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Silver Isotopes in Silver Suggest Phoenician Innovation in Metal Production

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Abstract: The current study presents Ag isotopic values of 45 silver artifacts with known Pb isotopic composition from the Southern Levant. These items originate from seven pre-coinage silver hoards, dating from the Middle Bronze Age IIC to the end of the Iron Age (~1650–600 BCE). These are the earliest silver artifacts analyzed for Ag isotopes; all former studies were performed on coins. All the sampled silver in this study contains relatively unfractionated Ag ($-2 \leq \varepsilon^{109}\mathrm{Ag} \leq 1.5$) that was more likely produced from hypogene, primary Ag-bearing minerals (e.g., galena and jarosite) and not from native, supergene silver. Four of the sampled hoards containing silver from Anatolia and the West Mediterranean (Iberia and Sardinia) are associated with the Phoenician quest for silver (~950–700 BCE). A significant amount of this Phoenician silver (12/28 items) plots within a narrower range of $-0.5 \leq \varepsilon^{109}\mathrm{Ag} \leq 0.5$. This is in contrast to non-Phoenician silver, which mostly underwent some degree of fractionation (16/17 items $\varepsilon^{109}\mathrm{Ag} \geq$ I0.5I). The results suggest that while all silver was exploited from primary ore sources, the Phoenicians dug deeper into the deposits, reaching ore minerals that did not undergo any weathering-associated fractionation. The results also call for further investigation regarding the influence of sealing and bundling in silver hoards on post-depositional fractionation of Ag isotopes.

Keywords: silver isotopes; silver hoards; Levant; Phoenicia; Ag-fractionation

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1. Introduction

For millennia, lead ores were mined to produce silver. The mining process included identifying potential areas for exploitation, the prospection of vertical shafts to provide access to veins of lead-rich minerals (the lead ore). Then, horizontal shafts that followed the direction of the vein were excavated [1,2]. Silver (Ag) was extracted from the lead ores by a two-step process: first smelting the ore in a furnace, instigating the reduction in the ore into metallic Pb–Ag, followed by cupellation, namely, oxidizing the alloy in a cupel for extracting Ag (and gold) and separating it from other metals. This technique, practiced from the 4th millennium BCE [3,4], enabled the extraction of silver from argentiferous galena (PbS) and cerussite ($PbCO_3$) lead ores [5].

The quest for metals, especially silver, was a crucial instigator of Phoenician early endeavors to the West Mediterranean at 950–800 BCE [6]. The Phoenician city-states in Lebanon and the northern shores of the southern Levant during the Iron Age (11th–6th centuries BCE), e.g., Tyre, Sidon and Byblos, 'Akko and Dor (for part of this period), shared political–economic traits and material culture (Figure 1; e.g., [7–14]). The Phoenicians are known for spreading to Europe long-lasting innovations, including the alphabet, murex-based purple dyeing and masterful craftsmanship (e.g., [7,15]). However, above all, the

Phoenicians are renowned for their seafaring prowess and far-flung trade, establishing colonies in North Africa, Sardinia and Iberia (e.g., [8,16–18]). Yet the Phoenicians were not mere traders. In the 9th century BCE, the Phoenicians extracted silver from jarosite ores in Iberia. They innovatively added external Pb from nearby ores to the Ag-rich jarosites to produce silver (see more below).

The basic silver-production process, which was based on cupellation, did not change and also remained in use throughout the Classical periods (e.g., [19,20]). As all cupelled silver contained Pb, lead isotopic analysis (LIA) has become the prevailing sourcing method for ancient silver. This method directly compares the Pb isotopic ratios of ores with those measured in archaeological artifacts (e.g., [21]). The chemical composition of the silver is less useful for provenance since most of the elements are either largely removed during production or their concentrations depend on the quality of the cupellation process [6,22]. A few elements (Pb, Au and Bi) can sometimes be used in order to identify idiosyncrasies resulting from the use of different ores [6,22–26].

Figure 1. Map of the Southern Levant showing sites with Bronze and Iron Age silver hoards. (Drawing by S. Matskevich; Reproduced after [25]).

Silver in the Near East was an important commodity and means of currency long before the invention of coinage (e.g., [25,27–29]). More than 40 silver hoards unearthed in the Southern Levant, remnants of 1400 years (~2000–600 BCE) during which silver was a central means of exchange in the region, form a large and accessible database (Figure 2; [25,27,28]). Based on Pb isotopic and chemical analyses of 250 items from 22 silver hoards, we identified the sources of silver in these hoards throughout the Bronze and Iron Ages [6,26,30,31]. We showed that during this long period, the sources of silver changed over time. In the Middle Bronze Age (~2000–1550 BCE), silver was brought to the Levant from Anatolia and the

Aegean [26]. During most of the Late Bronze Age (~1550–1250 BCE), gold probably replaced silver as the main currency, with some silver from Laurion, Greece, being used at the end of this period [26]. Following the Late Bronze Age collapse, throughout the Early Iron Age (~1200–950 BCE), silver was scarce and often mixed with Pb-rich copper. This affected the Pb isotopic composition of the silver items, and thus the origin of the silver has remained largely unknown [30]. The Phoenicians revived the trade-in silver in the mid-10th century BCE. They supplied silver to the Levant from the Taurus mountains in Anatolia, and from Iglesiente in south-west Sardinia and later from the Pyrite Belt in Iberia [6]. These long voyages lasted for ~300 years, through most of the Iron Age II A–C (~950–630 BCE); [31]. The quantities of silver brought by the Phoenicians to the Levant during this period ('the Phoenician period') greatly exceeded those traded in earlier and later periods [6,25,31]. Finally, at the very end of the Iron Age (~630–586 BCE), East-Greek merchants took over the supply of silver, bringing silver and copper from Laurion and Siphnos in the Aegean to the Levant and Egypt [31–33]. While the changing origins of silver found in the Levant have been widely discussed, we still have limited knowledge regarding the development of silver production practices and the exploitation of new ores. Mines are often illusive for this purpose, as later exploitations have overridden ancient exploitation attempts (e.g., [1,2]). Here we approached this question from the artifact point of view, based on silver isotopes.

Figure 2. Silver hoards analyzed in this study: (**a**) silver from the Shiloh hoard (without pendant), courtesy of the Israel Museum, Jerusalem. (**b**) Silver from hoard Tell el-'Ajjul 1312, courtesy of the Israel Antiquities Authority (Photo: Mariana Salzberger). (**c**) The Dor silver hoard image, © The Israel Museum by Ardon Bar-Hama (photographer) and the Tel Dor Expedition. (**d**) The 'Akko silver hoard image courtesy of Michael Eisenberg (photographer). (**e**) The 'Ein Hofez silver hoard image courtesy of the Israel Antiquities Authority, by Warhaftig Venezian (photographer). (**f**) The 'Arad silver hoard, courtesy of the Institute of Archaeology, Tel Aviv University (photographed by Sasha Flit). (**g**) Selected items from 'Ein Gedi hoard, © The Israel Museum, Jerusalem.

Silver isotope (SI) measurements have several applications in the study of ore formation processes [34–36]. According to [36], "isotopic fractionation of silver occurs (a) during low-temperature remobilization of Ag associated with redox reactions in the supergene (weathering) environment, and (b) among Ag-bearing mineral phases, including Ag-halides (bromargyrite, chlorargyrite, iodargyrite, boleite and pseudoboleite) and As-bearing sulfosalts (e.g., enargite, tennantite, proustite and polybasite)." As a result, the relative abundance of Ag isotopes sometimes varies within the same mine, from deep primary ores to supergene oxidized minerals or during different phases of mineralization. They also change with the nature of the ore deposits, e.g., hydrothermal versus sedimentary [34,36]. Several studies investigated the Ag isotopic variability of various hypogene and supergene silver-bearing minerals (including silver sulfides, sulfosalts, chlorides, hypo-

gene native silver and supergene native silver) from a large range of deposits and districts (e.g., [34,36–38]). No systematic Ag isotopic composition appears to characterize a specific type of deposit, geographic location, or mineralization age (see [36]).

The isotopic compositions of Ag are often measured as a relative difference between a sample and a mesured standard. They are expressed as ε^{109}Ag (ε^{109}Ag = 10,000 × $\{(^{109}Ag/^{107}Ag)_{sample} - (^{109}Ag/^{107}Ag)_{standard}\}/(^{109}Ag/^{107}Ag)_{standard}$; [37,39,40]; see more below). Sometimes, the δ^{109}Ag notation is used instead, where $1\delta^{109}$Ag = 10 × ε^{109}Ag [34,36].

Mathur et al. [34] and Arribas et al. [36] showed that worldwide, hypogene native Ag and acanthite/argentite (Ag_2S) Ag form a tight cluster that the supergene (supergene native Ag and Ag sulfosalts) data overlie and flank: The hypogene deposits, formed by high-temperature mineralization processes, have values that cluster around 0‰ ^{109}Ag (with a range of −4 ε^{109}Ag to + 4 ε^{109}Ag, namely ±0.4 δ^{109}Ag). On the other hand, the supergene deposits underwent some secondary reconstitution of precipitating silver that occurred at lower temperatures and might have involved redox reactions. Hence, Ag derived from these reactions contains a wider range of Ag isotopic composition in comparison to the source deposit (−12 ε^{109}Ag to 20 ε^{109}Ag; see [36]).

Silver isotopes, therefore, can be used in archaeology for geological classifications of the exploited ores. Thus far, all Ag isotope analyses in archaeology have been applied to silver coins. The results match the range of variation in hypogene silver minerals and not those of supergene secondary deposits. The ε^{109}Ag of Hellenistic and Early Roman (600–170 BCE) silver coins range between −1 and +2 ε^{109}Ag [39,40]. Within this time period, coins dating to 220–211 BCE all range between 0 and +0.5 ε^{109}Ag [39]. Medieval and modern coins range between ±2 ε^{109}Ag [37,38,41].

In this study, we analyzed silver isotopic ratios of hoarded silver in the Southern Levant from the Bronze and Iron Ages and compared the results to the Pb isotopic results obtained previously. As the silver hoards predate the invention of coinage, this dataset comprises the earliest reported Ag isotopes of archaeological silver items.

The preservation of Ag isotopes in ancient silver was also approached in this study since many of the items were sealed in bundles of cloth and/or cached in sealed ceramic vessels [25]. Milot et al. [40] showed that for ancient silver coins, silver in the patina is isotopically lighter due to the formation of Ag_2S, while the layer below the patina is isotopically heavier. This was explained by secondary, post-depositional variations, due mainly to underground interactions with soil–water during the prolonged burial in the ground. This is because Ag isotopic ratio is sensitive to low-temperature redox reactions [34,42]. Milot et al. [40] suggest that Ag isotopes of the core of the coins were not altered, yet this was based on buried (unsealed) coins only. Here, we had a unique opportunity to compare Ag isotopes of sealed and unsealed silver (see below). Although limited by the small size of the sample sets, we approached the question of whether oxidizing burial conditions also affected the cores of unsealed silver items.

2. Materials

Forty-five silver artifacts were selected for Ag isotopic analysis, all of known chemical and Pb isotopic compositions and generally not suspected to be alloyed or mixed with metals from different sources [33]. The results of the LIA of silver from the selected hoards (Figures 1 and 2) and their hoarding conditions are described below. The sampled silver dates to three different sub-periods:

(1) Middle/Late Bronze Age transitional period in the Southern Levant (MB IIC−LB I, ~1650–1500 BCE): hoards from Shiloh and Tell el-'Ajjul

The origin of silver in the Shiloh and Tell el-'Ajjul hoards has not been fully determined; however, LIA results suggest Anatolian/Aegean origin [26]. The Shiloh hoard was bundled and found on the floor of a storeroom [43]. It was not cached in a ceramic vessel. The silver in the Tell el-'Ajjul hoard was not found in bundles and was not hoarded in a ceramic vessel ([44]: 8; pl. XIX–XX). The jewelry in both hoards have Anatolian motifs, supporting the Anatolian origin of the silver within [26,43].

(2) The Iron Age II A–B (~950–700 BCE): hoards from Dor, 'Akko, 'Ein Hofez and Arad

The Dor and Akko hoards contain silver from the same origins, namely from Iglesiente, SW Sardinia (Dor_108, Dor_126, Dor_127, 'Akko_12, 'Akko_22) and Taurus 1A in Anatolia (Dor_122, Dor_52, 'Akko_13, 'Akko_2, 'Akko_221, 'Akko_5). Both hoards were found in Phoenician contexts and are therefore associated with Phoenician early endeavors to Anatolia and Sardinia in the Iron Age IIA. The silver in the Dor hoard was bundled, while the silver in the 'Akko hoard was not. Both hoards were placed in ceramic vessels and cached below unpaved floors; however, the Dor hoard was covered by a bowl, while the Akko hoard was not [6,25,45–47].

The 'Ein Hofez and 'Arad hoards contain silver from Iberia. For both hoards, LIA probably indicates the source of the Pb rather than the source of Ag. This is because the silver in Iberia was produced from jarosite at Rio Tinto, and external Pb from several ores around the peninsula was mobilized to Rio Tinto for this process ([6] and refs. within). The Pb from 'Ein Hofez silver sampled here originated mainly from Linares, SW Iberia ('Ein Hofez_112, 'Ein Hofez_164, 'Ein Hofez_171, 'Ein Hofez_176, 'Ein Hofez_91), but also contained Pb from additional origins within Iberia ('Ein Hofez_135, 'Ein Hofez_159, 'Ein Hofez_166, 'Ein Hofez_185). One silver item plotted within the Taurus 1A isotopic field, suggesting that it originated from Anatolia ('Ein Hofez_289). The Pb from Arad silver sampled here originated from Gador in southeast Iberia. The 'Ein Hofez hoard was not bundled and was found in unsealed ceramic vessels [48]. The 'Arad hoard was found in cloth bundles within a ceramic vessel [49]. Silver throughout the Iron Age IIA–B periods was acquired by the Phoenicians (from Tyre), who were probably the exclusive suppliers of silver to the region [6,26].

(3) The Late Iron Age IIC (~630–586 BCE): a hoard from 'Ein Gedi

The silver from the 'Ein Gedi hoard originated from Laurion, Greece, and was probably brought to the Levant by East Greek (Ionian) merchants [26]. The hoard was cached in a cooking pot, covered by a ceramic lamp under the floor of a room. The silver was not bundled ([50]; Figure 1).

3. Methods

3.1. Sample Perpetration

We used the National Institute of Standards and Technology (NIST) Standard Reference Material SRM978a as a standard for our measurements. It is supplied in the form of an $AgNO_3$ salt. This material was dissolved in water that was distilled twice and stored in 5% HNO_3 (1000 g/mL concentration) in a lightproof Teflon bottle.

For archaeological silver, we used silver drillings that were formerly obtained and dissolved: The silver (20–25 mg) was obtained using a 1-mm drill, and surface drilling materials were discarded to avoid external contamination. The silver was then dissolved in concentrated HNO_3 and diluted with 10 mL distilled water [6].

As mentioned in previous studies [34,37,51–53], the addition of palladium to correct for mass bias of the instrument is essential for accurate measurement of Ag isotopic ratio. Thus, the standard and Ag samples were doped with 10 ppm of palladium standard (NIST SRM3138). Both were prepared in a solution of 3% HNO_3, such that the final solutions contained 50 ppb Pd and 100 ppb Ag, equivalent to that of the Ag isotope reference standards ([52], p. 2156).

3.2. Ag Isotope Ratio Measurements

In order to overcome the drift of silver isotopic ratios, a sample-standard bracketing technique was employed in addition to external Pd-normalization. With standard-sample bracketing, the externally normalized $^{109}Ag/^{107}Ag$ ratio of a sample is referenced to the average fractionation corrected $^{109}Ag/^{107}Ag$ data of the standards (SRM978a) that were measured before and after each sample. As in earlier studies (see refs. above), the relative difference between the Ag isotopic compositions of the sample and the standard is then expressed as $\varepsilon^{109}Ag$.

All analyzed samples and standards were prepared for analysis on the day of use. This is because mixed solutions containing Ag and Pd are unstable, and Ag concentrations and isotope ratios were observed to change with time ([52], p. 2158). The samples were measured continuously from 26 February 2019 12:49 to 28 February 2019 00:32 using MC-ICP-MS (Neptune Thermo; Thermo Fisher, Bremen, Germany). We used four measurement blocks, each containing 10 acquisitions of 8.389 s integration time (one integration per cycle, 40 data points overall). ^{107}Ag was measured on the center cup and used for peak centering. ^{111}Cd was also measured to correct for interferences on Pd and had a typical response of 1.5E−5 volts or less. The ^{107}Ag, ^{109}Ag, ^{105}Pd and ^{108}Pd yielded signals that ranged between 1.5 and 2 volts. A mass bias correction was calculated using 1.18899 as the true value for ^{108}Pd/^{105}Pd. Operating conditions were optimized for maximum analyte signal intensity. On 27 February 2019 15:27, a new, fresh batch of doped samples and standards was used. In the course of the analysis, 59/61 of the ε^{109}Ag values were stable and varied within ±0.2 ε^{109}Ag (Figure 2).

4. Results

4.1. Chemical and Lead Isotope Analysis

Silver concentrations in the studied samples vary, ranging between 72 and 100 wt.% (Table 1). Low Ag values may indicate that the dissolved sample also contains corroded silver, which is insoluble (see more in [26] and below). Except for one item (Tell el-'Ajjul_1), containing 9.9 wt.% Cu (significantly beyond the limit of Cu expected for unalloyed silver, 5.5 wt% Cu; [6]), all the sampled items are not suspected to be mixed with Cu. Two additional items have Cu concentrations that are slightly above the expected for alloying, 'Ein Gedi_3 (5.9 wt.% Cu) and 'Ein Gedi_8 (5.6 wt.% Cu). The mixing with Cu in such small amounts is not expected to influence Ag isotopic ratios. In addition, in order to avoid mixing of Ag from different ores, we selected items that are all endmembers within the isotopic distribution of each hoard. Namely, they probably contain Ag from a single ore [6].

4.2. ε^{109}Ag of Archaeological Silver

The ε^{109}Ag results of the 45 silver items analyzed in this study range between −2 and +1.5 ε^{109}Ag (Figure 3). These results display a similar silver isotope variation as Hellenistic, Roman, Medieval and modern silver coins [37–41]. All these studies (including the current one) report ε^{109}*Ag* values that have narrower ranges than those reported for hypogene and supergene ores [34,36]. The reason for this phenomenon requires further investigation, which is beyond the scope of the current study.

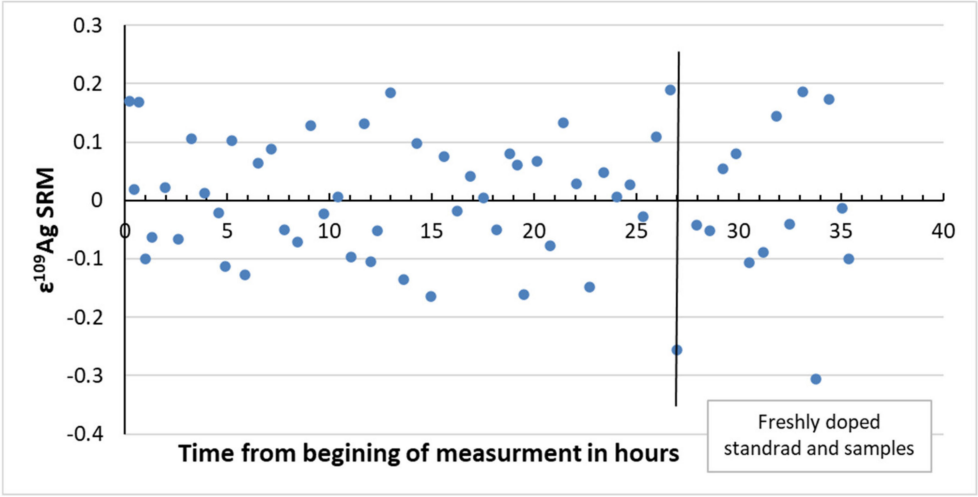

Figure 3. Results of ε^{109}Ag of bracketing standard versus time from beginning of measurement.

Table 1. The items sampled in this study, including their origin; chronology; type of hoarding (sealed/unsealed), bulk chemistry and LIA-based provenance of silver sampled in this study [6,26,31,33]; and ε^{109}Ag values. The hoards from Dor, 'Akko, 'Ein hofez and 'Arad are attributed to the Phoenicians [6,31].

Hoard	Period	Absolute Chronology	Sealed	Sample ID	LIA Provenance	type	Ag %	Cu%	Au%	Pb%	Bi %	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	ε^{109}Ag
Shiloh	MB IIC	~1650–1600 BCE	bundles	Shiloh 2	Anatolia/Aegean	cut ingot	97	3.5	0.04	0.2	0.1	18.858	15.685	38.988	2.0675	−1.39
				Shiloh 5	Anatolia/Aegean	cut ingot	94	3.1	0.1	0.1	0.3	18.850	15.682	39.010	2.0695	−1.29
				Shiloh 6	Anatolia/Aegean	cut ingot	86	3.7	0.1	1.3	0.2	18.858	15.677	38.892	2.0624	−1.38
				Shiloh 8	Anatolia/Aegean	cut ingot	93	5.2	0.1	0.7	0.1	18.851	15.678	38.846	2.0607	−1.36
Tell el-'Ajjul	MB IIC/LB I	~1600–1550 BCE	X	Tell el-'Ajjul 1	Anatolia/Aegean	rod	84	9.9	n.d.	0.2	0.1	18.855	15.684	38.938	2.0651	−0.67
				Tell el-'Ajjul 2	Anatolia/Aegean	rod	88	4.0	n.d.	0.4	0.1	18.898	15.689	39.063	2.0670	−0.63
				Tell el-'Ajjul 3	Anatolia/Aegean	rod	96	4.4	n.d.	0.4	0.1	18.815	15.684	38.911	2.0681	−0.53
				Tell el-'Ajjul 5	Anatolia/Aegean	rod	76	5.5	n.d.	0.4	0.3	18.779	15.672	38.776	2.0649	−0.86
				Tell el-'Ajjul 6	Anatolia/Aegean	rod	90	5.0	n.d.	0.4	0.2	18.841	15.682	38.958	2.0677	−0.97
				Tell el-'Ajjul 7b	Anatolia/Aegean	sheet	72	3.2	0.1	0.2	0.1	18.802	15.673	38.837	2.0656	−0.17
				Tell el-'Ajjul 9	Anatolia/Aegean	sheet	88	1.9	0.02	0.3	0.0	18.797	15.679	38.845	2.0666	−0.89
Dor	Iron Age IIA early	~950–900 BCE	bundles within sealed ceramic vessel	Dor 108	Iglisente, Sardinia	cut ingot	100	3.1	2.6	0.8	0.02	17.940	15.645	38.033	2.1200	0.03
				Dor 122	Taurus 1A, Anatolia	cut ingot	95 *	1.5	3.1	0.7	0.002	18.988	15.694	39.027	2.0554	0.06
				Dor 126	Iglisente, Sardinia	cut ingot	100	1.4	2.8	0.04	0.01	17.910	15.639	37.988	2.1210	−0.50
				Dor 127	Iglisente, Sardinia	cut ingot	95	0.8	2.2	0.5	0.004	17.906	15.642	37.991	2.1217	−0.37
				Dor 52	Taurus 1A, Anatolia	cut ingot	89	5.1	2.7	0.7	0.04	18.976	15.695	39.028	2.0567	−0.07
'Akko	Iron Age II	~950–815 BCE	usealed ceramic vessel	'Akko 12	Iglisente, Sardinia	cut ingot	84	2.0	n.d.	0.5	n.d.	17.894	15.633	37.966	2.1217	0.26
				'Akko 13	Taurus 1A, Anatolia	cut ingot	92	1.6	n.d.	0.9	n.d.	18.976	15.691	39.015	2.0560	0.94
				'Akko 2	Taurus 1A, Anatolia	cut ingot	88	0.5	n.d.	0.1	n.d.	18.964	15.688	39.003	2.0567	0.09
				'Akko 22	Iglisente, Sardinia	cut ingot	99 *	1.4	n.d.	0.03	n.d.	18.030	15.660	38.150	2.1160	−0.70

Table 1. *Cont.*

Hoard	Period	Absolute Chronology	Sealed	Sample ID	LIA Provenance	type	Ag %	Cu%	Au%	Pb%	Bi %	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$\varepsilon^{109}Ag$
				‘Akko 221	Taurus 1A, Anatolia	cut ingot	72	0.7	n.d.	0.3	n.d.	18.957	15.685	38.984	2.0564	1.07
				‘Akko 5	Taurus 1A, Anatolia	cut ingot	93	1.6	n.d.	0.5	n.d.	18.967	15.687	39.003	2.0564	0.98
‘Ein Hofez	Iron Age IIA late	~900–815 BCE	usealed ceramic vessel	‘Ein Hofez 112	Linares, Iberia **	cut ingot	90	0.5	n.d.	0.0	2.3	18.214	15.620	38.309	2.1032	−0.80
				‘Ein Hofez 135	mixed Pb ores in Iberia **	cut ingot	102	0.8	n.d.	0.1	1.1	18.502	15.644	38.632	2.0880	−0.75
				‘Ein Hofez 159	mixed Pb ores in Iberia **	cut ingot	92	0.4	n.d.	1.1	3.0	18.299	15.636	38.428	2.1000	−0.16
				‘Ein Hofez 164	Linares, Iberia **	cut ingot	77	0.2	n.d.	4.2	0.1	18.215	15.609	38.331	2.1044	−1.10
				‘Ein Hofez 166	mixed Pb ores in Iberia **	cut ingot	88	0.7	n.d.	0.2	0.04	18.356	15.621	38.455	2.0949	−0.53
				‘Ein Hofez 171	Linares, Iberia **	cut ingot	89	0.7	n.d.	3.1	0.7	18.180	15.600	38.280	2.1056	−0.17
				‘Ein Hofez 176	Linares, Iberia **	cut ingot	85	0.8	n.d.	0.3	0.2	18.220	15.614	38.305	2.1024	−0.94
				‘Ein Hofez 185	mixed Pb ores in Iberia **	cut ingot	87	0.5	n.d.	0.3	1.9	18.699	15.667	38.798	2.0748	−1.33
				‘Ein Hofez 289	Taurus 1A, Anatolia	cut ingot	89 *	0.9	n.d.	8.3	2.0	18.944	15.687	38.981	2.0577	−0.60
				‘Ein Hofez 91	Linares, Iberia **	cut ingot	97 *	0.4	n.d.	2.0	0.5	18.188	15.609	38.304	2.1060	0.58
‘Arad	Iron Age IIB	~815–700 BCE	usealed ceramic vessel	‘Arad 1	Gador, Iberia **	cut ingot	89	0.9	n.d.	0.7	0.9	18.342	15.666	38.522	2.1002	0.06
				‘Arad 19	Gador, Iberia **	cut ingot	96	0.9	n.d.	1.1	1.4	18.339	15.665	38.520	2.1005	−1.48
				‘Arad 2A	Gador, Iberia**	cut ingot	95	1.7	n.d.	0.3	0.8	18.335	15.668	38.520	2.1009	0.02
				‘Arad 2B	Gador, Iberia **	cut ingot	98	n.d.	n.d.	n.d.	n.d.	18.334	15.667	38.520	2.1010	−0.58
				‘Arad 3	Gador, Iberia **	cut ingot	100	1.6	n.d.	0.5	0.7	18.335	15.671	38.519	2.1009	0.09
				‘Arad 4	Gador, Iberia **	cut ingot	97 *	2.1	n.d.	0.1	1.1	18.331	15.665	38.510	2.1008	−1.47
				‘Arad 8	Gador, Iberia **	cut ingot	99	1.1	n.d.	0.2	0.6	18.349	15.668	38.526	2.0996	−1.56
‘Ein Gedi	Iron Age IIC	~700–586 BCE	sealed ceramic vessel	‘Ein Gedi 2	Lavrion, Greece	ingot	91	5.3	n.d.	3.1	0.2	18.855	15.682	38.865	2.0612	−1.59
				‘Ein Gedi 3	Lavrion, Greece	ingot	91 *	5.9	n.d.	3.5	0.2	18.841	15.680	38.853	2.0621	−1.66
				‘Ein Gedi 5	Lavrion, Greece	cut ingot	87	3.7	n.d.	3.8	0.1	18.840	15.678	38.835	2.0614	−1.63
				‘Ein Gedi 7	Lavrion, Greece	cut ingot	81	4.7	n.d.	3.4	0.2	18.843	15.683	38.876	2.0631	−1.41
				‘Ein Gedi 8	Lavrion, Greece	cut ingot	89	5.6	n.d.	3.6	0.1	18.842	15.680	38.852	2.0620	−1.55
				‘Ein Gedi 9	Lavrion, Greece	cut ingot	92*	4.0	n.d.	4.1	0.1	18.857	15.683	38.867	2.0612	−1.83

* Ag concentrations equal to the difference between the concentrations of other elements and 100%. ** Results indicate the source of Pb added to Ag-rich jarosite in Iberia [6,31].

The results are limited to the narrow isotopic range expected for hypogene ores, and none of the samples have Ag isotopic values typical of supergene deposits (see above). This suggests the use of galena or jarosite hypogene ores for the production of silver throughout the Bronze and Iron Ages, rather than native silver that is predominantly found in supergene ores ([54], p. 348).

4.3. ε^{109}Ag and the Archaeological Context

The 45 silver items analyzed for Ag isotopes can be grouped into three different time periods: Middle/Late Bronze Age transition, ~1650–1550 BCE (11/45), Iron Age IIA–B, ~950–700 BCE ("Phoenician"; 28/45) and Iron Age IIC, 700–586 BCE (6/45).

The ε^{109}Ag values coupled with ^{206}Pb/^{204}Pb ratios (Figure 4) indicate that Phoenician silver (red circles; Iron Age IIA–B) originated from three sources (Sardinia, Iberia and Anatolia) and have a wide ε^{109}Ag range from −1.6 to +1.1. The Middle/Late Bronze Age samples originate from Anatolia and/or the Aegean and have, in general, negative ε^{109}Ag (between −1.4 and −0.1), and the Iron Age IIC silver items are from the Aegean and have even more negative ε^{109}Ag values (between −1.4 and −1.9). Hence, strictly speaking, all analyzed hoards contain silver produced from primary hypogene ores that did not undergo significant fractionation [36].

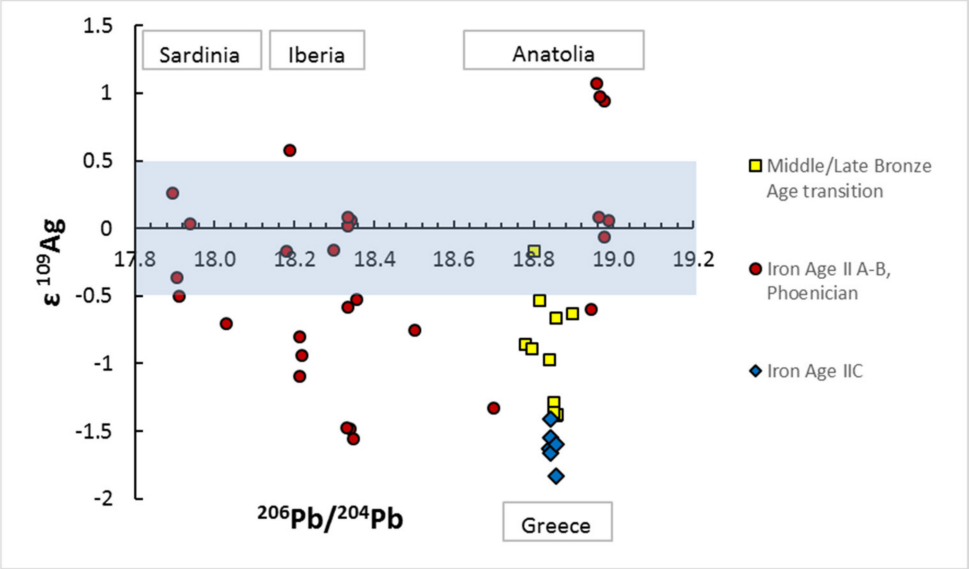

Figure 4. ^{206}Pb/^{204}Pb versus ε^{109}Ag in silver items from Bronze and Iron Age South-Levantine hoards. The results are marked according to the different time periods: yellow squares—Middle/Late Bronze Age transition; red circles—Iron Age IIA–B (Phoenician); blue rhombuses—Iron Age IIC. For Pb isotopic ratios and the content, context and chronology of the hoards, see [6,26,31,33].

Within the Ag isotopic range of hypogene ores, we differentiate here between the narrow range 0 ± 0.5 ε^{109}Ag, which is considered within the $\pm 2\sigma$ range of 0 ε^{109}Ag, namely unfractionated, and any value beyond that, which underwent some extent of fractionation. Silver of 0 ± 0.5 ε^{109}Ag was probably not exposed to weathering; hence, this silver probably originated from primary deeper ores than silver with $0.5 \leq \varepsilon^{109}$Ag or ε^{109}Ag ≤ -0.5.

Thirteen of the samples fall within the range of ± 0.5 ε^{109}Ag. These items originate from Sardinia (4/13), Iberia (5/13), the Aegean/Anatolia (1/13) and Taurus, Anatolia (3/13). The remaining 32 items plot beyond the range of ± 0.5 ε^{109}Ag, namely, the silver in these items underwent some fractionation. These include silver from Sardinia (1/32), Iberia (11/32), the Aegean/Anatolia (10/32), Greece, Laurion (6/32) and Taurus, Anatolia (4/32). Based on these results, as in previous studies, we did not find any correlation between the origin of the silver and their ε^{109}Ag value [37–41].

There is, however, a clear distinction between fractionated and unfractionated (0 ± 0.5) ε^{109}Ag according to their archaeological context: Twelve out of 13 samples that fall in the range of ± 0.5 ε^{109}Ag are from Phoenician silver hoards (dating between ~950 and 800 BCE). Moreover, while a large portion of the Phoenician silver did not undergo Ag isotope fractionation (12/28 sampled items), non-Phoenician silver mostly underwent Ag isotope fractionation (16/17; Figure 4). The results indicate, therefore, that Phoenicians also exploited deeper, less weathered ore sources, reaching unaltered ore minerals.

4.4. ε^{109}Ag and the Preservation of Silver

Post-burial weathering processes were found to highly affect the surface of silver items that were found in the sediments of archaeological sites [40]. This was attributed to interactions with groundwater and dissolved organic compounds, which lead to redox transformations of the near-surface silver, causing Ag isotopic fractionation at the surface of silver coins in comparison to their cores [40]. In this study, the silver was presumably sampled from the core of the items rather than the surface; however, as not all items reached a total sum of 100% in their elemental composition, we were concerned that sampling was not always clean of surface corrosion (see Table 1 and [26]).

We defined uncorroded silver as items with a total sum of elements that was $\geq$90 wt.%. Although most drillings had a total sum of 90–100 wt.%, eight items in this study displayed a lower sum, ranging between 72 and 89 wt.% (Tell el-'Ajjul_5, Tell el-'Ajjul_7, 'Akko_12, 'Akko_2, 'Akko_221, 'Ein Hofez_164, 'Ein Hofez_166 and 'Ein Hofez_176). These items are therefore suspected of containing some insoluble corrosion (e.g., AgCl) within the drillings and possibly additional corroded material from the surface of the item.

These results suggest that the silver in the hoards from Shiloh, Dor, 'Arad and 'Ein Gedi was better preserved than silver from the hoards of Tell el-'Ajjul, 'Akko and 'Ein Hofez. A possible explanation for this difference may be the method in which the silver was stored.

Hoarded silver was often stored within cloth bundles or sealed in ceramic vessels, practices that might have reduced the contact between the silver and the local soil. Other hoards that were unsealed may have been more exposed to corrosion and consequentially also to Ag isotopic fractionation on the surface of the items and immediately below it [40]. As hoarded silver is sampled for Ag isotopic composition in this study for the first time, we assess the effect of sealing and bundling on the exposure of the silver to post-depositional weathering processes by comparing contemporaneously sealed and unsealed silver. We attempt to determine whether sealed silver was less exposed to weathering processes than unsealed silver. Here we define four different levels of hoarding (Table 1; for a full description of hoard depositions, see [33]):

1. Sealed silver: Silver, which was cached in a ceramic vessel and covered by another one, therefore expected to be least exposed to weathering processes in the ground. These include the hoards from Dor (in which the silver was also bundled) and Ein 'Gedi;
2. Bundled silver: Silver hoarded in cloth bundles. The bundle preserves the silver in a tight cluster. The hoard itself may be exposed to underground fluids; however, the bundle and outer silver artifacts may protect the inner silver pieces. This includes the hoard from 'Arad (which was also cached within a ceramic vessel) and Shiloh;
3. Semi-sealed silver: Silver that was not wrapped in a bundle but rather cached in an open, uncovered ceramic vessel. These include the hoards from 'Ein Hofez and 'Akko. The presence of soil within the vessels of the 'Ein Hofez hoard (Y. Alexandre, personal communication) indicates that silver was stored in uncovered ceramic vessels, and thus was exposed to post-depositional weathering processes;
4. Unsealed silver: Silver that was not bundled and not stored in a ceramic vessel but rather buried directly within the ground. One hoard answers this description from Tell el-'Ajjul.

The results, as demonstrated in Figure 5, show that unsealed and semi-sealed silver has a wider range of ε^{109}Ag values compared with bundled and sealed silver. Semi-sealed

silver, which was hoarded in open ceramic vessels, displays the widest range of ε^{109}Ag values. This observation does not alter our original conclusions that Phoenician silver is less fractionated than Middle/Late Bronze Age and Iron IIC silver, as the same conclusions can be reached when considering sealed and bundled silver only (the colored items in Figure 5).

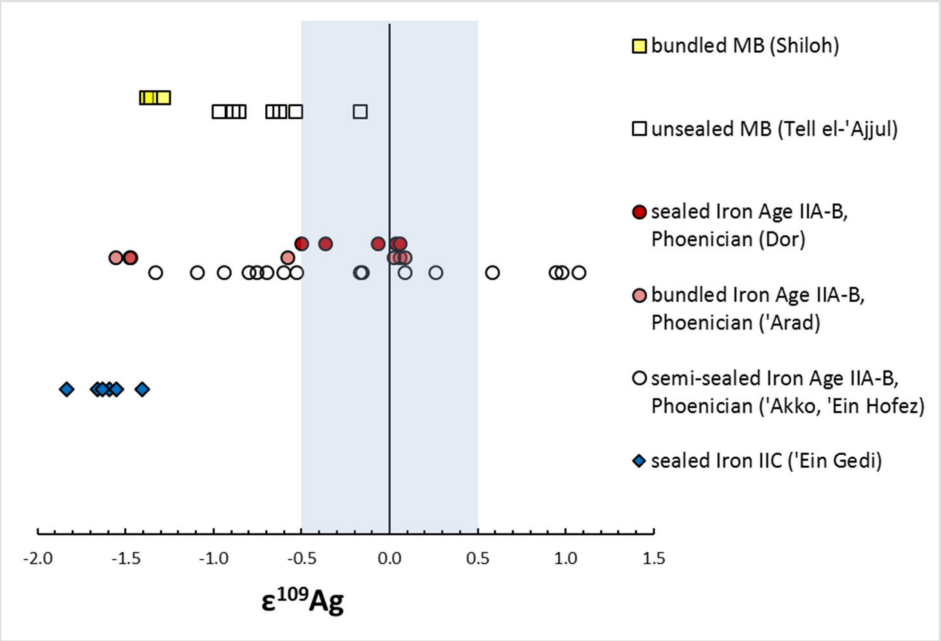

Figure 5. Ag isotopic composition of sealed and unsealed silver. The results are marked according to time periods: Squares—Middle/Late Bronze Age transition; Circles—Iron Age IIA–B (Phoenician); Rhombuses—Iron Age IIC. Color indicates sealed silver.

In addition, we observed that all the items that contain [Ag] < 90% originate from either semi-sealed or unsealed hoards (Tel el-'Ajjul, 'Ein Hofez and 'Akko; see list above), while all the sampled silver items from sealed and bundled hoards contain Ag $\geq$ 90%, and were probably better preserved. Therefore, it is possible that underground post-depositional burial processes affected the Ag isotopic compositions of unsealed and semi-sealed silver artifacts in the study, causing fractionation. Additional measurements are needed in order to quantify this effect and examine the association between hoarding technics and Ag isotopic compositions.

5. Discussion and Conclusions

The results support a long-held assumption that native silver was rare in antiquity (e.g., [5,55,56]) and that the source of silver throughout the Bronze and Iron Ages was from hypogene ores, rather than supergene ones where native silver primarily resides ([54], p. 348).

As previously mentioned, the Phoenicians brought silver to the Levant from Anatolia and Sardinia in the mid-10th century BCE and from Iberia during the 9th and 8th centuries BCE [6,31]. One of the yet unresolved questions regarding the Phoenician exploitation of metal resources is to what extent were they innovative? Did they bring about new production methods that enabled the exploitation of larger silver quantities, or were they merely fine sea traders and navigators who were able to acquire cheap silver in the West and mobilize it across the Mediterranean? As mentioned above, metal ores cannot always be dated based on the archaeological evidence on-site because recent mining often eliminated the remnants of ancient mining activities. Indeed, archaeology and LIA, insofar, provide limited knowledge regarding Phoenician silver production methods in Anatolia

and Sardinia. Regarding Anatolia, the quantities of Anatolian silver brought to the Southern Levant by the Phoenicians are by far much larger than in earlier periods; however, ores in Western Anatolia and in the Taurus Mountains were known to be major sources of silver since the 3rd millennium BCE, predating the Phoenician interest there (e.g., [57–60]). As for Sardinia, there is no clear evidence that silver was exploited in antiquity, and the activity in the mines was never dated [61–63]. In Iberia, in contrast to the above, silver production is unanimously considered a Phoenician innovation. Based on numerous finds in silver production sites, it was concluded that from ~800 BCE, silver was extracted from the abundant Pb-deficient argentiferous jarositic ores in the Iberian Pyritic Belt by Phoenicians, via the deliberate addition of Pb from other Iberian sources (e.g., [64–67]).

The results presented here suggest that a significant fraction of the silver exploited by the Phoenician did not undergo fractionation, namely, originated from deep hypogene silver ores in Anatolia, Sardinia and Iberia. On the other hand, during both preceding and following periods within the Bronze and Iron Ages, more fractionated silver was exploited, although also originating from hypogene ores. This is further demonstrated in an earlier study by [39], showing that primary, unfractionated silver originating from Iberia was circulating during the 3rd century BCE (Figure 2 in [39]). The Romans produced silver in Iberia from the 2nd century BCE onwards [68]. They improved the production process, as indicated by the chemical compositions of their slags [20,69], yet Albarede et al. [39] demonstrated that the silver produced by the Romans from the 2nd century BCE onwards was mostly fractionated. We carefully suggest that this indicates, again, the uniqueness of metal exploitation by the Phoenicians, who exploited deeper primary ores. The Ag isotopes are therefore evidence of the effort, originality and novelty that the Phoenicians invested in silver production. The large quantities of silver in the Levant attributed to the Phoenicians attest to the rewarding outcomes of these efforts [6,25].

The fact that Ag isotopes in many Phoenician silver items are unfractionated regardless of the origin or date of the silver suggests that the same exploitation methods were practiced in Anatolia and Sardinia in the 10th century BCE, as well as in Iberia in the 9th century BCE. The results further substantiate our previous suggestion that the Phoenicians were not only sailors. They appear to have acquired new metallurgical methods in Anatolia and introduced them to Sardinia and Iberia [6].

Finally, it is also possible that underground post-depositional processes slightly affect the Ag isotopic compositions of unsealed and semi-sealed silver; however, a larger database is still needed in order to confirm this hypothesis and quantify it.

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