exchangeable Zn, indicated limited sphalerite weathering (Tables S3 and S4 in ESM).

**Silver isotopic composition.** We identified relatively homogeneous Ag isotope patterns across both tailing's profiles (P1 and P2), as shown in Table 1. Most of the tailings had slightly positive  $\delta^{109}\text{Ag}$  values close to 0, ranging from  $-0.10$  to  $+0.26\text{‰}$  ( $\pm 0.1$ , 2SD), which thus overlapped within the measurement error. Comparing the compositions in the individual profile sections with those of the reference ore minerals ( $\delta^{109}\text{Ag}$  between  $-0.10$  and  $+0.06\text{‰}$ ), it shows that the Ag isotopic signatures are similar. The only pyrrhotite was depleted in the heavy isotope <sup>109</sup>Ag (enriched in <sup>107</sup>Ag), although insignificantly, making it comparable to the bottom of the profile P2 sampled in the tailing dam (depth: 310–320 cm). By contrast, the 40–50 cm sample from the same

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Table 1. Total element concentrations, water-soluble, exchangeable, oxalate-extractable and sulphide-associated concentrations of Ag or Mn/Fe ( $\text{Ag}_{\text{H}_2\text{O}}$ ,  $\text{Ag}_{\text{EX}}$ ,  $\text{Ag}_{\text{S}}$  and  $\text{Ag}_{\text{OX}}$ ), and Ag isotopic compositions (in  $\delta^{109}\text{Ag}$  relative to SRM NIST 978a) in the studied tailings and ore samples

Profile	Depth (cm)	$\text{pH}_{\text{H}_2\text{O}}$	Total Ag	Total Pb	Total Zn	Total Cd	$\text{Ag}_{\text{H}_2\text{O}}$ (mg/kg)	$\text{Ag}_{\text{EX}}$	$\text{Ag}_{\text{S}}$	$\text{Mn}_{\text{OX}}$ (g/kg)	$\text{Fe}_{\text{OX}}$ (g/kg)	$\delta^{109}\text{Ag}$ (‰)
P1	0–10	6.5	3.80	751	7 610	29.3	0.02	0.003	0.004	2.48	2.87	69.2 +0.13
	50–60	7.6	3.62	731	5 930	21.8	0.02	0.01	0.003	2.04	7.35	22.7 +0.06
	120–130	6.8	5.44	676	15 700	68.9	0.01	0.002	0.002	3.94	1.08	26.0 +0.14
	130–140	7.2	12.8	4 440	31 500	151	0.01	0.003	0.001	10.2	1.88	12.5 –0.06
	170–180	7.3	8.86	2 240	24 600	112	0.04	0.01	0.003	5.85	4.30	55.6 +0.05
	190–200	6.8	9.21	2 960	26 100	120	0.01	0.002	0.003	7.83	1.78	45.7 +0.08
	210–220	6.0	9.57	3 000	23 600	114	0.03	0.002	0.003	8.54	3.02	52.4 0
	250–260	7.2	5.99	1 670	23 600	116	0.05	0.005	0.003	4.65	2.61	35.9 +0.02
	290–300	7.3	6.79	1 820	15 400	101	0.01	0.003	0.003	4.23	2.06	32.8 +0.01
	0–10	7.3	9.26	2 410	23 900	160	0.05	0.03	0.002	5.92	3.01	25.8 +0.06
P2	40–50	7.2	15.1	3 360	18 600	123	0.01	0.17	0.001	9.48	2.54	26.9 +0.26
	80–90	7.2	4.41	953	31 200	105	0.07	0.04	0.003	2.80	3.36	21.6 +0.19
	130–140	7.1	6.06	997	26 400	107	0.09	0.04	0.003	4.09	2.90	44.5 +0.13
	180–190	7.2	16.4	5 240	28 300	150	0.10	0.004	0.002	9.21	1.89	15.2 +0.11
	250–260	7.3	9.0	4 030	13 700	75	0.02	0.002	0.002	7.39	2.61	32.8 +0.12
	290–300	7.3	16.3	5 220	32 300	147	0.09	0.004	0.003	10.8	2.53	44.9 +0.12
	310–320	7.3	14.5	4 500	29 600	136	0.07	0.002	0.002	11.7	4.03	35.9 –0.10
	320–330	7.4	9.58	3 510	20 500	108	0.05	0.002	0.002	7.85	2.30	26.4 +0.08
	Galena (PbS)	--	267	318 000	1 050	6.26	--	--	--	--	--	--
	Sphalerite (ZnS)	--	41.2	455	342 000	1 270	--	--	--	--	--	--
	Hematite ( $\text{Fe}_2\text{O}_3$ )	--	0.84	80.3	18 500	49.9	--	--	--	--	--	--
	Pyrite ( $\text{FeS}_2$ )	--	3.76	231	141	0.60	--	--	--	--	--	--
	Pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ )	--	61.5	8 571	4 810	17.7	--	--	--	--	--	--

All concentration data represent average values ( $n = 2$ ) with relative standard deviation (RSD)  $\leq 10\%$ ; -- not determined; the measured half concentrations of Pb and Zn in PbS and ZnS (i.e., relative to their stoichiometry) are the result of dilution errors; the  $\delta^{109}\text{Ag}$  values are assigned an error of  $\pm 0.1\%$  (2SD) that is based on the long-term external reproducibility achieved in our lab for SRM NIST 2782 (Industrial sludge); see Table S2 in Electronic Supplementary Material

profile was the only one that had increased  $\delta^{109}\text{Ag}$  factor of  $\sim +0.3\text{\textperthousand}$  (Table 1). Given the fact that Ag was systematically “insoluble” in the studied waste materials, any positive/negative isotopic shift cannot reflect Ag isotopic fractionation. Rather, it simply results from the input of source-specific geogenic silver, i.e., the observed Ag isotopic patterns in the tailings are inherited and reflect the predominant composition of Ag-bearing sulphides. Additionally, we did not observe any significant variations in  $\delta^{109}\text{Ag}$  among the different ore minerals, all of which showed values  $\sim 0\text{\textperthousand}$ . Therefore, the Namib Lead & Zinc ore deposit appears to exhibit a uniform isotopic signal approaching “positive zero” in relation to the Ag standard (SRM NIST 978a). This is quite surprising, since recent findings by e.g. Milot et al. (2022) and Wang et al. (2022) illustrate large Ag isotopic variabilities in galena ( $\leq 6\text{\textperthousand}$ ) within individual polymetallic systems. Their findings suggest a sequence of sulphide(s) formation with markedly different Ag isotopic compositions, namely, a spatial and/or temporal hydrothermal sequence. As for our case, one possible explanation is the isotopic homogenization that occurred during the high-T deposit’s metamorphism and associated Ag/element remobilisation and reprecipitation of sulphides from the fluids. Another explanation is that both MVT and SEDEX systems related to the Namib Lead & Zinc mine lack a significant vapour component during hydrothermal ore genesis (Basson et al. 2018). This could result in minimal Ag isotopic fractionation during sulphide formation, i.e., unlike in the volcanic massive sulphide (VMS) system (Mathur et al. 2018; Milot et al. 2022).

With regards to surface environments (soils, sediments, waste accumulations etc.), redox processes, i.e., interactions controlled by redox reactions (if they do occur), are considered the cause of Ag isotopic fractionation, analogous to other metal isotope systems (e.g., Bigalke et al. 2010; Mathur et al. 2018; Vejvodová et al. 2020; Vaněk et al. 2023). However, these processes were not identified in this study, and they are therefore considered insignificant.

**Environmental implications.** Silver is considered relatively harmless to humans, except in specific situations involving extreme Ag loads or doses. However, it can pose an environmental risk to microbiota, especially in the form of readily soluble Ag species capable of dissociation. Dissolved Ag(I) ions in the environment are persistent and highly toxic to prokaryotes, algae, freshwater and marine

invertebrates, fish etc. (Erickson et al. 1998; Fabrega et al. 2011; Padhye et al. 2023).

The Namib Lead & Zinc mine and its tailings are situated in an area affected by the extreme aridity of the Namib Desert (Figure 1) (Sracek et al. 2024). Therefore, except for the dispersion of fine-grained tailings into the environment due to wind erosion and other factors, the results show that Ag has minimal potential for solubilization and passive uptake by organisms, as well as potential toxicity. Consistent with previous findings by Lohmeier et al. (2024a, b) and Ettler et al. (2025), the vast majority of Ag and trace elements, mainly Pb and Zn, are associated with sulphides that have not undergone alterations in recent decades. Furthermore, Lohmeier et al. (2024a) concluded that the tailings mineralogy was comparable to that of the primary ore, highlighting the fact that previous processing technologies (flotation and/or flotation agents) did not modify the mineralogical assemblage. Given that the study area is underlain by carbonates and is virtually precipitation-free, it is reasonable to assume that the behaviour/fate of sulphides will remain stable in the future.

## CONCLUSION

This study conducted geochemical and isotopic investigations of Ag in mine waste (tailings) from the Namib Lead & Zinc mine in Namibia. It was determined that the concentrations of Ag and other trace elements (Pb, Zn and Cd) are high and vary significantly, as revealed within two deep profiles. The identified relationship between Ag and Pb concentrations in the tailings and ore samples shows that galena is the principal carrier of Ag. Most importantly, all mild extractions mobilised only a minimal amount of Ag (only up to 1 wt.% of the total amount). This suggests that most Ag is associated with geochemically stable phases (sulphides), which are not subjected to leaching and/or intensive weathering. Unlike other isotope studies, the present research demonstrates a homogeneous Ag isotopic signal for all the ore minerals and tailings with an average  $\delta^{109}\text{Ag}$  value of  $\sim 0\text{\textperthousand}$  ( $\pm 0.1$ , 2SD). Therefore, it provides new insights and clearly supports the further use of Ag isotopic data to track primary Ag sources, i.e., the source fingerprinting not only in arid regions in Africa, but also globally.

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**Data availability.** The source data are found in the Supplementary material associated with this paper and openly available at Zenodo: <https://zenodo.org/records/17977695>.

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