Appl Phys A (2009) 96: 701–711
DOI 10.1007/s00339-009-5163-9

Applied Physics A
Materials Science & Processing

A study of smalt and red lead discolouration in *Antiphonitis* wall paintings in Cyprus

Sister Daniilia · Elpida Minopoulou

Received: 6 May 2008 / Accepted: 24 February 2009 / Published online: 21 March 2009

Abstract The present analytical study focuses on the degradation phenomena observed in fifteenth century wall paintings of the Christ *Antiphonitis* monastery in Cyprus. Examination of ten fragments by means of optical microscopy (OM), scanning electron microscopy (SEM/EDS), μRaman and FTIR spectroscopy revealed smalt discolouration and loss, and transformation of red lead from orange Pb_3O_4 to black PbO_2. The chromatic changes have affected the aesthetic effect of the paintings insofar as these pigments were extensively used. The mechanisms of smalt weathering, i.e. leaching of alkali and formation of micro-cracks, are interpreted in relation to its chemical composition and to the aggressive environmental conditions. In addition, it is assumed that red lead degradation may have been induced not only by the effect of temperature, light and humidity but also by the presence of chlorine salts. These phenomena of pigment alteration and loss underline the unsuitability of smalt and minium on wall paintings, regardless of the painting technique (*fresco, fresco-secco, secco*).

PACS 33.20.Ea · 33.20.Fb · 61.43.Fs · 68.37.Hk · 91.65.An

1 Introduction

1.1 The wall paintings

The central church of the Christ *Antiphonitis* monastery in the district of Kyrenia Cyprus is decorated with wall paintings that date from the last decades of the fifteenth century [1]. Ten fragments from two large and elaborate scenes, the *Last Judgement* and the *Root of Jesse*, now exhibited in the halls of the Archbishop Makarios Foundation at Nicosia, were subject to examination. In the mid 1970s, these scenes were severed by means of a mechanic saw in order to be sold to private collectors in Germany. Thirty-two of the *Antiphonitis* fragments were returned to Cyprus in 1997 [2, 3].

Investigations into the painting technique were carried out with optical microscopy (OM), scanning electron microscopy (SEM/EDS), and micro-Raman and FTIR spectroscopy. Calcite, carbon black, yellow ochre, red ochre, green earth, cinnabar, red lead (minium) and smalt were identified in the painting of both scenes. It was further ascertained that the *Antiphonitis* painters employed a fresco-secco technique combining limewater and protein as binders [2]. In their current state of preservation the fragments were found to have been subjected to several degradation phenomena such as (i) smalt discolouration and loss; and (ii) transformation of orange red lead (Pb_3O_4) to black plattnerite (PbO_2). The purpose of this study is to investigate the causes and processes of smalt discolouration and red lead degradation, as well as their effect on the *Antiphonitis* fragments.

1.2 Smalt

Artificial in nature, smalt is a potash silicate. Its blue colour is the consequence of adding small amounts of cobalt (in the form of cobalt oxide) during manufacture. The use of smalt in painting dates from between the mid fourteenth and early nineteenth centuries. While cobalt ores were used for colouring glass in Egyptian and classical times [4–6], the earliest attested use of smalt as a blue pigment in the early

---

Sister Daniilia (✉) · E. Minopoulou
Ormylia Art Diagnosis Centre, Sacred Convent
of the Annunciation, 63071 Ormylia, Chalkidiki, Greece
e-mail: ormylia@artdiagnosis.gr
Fax: +30-23710-98402

post-Byzantine period, shortly after the fall of Constantinople, is in the *Antiphonitis* wall paintings.

Smalt is known to fade in paintings, but the degree to which this occurs varies even within the same painting. The reason for the fading has only quite recently become understood. The original assumption was that the fading resulted from cobalt leaching. However, when examining the paint cross sections of five sixteenth century paintings, Boon et al. [7] found potassium concentration is to be crucial to fading. The loss of potassium from smalt in oil paint was understood to be a leaching process which lowered the basicity of the glass below a critical level for colour maintenance. The colour change of smalt was thus acknowledged to be an indicator of a change in alkalinity inside the glass. On the basis of semi-quantitative SEM-EDX data, where the ratio of potassium to cobalt was 1:1 or higher, the colour did not fade. Potassium is strongly alkaline, so it was sug-

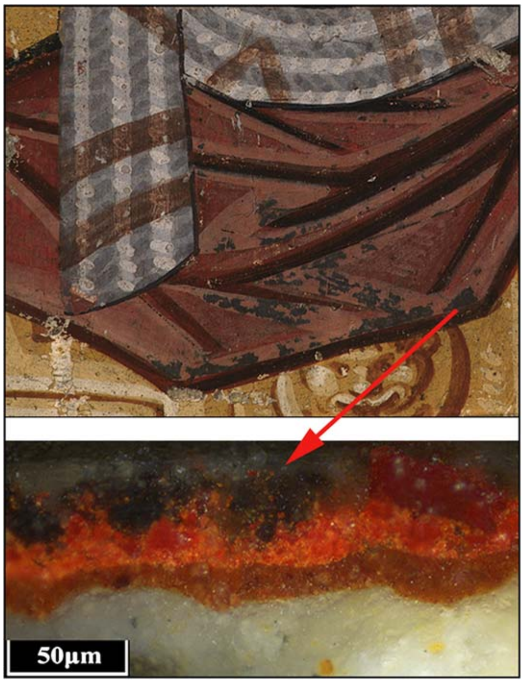


Fig. 1 Minium alteration detected on red garment (Protaton wall paintings) [13]

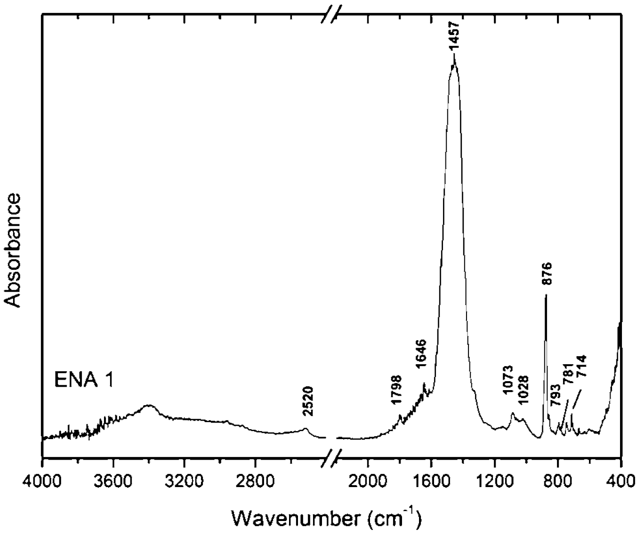


Fig. 4 FTIR spectrum of ENA1

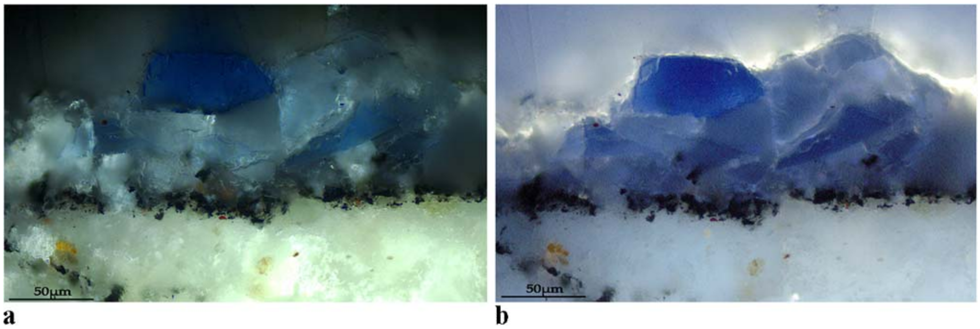


Fig. 2 Cross section in white reflected and under UV light of the gray-blue background (ENA1, *Judgement*)

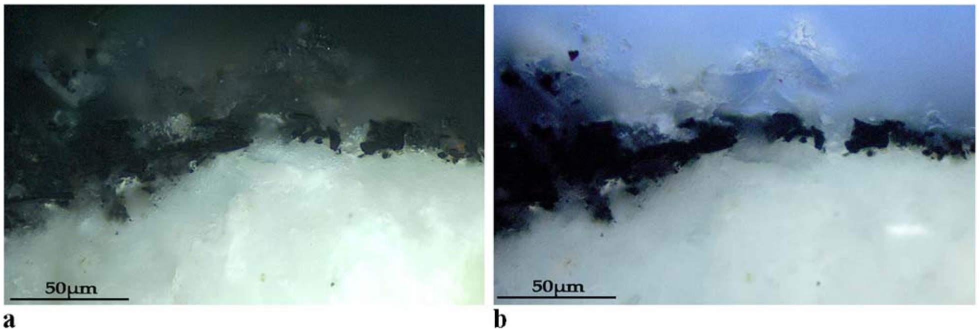


Fig. 3 Cross section in white reflected and under UV light of the gray background (ENA15, *Jesse*)

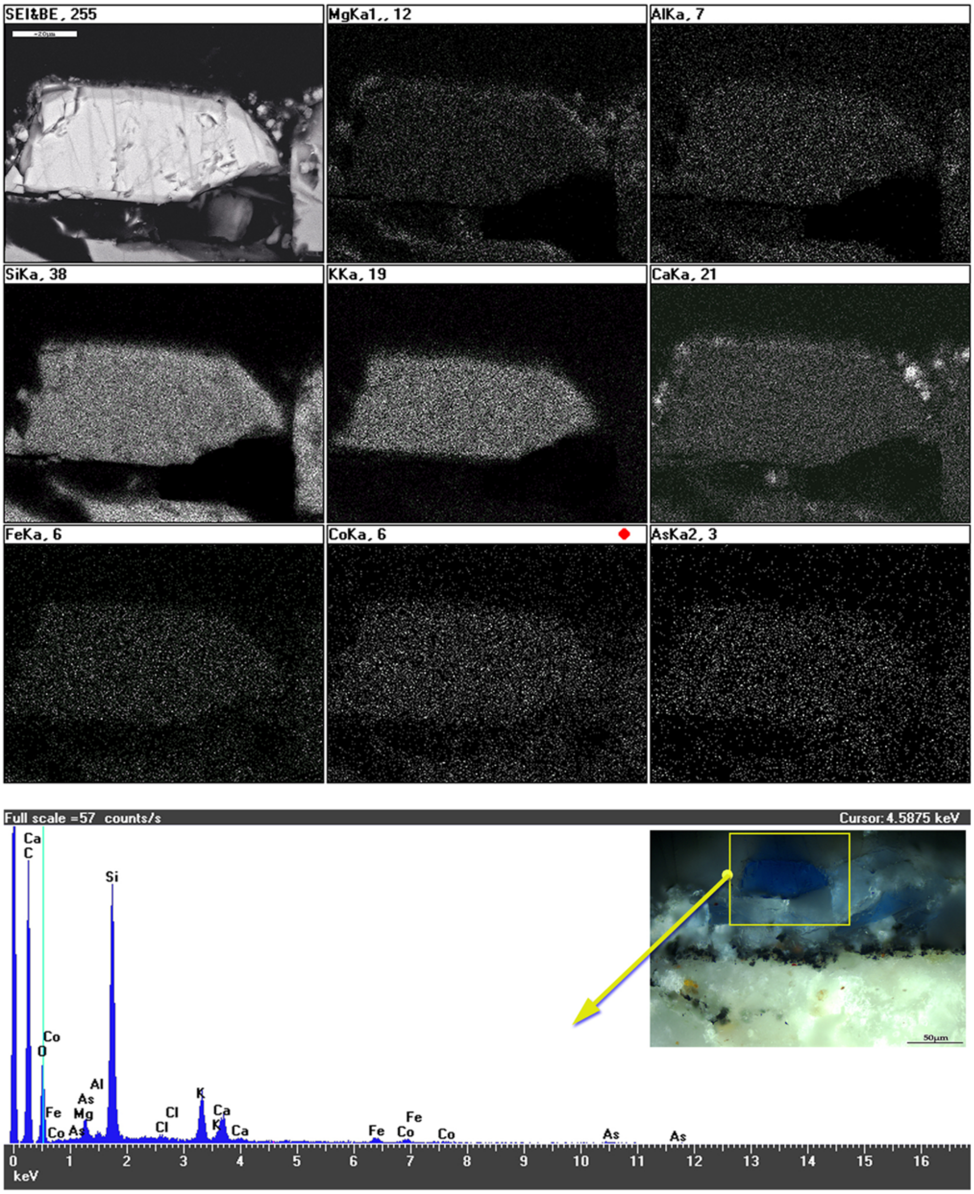


Fig. 5 BSE image of a smalt particle (ENA1, *Judgement*), X-ray maps, and the corresponding SEM spectrum with the cross section in reflected light

gested that a certain level of alkalinity is required to maintain smalt's blue colour. Azò et al. [8] investigated the state of conservation of smalt in two of Ciro Ferri's mural paintings with SEM-EDS. The pale blue colour of smalt, observed on the painting surface, was attributed to the presence of discoloured smalt grains. The decreased percentage of potassium and the contemporary increased percentage of calcium were strongly related to the discolouration of the smalt. SEM-EDS analysis excluded the migration of cobalt from the inside to the outside of the smalt grains.

Santopadre and Verita [9] noted that the alkali leaching process was the primary cause of smalt deterioration in two sixteenth century wall paintings in Rome by comparing SEM, optical microscopy and chemical analyses. They attributed the partial loss of colour in severely leached particles to three phenomena: (i) the formation of a network of cracks in the weathered layers (crizzling), leading to a diffuse reflection of incident light; (ii) a slight leaching of cobalt ions; and (iii) the lower extinction coefficient expected for Co^{2+} ions in dealkalized leached layers (acidic glass) compared with that in intact alkaline glass.

1.3 Red lead

Red lead, (also called minium), a lead-based bright orange pigment, has been known since antiquity [10]. It was used widely in medieval manuscripts and has been identified on wall paintings, polychrome sculpture and panel paintings [4, 11].

This pigment has the tendency to darken in water colour and wall paintings. Gettens and Stout [4] suggested the for-

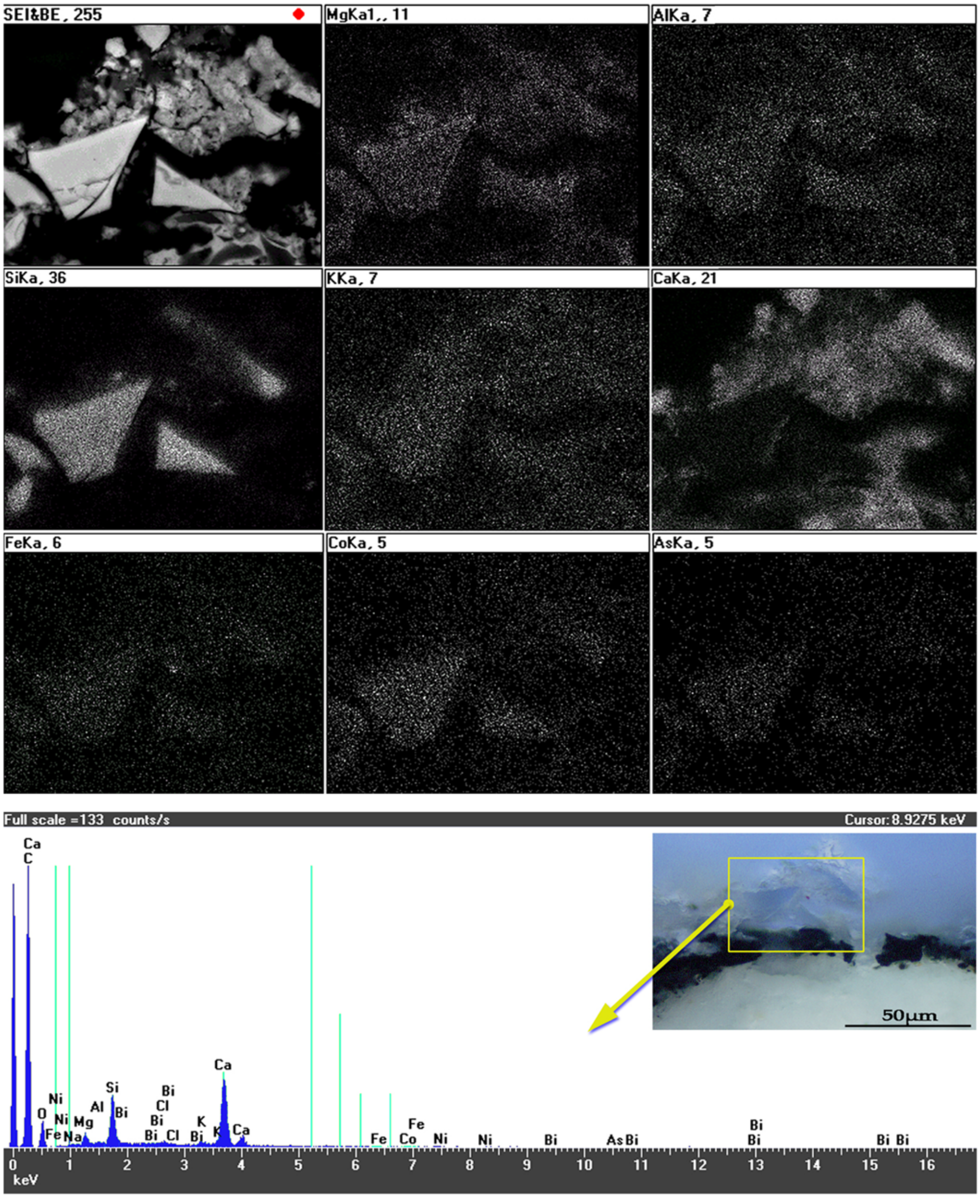


Fig. 6 BSE image of few smalt particles (ENA15, *JesseI*), X-ray maps, and the corresponding SEM spectrum with the cross section under UV light

mation of lead dioxide as a cause for this darkening. The darkening of lead tetroxide, however, may not be a simple matter of alteration to plattnerite. Moreover, exposure to light, rain and atmospheric carbon dioxide can lead to the formation of the basic lead carbonate (lead white), which gives a chalky surface. Minium is liable to discolour in the presence of hydrogen sulphide or reacts when mixed with sulphide containing pigments leading to the formation of black lead sulphide [10].

Burgio et al. [12] employed Raman microscopy in order to investigate pigment degradation in one Javanese and four Thai manuscripts. They surmised that the darkening of red entailing the formation of the black compound lead(II) sulphide was due to sulphur containing atmospheric pollutants. Eremin et al. [13] discovered darkened areas of red lead on a sixteenth century illustrated Japanese manuscript. The analyzed samples consisted of mixtures of the dark alteration product, secondary alteration products and primary red lead, with the last dominating. The only phases detected by Raman, FTIR or X-ray diffraction in the darkened samples were lead(II,IV) oxide and lead sulphate. The latter, a white phase, was thought to represent a further alteration product, either the oxidation of lead(II) sulphide or the alteration of lead(IV) oxide due to the sulphur species (presumably hydrogen sulphide). Scanning electron microscopy exhibited lead, sulphur and oxygen but could not identify the specific phases.

Daniilia et al. [14] detected minium alteration in Byzantine wall paintings of the Protaton, Mount Athos, by means of Raman spectroscopy. The chemical transformation of red lead to plattnerite, caused by the effects of light and humidity, resulted in grey spots on the Protaton's wall paintings (Fig. 1). The phenomenon of red lead pigment fading was also investigated by Aze et al. [15] through the study of an experimental fresco painting. Chemical modifications of the pigment induced fading and darkening phenomena after a 25-year natural ageing period. The alteration phases were studied by means of complementary micro-analysis techniques. Focused X-ray diffraction patterns revealed the transformation of red lead pigment into both cerussite (lead carbonate) and anglesite (lead sulphate). The distribution of Pb, S, O and Ca elements within the cross section was established using electron micro-probe analysis and correlated to micro-Raman semi-quantitative mappings of minium (Pb_3O_4), cerussite ($PbCO_3$), anglesite ($PbSO_4$) and calcite ($CaCO_3$) phases. The micro-structural characteristics of each lead containing phase were investigated by means of scanning electron microscopy observations of the sample cross section using backscattered electron imaging. The major role of atmospheric pollutants (SO_2, CO_2), together with water condensation on this kind of red pigment fading was emphasised.

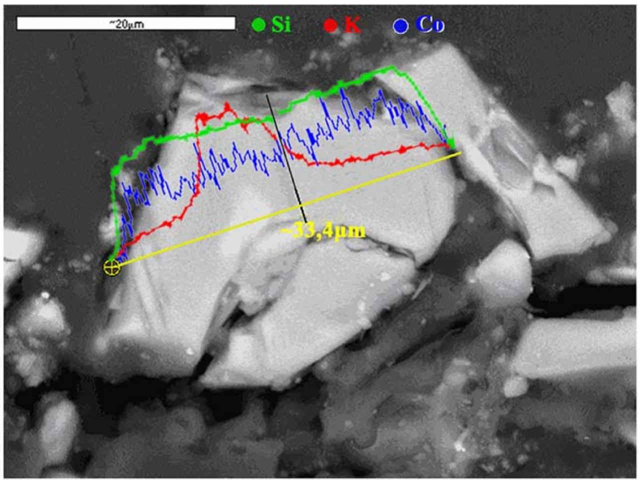


Fig. 7 BSE image of a weathered smalt grain (ENA1, *Judgement*) with line scan of Si, K and Co

2 Experimental

2.1 Samples

Four microsamples from the *Antiphonitis* wall paintings were analyzed for the investigation of smalt and minium degradation phenomena (Table 1). Two samples (ENA1, 4) were selected from the *Last Judgement* (henceforth, *Judgement*) and two (ENA13, 15) from the *Root of Jesse* (henceforth, *Jesse*).

2.2 Methodology

2.2.1 Optical microscopy

Samples were mounted in polyester transparent resin and the cross sections were ground and polished using a Struers Planopol-V machine. A Zeiss Axiotech 100 HD polarizing microscope, equipped with white reflected and ultraviolet

Table 1 Sample description

Sample	Scene	Description
ENA1	*Judgement*	Three martyrs: grey-blue background
ENA4		Three martyrs: light in red tunic of first martyr
ENA13	*Jesse*	King David: grey light in pink royal garment
ENA15		King David: grey background

Fig. 8 Cross section of the dark gray light in bearded Saint's tunic (ENA4, *Judgement*)

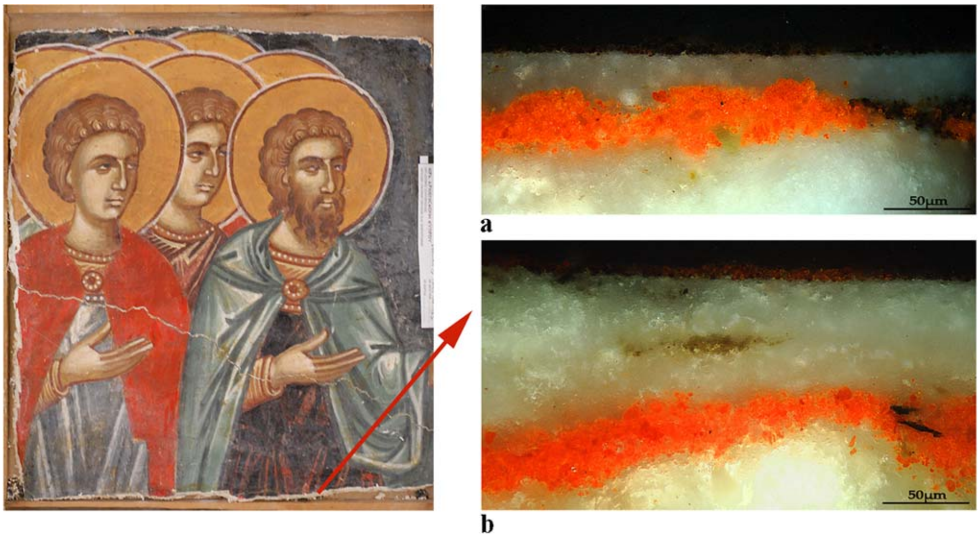


Fig. 9 Cross section of the dark gray light in King David's garment (ENA13, *Jesse*)

light as well as with a SPOT 2 1.4 digital cooled camera, was employed for observation and photography of the cross sections.

2.2.2 *μRaman spectroscopy*

Raman spectrum acquisition was achieved using a Renishaw System 1000 micro-Raman spectrometer comprising an Olympus BH-2 imaging microscope, a grating monochromator and a charged-coupled device (CCD) Peltier-cooled detector. A HeNe laser (632.8 nm) served as the excitation source and the beam emitted was focused using a 50× microscope objective. Low laser power (up to 2 mW) was used for spectra accumulation. A set of two notch filters with a cut-off edge of $\sim +100\ \text{cm}^{-1}$ was employed for the rejection of Rayleigh scattered light. The resolution was kept at $\sim 5\ \text{cm}^{-1}$.

2.2.3 *FTIR spectroscopy*

A Biorad FTS 175 FTIR spectrophotometer was employed for material identification. The free samples were ground finely with anhydrous potassium bromide and then pressed into pellets. The spectra were collected in absorbance mode at $4\ \text{cm}^{-1}$ resolution, representing averages of 64 scans.

2.2.4 *Scanning electron microscopy (SEM/EDS)*

Scanning electron microscopy (SEM) was carried out using a JEOL 6300 scanning electron microscope equipped with an energy dispersive X-ray (EDS) ISIS 2000 microanalytical system. An acceleration voltage of 20 kV was used and the probe current was 1000 pA. The elemental composition was determined using the prepared carbon coated cross sections, which were bombarded by a strongly accelerated and focalised electron beam in a vacuum (10^{-5} torr).

3 Results and discussion

3.1 Smalt discolouration and loss

Widespread loss of smalt together with pigment fading has been detected in the background of the *Antiphonitis* wall paintings. At present, the gray underpaint in the background of the wall paintings is preserved, whereas the upper blue layer of smalt is almost totally lost. Initially, this finding was ascertained by close observation of the paint surface and examination of the corresponding cross sections.

The optical microscopic examination of sample ENA1 taken from the background of *Judgement* revealed a blue layer 50–80 μm thick applied over a thin layer of carbon black (Fig. 2). In the cross section, both deep blue and almost colourless particles of smalt were observed, with irregular, sharp edges. The grains were most clearly recorded under UV light, allowing for the mapping of their distribution throughout the paint layer. In sample ENA15 taken from the background *of Jesse*, only a single thin layer of carbon black could be discerned (Fig. 3). A few small, colourless grains of smalt, were detected in the cross section under UV light.

Blue pigment was initially identified with FTIR spectroscopy through the Si–O absorption peaks at 1073 (Si–O stretching) and at $781\ \text{cm}^{-1}$ (Si–O bending) (Fig. 4) [16]. In the same spectrum (ENA1), the characteristic amide I mode of protein gave a weak peak at $1646\ \text{cm}^{-1}$. Calcite peaks were also recorded (2520, 1798, 1457, 876 and $714\ \text{cm}^{-1}$), while the weak aluminosilicate bands detected at 1028 and $793\ \text{cm}^{-1}$ could be attributed to yellow ochre, grains of which could be traced in the plaster (Fig. 2a). FTIR in combination with SEM/EDS analysis have demonstrated the ap-

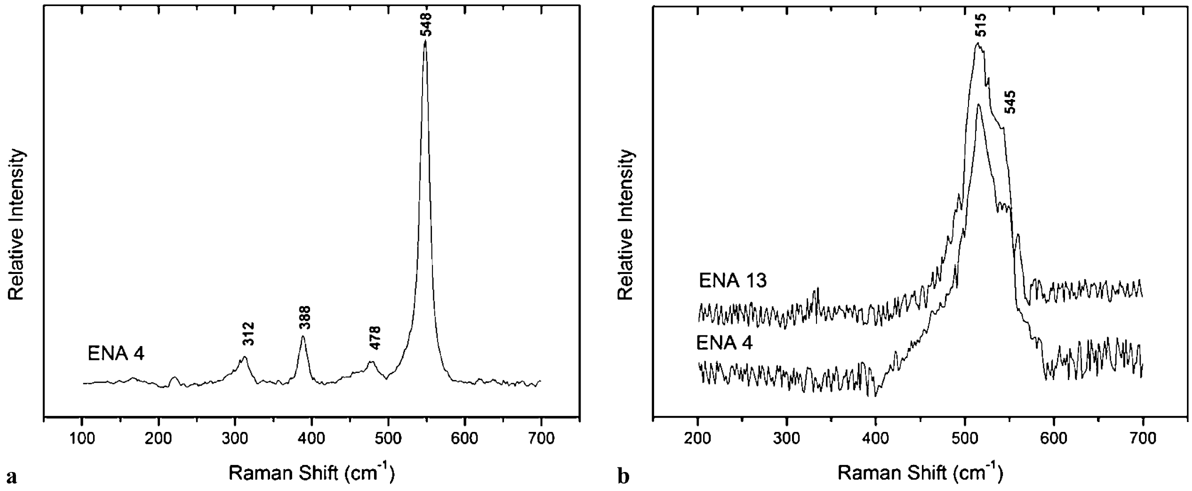
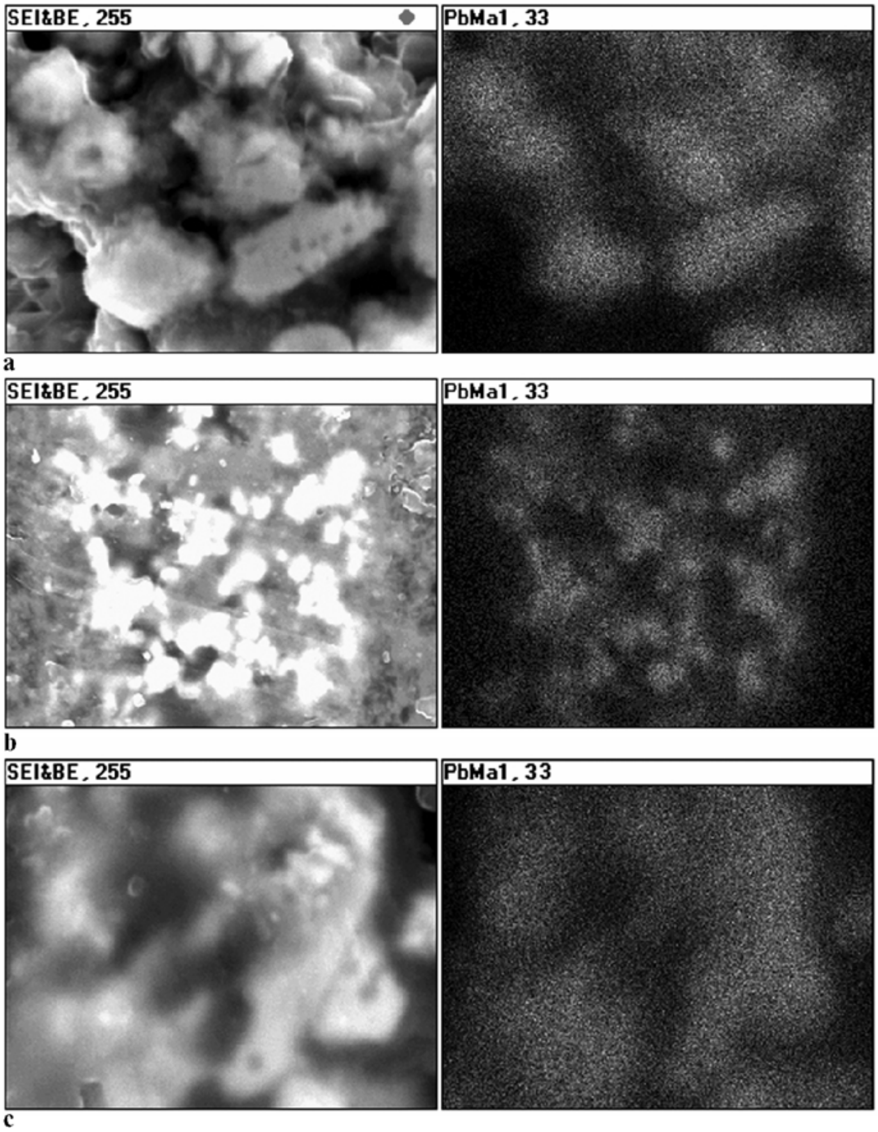


Fig. 10 Raman spectra from (**a**) unaltered minium (underpaint layer, Fig. 8); (**b**) altered minium (superficial layers, Figs. 8a, 9)

Fig. 11 BSE images and X-ray maps for Pb in the cross section of ENA4 (Fig. 8a) in areas of (**a**) the orange layer with unaltered minium; (**b**) the far right edge of the same layer with partially altered minium; and (**c**) the superficial black layer with totally altered minium



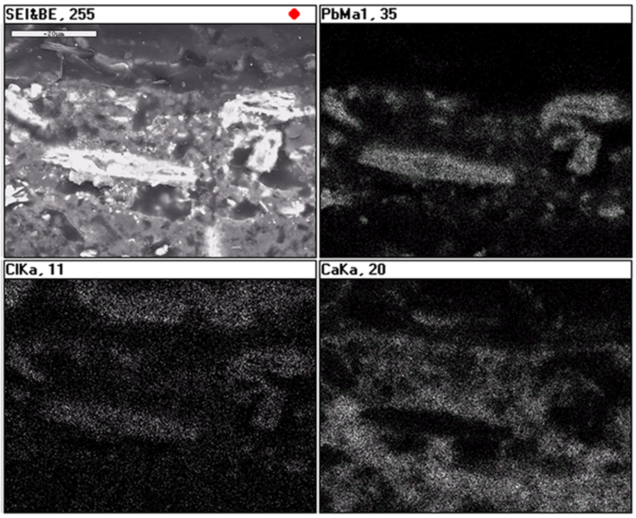


Fig. 12 BSE image and X-ray maps for Pb, Cl and Ca in the superficial paint layer of the cross section of ENA13 (Fig. 9) containing totally alterated minium

plication of a *fresco-secco* technique using limewater and protein as binders (Daniilia et al. [2, 18]).

The study and interpretation of smalt discolouration was carried out by SEM/EDS analysis on two cross sections. In the EDS spectra, the peaks of Si, K and Co, the main elements of smalt, as well as Mg, Al, Ca, Fe, and As were recorded (Figs. 5, 6). Elements such as Fe and As indicate the origin of cobalt oxide from the mineral cobaltite (Co,Fe)AsS, given the fact that there is no evidence of Ni (an element contained in the mineral smaltite [Co,Ni]As_{3-2}) in the EDS spectrum [5]. According to scholarly opinion the composition of smalt varies considerably in SiO_2 (65–71%, 66–72%), K_2O (16–21%, 10–21%), CoO (6–7%, 2–18%) and in impurities of other oxides (Al_2O_3, BaO, Bi_2O_3, CaO, CuO, Fe_2O_3, MgO, MnO, NiO, Na_2O). The presence of bismuth oxide in some of the grains analysed from the *Antiphonitis* wall paintings indicates the use of two types of smalt (Tables 2, 3).

SEM micrographs and X-ray maps of smalt particles in ENA1 and ENA15 (Figs. 5, 6) revealed several degrees of deterioration. Most pigment particles had suffered partial or even complete discolouration, whereas only few of them appeared intact. The percentage of potassium oxide, ranging from 12.8 to 17.3% (ENA1) and from 9.1 to 13.9% (ENA15) in intact areas decreased significantly in deteriorated areas (1.8–6.2% in ENA1 and 0.7–2.9% in ENA15), thereby signifying alkali leaching in weathered smalt particles (Tables 2, 3). As determined from X-ray maps, potassium depletion occurred in the boarders of discoloured smalt grains. In some cases depletion progressed to the core of the particles. The line scan of Si, K and Co in a smalt particle of ENA1 (Fig. 7) also confirmed the presence of K in the core of a weathered particle.

As to the detachment of smalt grains from the painting, it may be attributed: (i) to accidental removal during the several rescue interventions undertaken for the purposes of conservation, (ii) to a weakening of the binding power of the medium (protein)—this undergoes oxidative, chemical, photochemical and biochemical processes from environment, humidity, illumination and micro-organisms [17]. An analogous case has been reported in another post-Byzantine monument at Meteora, Greece, where smalt loss was also detected [18].

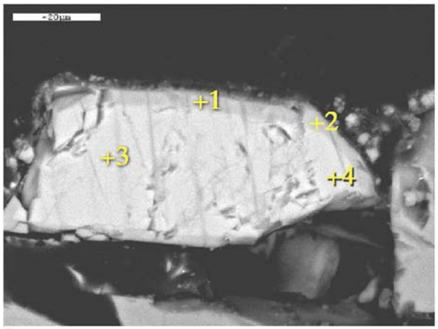
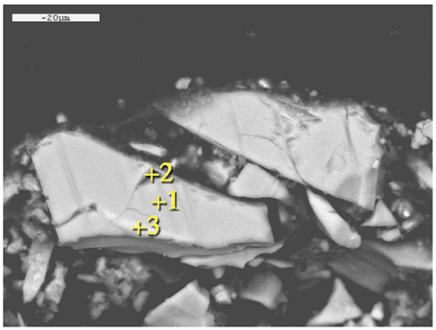
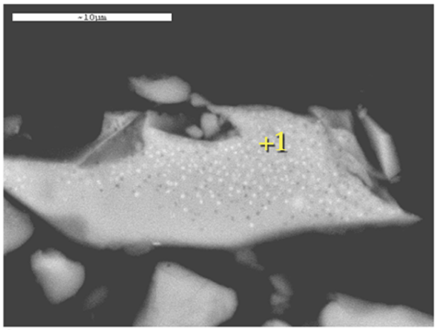
3.2 Red lead discolouration

In the current preservation state of the *Antiphonitis* wall paintings, the lights (luminous areas of the icons rendered in one, two or three colour shades) of certain red garments have acquired a dark gray hue (Figs. 8, 9), similar to what has been reported in Byzantine wall paintings [11, 13], where colour alterations of this kind where detected in a few dispersed areas. In the *Antiphonitis* fragments, however, the alteration is widespread.

The examination of characteristic cross sections from the lights of red and pink garments (ENA4, *Judgement*; ENA13, *Jesse*) revealed the presence of a superficial layer. Here pigment grains are black (Figs. 8a, 9), though some have taken on a brownish hue (Fig. 8b). Of note is the fact that in ENA4 (Fig. 8), taken from the edge of the fragment, an orange underpaint is preserved almost intact, whereas some grains in the right edge of the same layer have undergone alteration. This phenomenon is assumed to have occurred during the last thirty years after the last restoration treatment in 1973 [2]. When the fragment was detached from the wall painting, the edge of the underpaint layer became directly exposed to adverse environmental conditions.

Micro-Raman spectroscopy was employed to identify the pigment. In the spectrum—from unweathered grain from the underpaint (Fig. 10a)—characteristic Pb–O modes of minium were recorded at 312, 388, 478 and 548 cm^{-1} [19]. In the spectra from the black grains of the alterated pigment (ENA4, Judgement; ENA13, Jesse) the peak at 515 cm^{-1} underlined the presence of plattnerite (Fig. 10b) [13]. The shoulder at 543 cm^{-1} was attributed to the remaining red lead [20]. This transformation of red lead into plattnerite corresponds to the oxidation of lead(II) atoms originating from lead tetroxide Pb_3O_4—given also

Table 2 BSE images and chemical composition (wt% of the oxides) of a grain of smalt (**a**) partially leached; (**b**) almost leached and corroded; and (**c**) totally leached (ENA1, *Judgement*)

BSE image	Point	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	As_2O_3	Bi_2O_3
 **a**	1 leached	1.2	0.42	76.6	6.2	5.5	2.8	2.6	4.8	
	2 leached	1.2	0.38	76.3	5.8	5.0	3.5	2.6	5.4	
	3 intact	0.60	0.14	67.4	17.1	4.5	3.3	2.3	4.7	
	4 intact	0.97	0.25	66.9	17.3	4.7	3.1	2.4	4.4	
 **b**	1 leached	0.90	0.62	80.7	1.9	5.3	2.5	2.8	2.7	2.6
	2 corroded	1.5	0.25	78.5	2.4	6.4	2.8	3.7	1.9	2.6
	3 intact	1.1	0.26	70.1	12.8	5.2	2.3	3.0	2.6	2.6
 **c**	1 leached	1.1		74.7	1.8	3.5	1.8	4.2	8.6	4.3

as $Pb(^{II})_2(Pb(^{IV})O_4$—to the (IV) valence state [21] and may result from exposure to light, microbiological activity, or the presence of water or carbon dioxide [10, 22]. It should be noted that in the Raman spectra of the alterated pigment acquired from King David's mantle (ENA13), only the plattnerite peak at 515 cm^{-1} was recorded (Fig. 10b).

The micro-structural characteristics of each lead containing phase were investigated by means of scanning electron microscopy. Using backscattered electron imaging the distribution of the elements within the lead containing paint was examined (Figs. 11, 12).

In the BSE images and the X-ray maps of Pb in the cross section of ENA4 the dissolution of pigment crystals could be observed in the alterated state (Fig. 11b, c). It is also noteworthy that in the superficial paint layer of ENA13 (Fig. 12), consisting of totally alterated minium mixed with cinnabar and calcium carbonate, Cl^- anion was also detected. Its % abundance was particularly high in the surface of the sample (Table 4, point 2), whereas its presence on grains of alterated minium (Table 4, point 1) may indicate a possible effect on red lead transformation. The monument's location near the sea justifies the presence of these ions.

Table 3 BSE images and chemical composition (wt% of the oxides) of (**a**) two totally leached and corroded grains of smalt; (**b**) a totally leached grain of smalt; and (**c**) an almost intact grain of smalt (ENA15, *Jesse*)

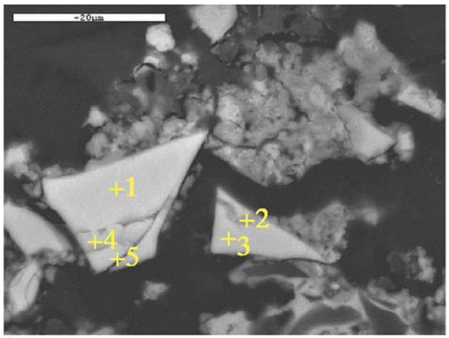
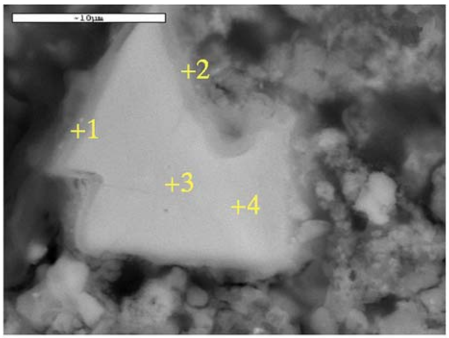
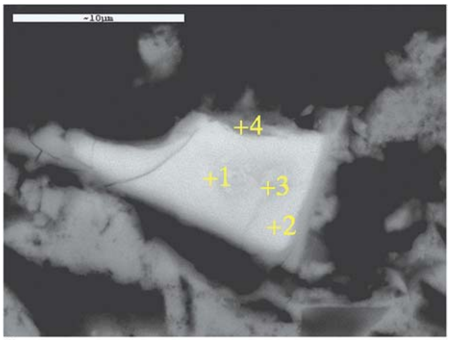
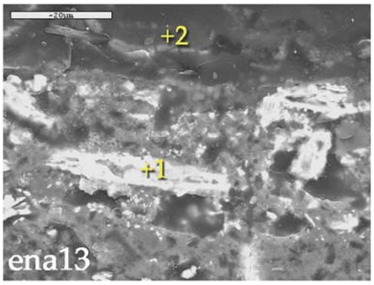
BSE image	Point	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	As_2O_3	Bi_2O_3
 **a**	1 leached	0.26	1.1	0.36	75.3	2.3	4.6	2.5	4.6	6.7	2.3
	2 corroded	0.17	0.43	0.28	81.1	1.0	4.3	2.0	2.9	4.5	3.3
	3 leached	0.38	1.4		80.1	1.0	5.6	2.0	3.7	3.1	2.8
	4 leached		1.6	0.97	73. 9	2.2	5.9	2.6	3.9	6.4	1.9
	5 corroded	0.17	3.6	2.0	65.8	2.9	14.8	1.2	2.7	8.2	
 **b**	1 leached	0.07	7.4	0.28	69.3	0.7	8.7	4.4	5.4	3.9	
	2 leached	1.2	9.8		73.4	0.7	5.4	2.6	3.3	4.1	
	3 leached	1.1	1.1		78.9	1.4	5.5	2.5	4.0	5.6	
	4 leached	1.3	1.3		80.1	1.1	5.2	2.2	3.6	5.6	
 **c**	1 intact	1.7	1.3	0.58	66.8	13.3	4.6	3.0	4.0	4.6	
	2 intact	2.3	3.0	0.74	64.1	11.9	5.9	2.8	4.5	4.7	
	3 intact	1.9	1.3	0.60	64.3	13.9	4.4	2.5	4.5	5.2	
	4 intact	1.4	2.7	0.67	65.4	9.1	8.0	2.1	4.1	5.9	

Table 4 Elemental analysis of ENA4 (*Judgement*) and ENA13 (*Jesse*)

BSE image	Point	Mg	Cl	Ca	Pb	Hg
	1	0.62	2.3	3.9	87.8	5.3
	2	3.7	43.0	40.3	2.9	6.2

4 Conclusions

The study of the *Antiphonitis* fragments has revealed (a) extensive loss and discolouration of smalt in the background of the wall paintings, and (b) blackening of the orange minium grains in the red and pink garments. Combining optical and scanning electron microscopy with Raman spectroscopy, the deterioration mechanisms of smalt and minium as well as their present state of preservation were thoroughly investigated.

These phenomena of pigment alteration and loss underline the unsuitability of smalt and minium on wall paintings, regardless of the painting technique (*fresco, fresco-secco, secco*). The irreversible alterations have significantly affected the aesthetic outcome of the wall paintings and unfavorable environmental conditions of preservation have been decisive for pigment chemical alterations. Smalt discolouration has advanced to a great extent and is almost entire. The effect of chlorine salts on the darkening of minium requires further investigation.

The above statements disclose the need for immediate preservation of the detached fragments and development of a conservation strategy that will prevent further pigment deterioration. It is therefore necessary to pay due attention to these unique artworks of the world's cultural heritage.

Acknowledgements Support by the European Commission through the European project INCO-CT-2005-015338 INFRARTSONIC (www.infrartsonic.org) is gratefully acknowledged.

References

1. A. Stylianou, J. Stylianou, *The Painted Churches of Cyprus* (Trigraph, London, 1985)
2. Sr. Daniilia, E. Minopoulou, Fr.D. Demosthenous, G. Karagiannis, J. Archaeol. Sci. **35**, 1695 (2008)
3. A. Papageorgiou, The church of Christ Antiphonetes in the village of Kalograia, Kyrenia. Committee for the Protection of the Cultural Heritage of Cyprus (1999), pp. 180–213
4. J. Gettens, G.L. Stout, *Painting Materials—a Short Encyclopaedia* (Dover, New York, 1966)
5. B. Muhlethaler, J. Thissen, *Artists' Pigments*, vol. 2 (Oxford University Press, New York, 1993), pp. 113–130
6. M. Richter, *Historical Polychromy, Polychrome Sculpture in Germany and Japan* (Hirmer, Munich, 2004), pp. 175–203
7. J.J. Boon, K. Keune, J. Van Der Weerd, M. Geldof, J.R.J. Van Asperen De Boer, Chimia **55**, 952 (2001)
8. D. Ajò, U. Casellato, E. Fiorin, P.A. Vigato, J. Cult. Herit. **5**, 333 (2004)
9. P. Santopadre, M. Verità, Stud. Conserv. **51**, 29 (2006)
10. E.W. Fitzhugh, *Artists' Pigments*, vol. 1 (National Gallery of Art, Washington, 1986), pp. 109–139
11. S. Sotiropoulou, Sr. Daniilia, C. Miliani, F. Rosi, L. Cartechini, D. Papanikola-Bakirtzis, Appl. Phys. A, Mater. **92**, 143 (2008)
12. L. Burgio, R.J.H. Clark, P.J. Gibbs, J. Raman Spectrosc. **30**, 181 (1999)
13. K. Eremin, J. Stenger, M. Li Green, J. Raman Spectrosc. **37**, 1119 (2006)
14. Sr. Daniilia, S. Sotiropoulou, D. Bikiaris, Y. Chryssoulakis, C. Salpistis, G. Karagiannis, B.A. Price, J.H. Carlson, J. Cult. Herit. **1**, 91 (2000)
15. S. Aze, J.M. Vallet, A. Baronnet, O. Grauby, Eur. J. Mineral. **18**, 835 (2006)
16. V. Ganitis, E. Pavlidou, F. Zorba, K.M. Paraskevopoulos, D. Bikiaris, J. Cult. Herit. **5**, 349 (2004)
17. F. Ospitali, A. Rattazzi, M.P. Colombini, A. Andreotti, G. Di Lonardo, J. Cult. Herit. **8**, 323 (2007)
18. Sr. Daniilia, E. Minopoulou, K.S. Andrikopoulos, A. Tsakalof, K. Bairachtari, J. Archaeol. Sci. **35**, 2474 (2008)
19. D.C. Smith, A. Barbet, J. Raman Spectrosc. **30**, 319 (1999)
20. L. Burgio, R.J.H. Clark, S. Firth, Analyst **126**, 222 (2001)
21. H.J. Terpstra, R.A. De Groot, C. Haas, J. Phys. Chem. Solids **58**, 561 (1997)
22. Y.P. Petushkova, N.N. Lyalikona, Stud. Conserv. **31**, 65 (1986)