



X-ray absorption spectroscopy of ultramarine pigments: A new analytical method for the polysulfide radical anion S_3^- chromophore

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ARTICLE INFO

Article history:

Received 24 August 2009

Accepted 17 November 2009

Available online 26 November 2009

Keywords:

Pigments
Ultramarine
XANES
Polysulfides
Radical anions

ABSTRACT

Blue and mauve ultramarine artists' pigments and their heat-treated products have been investigated by sulfur *K*-edge X-ray absorption. X-ray absorption near-edge structure spectra are dominated by features of reduced sulfur and sulfate species. There is also a pre-peak at about 2468.0 eV which reflects the presence of the unpaired electron on the polysulfide radical anion (S_3^-). Pre-peak intensity is directly proportional to the depth of blue coloration, and provides a new, independent method for estimating the proportion of ultramarine cage sites occupied by the blue chromophore. The occupancy of the polysulfide radical anion S_3^- is estimated to be 33% in an intense ultramarine blue pigment, 22% in a dark blue ultramarine pigment, and 1% in deep royal blue lazurite from Afghanistan. The more efficient development of color in lazurite is attributed to extensive annealing of the mineral structure in the natural environment.

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1. Introduction

Ultramarine pigments are chalcogen-bearing aluminosilicate clathrate compounds of the sodalite group, having a general formula $A_8[T_{12}O_{24}]X_2$ [1], where *T* are framework atoms (Al,Si), *A* cage cations (Na^+ , Ca^{2+}) and *X* cage anions (Cl^- , SO_4^{2-} , S_n^- , S_n^{2-}) and H_2O . The stability and safety of these pigments are the basis of their numerous industrial applications as coloring and whitening agents [2]. The most familiar pigment color is ultramarine blue, but a range of other colors may be prepared by manipulating chemical composition and preparation procedures. The sodalite cage (Fig. 1) accommodates a very wide range of cation and anion substituents; ultramarines containing Na, S, Ag, Ag–Na, Tl, Sr, Ba, Zn, Mn, Pb, and Se were synthesized in early research [3]. Ultramarine pigment compositions are based on the crystal chemistry of the royal blue sodalite mineral lazurite [$Na_6Ca_2Al_6Si_6O_{24}(S_n,SO_4)_2$] from the Sar-e-Sang locality, Afghanistan, which was prized as a blue pigment in antiquity when it was known as ultramarinum. Some idealized compositions suggested for synthetic ultramarine blue pigments include $Na_8Al_6Si_6O_{24}S_4$ [4], $Na_{6.9}Al_{5.6}Si_{6.4}O_{24}S_{2.0}$ [5], $Na_7Al_6Si_6O_{24}S_3$ [6], and $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$ [7], although actual compositions are usually complicated by minor amounts of impurities from starting materials.

Resonance Raman and electron paramagnetic resonance (EPR) studies have established that the color of ultramarine pigments is associated with reduced chalcogen species in the sodalite cages, particularly the polysulfide radical anions S_3^- , S_2^- and S_4^- [4–12]. The S_3^- radical anion is the blue chromophore, whereas yellow and red colors

have been attributed to S_2^- and S_4^- , respectively. Quantification of the proportion of sodalite cages occupied by the S_3^- radical in typical ultramarine blue pigment has been complicated by difficulty in the calibration of ultraviolet–visible reflectance spectra and EPR spins, and sample-to-sample variation. Only small amounts of this chromophore are responsible for the deep blue color of alkali chloride melts [13] and the blue-violet color of aluminoborosilicate glasses (≤ 10 ppm) [14]. However, spin densities inferred from EPR studies suggest that a significant proportion of the reduced sulfur content of deeply-colored ultramarines is indeed present as the S_3^- radical anion: e.g., 43% [6] and 15.8% [12], with higher estimates in earlier studies [6].

We presently investigate the chemical state of sulfur in several commercial ultramarine pigments using S *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy. This technique has previously been applied to the study of lazurite from Afghanistan and Baffin island, Canada [15], and Biakal, Russia [16]. Numerous studies have shown that synchrotron radiation XANES spectroscopy is a sensitive probe of the local structure and chemical state of sulfur in minerals and chemical compounds [15,17–22]. Sulfur *K*-edge XANES spectra are characterized by a prominent absorption edge feature which shifts systematically with oxidation state from 2469.5–2470 eV for S^{2-} in metal sulfides to near 2482 eV for S^{6+} in sulfates. However, this correlation is complicated for reduced sulfur species by an upward shift of up to 5 eV in the position of the *K* edge for the ionic monosulfides [22].

2. Experimental methods

A total of fourteen ultramarine artists' pigments were obtained from Sinopia, San Francisco, and Guerra Paint and Pigment Corp., New York, and four were selected for further study based largely on a preliminary

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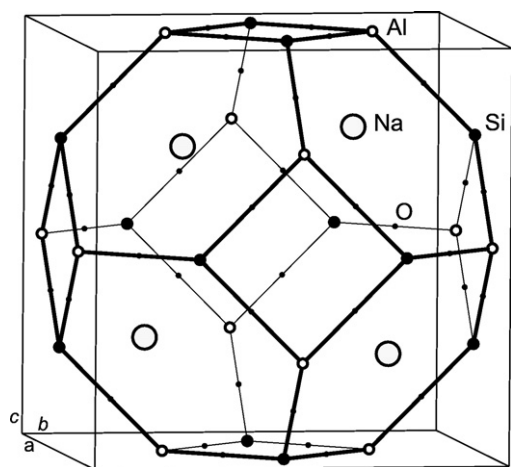


Fig. 1. Ideal sodalite-structure cage: cage anion has been omitted and sodium cations are located within cage in real structures.

powder X-ray diffraction study. These are presently referred to as 4501 (ultramarine blue), 4504 (dark blue), G5 (mauve), and G6 (heliotrope). Chemical analysis of the bulk pigments was made by Activation Laboratories Ltd., Ancaster, Ontario. To investigate the influence of temperature and air oxidation on the development of pigment color, approximately 0.5–1.0 g amounts of the pigments were transferred to either silica glass tubes or platinum foil and heated in a muffle furnace (Table 1). The glass tubes were either sealed under vacuum or left open to the muffle atmosphere. Temperatures investigated were from 500 to 900 °C, to encompass the temperature range for pigment preparation procedures, and run durations were from 2 to 24 h. Most glass tube experiments were pre-heated at 200–300 °C to remove excess volatile components.

Sulfur *K*-edge XANES spectra were collected at the Synchrotron Radiation Center (SRC; Aladdin storage ring), University of Wisconsin at Madison, using the double crystal monochromator beamline in fluorescence yield and total electron (current) yield detection modes as a function of incident photon energy. Samples were lightly crushed and uniformly spread on double-sided conducting carbon tape affixed to a clean stainless steel disk. The spectrometer geometry minimized the influence of variation in sample thickness and self absorption.

Table 1
Thermal treatment of pigments.

Experimental conditions					Color ^a
Expt.	Temperature (°C)	Time (h)	Container ^b	Pre-heating (°C)	
4501	(Pigment)				Ultramarine
4501-1	800	4	S	200	Ultramarine
4501-2	900	2	O	300	Cornflower
4501-3	800	4	O	200	Light blue
4501-4	900	3	F	–	Colorless
4504	(Pigment)				Dark blue
4504-1	800	24	S	200	Dark blue
4504-2	600	24	S	–	Dark blue
4504-3	900	2	O	300	Cornflower
4504-4	800	4	O	200	Powder blue
4504-5	900	3	F	–	Colorless
G5	(Pigment)				Mauve
G5-1	500	24	S	200	Cornflower
G5-2	900	2	O	300	Light blue
G5-3	900	2	O	300	Baby blue
G5-4	900	3	F	–	Colorless
G6	(Pigment)				Heliotrope
G6-1	600	24	S	200	Cornflower
G6-2	800	4	O	200	Baby blue
G6-3	900	2	O	300	Sky blue
G6-4	900	3	F	–	Colorless

^a Color shades obtained using standard color charts.

^b Container: S is sealed glass tube; O is open glass tube; F is Pt foil.

Current yield was measured at the sample surface and the fluorescence yield detector was positioned in front of the sample. Sample depths probed at the *S K* edge have been estimated to be only about 230 Å and 1000–2000 Å, respectively [23,24]. XANES spectra were collected from 2430 to 2530 eV, at intervals of 0.25 eV from 2461 to 2495 eV and 1.0 eV elsewhere, and averaged from two scans using a beamline data reduction program. The spectra were subsequently normalized against incident intensity (I_0), measured simultaneously, using BAN [25] and smoothed using a moving average of three data points. The edge peak of the total electron yield spectrum of the native sulfur standard was centered at 2472.0 eV [15].

3. Results

X-ray diffraction powder patterns of the four starting pigments and heat-treated products were dominated by reflections of a single sodalite-type phase. All of these materials were essentially single-phase ultramarines. Formulae deduced from the chemical analyses are: 4501— $\text{Na}_{4.1}\text{Ca}_{0.1}\text{K}_{0.1}\text{Al}_{3.5}\text{Si}_{8.5}\text{O}_{24}\text{S}^*_{3.0}(\text{SO}_4)_{0.2}$; 4504— $\text{Na}_{6.1}\text{Ca}_{0.1}\text{K}_{0.2}\text{Al}_{5.5}\text{Si}_{6.5}\text{O}_{24}\text{S}^*_{3.1}(\text{SO}_4)_{0.2}$; G5— $\text{Na}_{5.9}\text{Ca}_{0.1}\text{K}_{0.2}\text{Al}_{5.3}\text{Si}_{6.7}\text{O}_{24}\text{S}^*_{2.4}(\text{SO}_4)_{1.3}$; and G6— $\text{Na}_{4.6}\text{K}_{0.1}\text{Al}_{4.9}\text{Si}_{7.2}\text{O}_{24}\text{S}^*_{1.8}(\text{SO}_4)_{1.8}$, where S^* represents total reduced sulfur, and minor amounts of iron, titanium, magnesium, and manganese have been ignored. The compositions of the starting pigments represent a wide range in Al/Si ratio and are broadly consistent with three sulfur atoms per formula unit, present as reduced sulfur in the blue pigments and a mixture of reduced sulfur and sulfate in the mauve pigments. The calculated net positive charge available to bind anions in the sodalite cage is 0.9, 1.28, 1.08, and 0.06 per formula unit, for 4501, 4504, G5, and G6, respectively.

Sulfur *K*-edge XANES spectra for the starting pigments 4501, 4504 and G6 and their heat-treated products are reproduced in Fig. 2.

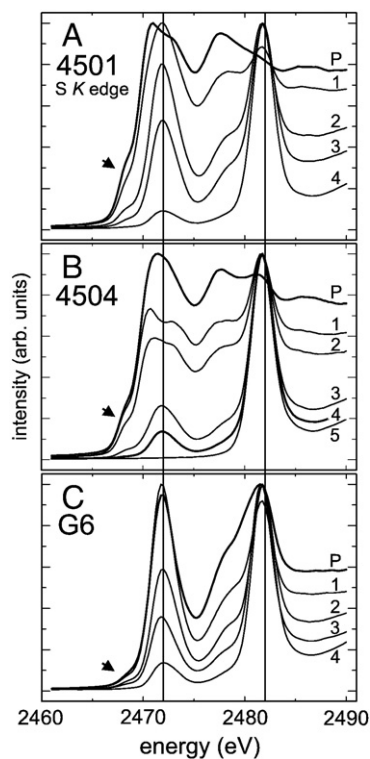


Fig. 2. Sulfur *K*-edge XANES spectra for ultramarine pigments (P) and their heat-treated products (1–5): (A) 4501, ultramarine; (B) 4504, dark blue; (C) G6, heliotrope; labels for heat-treated products correspond to the experiment numbers listed in Table 1 and spectra are arranged in a downward sequence of decreasing intensity of blue coloration; ruled lines locate edge peak positions for native sulfur and sulfate; arrow locates pre-peak associated with S_2^- ; spectra were recorded by fluorescence yield and have been normalized and smoothed.

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