

# Neutron Activation Analysis for Provenancing of Cultural Heritage Objects

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## Introduction

Provenancing of objects of the cultural heritage provides insights into the object's **place of origin**, its **manufacture** and **history of trade**. To reliably determine the provenance of an object by using its chemical composition or **chemical fingerprint**, it is important that all objects from a common origin have similar composition that is at the same time different from the composition of similar objects from different origin. This is usually the case for most **geological material** like pumice, obsidian, marble, limestone etc. For manufactured materials, like **ceramics**, the composition of the basic raw material (clay) is usually not completely preserved, but the recipe used in producing the clay paste can be equated with basic raw material of geochemical objects.

For the relation of a given sample to its origin or provenance, a well-established database of chemical fingerprints for comparison is fundamental.

At the Atominstitut in Vienna, such databases are maintained while at the same time it houses Austria's only research reactor necessary for Neutron Activation Analysis. This specifically qualifies the members of the Archaeometry group at the Atominstitut to provide reliable provenancing completely in-house.

## Ceramic Sherds

Provenancing of ceramics is somewhat different from work with geochemical materials. This is due to the custom of ancient potters of refining the basic raw clay to better suit their needs of manufacture. This is usually done by **levigating** (cleaning) and **tempering** of the raw clay. This process changes the original chemical composition of the raw clay. Provenancing of ceramics is thus usually done with respect to the clay paste produced and hence relates to the **recipe** employed at the workshop of origin.

The current database of ceramics at the Atominstitut contains data on approximately **1000 samples** from the Aegean, Egypt, Sudan, Mesopotamia and Japan.

## Statistical Evaluation

Especially in the case of ceramics, **multivariate statistical analysis** of the collected data is important. At the Atominstitut, a statistical filtering algorithm developed in Bonn (Mommsen et al. 1988) has been implemented and used successfully for grouping of ceramic samples (Sterba et al. 2009). This approach employs a modified Mahalanobis distance that takes into account **measurement errors** as well as a **dilution factor** (best relative fit). A simple visual tool for finding groups of samples are histograms of the Mahalanobis distance relative to a single samples (see Figure 4).

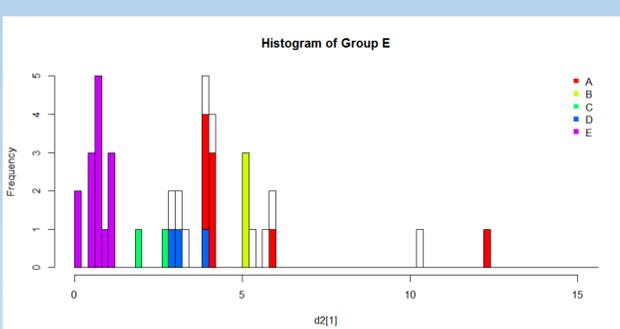


Figure 4: Histogram of Mahalanobis Distance of several ceramic sherds.

## Neutron Activation Analysis

Neutron Activation Analysis (NAA) is a radio-chemical method for **elemental bulk analysis**. Required sample sizes are approximately 150-200 mg, depending on homogeneity of the sample. Sampling procedures are usually either **drilling** with an alumina drill or breaking or cutting of a piece of 1x1 cm. For analysis, samples are packed in Suprasil™ quartz vials and irradiated in the neutron flux of the TRIGA Mk II research reactor of the Atominstitut in Vienna together with internationally certified reference materials. After irradiation, two measurements are performed on an HPGe detector for the quantification of the elements Na, Al, K, Sc, Cr, Mn, Fe, Co, Zn, As, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U, resulting in the **chemical fingerprint** of the sample.

For further details on measurement parameters and sample preparation see Steinhauser et al. (2006).

## Chemical Fingerprint

The **Chemical Fingerprint** fully describes the elemental composition of the sample measured. It consists of 25-30 elements which describe the bulk composition of the sample (see Figure 1). No chemical speciation is done. Since the elements used are of (geo)chemical significance, two samples that have the same chemical fingerprint, can be considered to originate from the **same basic raw material**. In the case of ceramics this indicates recipes, in the case of geological material, the **original outcrop**.

Once the chemical fingerprint of a given sample has been measured, it needs to be compared to other data to allow valid comparisons. Databases on raw materials (**pumice, obsidian**) and archaeological ceramics (Aegean, Egyptian, Nubian, Mesopotamian and Japanese) are currently built and maintained at the Atominstitut in Vienna (e.g. D'Ercole et al. 2017).

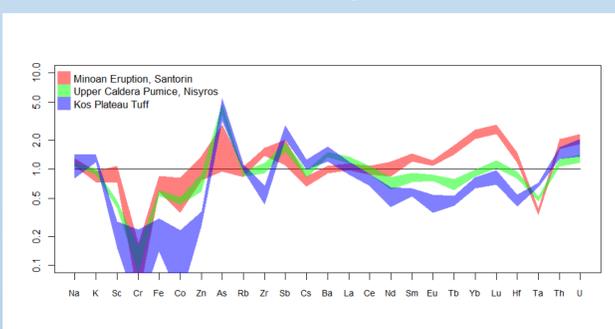


Figure 1: Example chemical fingerprints of three pumice producing volcanic eruptions.

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## Pumice

Pumice has been used as an **abrasive** since antiquity and thus has been traded. Since pumice producing volcanic eruptions are short events, identification of archaeologically stratified pumice provides a **maximum age** for the stratum as well as **trading information**. The database of chemical fingerprints of pumice deposits at the Atominstitut contains data on all major and most minor volcanic eruptions in the **Mediterranean**, including Italy, Greece and Turkey.

The most interesting volcanic eruption that coincidentally produced large amounts of pumice is the so-called **Minoan eruption of Santorin**, dated to ~1620 BC. While several older eruptions of the same volcano produced pumice at Santorin, a simple 4-element diagram can distinguish the older eruption products from the Minoan eruption (see Figure 2). Other diagrams easily identify the older eruptions products.

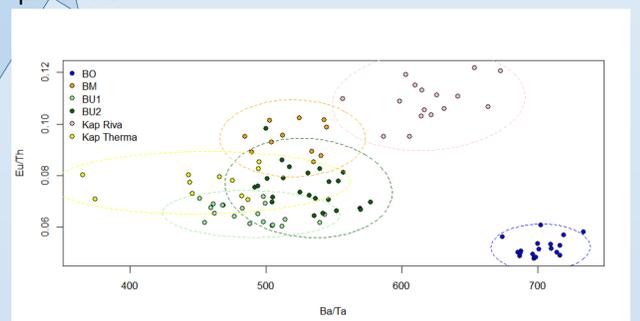


Figure 2: Distinction of Minoan eruption from older eruption products of Santorin.

## Obsidian

The natural volcanic glass **obsidian** is one of the classical objects of archaeometric analyses. The database on Obsidian sources at the Atominstitut comprises chemical fingerprints of Obsidian sources in **Central and Southern Europe**, i.e. Greece, Italy, Slovakia and Hungary. With the development of **OLDAPS** (Obsidian Least Destructive Analytical Provenancing System) a tool for the selection of the least destructive analytical method can be provided, that results in the best possible provenancing data.

As an example, a rumored third source of Obsidian on Milos island was investigated. Two well defined sources, namely Agia Nychia (Cape Bombarda) and Demenegakion exist on Milos (see Figure 3). As with many obsidian sources, the chemical fingerprints of the two sources are similar, but in this case easily distinguishable by comparison of Sc and Th. When the samples from the third, rumored source (Agios Ioannis) are compared to the well defined chemical fingerprints of the other two sources, it is clear that all of them are either from Demenegakion (10 samples) or from Agia Nychia (6 samples). (Mandl 2001, Bichler and Sterba 2012, Eder et al. 2013)

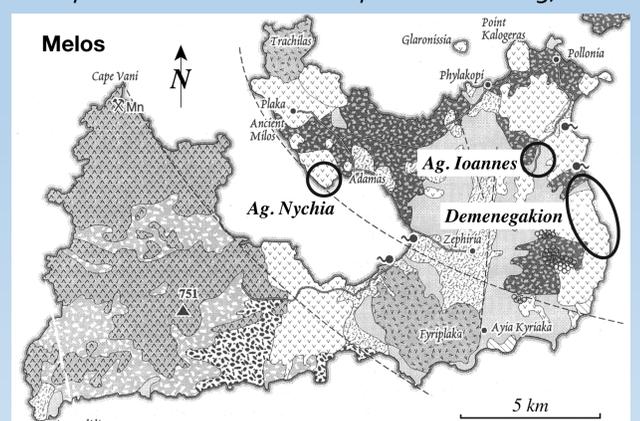


Figure 3: Locations of obsidian sources on Milos Island.