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A database of lead isotopic signatures of copper and lead ores for Europe and the Near East

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ABSTRACT

The objective of this synthesis work was to create a database compiling as many as possible of the lead isotope analyses performed to date on ores from copper and/or lead deposits.

The database is intended to be as exhaustive as possible and is based on existing compilations and enriched with data from various publications. The isotopic signatures are derived from geological and archaeological studies covering a large part of Europe, the Near East and the Urals.

The compiled data have been sorted and cleaned. Analyses performed on host rocks and deposits without copper and lead have been removed from the final compilation. Incomplete data have also been removed. A column is used to select only the signatures of high and/or low copper or lead deposits. A GPS coordinate (WGS 84) is indicated for each locality.

This database of approximately 7400 isotopic signatures is intended to be directly useable for provenance studies aimed at tracing the origin of copper and/or lead contained in artifacts.

The database produced is provided as a supplement to this article.

1. Introduction

The question of metal supply sources and the resulting exchange circuits is an important archaeological issue for understanding the socio-economic networks of ancient societies. The tracing of production sources *via* lead isotopy has thus been developed in the 60s (Grögler et al., 1966; Brill and Wampler, 1967) and has been used mainly since the 80s (e.g.: Oxalid database; Gale, 1980; Wagner et al., 1980; Pernicka et al., 1981; Stos-Gale and Gale, 1981; Pernicka et al., 1984) to identify the deposits from which the metal composing the archaeological artifacts originated. This type of study is possible because the lead isotopic signature of an ore is not modified by metallurgical processes (Cui and Wu, 2011; Pernicka, 2014). Thus, it is possible to assume that the object was produced from minerals from a specific deposit when the signatures of a deposit and an artifact are comparable.

Provenance studies are a valuable tool for understanding inter-regional exchanges, whatever the period. If this type of study can be carried out on iron, gold or silver artifacts, the majority of these works aim at defining the origin of copper or lead constituting an artifact (Pernicka, 2000; Artioli et al., 2020). The database therefore focuses on these two metals for which the bibliography is particularly abundant.

However, several limitations can be pointed out for this type of study

(Roberts, 2009; Villa, 2009; Baron and Coustures, 2018):

- the artifacts may have been recycled and/or may have been derived from a mixture of ores from several deposits;
- the signatures of certain regions are too close to be individualized;
- some regions are oversampled and others are undersampled or even unreferenced.

While the first two limitations mentioned are difficult to overcome, the last point discussed requires that each study take into account all available data. Failure to take into account the signatures of the mining district from which the artifact originates in the context of its study can only lead to an unsatisfactory result. In this regard Liu et al. (2018) cite as an example the Laurion mines for which the amount of isotopic signatures is very abundant and to which is associated a consequent copper production while little copper has been detected there.

Thus, in order to be able to trace the exchanges as well as possible, it is essential to have a solid reference system of lead isotopic signatures. This type of repository must be based on a compilation that is (i) as exhaustive as possible and (ii) cleaned to keep only relevant and error-free data.

The aim of the database is to provide a reliable support of mineral

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signatures directly useable for provenance studies aiming to investigate the origin of copper or lead in archaeological artifacts. It compiles analyses of European deposits but also of the Near East and part of Eurasia.

2. State of the art - existing databases

2.1. Open access LIA databases

Two major databases compiling isotopic analyses of lead are freely available and are regularly used in provenance studies: the Oxalid database and the B. Scaife compilation.

The Oxalid database is the result of the joint work of two research teams from the Universities of Oxford (UK) and Heidelberg (Germany). This database contains analyses carried out between 1975 and 2002. Initially, the aim of this work was to study the first metallurgies of the Mediterranean region (Stos-Gale and Gale, 2009). It does not therefore cover the whole of Europe (Fig. 1). The database is available online <http://oxalid.arch.ox.ac.uk/> and contains to date more than 2000 lead isotopic signatures of ores.

Another open access online database is the one compiled by Brett Scaife (<http://www.brettscaife.net/lead/data/index.html>). It also focuses on the Mediterranean region and the data are located in roughly the same areas as those referenced in Oxalid. The data mainly concern Cyprus and Greece, which have nearly 900 lead isotopic signatures. Italy is also strongly represented (about 500 signatures, including more than 400 for Sardinia alone). Turkey (143 signatures), Spain (90), Egypt (31), Syria (6 sediment analyses) and three data from the Maghreb complete this database.

Three other works on the scale of Europe and the Mediterranean rim

should be highlighted. These are the compilation of Thompson and Skaggs (2013) and the doctoral theses of Florence Cattin (2008) and Véronique Collin (1990). The work of Thompson and Skaggs (2013) compiles isotopic signatures of ores for Sardinia, the Iberian Peninsula and France. The two PhD theses previously cited present broad coverage of Europe, incorporating data for France and Germany in addition to the regions previously cited.

In addition to these large compilations, a hundred or so publications on more local scales, which were not included in the previous syntheses, have been added to the database. Although it is not possible to mention all of them, we should mention the work of Ernst Pernicka and his team for Eastern Europe (Pernicka et al., 1993) and the Eastern Alps (Pernicka et al., 2016), the IBERLID database for the Iberian Peninsula (García de Madinabeitia et al., 2021) and the work of Gilberto Artioli for the Western Alps (Artioli et al., 2016).

Finally, it should be noted that other database projects are currently being developed, including the GlobalID database (Klein et al., 2022) which is still under development. The associated metadata are very similar to those present in the database in the appendix of this document. However, the metals present in the analyzed deposits are listed without gradation according to whether the metal-bearing minerals are the major constituents of the ore deposit or not.

2.2. Consideration of signatures from geological studies

Although the analyses carried out within the scope of geological studies only concern very few of the mines exploited in archaeological times, their consideration remains interesting. Taking them into account therefore increases the amount of data available and it could be of

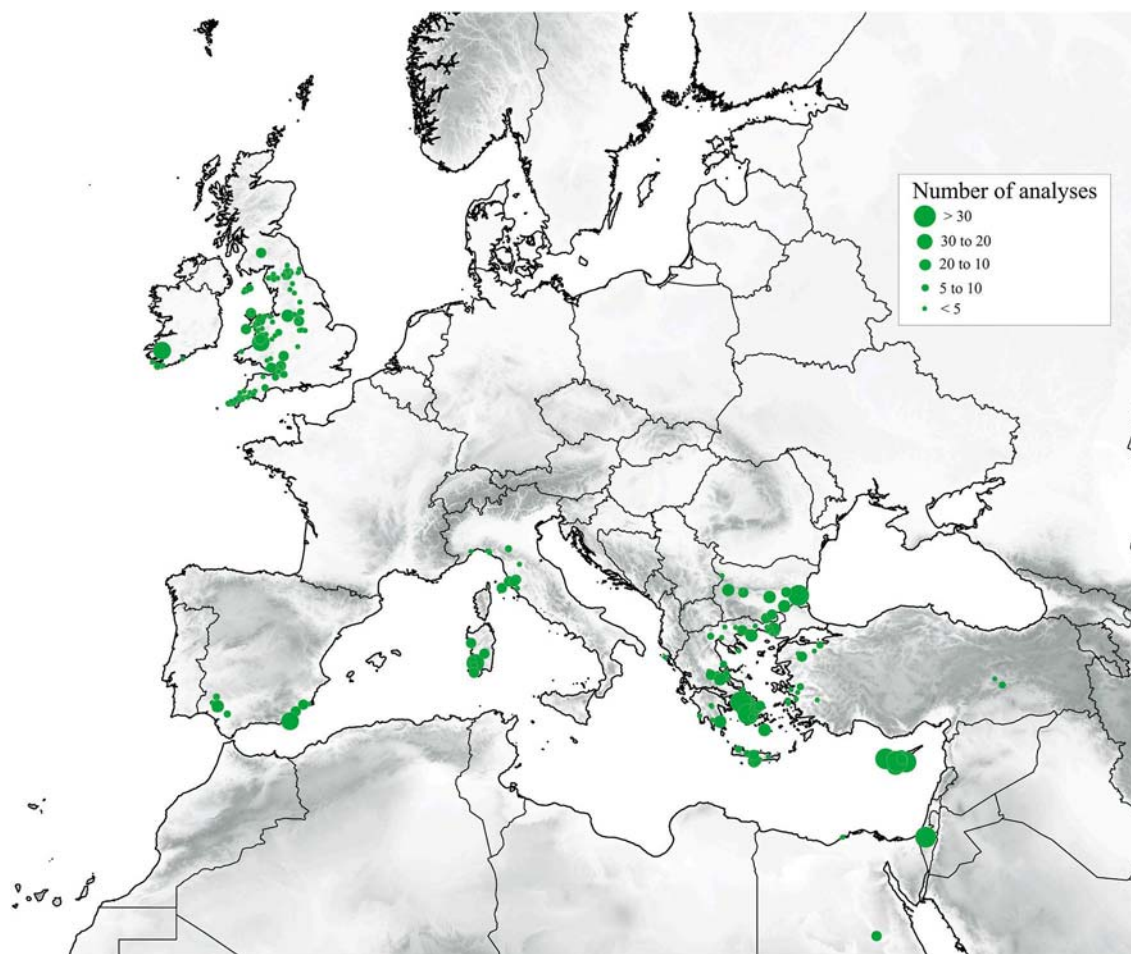


Fig. 1. Location of lead isotopic analyses of ores in the Oxalid database.

interest to compare the signature of artifacts with those of local deposits even if no mine has been discovered there to date.

Furthermore, the inclusion of data from the geological literature not only expands the amount of data available but also allows us to propose origins that are not linked to a geographic location but to a regional type of mineralization.

A fifth major database thus formed part of the skeleton of data compiled in this work. This is the work of [Blichert-Toft et al. \(2016\)](#). With more than 6000 data and covering a large part of Europe, this compilation aims to study the variations of lead isotopic signatures of the continental crust under the effect of major tectonic phenomena. Most of the data are from barren rocks, but some analyses concern deposits, particularly in Scandinavia.

This last remark is important because, although it is interesting to analyze rocks in the case of geological studies, the integration of signatures of sterile rocks can only bring a bias to archaeological provenance studies. Indeed, in order for the proposed provenance to be coherent, it must correspond to a mineralized zone (and therefore be exploitable for the substance traced).

Thus, it is necessary to clean the database created to keep only the lead isotopic signatures characteristic of ores.

3. Cleaning of the obtained database and addition of new metadata

Published data generally contain three isotope ratios ($^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ or $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$) and sometimes five ($^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$). The five isotope ratios can be recalculated from the three previously mentioned ratios.

It is therefore to be regretted that some of the published isotopic analyses cannot be included in the database created. Indeed, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are not always published (e.g. Montaigne silver mines ([Girard et al., 2010](#))). In this case the data are not considered because the provenance studies are based on at least three lead isotope ratios. Besides, the raw data are not always accessible (e.g. Cabrière mines ([Prange and Ambert, 2005](#))).

3.1. Removal of duplicates and addition of GPS coordinates

Pre-existing databases and publications generally contain at least:

- an identification code (ore identifier and/or analysis identifier), available in the "Sample Number" column;
- textual information about the location of the sample, available in the columns "Country", "Region" and "Sector details";
- the type of mineral analyzed, available in the "Mineral analyzed" column.

This data can be completed by various information, which varies according to the authors, such as the period of operation of the mine, a description of the deposit, the analytical margin of error, or the type of spectrometer used.

In cases where the assay numbers, geographic information, and isotopic ratios were identical, only one entry was retained. If one of the entries had more accurate isotope ratios (more digits after the decimal point), that entry was retained. This presence of duplicates is due to the fact that some analyses have been published several times.

The bibliographic references cited (columns "Sources" and "Full reference") are those of the original publications and not of the databases in which they appear.

Each entry in the database has been assigned a GPS coordinate (WGS 84) where this information was not originally provided. The GPS coordinates are ideally based on the maps provided in the original publications, but can also be derived from textual indications. The textual indications on which the search for GPS coordinates is based are reported in the metadata in the columns "Country", "Region" and "Sector details". This information may vary: not all publications specify the exact location.

If several lodes of the same mine have been analyzed, the GPS coordinates indicated correspond to the mine. GPS coordinates are shown in red if they are not accurate (only the region is indicated or several mines have the same name in the mining district).

3.2. Removal of isotopic ratios not corresponding to ores from copper or lead ore deposits

Provenance studies sometimes consider all the data available for a region (including analyses performed on the host rock of a mineralization, on waste rock or on deposits not containing the substance whose source is being sought). However, if it is possible to observe similarities between artifact signatures and this type of geological context, the question of the consistency of these comparisons may arise.

For example, [Budd et al. \(2000\)](#) interpreted the origin of copper artifacts as being from a granite containing tin but absolutely no copper. [Stos-Gale and Gale \(2010\)](#) consider the origin of Bronze Age Cypriot copper alloy artifacts as coming from non-copper silver deposits in the Montagne Noire (Massif Central, France).

The database was therefore sorted to separate analyses related to ores from copper and/or lead deposits from other types of data. The data corresponding to other types of ore deposits or rocks are nevertheless available in the sheet "no Pb and no Cu" of the Excel document provided in appendix. They can be used if the objectives of the study lend themselves to it and can constitute a source of complementary data.

Slag is also regularly not included in compilations of lead isotopic signatures of ores. Oxalid and IBERLID are exceptions. Metallurgical wastes, however, are numerous in these data sets: for example, Oxalid's "Ore Spain" file compiles analyses of: 12 litharge fragments, 50 copper slags and 101 ores. Metallurgical residues represent 44% of the signatures recorded. Still in Oxalid, some localities such as "Skouries/A. Ioannis slag heap" are represented only by slag signatures.

Isotopic signatures from such materials are regularly considered in provenance tracing studies ([Sayre et al., 1992](#); [Pernicka et al., 1993](#); [Begemann et al., 2003](#) or [Ling et al., 2019](#)). This is due to the fact that if a significant amount of slag is reported, it can be assumed to be from local production. However, the latter may have a different signature from local mineralization because they may be derived from a mixture of ores from several nearby operations exploiting deposits of different types and ages.

For a given period, the slag can thus provide precious clues as to the mixtures that were operated (mixtures of ores from several deposits but also addition of a flux (voluntary or not) to facilitate the metallurgical process). They thus sometimes present a signature closer to that of the finished products than the local deposits for a given period. One example is the Mitterberg slag in Austria, which is slightly different from the ore samples but better matches the archaeological sample data ([Pernicka et al., 2016](#)).

The inclusion of slag is therefore particularly interesting in cases where it is contemporary with the artifacts whose origin is being traced. However, it may be problematic to consider slag as marking the signature of local minerals if it is not contemporary with the artifacts. As such, the dating of analyzed slag is often uncertain. This is particularly the case for the slags in the Oxalid database, which warns the user about this: "Many of the slag heaps are situated well away from ore deposits, and may have acted as central places for smelting ores from many different ore deposits". This fact may explain why many databases of lead isotopic signatures of deposits do not include slag.

A database of the lead isotopic signature of metallurgical wastes (slag or litharge) and archaeological ores found outside the context of a mining chain of operations (settlement or burials, for example) from well-dated contexts would therefore be a particularly relevant work to complement the ores in source tracings. However, this would require research by chronological period. This is not the purpose of this study but it would be an interesting research perspective.

3.3. Research of geological data for the remaining entries

The remaining data (compiled in the “Directly useable data” sheet of the Excel document) were sorted to keep in the database only analyses of deposits containing at least traces of the presence of copper and/or lead.

This sorting is easy to carry out in the case of publications aiming to study one or more deposits because the geological contexts and mineralogical assemblages are described with precision.

However, as already pointed out by [Ixer \(1999\)](#), [Guénette-Beck and Serneels \(2010\)](#) and [Baron et al. \(2014\)](#) isotopic analyses from archaeological studies provide very little information about the deposits collected. The main minerals present in the deposit are almost never indicated and even more so, the mineralogical assemblages are only very rarely detailed.

A verification process was therefore undertaken for each site to determine whether or not it corresponds to a copper or lead mineralized zone. This work was based on the Mindat database of the Hudson Institute of Mineralogy (available here: <https://www.mindat.org/>). This website lists hundreds of thousands of mineralized deposits and showings around the world. It offers a large list of geological survey reports and scientific publications for each referenced site. Precise mineralogical assemblages can thus be found for almost all the deposits analyzed.

Other publications were searched for deposits and showings for which no publication was associated in the database and for sites not referenced in the database.

The corresponding metadata are available in the column “Main minerals/metals mined”.

However, in order to verify the presence or not of copper and/or lead minerals, it is necessary to know the precise location where the sample was collected. Data whose location was too vague (e.g. “Egypt” or “Saugerland”) were thus discarded. The same applies to about 400 deposit entries for which no other work mentions the name (it could be, for example, a bad transcription of the mine name in the source publication). These isotopic signatures have been gathered in the “incomplete metadata” sheet of the Excel document. The sites for which the location is too vague and those for which no deposit data have been found are listed.

For sites where the original deposit was identifiable, assays not related to mineralization containing at least traces of copper or lead were removed. This is the case for 270 entries, including about 40 analyses of copper ores from Cretan outcrops present in the Oxalid database, whereas the island has no deposits in the analyzed areas ([Spanakis, 2015](#)).

The remaining analyses then all correspond to ores from copper and/or lead ore deposits.

4. Distinction according to the quantity of copper and/or lead ores present in the deposit

Two columns in the database have been added to specify the presence or absence of copper and lead ores. These are the “Presence of Cu” and “Presence of Pb” columns respectively. These two columns can contain one of the following three texts: Cu/Pb major, Cu/Pb minor or No Cu/Pb ([Table 1](#)).

Copper and/or lead deposits are distinguished as “Cu major” and “Pb major”. Deposits with only very few copper and/or lead minerals are referred to as “Cu minor” and “Pb minor” respectively ([Fig. 2](#)).

Table 1

Database entries for copper and lead according to the richness of the deposit analyzed. It should be noted that a deposit may be both copper and lead bearing (this is the case for 60% of the analyses) or may contain only one of the two substances.

	Cu major	Cu minor	No Cu	Pb major	Pb minor	No Pb
Number of inputs	3539	2326	1485	3823	2041	1486

This distinction is not based on a threshold grade. Indeed, if there are thresholds to determine if a deposit is currently exploitable or not, it is not possible to know the exploitation thresholds for old periods. Considering a cut-off grade separating the “major” and “minor” designations does not therefore seem coherent.

Thus, the major and minor cut-offs are based on the fact that only rare copper and/or lead minerals have been reported (these are accessory minerals). On the contrary, when copper and/or lead minerals are described as main constituents of the deposit, the term “major” is associated with the analysis. In addition, some deposits may have several phases of mineralization: some lodes may therefore be rich in copper and/or lead minerals, while other lodes in the same deposit may contain almost none.

Thus, the analyses of Cu and Pb minor appear to be difficult to use by miners: they are too scattered, too little present. The quality of these data is therefore much lower than that of the data from the deposits (“major”). It will therefore be necessary to select them with caution in the context of a possible study.

However, their consideration may be interesting for several reasons.

Indeed, in some places, they can present more important accumulations: some deposits that are very poor in a substance may have an isotopic signature close to those of surrounding veins where the presence of these metals would be more important ([Marcoux \(1986\)](#) and [Zartman \(1974\)](#) refer to this phenomenon as regionalism). Furthermore, the choice to take into account signatures corresponding to deposits with very little enrichment of a substance also makes it possible to increase the amount of data available for an under-analyzed region.

Finally, as already mentioned, if no copper and/or lead mineral is present, it is indicated “No Cu” or “No Pb”.

If imprecise information has been indicated for a site, it will appear in red. The indications “No Pb?” and “No Cu?” correspond to cases where the ore analyzed (Mineral analyzed column) is indicated as being a lead or copper mineral while the deposit theoretically contains (almost) none.

Finally, it should be emphasized that if the database is cleaned and only the signatures corresponding to deposits have been kept, no sorting has been done to isolate the analyses according to their precision. However, the question of the possibility of taking into account the analyses carried out 20 years ago deserves to be asked.

5. Variable data accuracy in relation to the evolution of mass spectrometers

A difference in data accuracy is related to the evolution of mass spectrometers for measuring isotopic ratios. The progressive replacement in the 2000s of TIMS (Thermal Ionization Mass Spectrometry) by MC-ICP-MS (Multi-Collector Inductively Coupled Plasma Mass Spectrometry) has led to a very significant increase in the precision of measurements ([White et al., 2000](#)). The advent of the double-spike has thus made it possible in about 20 years to obtain at least a 10-fold increase in the accuracy of quantification of isotope ratios ([Taylor et al., 2015](#)).

Nevertheless, [Baker et al. \(2006\)](#) show that the signatures obtained by TIMS and MC-ICPMS are comparable. The data acquired by MC-ICPMS appear less diffuse than those acquired by TIMS.

[Vaxevanopoulos et al. \(2022\)](#) observe this same type of trend for ores from the Aegean rim. Their new measurements are consistent with older analyses from Oxalid but are less diffuse. They point out that studies to be published would show the same trend for the Iberian Peninsula.

The $^{207}\text{Pb}/^{204}\text{Pb}$ ratio appears to be the most impacted and would be significantly lower when measured with a conventional TIMS ([Cordier et al., 2016](#)).

However, if TIMS with an accuracy of $\pm 0.1\%$ on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is nowadays little used (e.g. [Bozkaya and Gökce \(2011\)](#) still use it), this type of analysis is still used but with methods of correction of the fractionation allowing a gain in precision.

If it is therefore preferable to favour recent and therefore less diffuse data, it is important to stress that some regions have mainly been the

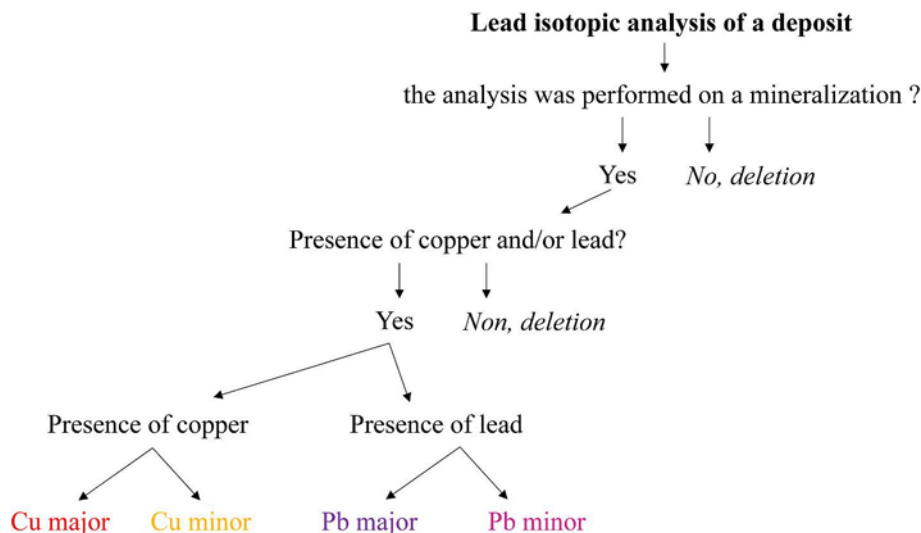


Fig. 2. Summary diagram of database cleanup. If an analysis is performed on a locality where there are no copper or lead ores in the form of at least flecks, the signature is removed from the database.

subject of analyses that are at least 20 years old: almost all of the lead isotope analyses available for Ireland, Great Britain, France, Cyprus, Greece, Scandinavia or the Oman Peninsula are old. If new analyses are performed for these areas, the value of favoring recent data is not insignificant.

According to this reasoning, the isotopic signatures of lead acquired in the past whose uncertainty on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is $\pm 0.29\%$, have not been taken into account (e.g: Delevaux et al. (1967)). Furthermore, while artifacts (Degryse and Vanhaecke, 2016) are sometimes analyzed by Laser ablation mass spectrometers (LA-ICP-MS), at present, no deposits located in the study area have been analyzed by this technique to define their lead isotopic signature.

Another point related to the analytical margin of error concerns analyses where only two decimal places after the decimal point are available for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio. In this case, the lack of precision makes them difficult to use. Those signatures have been isolated in a

separate sheet of the document in the appendix (called “Inaccurate isotopic data”). The user can then choose to consider them or not.

A final point to emphasize is that the ratios are interdependent: they must be retrievable by simple multiplication. Six cases where the ratios were not consistent with each other were identified and isolated in the “isotopic ratios not logical” sheet.

6. Result of the compilation - map view

This work has resulted in the creation of a database of about 7400 lead isotope signatures. The data covers Europe, the Near East and part of the Urals. The elaboration of a database on this scale had never been undertaken before. The inclusion of isotopic signatures from geosciences studies (46% of the total data) allows a better coverage of the study area. In particular, it allows us to cover France, the Maghreb and Scandinavia (Fig. 3) As previously mentioned, although few analyses have been

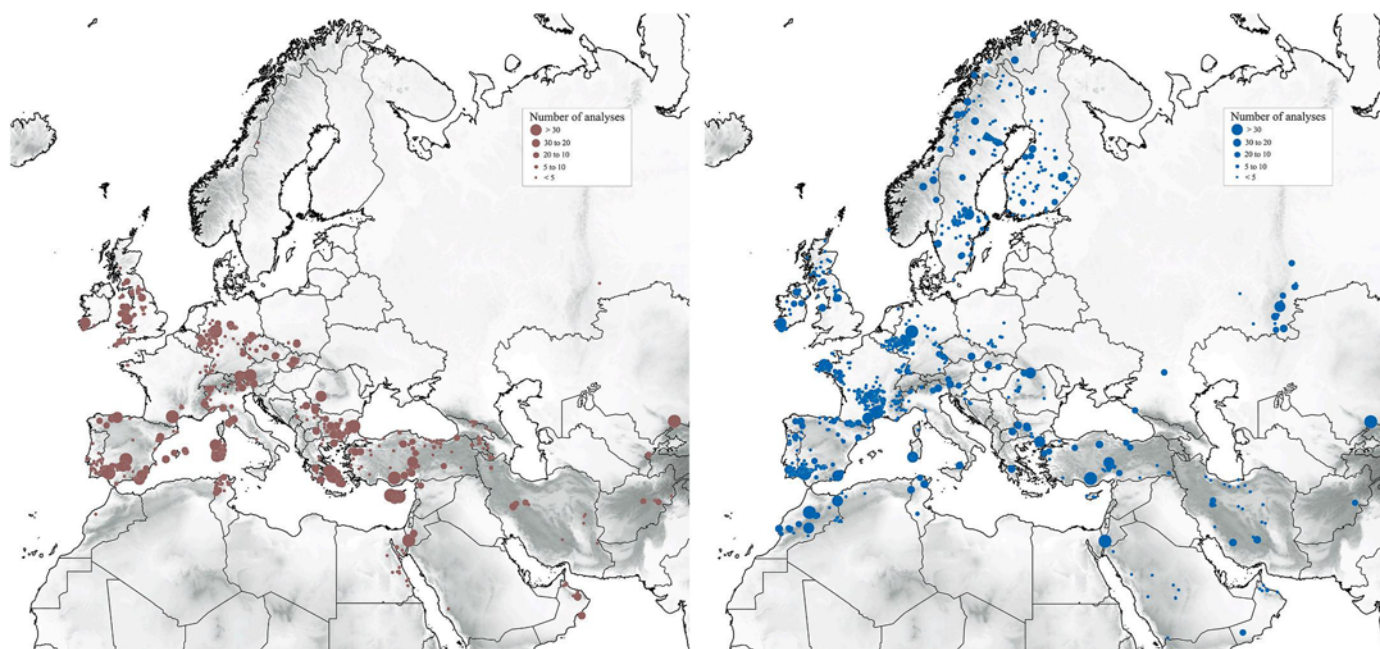


Fig. 3. Initial aim of the work from which the compiled signatures originate: on the left (brown circles) data from archaeological studies, on the right (blue circles) data from geological studies. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

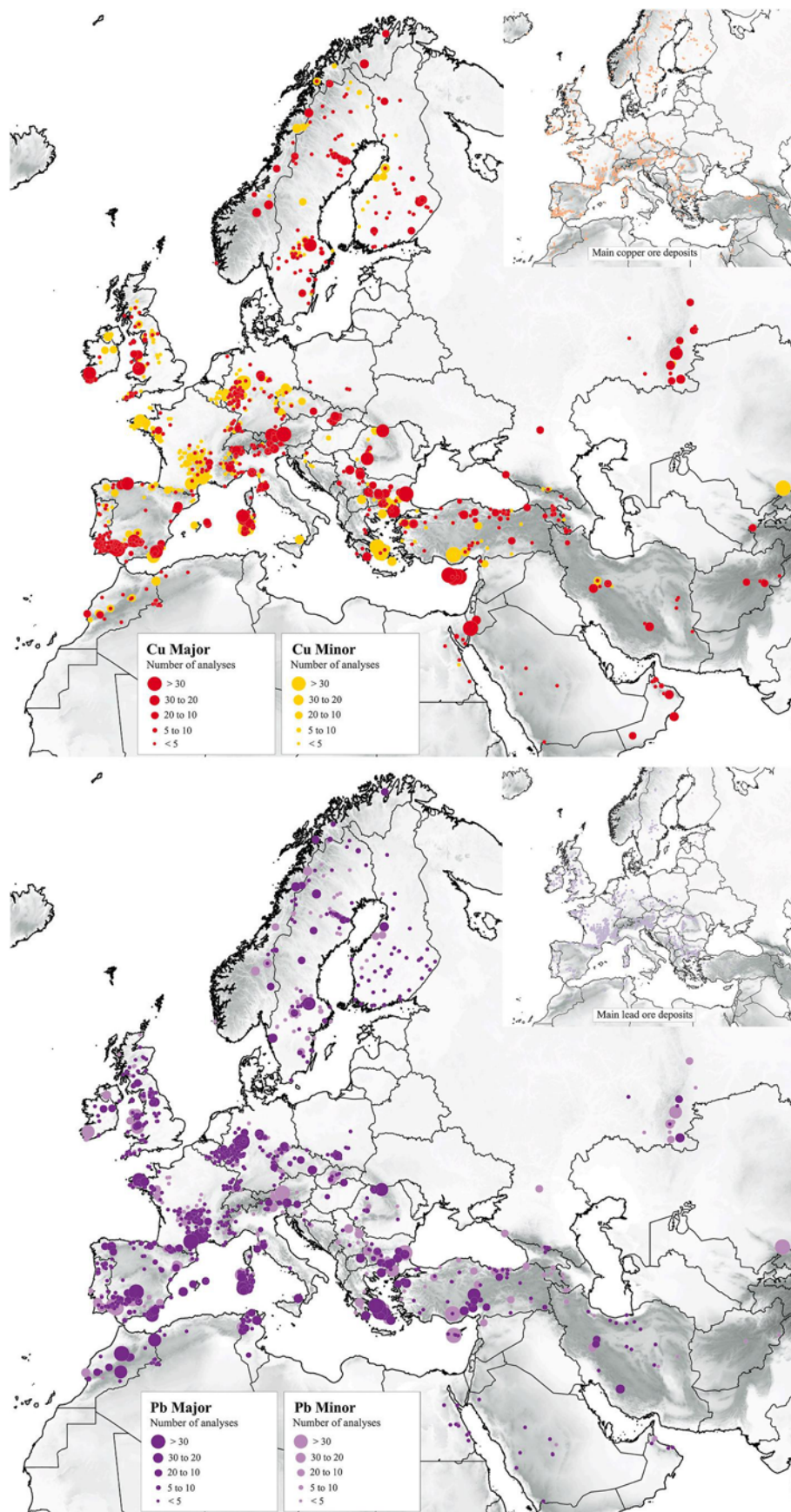


Fig. 4. Copper (top map) and lead (bottom map) ore deposits referenced in the database and mineralized showings in Europe (data from Promine (Cassard et al., 2015) and the US Geological Survey online database (<https://mrdata.usgs.gov/>)).

carried out by geologists on old mines, taking these data into account can be of interest, particularly to question possible local sources in the case where no old mine is known.

Moreover, this database offers the possibility to select only the signatures corresponding to copper and/or lead ore deposits. It thus makes it possible to consider only deposits that show at least traces of the metal whose origin we are trying to define.

However, although this bibliography and the cleaning of existing data show a good coverage of European copper and lead deposits, some regions remain under-sampled or even lacking in lead isotope analyses that would allow their mineralization to be characterized (Fig. 4).

Among the areas where very few analyses are available for copper are Poland and France, where the isotopic signatures of lead(-zinc) deposits are abundant but few analyses are available for copper deposits (except in the Alps). Also in France, Corsica has only one analysis despite the abundance of its copper and lead deposits. The northern and eastern part of Ireland has few signatures for copper, as do the Italian Calabria and the western Balkans (Albania in particular). Outside of Europe, the database is poor in isotopic signatures for the copper-lead deposits of Iran and Kazakhstan and for the copper deposits of Saudi Arabia and western Russia.

These gaps are not negligible and necessarily influence the proposed interpretations. Indeed, as mentioned in the introduction, if the region of origin of the ore used to shape an artifact is not known, the interpretation of its provenance may not yield any result or may be erroneous.

Thus, the lack of reference material available for France regularly leads to the impossibility of determining the provenance of protohistoric artifacts in the country. Let us quote for example the thesis work of Véronique Collin (1990) whose hundreds of analyses of Bronze Age artifacts discovered in a hoard 80 km from Paris (France) could not be associated with certainty to a producing region.

This problem illustrated here for France is true for the entire globe. A recent study proposed that copper present in Bronze Age artifacts found in China would come from South Africa (Sun et al., 2016). This result was criticized by (Liu et al., 2018) who state that the mineral signatures and artifact signatures do not match exactly and more importantly that Chinese mineral signatures are missing to propose an interpretation.

The addition of new data in future years could thus make it possible to define the provenance of certain artifacts whose regions of origin are not (sufficiently) documented.

It is also possible that artifacts for which a provenance was clearly identified could have their result modified if a new mining area added has a signature extremely close to another region. This difficulty in differentiating between similar signatures from distant regions is called overlap and contributes to the difficulty of attributing a provenance to an artifact.

7. Conclusion

The realization of isotopic analysis of lead has been growing for 50 years and so have the compilations of isotopic signature data. The need for reference data for provenance studies is indeed a key element to propose reliable provenances. However, the compilation of these data can present numerous difficulties, notably due to the presence of signatures that do not correspond to minerals and therefore do not allow us to propose solid results. In addition to the cleaning performed in this database, its main advantage lies in the selection of signatures from copper and lead mineralization only. It is thus possible to select only the signatures of deposits of one of these two metals or to take into account areas with very poor mineralization.

Thus, this work proposes more than 7350 lead isotopic signatures that can be directly used at the scale of Europe and the Near East.

However, if this database is cleaned, it does not allow a critical view of the results. In this respect, two main limitations must be taken into account. First, some regions remain under-sampled. Secondly, the lower precision of the lead isotopic signatures obtained with TIMS leads to a

higher dispersion of the signatures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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