

Of MOUSE and Men

Single-sided NMR in Cultural Heritage

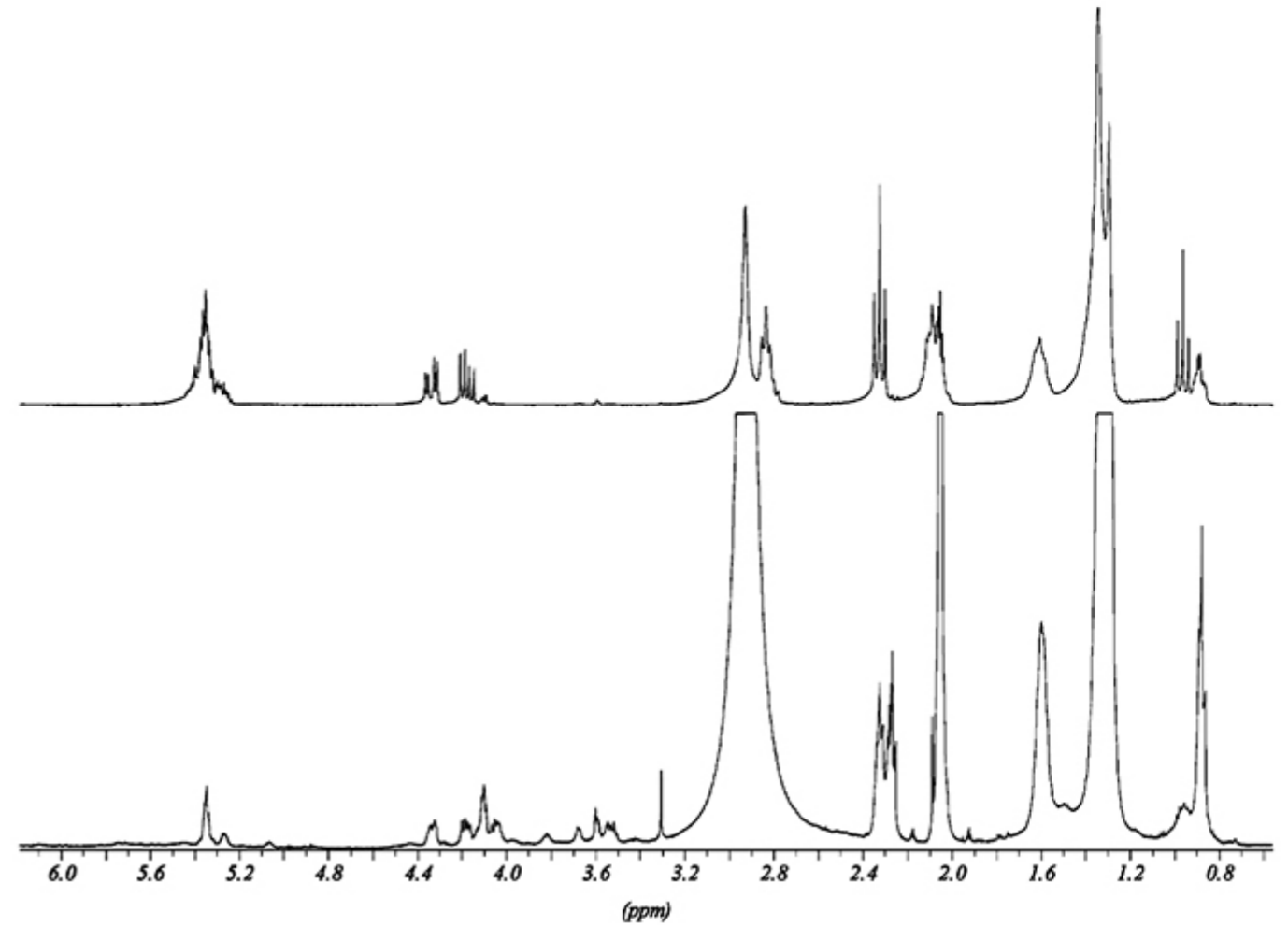
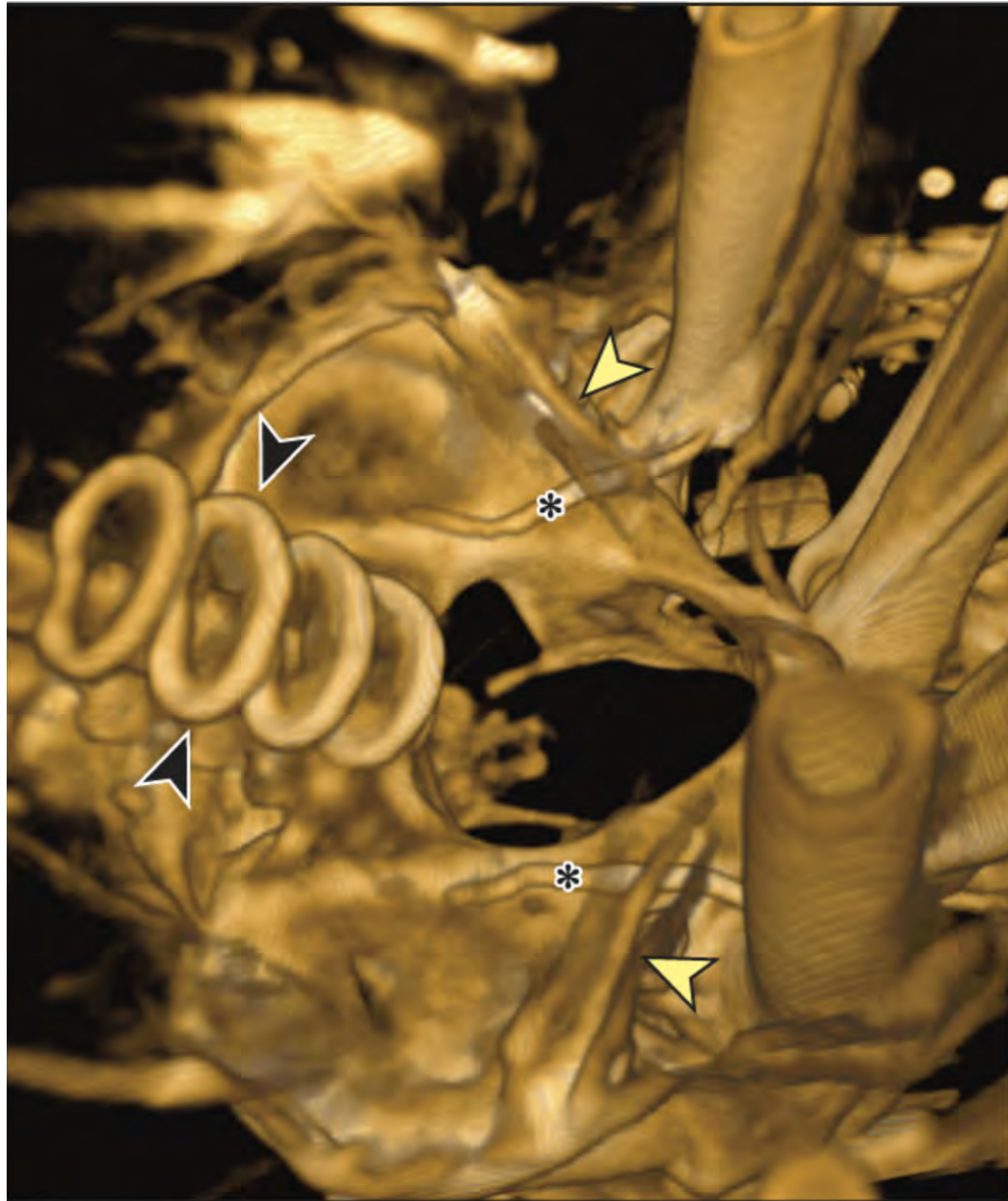
Tyler Meldrum

New Techniques for the Non-invasive Investigation of the Surface and Subsurface

Structure of Heritage Objects

Toruń, Poland; 25 June 2013

What Can NMR Contribute?



Rühli et al. Clinical Magnetic Resonance Imaging of Ancient Dry Human Mummies Without Rehydration. *J. Am. Med. Assoc.* **2007**. doi:10.1001/jama.298.22.2618-b
Spyros and Anglos. Study of aging in oil paintings by 1D and 2D NMR spectroscopy. *Anal. Chem.* **2004**. doi:10.1021/ac049350k

Shortcomings of NMR

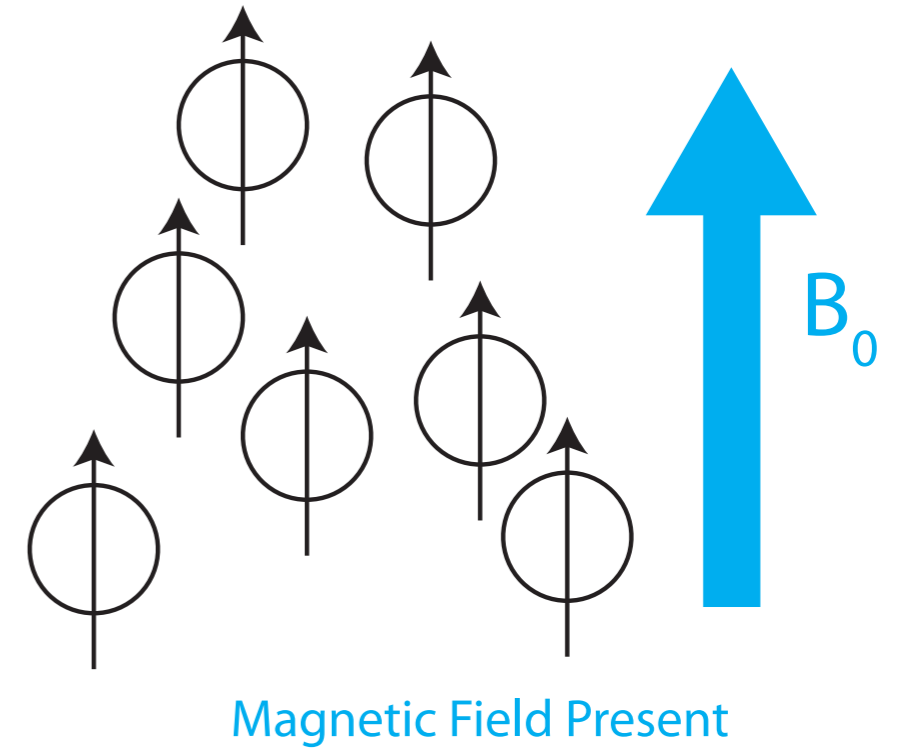


Expensive
Fixed in labs
Incompatibility with some samples



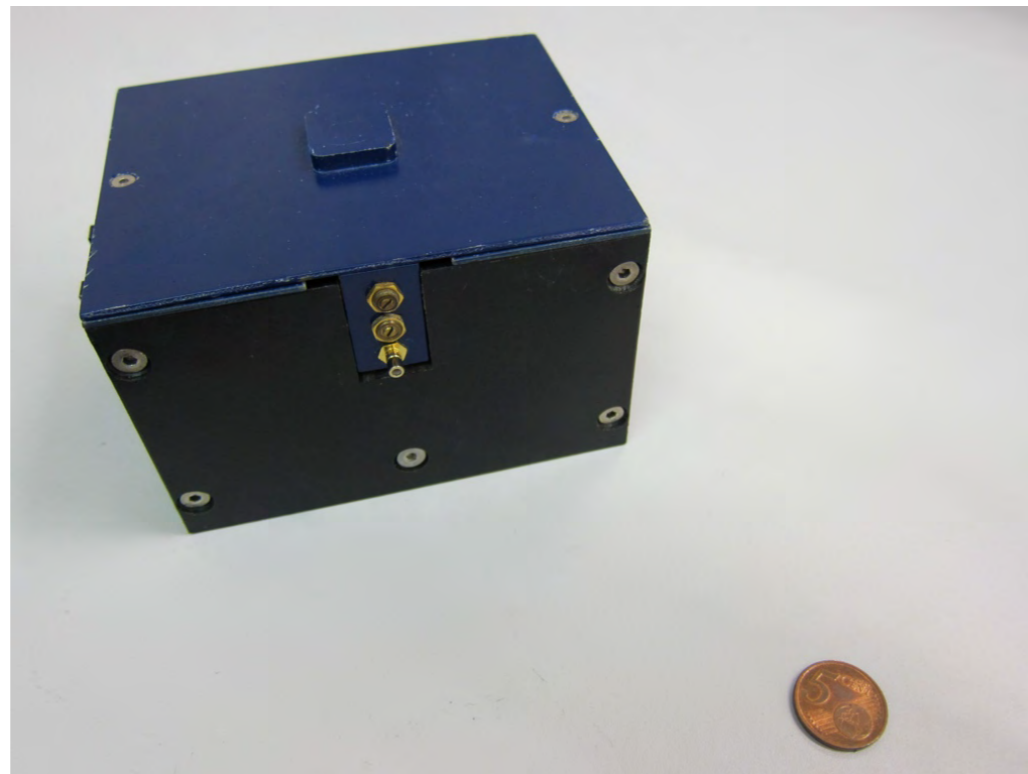
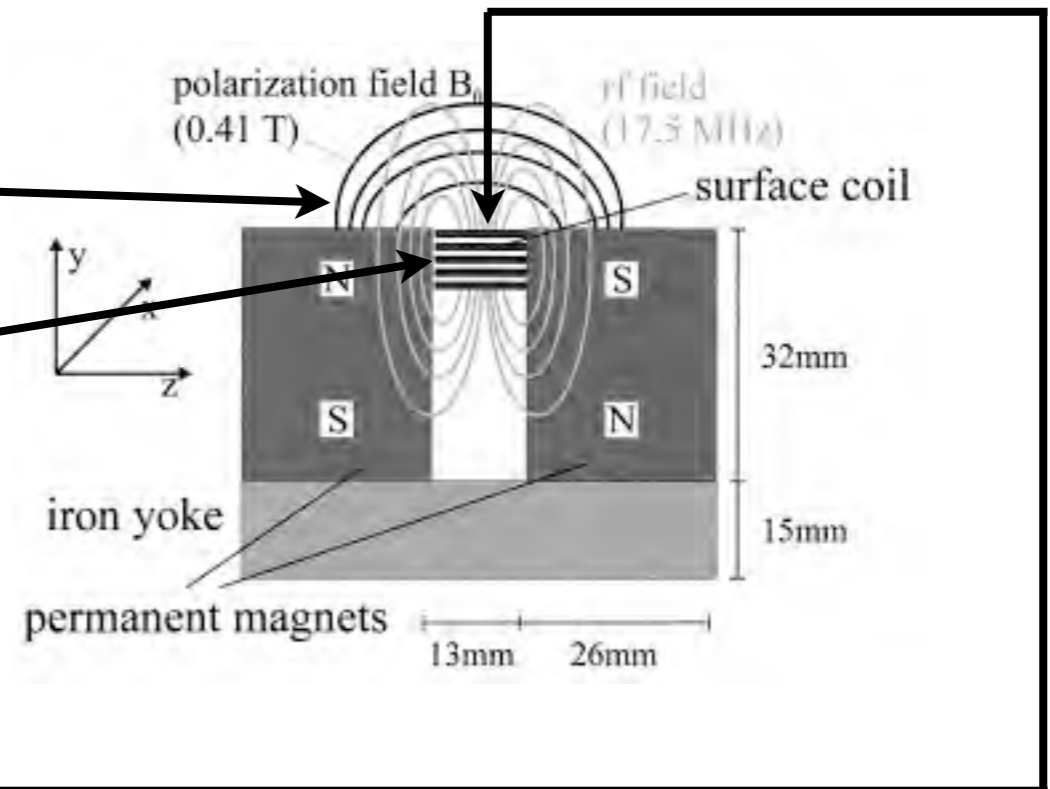
Essential NMR

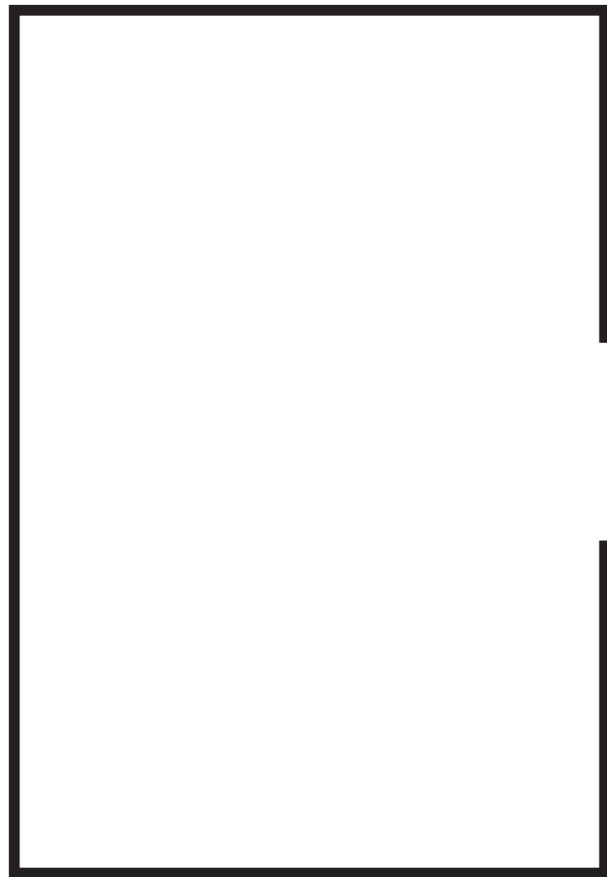
- Sample
- Magnetic field
- RF transmitter/receiver

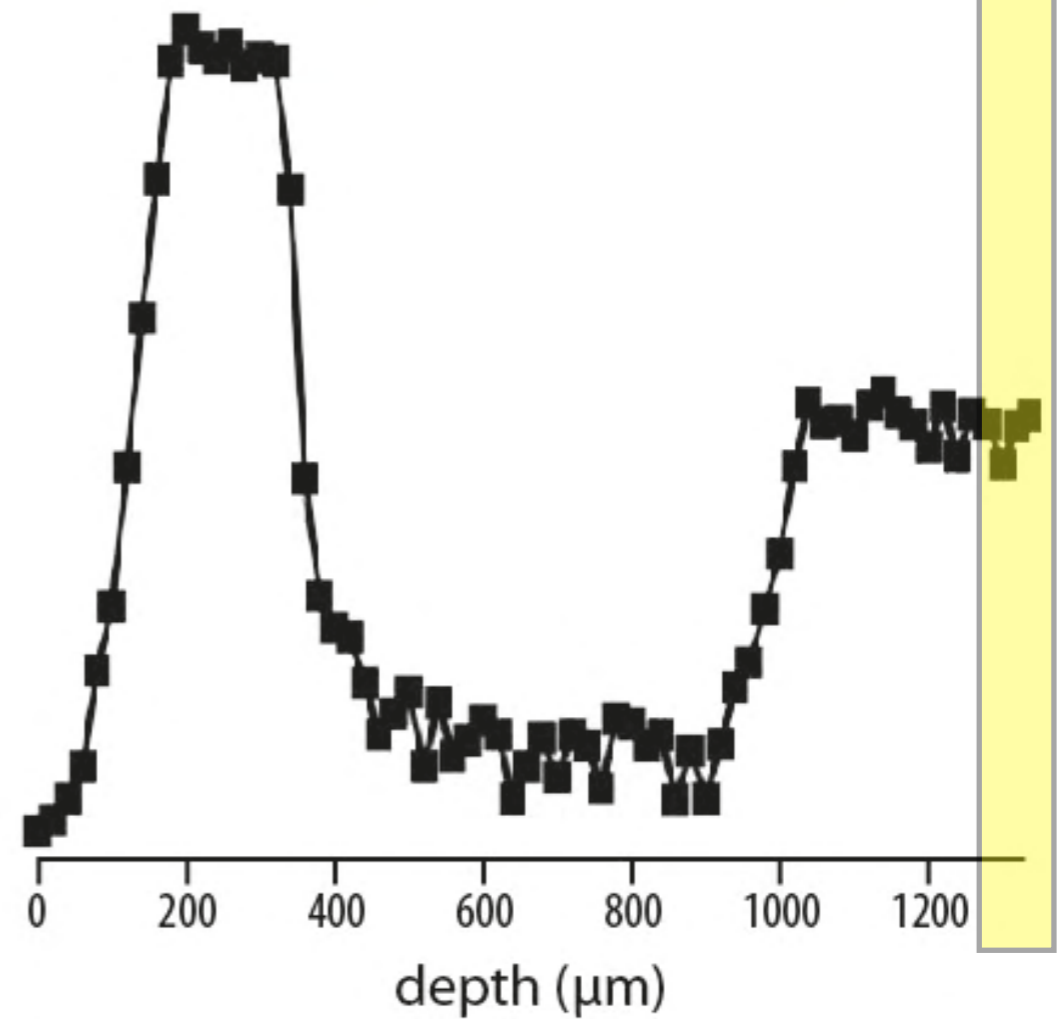
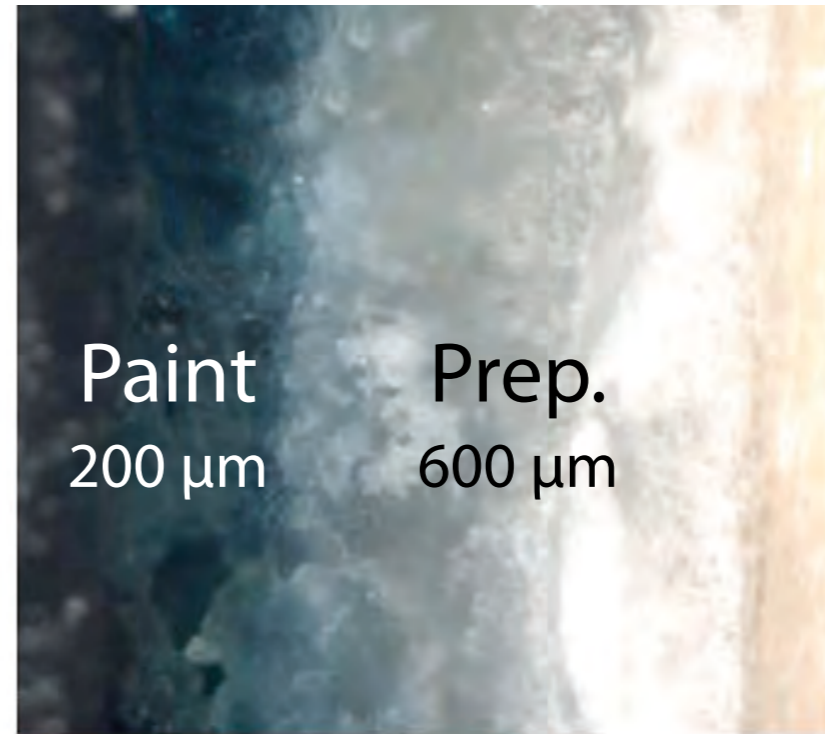
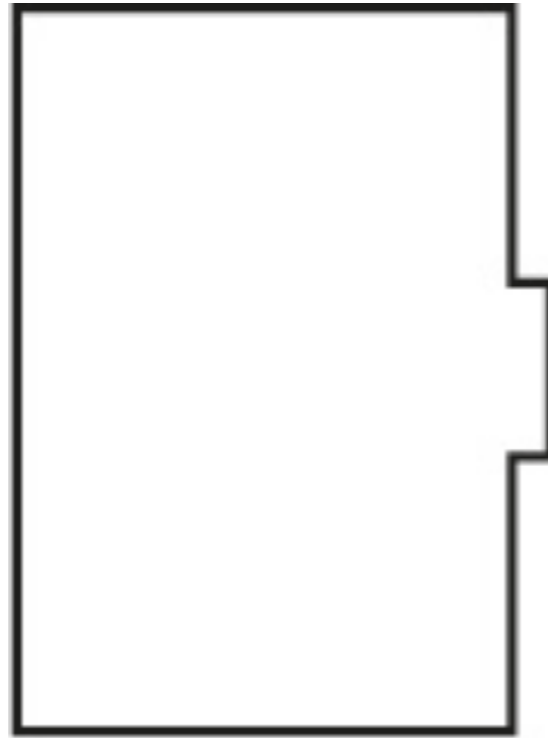


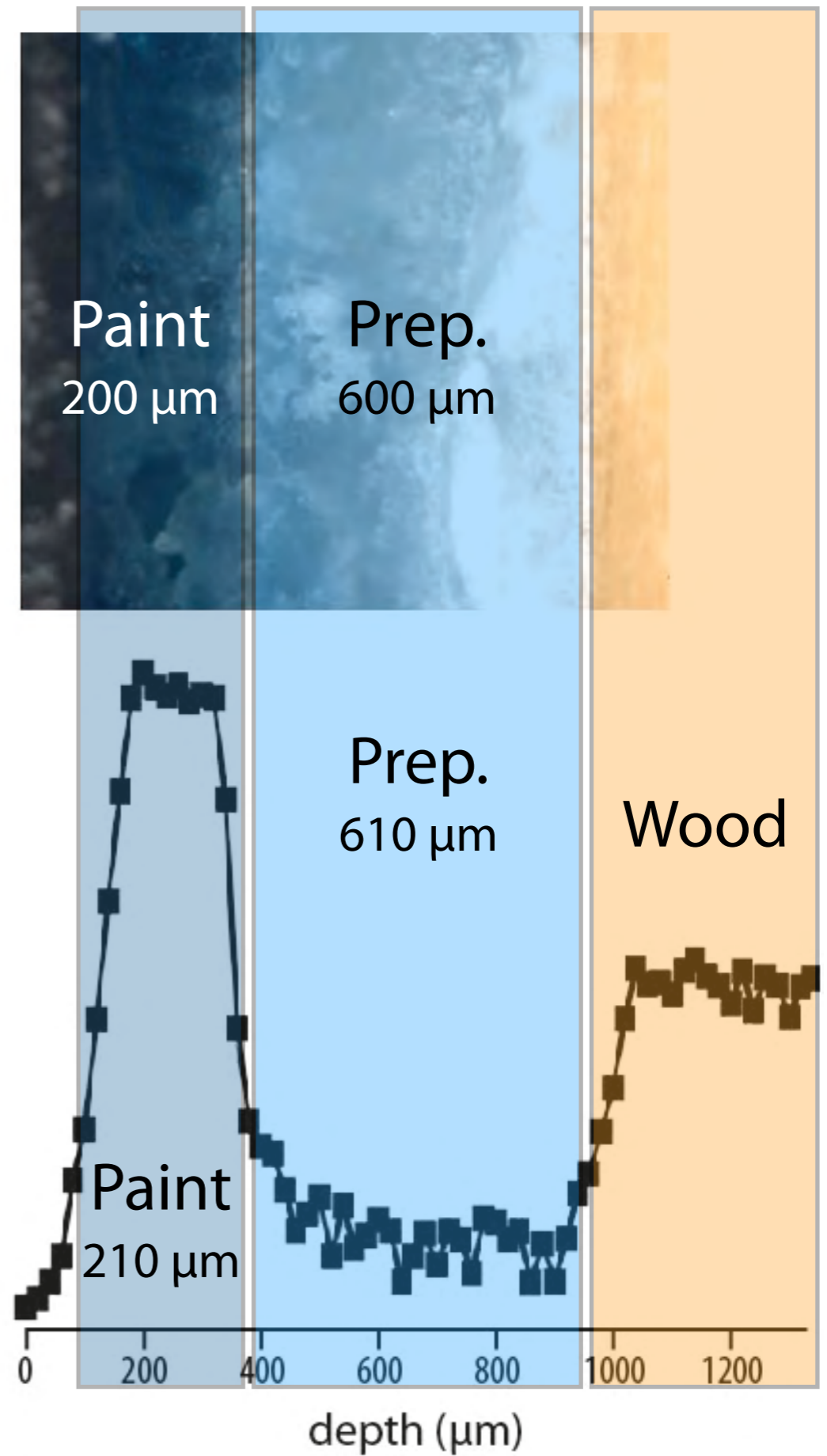
Open, Single-sided Magnets

- Magnetic field
- RF transmitter/receiver
- Sample







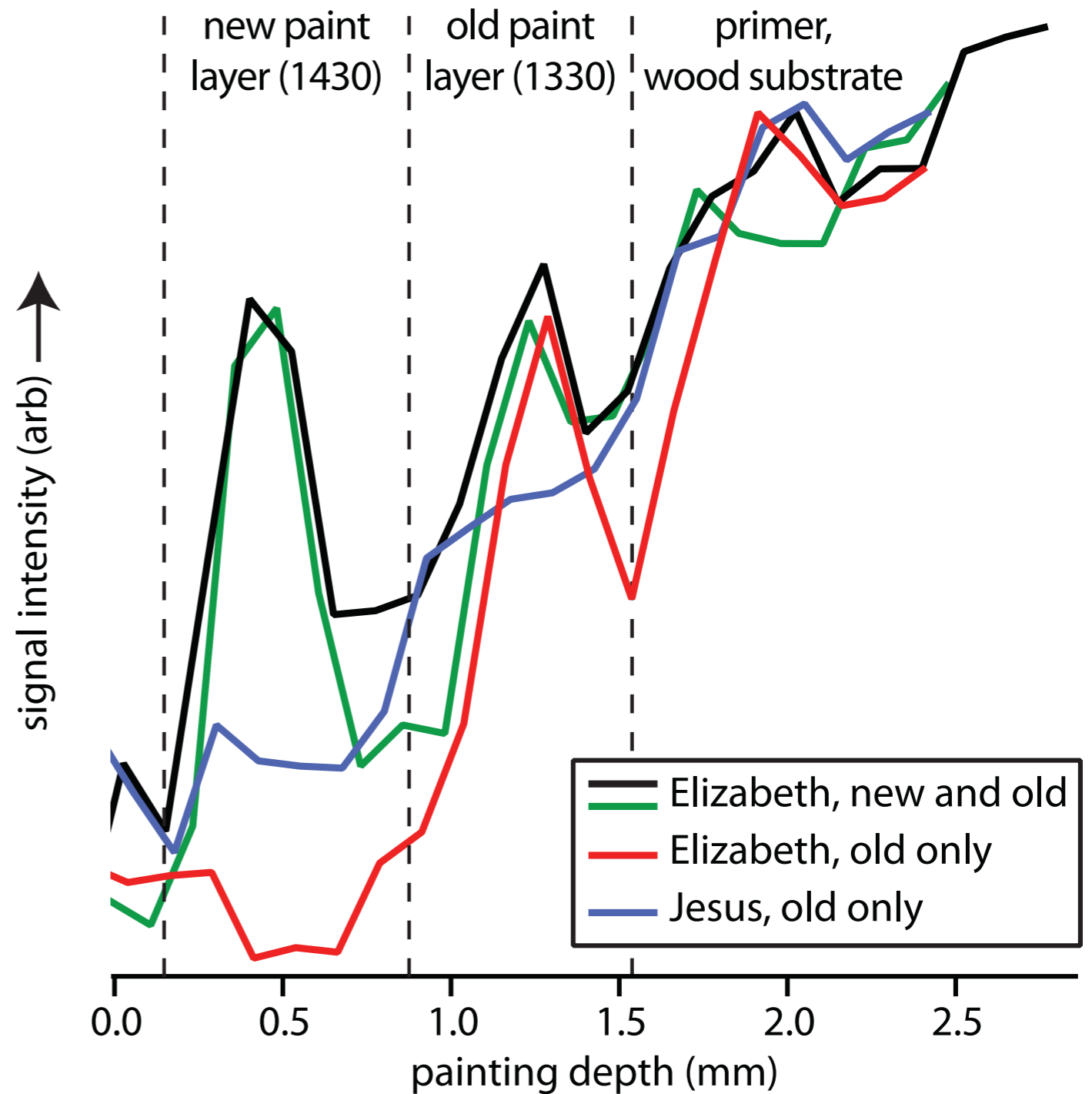


Wallraf-Richartz Museum

Elizabeth clothes the naked/Elizabeth cares for the sick
Painting on Fir, 1330/1430



Depth Profiles and Age of Paint Layers



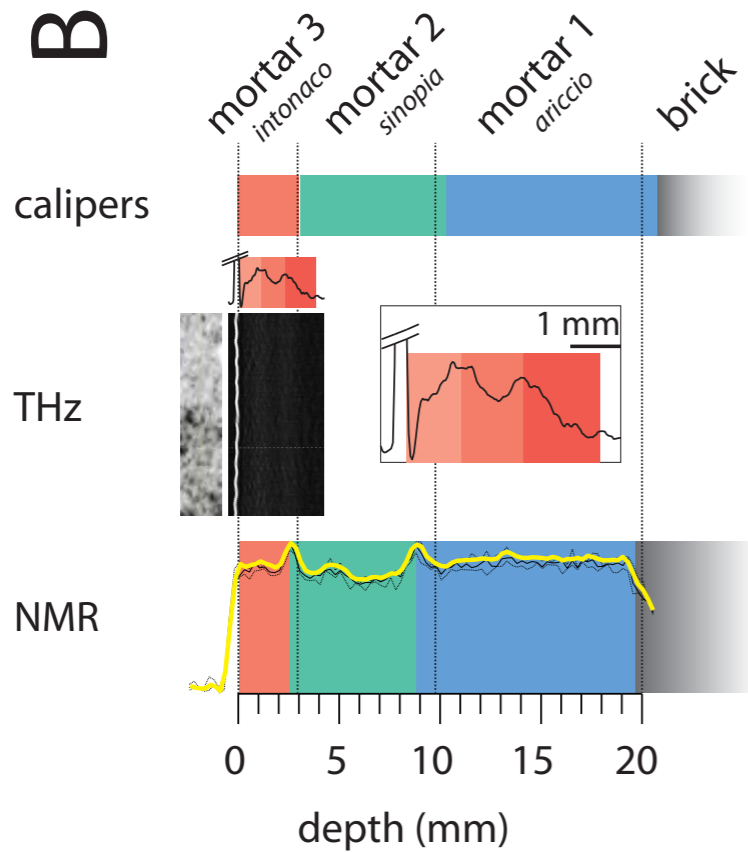
Frescoes

Nara, Japan



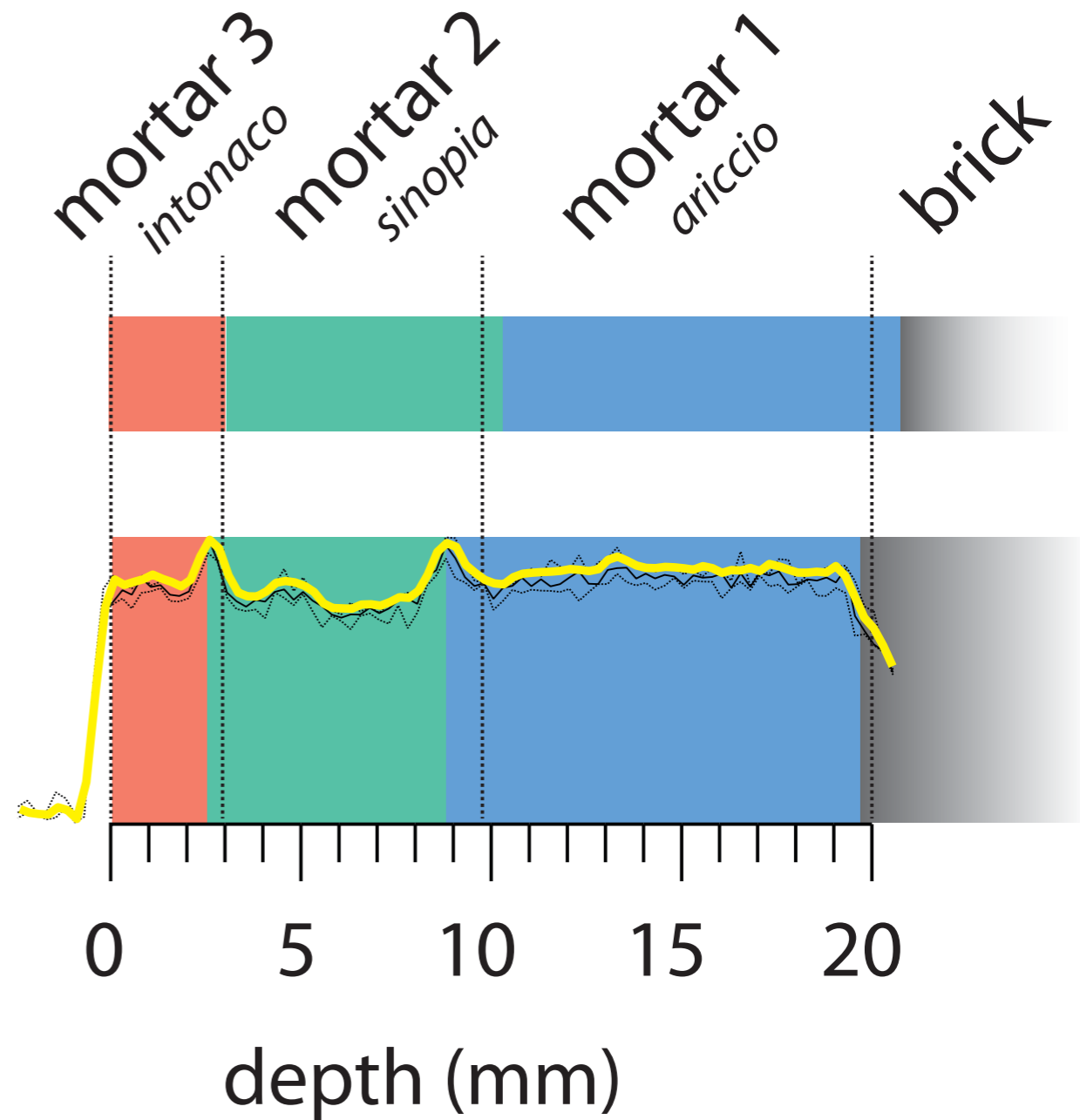
Frescoes

Buon Fresco Style (Florentine)



calipers

NMR

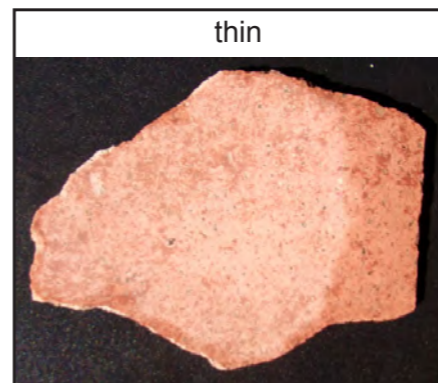
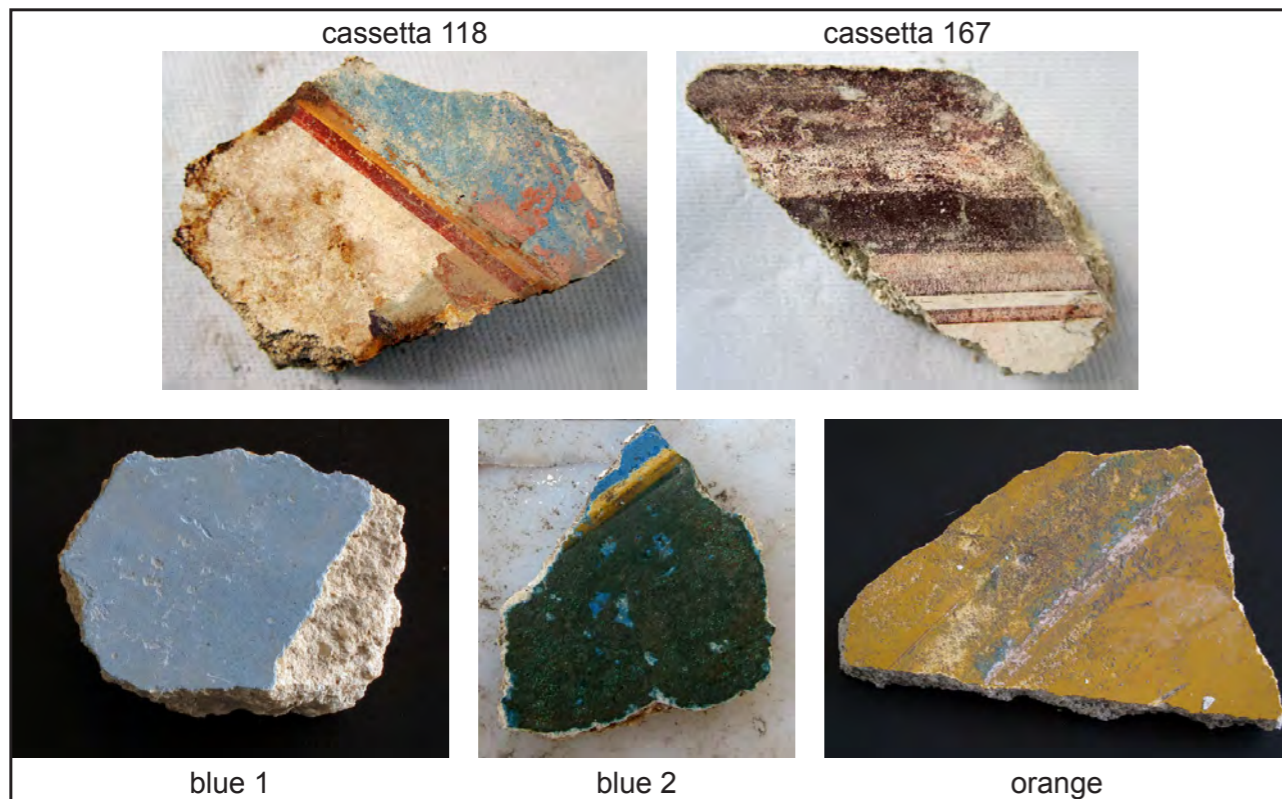
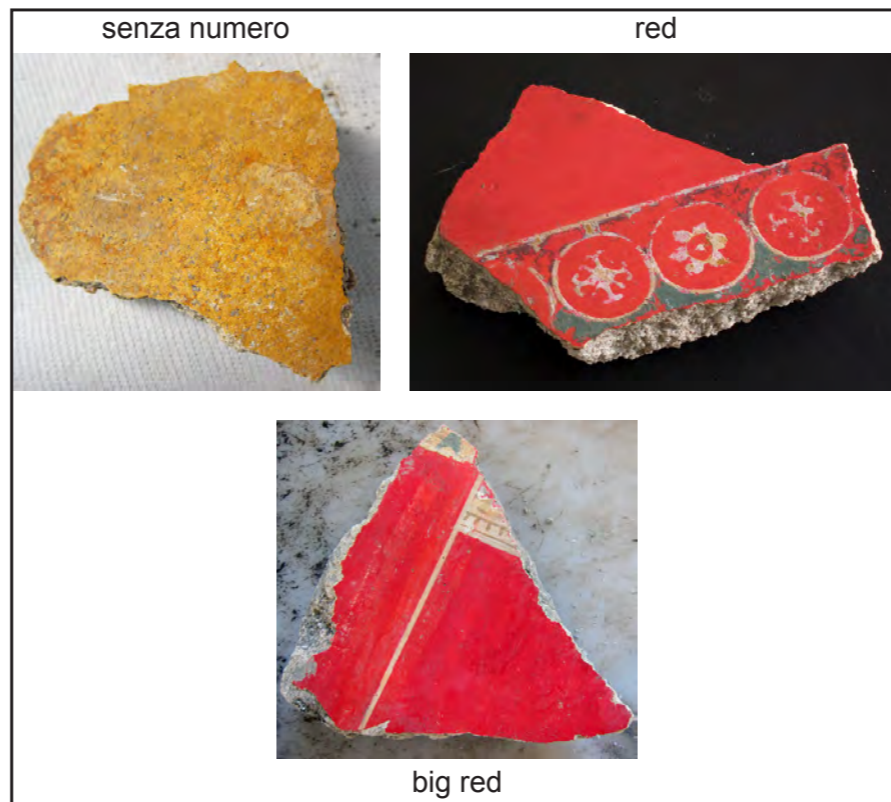
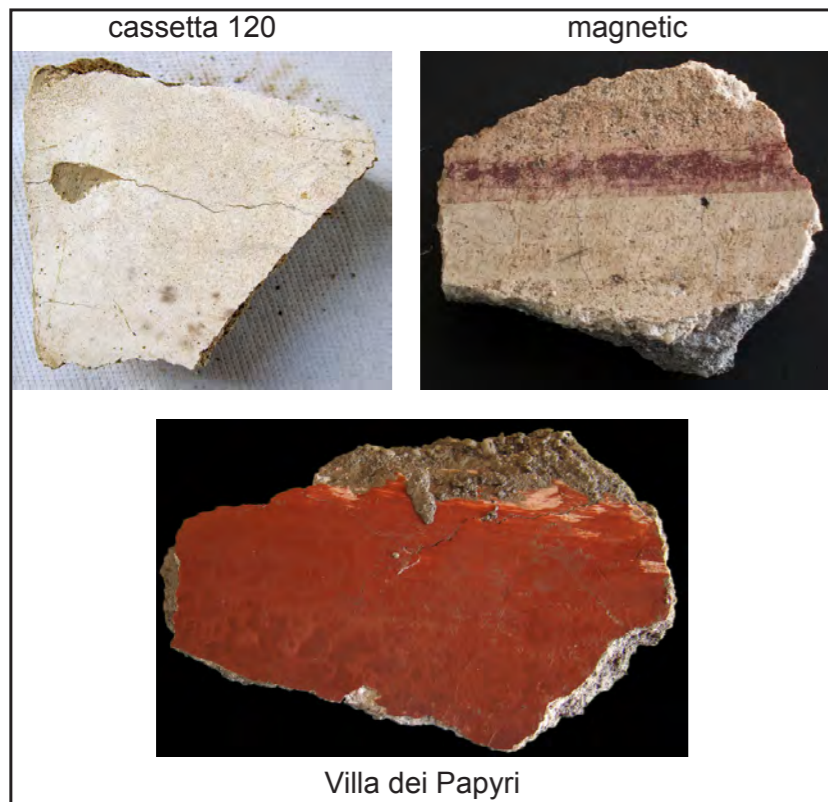


Wall Painting Fragments

Herculaneum, Italy

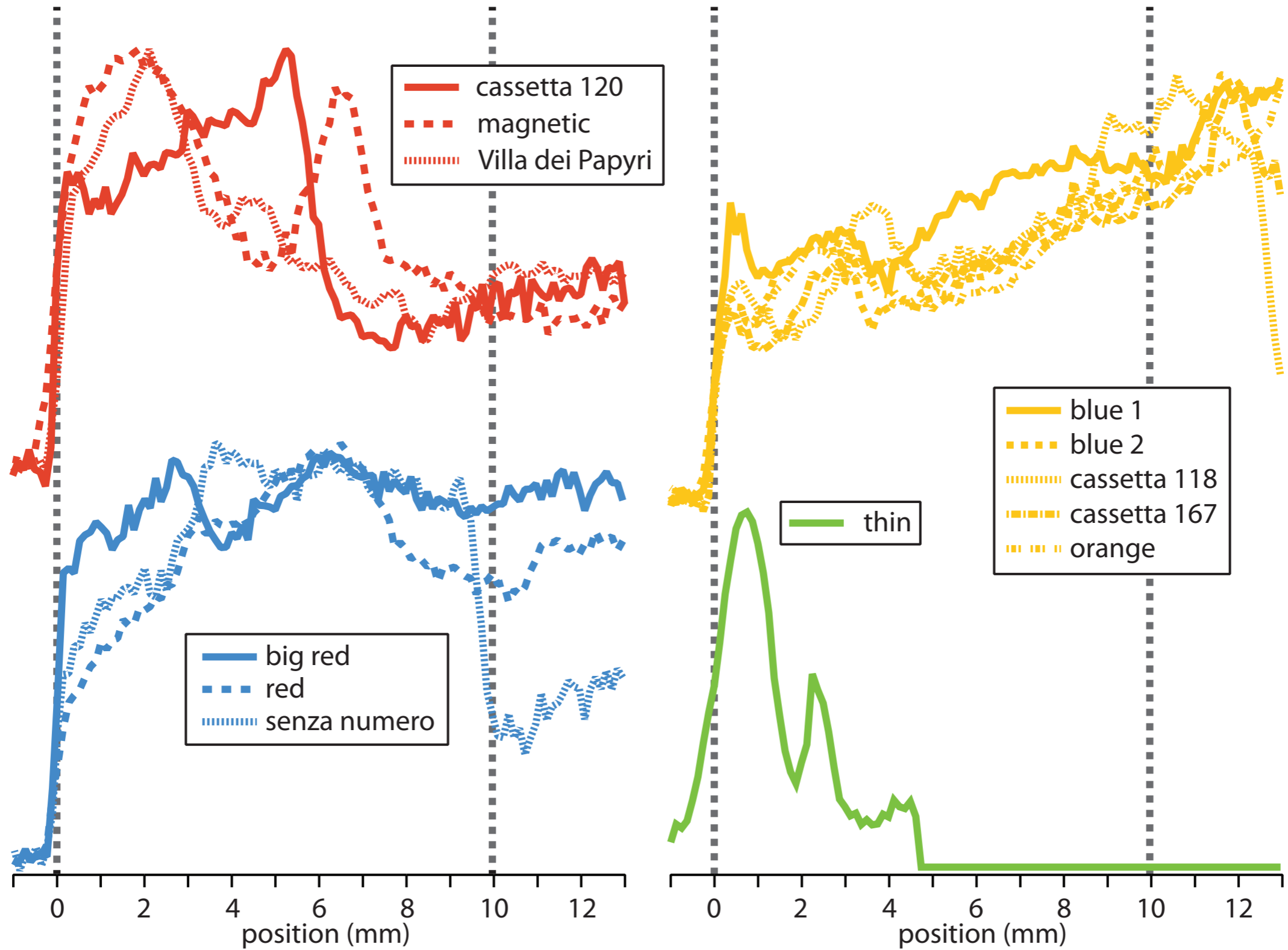


Fragment Profiles

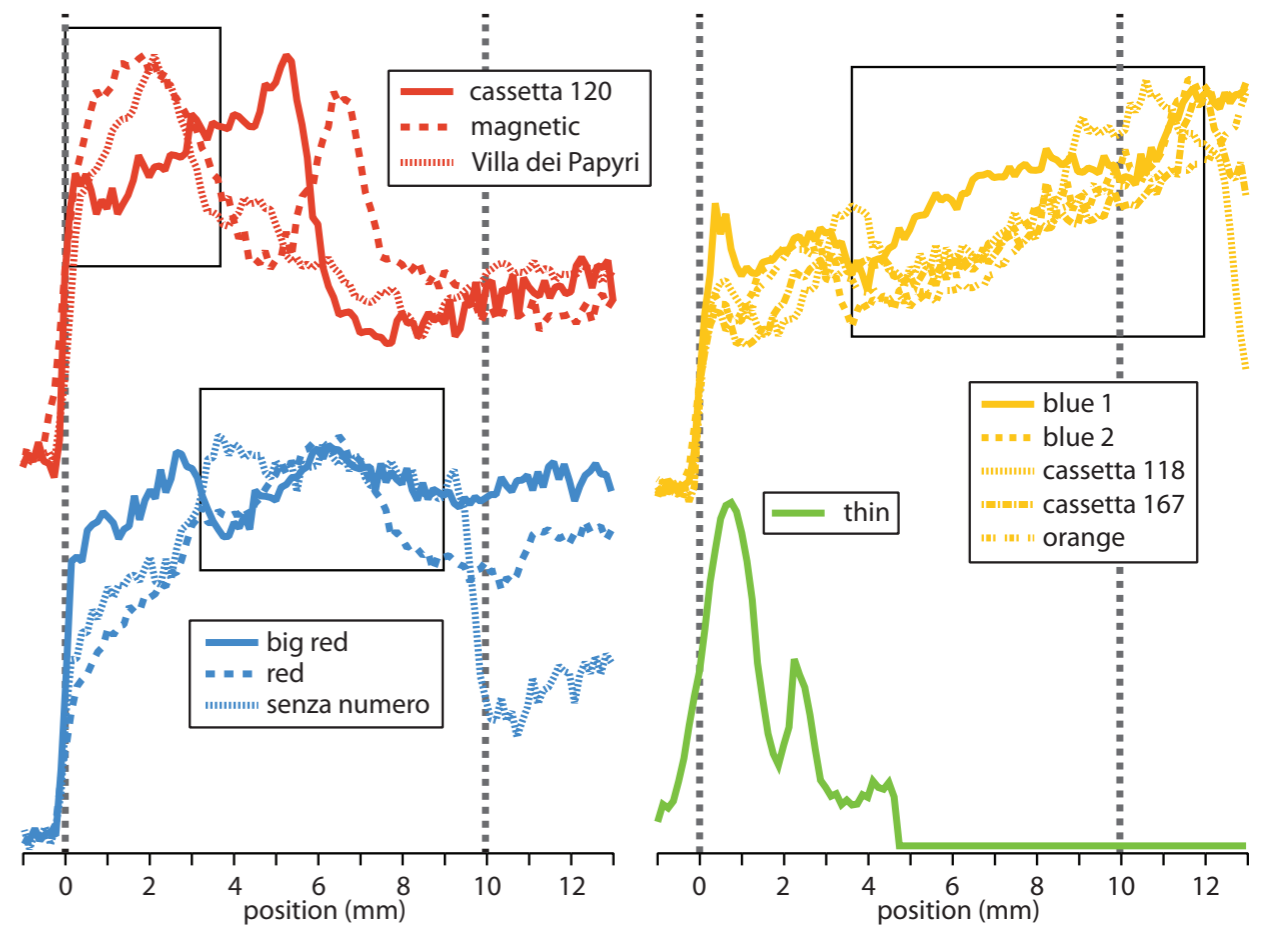
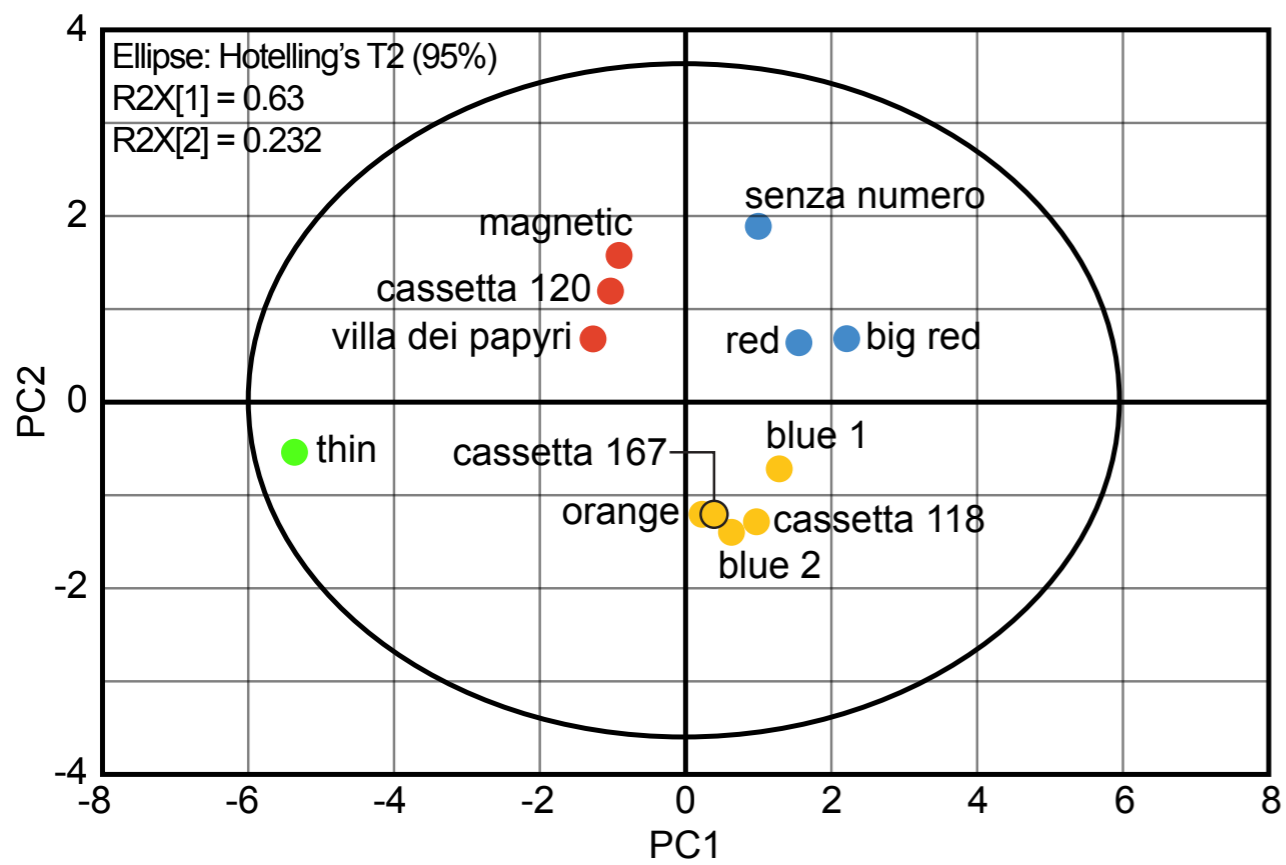


1 cm

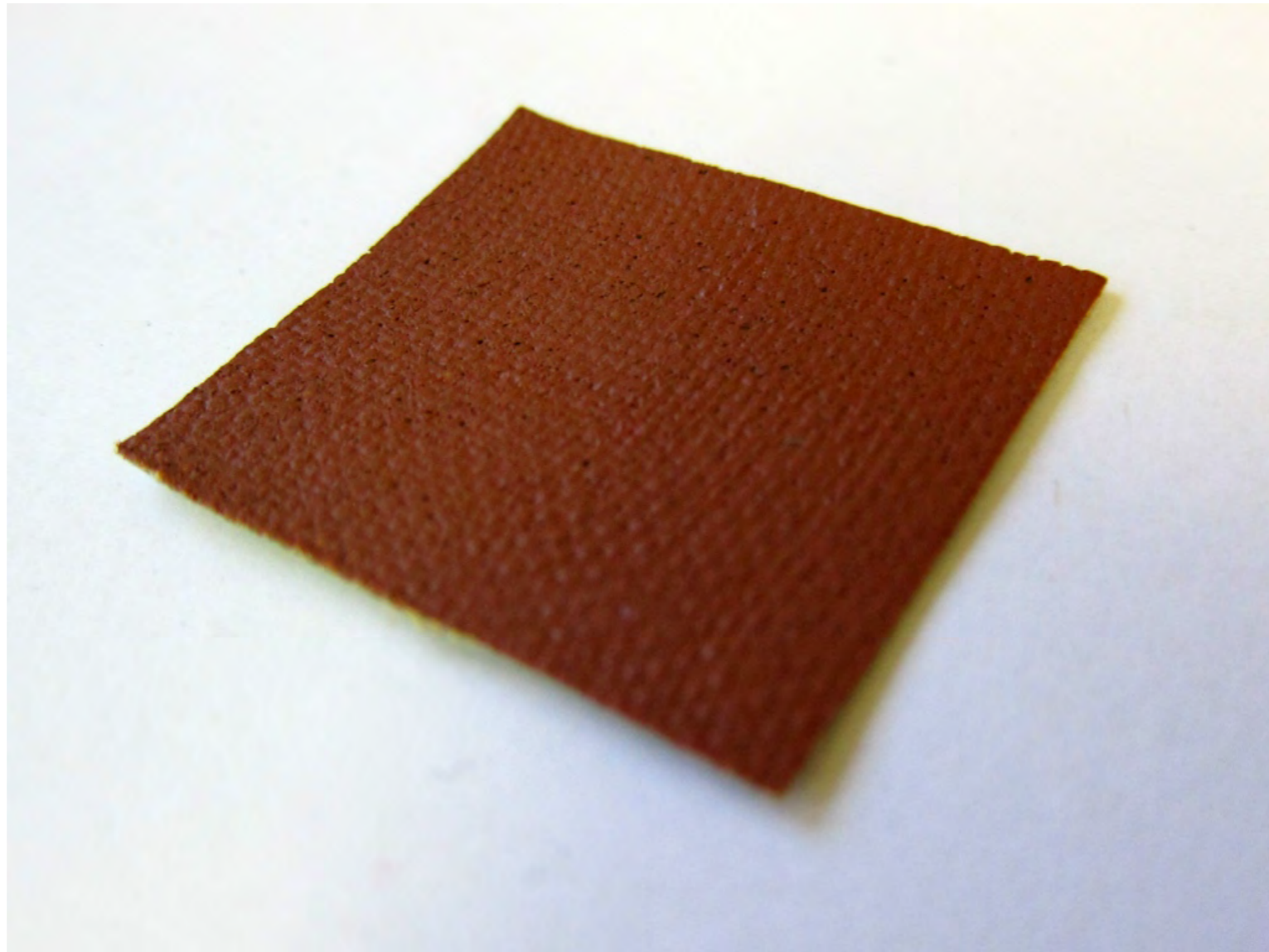
Fragment Profiles



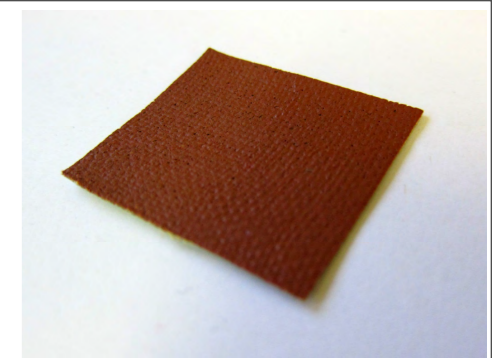
Principal Component Analysis



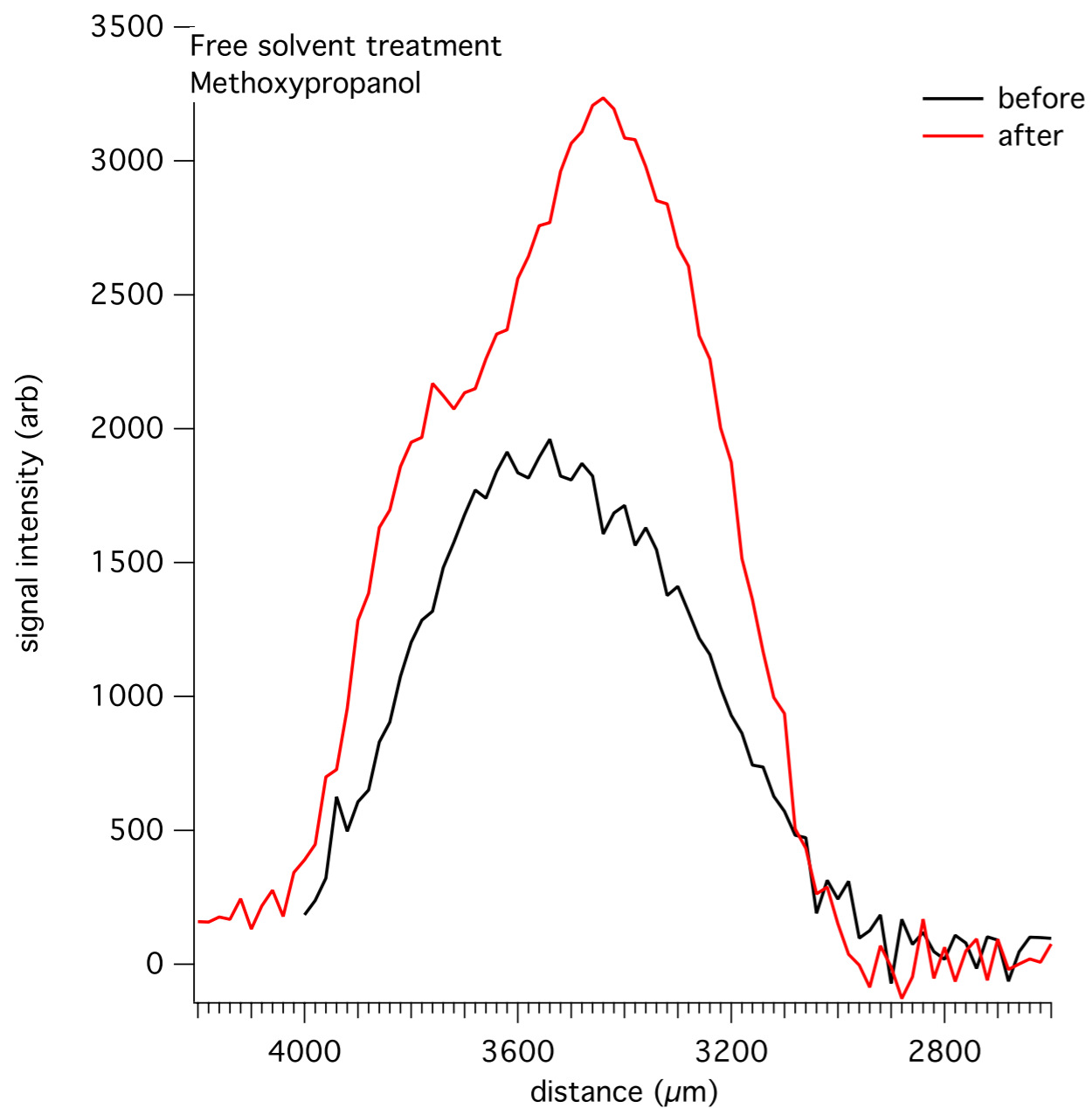
Cleaning Methods



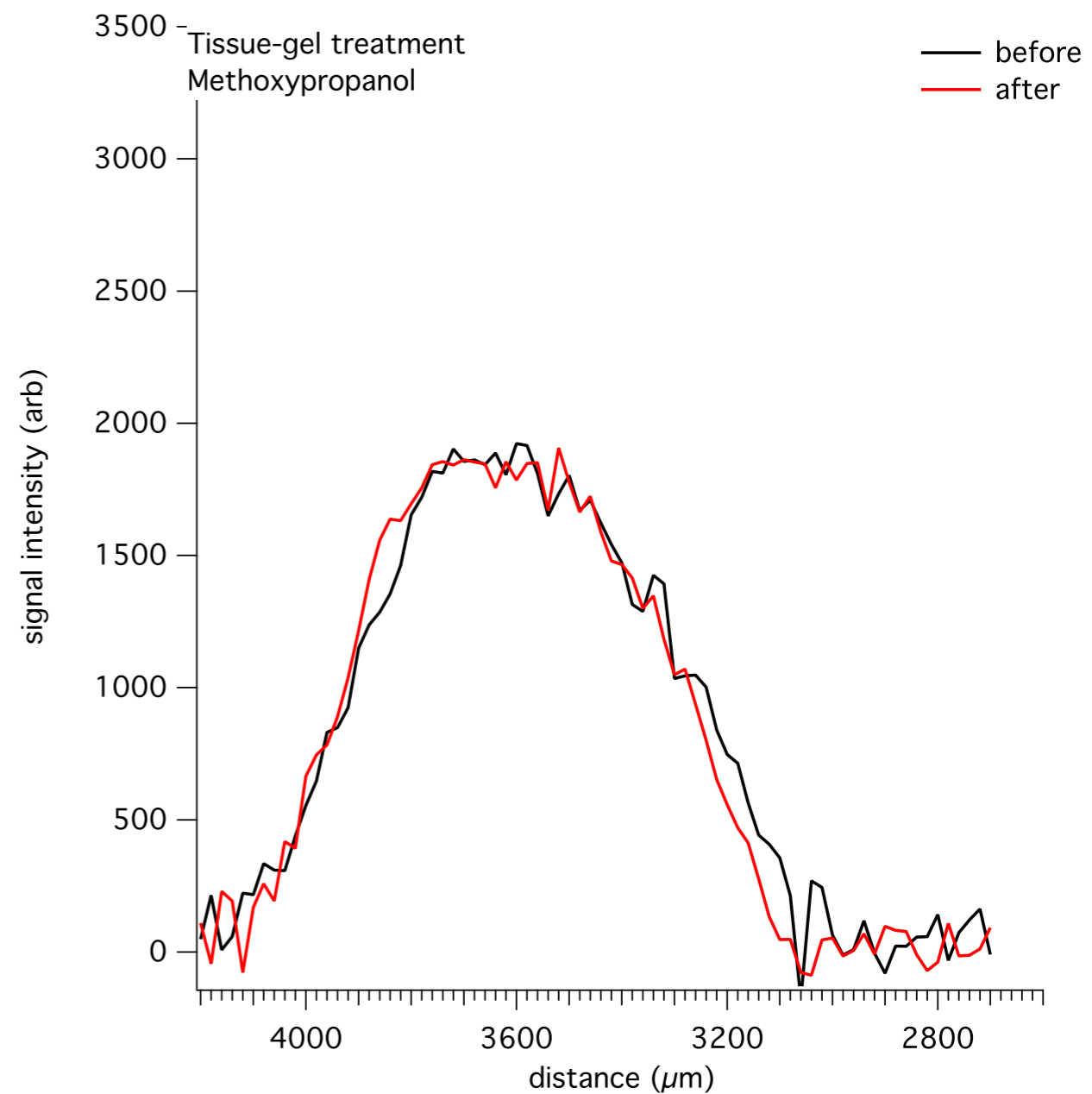
Cleaning Methods



Free solvent



Tissue-gel



NMR Relaxation

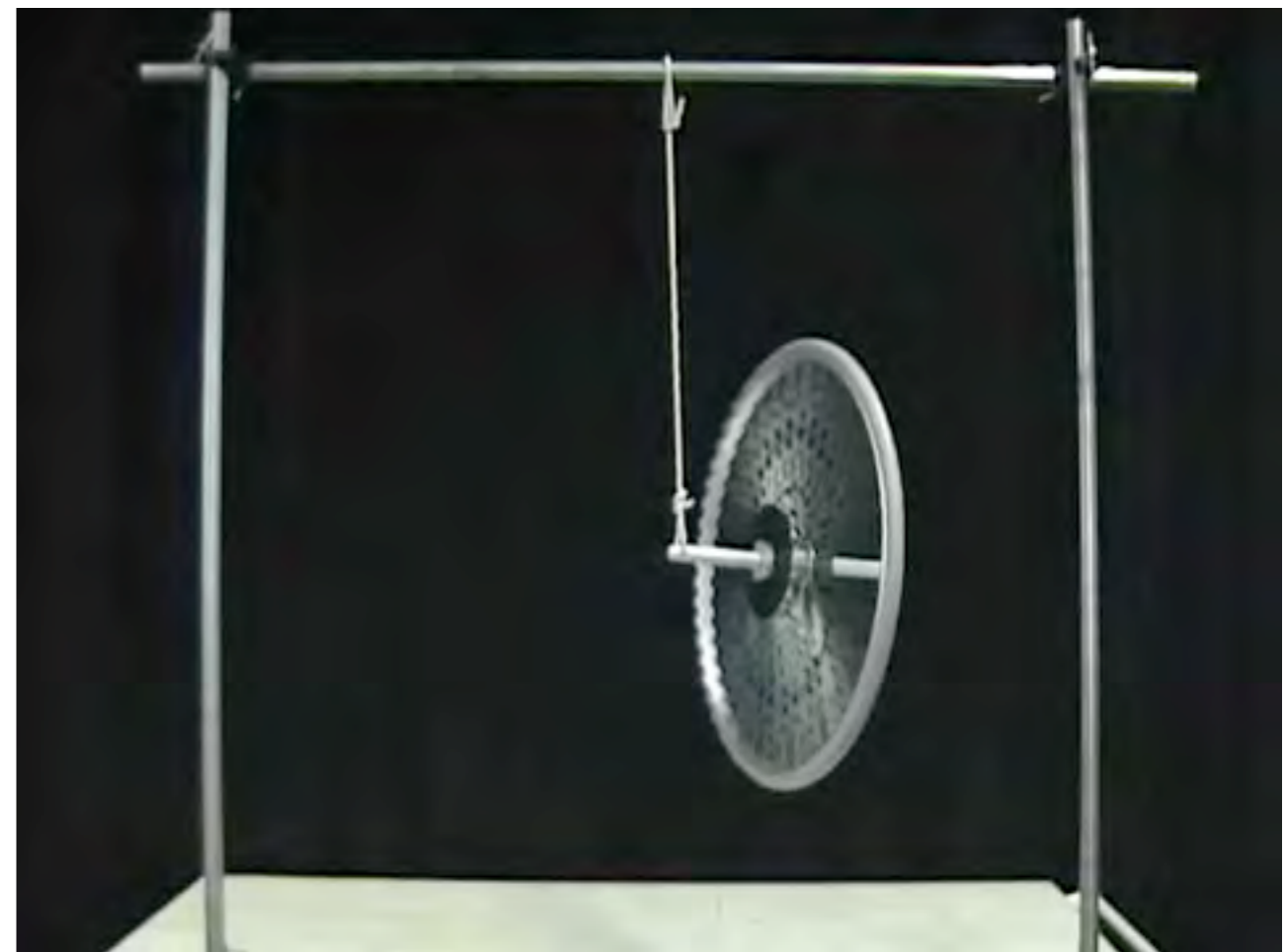
- T_1 returns to thermal equilibrium
- T_2 destroys coherence between spins

Relaxation times suggest physical properties of the sample

NMR Relaxation

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Pipenpooyse bruiloft, 1616

The Pipenpoy Wedding; Fries Museum, Leeuwarden NL



Pipenpooyse bruiloft, 1616

The Pipenpoy Wedding; Fries Museum, Leeuwarden NL

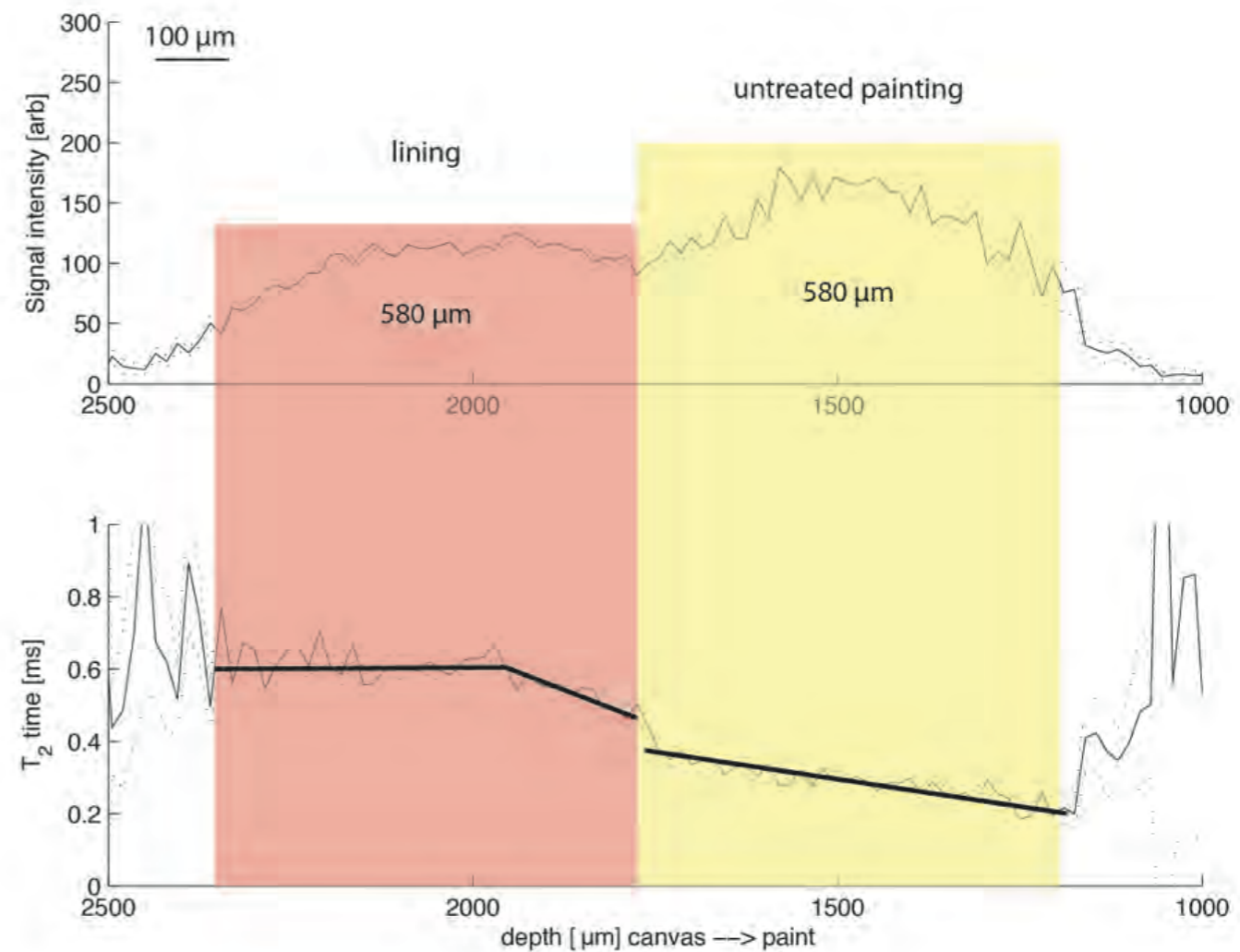
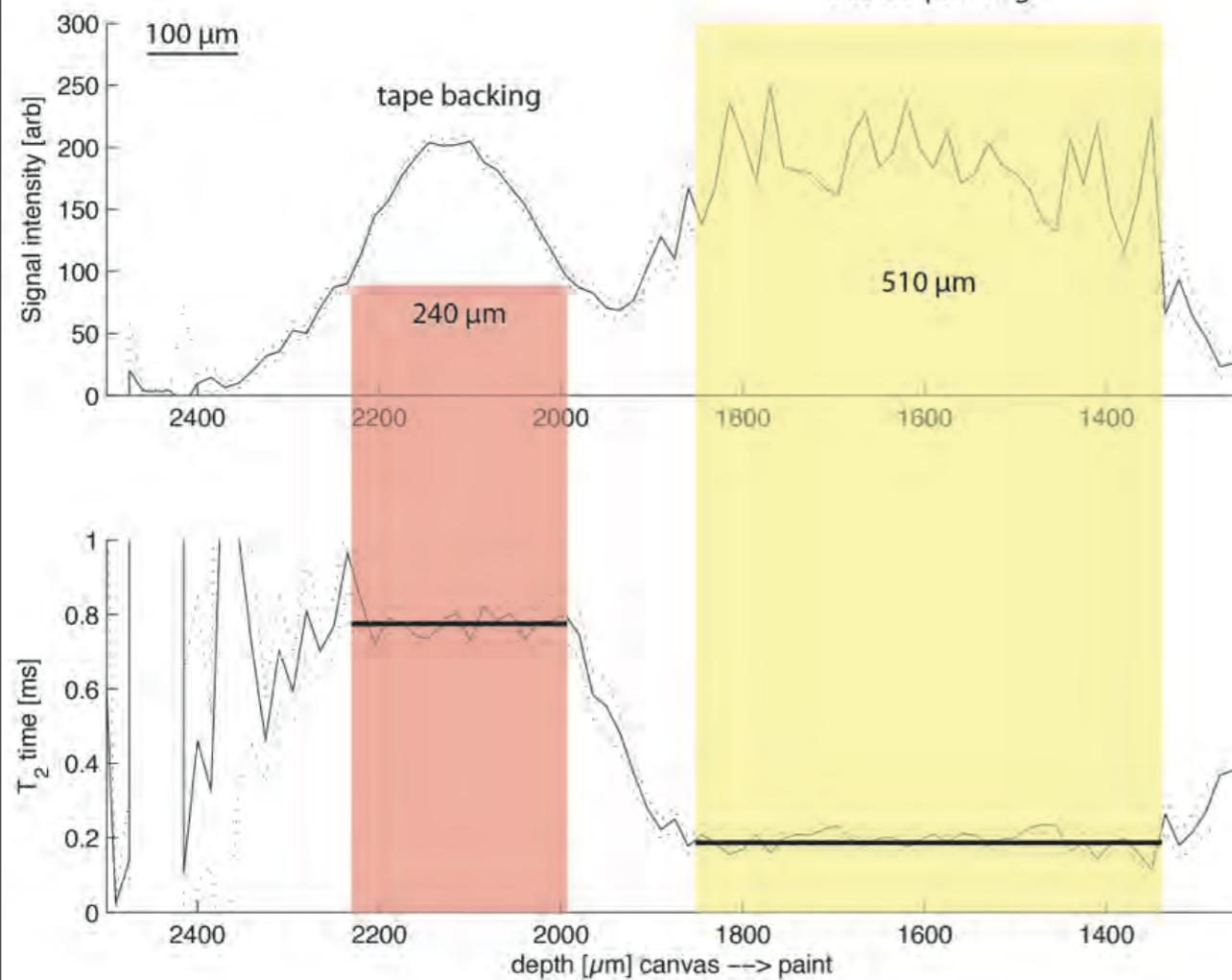


Pipenpooyse bruiloft, 1616

The Pipenpoy Wedding; Fries Museum, Leeuwarden NL



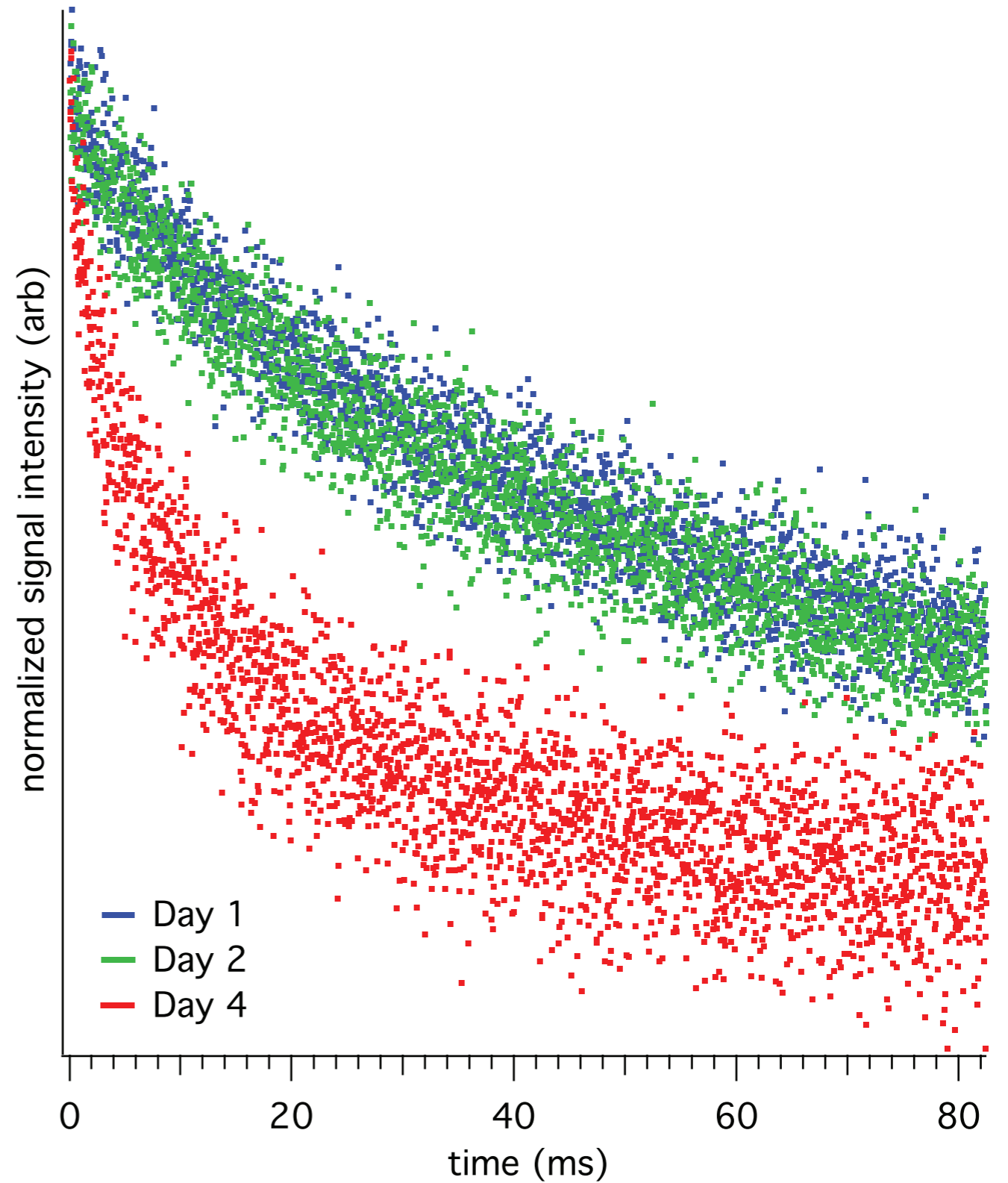
treated painting



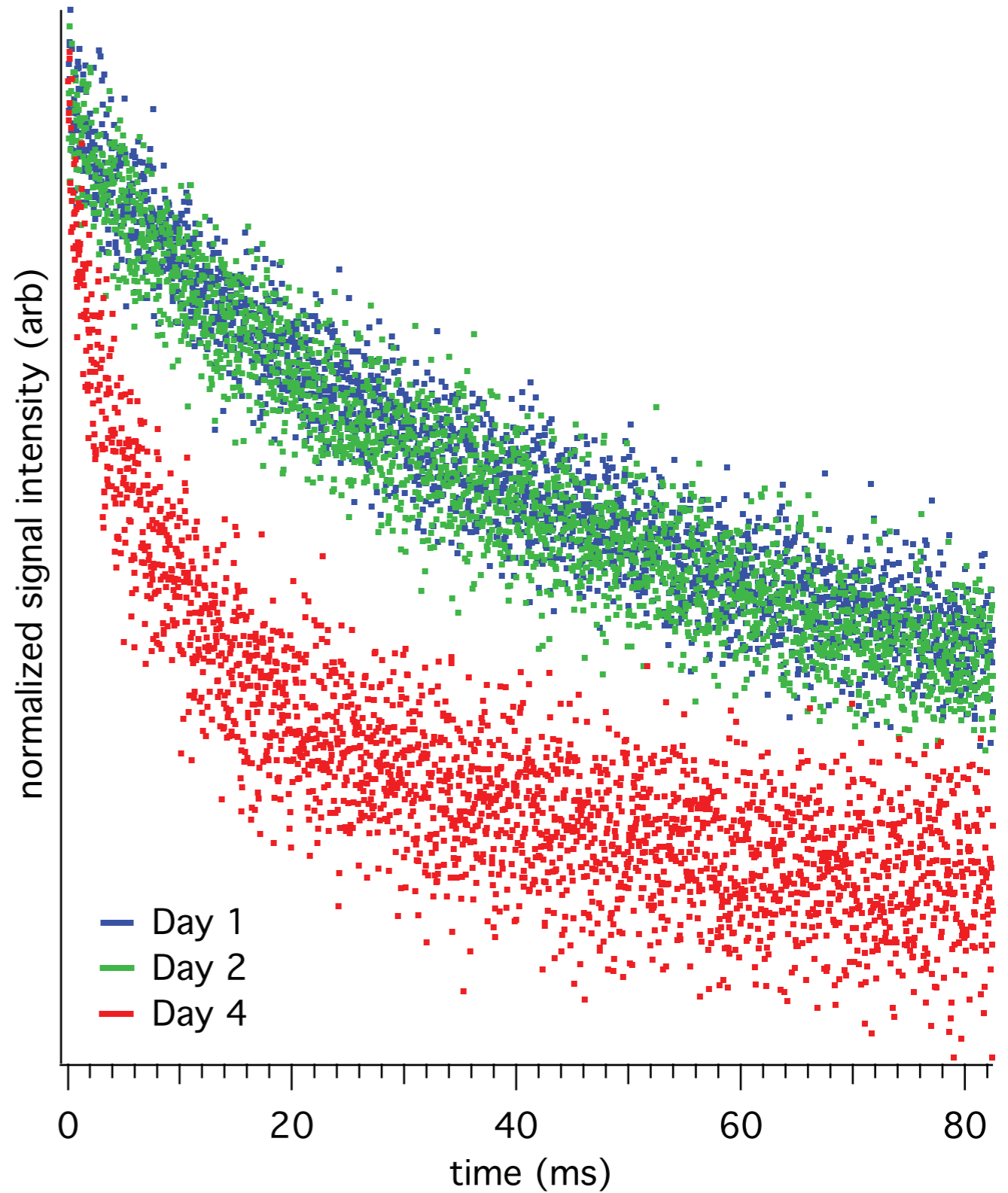
Le Bonheur de Vivre
H. Matisse, 1906



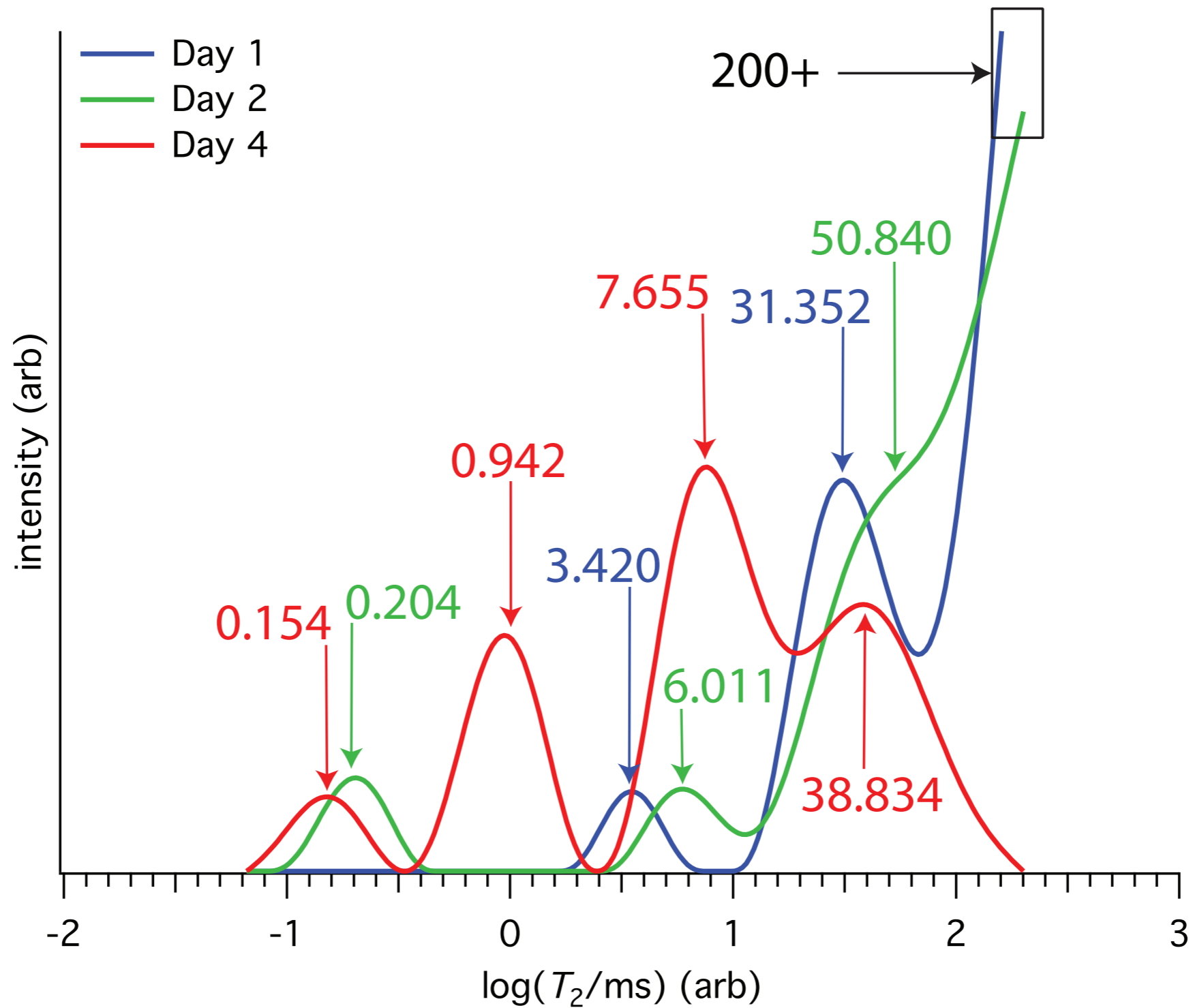
Cadmium Yellow Paint



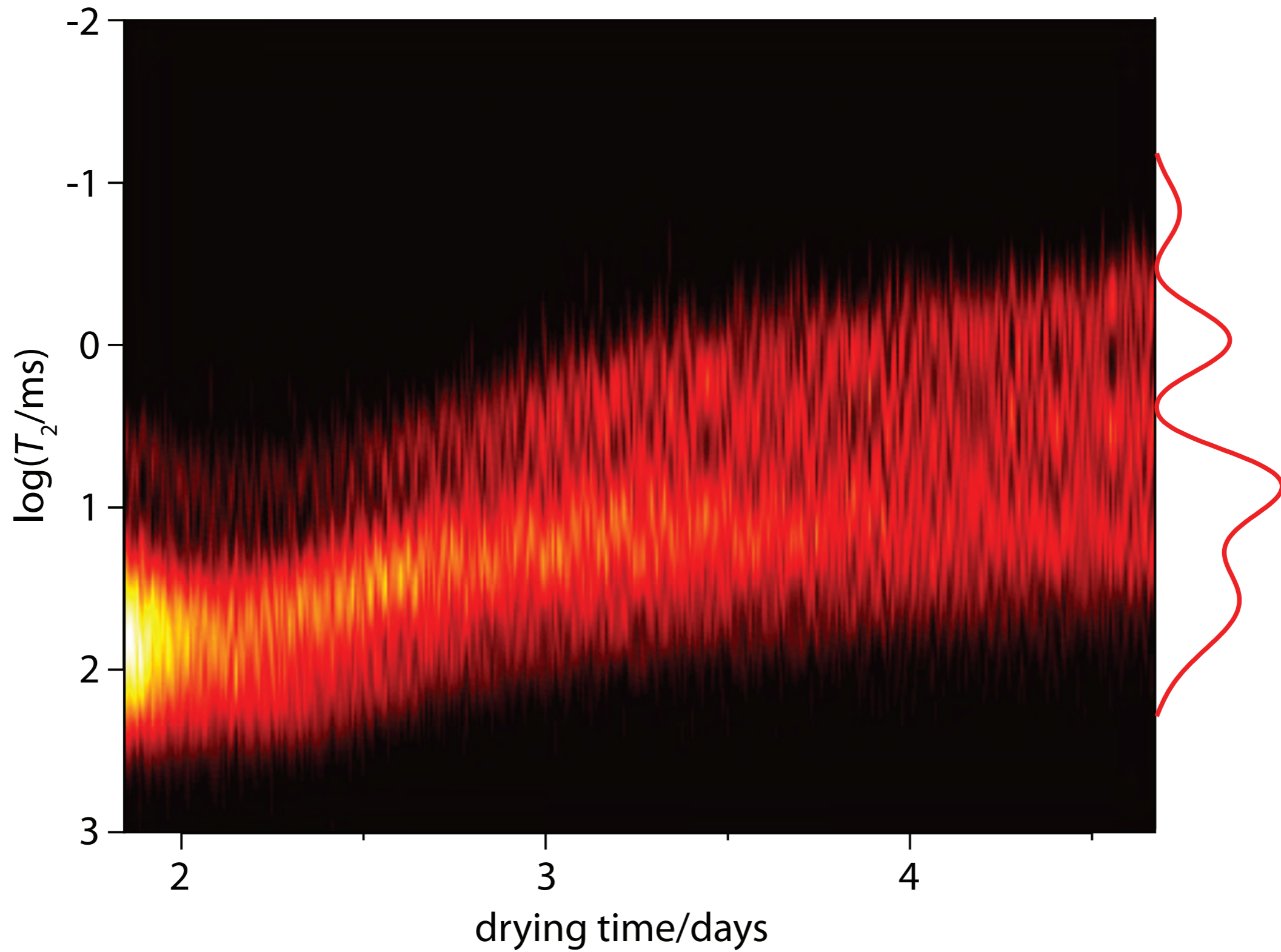
Cadmium Yellow Paint



Inverse Laplace Transformation

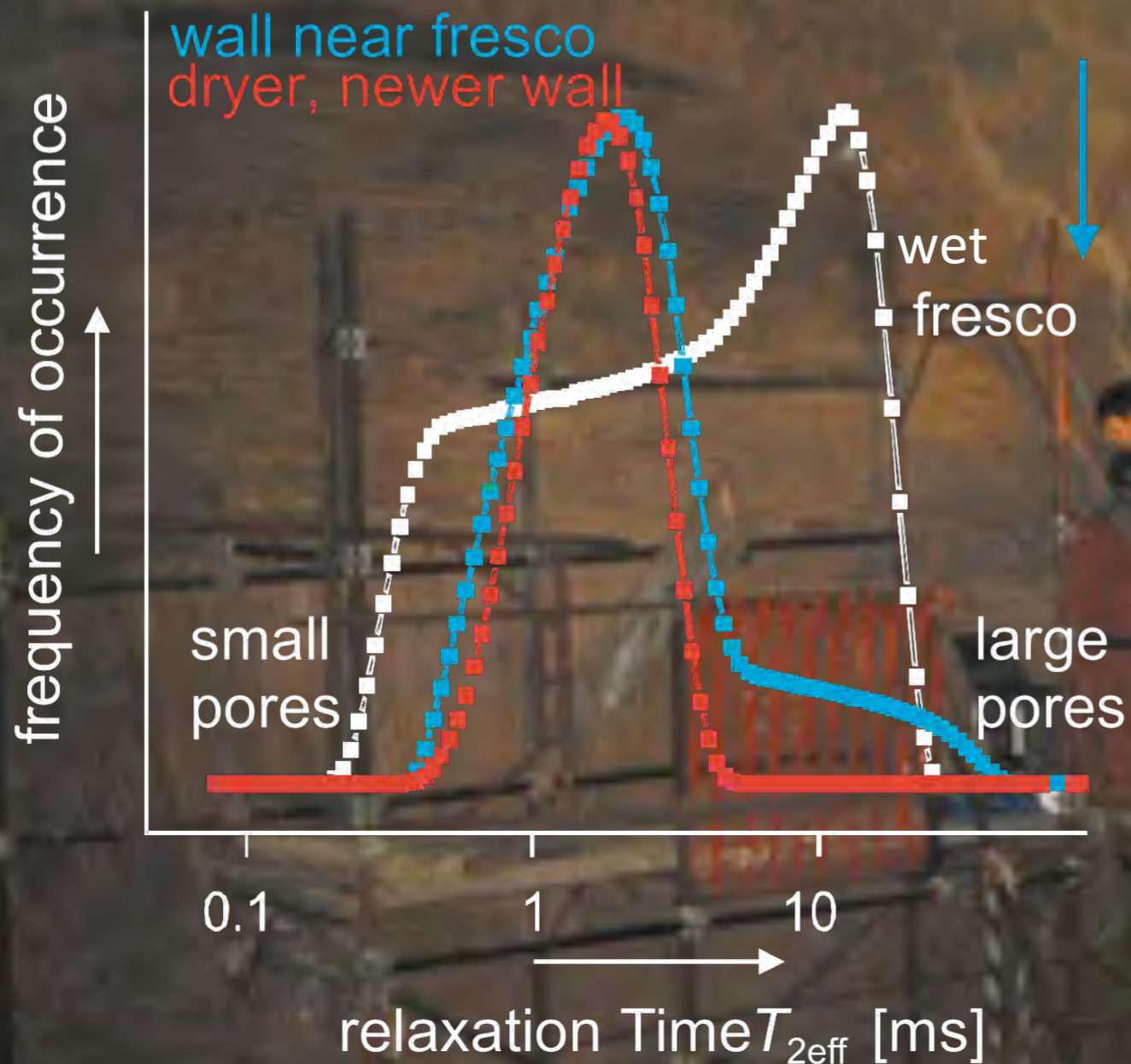


Time Evolution of Drying



Cryptoporticus at Colle Oppio, Rome

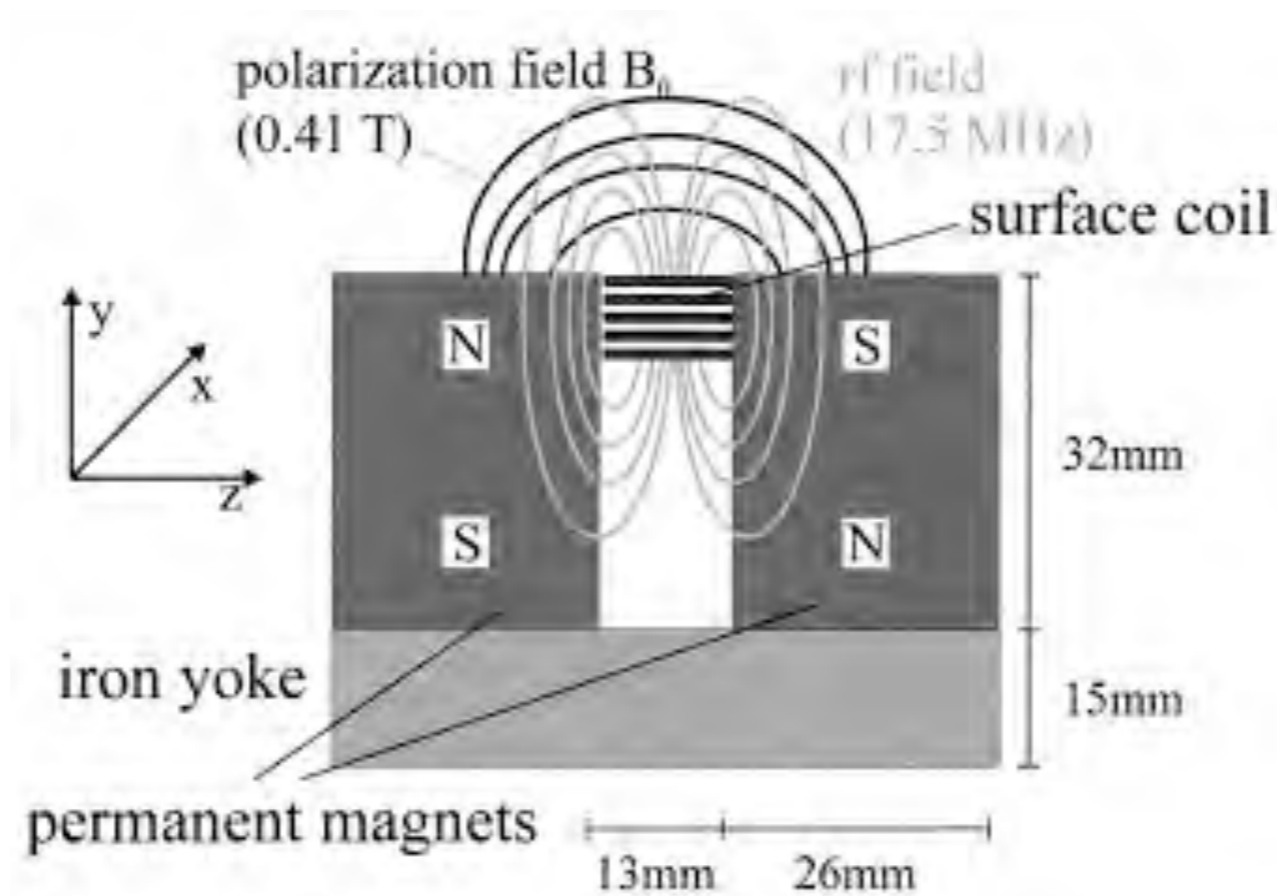
March 2002



S. Sharma et al. Analysis of historical porous building materials by the NMR-MOUSE. *Magn. Reson. Imag.* **2003**. doi: 10.1016/S0730-725X(03)00132-2

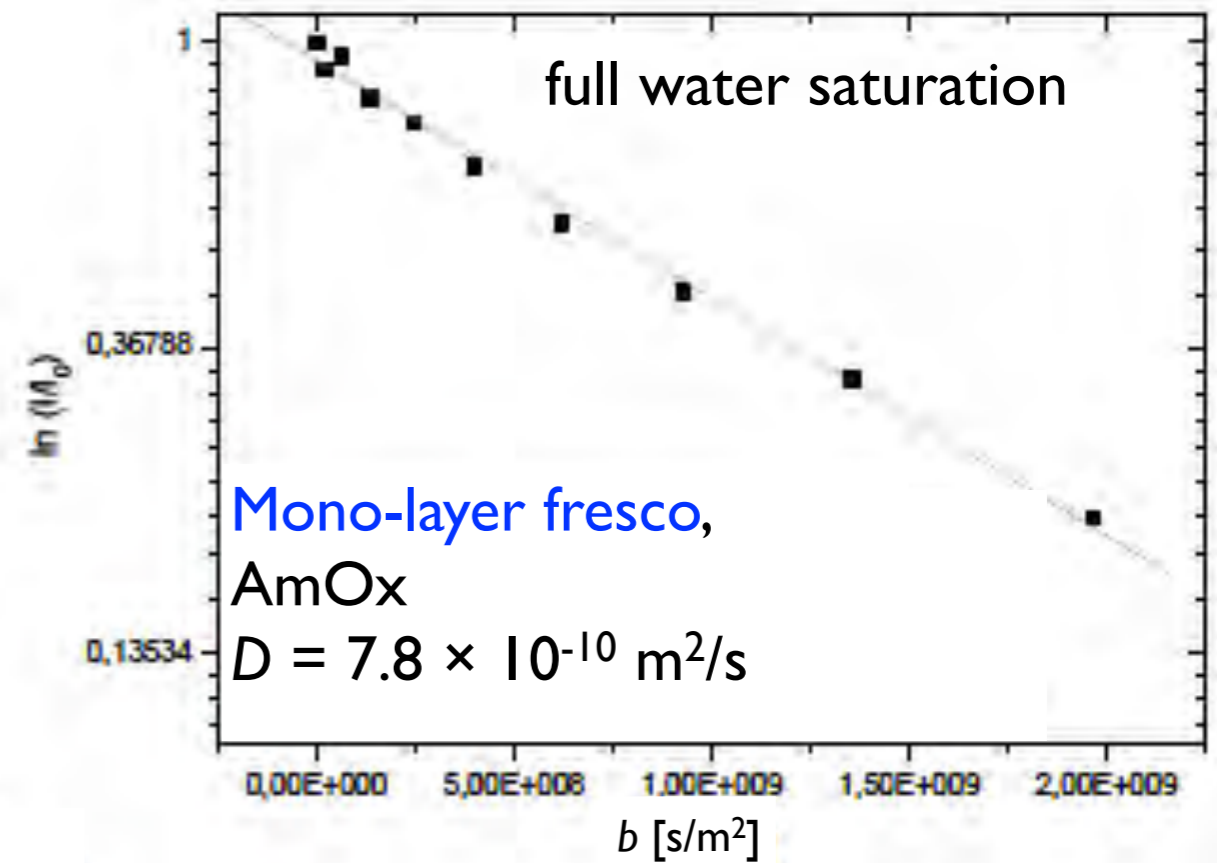
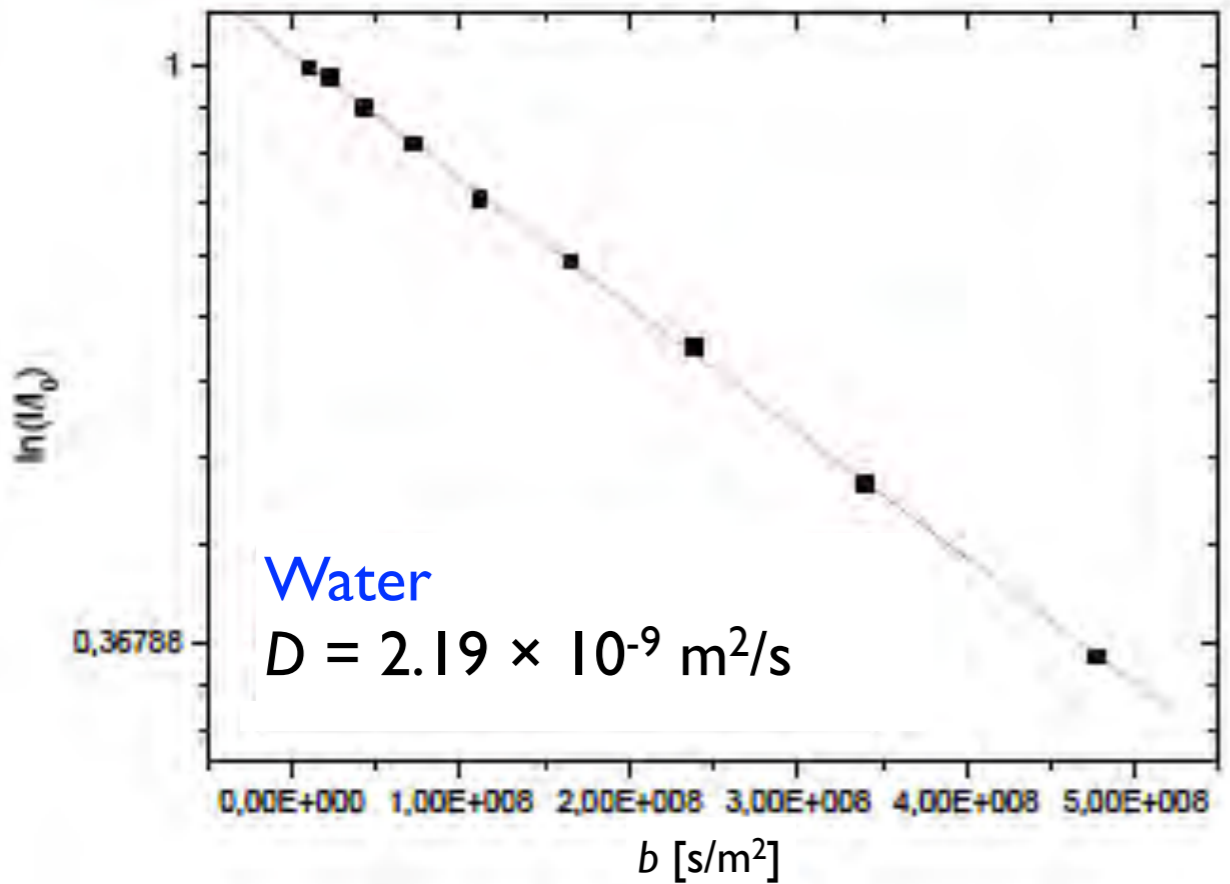
Measuring Molecular Motion

$$S \approx e^{-\frac{2}{3} S_0 \gamma^2 G^2 \delta^3 D}$$



Hürlimann, M.D. Diffusion and relaxation effects in general stray field NMR experiments. *J. Magn. Reson.* **2001**. doi:10.1006/jmre.2000.2263.
Song, Y-Q. Categories of coherence pathways for the CPMG sequence. *J. Magn. Reson.* **2002**. doi:10.1006/jmre.2002.2577.

Self-Diffusion Coefficients



Fresco models

Treatment, mono-layer	D [m ² /s]
Ammonium oxalate	7.8×10^{-10}
Ba(OH) ₂	8.5×10^{-10}
Salt only	13.0×10^{-10}
Pristine	6.5×10^{-10}

Treatment, multilayer	D [m ² /s]
Ammonium oxalate	7.7×10^{-10}
Ba(OH) ₂	7.5×10^{-10}
Pristine	72.0×10^{-10}

Secco models

Treatment, monolayer	D [m ² /s]
Ammonium oxalate	4.5×10^{-10}
Ba(OH) ₂	8.1×10^{-10}
Pristine	4.5×10^{-10}

Lower self-diffusion

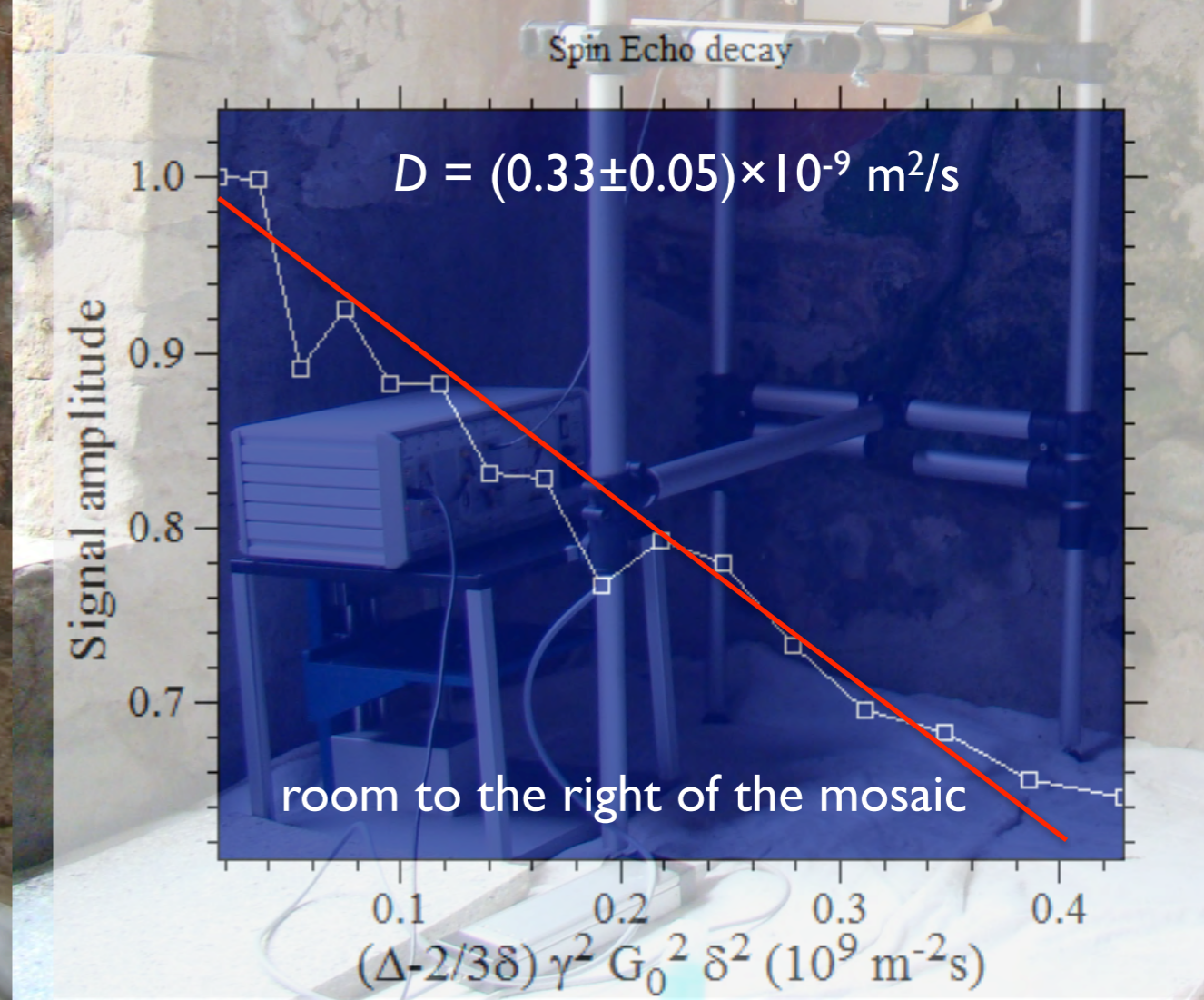
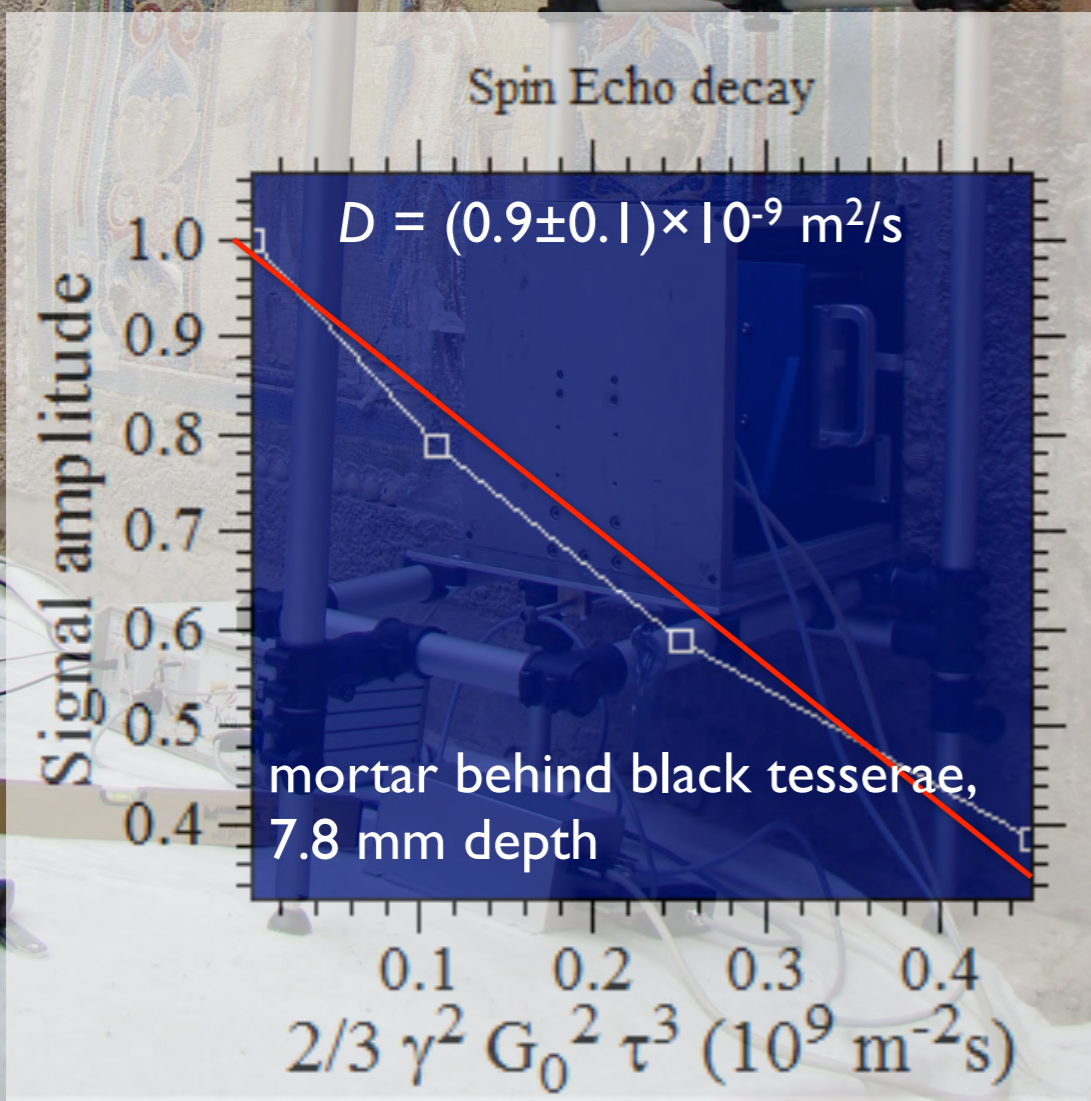
- in secco than in fresco
- for AmOx than for Ba(OH)₂

Herculaneum, Italy



Moisture Transport: Measurement of Diffusion

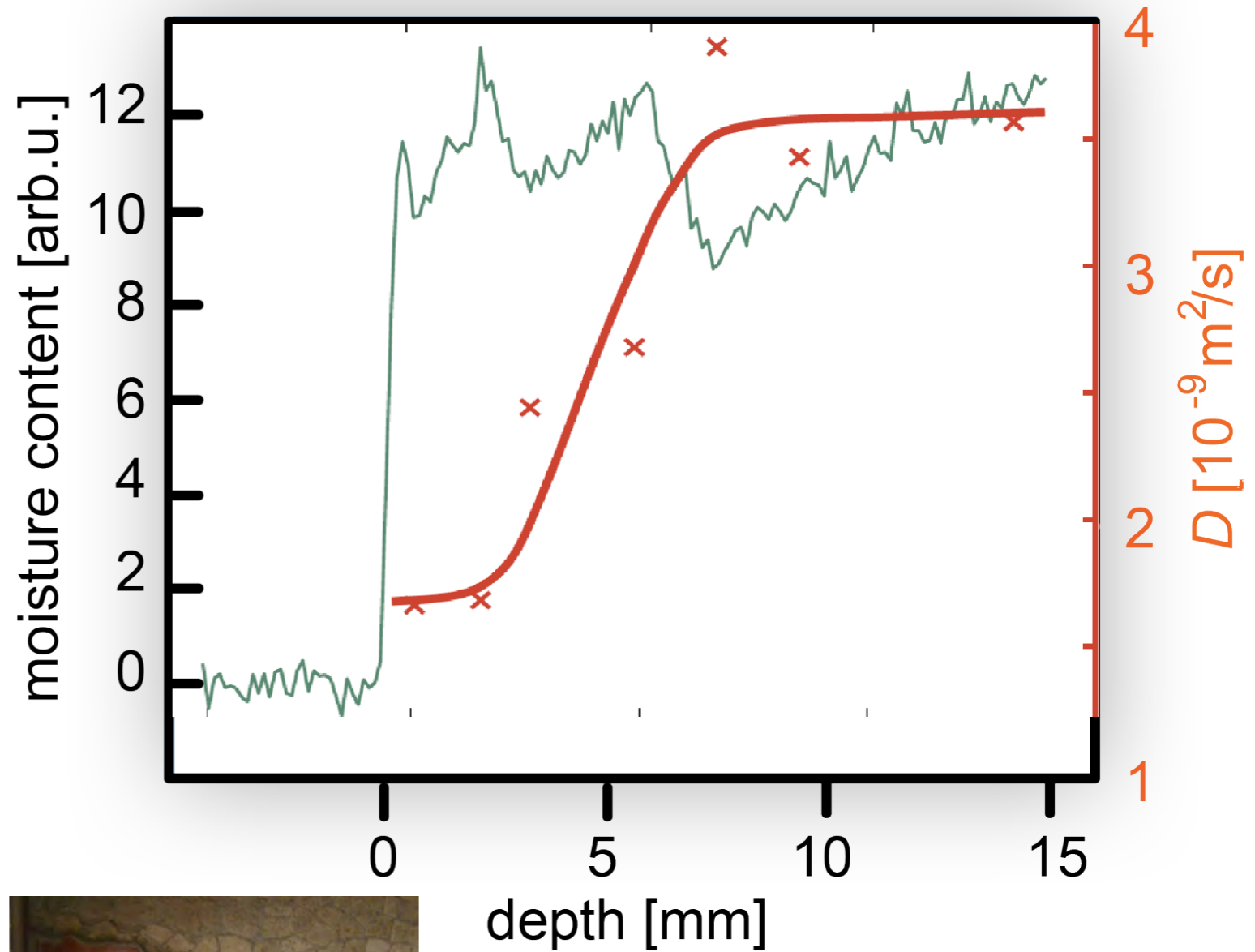
Self-diffusion of natural
moisture can be
determined *in situ*



Villa dei Papyri *Herculaneum, Italy*



Moisture Content and Mobility



Use profiles of **moisture content** (green) and of the **moisture mobility** (red) to model **moisture flux**

Acknowledgements

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Bernhard Blümich; *RWTH Aachen University*



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