Journal of Archaeological Science 75 (2016) 27–39

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

A lead-isotope database of copper ores from the Southeastern Alps: A tool for the investigation of prehistoric copper metallurgy

G. Artioli [a, *], I. Angelini [b], P. Nimis [a], I.M. Villa [c, d]

[a] Dipartimento di Geoscienze, Università degli Studi di Padova, 35131 Padova, Italy
[b] Dipartimento di Beni Culturali, Università degli Studi di Padova, 35131 Padova, Italy
[c] Centro Universitario Datazioni e Archeometria, Università di Milano Bicocca, 20126 Milano, Italy
[d] Institut für Geologie, Universität Bern, 3012 Bern, Switzerland

ARTICLE INFO

Article history:
Received 29 May 2016
Received in revised form
3 September 2016
Accepted 13 September 2016

Keywords:
Copper metallurgy
Copper ores
Eastern Alps
Eneolithic
Bronze age
Lead isotope analysis

ABSTRACT

The Southeastern Alps were an important source of copper metal in prehistory, at least from the Eneolithic and through the Bronze Age, as documented by the abundant and substantial presence of smelting slags. Evidence of mining activity is scarce, because of limited ad hoc investigation and because of the subsequent systematic erasing by post-Medieval exploitation. Moreover, until recently the profusion of archaeometallurgical and archaeological investigations focusing on the prehistoric exploitation of Northern Alpine, Central European, and Balkan ore sources has somehow obscured the early role of the Italian Southern Alps as a major copper producing area. The recent advances in the systematic characterization of the copper ores in the Southeastern Alps (including Alto Adige, Trentino, Veneto, and nearby regions) by lead isotope analysis, supported by mineralogical and geochemical interpretation, offer now the appropriate tools to re-evaluate the extent of prehistoric mining and the local patterns of ore exploitation. The developed database is a powerful tool to identify the metal derived from local production. It is suggested that (1) based on the abundance and chronological distribution of smelting slags evidence, two major periods of mining exploitation took place, the first in the middle of the 3rd millennium BC and the second during the Late Bronze Age; and (2) based on the discrimination of copper sources and the available analyses, most of the metal circulating in Northern Italy and in the greater Po Valley region was actually produced from Southern Alpine ores.

1. Introduction

The Italian Alps do not contain large copper deposits in modern industrial terms; nevertheless, they are host to a large number of relatively small copper and polymetallic copper-bearing deposits of different genetic type and geological age. Most of these copper occurrences would be of limited economic interest in the present global resource market, but many of them have been extensively exploited since prehistory, possibly since Late Neolithic times. As a matter of fact, copper metal objects were circulating in the area well before the Bronze Age, as the archaeological evidence clearly shows (e.g. Pedrotti, 2002: p. 213, Pearce, 2007; Angelini et al., 2013), also through spectacular finds such as the Iceman's copper axe (De Marinis, 1992; Fleckinger, 2003; Sperl, 2005). The latter finding stands as a landmark as it is the only directly datable Eneolithic copper axe in the Southern Alpine region.

The copper deposits which have allegedly been exploited in prehistory are mainly located in the Southeastern Alps (Nimis et al., 2012; Artioli et al., 2013), namely in the Trentino and Alto Adige/South Tyrol regions, which show substantial evidence of Copper Age (Perini, 1989; Pedrotti, 2002; Pearce, 2007; Angelini et al., 2013; Artioli et al., 2015) and Bronze Age (Weisgerber and Goldenberg, 2004; Cierny, 2008) smelting activities. Despite the intense prehistoric metallurgical activity, surprisingly few systematic investigations were carried out in order to define the geochemical and isotopic character of the Southern Alpine deposit for archaeometric and provenancing purposes. The attention to date has been mostly focused on the more northerly Austrian Alps (e.g. Lutz and Pernicka, 2013 and references therein). Significantly, in a recent review of available lead isotope data for the Alpine region (Ling et al., 2014), the authors clearly state: "The Eastern Alps in particular are known for large and rich deposits of copper (also

* Corresponding author.
E-mail address: gilberto.artioli@unipd.it (G. Artioli).

http://dx.doi.org/10.1016/j.jas.2016.09.005
0305-4403/

lead and silver). There is a well-documented exploitation throughout the Bronze Age of copper ores, mainly in Tyrol, …Over 300 lead isotope data that can be used for comparisons have been published for the Alpine copper ores, mainly from Austria (Höppner et al., 2005; Köppel and Schroll, 1983a,b; Schroll, 1997). Unfortunately, there are no lead isotope data published in numerical format for the mines in Mitterberg, the only published information about these ores is plotted as graphs (for example Pernicka, 2010, Fig. 8, p. 729). *There is also archaeometallurgical evidence of ancient copper mines in the Italian Alps, but there are no lead isotope data available for these ores* (Weisgerber and Goldenberg, 2004)." Actually, several lead isotope (hereafter LI) data for the Italian Western and Eastern Alps do exist in the literature (Cumming et al., 1987; Artioli et al., 2009; Nimis et al., 2012), nonetheless it is true that no systematic, archaeometry-oriented report of these data has yet been published in a major journal. Small to very small outcrops of copper minerals were probably widespread in the Alps. Wherever small-scale investigations were undertaken, it was demonstrated that literally hundreds of localities were accessed in the Bronze Age, for many of which Pb isotope data are available (e.g. Valais: Cattin et al., 2011; Austria: Höppner et al., 2005; Köppel and Schroll, 1983a,b; Schroll, 1997; Eastern Italian Alps: Artioli et al., 2013; Angelini et al., 2015; Western Italian Alps: Artioli et al., 2009).

The present review is meant (a) to release in a complete and organic form the lead isotope (hereafter LI) data collected in the last decade within the AAcP project (Alpine Archaeocopper Project: geo.geoscienze.unipd.it/aacp/welcome.html) pertaining to copper deposits in the Southeastern Alps, (b) to define reference isotopic groups for the area, (c) to provide a general geological and geochemical interpretation of the discrimination potential of the LI data for these deposits with respect to other European and Mediterranean copper sources exploited in antiquity, and (d) to show examples of provenancing application to prehistoric copper and bronze objects from Northern Italy. It is believed that these exercises will greatly contribute to clarify the picture of ancient metallurgical exploitation in the Alpine region.

2. The development of the database: ore selection and characterization

Copper-bearing ore samples from the Southeastern Alps were systematically collected during the last decade based on geological, historical, and mining information. The early investigations (Artioli et al., 2008a) focused on the geochemical discrimination of the ore sources, starting with a few samples of the most well-known deposits in the region. The Agordo mining area (Belluno, Veneto) in the heart of the Dolomiti Bellunesi, which used to be one of the fundamental metal producing areas of the Republic of Venice in the XVII and XVIII centuries, was first selected in order to calibrate the sampling and analytical protocols (Artioli et al., 2008b, 2012). The Agordo area in fact offers excellent occurrences of ores, smelting slags of various ages, and copper metal of unequivocal local origin, besides a wealth of historical information concerning mining sites and metallurgical activities. Agordo hosts one of the most famous Italian mining schools, founded in 1867, and preserves a wealth of information on historical mining and ore processing. The Agordo area was extensively surveyed and sampled in close collaboration with personnel of the mining school, mineral collectors and the local archaeological group (ARCA, Gruppo Archeologico Agordino). A large number of mineralogical, geochemical and isotopic analyses were performed on the samples from the Agordo mines (Valle Imperina, Sasso Negro, Valle del Mis, Passo di Vallés) and compared to the data obtained on local copper smelting slags related to Medieval and pre-industrial extraction activities and on raw copper fragments associated with the slags (Artioli et al., 2008b, Artioli et al. 2010, 2012; Giunti, 2011; Artioli et al., 2012). This preliminary test investigation allowed us to optimize the ore sampling and separation protocols, and to understand in detail the potentials and limits of the tracing parameters in linking the minerals to the extracted raw copper, through the smelting slags.

The research was then extended to the other known copper districts in the Trentino, Alto Adige/South Tyrol and Veneto regions. Recently, the main copper occurrences in the more easterly Friuli Venezia Giulia (Carnia area) and a few deposits from the more westerly Valcamonica area (Brescia, Lombardia) were also sampled and analysed. The reported data virtually include all occurrences of known copper mineralization in the explored regions. In fact, care was taken in covering all the different genetic typologies of deposits in a given area or mining district, so that the geochemical signature of any presently inaccessible deposit can be predicted from the present data on solid geological grounds. The project now plans to extend the survey further westward to the Central Alps.

Whenever possible each deposit was directly investigated in the field, and representative samples were collected from outcrops or mining dumps. Only in a few cases, when little or no copper ores were still accessible in the field, we had to rely on local private collections or museum specimens from a given locality. In a few cases, core samples from past mining exploration projects were made available.

Fig. 1 shows the location of the sampled mining sites, and Table 1 reports the detailed list of the analysed samples, together with geographical coordinates, locality names, as well as essential geological and mineralogical information.

3. Lead isotope analyses

The ore samples were mineralogically and petrographically characterized in polished sections by optical microscopy under reflected light and by X-ray powder diffraction (XRPD). Representative portions of the ore containing primary or secondary copper-bearing mineral assemblages (Table 1) were selected and then gently crushed. An adequate amount of mineral grains was then separated by handpicking under a binocular microscope, and their mineralogical composition checked by XRPD.

An aliquot of the separates (2–10 mg) was dissolved in aqua regia by high-pressure microwave digestion in sealed PTFE vessels. The dissolved lead was purified using the SrSpec™ resin (EIChroM Industries; Horwitz et al., 1992), following the same procedure described in Villa (2009). About 100 ml of resin are filled in a 3-mm diameter hand-made PTFE column. The height to width ratio is approximately 4. The sample solution is loaded in 0.5 ml 1 M HNO_3, 1.5 ml of which is also used to wash out the matrix metals, while Pb is very strongly retained on the resin. Pb is then eluted with 3 ml 0.01 M HNO_3 and is ready for analysis. Lead isotope analyses were performed with a Nu Instruments™ Multi-Collector-ICP-MS at the Institut für Geologie, University of Bern (Switzerland). The sample solution was ionized by introducing it into a 9000 K plasma. All elements were ionized simultaneously. Mass fractionation was monitored by adding a small quantity of Tl, which has a known $^{203}Tl/^{205}Tl$ ratio, is ionized together with and fractionated.

by the same mechanism as Pb, and does not interfere with Pb isotope measurements. Calibration was carried out using the NIST SRM 981 international standard. The results are reported in Table 2. Typical in-run relative uncertainties (2 SE of the mean) on $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ isotope ratios were smaller than 0.02%. The measured isotopic composition for SRM 981 were indistinguishable from the certified value and the recent, more precise literature measurements (Rehkämper and Mezger, 2000), so that no adjustment of the measured ratios was necessary.

The external reproducibility on the SRM 981 reference material