Heat Alteration of the Blue Pigment Aerinite: Application to Sixena's Romanesque Frescoes

/ JORDI IBÁÑEZ-INSA(1,*), NÚRIA ORIOLS (2), JOSEP J. ELVIRA (1), SOLEDAD ÁLVAREZ (1), FELICIÀ PLANA (3)

(1) Institut de Ciències de la Terra Jaume Almera (ICTJA-CSIC), Lluís Solé i Sabarís s/n, 08028 Barcelona, Catalonia, Spain
(2) Museu Nacional d'Art de Catalunya (MNAC), Palau Nacional, Parc de Montjuïc, 08038 Barcelona, Catalonia, Spain
(3) Institut de Diagnosi Ambiental i Estudis de l'Aigua (IDAEA-CSIC), Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain

INTRODUCTION

Aerinite is a bluish fibrous inosilicate mineral associated with the alteration of mafic igneous rocks. Previous work has provided detailed information about the mineralogy of aerinite, including its chemical composition and crystal structure (Azambre & Monchoux, 1988; Rius *et al.*, 2004; Rius *et al.*, 2009). Aerinite is particularly interesting as it was used between the XI-XV centuries in many Romanesque fresco wall paintings of Catalonia, Aragon, and Andorra (Palet & de Andrés, 1992).

From the point of view of art conservation, studies on heat-induced mineral pigment alterations may provide useful information regarding the original state of a painting damaged by a fire event (Rickerby, 1991). This type of studies may be relevant for the knowledge and preservation of damaged paintings and even for their restoration. A characteristic example of such alterations can be found in the Romanesque wall paintings from the Chapter House of the Monastery of Santa Maria de Sixena (Huesca, Aragón, Spain). These frescoes, painted between 1196 and 1208, were highly damaged after the fire of 1936, with a high loss of pictorial surface and important color alteration. The paintings were transferred to canvas and are now exhibited at the Museu Nacional d'Art de Catalunya (MNAC), in Barcelona (see Fig. 1).

Aerinite has been identified as one of the blue pigments employed in Sixena's paintings (Palet & de Andrés, 1992). In the frescoes exhibited at MNAC, there exists a relatively large, blue-colored section that was not strongly affected by fire. Spectroscopic infrared transmission measurements confirm that aerinite was employed in this composition. For the preservation and complete understanding of these paintings, it would be desirable to determine which sections of the fire-damaged frescoes were originally blue. For this purpose, the thermal behavior of aerinite should be well understood.

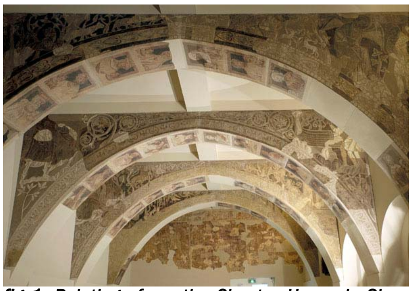

fig 1. *Paintings from the Chapter House in Sixena, on display at MNAC. ©MNAC – Museu Nacional d'Art de Catalunya. Barcelona. Photo by: Calveras / Mérida / Sagristà*

The aim of the present work is to investigate the heat-induced alterations of the mineral pigment aerinite. The chromatic alterations of aerinite samples are monitored as a function of temperature and x-ray diffraction (XRD) is employed to investigate the heat induced mineralogical transformations of this mineral pigment.

SAMPLES AND METHODS

Aerinite specimens from the Estopinyà area (Huesca, Aragon, Spain) were subject to 1 h thermal annealing at the following temperatures: 100º, 200º, 400º, 600º, 800º, and 1000ºC. Digital images of the annealed samples were obtained with conventional photographic techniques in order to record color alterations. For the XRD measurements, all samples were carefully hand-ground. XRD scans were recorded using a Bruker-AXS (Siemens) D5005 powder diffractometer equipped with a 2.2 kW sealed Cu x-ray source, a graphite monochromator to filter out the Cu Kβ radiation, and a NaI(Tl) scintillation detector. The scans were obtained between 4º and 60º (in 2θ) with a 0.05° step size and long integration times (6 seconds per step).

RESULTS AND DISCUSSION

The chemical alteration induced by heating of the mineral aerinite has an important bearing on the color of the annealed samples (Table I). At the lowest annealing temperatures, the blue color of aerinite is barely altered. At 400ºC the samples acquire a green hue, which tends to be yellow-brown above 600 ºC. At the highest temperature considered in this work (1000ºC), the samples become red-brown.

Remarkably, the colors of the aerinite samples annealed at temperatures ranging from 600ºC up to 1000ºC can be easily observed in-situ in the fire-damaged paintings from Sixena on display at MNAC. In particular, sections of the paintings that might be expected to be blue (following iconographic reasons) resemble very closely to the aerinite samples annealed at the higher temperatures.

The structural formula of aerinite as obtained from Syncrotron Powder Diffraction measurements on samples from the Estopinyà area is $Ca_{5.1}Na_{0.5}(Fe^{3+}AlFe^{2+}{}_{1.7}Mg_{0.3})(Al_{5.1}Mg_{0.7})[Si_{12}O_{36}(OH)_{12}H][(CO_3)_{1.2}(H_2O)_{12}]$ (Rius *et al.*, 2004). Note however that, owing to the chemical variability of aerinite, different structural results are obtained on specimens from other locations (Rius *et al.*, 2009). On account of its chemical composition, it can be expected that upon heating, aerinite will suffer a loss of H_2O, OH and CO_3 groups at low or medium temperatures. At sufficiently elevated temperatures, the reorganization and recrystallization of the remaining atomic species may be expected to yield Ca, Fe, Mg, and Na

palabras clave: Aerinita, Arte románico, Difracción de rayos X en polvo, Pigmento mineral azul	***key words:*** Aerinite, Romanesque art, X-ray powder diffraction, Blue mineral pigment

* corresponding author: **jibanez@ictja.csic.es**

Temperature	*not annealed*	*100 ºC*	*200 ºC*	*400 ºC*	*600 ºC*	*800 ºC*	*1000 ºC*
Color	blue	blue	bluish	greenish	yellowish-brown-	light brown	brownish-red
Phases detected by X-ray diffraction	aerinite other phases	aerinite other phases	aerinite other phases	other phases	other phases	augite other phases	plagioclase, hematite, other phases

Table 1. *Results of the heating tests on aerinite as a function of annealing temperature. 'Other phases' refers to minority, accompanying minerals like quartz or diopside that are observed in all the XRD scans, also in the non-annealed aerinite sample.*

aluminosilicates.

Fig. 2 shows selected XRD scans of non-annealed aerinite together with aerinite samples annealed at different temperatures. The XRD spectrum of the untreated aerinite sample displays peaks from this phase as well as from other minerals present in the powder: quartz, feldspars (microcline and plagioclase), augite (close to the diopside end-member) and mesolite. The latter, which is a tectosilicate mineral associated to aerinite, is no longer detected in the annealed material.

With increasing temperature (Fig. 2), the intensity of the XRD reflections from aerinite is lowered, while the peaks from quartz and augite remain basically unchanged. At 600ºC, no signal from aerinite is detected. At 800 ºC, the XRD peaks augite, with general formula $Ca(Fe,Mg)Si_2O_6$, are sizably more intense. We attribute this observation to the partial recrystallization of the atomic species that remain after the degradation of aerinite. It should be noted that the temperature required for the growth of the Mg-rich and Fe-rich end members of the augite solid solution (diopside and hedenbergite) is in the 800-950ºC range (Deer *et al.*, 1992). In the XRD scans of the sample annealed at 1000ºC, strong peaks from Ca-rich albite also emerge (see Fig. 2). Note that the Ca-rich (ordered) low albites are expected to crystallize at around 1000-1100ºC (Deer *et al.,* 1992). Hematite peaks also show up in the XRD spectra of the sample annealed up to 1000ºC. This result is consistent with the red-brown color acquired by this sample. While at 800 ºC the XRD patterns of augite are closer to those of hedenbergite (Fe-rich end of augite) and no hematite reflections are observed, at 1000ºC the peaks assigned to augite are closer to those of diopside (Mg-rich end of augite). This suggests that at such elevated temperatures Fe is fully oxidized, giving rise to the hematite phase, while the rest of species are incorporated into the felsic (plagioclase) feldspar. In contrast, at lower temperatures (800ºC) Fe, and also the rest of cations from the original aerinite (Ca, Mg, Na), seem to be mainly incorporated in the hedenbergite phase. This result is compatible with the brownish color displayed by the sample annealed at 800ºC.

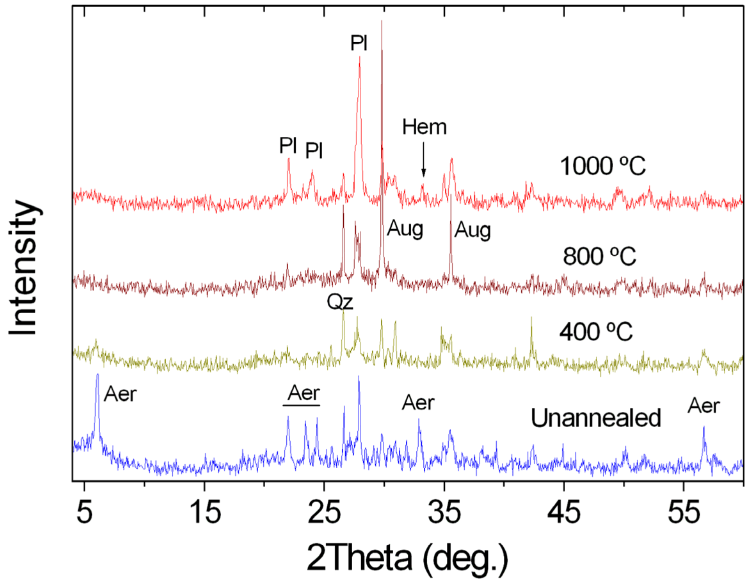

fig 2. *X-ray diffraction scans from aerinite samples annealed at different temperatures. Aer= aerinite, Qz= quartz, Aug=augite,Pl=plagioclase, Hem=Hematite.*

CONCLUSIONS

The blue pigment aerinite, widely employed in Romanesque paintings in the region of the southern Pyrenees, undergoes important heat-induced color alterations. The color acquired by aerinite samples after thermal annealing is found in-situ in the frescoes of Sixena, which were badly damaged several decades ago. We have used XRD to monitor the mineralogical alterations of the pigment aerinite upon heating. The XRD data suggest that aerinite is totally degraded above 400ºC. At 800ºC recrystallization yields Fe-rich augite. At 1000ºC Fe is mainly found as hematite, whereas the rest of cationic species give rise to (felsic) plagioclase feldspars.

ACKNOWLEDGEMENTS

Work performed in collaboration with Rosa M. Gasol (painting conservator-restorer at Oficina del Patrimoni Cultural, Àrea de Coneixement i Noves Tecnologies, Diputació de Barcelona) and The Romanesque Art Area of Museu Nacional d'Art de Catalunya (MNAC). Work supervised by Mireia Mestre, Head of MNAC's Conservation and Restoration Department.

REFERENCES.

Azambre, B. & Monchoux, P. (1988): Précisions minéralogiques sur l'aérinite: nouvelle occurrence à Saint-Pandelon (Landes, France). Bull. Minéral. ***111****, 39-47.*

Deer, W.A., Howie, R.A., Zussman, J. (1992): An introduction to the rock-forming minerals. 2nd ed, Longman, Harlow, 696 p..

Palet, A. & de Andrés, J. (1992): The Identification of Aerinite as a Blue Pigment in the Romanesque Frescoes of the Pyrenean Region. Studies in Conservation, ***37****, 132-136*

Rickerby, S. (1991): Heat alterations to pigments painted in the fresco technique. The Conservator. ***15****, 39-44.*

Rius, J., Elkaim, E. Torrelles, X. (2004): Structure determination of the blue mineral pigment aerinite from synchrotron powder diffraction data: The solution of an old riddle. Eur. J. Mineral., ***16****, 127-134.*

Rius, J., Crespi, A., Roig, A., Melgarejo, J.C. (2009): Crystal-structure refinement of Fe^{3+}-rich aerinite from synchrotron powder diffraction and Mössbauer data. Eur. J. Mineral. , ***21****, 233–240.*