

An *in Situ* X-ray Powder Thermodiffraction Study of Azurite Decarbonation

/ CAROLINA CARDELL (1*), AFRICA YEBRA-RODRÍGUEZ (2), PEDRO ALVAREZ-LLORET (1), ISABEL GUERRA (3), J. DANIEL MARTÍN-RAMOS (1)

(1) Department of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain

(2) Department of Geology, Faculty of Experimental Science, University of Jaen, Campus Las Lagunillas, s/n, 23071 Jaén, Spain

(3) Scientific Instrumentation Centre, University of Granada, Campus Fuentenueva, 18071 Granada, Spain

INTRODUCTION.

For centuries Azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, has been used extensively as a pigment, particularly during the Middle Ages and Renaissance in canvas, manuscripts, glasses, ceramics and glazes. Thermal analyses of historical mineral pigments remain limited, particularly using modern thermo-analytical techniques (Frost et al., 2002), despite numerous studies of thermal decomposition of copper carbonates (e.g. azurite and malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) as catalyst precursors (Ding et al., 2002).

This paper presents the results of an *in situ* thermal decomposition experiment of an azurite pigment (Kremer Pigments GmbH & Co. KG. Ref. 10200 Cl: PB 30 -77420, with particle size 0–120 μm) using X-ray powder thermodiffraction (XRTD) by increasing temperature (T) from 30 to 220 °C. The experiment aimed to characterize (a) time-resolved *in situ* decarbonation of azurite up to ~ 220 °C, and (b) volumetric dilatation coefficients for thermal expansion of azurite. Furthermore, the study intended to demonstrate that XRTD is a suitable technique to investigate thermo- and photo-sensitive historical pigments, and show the benefits of combining 2D XRTD mapping with DSC and SEM-EDX to better visualize and characterize the phase transformations occurring in mineral pigments (Yebra-Rodríguez et al. 2009).

According to the literature thermal decomposition of azurite takes place in six stages at 205, 321, 332, 345, 362 and 842 °C (Frost et al., 2002, Ding et al., 2002). Rickerby (1991) pointed out that azurite blackens into tenorite (CuO) above 300 °C, and that the transformation depends on grain size. Recently Mattei et al. (2008) studied laser-induced degradation of azurite

transformation into tenorite only below the critical size of 25 μm .

ANALYTICAL TECHNIQUES.

In situ XRD data were acquired using a Philips PW1710/00 X-ray diffractometer with PW1712 communication card via RS232 serial port, full-duplex controlled by the X Powder PLUS software. The heating device is composed of an halogen lamp (Philips Capsule-line Pro 75 W, 12 V) that heats the XRD chamber up to 230 °C, a Pt-1000 probe for T monitoring (0.5 °C precision), and a software-controlled thermostat with digital T selection. A detailed description of the heating system is described elsewhere (Cardell et al., 2007). The XRD patterns were scanned over $10^\circ < 2\theta < 55^\circ$ range, with 0.1 goniometric rate and 0.4 s integration time. The scan mode was continuous using $\text{CuK}\alpha$ radiation. The voltage was 40 kV, and the tube current 40 mA. Diffraction patterns were collected at 10 °C increments between 30 and 220 °C. Phase transformation was simply detected by the appearance/disappearance of characteristic peaks in the XRD patterns.

Thermal analysis performed with DSC (DSC 822e/700 Mettler Toledo) was applied on samples after drying by vacuum heating at 80 °C during 48 h (heating rate: 10 °C/min over a T range of 25–600 °C).

The chemical composition of the mineral phases was identified with a SEM Leo 1430VP (VP-SEM) scanning electron microscope, coupled with an EDX microanalysis Inca 350 version 17 Oxford Instrument, which allows identification of elements with low atomic numbers, including carbon. EDX working conditions were 500 pA

filament current, 20 keV beam energy, and 10 eV/ch resolution for pinpoint analyses.

RESULTS AND DISCUSSION.

The results of our azurite XRTD experiment show that while the surface of the studied sample remained blue (i.e. azurite), a black powder, identified as tenorite, formed at the bottom of the sample, in contact with the glass sample holder. This finding indicates that thermal decomposition of azurite took place during the test at an XRD chamber T of only ~ 220°C, far below that reported for azurite decarbonation. It seems that absorption of X-rays heated the glass sample holder, and thermal conduction led to a T gradient in the sample, and transformation of azurite into tenorite at the point of contact between sample and holder.

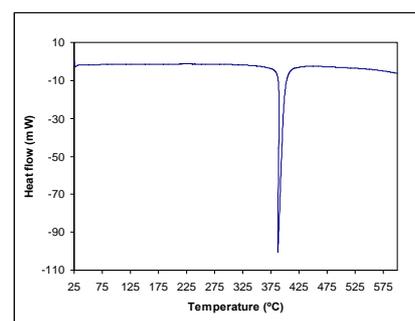


fig 1. DSC heating process of the azurite pigment.

The DSC analysis of the azurite displayed an endothermic peak at ~ 387.19 °C which corresponds to its melting point. This process took place rapidly and thermal decomposition was complete by 420 °C. This result corroborates the idea that, irrespective of the T attained in the TXRD chamber (~ 220 °C), the glass sample holder achieved a T surpassing the azurite melting T required for decomposition to

tenorite. This result agrees with previous studies which showed that tenorite is formed at ~ 384 °C from decarbonation of azurite (loss of carbon dioxide; Frost, et al., 2002). On the other hand, the SEM-EDX analyses of both azurite and tenorite were done to obtain their spectral features.

CONCLUSIONS.

This study provides insight into the interactions between azurite and glass at low temperatures up to ~ 400 °C, with implications for studies related to coloured ancient glass artefacts, archaeological and medieval stained glasses, and glass-making experiments.

Moreover, the conducted experiment draws attention to the need to use special sample holders to avoid heating the sample by minimizing either X-ray absorption, or thermal conduction, or both.

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