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CHEMICAL AND ISOTOPIC TRACERS IN ALPINE COPPER DEPOSITS: GEOCHEMICAL LINKS BETWEEN MINES AND METAL

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With 7 figures

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Abstract

Tracing the provenance of ore minerals used in prehistoric and historic times for copper smelting and extraction is a very hot topic in modern archaeometallurgy. To aid metal provenancing studies, a database of fully characterized Alpine copper mineralisations is being developed as the fundamental reference frame for metal extraction and diffusion in the past. A preliminary account of the protocols and scopes guiding the database development is presented, together with the advanced strategies of multivariate chemometric techniques presently used to interrogate the database and discriminate the ore mineral provenance. It is prospected that the availability of such unprecedented and complete amount of data of Alpine copper deposits may also yield interesting information concerning the geochemical and minerogenetic intepretation of the deposits themselves. Examples of archaeometallurgical applications are provided concerning copper metal provenance from the Agordo area, Veneto, and the recently found prehistoric slags from Milland/Millan, South Tyrol/Alto Adige.

1. Introduction

The provenance of materials is one of the basic questions that archaeologists pose to modern analytical archaeometry (Renfrew and Bahn, 2000). As far as metals are concerned, the vast majority of provenance studies have been based on lead isotope measurements (Gale, 2000; Hauptmann, 2007), simply because the lead isotope systematics of ores and rocks has been widely studied, and reliable models are available to interpret the petrological and geochemical data for chronological and petrogenetic problems. Other large-scale series of analytical studies attempted the chemical classification of ancient metals based on a dozen or so chalcophile elements (Junghans et al. 1968-1974), in the hope that the chemistry of the early copper and bronze objects could be rationalized in terms of a few basic groups reflecting the exploitation of the known metallogenic provinces, already well characterzed and studied from the geological and minerogenetic points of view. The elemental data obtained on the metal objects are generally compared to the elemental abundances measured on representative specimes of the ores, the concentrations of the different elements spanning several orders of magnitudes, and the concentration patterns are taken as indicative of the source (Ixer, 1999; Pernicka, 1999), assuming that the chalcophile elements follow copper during the pyrotechnological smelting processes and there is no fractionation during the copper metal reduction (Pernicka, 2004 and references therein).

However, in both types of study the real story seems to be much more complicated than expected. In the case of the lead isotopes, interpretation problems and inadequate databases of reference samples have often given rise to longlasting controversies (Scaife et al., 1999), and in the case of the chemical tracers, the large numbers of observed metal groups have opened a number of classification and interpretative problems (Waterbolk and Butler, 1965; Pernicka 2004). Furthermore, the use of the copper isotopes ratio has been recently proposed as an additional tracer for the copper ores (Gale et al., 1999), although the use of the copper isotopes as geological and archeometallurgical tracers is still in its infancy (Zhu et al., 2000; Colpani et al., 2007).

In general, archaeometallurgical provenance studies to date have mainly focused on prehistoric or protohistoric copper and early bronze, because later materials and objects are known to incorporate a large amount of metal recycling and mixing, making the issues very complicated. Even when limiting the investigation to the very early copper metallurgy, when copper recycling may pherhaps be excluded, a number of other issues must necessarily be considered, such as the analytical difficulties and the poor statistical significance of the data due to the extreme heterogeneity of the samples, both the ores and the metal artefacts themselves.

To face such complicated issues using a comprehensive approach, an extensive project was initially launched through a collaboration of three research groups: the mineral deposit group at the University of Padova (formerly in Milano), the analytical chemistry group at the University of Insubria (Como), the Museum of Nature of South Tyrol/Alto Adige (Bozen/Bolzano, www.museonatura.it/en/default.asp) and the South Tyrol Museum of Archaeology (Bozen/Bolzano). The collaboration, initially focused on the Eastern Alps mineralizations, has successively been extended to other areas, with the collaboration of other research groups, so that the database now includes most copper deposits of the Western Alps (Piemonte, Val d'Aosta) and Liguria. Further expansion of the project is in progress to include other possible source areas of prehistoric copper.

We here report the strategies used for the database development, and two successful applications to prehistoric slags and raw copper metals.

2. The database of Alpine copper mines: analytical protocols and status

Ore Samples

In the early stages of the project, some of the most well known copper deposits in the Eastern Alps were selected (Fig. 1: *Prettau/Predoi*, Ahrntal/Valle Aurina, Bozen/Bolzano; *Pfundererberg/Montefondoli*, Klausen/Chiusa, Bozen/Bolzano; *Grua vo Hardömbl*, Valle dei Mocheni, Trento; *Martell/Val Martello*, Bozen/Bolzano*; Eyrs/Oris,* Vinschgau/Val Venosta, Bozen/Bolzano*;* and *Stilfs/Stelvio*, Vinschgau/Val Venosta, Bozen/Bolzano; *Valle Imperina*, Agordo, Belluno) and compared with very different minerogenetic deposits from the French Queiras (*Saint Veran*) and the Ligurian Apennines (*Libiola, Monte Loreto*). These earlier investigations (Colpani et al., 2007) were primarily meant to check the performance of the different geochemical and isotopic tracers in the discrimination of the ores sampled from rather different geological settings.

All samples were first hand collected by the research team at the mines and special care was devoted to the selection and characterization of the

Fig. 1: Map of the investigated copper mines in the Eastern and Southern Alps.

19b	Dolostones and limestones
21a	Basement rocks: phyllites with interbedded porphyroids and greenstones
21c	Basement rocks: paragneisses
22a	Marbles
22b	Amphibolites and greenstones
28	Tectonic melanges of Austroalpine basement silices and Piedmont-Ligurian calcschist and metaophiolites
31	Undifferentiated flysch supraophiolithic cover (Cretaceous-Upper Jurassic) pillowed metabasalts and serpentinites
35a	Undifferentiated calcschist
41a	Augengneissess and massive metagranitoids from Late Hercynian intrusions
53b	Valais calcschist Units
94c	Siliciclastic, locally nummulitic, turbidites
98	Adamello and Miagliano calcalkaline plutons
100	Mesozoic basinal and pelagic deposits
101b	Mesozoic shelf deposits
102	Platform and basinal deposits
104	Undifferentiated, mainly clastic, alluvial and shallow marine deposits
105a	Rhyolites, rhyodacites, dacites and minor andesites
105b	Granitoids
106	Phyllites and micaschists

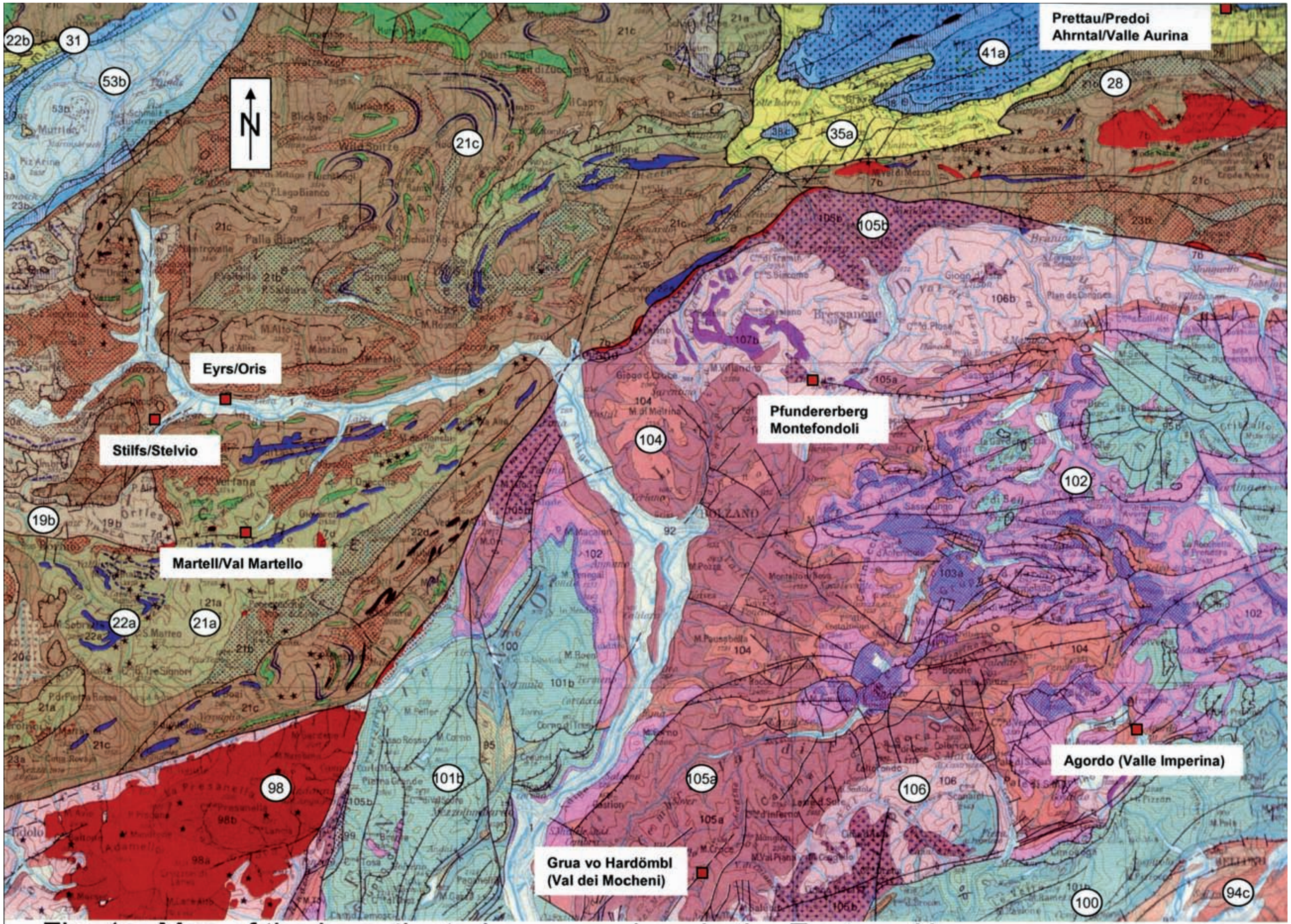

Fig. 1a. Map of the investigated copper mines in the Eastern Alps.

(From: Structural model of Italy, „La ricerca scientifica", n. 114, vol. 3, C.N.R. 1983) samples, in order to be fully representative of the sampled ores. At each mine, following accurate field and mineralogical work, the samples were distinguished between (a) primary Cu-ore mineralization of the deposit (usually chalcopyrite, apart from the Saint Veran mine, where the primary sulphide is bornite), (b) remobilized Cu-sulphides (usually second-generation chalcopyrite), (c) secondary minerals produced by alteration (commonly azurite, malachite, brochantite, chrysocolla, etc.), and (d) native copper. For each mine, depending on ore availability and local minerogenetic processes, a number of samples in the range 5-10 underwent subsequent mineralogical and petrological characterization by ore mineral separation, X-ray powder diffraction identification of the crystal phases, petrographic texture analysis by reflected light optical microscopy, and preliminary chemical analysis by SEM-EDS.

Chemical and isotopic analytical protocols

The fully characterized samples were then prepared for subsequent measurements by mass spectrometry using an ICP-QMS (X serieII – Thermo Electron) equipped whit a collision cell (CC). Collision cell technology was used to avoid mass interferences on analyte ions caused by argon ions (Ar^+) and argon molecular ions ($ArAr^+$, $ArCl^+$, ArO^+...) via reaction with collision gases H_2/He 8% in an RF hexapole (Feldmann et al. 1999). Besides the commonly used Pb-isotope ratios (^{204}Pb/^{206}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb), the analyses performed by ICP-QMS mass spectrometry measured in all samples the abundances of about 60 minor and trace elements, including most transition metals and chalcophile elements, and the rare earth elements. Furthermore, the feasibility of the routine reliable measurement of the ^{65}Cu/^{63}Cu isotope ratio (Ciceri et al., 2005) and its eventual use as a possible ore tracer was tested (Colpani et al., 2007).

The adopted measurement protocol encompasses **(a)** decontamination of the mineral powder by chemical etching, **(b)** complete dissolution by high pressure microwave digestion, **(c)** quantitative measurements of the minor and trace elements performed by external calibration methods based on ICP Multi-element Standard Solution VI (30 elements - Merk Certipur), a REE multi-element solution (Carlo Erba) and single certified standards solutions for Au, Pd, Pt (Fluka), Ti, Ir, Rh (Aldrich) and Sb (Merck) were used. All the solutions were prepared with ultra pure water (18.2MΩ*cm - TOC 4 mg/L - MilliQ Millipore) and HNO_3 (TraceSelect =69.0% - Fluka). The use of clean conditions (class 100 laminar flow hood for all the manipulations of standard solutions and samples, ultrapure reagents and water) allowed to reach extremely low limits of detection (LOD) for most elements. For example the LOD for platinum group elements (PGE) in solution are in the range 0.1-1.0 ppt. **(d)** dilution of the solution to Cu concentration of about 100 µg/l to obtain the same response in counts per second (ICPS) on m/z 63 and 65 mass channels, **(e)** measurement of the ^{65}Cu/^{63}Cu isotope ratio were performed using a modification of the method adopted by Begley and Sharp (1997) to correct the instrumental drift and the mass bias, using as the external control the standard NIST SRM 976 (certified to ^{63}Cu/^{65}Cu = 2.2440 ± 0.0021 (1σ)). In brief, the control standard was read every three sample measurements. In this operational mode, each cycle (standard-sample-sample-sample) was repeated three times to obtain satisfactory statistical standard deviations in the range 0.0003-0.0008 (1σ) on the isotopic ratio ^{65}Cu/^{b}Cu (Ciceri et al., 2005). The dead time evaluated for the detector of the ICP system was about 15 ns, and no proper correction was applied (Held & Taylor 1999; Nelms et al. 2001), furthermore by using the same concentration of copper in each solution, the effect of dead time was minimized. A blank solution was read to perform baseline correction. Matrix effects were investigated but no correction was necessary, thus also sample pre-treatments were not necessary. Isobaric interferences by molecular ions of Zn, Ti, V and Na were evaluated. The repeatability of the analytical method was investigated on two different samples obtaining a good instrumental response. Three samples prepared and measured following the above protocol were sent to the Laboratoire de Sciences de la Terre, ENS Lyon, France for measurement by MC-ICP-MS technique (Marèchal et al. 1999) and independent cross-checking. Of course the copper isotope abundances obtained by the multi-collector technique show better instrumental precision (i.e. 1σ values on the ^{65}Cu/^{63}Cu ratio of about 0.0001), though the absolute values and reproducibility were comparable to the values measured in our laboratory. This means that, although much more precise data can be obtained with MC-ICP-MS, ICP-QMS Cu ratios are equally reliable in terms of accuracy. **(f)** dilution of the sample and standard solutions to Pb concentration of about 10 µg/l and acidification with 2% nitric acid, **(g)** measurement of the $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ isotope ratios. The measurement of the Pb isotope ratios is performed by the bracketing technique using the NIST SRM981 standard as isotopic reference for correction of instrumental mass bias and to optimize instrumental conditions. The following isotopes are measured: ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb. The ^{202}Hg isotope is measured to correct for the overlapping isobaric isotopes at mass 204. Blank values are also always measured and subtracted to each measured values on the samples, which are also corrected for instrumental dead time. The statistical mean final value for each sample is the average of three separate replicate measurements each one obtained on a series of 10 instrumental read outs. The statistical analysis defines and eliminates the outliers following the Huber moving average method. The precision obtained on the Pb isotopic ratios is as follows: $^{204}Pb/^{206}Pb \pm 0.00013$, $^{207}Pb/^{206}Pb \pm 0.00036$, $^{208}Pb/^{206}Pb \pm 0.00060$, which is comparable with the values commonly reported in the geologic and archaeometric literature.

Preliminary results

The detailed results of these earlier studies have been extensively discussed in the reported papers and they will only be briefly summarized here:

(1) the Cu isotopes alone cannot be considered as discriminant for the provenancing of the ore mineralization. There is a measured trend of decrease in the $\delta^{65}Cu‰ = [(^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{NIST}]*1000$ roughly proportional to the temperature of formation of the primary ore, in line with previous observations (Larson et al., 2003), though the variation in the $\delta^{65}Cu‰$ values observed within a single ore body is often comparable with the ranges observed in different mines. However, even if the $^{65}Cu/^{63}Cu$ isotope ratio alone can not be used for provenancing, the observed trend ensures that the Cu-isotope measurement does carry some weight in the total discrimination using multiple parameters (see below).

(2) In agreement with the previous observation, in each copper deposit there is a consistent and systematic decrease in $\delta^{65}Cu‰$ values following the temperature of formation of the different minerals. That is chalcopyrite and bornite show higher values than the secondary minerals present in the same mine, and both have higher values than native copper, if present. This observation ensures that the measurement of the $^{65}Cu/^{63}Cu$ isotope ratio, along with other geochemical parameters, contributes to the discrimination of the type of minerals involved.

(3) As frequently discussed in the literature (Gale, 2000), the measurement of the Pb-isotope ratios of a rock yields information on the age of formation, and possibly on the original reservoir or mixing of the sources of the genetic fluids. Accordingly, the use of the Pb-isotopes alone for unambiguous location of the ore source is not possible, because of the presence of co-genetic ore deposits frequently distributed over large geographical areas. Nonetheless, the measurement of the $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ ratios yields precise information on the age and type of the deposit, thus helping in the definition of the possible geological sources. As in the case of the Cu-isotope data, the insertion of the Pb-isotope data in the ore database has substantial weight in the discrimination procedure.

(4) Finally, the measurement of the large suite of minor and trace elements contained in the ore minerals contain a wealth of information related to the geologic, geochemical, and minerogenetic processes of the ore minerals themselves. Traditionally, archaeometallurgical analyses are confined to some of the most common elements associated with copper in the primary sulphides (Cr, Mn, Fe, Co, Ni, Zn, Ag, Sn, Pb, As, Sb, Bi), and contained in quantities (>1000 ppm) easily measured by readily available analytical techniques such as ICP-OES, XRF, or AAS. These elements are of course invaluable markers of the formation processes and mineral paragenesis of the ore, although there are a number of other elements, often contained in much smaller abundances (down to a few ppm or less) that may be significant tracers as well. The geochemistry of these minor elements cannot be of course discussed in details in this context, but the performed multivariate analysis described below clearly shows that some elements that are rarely analysed by conventional archaeometallurgical protocols (for example Ga, Ge, In, Hg, Tl, Te, Rh, Pd, Pt and all

the REE) have a significant weight as ore tracers. Many of these trace elements are present in very low amounts (commonly in the range 0.1-100 ppm, well above the LOD), however it is to be considered that it is not the absolute concentration that is important for the statistical analysis, but rather the correlation statistics among groups of elements. It is indeed the correlation information, combined to the isotope data that greatly contributes to the discriminating potential contained in the database.

Status of the database

After the preliminary study and the development of the protocols of interrogation of the database, the main effort now is to enlarge the ore database so that it may effectively become the reference source for the Alpine copper deposits. At the moment the characterization and analytical efforts are devoted to the Western Alps deposits located in the Piemonte and Val D'Aosta areas. At the same time an increasing number of ore minerals from Tyrol, Trentino, Veneto, and Friuli are being analysed to complete the source data for the Italian Eastern and Southern Alps.

3. The discrimination of the mines and ores: advanced multivariate data analysis

The chemical and isotopic data are arranged into a matrix characterised by samples as objects (rows) and chemical measurements as variables (columns) in order to carry out chemometric calculation. Data are treated with the chemometric software "The Unscrambler Version 9.5" (CAMO AS, Trondheim, Norway). Data pre-treatment, PCA (Wold et al. 1987) and PLS-DA (Esbensen, 2002, Geladi et al., 1986) models are performed as implemented in the software. Prior to any modelling autoscaling was applied in order to give all variables (major and minor elements, ^{65}Cu/^{63}Cu ratio) the same chance to influence the estimation of the components. Models are validated by cross-validation (using the leave-one-out approach) and the optimum number of components is evaluated with the default criterion of the program together with the interpretation of the plot of the residual variance versus the number of factors and by the Root Mean Square Error of Cross Validation (RMSECV). More details of the analysis and the flow chart of the discrimination strategy are reported in Giussani et al. (2007).

As the Pb-isotope data are not yet available for all samples, they were excluded in the present modelling, although preliminary tests show that they significantly contribute to the analysis and the discrimination strategy. Exploratory PCA analysis allowed investigation of similar features or differences among the samples, without imposing any prior knowledge on the model. The model allows definition of a few new variables, called Principal Components, accounting for the relevant chemical information. The first exploratory analysis carried out on all the investigated chemicals is already sufficient to adequately discriminate the samples into two groups (up to 44% of the information in the first two PC): Primary minerals (i.e. the mineral types a, b above) and secondary minerals (i.e the mineral types c, d above). A starting PLS-DA model was therefore built in order to classify samples according to their primary or secondary character. If there are only two classes to separate, as in this case, the PLS model uses one response variable, which codes for class membership as follows: 0 for members of one class, +1 for members of the other one. The obtained PLS for one y-variable (PLS1) algorithm was then used for classification. The model is able to correctly classify almost all samples according to their mineralogical type with the two principal components (99% of the variability of y explained) with an RMSECV of 0.13.

Simple unsupervised PCA analysis however is not able to adequately discriminate the provenance area of all samples. Therefore a combined PCA and PLS-DA strategy was developed to obtain complete discrimination of all the investigated ore deposits. That is a specific model is defined with the aim to discriminate samples from a specific deposit from all the other samples (as an example the discriminating score plot for the Saint Veran area is reported in Fig. 2), then the discriminated samples of that specific deposits are eliminated from the dataset, and the operation is repeated until all samples have been discriminated by at least one deposit model.

The very interesting part of the study resides in the fact that each deposit is described by a different set of variables, and the weight (i.e. the discriminating power) that each variable has during the analysis can be adequately evaluated through the loading plot. The geochemical significance of each loading plot is irrelevant for the bare statistical discriminating purposes, although it carries a wealth of geological and minerogenetic information that is presently analysed in the frame of the Alpine geological history and tectonics, in order to make each discriminating model meaningful. It is expected that the investigation will contribute substantial minerogenetic information on the formation processes of the deposits.

4. Metal provenancing: the Agordo case

After developing the discriminant models for the ore deposits, the method was tested by exploring the feasibility of provenancing a fragment of smelted copper found in the Agordo area. The copper fragment (sample PA06) was found in the Valle Imperina area, and it was selected because of the very high probability that it was smelted from local ores in historical times, possibly after the 15th century during the operation of the local furnaces by the Republic of Venice.

The copper sample was analytically treated and processed exactly as the ore samples. Of all the developed discriminant models of the deposits, the one selected to separate and identify the Agordo ores is perfectly applicable also to the copper samples (Fig. 3), clearly indicating that the metal was extracted from the local ores. Further discrimination within the Agordo data indicates that the copper was smelted from chalcopyrite, rather than bornite or secondary malachite/brochantite, and that the chalcopyrite is most likely from the Valle Imperina mines. The loadings plot for the principal components used for the discrimination of the Agordo samples is shown in Fig. 4. Although complete interpretation is in progress, it can be readily appreciated that the REE elements are clustered in the upper left corner and therefore they have substantial weight in both the PC1 and the PC2 components. Furthermore some of the chalcophile elements, especially As, Ag, Cd, Sn, Tl, Pb, and some of the siderophiles (Ge) are grouped on the right end of the diagram, indicating a substantial weight in the PC1 component.

Very similar information is obtained using the Pb isotope ratios (Figs. 5 and 6). The values of the Pb isotope data obtained on the copper fragments systematically plot together with the values of the chalcopyrite samples collected in the Valle Imperina

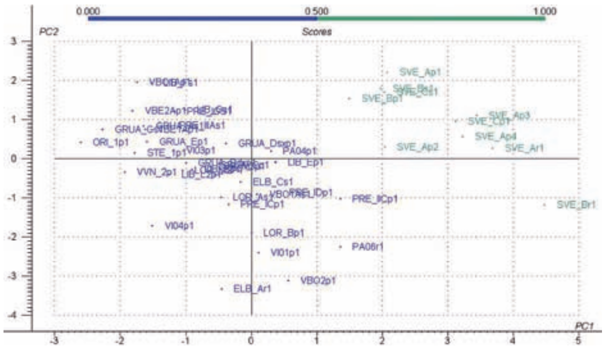

Fig. 2: Score plot of the discriminating model used to separate the Saint Veran samples.

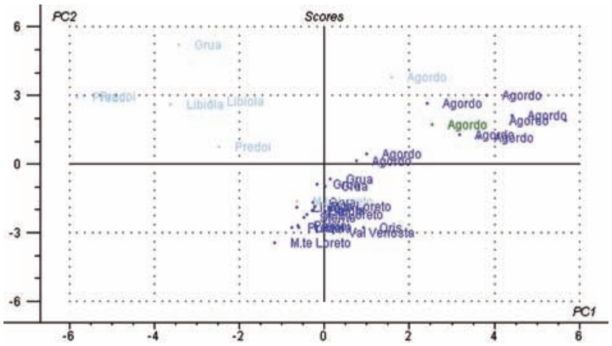

Fig. 3: Score plot of the discriminating model used to separate the Agordo samples. The green point (sample PA06) is the smelted copper sample used in the provenance test.

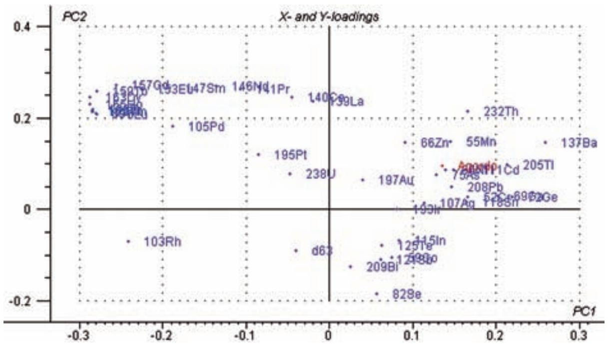

Fig. 4: Loading plot of the PLS-DA components used to discriminate the Agordo samples (Fig. 3).

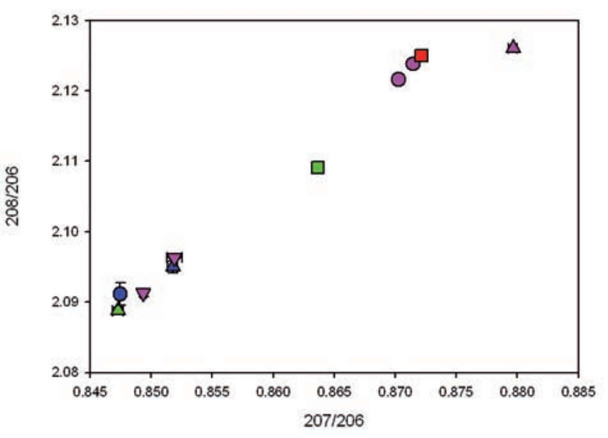

Fig. 5: Diagram of the $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ isotopic ratios. Error bars are indicated but constantly smaller than the data points. The colour of the data points is related to the mineral: magenta/chalcopyrite, blue/bornite, green/malachite. The symbol is related to the mines: circle/Valle Imperina, upper triangle/Valbona, square and lower triangle/Pattine. All mines are located in the Agordo area. The red square indicates the smelted copper sample.

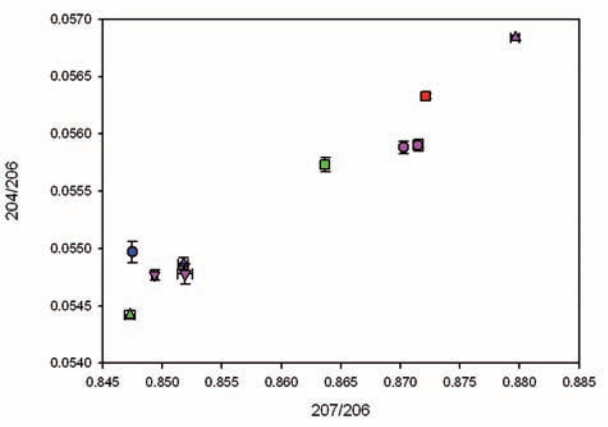

Fig. 6: Diagram of the $^{204}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ isotopic ratios. Symbols and colours as in Fig. 5.

mines, and seem to show a distinctive signature with respect to chalcopyrite and other sulphides (bornite) and secondary minerals (brochantite, malachite, posnjakite) collected in the other mines of the area.

5. Linking slags and metal: the Milland/Millan case

The discriminating power of the database was tentatively applied also to the provenancing of an important find of smelted copper: the only known semiworked copper fragment associated with Eneolithic copper slags in Europe. The copper sample (BFO60-15) was found during the rescue excavation of a site near Milland/Millan (Brixen/Bressanone, Bozen/Bolzano, Italy) dated to about 2700 BC (Dal Ri et al., 2005) yelding a large number of slags produced during Eneolithic smelting of copper from a sphalerite/galena-rich chalcopyrite ore (Colpani et al, 2008).

As in the Agordo case, a small portion of the copper fragment was analysed as the ore samples. The discriminating model of the copper deposits that best describes the data measured on the Millan copper sample is the one derived to separate and identify the investigated mineral samples from the Vinschgau/Val Venosta, that are the Eyrs/Oris, Martell/Val Martello, and Stilfs/Stelvio mines (Fig. 7). There is therefore a strong indication that the ore minerals used to produce the copper fragment were extracted from some deposits of the Val Venosta, an area located about 80 km to the West of the archaeometallurgical site of Millan.

The results support earlier claims that the copper metal fragment is genetically unrelated to the large amount of associated slags found in the excavation, since the Vinschgau/Val Venosta ores have a rather different mineralogical character than the sphalerite-rich chalcopyrite used for the slag production, which was probably mined in the Brixen/Bressanone area. The copper metal was thus either locally produced using a different charge imported from the Vinschgau/Val Venosta, or smelted elsewhere.

6. Conclusions and future perspectives

The intensive analytical and interpretative effort devoted in the last few years towards the development of a geochemical database of the Alpine copper deposit is now starting to produce interesting results. Albeit far from being complete, the database represents an essential unifying tool for the interpretation of ore extraction and metal diffusion in the past.

The application of PCA and PLS-DA analyses to the geochemical and isotopic data proved to be a very powerful implement to discriminate the ore source areas and their geochemical character. The presented preliminary applications to copper metal samples seem to indicate that the analysis can be successfully performed on archaeometallurgical specimens for provenancing and diffusion investigations.

Future efforts are directed towards (1) completion of the mine database, (2) investigation of archaeological copper slags, (3) deeper interpretation of the geochemical tracers and of their behaviour during the smelting processes.

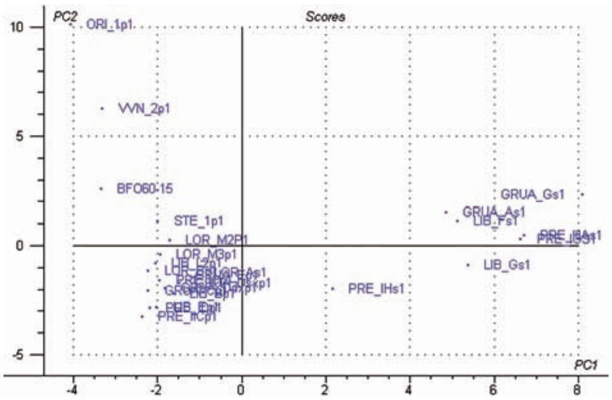

Fig. 7: Score plot for the semiworked metal (sample BFO60-15) found at the Milland/Millan site, near Brixen/Bressanone, Bozen/Bolzano, Italy.

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