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

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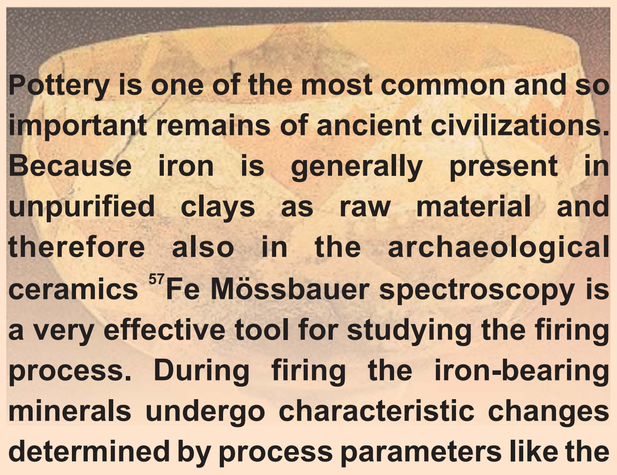
Introduction



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 ^{57}Fe 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.

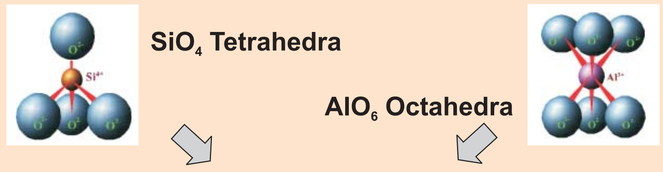
- Albania -
a country with rich cultural heritage

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

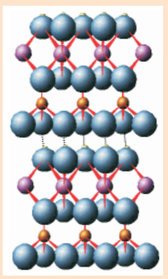
Clay Minerals

- Phyllosilicates

Basic Subunits



Structural Networking



Kaolinite
1:1 silicate clay mineral

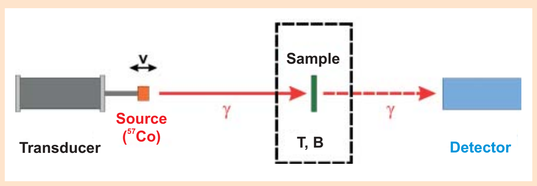
Fe^{2+} ions on octahedral sites

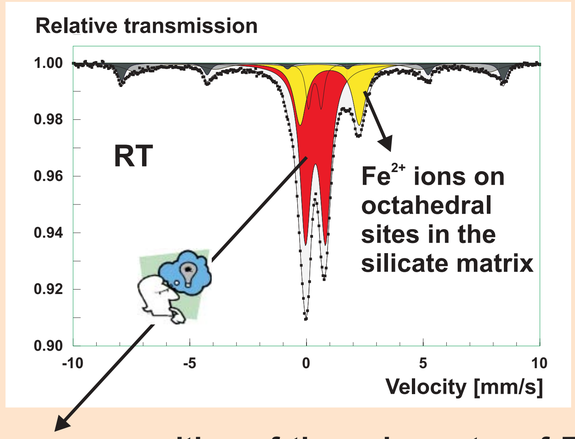
Fe^{3+} ions on tetrahedral and octahedral sites

- Iron(III) oxides and hydroxides

Mössbauer Spectroscopy

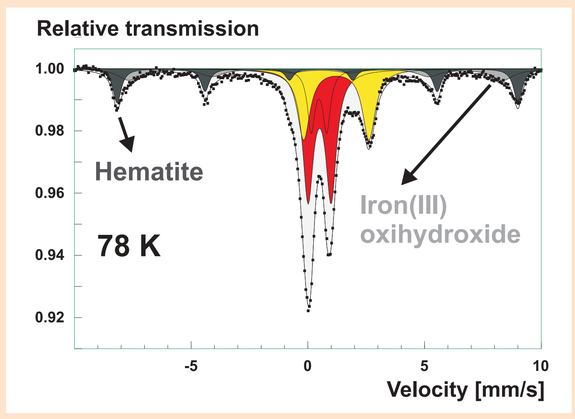
Experimental:
Measurement of the powdered sherd samples in transmission geometry at room temperature (RT)





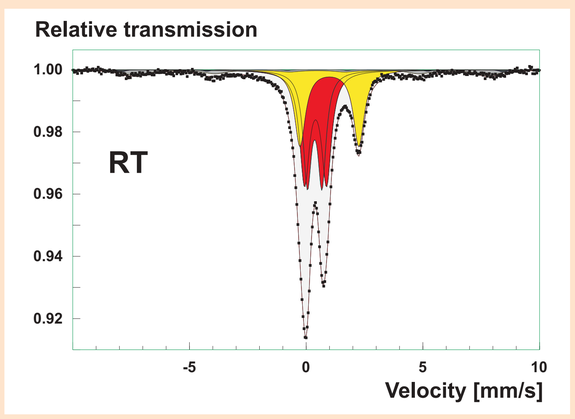
Problem: strong superposition of the subspectra of Fe^{3+} ions in the silicate matrix and superparamagnetic iron(III) oxides and hydroxides

Solution I:
Measurement at low temperatures
⇨ Blocking of superparamagnetic iron(III) oxide and hydroxide particles



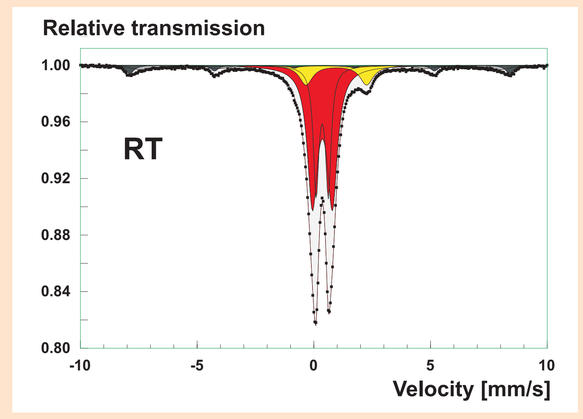
Fractional intensity of the sextets increases from 19,1 % at RT to 28.6 % at 78 K; Fe^{3+}/Fe^{2+} ratio decreases from 2,71 to 1,98

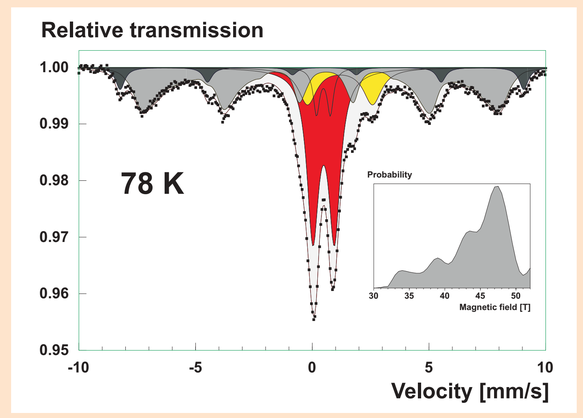
Solution II:
Chemical extraction with bicarbonate-buffered sodium dithionite
⇨ Selective dissolution of oxidic iron



Fractional intensity of the sextets decreases from 19.1 to 9.8 %; Fe^{3+}/Fe^{2+} 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

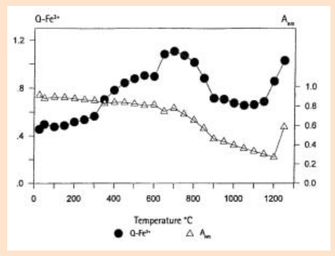
- raw material
- process parameters like
  - firing temperature
  - kiln atmosphere
  - duration of firing

Most relevant hyperfine parameters:

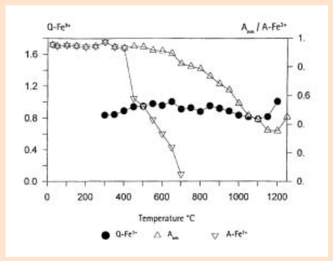
- quadrupole splitting of the Fe^{3+} doublet, Q-Fe^{3+}
- nonmagnetic fraction in the spectra, A_{nm}
- Fraction of Fe^{2+}, A-Fe^{2+}

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.)



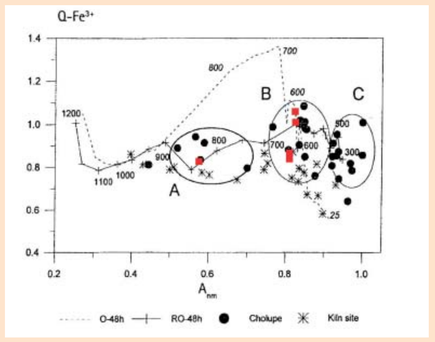
Firing of clay Batan Grande in air for 48 h



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

increased Q-Fe^{3+} 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.

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