Provenance of Early Bronze Age Metal Artefacts in Western Switzerland Using Elemental and Lead Isotopic Compositions and their Possible Relation with Copper Minerals of the Nearby Valais

Florence Cattin¹, ², Barbara Guénette-Beck³, Philippe Curdy⁴, Nicolas Meisser⁵, Stefan Ansermet⁶, Beda Hofmann⁶, Rainer Kündig⁷, Vera Hubert⁸, Marie Wörle⁸, Kathrin Hametner⁹, Detlef Günther⁹, Adrian Wichser¹⁰, Andrea Ulrich¹⁰, Igor M. Villa¹¹,¹², Marie Besse¹

¹ Laboratory of Prehistoric Archaeology and Human Peopling, Department of Anthropology, University of Geneva, 12 Gustave-Revilliod, CH-1211 Genève, Switzerland
² Present address: Geology, Earth and Environmental Sciences, Katholieke Universiteit Leuven, Celestijnenlaan 200 E, B-3001 Heverlee, Belgium
³ Geosciences Department, University of Fribourg, Musée 6, CH-1700 Fribourg, Switzerland
⁴ Musées cantonaux du Valais, Rue des Châteaux 14, CH-1950 Sion, Switzerland
⁵ Musée cantonal de géologie, Quartier UNIL – Dorigny, bâtiment Anthropole, CH-1015 Lausanne, Switzerland
⁶ Natural History Museum in Bern, Bernastrasse 15, CH-3005 Bern, Switzerland
⁷ Schweizerische Geotechnische Kommission, ETH Zurich, Sonneggstrasse 5, CH-8092 Zürich, Switzerland
⁸ Swiss National Museum, Sammlungszentrum, Lindenmoosstrasse 1, CH-8910 Affoltern a. Albis, Switzerland
⁹ ETH Zurich, Department of Chemistry and Applied Bioscience, Laboratory of Inorganic Chemistry, HCI G113, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
¹⁰ Empa - Swiss Federal Laboratories for Material Testing and Research, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland
¹¹ Institut für Geologie, Universität Bern, Baltzerstrasse 3, CH-3012 Bern, Switzerland
¹² Dipartimento di Scienze Geologiche e Geotecnologie, Università di Milano Bicocca, I-20126 Milano, Italy

Florence Cattin (corresponding author) – mail@florencecattin.com, tel. +32 16 327259, postal address: Celestijnelaan 200 E, B-3001 Heverlee, Belgium
Barbara Guénette-Beck – barbara.guenette@gmail.com
Philippe Curdy – Philippe.Curvy@admin.vs.ch
Nicolas Meisser – Nicolas.Meisser@unil.ch
Stefan Ansermet – Stefan.Ansermet@unil.ch
Beda Hofmann – beda.hofmann@geo.unibe.ch
Rainer Kündig – kuendig@erdw.ethz.ch
Vera Hubert – Vera.Hubert@snm.admin.ch
Marie Wörle – Marie.Woerle@slm.admin.ch
Kathrin Hametner – hametner@inorg.chem.ethz.ch
Detlef Günther – guenther@inorg.chem.ethz.ch

Published in "Journal of Archaeological Science  doi:10.1016/j.jas.2010.12.016, 2011" which should be cited to refer to this work.

http://doc.rero.ch
ABSTRACT

Ten Early Bronze Age (BzA1, 2200-2000 BC) copper artefacts from the central Valais region from Switzerland were studied for their elemental composition and lead isotope ratios. In order to answer the archaeological question of a local copper supply, a database for copper minerals across the Valais (Switzerland) has been established. This database contains 69 data on lead isotope ratios as well as additional information on the minerals and geochemical associations for copper minerals from 38 locations in the Valais. Comparisons of the artefacts were also made with data pertaining to minerals from various deposits from Europe and Anatolia taken from the literature. The provenance of the materials is very diverse. Some of the data are compatible with the data from the copper mineral deposits of the Valais region. Moreover, three copper lunulae were identified as possibly Tuscan, which demonstrates contacts between Italy and the Valais region. This pattern also establishes a multiplicity of provenances for the metal and cultural influences in the Alpine environment of the Rhone Valley of Switzerland at the beginning of the Early Bronze Age.

KEYWORDS

Early Bronze Age, Valais (Switzerland), copper artefacts, copper ores, material provenance, database, lead isotope ratios, elemental composition, ICP-MS inductively coupled plasma mass spectrometry, LA laser ablation

1. INTRODUCTION

In the context of the European Alps at the beginning of the Early Bronze Age (BzA1, 2200-2000 BC), some specific areas are affected by a particularly early appearance of an abundance of copper objects: the Singen necropolis in Germany, the Franzhausen and Gemeinlebarn cemeteries in Austria, and the central Valais region in Switzerland (fig. 1). Currently, the research concerning these Early Bronze Age centres lacks a satisfying explanation for such abundant copper artefact findings. Similar manufacturing techniques and artefact types may indicate both circulation of objects and the transfer of knowledge between the different regions. In order to evaluate the possibility of inter-regional links between these major Early Bronze Age sites, detailed archaeological research coupled with archaeometric investigations for all regions is necessary. This paper focuses primarily on the Valais region in Switzerland, for which 29 copper artefacts attributed strictly to the BzA1 are known. The goal of this work is to thoroughly investigate two major propositions that could explain this early and significant presence of copper in the Valais region: (1) a local ore supply with on-site manufacturing, (2) an extensive external influx of raw materials and/or artefacts from outside regions. From a broader perspective,
this initial research pertaining to copper provenance also seeks to address the questions concerning social, economic, technological, and cultural networks during the beginning of the Early Bronze Age in the Valais region. These networks may very well be shown to have impacted the rapid development of a new social system in the Alps region and its surroundings, as evidenced by David-Elbiali and David (2010).

First, one possible reason for the early emergence of this Valaisan centre is a probable local ore supply and manufacturing techniques. Regarding the local ore supply, the copper deposits in the Valais region of the Swiss Alps, and in particular those of the Val d’Anniviers, have been the subject of previous proposals by researchers who suggested that they were possible procurement sources for copper during prehistory (Gallay 2008; Rychner and Fasnacht 1998). In fact, their exploitation has been put forth as a hypothesis to explain the rapid development of the Culture du Rhône in Western Switzerland, and its ensuing prosperity (Gallay 2008). However, in this region, evidence of mining activities exists but is either primarily related to later time periods (i.e. during the 16th to 20th centuries AD) or is undated. About manufacturing techniques, evidence for copper production is rare. Residual traces of furnaces and slags have been found at Zeneggen/Kasteltsguggen (Valais, Switzerland) (Gallay 2008), but were attributed to either the Middle or the beginning of the Late Bronze Age.

Thus, the absence of clear evidence for Neolithic/Early Bronze Age copper mining and processing in the Valais suggests that a more dispersed or wide ranging transfer network of objects is more likely. According to the second proposition mentioned above, the high concentration of copper artefacts in the Valais may be linked to an external influx, whose physical nature (artefacts, raw materials—in the form of ingots or ores—and/or techniques), mode of transport (mobility of goods, people, ideas or know-how), and origin need to be more clearly defined. Thus far, little is known of the path of distribution or the dominant regions of influence in this area. However, in the Alpine area and its surroundings, the presence of artefacts of similar types attests to some interaction between different regions. Even if the typology of some copper artefacts, such as copper pins with a paddle shaped head, closely resembles the discoveries in southern Germany (e.g. in the Straubing and Singen groups), connections that affected central Valais at the beginning of the Early Bronze Age remain, for the most part, poorly defined (David-Elbiali 1998).

Archaeometric studies of a collection of 14 Early Bronze Age (BzA1) metal artefacts from Western Switzerland were previously conducted by the Stuttgart research group (Junghans et al. 1960, 1968-1974). Using elemental composition on more than 22000 artefacts across Europe, they intended to shed light upon the origin and development of metallurgy in Europe. The investigation concerning these Early Bronze Age artefacts from Western Switzerland highlighted, on the one hand, relationships with German artefacts that were deduced from similar compositional patterns (groups A and B2, characterized mainly by arsenic >250 mg/kg, antimony >1200 mg/kg and silver >1000 mg/kg contents typical for copper issued from fahlores), and, on the other hand, a clear difference given the absence of such groups as C2, C2 AB, C2C, C2D, which are defined as fahlores and contain a high bismuth content, superior or equal to 200 mg/kg (Junghans et al. 1968-1974). The accentuation of a specific development in Western Switzerland was demonstrated for the late phase of the Early Bronze Age (Junghans et al. 1968-1974),
in tandem with the development of local types and the maintenance of technology using sheets of metal (e.g. “épingles tréflées”). During the late phase of the Early Bronze Age, the authors detected changes in the compositional patterns, which they linked to an influence from south-eastern Europe and the Mycenaean world. Despite the fact that these compositional pattern groups remain in use as a classification tool, the Stuttgart studies do not sufficiently fulfil all aspects of the scientific goals concerning the origin and development of metallurgy in Europe, and more specifically in Western Switzerland. As exemplified by more recent research studies in the Alpine area, the use of lead isotope ratios and the elemental composition for sourcing studies gives new weight to the question of copper circulation in prehistory (Artioli et al. 2009; Cattin 2008, 2009; Cattin et al. 2009b; Höppner et al. 2005; Niederschlag et al. 2003). In parallel to these archaeometric studies, surveys and fieldwork studies supplied new information concerning the prehistoric mining activities and ore processing in Austria (Krauss 2003; Rieser and Schrattenthaler 2004; Stöllner et al. 2004), Eastern Switzerland (Schaer 2003; Schaer and Fasnacht 2002), France (Bailly-Maître and Gonon 2006; Barge et al. 2003), and Italy (Artioli et al. 2007; Poggiani Keller 1999-2000; Poggiani Keller et al. 2006).

It is now necessary, within this research context, to undertake a thorough evaluation of the mining potential in the Valais region, including archaeological survey, field excavations, and the identification of possible procurement sources for Valaisan artefactual copper using analytical methods providing access to the elemental and isotope compositions. A major problem concerning the recognition of direct evidence of mining activities in the Valais is the possibility of destruction by more recent activities and/or the disappearance of evidence under later concentrations of mining waste. Therefore, comparison of the metal compositions of artefacts and ores using lead isotope ratios and chemical elements is known to be the most promising way to identify and narrow potential provenances, and to exclude those which are incompatible (Stos-Gale and Gale 2009). Thus, the comparison of an archaeological data set from the Valais region with a database for Valaisan minerals is supposed to provide new indications for the development of a local supply. Indeed, a significant database on silver and lead minerals has been elaborated within the archaeometric research program of Guénette-Beck (2005). However, it does not fulfil adequately the conditions for an application to copper sourcing, since the lead isotopic signatures of different types of minerals may be subject to distinct mineralization events. Hence, as a prerequisite for the sourcing studies and for a possible highlight of local ore mining, we obtained new lead isotope data for copper minerals across the Valais in order to allow a comparison with the copper-based artefacts. Additionally, we aimed to gather comparative information on ores from across Europe and Anatolia from the literature to shed new light on potential copper transfer over longer distances.

2. THE CULTURAL CONTEXT OF THE EARLY BRONZE AGE IN THE EUROPEAN ALPS

In the areas surrounding the Alps, the Bronze Age begins at about 2200 BC. During the initial phase of the Early Bronze Age, several cultural groups occupied well-defined areas in the peripheral regions of the Alps (David-Elbiali 2000): the Leithaprodersdorf group at the east end of the Alpine arc, the Unterwölbling, Straubing and Singen groups to the
north of the Eastern Alps, the Bronze ancien rhodanien in the middle Rhône Valley, the Campaniforme barbelé or Epicampaniforme in Provence (France), the Polada culture on the southern edge of Lake Garda (Italy), and the Ljubljana culture in Slovenia. The main Alpine valleys also show evidence of a scarce human presence for this same period. In the Grisons (Switzerland), this evidence is attributed to the “inner Alpine groups”.

In Western Switzerland, the Rhône Valley is settled at least since the Middle Neolithic (Gallay 2008). David-Elbiali (1998, 2000) attributes the archaeological discoveries linked to the beginning of the Early Bronze Age to the Preliminary Phase of the Culture du Rhône (BzA1). This phase is dated between 2200 BC and 2000 BC on the basis of a new chrono-typological classification system. The sites are primarily found in the central Valais region with the exception of two external finds (fig. 1): a single pin with a decorated paddle shaped head found in the commune of Etrembières (Haute-Savoie, France; David-Elbiali 2000); and a tomb in Thun-Wiler (canton of Bern, Switzerland; Hafner and Suter 1997). Various copper items such as bracelets with spiral-ends made from wire, disk-head pins, paddle shaped head pins (with or without a rolled end), and curl rings and pendants (lunulæ) from sheets of metal, have been recovered. Some of these artefacts are decorated with engraved geometric motifs composed of parallel lines, hatched bands, and rows of hatched triangles.

3. EXPERIMENTAL

3.1. Selection of the copper artefacts

This study is based on a collection of ten archaeological ornaments representative of the first phase of the Early Bronze Age (commonly abbreviated BzA1, 2200-2000 BC)(fig. 2). The objects have been selected from three sepulchral sites found in the central Valais region of Switzerland. Two pins with a paddle shaped head and five lunulæ originate from the site of Ayent/Les Places. Tomb 2 from Conthey/Sensine furnished a pin with a paddle shaped head. A small deposit in the dolmen MXI at Sion/Petit-Chasseur produced a pin with a paddle shaped head and “à tige en sabre” as well as a ring made of a thin rolled sheet of metal. The material can be attributed to the BzA1 phase on the basis of stratigraphic and/or chrono-typological considerations (David-Elbiali 2000).

3.2. The lead isotope database for the Valais region and Europe

The Valais is part of the alpine system, for which the highly complex orogenesis is well-known. Its relief results from the collision of the European and Apulo-African plates, which involved two oceans (Valais and Piemonte) and a micro-continent (Briançonnais). In turn, these plates already had a complex history dating back around two billion years. The intense folding that occurred led to the thrust and overlapping of sediments and crystalline bedrock, sometimes over hundreds of kilometres. At the same time, deep strata underwent significant metamorphosis, gradually weakening from the internal to the external Alps. This turbulent genesis is naturally reflected in the multiple characteristics of mineralizations; when we consider the morphology, the nature of the host rock, the mineralogy, the chemical composition and the geological history.
The lead isotope field of the copper minerals in the Valais is thus foreseen to be very variable. In order to document the lead isotope variability, we chose to document most of the Valaisan copper mineralizations reported by the Swiss Geological Commission (Schweizerische Geotechnische Kommission), having the corollary of a mean of about two samples per ore body. This sampling procedure aimed at allowing a general overall picture of the lead isotope field of the copper minerals in the Valais. The sampling of the minerals has been based on the geological collections from the Musée cantonal de géologie in Lausanne, Switzerland and from the Naturhistorisches Museum in Bern, Switzerland.

A description of the 38 investigated Valaisan mineralizations is detailed in the online supporting material. It includes the geographical and geological locations, the minerals the geochemical associations, and the lead isotope ratios. The strong representation of the Val d’Anniviers, Val de Zinal and Val de Moiry depends on the high density of copper outcrops. The investigated ore bodies appear in two geological domains: the Penninic Domain (Middle, Upper, and Lower) and the Helvetic Domain. Generally, the copper minerals – mainly chalcopyrite and minerals of the tennantite-tetraedrite series – are associated with secondary minerals (malachite, azurite), and other additional minerals that will influence the geochemical associations.

Additionally, a large database has been established for metallic minerals across Europe, and Anatolia in order to allow a comparison of the archaeological artefacts with all the available ore sources data (see references in Cattin et al. 2009b, database provided on request; see also Cattin et al. 2009a for additional references). As very little is currently known about copper networks during the Early Bronze Age, we selected the published data without a priori knowledge of the mines that either were, or could have been, exploited prehistorically. The database contains data concerning lead isotope ratios as well as the type of the copper minerals from different locations. The data from the different locations has been separated into 18 geographic regions to allow for the classification and allocation of the objects. Unless otherwise indicated, these data are assumed to have an analytical uncertainty of 0.1 %.

4. ANALYTICAL METHODS

For the mineral samples, previous analytical work (see references in online supporting material) allowed the description of the minerals and geochemical associations present in the investigated mineralizations. Thus, solely lead isotope ratios were newly determined, in contrast to the archaeological artefacts, which were characterized for both lead isotope ratios and for elemental composition. For this study, three different types of analyses were carried out. The determination of the lead isotope ratios was performed after the digestion of the samples and the pre-concentration using a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). The MC-ICP-MS technique provides the best performance for isotope ratio determinations in terms of precision (Niederschlag 2003; Klein et al. 2004; Ulrich et al. 2004). In addition, the elemental composition of the solid artefacts was directly determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) or through x-ray fluorescence. The primary advantages of
Laser ablation include an increased sensitivity compared to common x-ray techniques, a minimum of invasiveness, and the absence of sample preparation prior to analysis.

For the determination of the lead isotope ratios, 1-3 mg of material was sampled from both the archaeological artefacts and the minerals within the laboratories of the owning institutions. All samples were obtained by either scraping with a scalpel or by drilling with a 1 mm diameter bit drill column. After removal of the corroded surface, the core metal shavings were separated from the remaining corroded material under a binocular microscope. Lead isotope analyses were performed using a Nu Instruments™ multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Laboratory of Isotope Geology at the University of Bern. The samples were previously dissolved in aqua regia and pre-concentrated using a cation exchange resin according to the procedure by Villa (2009). All samples were spiked with thallium for correction of the mass bias. The measured values of NIST SRM 981 compare favourably with those reported in the literature (Tab. 1). Thus, we are able to present here the measured values without any further bias correction. The errors indicated for individual analyses (artefacts in table 2; minerals in online supporting material D) are calculated as the square root of the square in-run error plus the square of the dispersion of the standard measurements for the corresponding day of analysis.

In addition to the above mentioned analyses performed by optical emission spectrometry OES (Junghans et al. 1968-1974) and X-ray fluorescence spectrometry XRF (Siemens wavelength-dispersive instrument; Voute 1995), new element concentrations were determined using LA-ICP-MS. Two different instrumentations were used for the LA-ICP-MS analysis in two different laboratories at ETHZ Swiss Federal Institutes of Technology Zürich and at EMPA Swiss Federal laboratories for Material Technology and Research. For the analysis at ETHZ, an ArF 193 nm excimer laser (Lambda Physik, Göttingen, Germany) equipped with homogenisation optics and microscope ( Günther et al. 1997) was used for laser ablation. An average laser spot of 80 μm was selected for analysis (n = 5). The laser was operated at a frequency of 4 Hz. An in-house built ablation chamber with a length of 30 cm long and 3.5 cm wide was used for hosting the samples. He (1 L/min) was used as carrier gas which was mixed with 0.8 L/min Ar before entering the ICP. The laser system was coupled to a quadrupole ICP-MS (ELAN 6100 DRC II, Perkin Elmer, Norwalk, USA). The concentrations were determined using the reference material BAM 386 and NIST 610 for calibration.

At the EMPA an in-house modified 266 nm Nd:YAG LASER (Quanta-Ray DCR-11, Spectra-Physics), running at 10 Hz and 4 mJ pulse-1, was used in combination with a quadrupole ICP-MS (Elan 6000 PE/Sciex) (for more details, see Barrelet et al. 2008). The ICP-MS was operated under standard hot plasma conditions. The gas flow rates were set to a value of 0.95 L/min for the carrier gas, 16 L/min for the plasma, and 1 L/min for the auxiliary gas. The RF power was set to 1200 W. In order to account for the heterogeneity of the copper-based samples, the aperture was set to a spot size of about 300 μm. An external calibration strategy with well characterised matrix-matched standards and standard reference materials with similar chemical and physical properties was chosen for the laser ablation analysis of the archaeological samples. Therefore, different certified standard reference materials, i.e. BAM 211, BAM 227, CRM BNF C50.01-2, as well as
one self-analysed copper alloy, i.e. the copper-tin-lead alloy G-SnBz10, were used as the calibration standard. A mountable laser cell developed by EMPA, which also allows direct mounting of the cell on larger objects, was used for all the LA-ICP-MS analyses. The cell design is an advanced prototype of the mountable cell reported by Devos et al. (1999).

5. RESULTS AND DISCUSSION

The results of the chemical composition of the objects are summarized in table 3. The analyses published in the SAM project (Junghans et al. 1964, 1968-1974) are presented along with the new ones obtained by LA-ICP-MS techniques. An evaluation of the SAM data was performed by Pernicka (1984); he found that the data were in general of acceptable quality, with the exception of antimony due to interferences from iron. This result was reaffirmed recently (Müller, Pernicka 2009). The discrepancies with the new data may be explained by the differences in the analytical equipment (emission spectroscopy versus mass spectrometry), the sampling procedures, e.g. punctual analyses by laser ablation are more affected by micro variations in the matrix (especially lead inclusions), the detection limits, and the analytical accuracy and precision. As a classifying tool, the compositional patterns are listed in table 4 and sorted according to the groups defined by Junghans et al. (1968-1974) and the copper types described by Pernicka (1990). These classifications are based on the elements arsenic, antimony, silver, nickel and bismuth. Thus, they do not enable discrimination between unalloyed copper and bronze. As a confirmation of the suitability of the SAM chemical analyses for this study, both replicate analyses with old and new methods are in complete accordance within the copper types defined by Pernicka (1990), which are therefore chosen at the interpretation stage. The lead isotope ratios are presented in table 2.

5.1. Compositional patterns of the artefacts

The artefacts can be sorted into three typological groups on the basis of object type (tab. 3): group A is made up of five lunulae (740d, 740e, 740f, 740g, 740h); group B is composed of four pins (733, 735, 40249, A-11603); and group C is represented by a single ring (40250).

Whereas the pins and the ring (groups B and C) are composed of unalloyed copper, a differentiation can be observed in group A on the basis of tin content. The lunulae are of two types: (I) copper (740d, 740f, 740h), and (II) copper/tin composition, with a content of 39000 mg/kg and 22000 mg/kg of tin for lunulae 740e and 740g respectively; the copper/tin composition of group A(II) figures as an outlier in the data set from the beginning of the Early Bronze Age (BzA1). Such tin content is found in Late Neolithic and Bell Beaker contexts throughout Europe, and may not necessarily be the result of alloying (Cattin et al. 2009b). Within contemporaneous contexts from the beginning of the Early Bronze Age, some specific daggers found in the Singen necropolis (Konstanz, Germany), named “Atlantic”, present a higher content, between 50000 and 90000 mg/kg tin (Krause 1988).

The copper types (tab. 4) fit the metallic patterns determined in the well-studied
Northeastern Alpine area and are commonly used as a reference for the surrounding regions (Krause 1988; Krause and Pernicka 1998; Krause 2003). In group A(I), the purity of the copper does not allow for any indication of the type of source minerals; this could be due to the scarcity of mineralogical associations in the ore source (e.g. oxide minerals or native copper), as acquired during the metallurgical process through refining of ores with a high content of associated minerals (e.g. minerals from the tennantite-tetrahedrite series). As for group A(I), the compositional pattern of group A(II) provides no specific indication of the type of the source minerals due to the very low trace element contents.

According to table 4, the four pins of group B correspond to the fahlore type copper with nickel defined by Pernicka (1990). This is in accordance with their very high contents of arsenic, antimony, and silver, as shown in table 3. The pin with a “tige en sabre” (40249) contains less arsenic. We suggest that they were all manufactured with a copper smelted from ores of the tennantite-tetrahedrite series, and more specifically from the argentiferous tetrahedrite for those with a higher content of silver. It is also pertinent to mention here the particularly high content of nickel in the composition of the pins, somewhat similar to that of the cobalt content. A good parallel of this composition, with relatively high contents of arsenic, antimony, silver, and nickel, is found in the artefactual copper from the Singen cemetery (Konstanz, Germany), where a specific sub-group within the fahlore copper type has been identified: the “Singen Metall” (Krause 1988).

The ring from group C has a very high arsenic content (15900 mg/kg) whereas silver, antimony, and nickel are all one order of magnitude lower. This is consistent with the smelting from ores of the tennantite-tetrahedrite series.

5.2. Lead isotope patterns of the artefacts

For the description and interpretation of the data (detailed in table 2), the lead isotope ratios of minerals and artefacts are represented graphically. In regard to the lead isotope ratios on the \( ^{208}\text{Pb}/^{206}\text{Pb} \) and \( ^{207}\text{Pb}/^{206}\text{Pb} \), \( ^{207}\text{Pb}/^{204}\text{Pb} \) and \( ^{206}\text{Pb}/^{204}\text{Pb} \) scatter diagrams (fig. 3 and 4), three out of the five lunulae -group A(I), i.e. 740d, 740f, 740h- appear to cluster together. Thus, they derive very probably from the same ore lot or charge, and perhaps even the same ore source or mine.

The two lunulae 740e and 740g from group A(II) are close together on the graphs of figures 3 and 4, and they appear in an area which is distinct from group A(I). It is more likely that the variation in the lead isotope ratios between groups A(I) and A(II) is due to a different ore lot or ore source than to a difference in the manufacturing process. It is well known that fluxes, additives and smelting conditions influence the elemental pattern (Pernicka 1990, 1999). In terms of the lead isotopes, it has been shown that the chemical reactions in smelting and refining do not alter the initial ratios (Gale and Stos-Gale 2000). However, other components such as fuel wood or furnace clay might influence the later lead isotope ratio of the metal. Since the lead content of the copper minerals usually appears in the range between 300 to 5800 mg/kg (tab. 5), but the lead content in the other materials varies in the lower ppb (\( \mu \text{g/kg} \)) to ppm (mg/kg) range only, the influence of the other ingredients is assumed to be negligible. For example metal contents of plant materials like wood is relatively low and primarily dominated by alkaline and earth
alkaline metals such as K or Ca (Ulrich et al. 2009), whereas heavy metal elements like lead contents are normally at the μg/kg to lower mg/kg levels (Hagemeyer 1992). Even in the more anthropogenic influenced 20th century soils, which show an enhanced lead accumulation due to emissions of lead in fuel, the lead content does not typically exceed maximum concentrations of 20 – 100 mg/kg (Walthert et al. 2003).

In regard to the pins of group B (733, 735, 40249, A-11603), and the ring of group C (40250) on figures 3 and 4, the different lead isotope ratios show that it is probable that they were manufactured using copper from different sources than the lunulae.

5.3. The database of Valaisan copper minerals and its application to sourcing studies

The copper minerals exhibit a variation ranging from 0.9188 to 2.2032 for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio, from 0.3973 to 0.9432 for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, from 15.423 to 16.921 for the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio and from 16.352 to 42.591 for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio. In fact, as exemplified by the ratios $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, the scattering of the data reflects mainly an intense recycling with a radiogenic lead contribution. The radiogenic nature of some of the data is explained by the massive presence of uranium in the mines of Grand-Alou (Nendaz), La Creusaz/Les Marécottes (Salvan), the Col des Mines (Riddes), and Grand Alou-Plan du Fou (Isérables/Nendaz). Thus, the lead isotope signatures have been intensively enriched with uranium. In fact, for ore bodies issued from a totally or partially sedimentary process, like Six-Blanc (Orsières), a radiogenic signature is a common fact due to the presence of minerals with a high uranium content in the host sediments. After radiogenic lead is released by these sediments, it subsequently precipitates with the copper, and regularly gives to the copper a paradoxical future age. Conversely, for the mineralization of Heiligkreuz, also from a sedimentary process, the age deduced from the lead isotope analysis is older than the expected Triassic age (about 230 MA) of the mineralization. The comparison of the lead isotopic data of the mineralizations with the lead evolution model of Kramers and Tolstikhin (1997) mirror their known origin as mixtures between the old upper crust and the young upper crust. Only Laulosses’ datum (Ayer) seems to be reflecting an origin in more basic (mantle-like) rocks. The mineralization of Schonec shows very “old” signatures that are very surprising in the context of the Alpine orogenesis.

The comparison of the Valaisan copper minerals taken as a whole with selected mining areas within the Alps and across Europe shows numerous overlaps (Cattin et al. 2010). In regards to this result, it would be theoretically worthwhile to consider each mine in the Valais in contrast to all European mineralizations included in the database, to get a better idea of overlaps or incompatibilities. It is generally admitted that a substantial number of about 30-50 analyses per ore body is necessary (Gale 1989). A mean of two analyses for each mineralization – as presented here – is not enough to define each isotopic field, because a small variation of the data can either be due to a real small range in the isotopic ratios, or represent a part of the whole field. However, the Valaisan data at the regional scale are distinct enough in some areas to tell one from the other. This is exemplified by the Italian data from Tuscany and the Apuan Alps (Stos-Gale et Gale 1992; Stos et al. 1995; Lattanzi et al. 1992), that show no overlaps with the Valaisan data.
Additionally, some mineralizations show a greater variation in their lead isotopic data, as for example Baicolliou, Bourrimonts, Grand Alou-Plan du Fou, Lapine Rousse, Pétolliou, and Tignousa. As the isotopic fields that show a wide range are less robust in terms of a possible provenance, these ore bodies are not suited for provenance studies using lead isotope ratios.

5.4 A possible local copper supply during the beginning of the Early Bronze Age

In general, the Valaisan copper deposits’ signatures are spread out enough to cover almost the entire Alpine field. However, despite the spread of the geological data that can be observed on figures 5 and 6, almost all the studied archaeological objects appear in the densest zone of the minerals from the Valais region. Thus, at this scale, the hypothesis of a local supply source is compatible with the data.

A closer look reveals the compatibility of only one analysis with a specific Valaisan mineralization: the lunula 740e from copper/tin group A(II) with the copper/lead/zinc mineralization of Massaschlucht “Massagrube” (Brig, Valais), whose isotopic field is defined by two analyses on copper minerals and two analyses on lead minerals (tab. 6). The elemental analysis of lunula 740e can be seen on table 3. It indicates a lead content of 4100 mg/kg, which is in perfect accordance with the expected geochemical associations in the Massaschlucht “Massagrube” mineralization (see online supporting material). If the copper of the lunula 740e could be consistent with an origin from this mine, the same cannot be said for the lunula 740g.

In summary, although other alternatives cannot be ruled out in the quest to explain the massive presence of copper artefacts in the central Valais region during the beginning of the Early Bronze Age (such as the social value of technical know-how, political and military dominance, or the control over transport and communication routes), it is likely that the exploitation of one or more local copper resources lead partly to economic prosperity, the expression of which is obvious in the depositing of valuable copper artefacts in tombs. For the remainder of the artefacts, the absence of a perfect concordance with the Valaisan mines analysed thus far does not weaken the hypothesis concerning mining activities for the investigated period in the Valais region. Ores or ingots from several sources could have been mixed during the time that inevitably passed between the mining of the ore and the production of the artefacts. However, lead isotope data suggest that the artefactual copper might be linked to local mining activities as well as to trade with other mining districts.

5.5. Evidence of circulation networks during the beginning of the Early Bronze Age

Given the compatibility of the data with the Valaisan mineralizations, as shown above on figures 5 and 6, we consider a local ore exploitation to be more likely than intensive exterior supply. However, it can not be denied that each single analysis for the BzA1 artefacts is also compatible with numerous mineral data from across Europe and Anatolia, even more so if we consider the possibility of the mixing of ores and recycling of metal of different provenances. A pattern of under-constrained signatures due to mixing was described for Imperial Roman lead and obscured the identification of the sources (Boni et
However, we must note that industrial mining and trading was likely much more developed in Imperial Roman times than at the end of the third millennium BC.

The group A(I), with the three lunulae, does appear to warrant a closer look. The similar lead isotope ratios and the identical chemical composition both indicate that the lunulae may share a similar type of source ore and/or manufacturing process, as well as a similar provenance. However, as shown on figures 5 and 6, the lead isotope ratios are not compatible with any of the Valaisian mineralizations, especially on account of their high $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, and the hypothesis of mixing would require an even more extreme source which is not documented. Hence, the lead isotope ratios of the objects were compared graphically with those of minerals from other possible exterior sources. It appears that the lead isotope ratios of the group A(I) plot in a very unusual Pb isotopic area. The comparison with the ore database, based on literary data, permits the exclusion of several regions as possible supply sources: Anatolia, Austria, Cyprus, Czech Republic, England, France, Germany, Greece, Ireland, Macedonia, Sardinia, Serbia, Slovakia, and Wales. Among all available possibilities, only the data deriving from Bulgaria, Italy, and Spain match the artefacts (fig. 7). Since Bulgaria is quite distant from the Valais region and the data of the mine of Lerkavitsa (central Rhodope, Bulgaria)(Gale et al. 2000) is based on analyses of galena only, it was also excluded. Contrary to this, the Massa Marittima, Campiglia Marittima, and Bocchegiano mining districts in Tuscany, Italy (Stos-Gale and Gale 1992; Stos-Gale et al. 1995), and the Pozo de Aquja mine (Mazzaron, Murcia) (Stos-Gale et al. 1995) in the south of Spain present analyses of various copper minerals (sulfide and oxide minerals). Given the purity of the artefact copper, neither of these possibilities could be excluded. Nevertheless, their nickel content allows for the exclusion of the Mazzaron district, where nickel is absent.

Thus, the Tuscan mining district (Italy), which is primarily known for its Etruscan and Medieval activities (Chiarantini et al. 2009; Costagliola et al. 2008), appears to be a good candidate for the provenance of the copper of the lunulae from group A(I). The discovery of a copper ingot related to the Early Bronze Age near Serrabottini (Massa Marittima, Tuscany) proves that this mining district was in all likelihood exploited earlier (Aranguren and Sozzi 2005; Aranguren et al. 2007). Moreover, in this region ore smelting is demonstrated by Eneolithic copper slags from San Carlo and Orti Bottagone (Artioli et al. 2007). Several other artefacts support ancient activities in Tuscany: a copper ingot from Cugnano (Monterotondo Marittimo, north of Massa Marittima, Tuscany, Italy); a stone hammer from Massa Marittima, which is similar to hammers found at Libiola and Monte Loreto where mining activities were undertaken during the second part of the fourth millennium BC, and, only at Monte Loreto during the first part of the third millennium BC (Maggi and Pearce 2005); axes and ingots hoards in the Campiglia Marittima area (Aranguren and Sozzi 2005). Last but not least, this mining district has already been proposed as a source for eight Ligurian artefacts from the Chalcolithic, the Bronze Age, and the Iron Age (Campana et al. 1996). Hence, as our data show, the Tuscan economy, at least at the end of the third millennium BC, extended far further across the Alps.

This archaeological and archaeometric evidence strongly supports the identification of a Tuscan source for the metal of the three lunulae from Ayent/Les Places (740d, 740f,
740h). While this type of lunulae appears primarily in central Valais (nine occurrences at Ayent/Les Places and one at Conthey/Sensine, tomb 2), some very similar pieces were recovered at Arbedo/Castione (Ticino, Switzerland), Saint-Martin de Corléans (Aosta, Italy), in the Singen necropolis (Germany), in two tombs in Upper Bavaria (Munich and Raisting, Germany), and on the edge of Lake Ledro (Italy) (David-Elbiali 2000; Mezzena 1997; Primas 1997; Rageth 1974). Their low numbers do not allow for the defining of a cultural origin zone of this type with certainty. Even though no evidence for any occurrences of this type of artefact have been found in Tuscany thus far, the specific isotopic signature strongly indicates a likelihood that the origin of the metal is Tuscan. It must be underlined here that the typological criterion is distinct from the isotopic and technological ones: the lead isotope analyses of the two other lunulae 740e and 740g from Ayent/Les Places do not overlap with those of the Tuscan ores, and their copper is alloyed with tin.

5.6. The quest for the cultural components of the Early Bronze Age in the central Valais

As shown by this study, the copper objects found in the central Valais region suggest diverse origins for the metal, not only in the Valais itself, but also in Tuscany. A relationship is supported by the presence of the megalithic complex in Saint-Martin-de-Corléans (Val d’Aosta, Italy), whose architecture, artefacts and funerary rituals show similarities with the necropolis of Sion/Petit-Chasseur (Gallay and Chaix 1984; Mezzena 1997; Mollo Mezzena 1997). Other discoveries reinforce a connection with the southern Alpine area. A cup fragment from Zampon/Noale shows parallels with the early phase of the northern Italian Polada culture (David-Elbiali 2000). The presence of the pin “à tige en sabre” 40249 also supports this impression, due to the presence of similar objects at Sorbara-Asola (Mantua, Italy) (Baioni 2005).

While some of the Valaisan Early Bronze Age cultural components show a relationship with the south of the Alps, a central European influence cannot be clearly ruled out. The four pins with a “Singen Metall” composition are evidence of shared economic and cultural networks. Their comparison with 105 lead isotope ratios of Unetician bronze objects published by Niederschlag et al. (2003) shows that the pins with a paddle shaped head 733 and 735 likely correspond to the main concentration of data. Given the distribution of the pins with a paddle shaped head in Europe, the majority of which were found in the Middle and Upper Danube region, as well as on the Middle Rhine area (David-Elbiali 2000), a link with the economy of the northern sphere of the Early Bronze Age is conceivable. The circulation routes, direction of travel and the nature of these contacts remain unclear. Given the lack of metal artefacts for the beginning of the Early Bronze Age in the Swiss Plateau, which would have been an alternative route from central Europe to the Valais, northern Italy may have acted as a relay area for central European influences.

6. CONCLUSION

Ten objects from the central Valais region, all representative of the beginning of the Early Bronze Age, were analysed for their elemental composition and lead isotope ratios. Additionally, previously lacking data for a lead isotope reference database of copper
minerals in the Valais are provided. The provenance studies support the hypothesis of a copper supply from several different sources. The copper of three lunulae all appear to have the composition of Tuscan minerals, which indicates that mining activities were conducted in this region during the Early Bronze Age, despite the lack of clear evidence for mining dating back to this period. Additionally, a good correspondence of the lunula 740e is given by the copper/lead/zinc mineralization of Massaschlucht “Massagrube” (Brig) in the Valais. Thus, the current state of the research suggests that the two initial propositions of an external influx and a local ore supply, to explain the particularly early and rich appearance of copper objects in the central Valais region, remain both valid, and in all likelihood concomitant.

In regard to the comparison of the Valaisan mineral data with the studied artefacts whose provenance could not be clearly identified, a local supply is compatible with the Valaisan lead isotopic field taken as a whole, although other sources in the Western Mediterranean and in continental Europe can not be ruled out, specifically considering that the mixing of ores and recycling of metal of different provenances is likely. Thus, additional data will be required for each Valaisian mineralization in order to increase the delimitation and robustness of each isotopic field and, therein, the weight of the possible proposed sources. In parallel, additional investigations focussing on the elemental composition of mineralizations could provide indications for provenance through the definition of regional chemical markers and should be the central focus of future projects on Valaisan copper minerals. Also, the use of other isotopic tracers should be evaluated in the context of the Valaisan copper minerals and of the metallurgical processes in use during the Early Bronze Age. Finally, it would be worthwhile to conduct archaeological surveys and excavations, especially in the region surrounding the mineralization of Massaschlucht “Massagrube” (Brig, Valais) to find out whether or not this ore body was mined during the Early Bronze Age, as is suggested by the corresponding metallic composition of the lunula 740e.

This study also raises the question of the role of the central Valais region within the copper distribution networks during the beginning of the Early Bronze Age. The other specific areas that are affected by a particularly early and rich appearance of copper objects within the region of the Alps share similar manufacturing techniques and object types that might indicate an active knowledge transfer and material circulation between the different regions. To evaluate possible inter-regional exchanges, an ongoing research project is now being conducted by one of the authors (F.C.), M. Merkl and Ch. Strahm on a subset of the artefacts from the Singen cemetery (Germany). The analysis of the metallic composition should shed light on the existence of common extra-local networks in combination with a local copper supply. A central motivation will be to ascertain to what extent these diverse economic ties resulted in cultural influence that could be shown to be primordial in the emergence and the development of the Culture du Rhône.

ACKNOWLEDGMENTS

This research was founded by the Swiss National Science Foundation (PP001-102710, PBGEP-123575). This work was also made possible through the support of the Action
COST G-8 n° 05.0082 (M. Wörle, Swiss National Museum in Zurich, and M. Besse, University of Geneva), the Fondation Ernst & Lucie Schmidheiny, the Fondation Dr Ignace Mariétan, the Fondation Marc Birkigt, the Direction régionale des affaires culturelles, Provence-Alpes-Côte d’Azur (H. Barge), the Swiss National Museum in Zurich (S. Van Willigen). Their financial and material support is gratefully acknowledged. We also want to thank V. Köppel, F. Monna and M. Prange for the (unpublished) LI electronic data they have provided, A. Thompson and B. Scott who kindly helped to improve the English text, and T. Rehren and the anonymous reviewers for their stimulating comments.

REFERENCES


Cattin, F., Villa I.M., Besse M., 2009b. Copper supply during the Final Neolithic at the Saint-Blaise/Bains des Dames site (Neuchâtel, Switzerland), in: Cattin, F., Guénette-Beck, B., Besse, M., Serneels, V.


We focus on the north Alpine metallurgy at the beginning of the Early Bronze Age.
Elemental composition and LI ratios of copper artefacts are investigated.
A database of copper ores from the Valais (Switzerland) is elaborated for comparison.
A local ore supply is compatible with the artefactual data.
Provenance studies using literature data support a (Tuscan?) external influx.
TABLES

Tab. 1: Measured values of NIST SRM 981 from different literature sources compared with those obtained in this study. Analytical errors (2 sigma) refer to the least significant digits and results shown in italics were calculated from the data given in the original publication.

Tab. 2: Lead isotope ratios for the objects studied (analytical uncertainties are shown as 2 sigma and refer to the least significant digits). Conservation location: MCVS: Musées cantonaux du Valais, Sion; SNM: Swiss National Museum, Zurich.


Tab. 4: Chemical analyses sorted according to the copper groups and copper types as defined by Pernicka (1990) and Junghans et al. (1968-1974) respectively. Conservation location: MCVS: Musées cantonaux du Valais, Sion; SNM: Swiss National Museum, Zurich.

Tab. 5: Pb content of various Cu bearing bulk ore from studied area.

Tab. 6: Lead isotope ratios of the Massaschlucht mine (Valais, Switzerland).

FIGURES

Fig. 1: Sites with numerous copper artefacts: (1) the Central Valais, Switzerland, (2) the Singen cemetery, Germany, (3) the Franzhausen and (4) Gemeinlebarn cemeteries, Austria. Main localities mentioned in text: (a) Etrembières, France, (b) Saint-Martin-de-Corléans, Italy, (c) Alagna Valsesia, Italy, (d) Zeneggen/Kastellschuggen, Switzerland, (e) Thun-Wiler, Switzerland.

Fig. 2: Drawings of the ten archaeological objects studied. 1: Conthey/Sensine, tombe 2 (A-11603); 2: Ayent/Les Places (733); 3: Ayent/Les Places (735); 4: Sion/Petit-Chasseur, M XI Dépôt 1 (40249); 5: Sion/Petit-Chasseur, M XI Dépôt 1 (40250); 6: Ayent/Les Places (740 f); 7: Ayent/Les Places (740 d); 8: Ayent/Les Places (740 h); 9: Ayent/Les Places (740 e); 10: Ayent/Les Places (740 g). 1: from David-Elbiali (2000), modified; 2, 3: from Bocksberger (1964), modified; 4, 5: from Gallay and Chaix (1984), modified; 6-10: F. Cattin, S. Broccard.

Fig. 3: Comparison of the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Artefacts from the Early Bronze Age (BzA1). Error is smaller than the symbols.

Fig. 4: Comparison of the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Artefacts from the Early Bronze Age (BzA1).

Fig. 5: Comparison of the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Artefacts from the Early Bronze Age (BzA1) and copper ores from the Valais region. The lead isotope field of the mine of Massaschlucht “Massagrube” (Brig, Valais) is drawn on the basis of two analyses on copper minerals and two analyses on lead minerals. Error is smaller than the symbols.

Fig. 6: Comparison of the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Artefacts from the Early Bronze Age (BzA1) and copper minerals from the Valais region. The lead isotope field of the mine of Massaschlucht “Massagrube” (Brig, Valais) is drawn on the basis of two analyses on copper minerals and two analyses on lead minerals.

Fig. 7: Comparison of the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, and $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Lunulæ 740 d, 740 f, and 740 h from the Early Bronze Age (BzA1), and minerals from the European database discussed in the text (literary sources are assumed to have an analytical uncertainty of 0.1%).
<table>
<thead>
<tr>
<th>Study</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{206}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Todt et al. (1996)</td>
<td>36.7006 ±34</td>
<td>15.4891 ±9</td>
<td>16.9356 ±7</td>
<td>2.16701 ±13</td>
</tr>
<tr>
<td>White et al. (2000)</td>
<td>36.6825 ±78</td>
<td>15.4899 ±39</td>
<td>16.9467 ±76</td>
<td>2.1646 ±8</td>
</tr>
<tr>
<td>This study (n=53)</td>
<td>36.720 ±2</td>
<td>15.496 ±2</td>
<td>16.942 ±1</td>
<td>2.16730 ±10</td>
</tr>
</tbody>
</table>
$^{207}\text{Pb}/^{206}\text{Pb}$

- 0.914750 ±35
- 0.914623 ±37
- 0.914685 ±49
- 0.91459 ±13
- 0.914585 ±4
- 0.91469 ±7
- 0.91404
- 0.91467 ±5
<table>
<thead>
<tr>
<th>Acquisition number</th>
<th>Conservation location</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{206}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{206}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group A: five lunulae (copper and copper/tin composition)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (I): three lunulae of unalloyed copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 d</td>
<td>MCVS</td>
<td>39.066±33</td>
<td>15.700±13</td>
<td>18.755±11</td>
<td>2.08302±34</td>
<td>0.83719±7</td>
</tr>
<tr>
<td>740 f</td>
<td>MCVS</td>
<td>38.995±21</td>
<td>15.698±8</td>
<td>18.742±10</td>
<td>2.08070±34</td>
<td>0.83758±12</td>
</tr>
<tr>
<td>740 h</td>
<td>MCVS</td>
<td>39.055±26</td>
<td>15.702±10</td>
<td>18.760±9</td>
<td>2.08181±48</td>
<td>0.83704±17</td>
</tr>
<tr>
<td>- (II): two lunulae of copper/tin alloy (bronze)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 e</td>
<td>MCVS</td>
<td>38.592±21</td>
<td>15.653±8</td>
<td>18.732±8</td>
<td>2.06024±36</td>
<td>0.83560±11</td>
</tr>
<tr>
<td>740 g</td>
<td>MCVS</td>
<td>38.707±21</td>
<td>15.649±10</td>
<td>18.771±9</td>
<td>2.06236±31</td>
<td>0.83375±13</td>
</tr>
<tr>
<td><strong>Group B: four pins (copper)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>733</td>
<td>MCVS</td>
<td>38.487±24</td>
<td>15.667±10</td>
<td>18.373±33</td>
<td>2.09535±46</td>
<td>0.85290±13</td>
</tr>
<tr>
<td>735</td>
<td>MCVS</td>
<td>38.516±176</td>
<td>15.672±70</td>
<td>18.396±81</td>
<td>2.09386±68</td>
<td>0.85184±28</td>
</tr>
<tr>
<td>40249</td>
<td>MCVS</td>
<td>38.556±77</td>
<td>15.709±32</td>
<td>18.423±38</td>
<td>2.09286±26</td>
<td>0.85270±9</td>
</tr>
<tr>
<td>A-11603</td>
<td>SNM</td>
<td>38.473±36</td>
<td>15.609±14</td>
<td>18.418±15</td>
<td>2.08896±92</td>
<td>0.84747±15</td>
</tr>
<tr>
<td><strong>Group C: one ring (copper)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40250</td>
<td>MCVS</td>
<td>38.490±6</td>
<td>15.681±2</td>
<td>18.242±1</td>
<td>2.11001±23</td>
<td>0.85962±6</td>
</tr>
<tr>
<td>Acquisition number</td>
<td>Conservation location</td>
<td>Laboratory of analysis</td>
<td>Analysis number</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------</td>
<td>------------------------</td>
<td>----------------</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td><strong>Group A:</strong> five lunulae (copper and copper/tin composition)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (I): three lunulae of unalloyed copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 d</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4241</td>
<td>Traces</td>
<td>n.d.</td>
<td>Traces</td>
</tr>
<tr>
<td></td>
<td>SNM/ETH</td>
<td>MAS 468</td>
<td>56</td>
<td>0.3</td>
<td>6</td>
<td>244</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>25</td>
<td>0.2</td>
<td>5</td>
<td>123</td>
<td>3060</td>
</tr>
<tr>
<td>740 f</td>
<td>MCVS</td>
<td>SNM/ETH</td>
<td>MAS 466</td>
<td>31</td>
<td>0.8</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>9</td>
<td>0.2</td>
<td>29</td>
<td>340</td>
<td>16</td>
</tr>
<tr>
<td>740 h</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4242</td>
<td>Traces</td>
<td>n.d.</td>
<td>Traces</td>
</tr>
<tr>
<td></td>
<td>SNM/ETH</td>
<td>MAS 465</td>
<td>37</td>
<td>0.6</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>12</td>
<td>0.1</td>
<td>6</td>
<td>7</td>
<td>81</td>
</tr>
<tr>
<td>- (II): two lunulae of copper/tin alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 e</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4238</td>
<td>Traces</td>
<td>n.d.</td>
<td>Traces</td>
</tr>
<tr>
<td>740 g</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4239</td>
<td>Traces</td>
<td>n.d.</td>
<td>1100</td>
</tr>
<tr>
<td><strong>Group B:</strong> four pins (copper)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>733</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4184</td>
<td>n.d.</td>
<td>620</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>SNM/ETH</td>
<td>MCA 733</td>
<td>38</td>
<td>940</td>
<td>21300</td>
<td>361</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>19</td>
<td>813</td>
<td>4800</td>
<td>326</td>
<td>21</td>
</tr>
<tr>
<td>735</td>
<td>MCVS</td>
<td>SAM *</td>
<td>SAM 4186</td>
<td>Traces</td>
<td>530</td>
<td>16000</td>
</tr>
<tr>
<td></td>
<td>SNM/ETH</td>
<td>MCA 735</td>
<td>240</td>
<td>347</td>
<td>10800</td>
<td>346</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>354</td>
<td>86</td>
<td>1900</td>
<td>142</td>
<td>15</td>
</tr>
<tr>
<td>40249</td>
<td>MCVS</td>
<td>EMPA</td>
<td>40249</td>
<td>&lt;100</td>
<td>1170</td>
<td>12200</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Group C:</strong> one ring (copper)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40250</td>
<td>MCVS</td>
<td>SNM/ETH</td>
<td>40250</td>
<td>44</td>
<td>5</td>
<td>1670</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>47</td>
<td>1</td>
<td>80</td>
<td>35</td>
<td>1770</td>
</tr>
</tbody>
</table>

*Published data from Junghans et al. (1968-1974).*
<table>
<thead>
<tr>
<th>Acquisition number</th>
<th>Conservation location</th>
<th>Copper type (Pernicka 1990)</th>
<th>Copper group (Junghans et al. 1968-1974)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A: five lunulae (copper and copper/tin composition)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (I): three lunulae of unalloyed copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 d</td>
<td>MCVS</td>
<td>Pure copper</td>
<td>E00/C1A</td>
</tr>
<tr>
<td>740 f</td>
<td>MCVS</td>
<td>Pure copper</td>
<td>E00</td>
</tr>
<tr>
<td>740 h</td>
<td>MCVS</td>
<td>Pure copper</td>
<td>E00</td>
</tr>
<tr>
<td>- (II): two lunulae of copper/tin alloy (bronze)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740 e</td>
<td>MCVS</td>
<td>Pure copper</td>
<td>E00</td>
</tr>
<tr>
<td>740 g</td>
<td>MCVS</td>
<td>Pure copper</td>
<td>E00</td>
</tr>
<tr>
<td>Group B: four pins (copper)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>733</td>
<td>MCVS</td>
<td>Fahlore type copper with nickel</td>
<td>B2/A1</td>
</tr>
<tr>
<td>735</td>
<td>MCVS</td>
<td>Fahlore type copper with nickel</td>
<td>A/A</td>
</tr>
<tr>
<td>40249</td>
<td>MCVS</td>
<td>Fahlore type copper with nickel</td>
<td>A</td>
</tr>
<tr>
<td>A-11603</td>
<td>SNM</td>
<td>Fahlore type copper with nickel</td>
<td>A/undefined</td>
</tr>
<tr>
<td>Group C: one ring (copper)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40250</td>
<td>MCVS</td>
<td>Fahlore type copper without nickel</td>
<td>C6A</td>
</tr>
</tbody>
</table>

1From published data (Junghans et al. 1968-1974 - OES).
2From new data, this study (Swiss national museum/ETH, Zurich, Cattin, Wörle, Besse, Hubert, Günther, Hametner, 2005 – LA-ICP-MS).
3From new data, this study (Swiss national museum, Zurich, Voute, 1978-1980 – XRF on core metal).
<table>
<thead>
<tr>
<th>Name of mineralization</th>
<th>mg/kg [ppm]</th>
<th>hand-splitted</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baicolliou</td>
<td>4900; 2000; 900</td>
<td>Yes</td>
<td>Halm (1945); WC Halm (1945)</td>
</tr>
<tr>
<td>Biolec</td>
<td>300</td>
<td>Yes</td>
<td>Halm (1945)</td>
</tr>
<tr>
<td>Laulosses</td>
<td>497; 10; 5; 73; 19; 54; 30; 42; 2</td>
<td>No</td>
<td>Woodtli et al. (1945)</td>
</tr>
<tr>
<td>Pétolliou</td>
<td>500</td>
<td>Yes</td>
<td>Halm (1945)</td>
</tr>
<tr>
<td>Pont-du-Bois</td>
<td>5800</td>
<td>Yes</td>
<td>Woodtli et al. (1945)</td>
</tr>
<tr>
<td>La Creusaz/Les Marécottes</td>
<td>1808; 935; 442; 1558</td>
<td>No</td>
<td>Meisser (2003)</td>
</tr>
<tr>
<td>Acquisition number</td>
<td>Analysis number</td>
<td>Analysed mineral</td>
<td>$^{206}\text{Pb}/^{204}\text{Pb}$</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------</td>
<td>------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Natural History Museum Bern, NMBE 6939</td>
<td>6939</td>
<td>Cp, gn</td>
<td>38.558 ±14</td>
</tr>
<tr>
<td>Natural History Museum Bern, NMBE A1410</td>
<td>A1410</td>
<td>Cp, gn</td>
<td>38.559 ±15</td>
</tr>
<tr>
<td>Geotech. Commission Zurich</td>
<td></td>
<td>Gn</td>
<td>38.575 ±28</td>
</tr>
</tbody>
</table>

Young upper crust (Kramers and Tolstikhin 1997)
Copper minerals from the Valais
Archaeological artefacts from the BzA1
Pb isotopic field of the Massaschlucht mine (Valais)
Copper minerals from the Valais
Archaeological artefacts from the BzA1
Pb isotopic field of the Massaschlucht mine (Valais)
Young upper crust (Kramers and Tolstikhin 1997)
Young upper crust (lead source evolution model from Kramers and Tolstikhin 1997)

Lerkavitsa (Central Rhodope, Bulgaria) (Gale et al. 2000)
La Pesta mine (Massa Marittima, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Lanzi mine (Campiglia Marittima, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Temperino mine (Campiglia Marittima, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Capanne Vecchie mine (Massa Marittima, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Balarino mine (Boccheggiano, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Pozo de Aquja mine (Mazzaron, Murcia, Spain) (Stos-Gale et al. 1995)
Early Bronze Age artefacts (this study)
Capanne Vecchie mine (Massa Marittima, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Balarino mine (Boccheggiano, Tuscany, Italy) (Stos-Gale and Gale 1992; Stos-Gale et al. 1995)
Pozo de Aquja mine (Mazzaron, Murcia, Spain) (Stos-Gale et al. 1995)