Eur. J. Mineral.
2006, **18**, 835-843

The fading of red lead pigment in wall paintings: tracking the physico-chemical transformations by means of complementary micro-analysis techniques

SÉBASTIEN AZE[1]*, JEAN-MARC VALLET[1], ALAIN BARONNET[2] and OLIVIER GRAUBY[2]

[1]Laboratoire du Centre Interrégional de Conservation et Restauration du Patrimoine (CICRP)
21 rue Guibal, F-13003 Marseille, France
[2]Centre de Recherche sur la Matière Condensée et les Nanomatériaux (CRMCN-CNRS),
Campus de Luminy, F-13288 Marseille cedex 9, France

Abstract: The phenomenon of red lead pigment fading in wall paintings was investigated through the study of an experimental fresco painting. Chemical modifications of the pigment induced a local fading of the pictorial layer after a 25-years natural ageing period. Representative features of the alteration phases, including composition and structural information, were obtained by applying complementary micro-analysis techniques to the study of a single paint sample. Focused X-ray diffraction patterns of small areas were collected using a highly sensitive detector, revealing 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 such a red pigment fading is emphasised.

Key-words: chromatic alteration, red lead, experimental fresco painting, natural ageing, micro-analysis.

Introduction

Considered by art historians as one of the earliest artificial pigments, red lead has been widely employed in artworks. Numerous authors mention the presence of red lead on manuscript illuminations or miniatures (Clark & Gibbs, 1998; Bruni *et al.*, 1999; Andalo *et al.*, 2000), canvas paintings (Domenech-Carbó *et al.*, 2000), but especially in wall paintings (Edwards *et al.*, 1999; Daniilia *et al.*, 2000; Klockenkämper *et al.*, 2000). The pigment was traditionally used either as a pure colour or in mixture with other pigments, such as red ochre (Cam & Fan, 2000; Perez-Alonso *et al.*, 2004), vermilion (Burgio *et al.*, 2003), and orpiment (Bruni *et al.*, 2001).

Natural ageing of red lead in paintings often cause the formation of either dark or white stains, which are strongly harmful to both the conservation and legibility of the artwork. This phenomenon has been widely documented since the publication of Cennino Cennini's *Libro dell'Arte*, written at the end of the 14th century (Thompson, 1960). Several hypotheses, sometimes contradictory, have been proposed to explain the formation of degradation products. Either environmental parameters (humidity, light, pollutants, microbial activity) or intrinsic features (nature of the binding media, pictorial technique) are supposed to influence both composition and formation kinetics of the alteration products (Petushkova & Lyalikova, 1986; Feng *et al.*, 1999). Several black minerals, mainly plattnerite (lead dioxide) and galena (lead sulphide) have been identified in darkened red lead-containing wall paintings executed in the true fresco or related lime techniques (Hwang *et al.*, 1993; Brill *et al.*, 1993). When applied with an organic binder, such as animal glue or oil medium, red lead may be transformed into lead carbonate, producing whitish discolorations (Saunders *et al.*, 2002). The mechanisms of these transformations are still misunderstood, as well as the conditions under which they might occur. No explicit conservation protocol, which might reduce the influences of both intrinsic and extrinsic factors, has been established (Fitzhugh, 1985). Moreover, no specific method has been proposed for the restoration of red lead-containing paintings.

This work attempts to take advantage of the several small-scale analysis techniques that are now commonly used by geologists and materials scientists. In order to elucidate the colour change processes, both composition and structure of the alteration were investigated. Complementary methods were employed to study a single

*E-mail: sebastien.aze@cicrp.fr

0935-1221/06/0018-0835 $ 4.05
DOI: 10.1127/0935-1221/2006/0018-0835