SELECTIVE MULTI-ELEMENT ANALYSIS OF THE CLAY FRACTION IN ANCIENT POTTERY BY LASER ABLATION – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

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Introduction
In the past two decades, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) has become an interesting alternative to the bulk solution methods for elemental analysis of pottery clay with the aim of provenance determination.

Advantages Challenges
No digestion step Direct solid sampling without internal standard
Spatially resolved analysis Limited amount of clay reference materials

The current study investigates the capabilities and limitations of selective LA-ICP-MS analysis of the clay fraction in thin sections of sediments and pottery in comparison to those of the more common bulk analysis techniques.

Materials and methods

1) A pressed, biased and polished pellet of NIST SRM 679 Brick Clay has been analysed repeatedly by LA-ICP-MS and the data was processed with different calibration approaches based on a calibration set of glass standards. The elemental concentration results were compared with the reference values from the GeoREM database.

2) The clay fraction in 30 thin sections of pottery from the middle Neolithic site Spiere-de-Hel has been analysed by LA-ICP-MS and the results are compared to those obtained in previous bulk analyses of the same pottery by inductively coupled plasma – optical emission spectroscopy (ICP-OES).2,3

The instrumentation used for the LA-ICP-MS analyses consists of an Analyte G2 Act*Ascimer-based deep UV laser system from Toledyne Celas Technologies and an Xseries II quadrupole based ICP-mass spectrometer from ThermoScientific.

1) Choice of calibration method

Differences in ablation behaviour between clay material and glass cause concentration values that are systematically biased when using external calibration without internal standard (IS) correction. A sum normalization approach whereby the concentration of Si as internal standard is initially estimated to be 30 weight percent (wt%) and is afterwards corrected by assuming the sum of all oxide concentrations to be 100 wt% produces nearly identical results as an external calibration approach whereby the bulk Si concentration from the certificate is artificially increased by 30 wt%.

Conclusions and outlook

1) LA-ICP-MS analysis effectively excludes inclusions in pottery clay from the analysis. This implies that temper added by the potter which could complicate comparison between pottery and sediment can be avoided.

Future research will shed light on the high recovery for some elements in the NIST SRM 679 Brick Clay. In addition, LA-ICP-MS analysis on thin sections of sediments from the direct surrounding of the site Spiere-de-Hel will be performed in order to compare the chemical composition with that of the pottery to answer hypotheses of plausible provenance.

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References