

**ARAGONITE IN ROMAN WALL PAINTINGS OF THE VIII<sup>a</sup> REGIO, AEMILIA, AND X<sup>a</sup> REGIO, VENETIA ET HISTRIA**

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*Summary* - In the Roman wall paintings different white colours were used, named *Paraetonium*, *Melinum*, *Anularia*, *Eretria*, *Argentaria*, etc. FTIR, Raman spectroscopy and X-Ray diffraction were applied to study different white pigments, such as calcite, aragonite, dolomite and huntite, white carbonates present in archaeological findings from roman walls in the Mediterranean region. This study showed that it is possible to distinguish and identify these components in white colours. About 450 samples of Roman wall paintings were analysed and it was observed that often aragonite is associated to precious coloured pigments. On the basis of the obtained results some considerations about the period in which the different kinds of white pigments were used are proposed.

**INTRODUCTION**

One of the main questions concerning ancient paintings is the definition of the nature of the pigments used. The stylistic study of the pictorial pattern of a painting can give information about the artistic quality of the piecework and its execution period, while the analysis of the materials used constitutes the fundamentals of the study and the essential condition for its conservation.

The chemical and mineralogical analyses can give useful information for the definition of the palette of colours available in the region and in the period in which the paint was done, and can define the social-economical situation of the client of the painting. Moreover, the analysis of the pigments can contribute to the knowledge of the techniques used in the preparation of the paints and on its application modes, to their origin, to the commercial exchanges and to the cultural influences among different regions.

In the Roman texts by Vitruvius (*De Architectura*)<sup>1</sup> and Pliny the Elder (*Historia Naturalis*)<sup>2</sup>, there are some uncertainties about the names used to define some pigments and the characteristics of the components of the colours. Some definitions are suggested by modern researchers, such as Augusti<sup>3</sup>, Giovanoli<sup>4</sup>, Frizot<sup>5</sup>, Delamare<sup>6</sup>, Barbet<sup>7,8</sup>, Guineau<sup>9</sup>, Béarat<sup>10-12</sup>, Blauer-Bohm<sup>13</sup>, Osborne<sup>14</sup>, Damiani<sup>15</sup> and Edreira<sup>16</sup>. Vitruvius and Pliny mentioned white pigments with several different names, such as *Paraetonium*, *Melinum*, *Cerussa*, *Eretria*, *Selinusia*, *Argentaria*, etc.

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Some authors consider satisfactory to define the white pigments as calcite, without other details, notwithstanding different roman names could suggest the correspondence to different nature, quality and price.

From chemical and mineralogical point of view, a white line or band, present in a fragment of roman wall painting, could be constituted by calcite ( $\text{CaCO}_3$ , trigonal), by aragonite ( $\text{CaCO}_3$ , rhombic), by dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) or, less often, by huntite ( $\text{CaMg}_3(\text{CO}_3)_4$ ). Such line or band could, however, be done also with cerussite (lead basic carbonate,  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) or with gypsum (calcium sulphate hydrate,  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ).

This paper presents the results of the analysis carried out on about 450 wall painting samples coming from different sites from northern Italy, in the regions corresponding to the *VIII<sup>a</sup> Regio* (*Aemilia*) and *X<sup>a</sup> Regio* (*Venetia et Histria*) of the Roman Empire. Most of the samples come from infill gullets. The study here presented aims to the experimental identification and differentiation between calcite, aragonite, dolomite and huntite. Particular attention was given to define the presence or not of aragonite as component of the white colour, in order to verify if there is a correlation between this pigment and period of execution, geographical context, type and quality of the painting.

The main analytical techniques used were infra-red spectroscopy in Fourier transform (FTIR) and Raman spectroscopy; in some cases X-ray diffraction was used. Concerning these techniques, the spectra for all the white compounds above-mentioned are known and available in specialized data base. Moreover, Scanning Electron Microscopy (SEM) was employed, as a complementary technique.

## EXPERIMENTAL

### *Samples*

The samples analysed in this work came from the Roman *VIII<sup>a</sup>* and the *X<sup>a</sup> Regio* in Italy (see Fig. 1). Concerning the *X<sup>a</sup> Regio, Venetia et Histria*, the samples were collected in the following sites: one site in Vicenza (*Vicetia* – S. Biagio)<sup>17,20</sup> two sites in Pordenone, north of *Concordia* (Torre and S. Vito), one site in Trieste (*Tergeste* – Crosada), one site in Padova (*Patavium* – Montegrotto)<sup>20</sup>; ten sites in Verona (*Verona* - Borgo Tascherio, Piazza Vescovado, S. Cosimo, Via Garibaldi, Vicolo Agnello, Via Rensi, Via Cantore, Piazza Nogara, Via Tazzoli and Sant’Alessio)<sup>21</sup>. As far as the *VIII<sup>a</sup> Regio, Aemilia* is concerned, the studied sites were: three in Parma (Church of S. Pietro Martire, Palazzo Vescovile, Palazzo San Vitale and Cassa di Risparmio), three in Reggio Emilia (*Regium* - Via Mazzini, Credito Emiliano, Le Grazie), one in Modena (*Mutina*) (Via Farini) and two in Bologna (*Bononia-Felsina*) (Via Ca’ Selvatica, Via Testoni).

Fig. 1 presents the map of the northern Italy during the Roman Empire and the cities where the samples were collected.

### *Scanning Electron Microscopy (SEM)*

SEM images were taken using a Jeol (Tokyo, Japan) JSM 5600 LV instrument. The images were obtained under low vacuum conditions, where samples did not present charging effects; in such a way it was not necessary to cover the samples with a high conductance thin film (gold or graphite films). A fragment of the sample, or a small amount (some milligrams) of painting layer scraped from the wall fragment, was put inside the special cavity of the instrument.



FIGURE 1 – Map of North Italy in the Roman period.

#### *Infrared spectroscopy (FT-IR)*

Absorption and transmittance spectra in the IR region were collected with a Perkin Elmer FTIR Spectrum One spectrometer. Thirty-two signal-averaged scans were acquired for each sample. A few milligrams of each sample were mixed with a KBr (IR grade, Merk) pellet of 12 mm diameter and pressed which 10 ton for 3 min. The resolution of this instrument is of  $2\text{ cm}^{-1}$ .

#### *Raman spectroscopy*

Raman spectra of the samples were recorded in the range of  $1100 - 100\text{ cm}^{-1}$ , in order to detect the wavenumber of some of the fundamental components of  $\text{CO}_3^{2-}$  ion and the principal reticular bands. The measurements were carried out directly on the wall fragment with a Labram microscope (Jobin Yvon.Horiba), equipped with a red Helium-Neon LASER, operating in the following conditions: *wavelength radiation of 632.8 nm*, maximum power of 5 mW, hole of 500 nm, detector CCD of  $1026 \times 256$  pixel cooled by the Peltier effect, resolution of  $2\text{ cm}^{-1}$ . The spatial resolution produced was of the order of a micron.

#### *X-Ray diffraction (XRD)*

XRD was used to identify the different crystalline phases present in the samples. A Philips PW1352 diffractometer with a incident radiation of Cu  $K\alpha$  Ni-filtered, operating with a current of 20 mA at 40 kV was used for the XRD analysis. The diffractograms were recorded by continuous scanning from an initial angle of  $5^\circ [2\theta]$  and a final angle of  $52^\circ [2\theta]$ , with sensitivity of 400 cps and scan rate of  $1^\circ\text{ min}^{-1}$ . The identification of the crystalline phases were carried out using the data base PDF (Mineral Powder Diffraction File, International Centre for Diffraction Data), where all the characteristic  $d$  values, the relative peak intensity and other specific parameters for each crystalline phase are presented.

## RESULTS AND DISCUSSION

Fig. 2 presents the SEM image (x 1000) of a wall painting sample containing aragonite, where the characteristic needle structure is evident<sup>11</sup>.

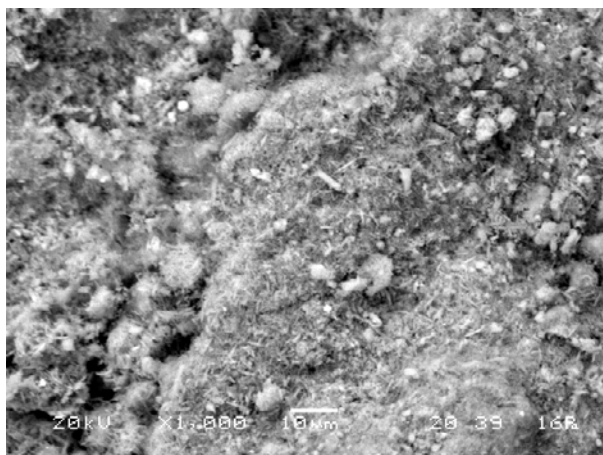


FIGURE 2 – SEM image of a white of aragonite (x 1000).

In the following, FTIR and Raman spectra of a series of four white carbonates, calcite, aragonite, dolomite and huntite, are reported as standards. These carbonates are present in archaeological findings from roman walls in the Mediterranean region. Dolomite and aragonite are found with calcite in a wide number of archaeological sites, while huntite is a white pigment found in Egyptian<sup>22</sup> and Pompeian<sup>23</sup> wall paintings.

Fig. 3 shows the FTIR spectra of the above mentioned four white carbonates. All these carbonates present bands around  $1400\text{ cm}^{-1}$  (stretching of  $\text{CO}_3^{2-}$ ) and between  $800$  and  $700\text{ cm}^{-1}$  (deformation of  $\text{CO}_3^{2-}$ ). Spectrum a) corresponds to calcite and presents the well-known components at  $1429$ ,  $875$  and  $710\text{ cm}^{-1}$ . Spectrum b), obtained for an aragonite sample from Bohemia (kindly given by the Section of Geomineralogy of the Department of Environmental

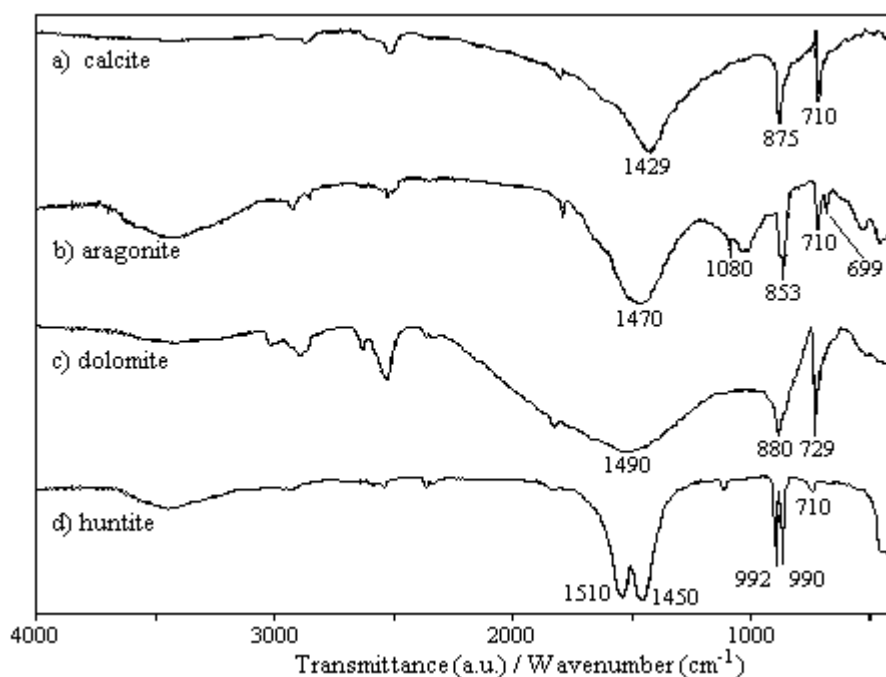


FIGURE 3 – FTIR spectra of calcite, aragonite, dolomite and huntite.

Sciences of Venice University) presents the characteristic bands of carbonate group at  $1470\text{ cm}^{-1}$ , at  $1080\text{ cm}^{-1}$  (symmetric stretching of  $\text{CO}_3^{2-}$ ) and at  $853$  and  $699\text{ cm}^{-1}$  (deformation of the planar ion  $\text{CO}_3^{2-}$ ). Spectrum c) was obtained from a mineralogical dolomite sample,  $\text{CaMg}(\text{CO}_3)_2$  and presents the deformation bands of  $\text{CO}_3^{2-}$  at  $883$  and  $728\text{ cm}^{-1}$ : these frequencies are clearly distinguishable from those of calcite and aragonite. The reported spectrum d) was obtained for a sample of huntite. Huntite presents a quite singular spectrum with two pairs of bands corresponding to anti-symmetric vibration centred around  $1480\text{ cm}^{-1}$  and around  $900\text{ cm}^{-1}$ . FTIR spectra of other white pigments, such as gypsum and cerussite (hydroxy carbonate of lead) are well known in the literature. No investigation has been performed in the FTIR far infrared range ( $< 150\text{ cm}^{-1}$ ), owing to the absence of interesting signals for the studied carbonates<sup>24</sup>.

Fig. 4 reports the Raman spectra of the same four carbonates. The analysis of this figure shows that on the basis of the frequencies and the relative intensity of the peaks, the four carbonates can be distinguished in a simple way, as well as by IR spectra. Moreover, it is possible to identify the fundamental role of the reticular bands situated at low wave numbers (lower than  $400\text{ cm}^{-1}$ ), a zone unusual for IR spectroscopy. It is worth to note that in Raman spectroscopy the bands around  $1400\text{ cm}^{-1}$  are not always observed, while in the case of aragonite the band at  $1080\text{ cm}^{-1}$  is the more intense component of the spectra; two other weaker bands are present at  $704$  and  $700\text{ cm}^{-1}$ . From the observation of figures 3 and 4, it is evident that both the techniques, FTIR and Raman spectroscopy, are suitable to distinguish among the carbonate species present in the painting.

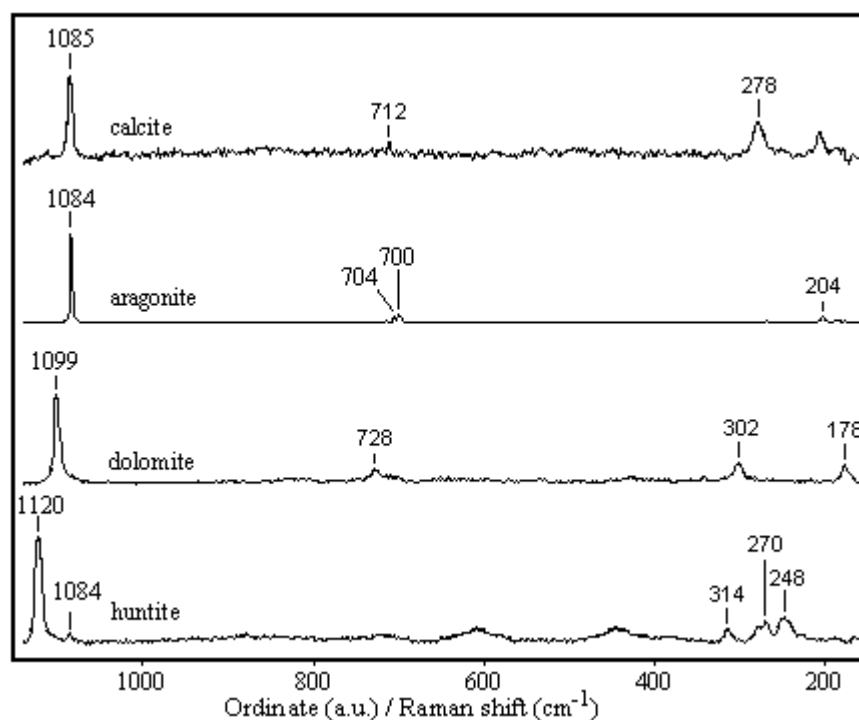


FIGURE 4 – Raman spectra of calcite, aragonite, dolomite and huntite.

It's worth to note that the utilised Raman technique is non-destructive and allows the analysis of a very small superficial area of the sample, without any pre-treatment. On the contrary, FTIR technique needs the mechanical removal of a few milligrams amount of sample to obtain the pellet to analyse; the obtained FTIR spectrum results from the averaged composition of the

removed sample, rather than from the particular composition of a very small sample area, as for the Raman spectra. The choice of the technique depends on the availability of the instruments, on the type of samples and on the experience of the researcher.

As shown in Fig. 5, the X-ray diffraction spectra obtained for the four studied carbonates are different and allow one to distinguish the components. However, this technique is time consuming, requires higher amounts of sample and is less sensitive, particularly in the analysis of a mixture of compounds.

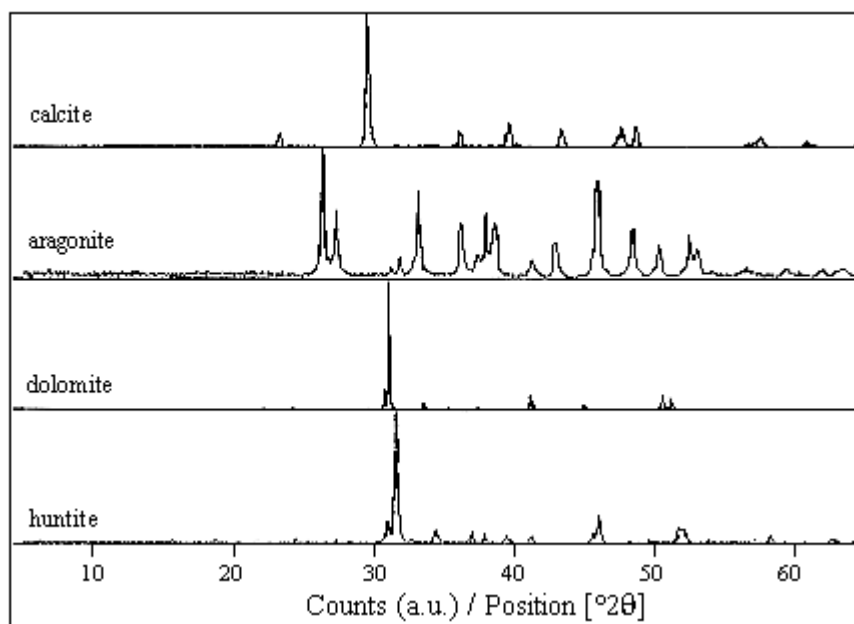


FIGURE 5 – X-Ray spectra of calcite, aragonite, dolomite and huntite.

Fig. 6 presents a FTIR spectrum of a white band present in a wall painting fragment with grey, blue and white bands, from the Vicenza site.

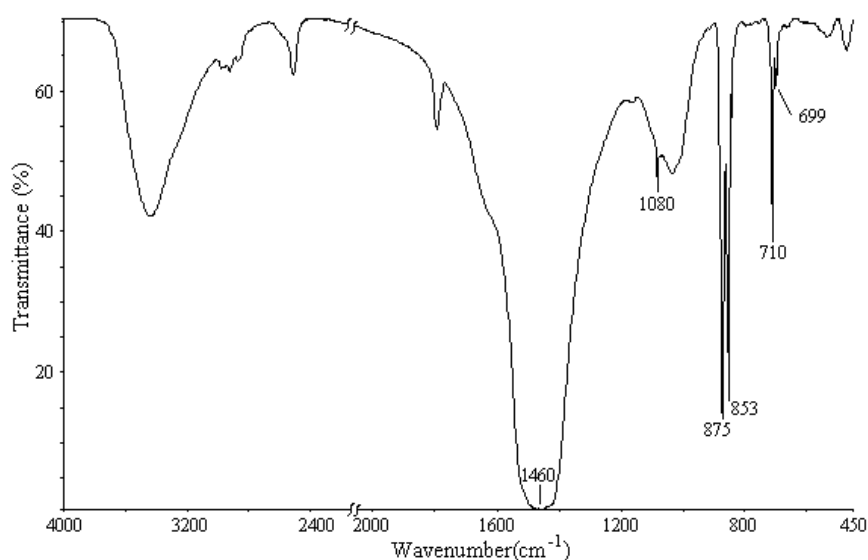


FIGURE 6 – FTIR spectrum of a white from a grey, blue and white Roman wall painting fragment from Vicenza.



In this figure it is possible to identify two bands of the same intensity at 875 and 853  $\text{cm}^{-1}$ , which can be ascribed to calcite and aragonite, respectively. The same consideration can be done for the bands at 710 and 699  $\text{cm}^{-1}$ , even if in this case they present different intensities. The large and intense band centred at 1460  $\text{cm}^{-1}$  results from superposition of the bands ascribed to aragonite and calcite.

Fig. 7 presents a FTIR spectrum of a white strip present in a wall painting fragment from a site of Verona (Piazza Vescovado). It is possible to identify two bands of comparable intensity at 880 and 875  $\text{cm}^{-1}$ , which can be ascribed to dolomite and calcite, respectively, as well as the two bands at 729 and 710  $\text{cm}^{-1}$ . The large and intense band centred at 1456  $\text{cm}^{-1}$  results from superposition of two bands ascribed to dolomite and calcite. No signal attributable to aragonite is present in this case.

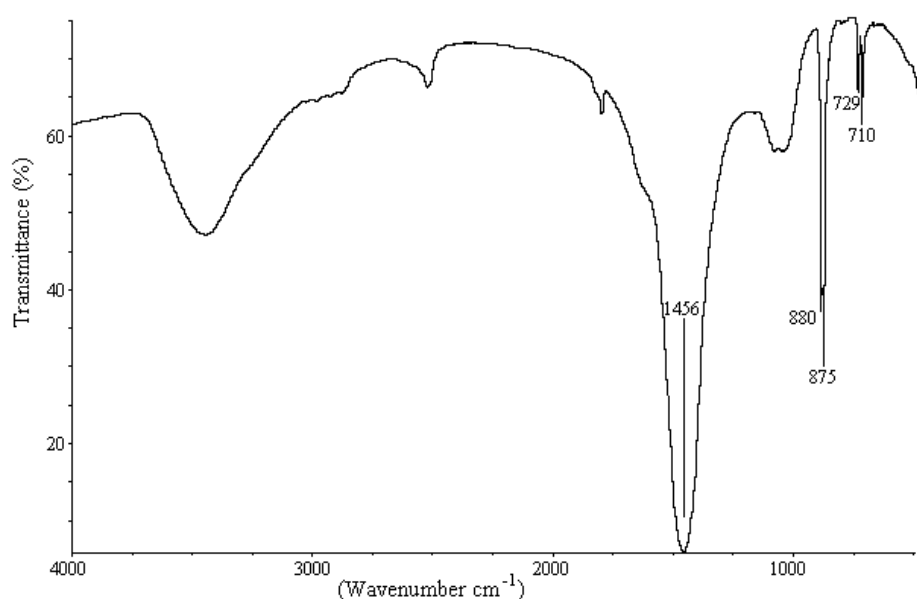


FIGURE 7.- FTIR spectrum of a white strip in a Roman wall painting fragment from Verona (Piazza Vescovado).

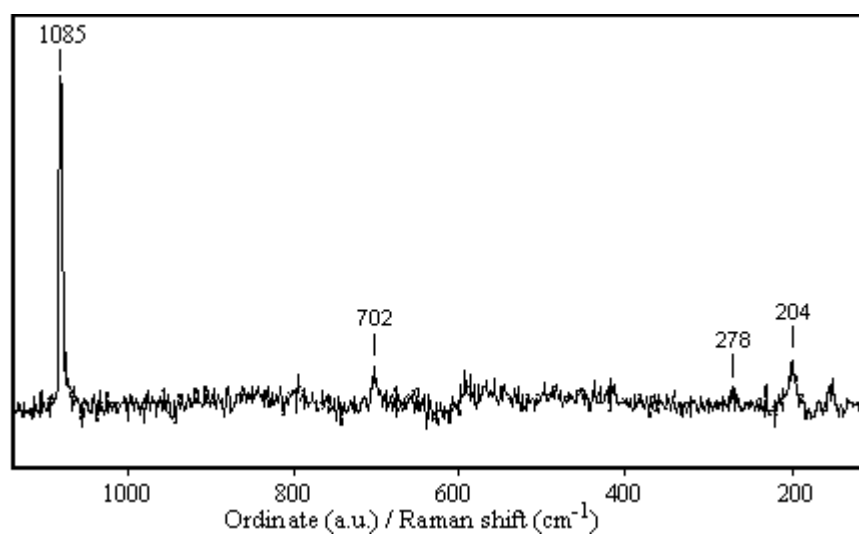


FIGURE 8 – Raman spectrum of a white Roman wall painting fragment from Bologna.

In this figure it is possible to identify the bands of 204 and 702  $\text{cm}^{-1}$  ascribed to aragonite and the band at 278 ascribed to calcite.

The results indicating the presence of aragonite in the samples from the *X<sup>a</sup> Regio* and *VIII<sup>a</sup> Regio* are summarized in Tables 1 and 2, respectively. In these Tables the cities of provenance, the number of samples, the sites where it was ascertained the use of aragonite as white pigment, and the colours and the type of pigments associated with aragonite are reported. In the samples where aragonite is present, the FTIR absorbance peak observed at 853  $\text{cm}^{-1}$  is rarely higher than the absorbance peak at 875  $\text{cm}^{-1}$  and characteristic of calcite; this suggests that aragonite was present always associated to calcite, whose origin could be natural, from a mixing in the preparation of the colour, or due to the diffusion from the fresh plaster lying below.

From the analysis of the results presented in Tables 1 and 2, it is possible to state that in the *VIII<sup>a</sup>* and *X<sup>a</sup> Regio* aragonite was the white pigment more often used for the white lines, and was also used together with precious pigments, such as Egyptian blue (*caeruleum*) and cinnabar in decorative rich paintings (see Table 1). These results are in agreement with those found for Roman sites of Switzerland (*Helvetia*)<sup>10-12</sup>. However, in the samples studied in the present work aragonite is often found associated with other pigments, such as green (Pordenone, Padova, Verona and Modena), yellow of goethite (one case in Modena); red to obtain a pink colour (Pordenone), and also in a violet colour (Montegrotto).

The association of aragonite with cinnabar was found in Verona and Trieste, but not in Padova, Vicenza and Pordenone; this result is in contrast with Béarat's statement that aragonite was always used as *sous-couche* for cinnabar<sup>11</sup>.

It is worth to note, as shown in Table 3, that aragonite is absent in cases where precious pigments, such as cinnabar, are present (Padova and Pordenone), as well as in three sites from Verona, where no expensive pigments were used; however, such latter "domus" are probably from the I<sup>o</sup> century b.c.<sup>21</sup>.

From the above reported results we can observe that the white pigments present in the samples can be found either alone, associated with white pigments, or mixed with other coloured pigments to clear them. These white pigments can be: calcite, coming by diffusion from the underlying plaster (*intonachino*, always constituted by pure calcite), or used on purpose as white pigment (see Table 3); dolomite, used as white pigment for white bands and strips, always associated with calcite and never associated with other colours (see Table 3); aragonite, always associated with calcite, specially used for the white lines and often mixed with precious pigments, (see Tables 1 and 2).

The overall results of this investigation suggest that aragonite was used on purpose for white bands and to clear colours, not excluding its use to apply colours with the technique "*a secco*", instead of "*a fresco*". This is supported by the fact that aragonite is always present in large amount as paint-layers white or coloured superimposed to underlying painting surfaces.

The analyses of the wall painting fragments, mostly from infill gullets in the ground, cannot give a date of the painting. However the archaeological data available at least for Montegrotto<sup>25</sup>, for the different *domus* from Verona<sup>21</sup> (reported in Table 3) and for the *domus* of Cosa at Grosseto<sup>15</sup>, suggest that white colours based on aragonite diffused in the Roman paintings from the Augustan period. Indeed, in *domus* from b.c. centuries (see Table 3), calcite and dolomite are used as white colours, while aragonite is not present.

The data seem to indicate a progressive increase of the use of whites based on aragonite along the time from the Augustan period, to become the most important white pigment in the Roman palette during the imperial period. The comparison of the white pigments found in this study with those from the Naples museum suggests that in the imperial period, in the *VIII<sup>a</sup>* and *X<sup>a</sup> Regio* the white pigment used by the painters was a "*creta calcarea*"<sup>3</sup>, such as *selinusia*, *melinum* or *paraetonium*. This latter was almost exclusively constituted by aragonite.



TABLE 1. - Colours and pigments associated with aragonite in the samples from *X<sup>a</sup> Regio*.

City	Number of Samples	Sites	Colours and patterns present in each group of samples	Associated pigments (A = Aragonite; C = Calcite)
Vicenza	45	S. Biagio	blue	Egyptian blue, A + C
			white braids	A + C
			white bands	A + C
Pordenone	15	S. Vito	green	celadonite, A + C
			pink	hematite, A + C
			floral decoration	A + C
Trieste	15	Crosada	red over black	hematite, A + C
			brilliant red	cinnabar, A + C
Padova	15	Montegrotto (excavation S)	blue	Egyptian blue, A + C
			white band	A + C
			green band	celadonite, A + C
			white braid over violet	A + C
Verona	10	S. Cosimo	blue	Egyptian blue, A + C
			brilliant red	cinnabar, A + C
	10	Via Garibaldi	white braids	A + C
	30	Vicolo Agnello	brilliant red	cinnabar, A + C
			daisy motif	A + C
	15	Via Rensi	white line	A + C
	25	Via Cantore	green	celadonite, A + C
	10	Piazza Nogara	black gray	carbon black, A + C
	15	Sant' Alessio	white braids	A + C
green			celadonite, A + C	
yellow motif			goethite, A + C	

TABLE 2. - Colours and pigments associated with aragonite in the samples from *VIII<sup>a</sup> Regio*.

City	Number of Samples	Sites	Colours and patterns present in each group of samples	Associated pigments (C = Calcite; A = Aragonite)
Parma	50	Palazzo San Vitale	red	hematite, cinnabar, A+C
		Cassa di Risparmio	white	A + C
Reggio E.	50	Via Mazzini	white line over red	A + C and cinnabar
		Credito Emiliano	white line over yellow	A + C and goethite
			white line over black	A + C and carbon black
			border of blue	Egyptian blue, A + C
Modena	30	Via Farini	intense green	green earth, Eg. blue, A+C
			yellow	goethite, A + C
			red	hematite, cinnabar, A + C
Bologna	30	Via Testoni	white over yellow	A + C and goethite
			white over red	A + C and hematite

TABLE 3.- Sites and cities where aragonite was not found

City	Number of Samples	Site	White pigment
Verona	15	Borgo Tascherio	calcite
	15	Piazza Vescovado	calcite and dolomite
	15	Via Tazzoli	calcite and dolomite
Padova	25	Montegrotto (excavation P)	calcite
Pordenone	20	Torre	calcite

Some hypotheses can be done to explain the prevailing use of aragonite in the imperial period, such as the particular features of aragonite as a good medium for the “*a secco*” painting technique, together with a higher availability of “*creta calcarea*”. The presence of aragonite is certainly an indication of the refinement in the decoration of the *domus*, its absence being often associated to the absence of other precious pigments. These and other circumstances could be accompanied by a change of taste or, more probably, of the economical conditions that made possible the use of a more specific white pigment, and not simply calcite or dolomite.

Finally we observed that in the VIII<sup>a</sup> and X<sup>a</sup> Regio the painters used almost the same criteria and the same materials used in the Roman Switzerland (*Helvetia*)<sup>3</sup> and France (*Gallia*)<sup>9</sup>.

This is a corroboration of the concept that the Roman Empire should be a place where the culture and the technology could easily circulate. Certainly there were some regional differences, but there was a common culture, a common taste and a diffusion of the knowledge and of the art.

## CONCLUSIONS

The spectroscopic methods of analysis applied to the identification of white pigments of ancient Roman wall paintings here proposed, revealed very suitable for the certain identification and discrimination of the different species of carbonates used as white colours. The application of this analysis on a wide number of samples allowed us to classify white pigments from several cities and sites of the Roman period together with the associated colours and pigments. In particular, the use of aragonite seems to have diffused beginning from the Augustan period, often connected to rich pigments and refined paintings, while aragonite was not found in paintings from b.C. Roman period. All the obtained results allowed us to state that the proposed methods of analysis can give information of archaeological interest for the knowledge of type, period and geographical diffusion of the materials used for the paintings, as well as about the diffusion of culture and technology in the Roman Empire.

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