

What Mössbauer spectroscopy can tell us about ancient pottery production in Albania...

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Introduction

Pottery is one of the most common and so important remains of ancient civilizations. Because iron is generally present in unpurified clays as raw material and therefore also in the archaeological ceramics ⁵⁷Fe Mössbauer spectroscopy is a very effective tool for studying the firing process. During firing the iron-bearing minerals undergo characteristic changes determined by process parameters like the kiln atmosphere, the firing temperature and the duration of firing. Aim is the reconstruction of the original production process by combining the results of an extensive phase analysis of the ancient pottery by Mössbauer spectroscopy and additional techniques with those of laboratory and field firing experiments and the archaeological evaluation of the finds.

- Albania - a country with rich cultural heritage

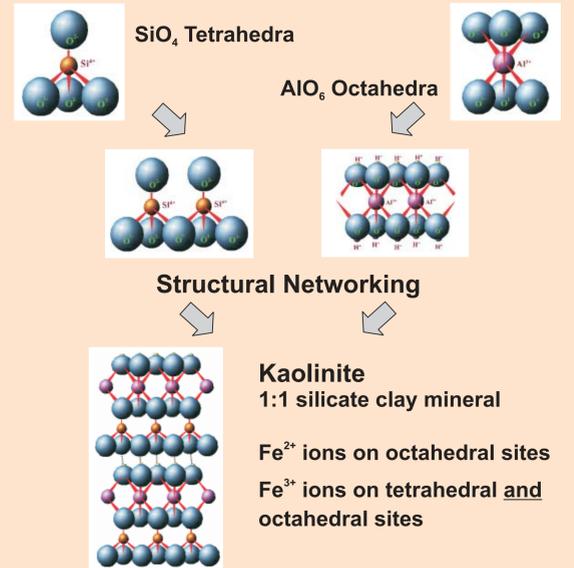


Study of samples from three different Albanian excavation sites: Apollonia, Durres and Belsh (4th to 2th century B.C.)

Clay Minerals

• Phyllosilicates

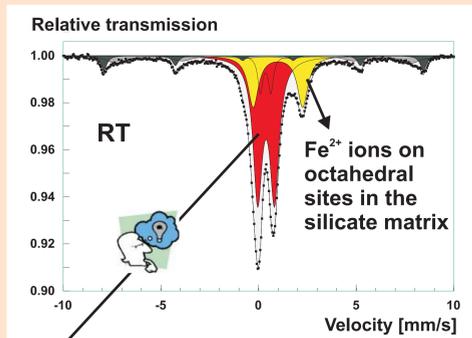
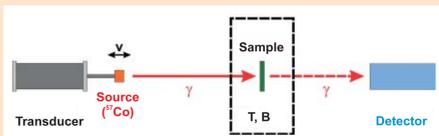
Basic Subunits



• Iron(III) oxides and hydroxides

Experimental:

Measurement of the powdered sherd samples in transmission geometry at room temperature (RT)

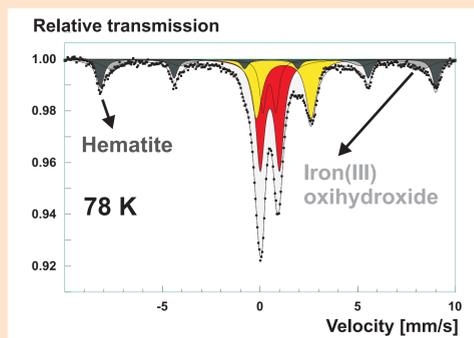


Problem: strong superposition of the subspectra of Fe³⁺ ions in the silicate matrix and superparamagnetic iron(III) oxides and hydroxides

Solution I:

Measurement at low temperatures

⇒ Blocking of superparamagnetic iron(III) oxide and hydroxide particles

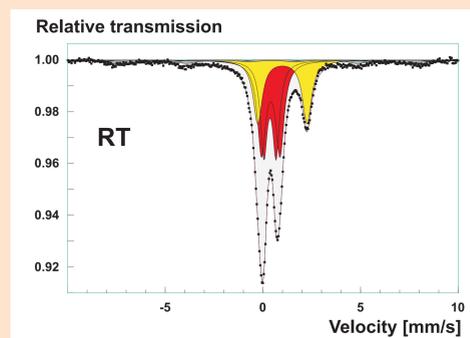


Fractional intensity of the sextets increases from 19,1 % at RT to 28,6 % at 78 K; Fe³⁺/Fe²⁺ ratio decreases from 2,71 to 1,98

Solution II:

Chemical extraction with bicarbonate-buffered sodium dithionite

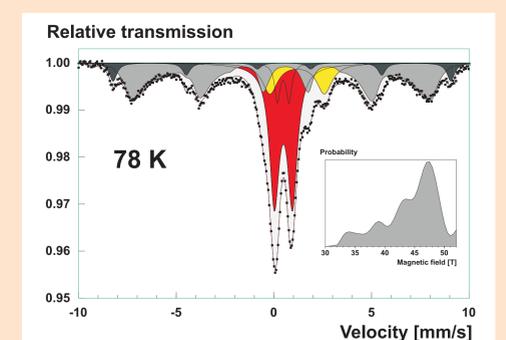
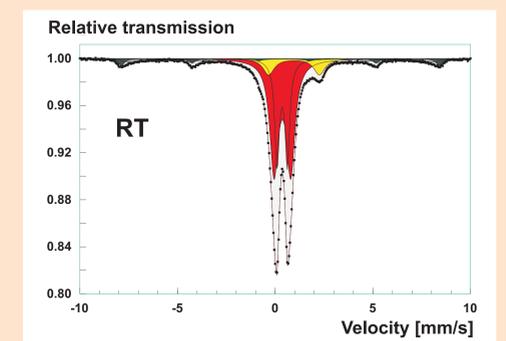
⇒ Selective dissolution of oxidic iron



Fractional intensity of the sextets decreases from 19.1 to 9.8 %; Fe³⁺/Fe²⁺ ratio decreases from 2.71 to 2.39

Special case:

Ceramic sherds found in a lake at Belsh



Dominant appearance of mostly superparamagnetic iron(III) oxihydroxides
⇒ Strong weathering process during the burial in a moist environment

Results

Mineralogical composition of archaeological ceramics determined by

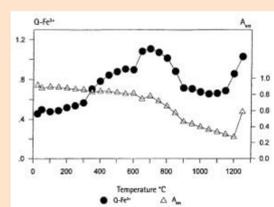
- raw material
- process parameters like
 - firing temperature
 - kiln atmosphere
 - duration of firing

Most relevant hyperfine parameters:

- quadrupole splitting of the Fe³⁺ doublet, Q-Fe³⁺
- nonmagnetic fraction in the spectra, A_{nm}
- Fraction of Fe²⁺, A-Fe²⁺

Aim: Reconstruction of the original production process by combining the results of the phase analysis with those of laboratory and field firing experiments

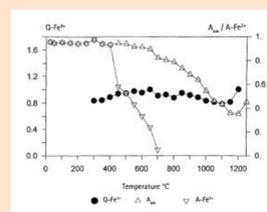
Results of extensive studies with Peruvian ceramics and clays for reconstruction of the Precolumbian firing technology (U. Wagner et al.)



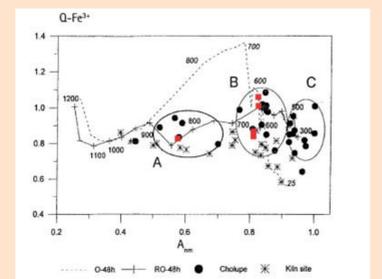
Firing of Clay Batán Grande in air for 48 h after a preceding 3 h reduction

increased Q-Fe³⁺ compared to fresh clays due to decrease of the symmetry of the ligand environment of the iron atoms caused by dehydroxilation of the octahedral layers in the clay minerals and the beginning breakdown of the clay structure.

Firing of clay Batán Grande in air for 48 h



Comparison of RT Mössbauer data of sherds found at Belsh (red) with the reference data



Oxidation process after preceding reduction found for the studied Albanian ceramics