Scuola universitaria professionale della Svizzera italiana
Dipartimento ambiente costruzioni e design
Istituto materiali e costruzioni

SUPSI

Powder characterization by QUALX

Application of XRPD analysis in cultural heritage studies

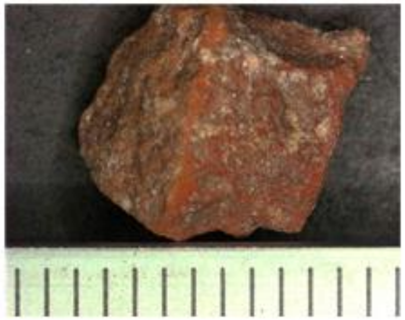
Giovanni Cavallo, PhD

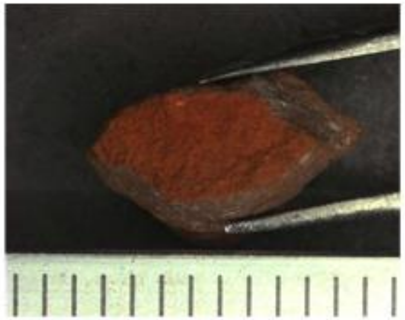
IC CI
CNR Istituto di Cristallografia

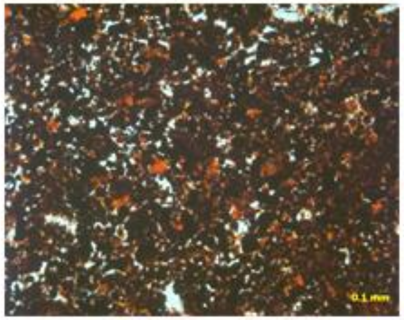
BARI

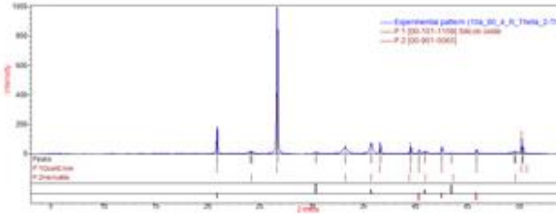
Polytechnic of Bari, 2nd of October 2019

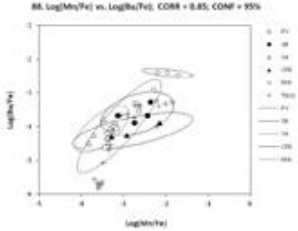
Premise

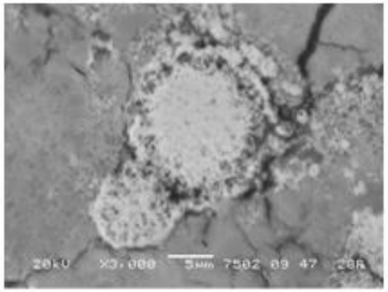


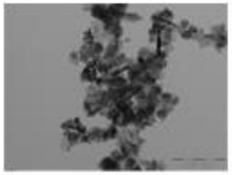












Premise

Pyrotechnology during Prehistory

Ancient pharmacy of *Santa Maria della Scala* in Rome

Pyrotechnology during Prehistory

CONTENTS

- Introduction
- Basics of goethite-hematite heat induced transformations and archaeological evidence
- Experimental: Natural heated goethite from *Ponte di Veja* (Mt Lessini, NE Italy)
- Concluding remarks

INTRODUCTION

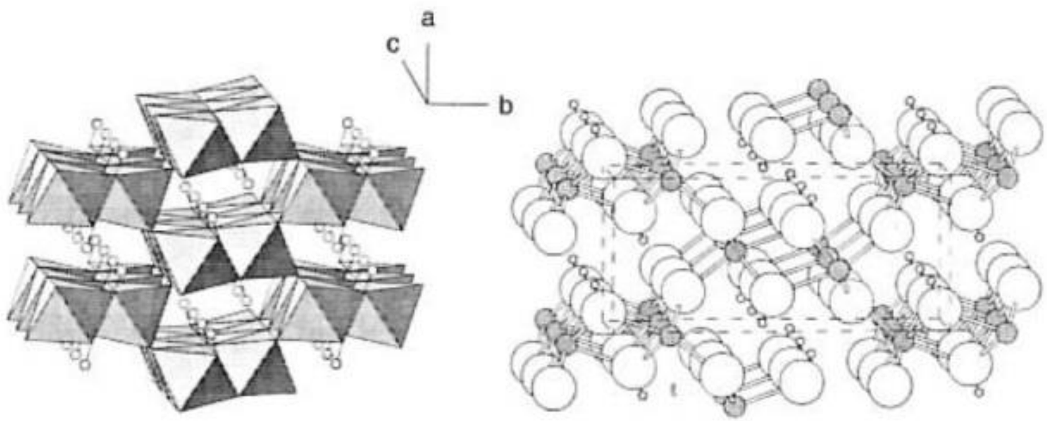
Evidence of red ochre by heating in some archaeological contexts:

- Mousterian levels of Es-Skhul, Mount Carmel, Israel, 100 kyr (Salomon et al., 2012);
- Epigravettian Dalmeri rockshelter, Italy (Gialanella et al., 2011) Troubat (French Pyrenees) 10kyr BP (Pomiés et al., 1999);
- Late Epigravettian Tagliente rockshelter and (Proto)Aurignatian Fumane cave, Italy (Cavallo et al., 2018).

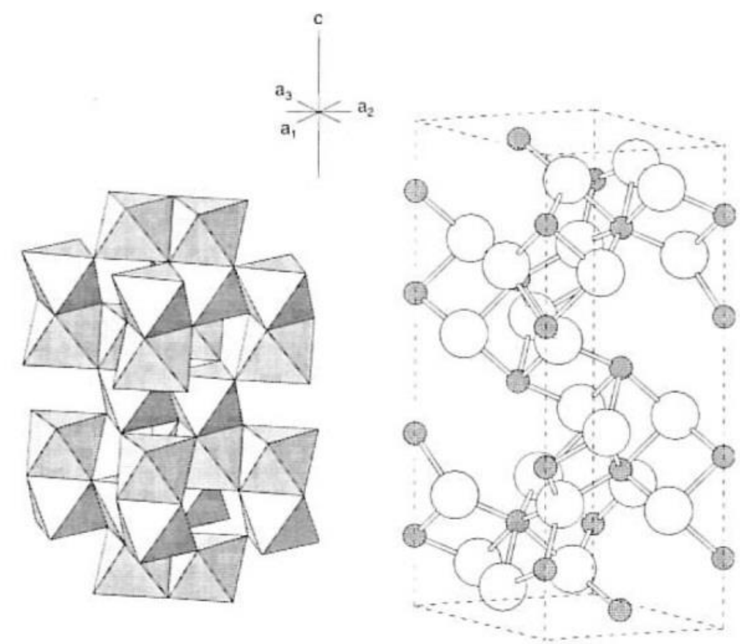
BASICS OF THE HEATING PROCESS

$$2FeOOH \xrightarrow{200\ ^{\circ}C} Fe_2O_3 + H_2O$$

Goethite *Hematite*



Crystal structure of **goethite** (orthorhombic). Arrangement of face-sharing $FeO_3(OH)_3$ octahedral (left) and ball and stick model (right)

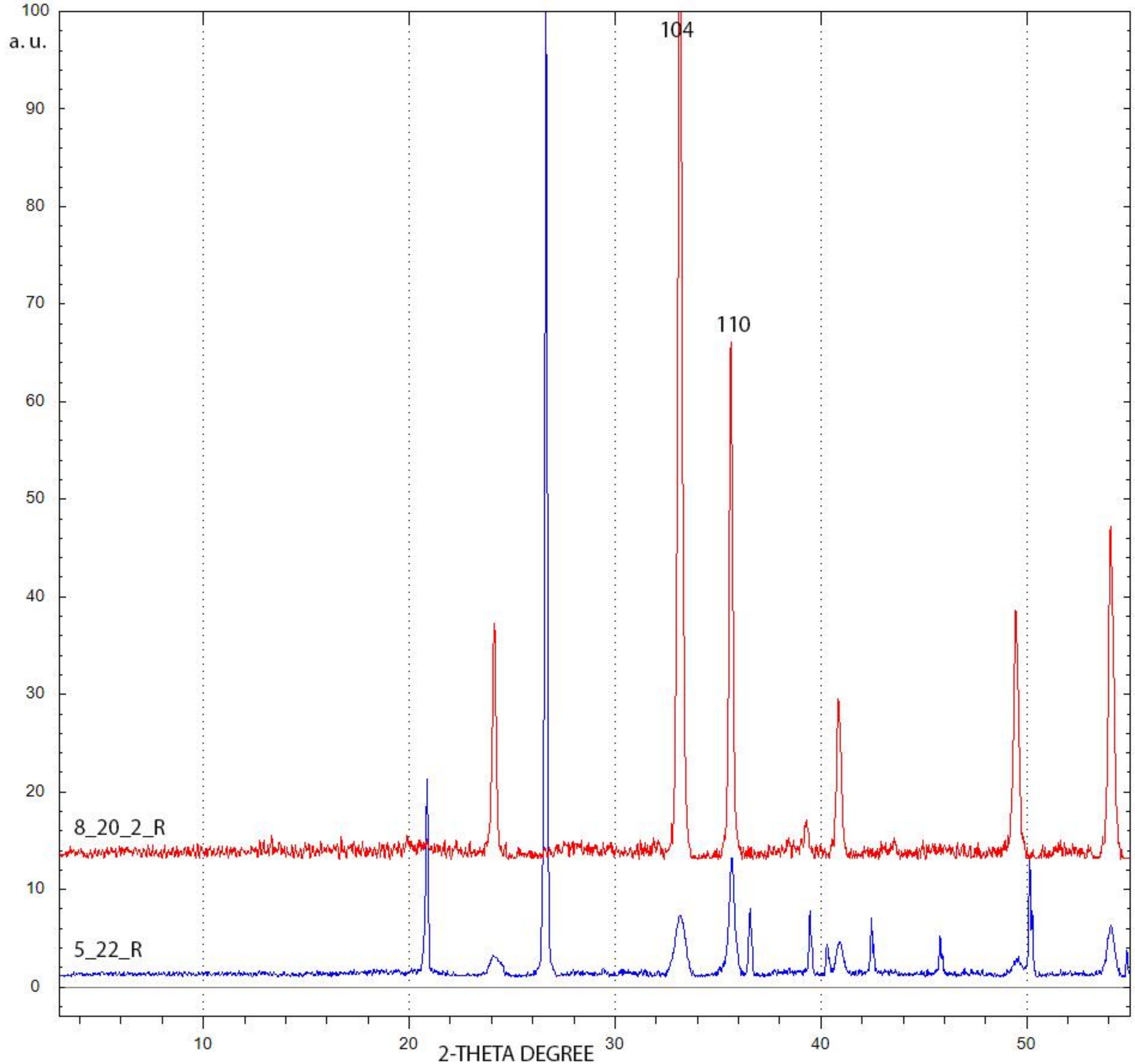


Crystal structure of **hematite** (rhomboehdral). Arrangement of edge-sharing FeO_6 octahedral (left) and ball and stick model (right)

BASICS OF THE HEATING PROCESS

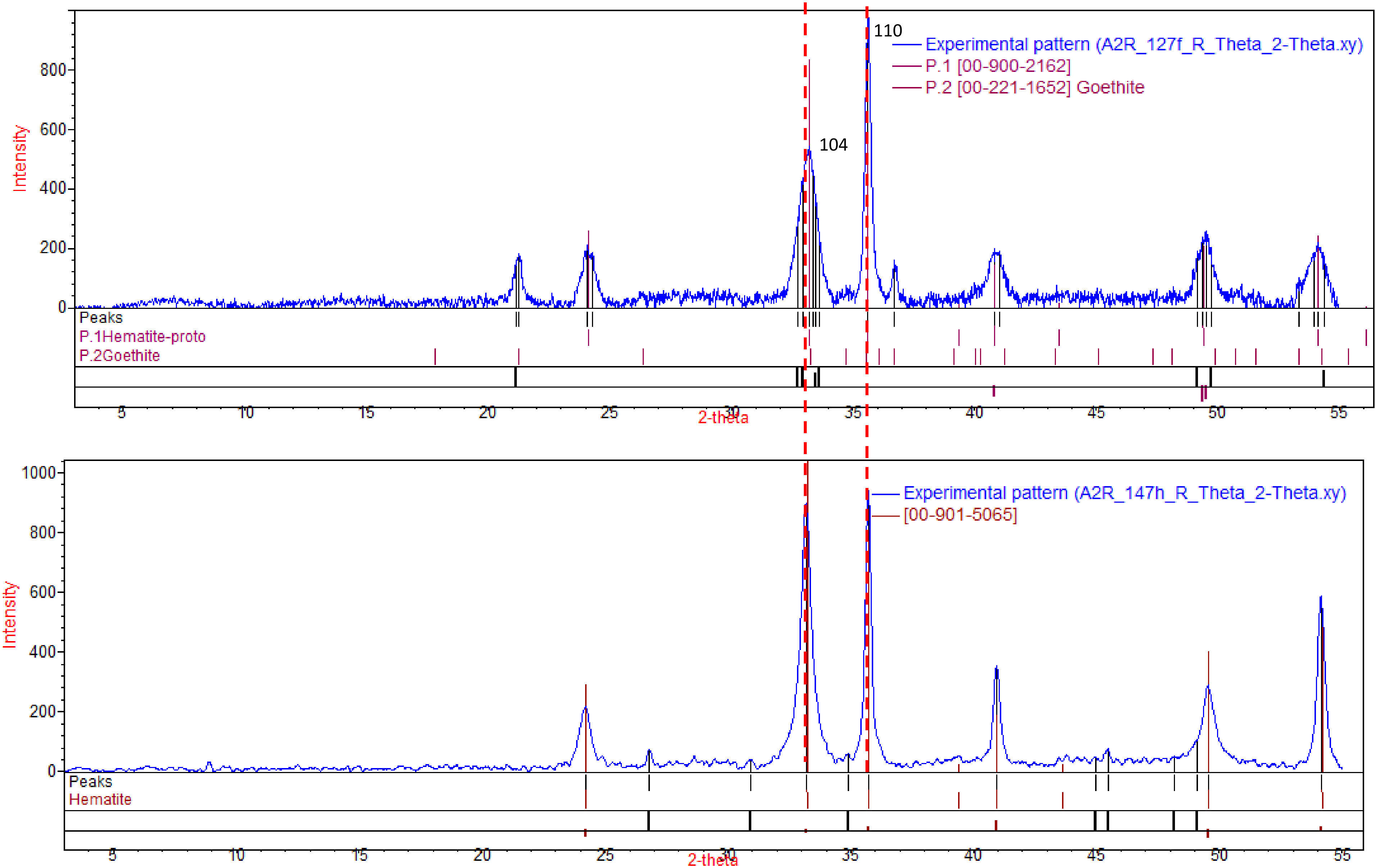
- Roocksby (1951) non-uniform broadening of the powder diffraction peaks
- Bunal et al. (1958) topotactic transformation
- Francombe and Roocksby (1959) unit-cell relationships between Gth and Hem
- Watari et al. (1979) TEM to study transformations – formation of pores
- Goss (1987) elongated and parallel pores developed during the dehydration of Gth
- Wolska (1981) and Wolska & Schwertmann (1989) formation of an intermediate phase called proto-hematite with chemical formula α-$Fe_{2-x/3}(OH)_xO_{3-x}$

XRPD



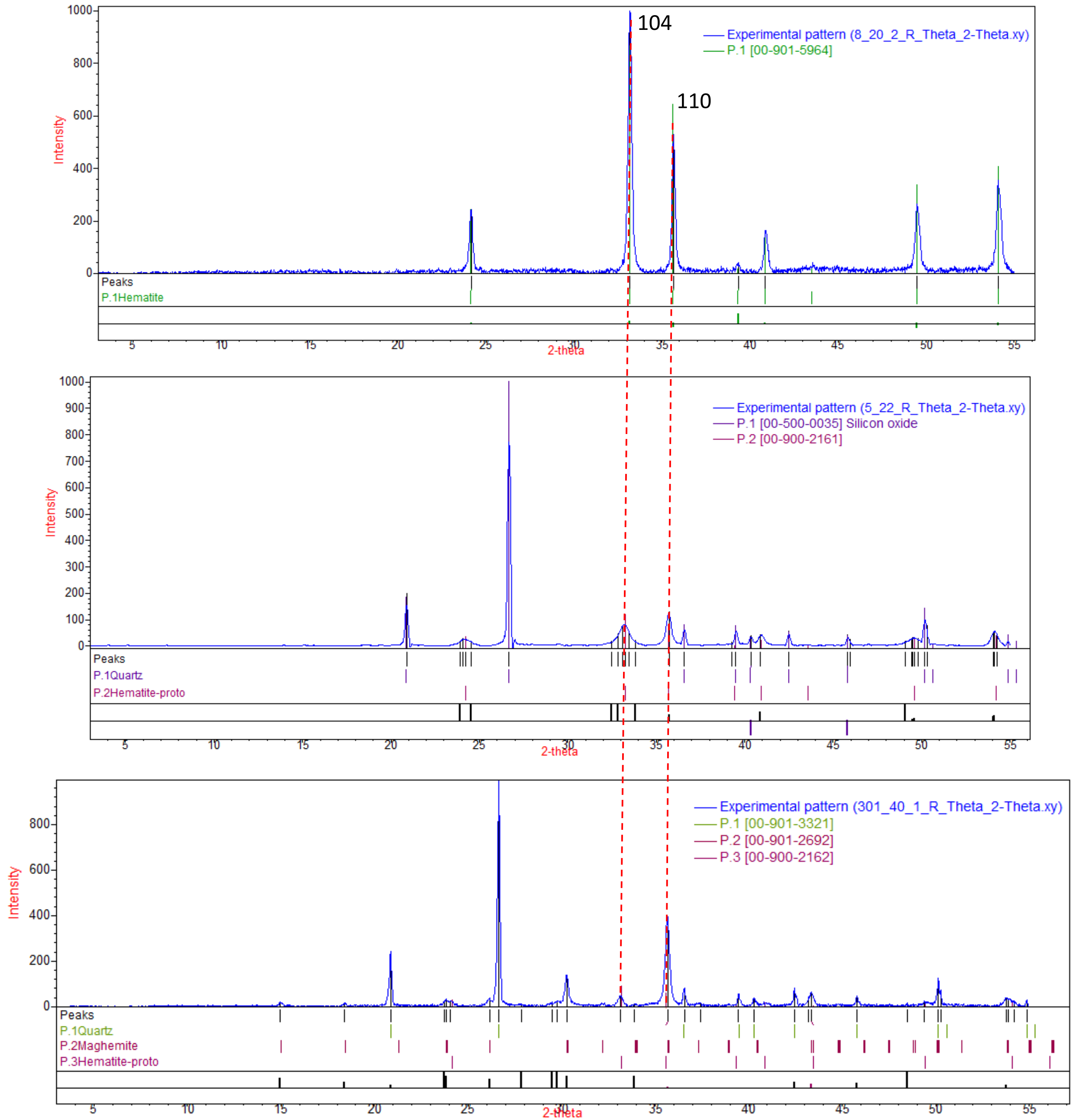
100
a. u.
90
80
70
60
50
40
30
20
10
0
104
110
8_20_2_R
5_22_R
10
20
30
40
50
2-THETA DEGREE

XRPD

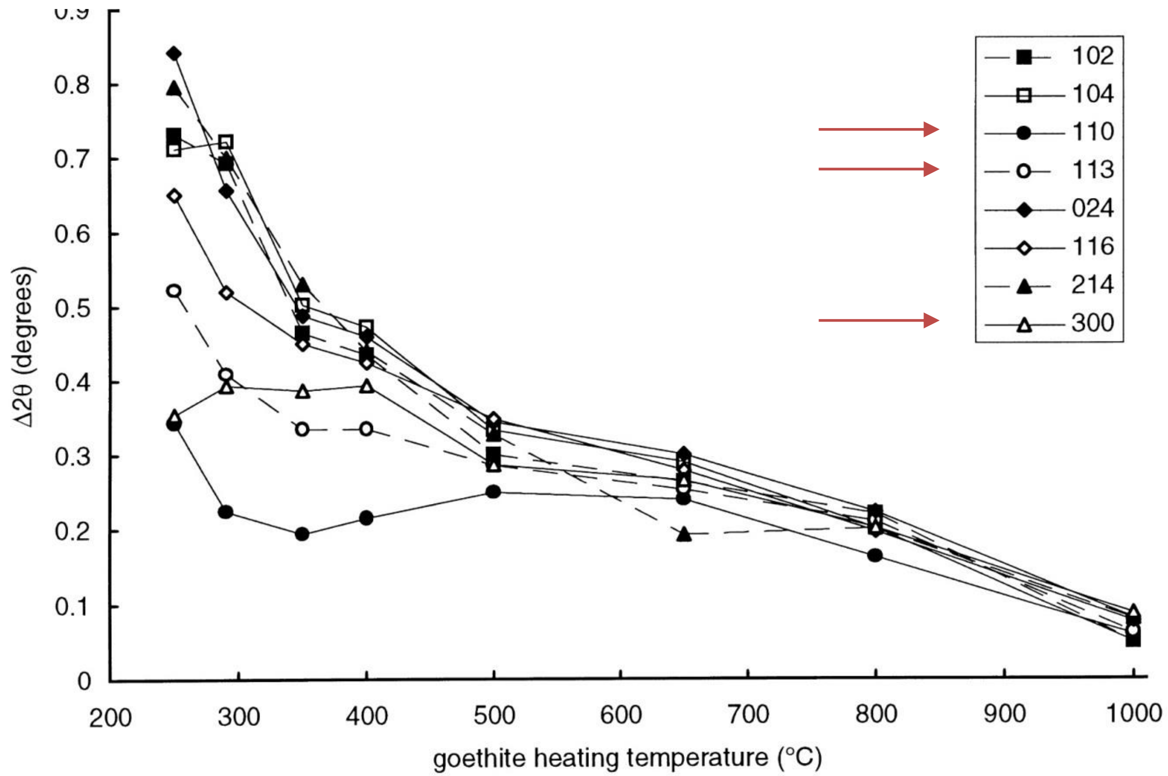


110
104
Experimental pattern (A2R_127f_R_Theta_2-Theta.xy)
P.1 [00-900-2162]
P.2 [00-221-1652] Goethite
Intensity
Peaks
P.1Hematite-proto
P.2Goethite
2-theta
Experimental pattern (A2R_147h_R_Theta_2-Theta.xy)
[00-901-5065]
Intensity
Peaks
Hematite
2-theta

XRPD

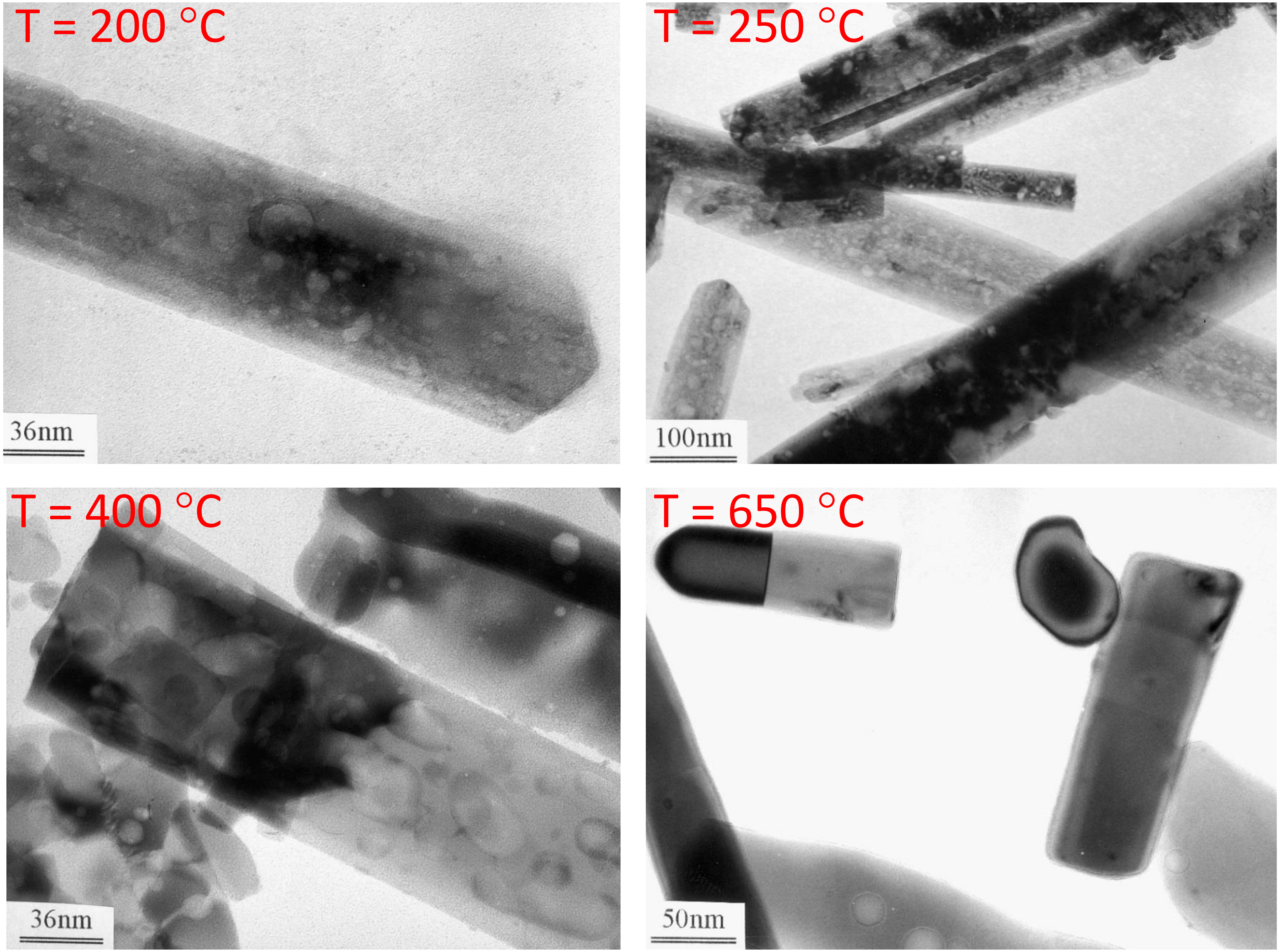

104
110
Experimental pattern (8_20_2_R_Theta_2-Theta.xy)
P.1 [00-901-5964]
Peaks
P.1Hematite
Intensity
2-theta
Experimental pattern (5_22_R_Theta_2-Theta.xy)
P.1 [00-500-0035] Silicon oxide
P.2 [00-900-2161]
Peaks
P.1Quartz
P.2Hematite-proto
Intensity
2-theta
Experimental pattern (301_40_1_R_Theta_2-Theta.xy)
P.1 [00-901-3321]
P.2 [00-901-2692]
P.3 [00-900-2162]
Peaks
P.1Quartz
P.2Maghemite
P.3Hematite-proto
Intensity
2-theta

BASICS OF THE HEATING PROCESS



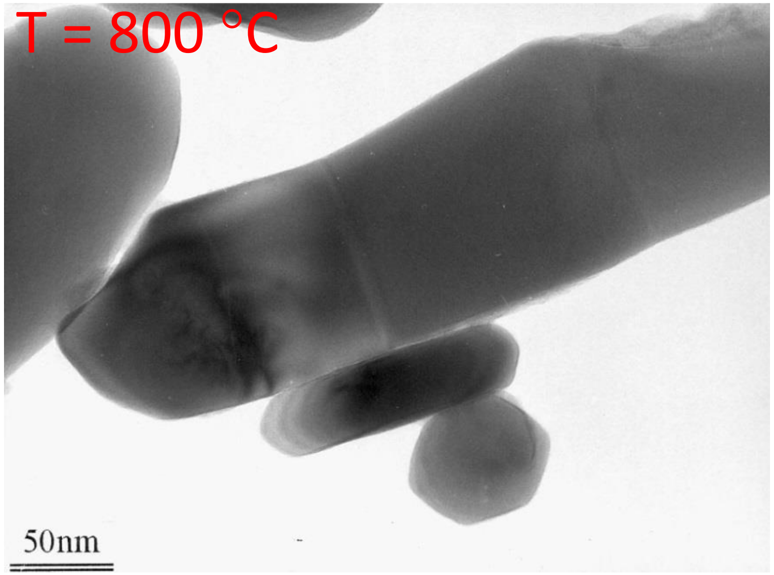
Widths of heated syntethic goethite main peaks at different temperatures (Pomiès et al., 1998)

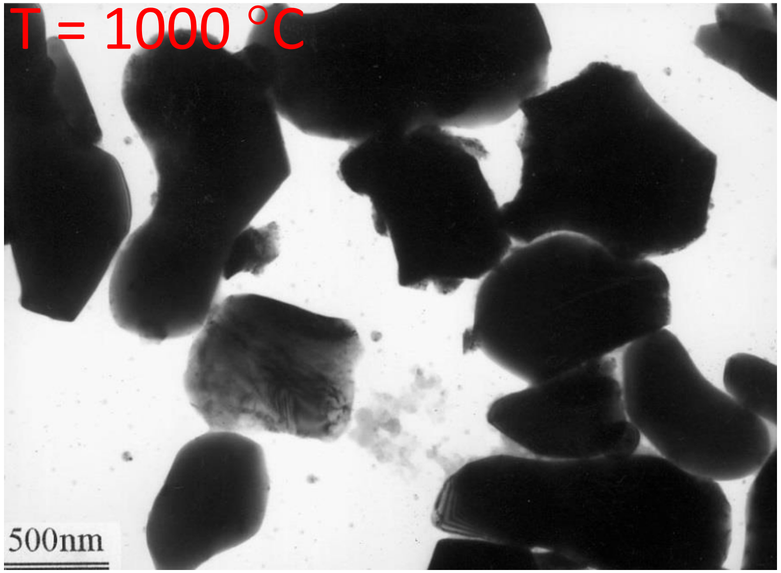
BASICS OF THE HEATING PROCESS

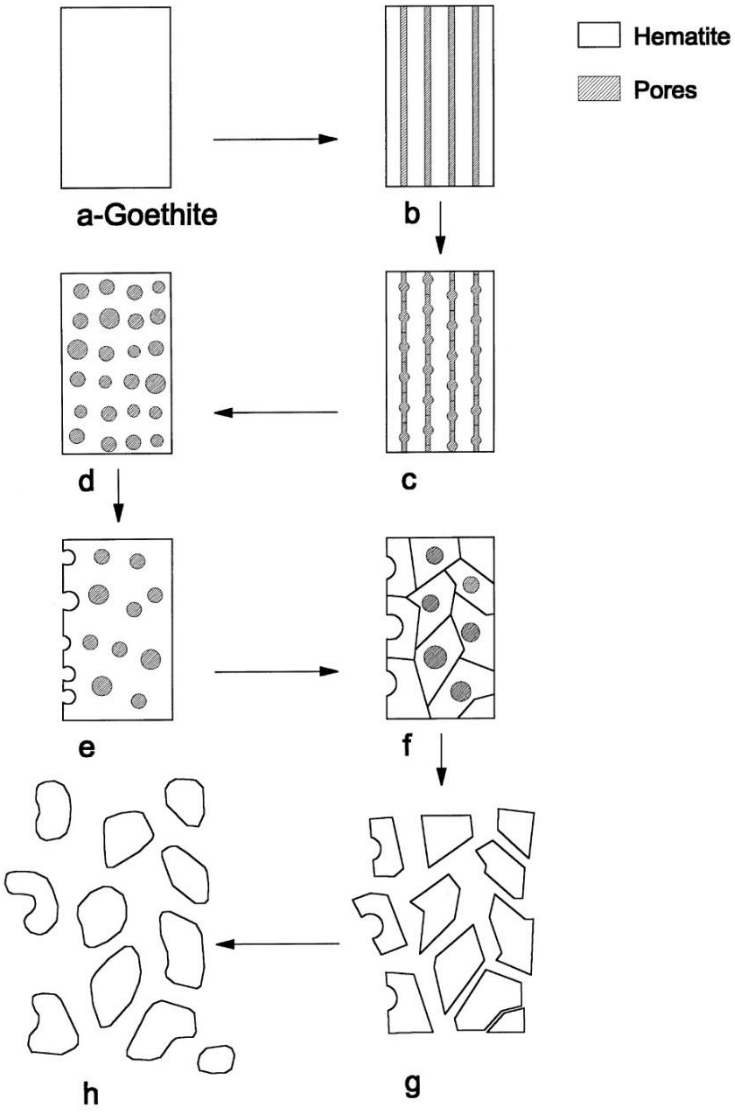


Pomiès et al. (1999)
Journal Eur. Ceramic. Soc, 19:1605-1614

BASICS OF THE HEATING PROCESS

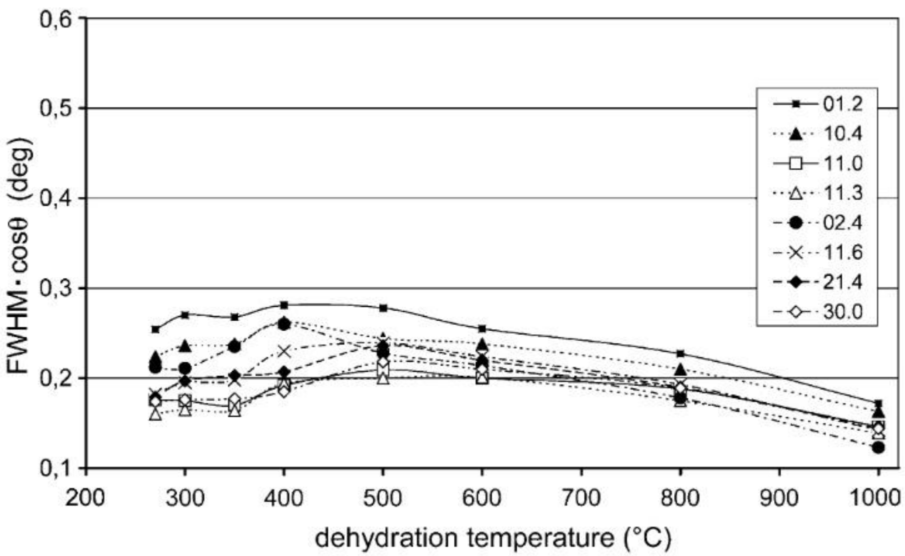


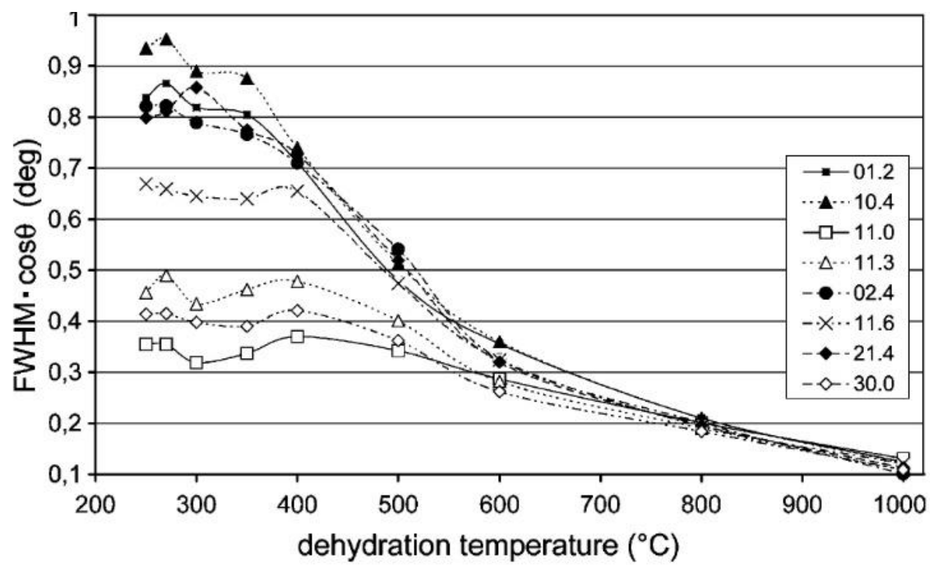




Pomiès et al. (1999)
Journal Eur. Ceramic. Soc, 19:1605-1614

EXPERIMENTAL: MOTIVATIONS



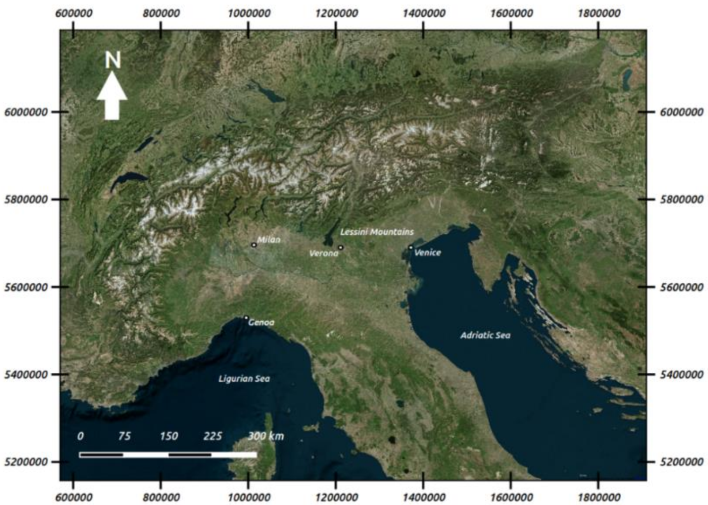


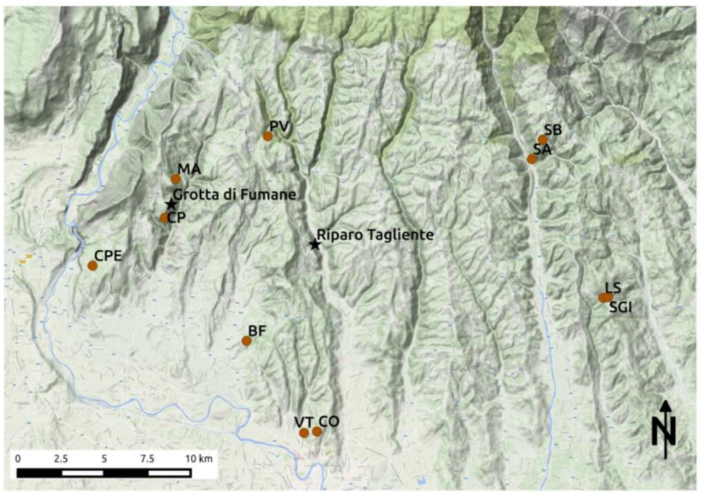
Natural Gth

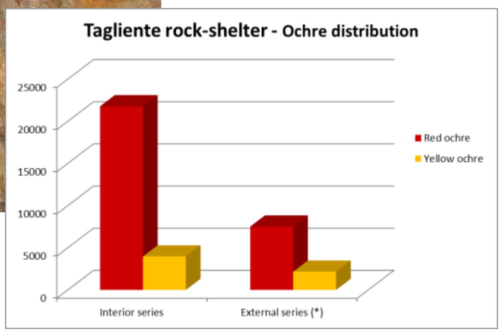
Synthetic Gth

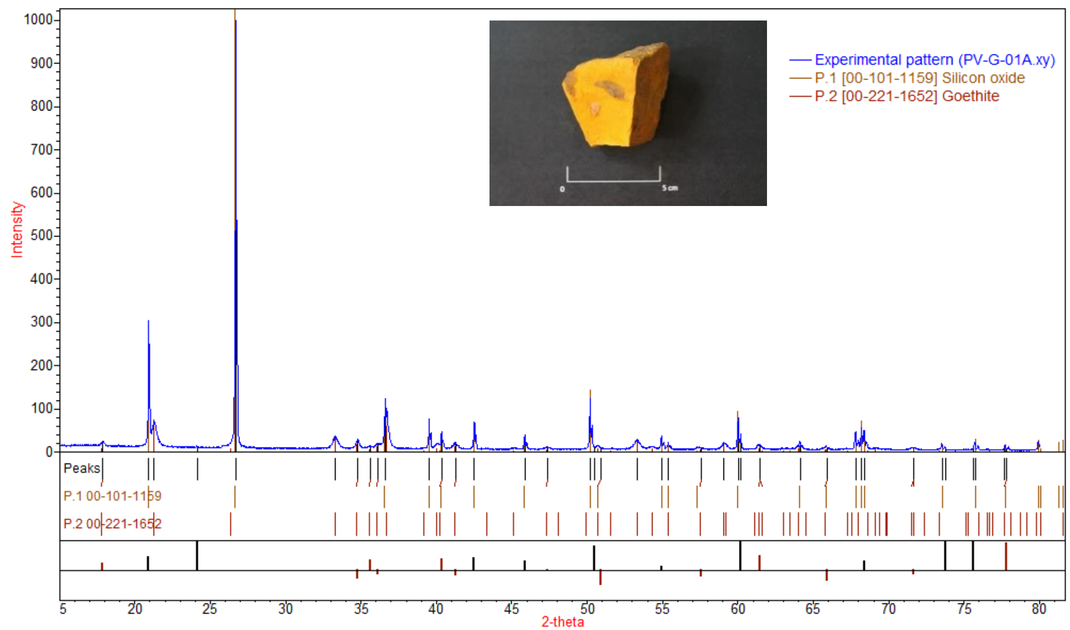
Löffler and Mader (2006)
Jour Eur Ceramic Society, 26:131-139

EXPERIMENTAL

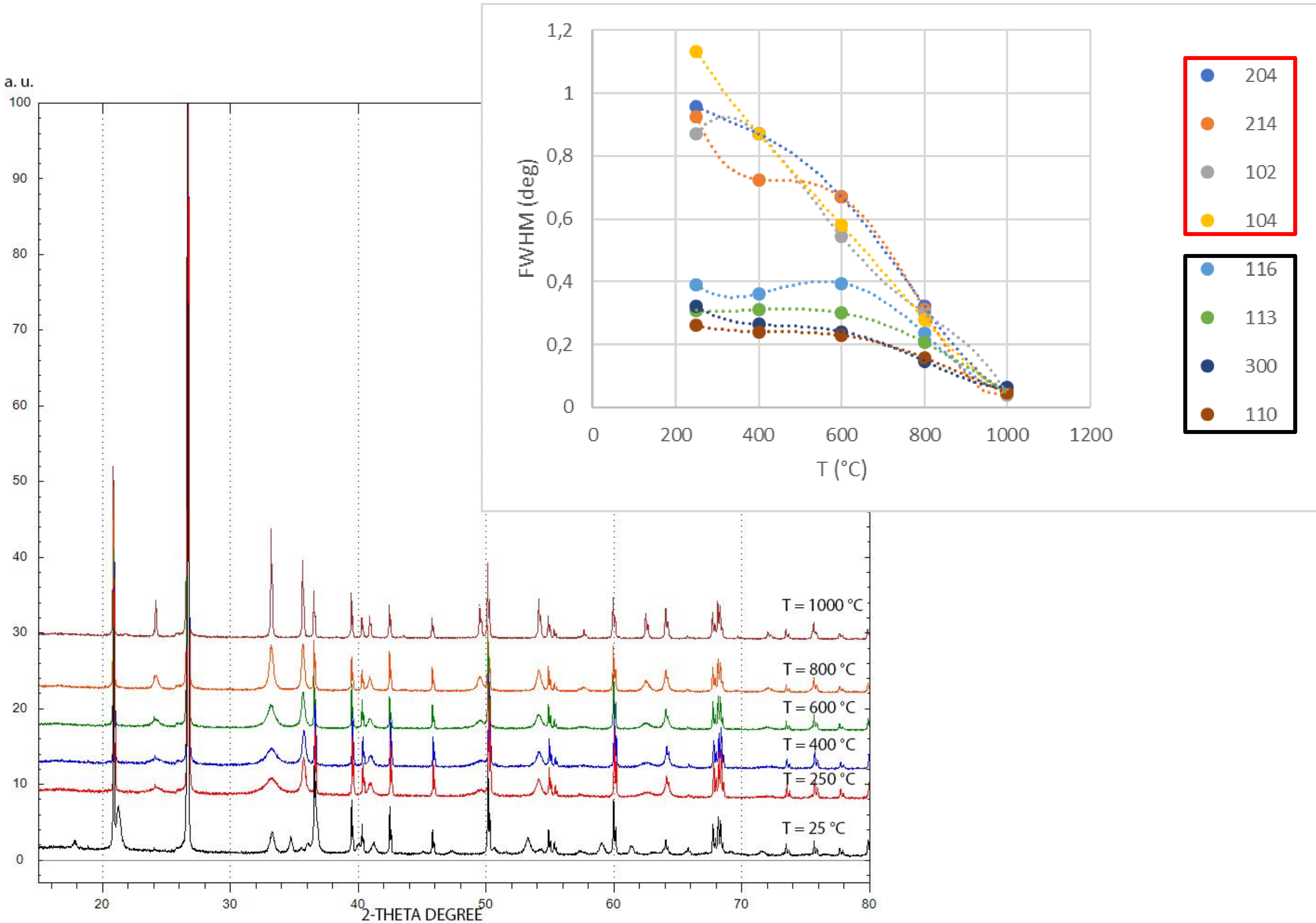




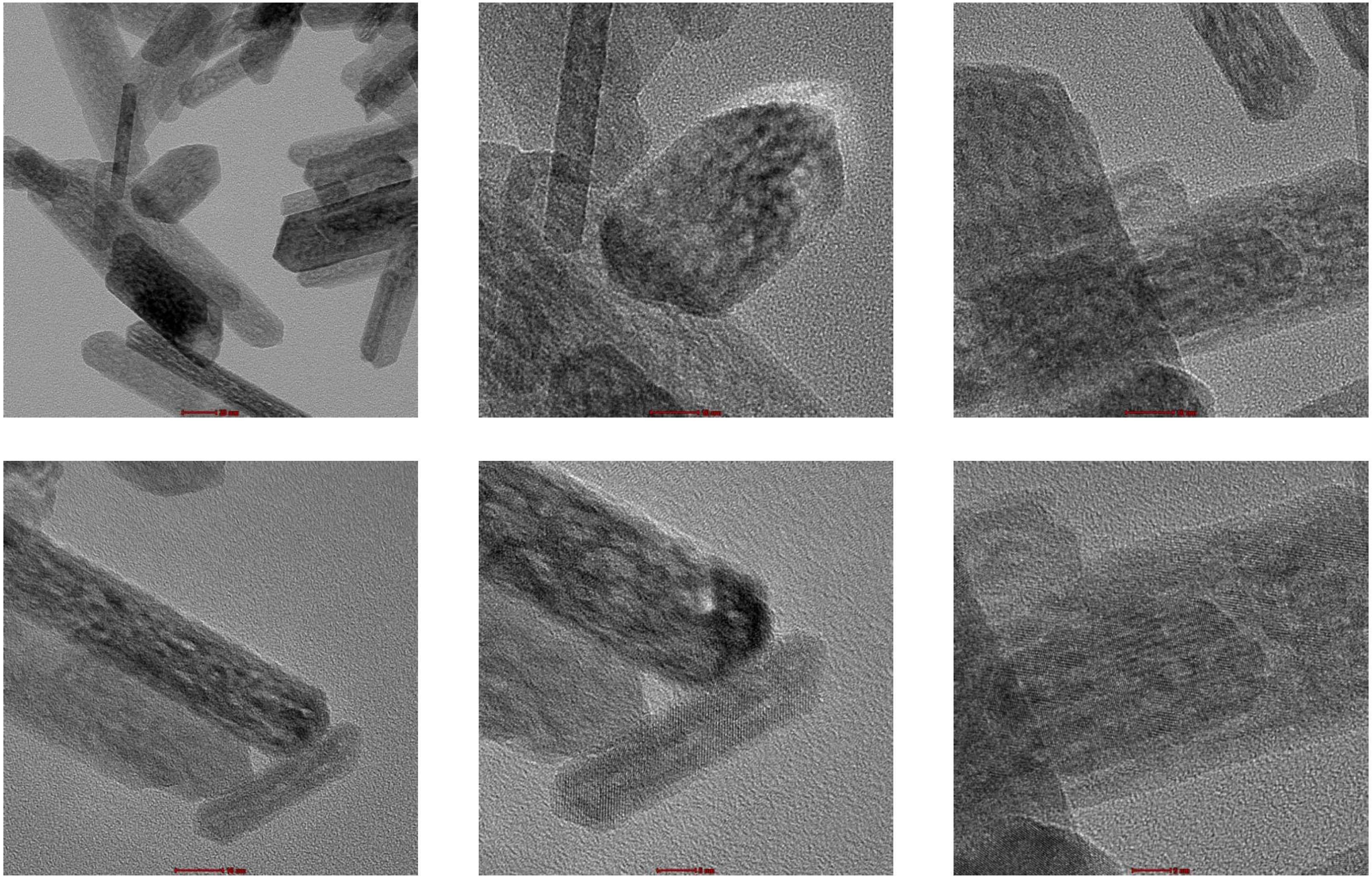




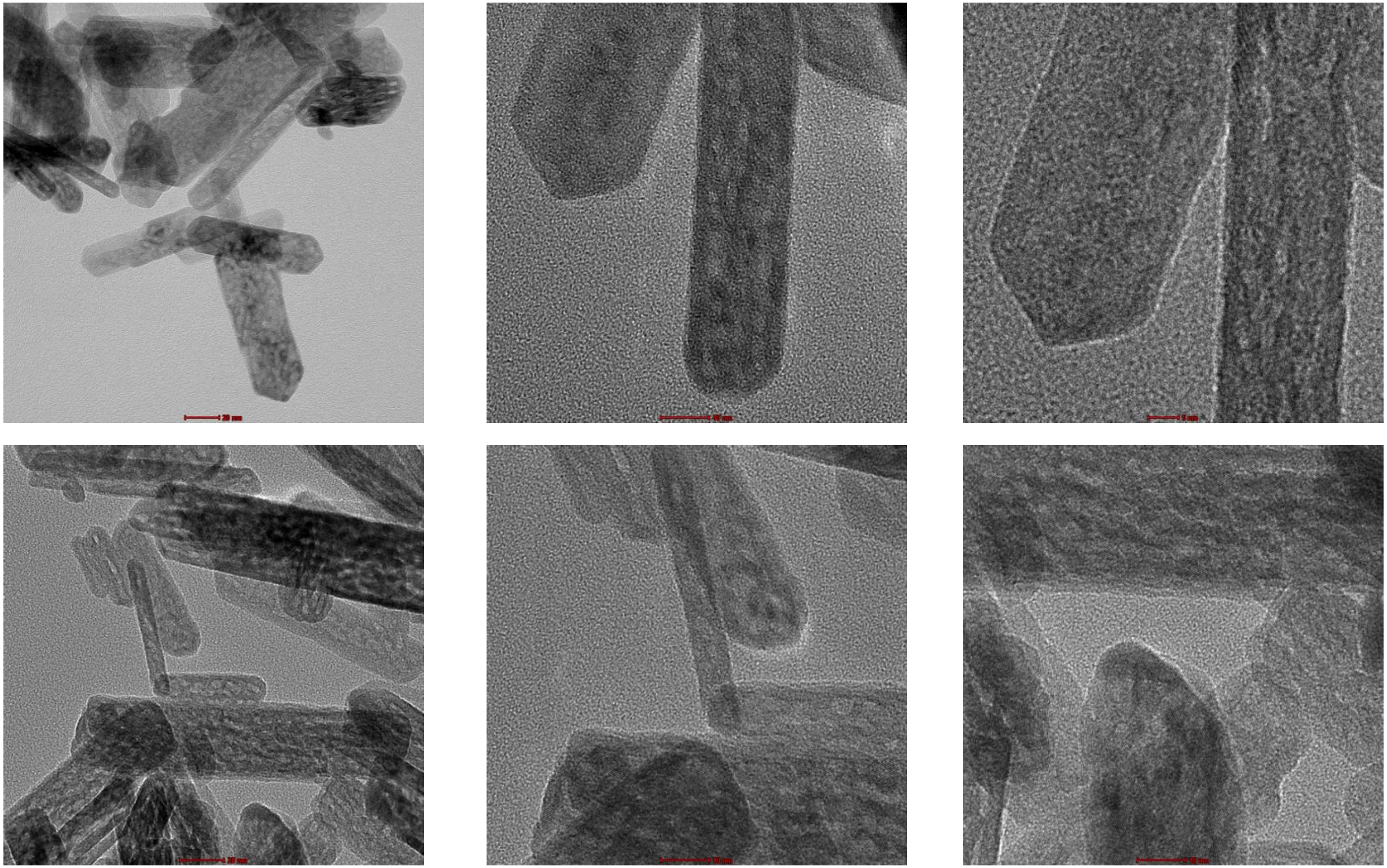
EXPERIMENTAL - XRPD



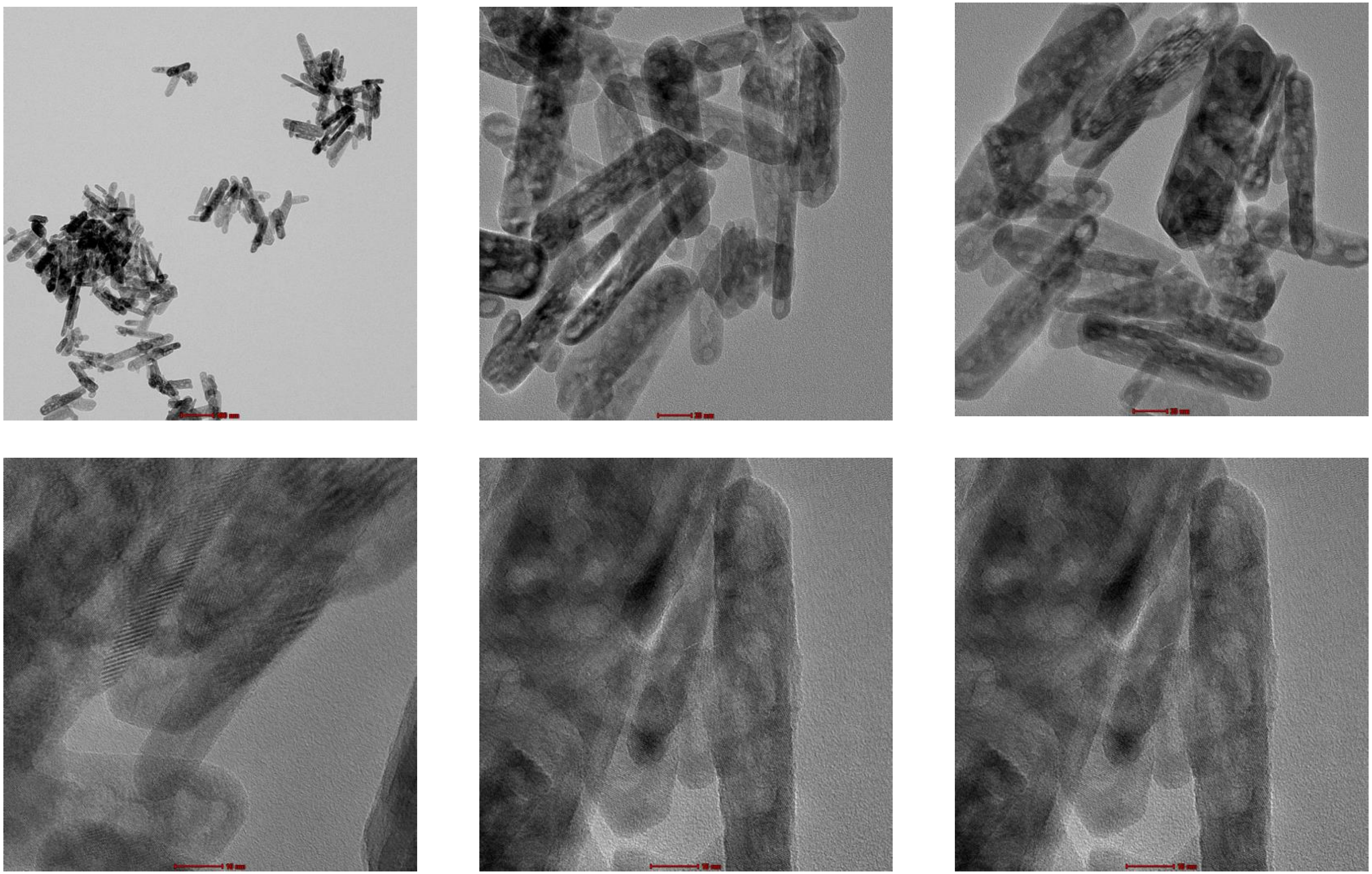
TEM - HT 250°C



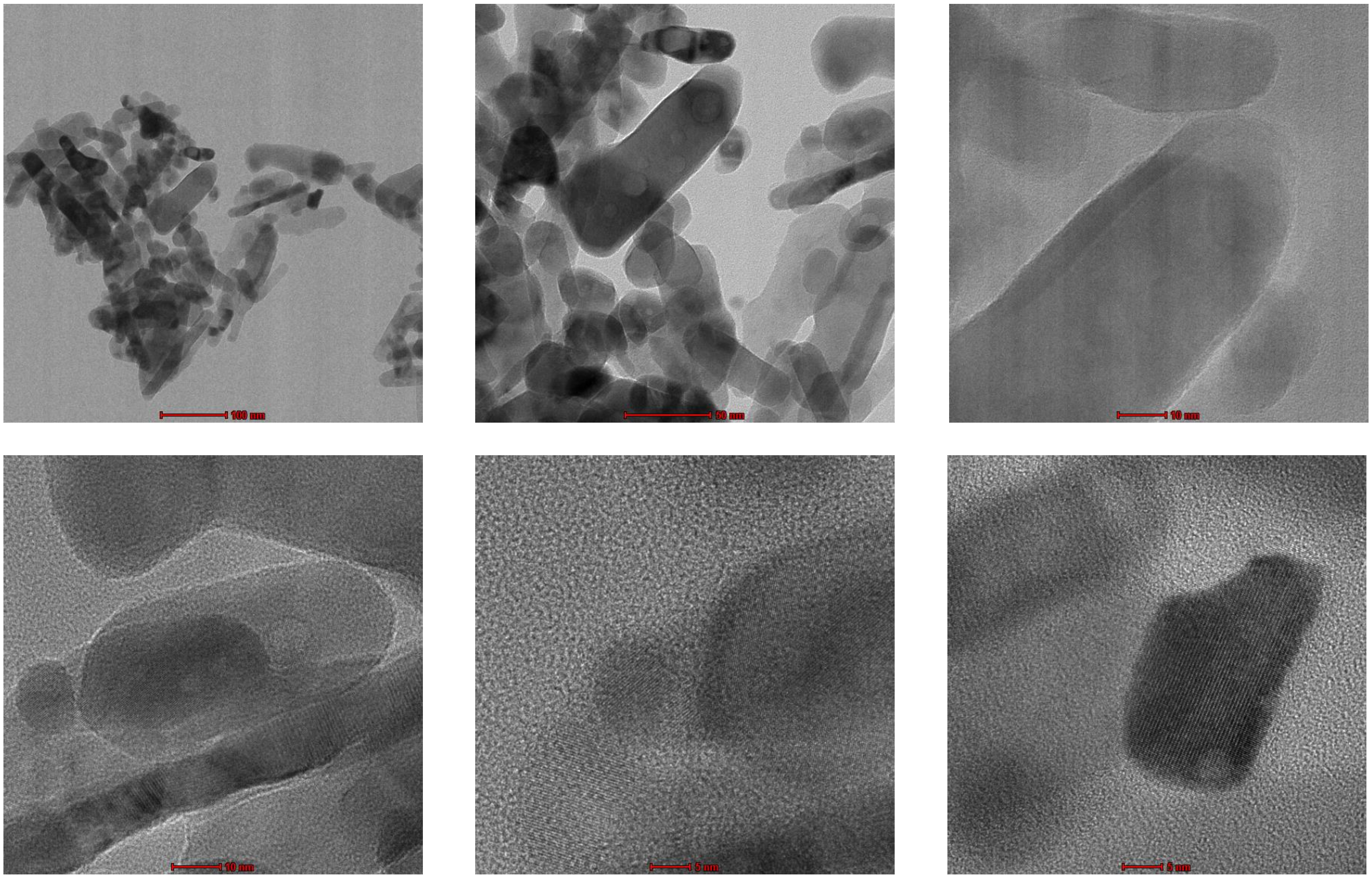
TEM - HT 400°C



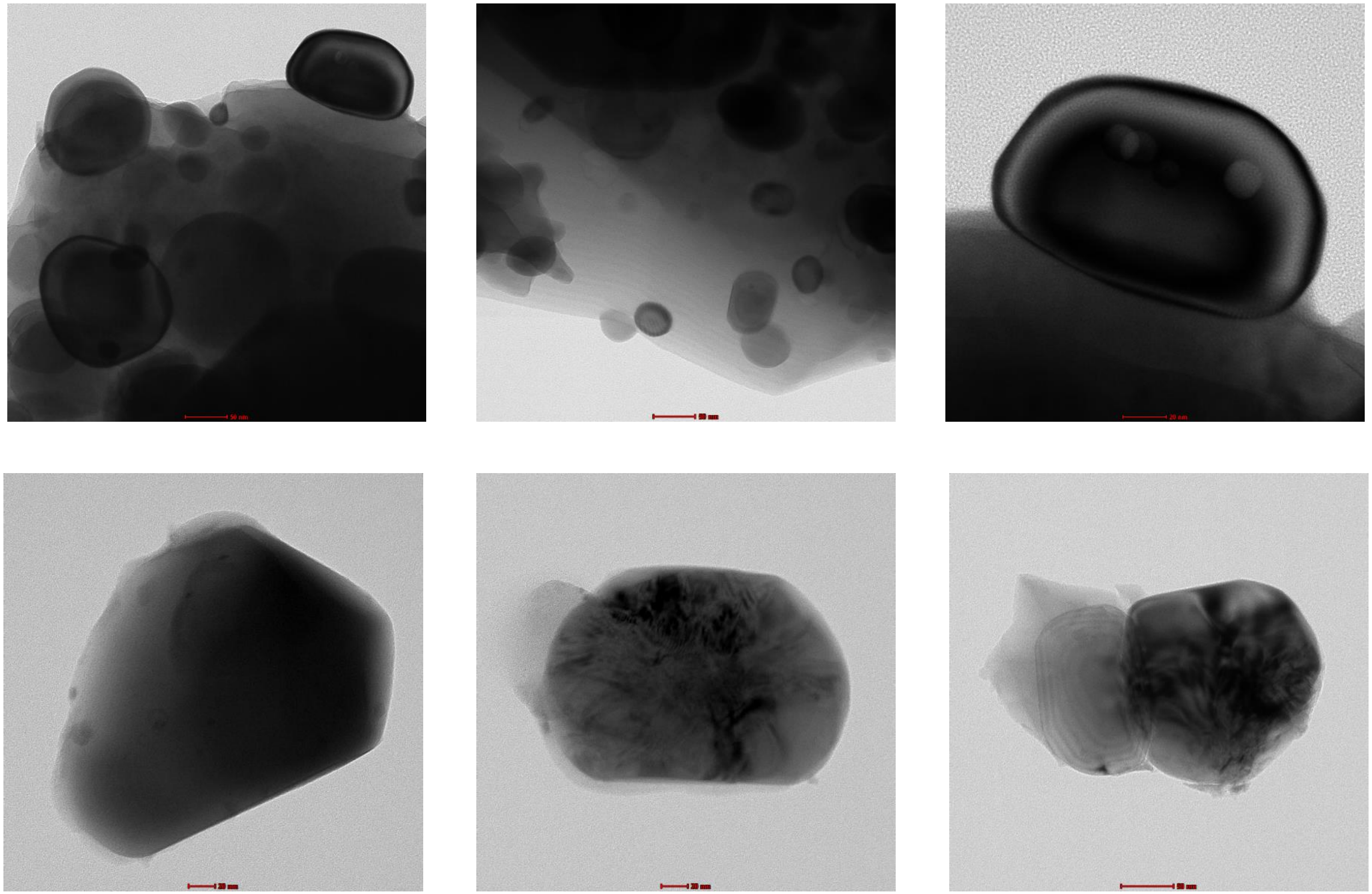
TEM - HT 600°C



TEM - HT 800°C



TEM - HT 1000°C



CONCLUDING REMARKS

- Selective broadening of peaks in XRPD profile occurs also in natural heat treated Gth confirming possible evidence of HT;
- The formation of pores of nanometric diameter due to the loss of water in Gth crystal lattice proves HT;
- The behavior of natural and synthetic Gth after HT is comparable;
- On the basis of the morphology and size of the pores, crystal size and morphology, FWHM, the ranges of heat temperatures can be estimated.

Ancient pharmacy of *Santa Maria alla Scala* in Rome

Aboca MUSEUM

Ancient pharmacy of *Santa Maria alla Scala* in Rome

CONTENTS

- Introduction
- Analysed materials
- Pigments, cosmetics, medicines
- Concluding remarks

Premise

The last books written by Pliny the Elder (24-79 AD) are devoted to the mineral realm. The author refers to minerals as self-transforming substances with biological vitality inspiring the Renaissance alchemists.
The figurative arts are part of this process of transformation being privileged places of the material processing: metal and gems are transformed by goldsmith and jeweller; marble by sculptor; earthy pigments are transformed by painter. According to Pliny, **art is a natural product**.

Introduction

The beginning of *pharmacognosy* (medicines from natural sources) can be traced in the *Iliad* where *pharmaka* are divided into three main groups:

1. ***pharmaka ipia*** (plant extracts to care the panic)
2. ***pharmaka androphona*** (murderous and life-destroying)
3. ***pharmaka lygra*** (plant extracts affecting the brain)

The verb ***Pharmasso*** means to treat by using *pharmaka* and to dye/colour wool.

(Photos-Jones and Hall, 2011)

Introduction

Internal view of a historical pharmacy as illustrated on the Kassel and Marburg *Taxa* of 1564 (from Burmester et al., 2010).

Introduction

Introduction

Research goals

Physicochemical analysis of the drugs, fragrances and pigments (231 samples).

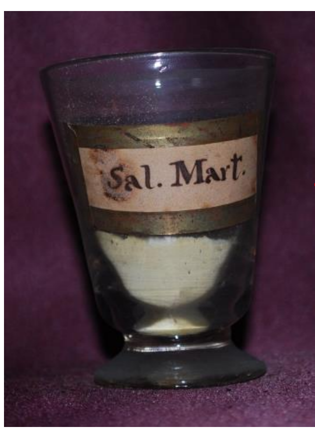
The study of written and pictorial sources: ancient Greco-Roman, Medieval and Modern.

Mythical-religious: beliefs, world-views, magical practices and rituals.

To favour the reappraisal, preservation and visibility of the Ancient Pharmaceutical Laboratory of *Santa Maria della Scala*, Rome

Research goals

Materials



GROUP	COMPOUNDS	THE MOST ABUNDANT DRUGS CONSERVED FOR EACH GROUP, IN ACCORDANCE WITH THE NAME REGISTERED ON THE LABEL OF THE CONTAINER
Group 1	Complex formulations	Antym Diaphor; Trocisc. Alb. Rax.; Pietra divina; Mutriforte Palay; Granat P.P.; Anthiemet. P.P
Group 2	Mercury	Princip. Alb.; Precip. Rub.; Marcas. Arg. Grc.; Mercurio Solub. del Mosc.; Cinabr. Nativ.; Cinabr. Fact.; Pulv. Absorbent Ven.
Group 3	Antimony	Sulph. Aur Antym.; Antym Diaphor.; Antymon. Diaphor Mart.; Sulph Aurat Antim.; Stomat. Poter; Anthiemet. P.P; Kerm. Minerv: Pro Veter; Reg. di Antimonio.
Group 4	Iron	Pulv. adcas. Mesne; Magist. Mart A.A.; Pulv. Cahet. Arnol; Lapis. Castrac; Antymon. Diaphor Mart.; Bol Armen; Ossido di Megane; Terr. Lemn.; Pulv. Astringent; Magist. Mart. Ap.; Lap. Hematit. PP.
Group 5	Organic compounds	Tint. di Cascarilla; Cascaril; Estratto di Cocca; Gumin. Kui?; Resin Mechioar; Mirabol Citrin; Gran Paradis; Lans. Fel. Rubr.; Benzoin; Gumm. Gut; Mechoacan; Gumm. Dragant; Corn. Cerv. PR.; Lig. Aloe; Res Guajac; Viper Pulv.; Sarcocoll; Anis Stellat; Guaiaco Resin.; Oss. Cord. Cerv.; Balsam. Peruvin; Ladon; Resin Scamon.
Group 6	Salts	Sal Vener; Sal Pimpinell; Sal Corall; Sal Guajac; Sal Escorz Ner; Sal Beccabung; Sal Hyosciam; Sal Peon; Sal Ormin; Sal Juvartel; Sal Eliotrop; Sal Juvartel; Sal Asparag; Sal Caryoph; Sal Dictam Cret.; Sal Polychr; Sal Absynt; Sal Centaur; Sal Tanasell; Sal Tartar Solub.; Sal Anonid; Sal Capill Vener; Sal Agrimon; Sal Rest. Capr.; Sal Scabios; Sal Apet.; Sal Goniz; Sal Fenaot; Sal Junyp; Sal Carlin; Sal Androsdem; Sal Tartar F.; Sal Chichor; Sal Balsamin; Sal Achant; Sal. Digest. Sylv.; Sal Anet; Sal Mirabit; Sal Aquileg; Sal Cyan; Sal Barden; Sal Corocop; Sal Hyperic; Sal Lentise; Sal Chin; Sal Theriacal.
Group 7	Gems	Margarit; Hyacint; Granat; Smerald; Pietre Preziose; Rubin; Saphyr; Topat; Lapislazuli.

Methodology

Preliminary documentation (UniVA)

HH-XRF (LAMS, UPMC, Paris)

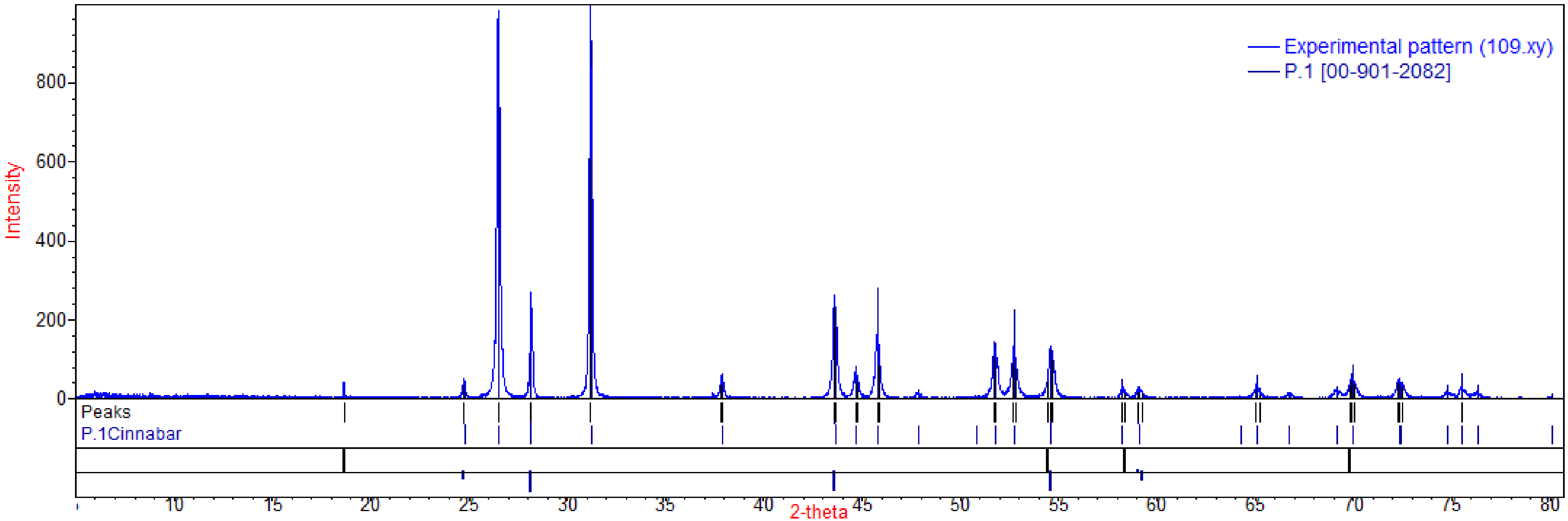
PLM (Supsi)

XRPD (Supsi and UniVA)
Bruker D8 Advance system; 40KV 40mA Cu anode (CuKα = 1.5418 Å); 2θ range=5-80°, step size 0.02°, scan speed 0.5°min^{-1}. QualX2.0 (Altomare *et al.*, 2015. *Jour Appl Crys*, 48, 598-603).

GC/MS and HPLC (Perugia, Cà Foscari Venice)

Results and comments

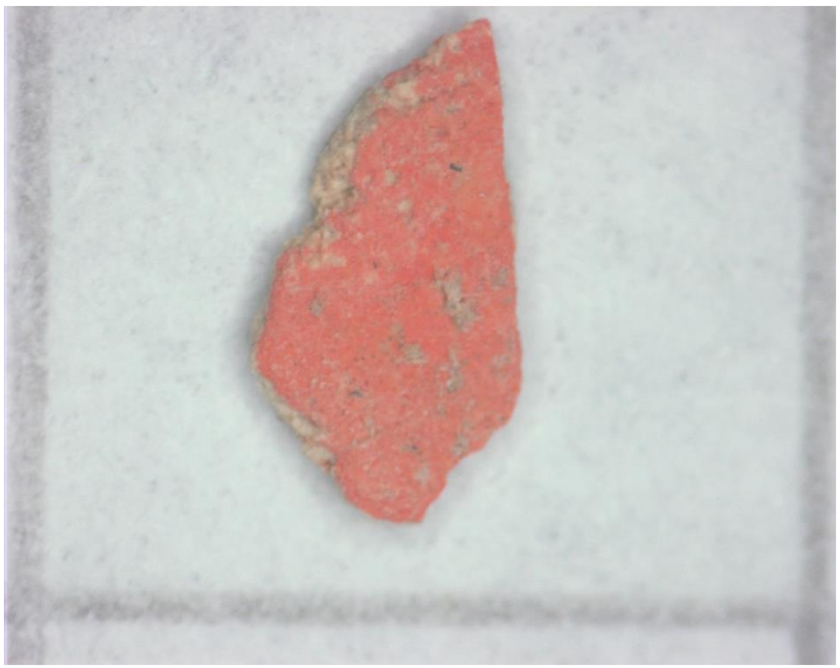
Hg-based compounds



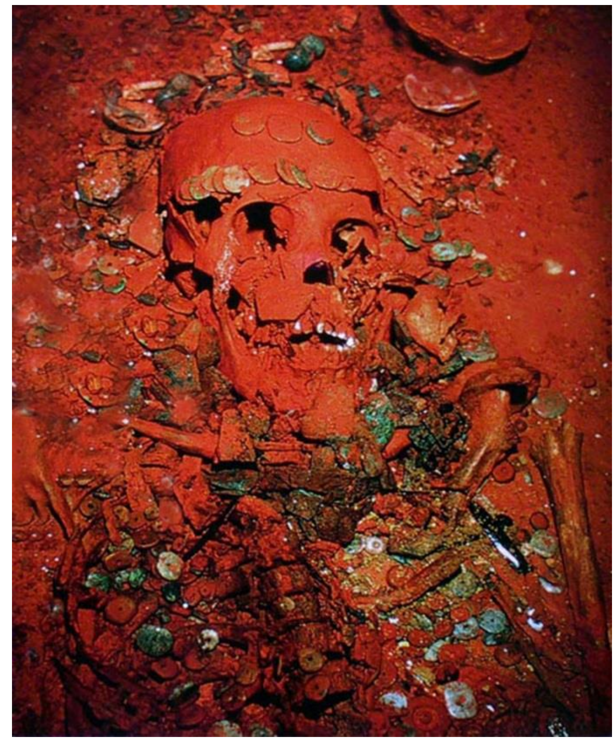
Cinnabar is red pigment well known to Romans but also in Greece at least since 6th century B.C. (Gettens et al., 1993). Notwithstanding, mercury is a well known toxic heavy metal, cinnabar has been used for 2000 years in traditional Chinese and Indian Ayurvedic medicines (Liu et al., 2008).

Results and comments

Hg-based compounds



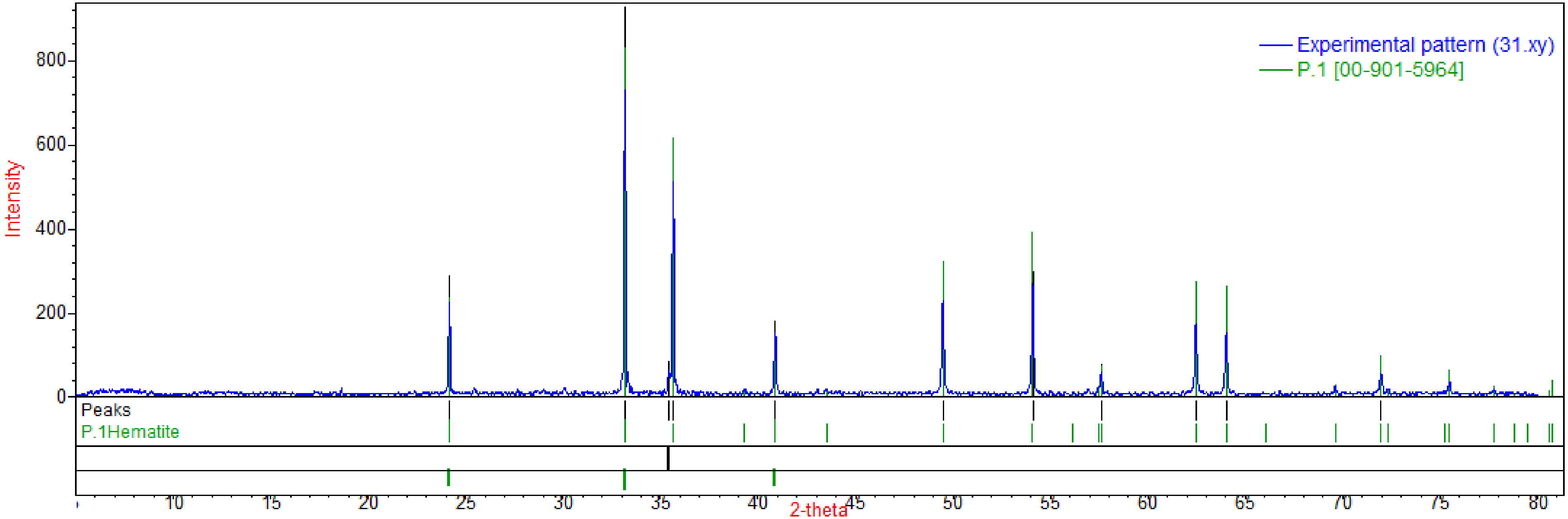
Wall painting fragment, Chupiquaro
(image 4 mm width)



The red Queen, Palenque

Results and comments

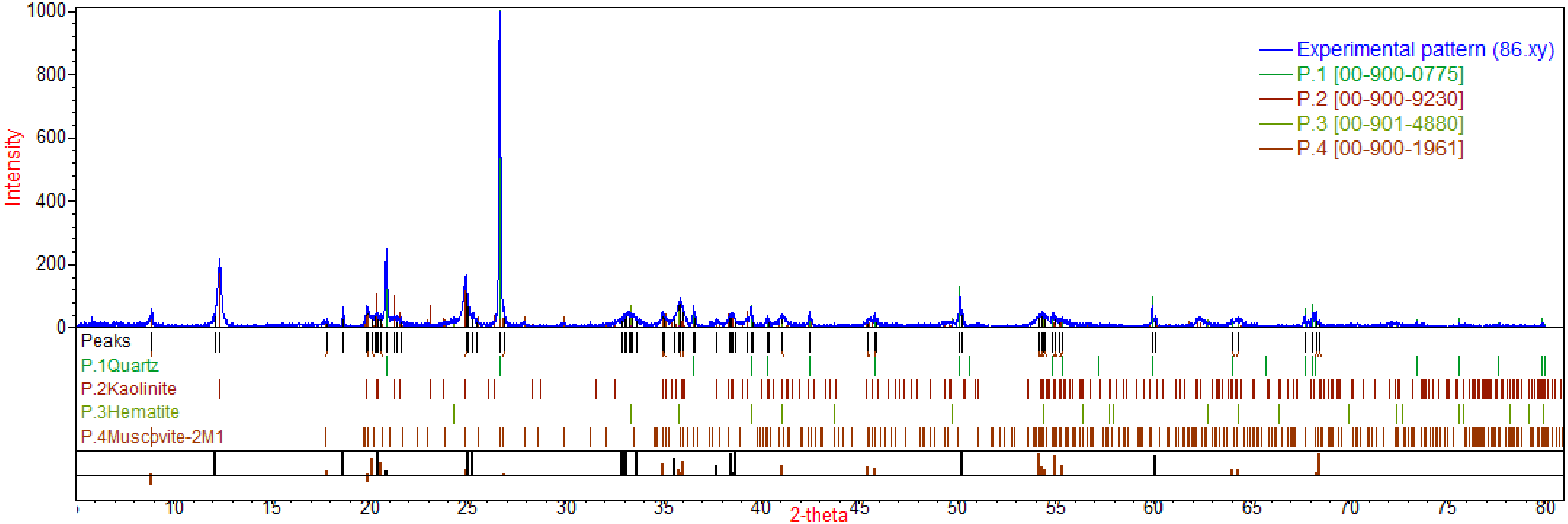
Fe-based compounds



Hematite, beside its use since Prehistory as pigment and other utilitarian and not utilitarian applications (Cavallo, 2016), was maybe the first mineral medicine used by early human beings (Velo, 1984).

Results and comments

Fe-based compounds



Results and comments

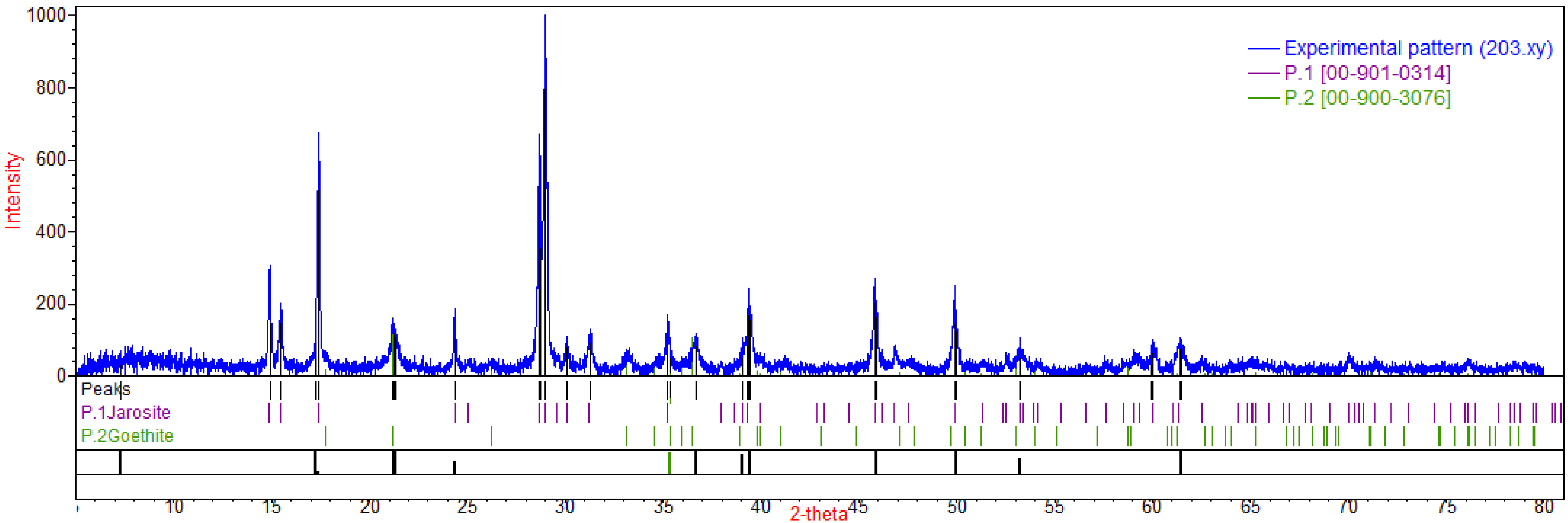
Fe-based compounds

Ethnographic evidence of hematite based compounds use

Roman wall painting (Ercolano, Italy)

Results and comments

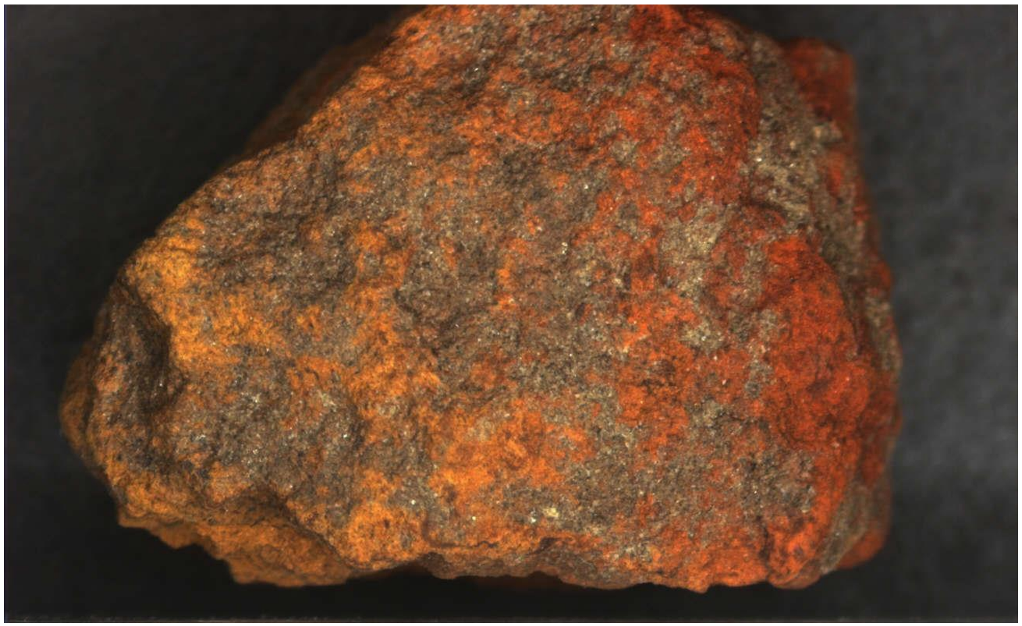
Fe-based compounds



Jarosite was used as yellow pigment since Middle Paleolithic (of Iberia) corresponding to 50000 years B. P. (Zilhão et al., 2010). It is important to point out that jarosite in association with goethite is called “Pulvis Astringent” (Astringent powder; sample 203), indicating its possible use in pharmacology. On the other hand, jarosite was used as cosmetic (and pigment) in the Roman world (Ambers, 2004; Gamberini et al., 2008).

Results and comments

Fe-based compounds

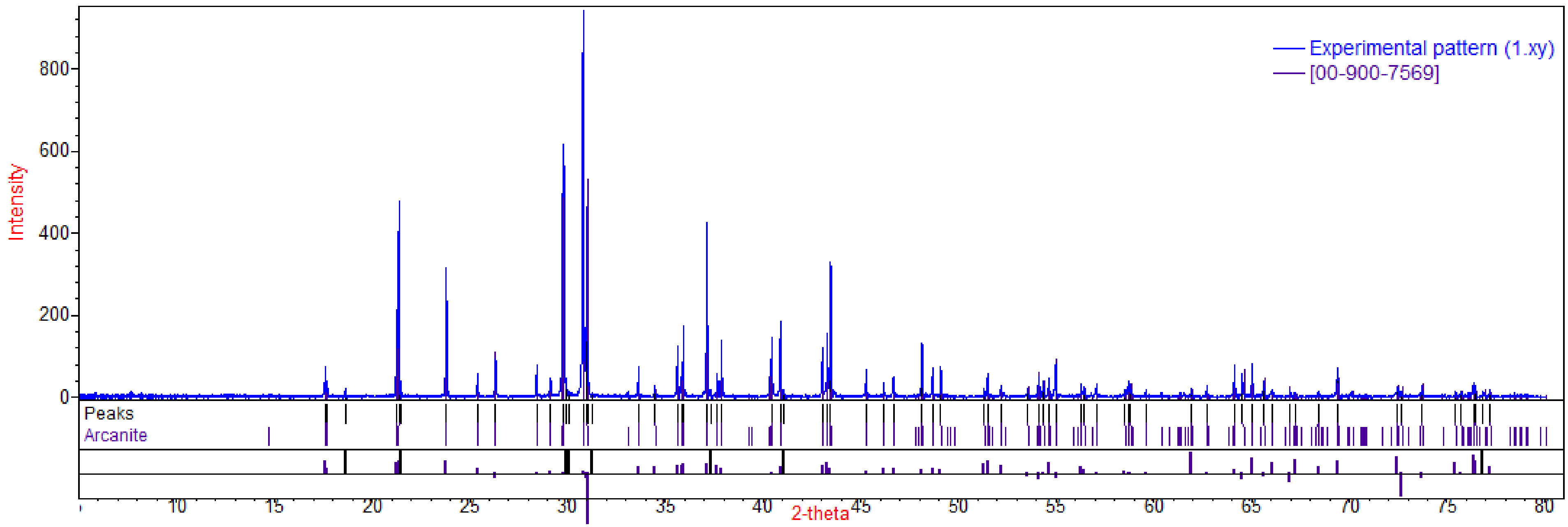


Partially heated archaeological ochre fragment from Tagliente rockshelter (image 13 mm width)

Painted plaster (St Giovanni church, Cevio, Switzerland)

Results and comments

Salts



The name of this salt derives from the Latin *Arcanum duplicatum* (double secret), a Medieval alchemical name.

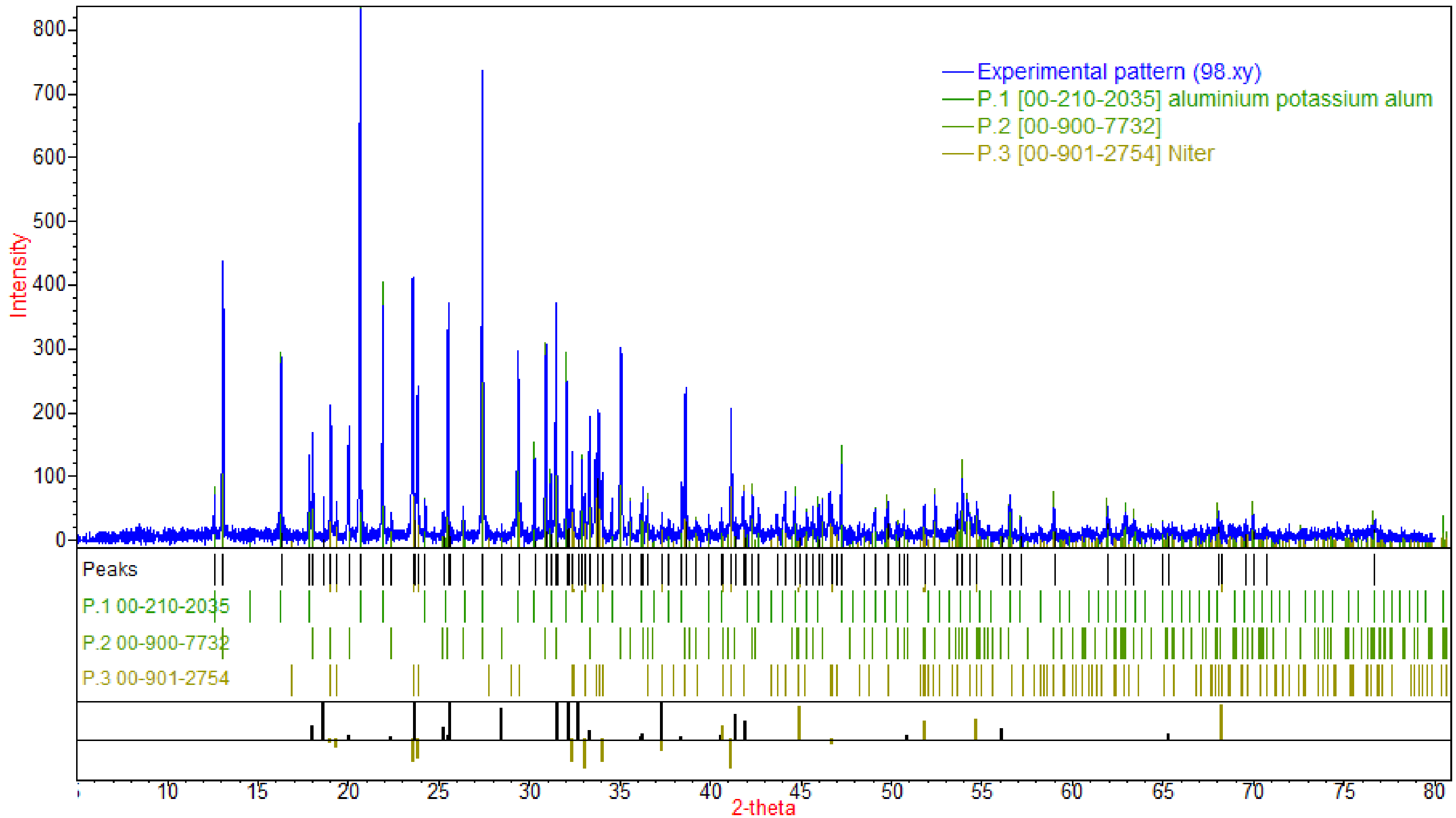
Results and comments

Chemical group	Chemical sub-group	Label (reported on the glass container)	Minerals (XRPD)
SULPHATES	K-sulphate	**1** Sal. Vener; **2** Sal Pimpinell; **4** Sal Guajac; **9** Sal Escorz Ner; **10** Sal Beccabung; **11** Sal Hyosciam; **12** Sal Ormin; **13** Sal Peon; **16** Sal Eliotrop; **17** Sal Asparag; **21** Sal Caryoph; **22** Sal Dictam Cret; **24** Sal Polychr; **29** Sal Absynt; **33** Sal Centaur; **45** Sal Tanasell; **52** Sal Tartar Solub.; **53** Sal Anonid; **54** Sal Capill Vener; **58** Sal Agrimon; **60** Sal Rest. Capr; **61** Sal Scabios; **65** Sal Alchimill; **68** Sal Goniz; **72.** Sal Junyp **76** Anacard; **78** Marcas. Arg. Grc.; **79** Sal Androsdem; **84** Sal Tartar F.; **91** Sal Chichor; **96** Sal Balsamin; **97** Sal Achant; **102** Sal. Digest. Sylv.; **124** Sal Mirabit.; **125** Sal Aquileg; **131** Sal de cluob. Mynsich? **133** Sal Cyan; **134** Sal Barden; **136** Sal. Corocop; **144** Sal Hyperlc?/Hyperic? **146** Sal. Card. Benect/Benecl?; **147** Sal Eder. Terr?; **151** Sal Herniar; **152** Cinabr. Fact.; **154** Sal Betton; **155** Sal Chin.; **156** Sal Tanacet; **157** Sal Lentise; **158** Sal Taraxac; **159** Sal Soldanell; **161** Sal Parietar; **168** Sal Mart; **169** Sal Alliar; **172** Sal Feber; **175** Semi di Felandro Aquatico; **179** Sal. Acler. Terr; **180** Sal Genist; **183** Sal Polii Mont.; **184** Sal Bistort; **194** Sal Absynt; **196** Sal Abrotan; **204** Sal (?); **206** Sal Agrimon; **207** Sale di Card. Benect; **208** Sal Alchecheg; **209** Sal Acanth; **210** Sal Tanacet; **212** Sal Nasturt Aq.; **215** Sal Fragor; **217** Sal Sub Fabar; **220** Arcanum?; **221** Sal Pimpinell.	**Arcanite**
	AlK-sulphate	**94.** Especific. Elvet.	**Alum**
CHLORIDES	Na-chloride	**62** Sal Apet;	**Halite**
	Na- and K-chlorides	**71** Sal Fenaot;	**Halite + Sylvite**
	Hg-chloride	**35** Princip. Alb.;	**Calomel**
	Hg-chloride and Hg-oxychloride	**122** Mercurio Solub. del Mosc;	**Eglestonite and Calomel**
	NH_4-chloride	**205** F. Hydroc. Amm.;	**Sal ammoniac**
CARBONATES	Ca-carbonates	**70** Margarit; **116** Mutriforte Palay?	**Aragonite + Calcite**
	Pb-carbonates	**73.** Trocisc. Alb. Rax.	**Hydrocerussite and Cerussite?**

Results and comments

PHOSPHATES	Ca-phosphates	**113.** Corn. Cerv. PR.; **138.** Calomel Turc [*];	**Hydroxylapatite**
		163. *No name*	**Monetite**
BORATES	Na-(tetra)borate	**187.** Borat Sod.	**Tintalconite**
SULPHIDES	Hg-sulphide	**109** Cinbr. Antymon.; **148** Cinabr. Nativ.; **152** Cinabr. Fact.	**Cinnabar**
OXIDES	Fe-oxide	**31** Pulv. Cahet. Arnol; **222** Lap. Hematit. PP.;	**Hematite**
		218 Magist. Mart. Ap.;	**Maghemite? Magnetite?**
	Si-oxide	**46** Sardon	**Quartz**
	Si- and (Fe,Mn)-oxides	**127** Ossido di Megane	**Quartz and bixbyite**
	Sn-oxide	**137** Anthiemet. P.P.	**Cassiterite and (?)**
MIXTURES	Salts	**15.** Sal Juvartel; **214.** Sal Theriacal	**Sylvite+Aphthitalite+Arcanite**
		110. Sal. Anet	**Arcanite + aphthitalite**
		98. Pietra divina	**Alum + Niter + kaliochalcite**
	Other	**86.** Bol Armen	**Quartz+Illite/(Muscovite)+ Kaolinite+Hematite**
		140. Protossido di Piombo	**Litarge + cerussite (?)**
		190. Pulv. Absorbent Ven.	**Cinnabar + jarosite + pyrrhotite**
		203. Pulv. Astringent	**Jarosite + Goethite**

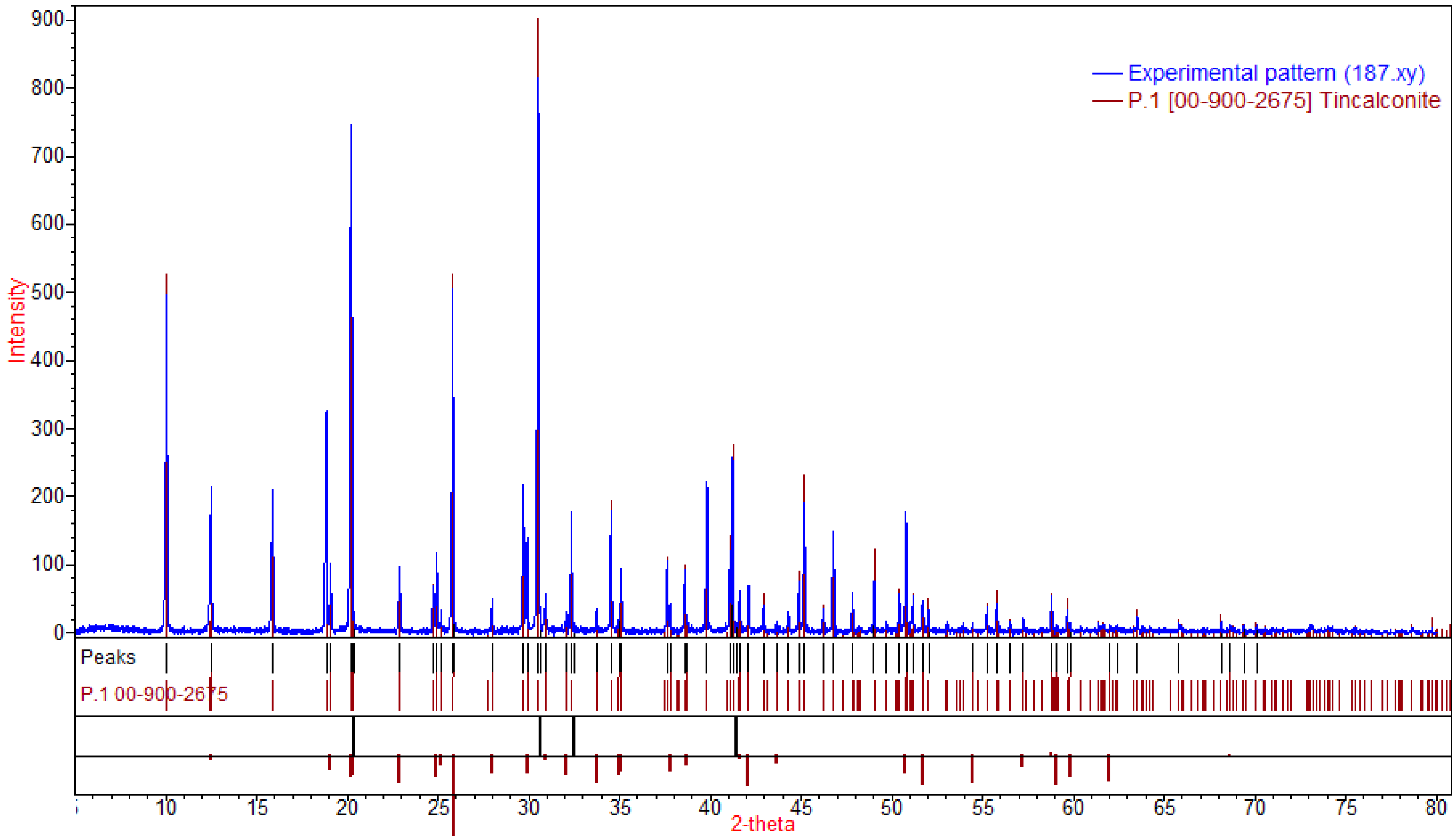
Results and comments



Finally, the composition of Pietra divina (Divine stone, sample 98) matches very well that reported in Testi (1980) composed of Alum-K $KAl(SO_4)_2 \cdot 12(H_2O)$, niter KNO_3 , Kaliochalcite $KCu_2(SO_4)OH$, according to the following proportion 1:1:1.

Cavallo and Vazquèz (2018)
Powder Diffraction Journal, 33(4), 270-278.

Results and comments



Tintalconite, a pseudomorph of borax [$Na_2(B_4O_7)\cdot 10H_2O$], belongs to the borate group used as flux in cobalt ore processing for blue pigment manufacture process (Matin and Pollard, 2017), and more in general in melting processes. Moreover, the use of boric acid (after dissolution of borates in water) is well known for its antiseptic properties and eye salves; recent applications as antibacterial agent are very promising (Photos-Jones et al., 2015). Finally, it was also an alchemical compound (Testi, 1980).

Concluding remarks

Most of the analysed samples (~50%) are salts, mainly arcanite (K_2SO_4).

Many minerals used as pigments were identified such as cinnabar, hematite, goethite, jarosite, armenian bole, azurite, (calcite, aragonite, lead white, hydroxilapatite).

The correspondence between the label on the glass container and the mineral is good except for a few cases.

The pharmacy supplied both medicines and pigments as in other cases in Italy and beyond the Alps.

Acknowledgments

Acknowledgments