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A multivariate approach to the study of orichalcum ingots from the underwater Gela's archaeological site

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ABSTRACT

In this work a careful ICP-OES and ICP-MS investigation of 38 ancient ingots has been performed to determine both major components and trace elements content to find a correlation between the observed different features and the composition.
The ingots, recovered in an underwater archaeological site of various finds near Gela (CL, Italy), were previously investigated by X-Ray Fluorescence (XRF) spectroscopy to know the composition of the alloy and it was found that the major elements were copper and zinc, in a ratio compatible with the famous orichalcum similar to the contemporary brass that was considered a precious metal in ancient times. The discovery of huge amount this alloy is extraordinary.
Following a chemometric approach at first, the use of Principal Component Analysis (PCA) and Cluster Analysis (CA) allowed us to highlight three well-defined groups of ingots and to point out three ingots that appeared outlier with respect to the whole sample set. Linear Discriminant Analysis (LDA) and Soft Independent Modeling of Class Analogy (SIMCA) enabled us to confirm the difference between the hypothesized groups. The prediction power of the variables computed by SIMCA allowed us pointing out some elements able to differentiate each group.
The three well-defined groups of ingots resulting from the chemometric analysis were in agreement with the observations of some morphological parameters such as ingot shape, width, and length and weight and by the presence of different kind of patina.
The appearance of three distinctive families of ingots can indicate different geographical location of the furnace, different technology stages and/or different raw material used in melting process and the morphology is indicative of cast diverse technologies. These findings can signify the starting point for giving important insights in the archaeometric study of the orichalcum ingots regarding the provenience and the manufacture technologies.

1. Introduction

The present work concerns the deepening of knowledge about the treasure of 40 antique ingots recovered from the seabed near Gela in the southern coast of Sicily in 2015 [1]. In a previous paper, by analysing the contest of the discovery it has been done the assumption that the ingots are part of a precious cargo transported in an ancient ship that was wrecked near the Gela coast [2]. This ship was dated to the end of VI century BC according to the pottery found nearby. A photo of the context of the discovery is showed in Fig. 1.

As example the photo of five representative ingots is reported in Fig. 2.

Ingots morphology suggested a casting mono-valve mold production. The mold contact surface is poorly defined, indicating the use of a rough refractory material. It can be excluded that two ingots were prepared by using the same mold. The presence of ripples on the surface exposed to the air during the cooling process, consequence of a rapid solidification of the melted alloy, indicated that the temperature was near the melting temperature. The presence of numerous impurities among the ripples was attributed to a separation process that

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Fig. 1. Photo of the context of the discovery.

underwent during the fusion. This suggested that a recasting of already machined objects was not used in order to obtain the ingots, therefore a primary production of the alloy could be assumed. All these findings suggested a rudimentary mold production compatible with the age of the ship.

In the previous work a preliminary investigation on 38 ingots was performed in situ by using a portable Energy dispersive X-Ray Fluorescence (XRF) instrument in order to determine the composition of the alloy. Results evidenced that all the ingots are constitutes by an alloy whose major elements are copper and zinc. The weight ratio between the two metals, Cu/Zn, varies between 2.7 and 5.7; these values are compatible with the composition of the famous orichalcum, considered a precious metal in ancient times. This results supports the hypothesis that, according to the pottery found nearby, this precious cargo was transported in an ancient ship dated to the end of VI century BC. This finding, archaeologically speaking, is very important because, to our knowledge, it is the first time that orichalcum is found in the shape of ingots and in so large amount. In the Greek world, orichalcum was the rarest and most expensive alloy, the value was second after gold and silver. It had previously been found only in small items; however, Plato wrote that the walls of mythical Atlantis were plastered with orichalcum, a metal connected with the Gods, according to poets of archaic Greece. The production of orichalcum from the antiquity up to XVI century was realized by the so called cementation process. This consists in a series of chemical reactions in a more or less closed crucible at temperature of 1000 ± 100 °C. The Zn contained in zinc ores such as sphalerite (ZnS_2) or smithsonite ($ZnCO_3$) is firstly reduced by heating and subsequently the vapor of reduced Zn partly diffuse in the Cu to form the Cu-Zn alloy. The temperature should be confined between 917° (Zn vapors) and 1083° (melting point of Cu) [3,4].

Recently Fan and others [5] showed that malachite [$Cu_2(CO_3)(OH)_2$], calamite [Zinc carbonate $ZnCO_3$ or smithsonite and zinc silicate $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ or hemimorphite.] and charcoal form brass when warmed in a closed device. The product composition depends on the temperature "When the temperature is 800 °C, the brass formed contains Zn less than 5%; when the temperature is 850 °C, the formed brass contains Zn more than 10%; when the temperature is over 900 °C, the Zn content of formed brass can exceed 20%". A little bit higher temperature is needed to obtain brass by fusion. Furthermore the raw materials can contain other minority minerals that are characteristic of the cave.

The composition of the alloy can be investigated by various techniques. The XRF spectrometry, already applied to the study of the ingots in the previous work [2] is a non-invasive and non-destructive technique, in addition it can be performed by portable instruments, but unfortunately it can give information only on the main elements [6].

Relevant information about the origin of the raw materials and the production techniques may be obtained by more sophisticated analyses of the ingots and of their trace elements [7]. For this purpose, it was important that the authorities perceived that such knowledge is worth of the sacrifice of few milligrams of orichalcum ingots. As the valuation of trace elements is very important for an accurate multi-elemental fingerprint of the sample, in order to obtain plentiful analytical data to be examined by means of chemometric methods [8,9], analysis of main and trace elements were performed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) respectively. One of the advantages of the use these techniques is the higher detection power attained, resulting in much improved limits of quantification, which can be particularly relevant for elements present at trace levels in micro samples. Both ICP methods, require small sample amounts that were sampled by drilling a micro well on each ingot [10].

Other techniques could provide with the same or a better accuracy the concentration of the trace elements, but the main reason to use ICP-OES and ICP-MS techniques was the common presence of these instrumentations in the modern analytical laboratories, and the established use for the high quality measurements concerning metal samples [11,12]. Furthermore ICP techniques have been widely used to analyse ancient metal objects [13–15] thus the results obtained in

Fig. 2. Photo of 5 representative ingots.