Mössbauer Studies in Archaeology: A preliminary description

1. Introduction

If applied in a systematic fashion Mössbauer spectroscopy is a valuable tool in the study of prehistoric artifacts (Hyperfine Interactions 154: 5-33, 2004). In Munich we have applied Mössbauer spectroscopy to describe the material properties of a large amount of Celtic and Andean pottery and tried to interpret them in an archaeological context.

The stable iron isotope ^{57}Fe is the testing probe in the Mössbauer measurements. Since iron is generally present in clay and ceramics in a concentration of several percent, measurements are possible on a routine basis (Hyperfine Interactions 154: 83-94, 2004). Hyperfine interactions between the ^{57}Fe nuclei and the surrounding electrons are measured and yield characteristic parameters that describe the chemical and physical state of the iron in solids. This specifically refers to the valence state of the iron atoms, the symmetry of their environment and the type and magnetic properties of iron compounds.

The aim of Mössbauer studies of ceramic materials is to obtain information on the firing conditions (temperature and kiln atmosphere) and to some extent, also on the raw materials used in making the pottery. In this context, laboratory model experiments on appropriate clays are essential and have been performed systematically: In model experiments systematic studies of clay samples fired at temperatures increasing from 100 °C to 1200 °C in steps of 50 °C were carried out (Hyperfine Interactions 154: 83-94 and 121-141, 2004). By firing in oxygen-rich and oxygen-depleted atmospheres possible kiln environments were simulated.

Some features of ceramic finds can only be studied when spectra are measured both at room temperature (RT) and at liquid helium temperature (4.2K). Differently colored layers, which are frequently observed in sherds, have to be studied separately. Occasionally samples were measured in an external magnetic field of 6 Tesla in order to help in the identification of magnetic components. Finally spectra of samples from controlled laboratory firing experiments on appropriate clays can be compared with the spectra obtained from archaeological ceramics. In this way ancient firing techniques can be assessed.

2. Study of model materials

In the study of the sherds excavated in a Sicán cemetery at Huaca Loro, we can rely on a previous extensive investigation of several clay specimens from the nearby workshop of Huaca Sialupe. Samples of ancient clays found at the excavation site of the workshop and of a recently collected clay were studied as well as samples from sherds already finished but not yet fired vessels (Hyperfine Interactions 150: 73-89, 91-105,107-123 and 125-139, 2003).

The Mössbauer spectra thus yield characteristic parameters, which reflect the valency and local symmetry of the environment of the iron atoms (Fig.1). They also give information on the magnetic properties of the iron compounds. With supplementary methods, like X-ray diffraction and optical thin section microscopy, non iron-bearing minerals and oxides present in ceramics can often be identified. In this way conclusions can be drawn on the type of raw materials and on the treatment during pottery production.

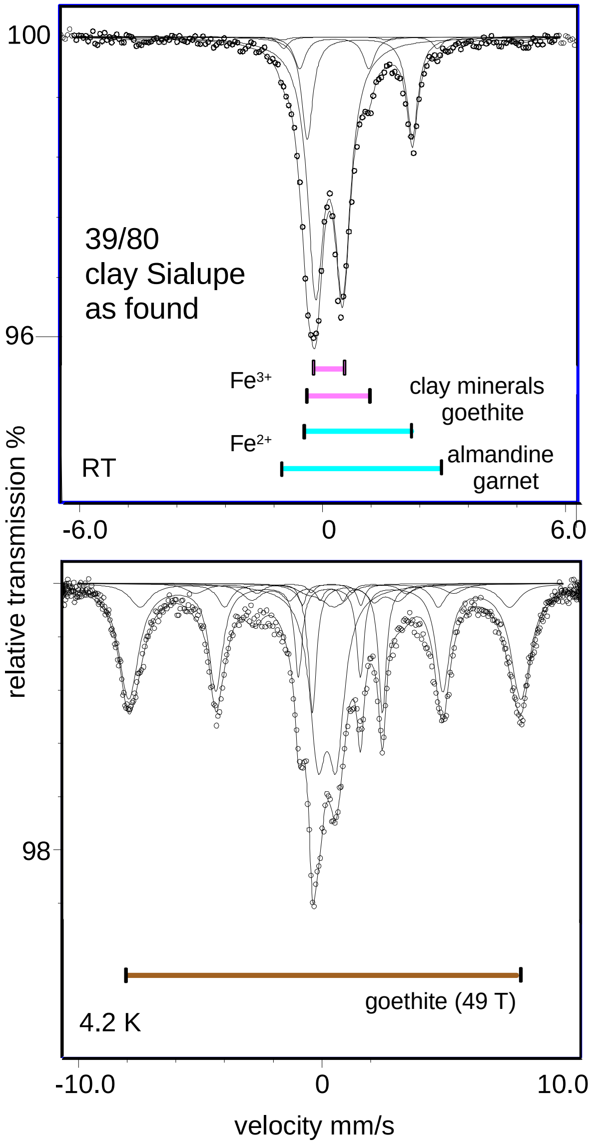


Fig. 1: Mössbauer spectra of clay from Sialupe taken at RT (top) and 4.2K (bottom). The different components are marked by bars. Part of the central doublet observed at RT belongs to superparamagnetic goethite, which orders magnetically at 4.2K with a characteristic magnetic hyperfine field of 49 Tesla.

During the firing of clay at increasing temperatures chemical and physical transformations occur and the Mössbauer parameters undergo characteristic changes. Their behaviour in oxidizing, reducing and changing atmospheres was studied systematically in laboratory experiments and serves as reference to assess the firing conditions in antiquity. The different processes taking place at increasing temperatures during firing in air (O) are explained in Fig. 2 for clay 39/80 from Sialupe. Two sensitive parameters are the electric quadrupole splitting of the trivalent iron at RT and the fraction of the spectral area that does not show magnetic hyperfine splitting at RT.

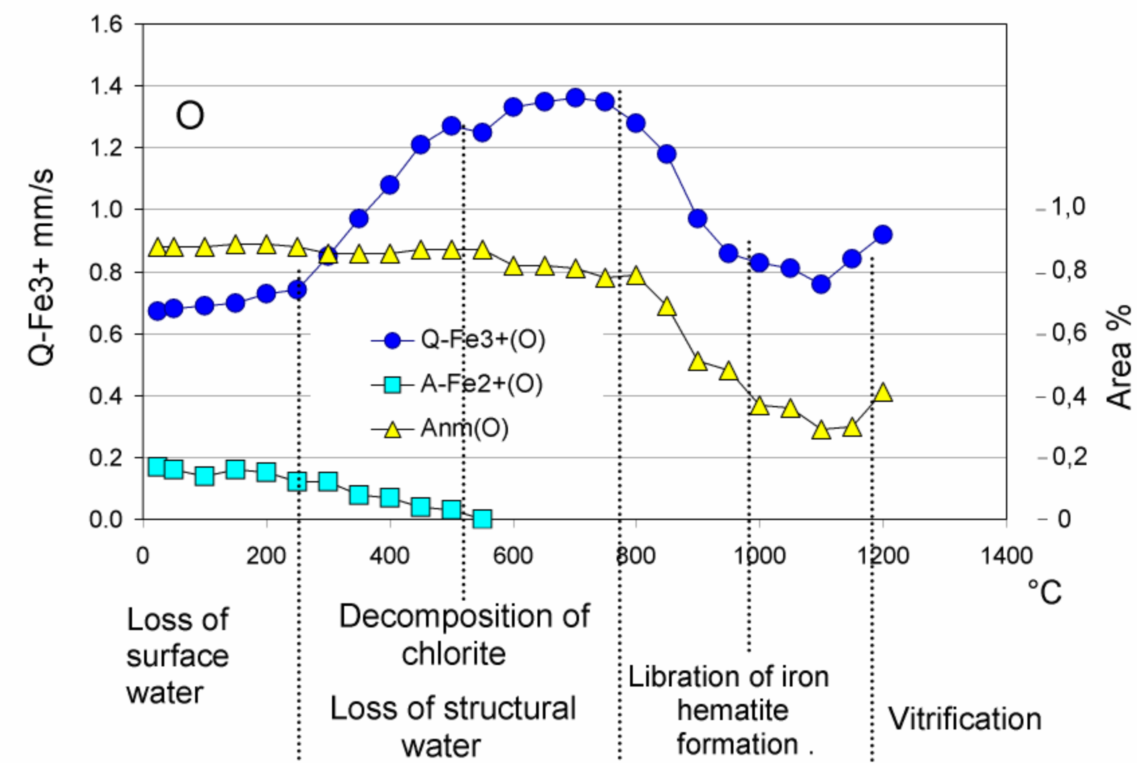


Fig.2: RT Mössbauer parameters observed for clay Sialupe (39/80) subjected to firing in air (O). Q-Fe^{3+} is the quadrupole splitting for the main Fe^{3+} doublet, A_{nm} is the cumulated fractional area of all species that show no magnetic splitting, A-Fe^{2+} the fractional area of Fe^{2+} species.

Heating the clay in the temperature region between RT and 300 °C causes some weight loss due to loss of surface water. During this, the Mössbauer parameters change only slightly. The quadrupole splitting Q-Fe^{3+} starts to increase drastically in the temperature region between 300 and 500 °C due to the loss of structural water from the clay matrix, which causes a decrease in local symmetry. Fe^{2+} disappears due to oxidation. The kink at 600 °C arises from the decomposition of chlorite. Above 800 °C the clay matrix breaks down and the librated iron atoms start to form hematite. Accordingly, the area of nonmagnetic species decreases. At still higher temperatures mineral formation and vitrification becomes dominant.

The parameters in Fig.2 were taken from the spectra shown as threedimensional plots of the RT Mössbauer spectra measured after firing in air (O) and shown in Fig.3. This figure also shows spectra obtained after firing in air of a sample first reduced at 800 °C (RO) and after reduction at different temperatures (R). Fig.3 thus gives an idea about the variety of the spectra observed after firing in different atmospheres.

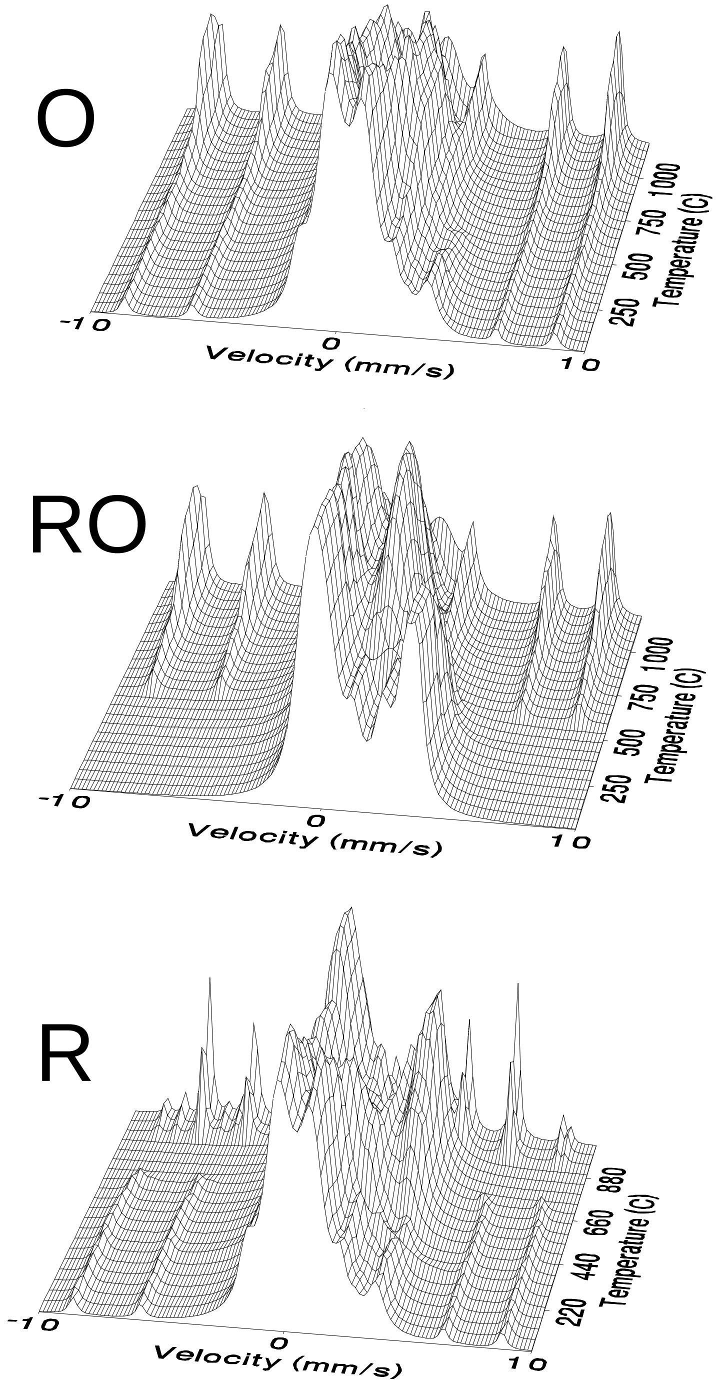
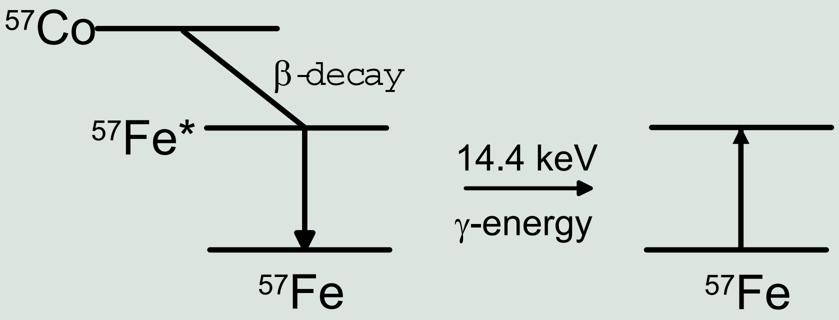


Fig.3: Threedimensional mountain plots of the RT Mössbauer spectra of clay Sialupe (39/80) fired in air for 48 h (O, top), fired in air for 48 h after a preceding reduction at 800 °C for 3 h (RO, middle), and fired in a reducing environment for 3 h (R, bottom). Metallic iron is formed in the latter case above 900 “C and can be easily identified by its small magnetic hyperfine field.

Principle of Mössbauer Measurement



source

absorber

^{57}Co

β-decay

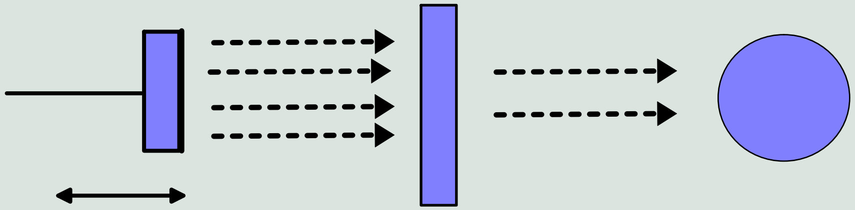
^{57}Fe*

14.4 keV

γ-energy

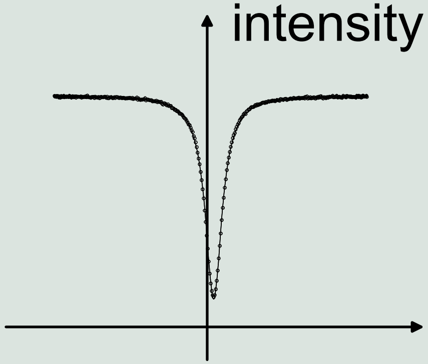
^{57}Fe

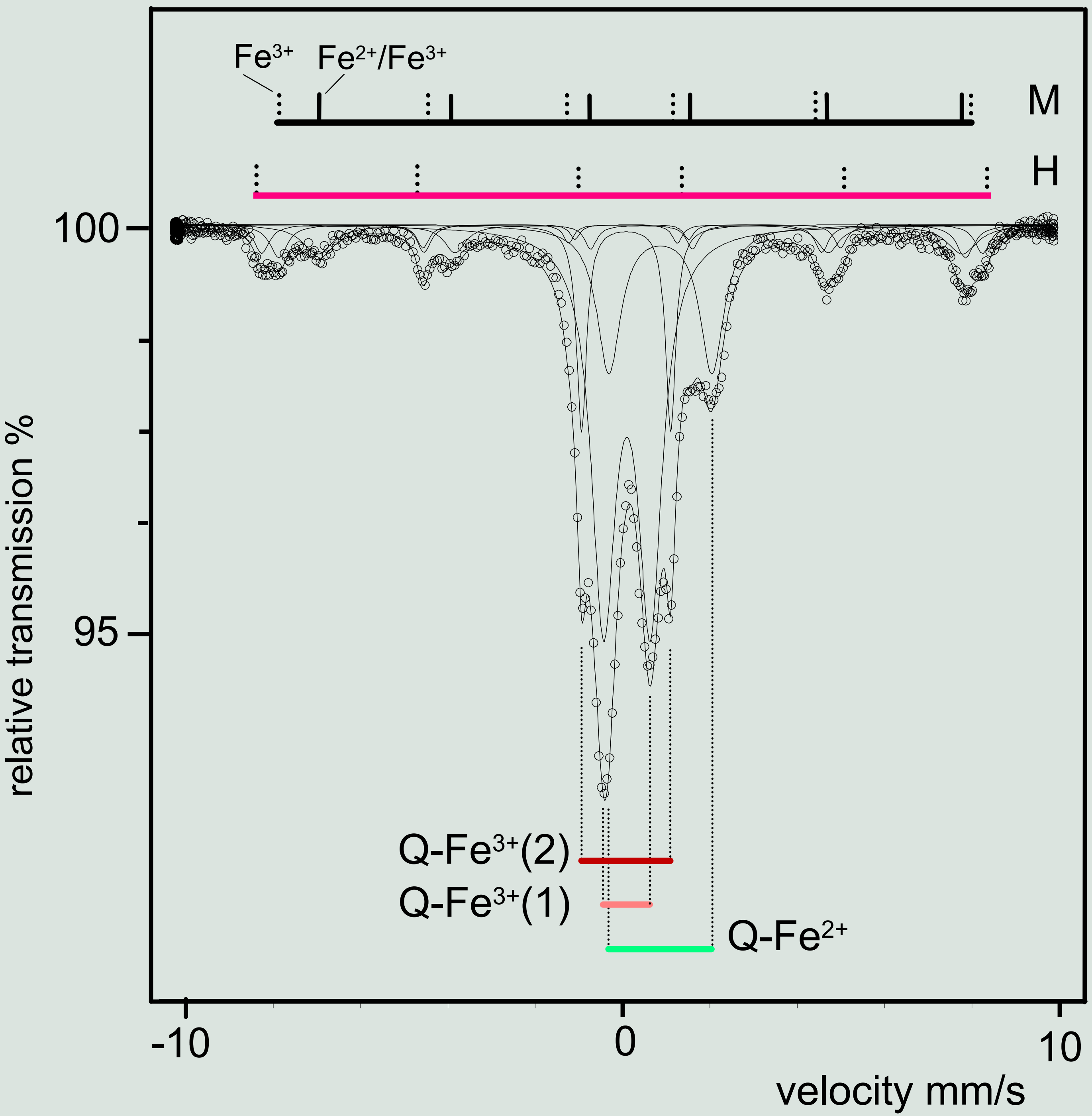
^{57}Fe



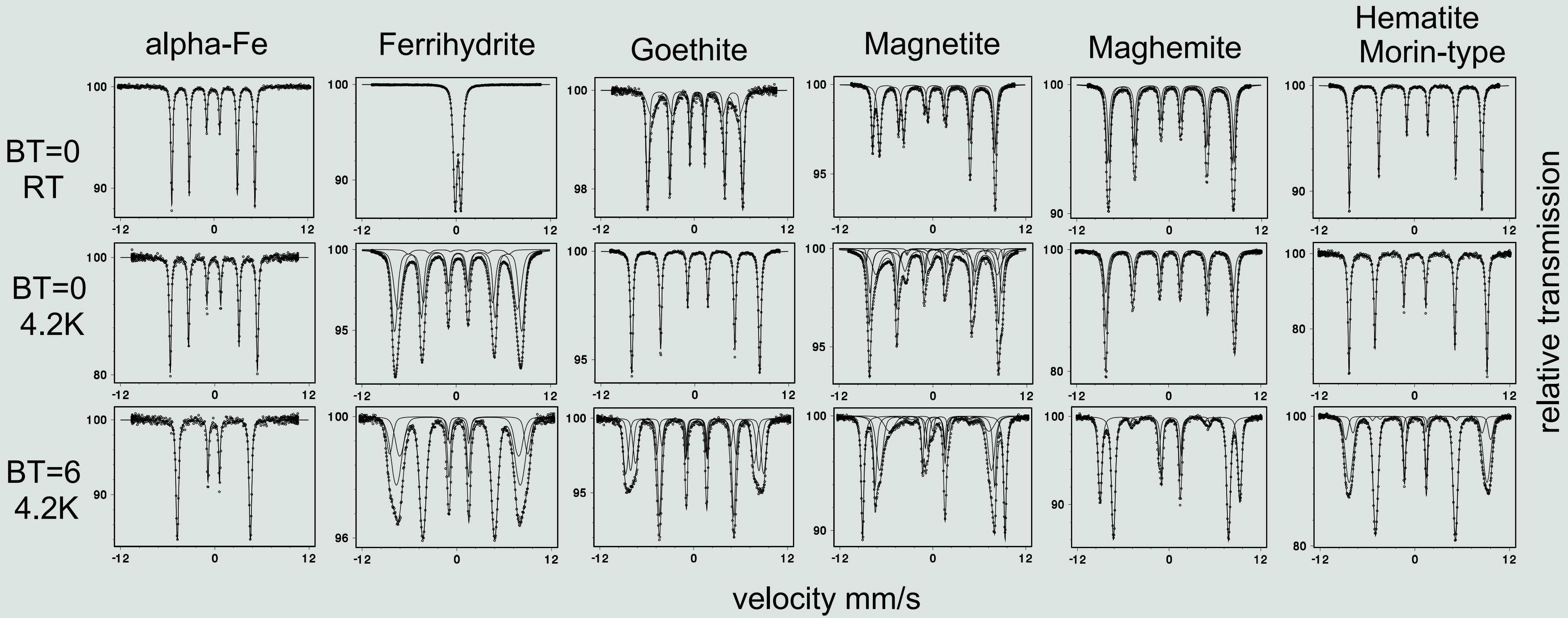
source absorber detector

Doppler velocity



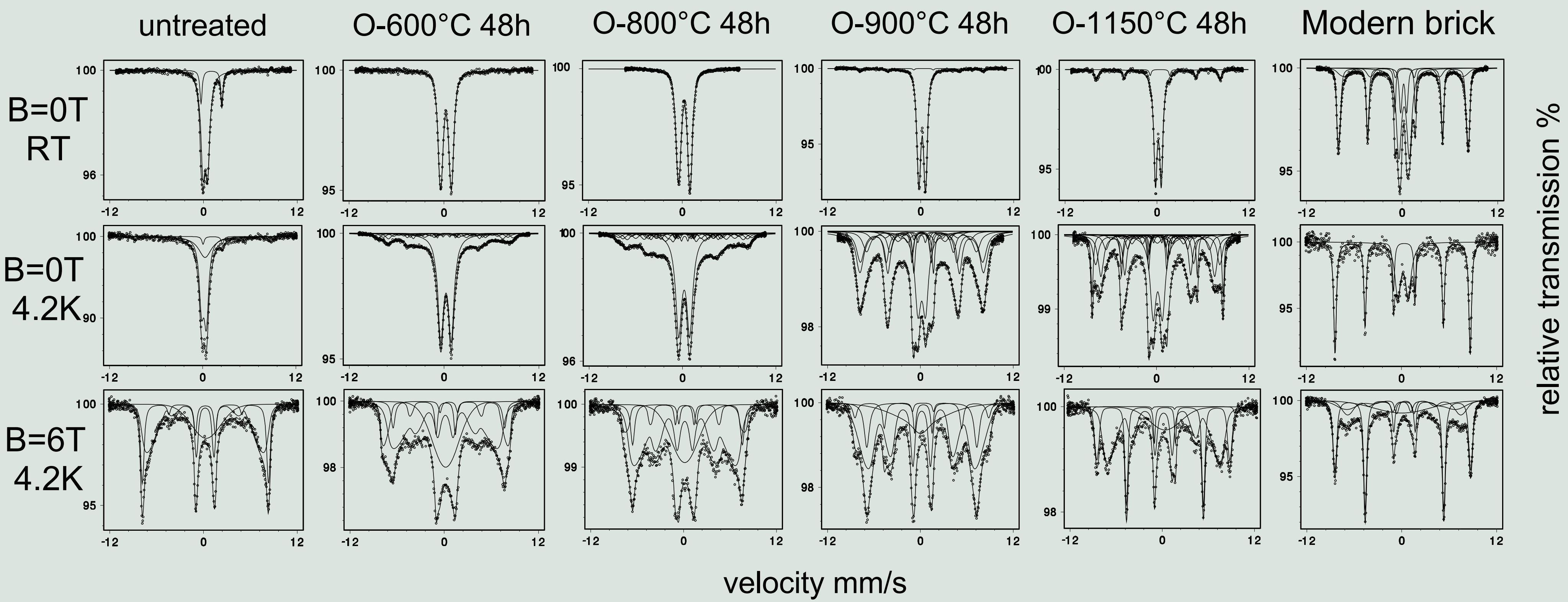


Mössbauer spectrum
of a sherd from the
Galeria de las Ofrendas
(13/73) Type Floral

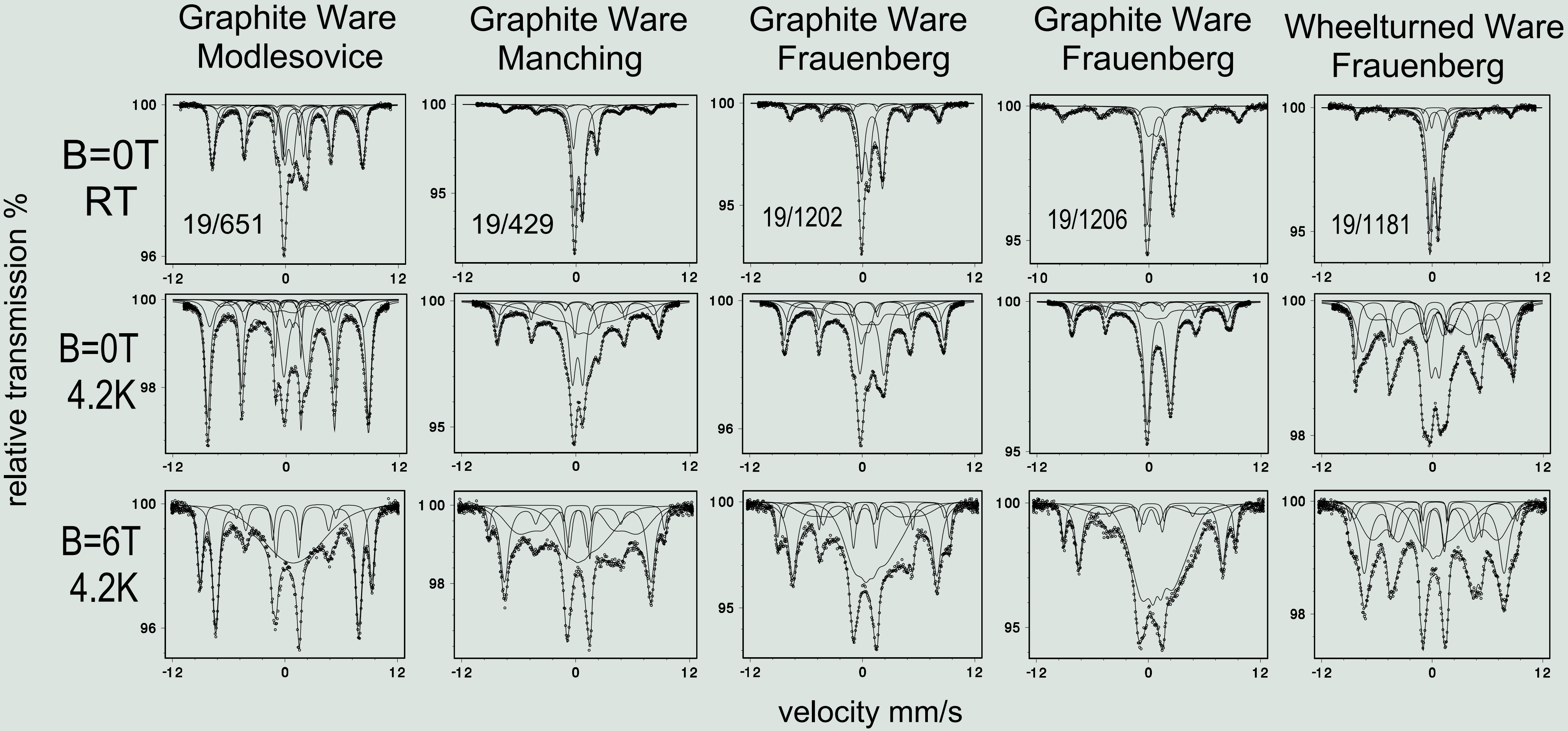


Mössbauer patterns of various iron oxides, as found in clays and ceramics, measured at room temperature (RT, top), at liquid helium temperature (4.2K, middle) and at 4.2K in an external magnetic field of 6T.

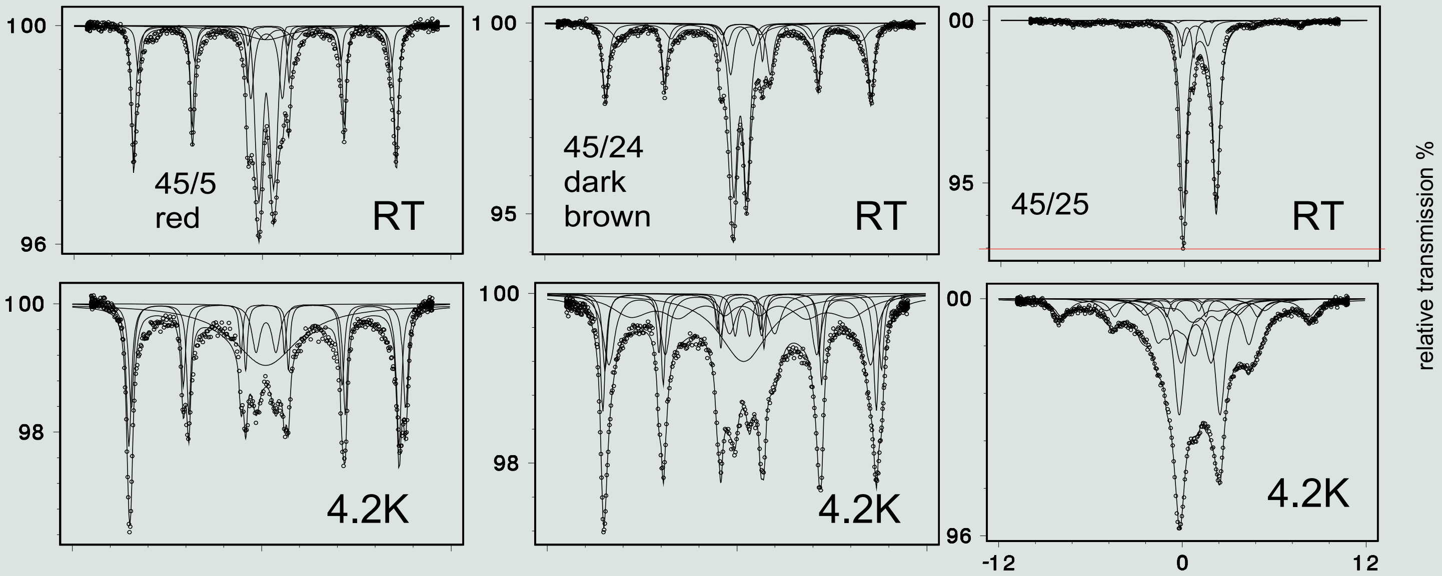
Montmorillonite

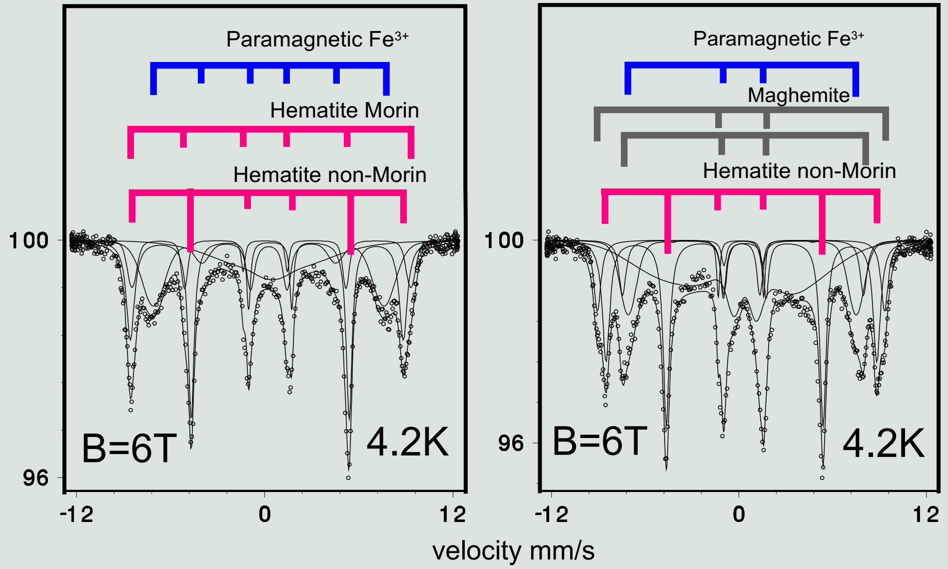


Mössbauer patterns of untreated montmorillonite and after heating it in air for 48 h at increasing temperatures measured at room temperature (RT, top), at liquid helium temperature (4.2K, middle) and at 4.2K in an external magnetic field of 6T. The spectra of a modern brick are shown at the right.



Mössbauer patterns of Celtic pottery measured at room temperature (RT, top), at liquid helium temperature (4.2K, middle) and at 4.2K in an external magnetic field of 6T.





Mössbauer spectra of 2 sherds from Pachacamac taken at RT (top) and at 4.2K (middle).

The explanation of the individual components in the Mössbauer spectra measured at 4.2K in an external field of 6 Tesla is shown at the bottom. The presence of maghemite in sherd 45/24 is unambiguously revealed.