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Novel sampling techniques for trace element quantification in ancient copper artifacts using laser ablation inductively coupled plasma mass spectrometry

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ABSTRACT

Elemental analyses using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) have great potential in archaeometric research due to the quasi-nondestructive sampling and excellent sensitivity of the method. However, the application of LA-ICPMS in cultural heritage research is often limited because samples are too large to fit within an ablation cell or cannot be moved to the laboratory. This work reports the development of analytical routines that allow trace element quantification in ancient copper artifacts regardless their mobility, size or geometry.

In this study, the LA sampling step was performed in ambient air using a portable laser ablation device (pLA). The LA module was placed on the object of interest and the laser-generated aerosol was either directly transferred into the ICPMS via a large-capacity gas exchange device (GED) or collected on polycarbonate membrane filters, which were later analyzed by LA-ICPMS. The analytical performances of both approaches were assessed using various copper reference materials. The laboratory-based, ablation-cell-independent pLA-GED-ICPMS method, yielded accuracies comparable to those obtained via conventional LA-ICPMS (±10%). Good performances (±30%) were also obtained with the pLA + filter sampling approach and subsequent LA-ICPMS analysis. Limits of detection for both approaches were in the low µg/g or sub- µg/g range, making these methods interesting for trace element analysis.

After validating these laser-based techniques on an ancient copper object whose elemental composition had previously been determined by graphite furnace atomic absorption spectroscopy (GFAAS), five Neolithic copper artifacts found in Switzerland and France were analyzed using the pLA + filter sampling approach. A copper dagger found in Lattrigen, Switzerland was analyzed using the pLA-GED-ICPMS method. Furthermore, the laser-induced sample damage was investigated.

The trace element profiles of the objects under investigation were compared to those of well-characterized copper artifacts. Thus, the chronological and cultural background of these artifacts could be determined. One group of copper artifacts showed high arsenic concentrations (up to 1% [w/w]) and could be attributed to "*Mondsee copper*", which was particularly common in the eastern Alps during the Middle European Late Neolithic. Other objects under investigation showed trace element concentrations, which are typical for the Late Neolithic north of the Alps. One artifact had a composition typical for objects from the Late Neolithic of Southern France.

1. Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is a versatile and powerful technique for elemental

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analyses of solid samples in a quasi-nondestructive manner (Koch and Günther, 2011). In particular, LA-ICPMS is interesting for archaeometric research where the elemental composition of an artifact can provide crucial information about its origin, age, way of production, or authenticity (Edwards and Vandenabeele, 2012; Resano et al., 2010a). However, in standard LA-ICPMS analyses, sample sizes are restricted to the dimensions of an enclosing ablation cell. Furthermore, conventional LA-ICPMS is laboratory-based, which prohibits its application in museums or at excavation sites. In order to allow the analysis of arbitrarily sized objects, ablation cells that can be attached to sample surfaces in an airtight manner have been developed (Devos et al., 1999; Wagner and Jedral, 2011). Alternatively, LA can be carried out in ambient air with the laser-generated aerosol guided into the ICPMS via a large-capacity gas exchange device (GED), so that a sealed ablation cell is no longer required (Kovacs et al., 2010). The suitability of this LA-GED-ICPMS setup was demonstrated for spatially resolved analyses of large-scale stalagmites (Tabersky et al., 2013), as well as for isotopic analyses of arbitrarily sized objects (Dorta et al., 2013). A recently published study reported the development of a portable laser ablation device (pLA), which enables mobile LA-sampling and collection of laser-generated aerosols with subsequent quantitative LA-ICPMS analysis of the collected aerosol carried out in the laboratory (Glaus et al., 2012). The suitability of this approach was demonstrated for trace element analyses of glass, ceramics and gold samples. Compared to other portable techniques, such as X-ray fluorescence spectroscopy (XRF) and laser induced breakdown spectroscopy (LIBS), multiple orders of magnitude lower limits of detection can be obtained (Glaus et al., 2012). Additionally, the LA-based method allows accurate isotopic analyses, which was demonstrated for Pb isotope ratio determinations in ancient Chinese ceramics, including a terracotta warrior in Xi'an (Glaus et al., 2013).

Elemental analyses of archaeological copper artifacts can be challenging due to several reasons. Heavy surface corrosion and possible heterogeneity of the metal/alloy make representative sampling difficult. Trace element concentrations are typically low. Apart from copper as matrix element, concentrations commonly vary from 1000 to 0.1 μg/g. XRF allows non-invasive analyses of objects (in cases where an oxidation layer does not have to be removed). However, this technique is not sensitive enough to quantify trace element concentrations below 1 μg/g. Therefore, destructive sampling followed by sample digestion and liquid analysis is frequently carried out (e.g. by graphite furnace atomic absorption spectroscopy (GFAAS) or inductively coupled plasma optical emission spectroscopy (ICPOES) (Giumlia-Mair, 2005)). Apart from the obvious sample damage, these techniques are time consuming. Moreover, drilling samples cannot be taken from objects that are very thin or small. Owing to their non-destructive nature, their multi-element detection capabilities and high sensitivity, methods relying on nuclear physics such as instrumental neutron activation analysis (INAA) and particle induced x-ray emission (PIXE) have been widely used in the field of archaeometry during the last decades (Fleming and Swann, 2000; Gersch et al., 1998; Glascock and Neff, 2003; Moreau and Hancock, 1999). However, these facilities are not readily available and often require a particle accelerator. Therefore LA-ICPMS has been introduced and successfully applied for the analysis of various copper objects in previous studies (Cevey et al., 2006; Dussubieux, 2007; Dussubieux et al., 2008; Lattanzi, 2008).

In this work, the analytical performances of the pLA + filter sampling LA-ICPMS approach and the pLA-GED-ICPMS setup were assessed by performing trace element quantification of copper standard reference materials and an ancient copper artifact. Finally, these two novel sampling techniques were applied to assess the trace element composition of seven copper artifacts found at Neolithic sites in Switzerland and France. An allocation to a certain artisanship was made.

2. Methods and materials

2.1. Portable laser ablation sampling

An overview of the two pLA-based elemental quantification techniques applied in this study is presented in Fig. 1. In the first technique, the pLA sampling device was connected directly to the ICPMS instrument using a large-capacity gas exchange device (GED) (Nishiguchi et al., 2008). In the second method, a previously reported pLA + filer sampling technique was optimized and applied for trace element analysis of copper materials. Both methods are described in detail in the following subchapters. The pLA system applied in both setups consisted of a portable, diode-pumped solid-state 532-nm laser unit (Wedge HB 532, Bright Solutions SRL, Cura Carpignano, Italy), which provides a pulse duration of less than 1 ns. The light was coupled into an optical fiber (length 2 m, core diameter 450 μm, Ocean Optics Inc., Dunedin, FL, USA) and guided into a custom-built laser-ablation module. The system has been described and characterized in detail in a previous study (Glaus et al., 2012). For this study, a custom-built tripod with micro screws was added to the setup to allow precise positioning of the pLA module on the sample. The laser focus was adjusted to a few hundreds of micrometers below the open end of the pLA module. This allowed the pLA module to be positioned directly above the object of interest without touching it. A CCD camera was used for online sample observation. The camera focus and the focus of the laser beam were aligned, which enabled the laser beam to be precisely focused, even on rough surfaces.

2.2. Online aerosol analysis

The pLA sampling device was coupled to the ICPMS via a large-capacity gas exchange device (GED), which exchanged the ambient air by argon. Tygon tubing (3 mm inner diameter) was used to connect the pLA module with the GED. A membrane pump (NMP 05, during the work replaced with NMS 020, KNF Neuberger AG, Balterswil, Switzerland) transported the aerosol in a continuous flow into the GED-ICPMS. The operating conditions of the GED were very similar to those used by Tabersky et al. (Tabersky et al., 2013). The ICPMS conditions are given in Table 3 and the pLA parameters are identical to the ones applied for the pLA filter sampling (Table 1), apart from the ablation frequency, which was set to 10 Hz. Although the pLA-GED-ICPMS approach described here is featuring the pLA sampling device, the whole setup is not portable anymore and analyses have to be carried out in a laboratory environment. However, pLA-GED-ICPMS still offers advantages over conventional laboratory based LA-ICPMS instrumentation and previously reported open-cell LA-sampling approaches. The ablation module can be positioned very flexibly with respect to sample surfaces. There are no limitations regarding sample size and flat sample surfaces are no longer a prerequisite.

The online coupling of the pLA sampling device to the ICPMS offered the possibility for depth profiling of corrosion layers. This setup enabled precise removal of oxidation layers and efficient sampling of bulk material by online monitoring signal intensities. For example, transient pLA-GED-ICPMS signals recorded from a corroded copper sample (a Bronze Age needle fragment from an unknown excavation site), which are presented in Fig. 2, indicate a significant compositional difference between the corrosion layer and the bulk material. The signal intensities of $^{29}Si^{+}$ and $^{109}Ag^{+}$ increased sharply during the first few pulses and dropped again to a