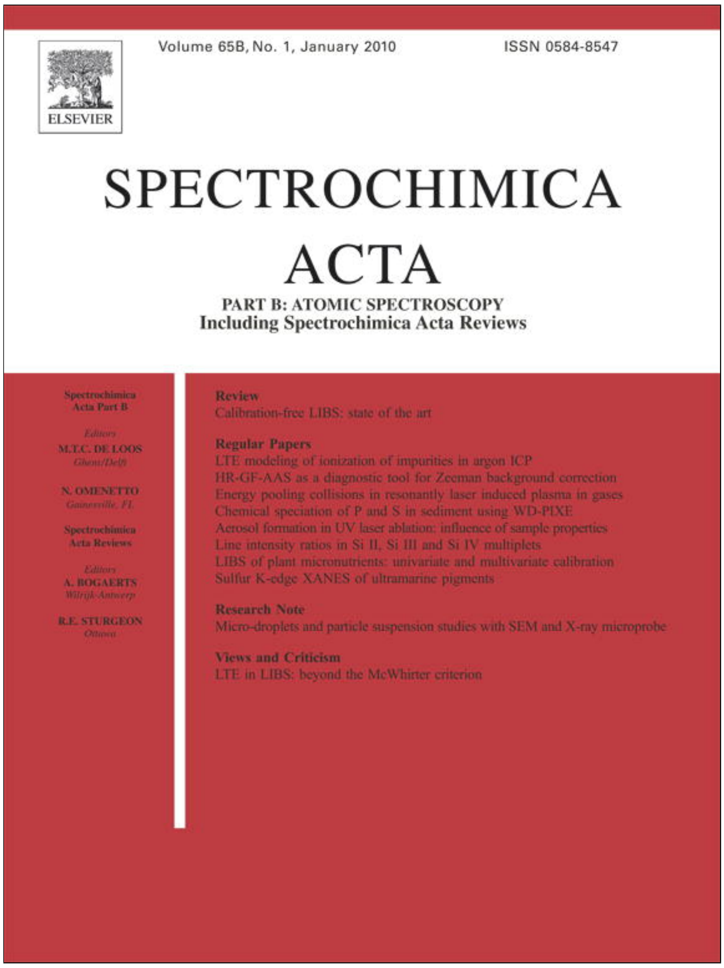

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X-ray absorption spectroscopy of ultramarine pigments: A new analytical method for the polysulfide radical anion S_3^- chromophore

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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.

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 ($\leq$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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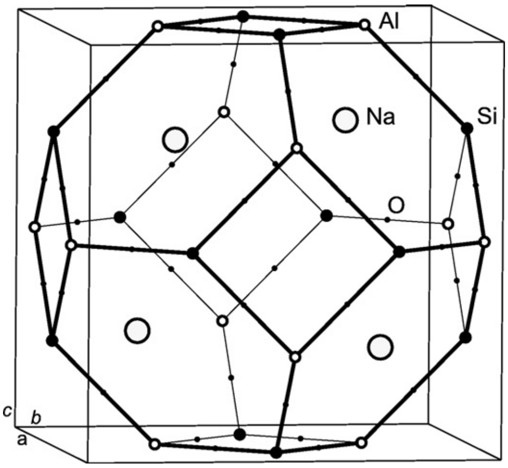

Fig. 1. Ideal sodalite-structure cage: cage anion has been omitted and sodium cations are located within cage in real structures.

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. 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_o), 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].

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.

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—$Na_{4.1}Ca_{0.1}K_{0.1}Al_{3.5}Si_{8.5}O_{24}S^*_{3.0}(SO_4)_{0.2}$; 4504— $Na_{6.1}Ca_{0.1}K_{0.2}Al_{5.5}Si_{6.5}O_{24}S^*_{3.1}(SO_4)_{0.2}$; G5— $Na_{5.9}Ca_{0.1}K_{0.2}Al_{5.3}Si_{6.7}O_{24}S^*_{2.4}(SO_4)_{1.3}$; and G6— $Na_{4.6}K_{0.1}Al_{4.9}Si_{7.2}O_{24}S^*_{1.8}(SO_4)_{1.8}$, 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.

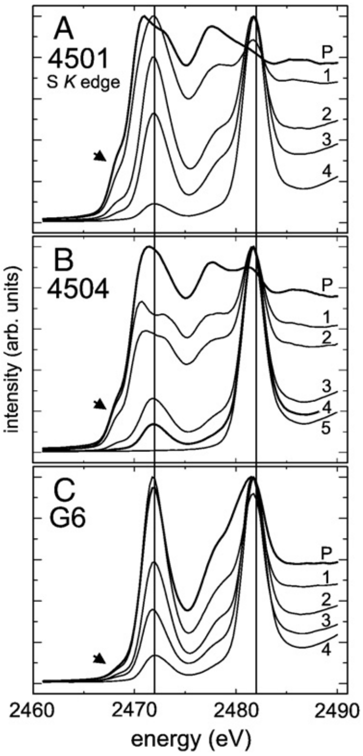

Fig. 2. Sulfur *K*-edge XANES spectra for ultramarine pigments (P) and their heat-treated products (1–5): (A) 4501, ultramarine; (B) 4504, dark blue; (C) G6, heliotrope; labels for heat-treated products correspond to the experiment numbers listed in Table 1 and spectra are arranged in a downward sequence of decreasing intensity of blue coloration; ruled lines locate edge peak positions for native sulfur and sulfate; arrow locates pre-peak associated with S_3^-; spectra were recorded by fluorescence yield and have been normalized and smoothed.

XANES spectra for G5 were generally similar to corresponding spectra for G6. All XANES spectra were collected using the fluorescence yield mode because the background to the spectra collected simultaneously by current yield was irregular. This problem was tentatively attributed to electrostatic charging at the surface of the nanoscale ultramarine particles, since it was not encountered for the native sulfur and $CaSO_4.2H_2O$ standards measured as the first and last samples of the beamtime session, respectively.

Heat treatment of the pigments to 200–300 °C resulted in no apparent change in either color or composition [2], other than loss of some volatiles. However, considerable change occurred at the higher temperatures investigated, and there was a marked difference between the products from sealed and open tube experiments. Consistent with earlier studies [6,12], heat treatment of blue pigments in sealed tubes to 600–800 °C resulted in intensification of color, to deep ultramarine for pigment 4501 (spectrum 1 in Fig. 2A) and deep dark blue for pigment 4504 (1 and 2 in Fig. 2B). On the other hand, mauve pigments heated to 500–600 °C changed color to cornflower blue (spectrum 1 in Fig. 2C). Heating of both blue and mauve pigments in open tubes resulted in progressively lighter shades of blue with increasing access to air. The products of the platinum foil experiments were colorless with, perhaps, a slight tinge of blue, corresponding to the loss of most, if not all, of the reduced sulfur species by volatilization and oxidation to sulfate (spectrum 4 in Fig. 2A,C and 5 in Fig. 2B).

4. Discussion

Interpretation of S *K*-edge XANES for ultramarines is complicated by the lack of reference compounds to adequately account for the encapsulation and isolation of reduced sulfur species in clathrate cages. The XANES spectra reveal the presence of reduced sulfur (peaks near 2472 eV) and sulfate (peak at 2481–2482 eV) species and possibly sulfite as well at about 2477.5 eV, and most have a low-energy shoulder to the edge peak for reduced sulfur centered near 2468.0 eV. These compound spectra may be deconvoluted using a stepped edge jump and Gaussian component peaks [18] (Fig. 3). The reduced sulfur region of the spectrum for the ultramarine blue pigment 4501 has two principal components, at 2470.4 eV and 2472.4 eV (B and C in Fig. 3). Component C is probably attributable to elemental sulfur, as encapsulated neutral clusters, whereas component B likely includes a contribution from the polysulfide radical anion (S_3^-). Note that the XANES spectra of the untreated ultramarine blue pigments (P in Fig. 2A,B) are similar to that of native sulfur [22] and the low net positive charges deduced for these pigments do not favor high contents of reduced anion species. Although a broad feature in S *K*-edge XANES at 2477–2478 eV has been interpreted to represent sulfur of intermediate oxidation state [16,18] and sulfur dioxide is an intermediate product in the oxidation step of ultramarine synthesis [2], components D and E must include a large contribution from multiple scattering with neighboring atoms, which results in a strong post-edge feature in spectra of sulfides and native sulfur [22]. The XANES spectra of the two mauve pigments G5 (not illustrated) and G6 (spectrum P in Fig. 2C) are characterized by edge peaks for elemental sulfur or polysulfide (at 2472 eV) and sulfate (near 2481 eV), and possibly thiosulfate as well.

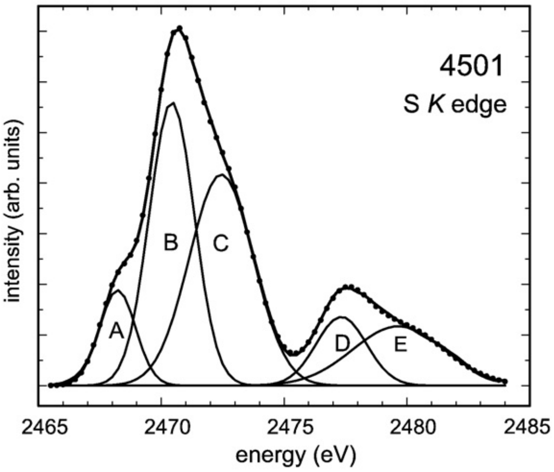

Fig. 3. Deconvoluted S *K*-edge XANES spectrum for ultramarine pigment 4501: A to E are Gaussian components from unconstrained least-squares refinement; spectrum recorded by fluorescence yield.

The contribution of sulfate to these S *K*-edge XANES spectra may be accounted for quantitatively by subtraction of the normalized spectrum for pigment 4504 calcined on platinum foil (5 in Fig. 2B). This spectrum has a flat background in the reduced sulfur region and an edge peak centered at 2481.7 eV. Using this method, there appears to be only 5% sulfate in pigment 4501 and 12% in pigment 4504. The proportion of sulfate increases progressively with more extensive heat treatment and exposure to air, and this coincides with a progressive fading of the blue color for open tube experiments (spectra 2 and 3 in Fig. 2A,C, and 3 and 4 in Fig. 2B) to colorless for platinum foil experiments.

The shoulder centered at about 2468.0 eV is a distinctive, and perhaps unique, feature of the present S *K*-edge XANES spectra, and represents an absorption peak below the energy threshold for reduced sulfur species (Fig. 2). This pre-peak is present ubiquitously in the spectra of all colored samples. It is most intense for the ultramarine blue and dark blue pigments (4501 and 4504, respectively), and decreases in intensity with decrease in the proportion of reduced sulfide and progressive fading of the blue coloration. Also, it is only weakly present in the spectra of mauve pigments (G5 and G6). Therefore, we assume that the pre-peak is associated with the S_3^- polysulfide radical anion chromophore. The extra electron on the radical anion is antibonding in character (π^*) and delocalized [5]. We speculate that this results in a structured energy band with an unoccupied region located in the forbidden energy gap.

The pre-peak in S *K*-edge XANES of ultramarine pigments is analogous to the familiar pre-peak in *K*-edge XANES spectra of high-spin transition-metal oxides [26–28], with the significant difference that the latter is associated with transition of the core electron to either 3*d* states or 4*p* states hybridized with 3*d* states, depending on coordination geometry [27]. The $1s \rightarrow 3d$ transition violates the atomic selection rules in the electric dipole approximation ($L = \pm 1$), but is weakly allowed by distortion of the stereochemical environment of the absorber metal atom for octahedral symmetry. On the other hand, the intense pre-peak of some tetrahedral metal oxide clusters appears to be attributable to transition to the *p* component of 3*d*–4*p* hybridized orbitals [27]. The $1s \rightarrow 3p(\pi^*)$ transition presently suggested for the ultramarine pigments is an allowed transition. This pre-peak is not related to iron and base-metal sulfide impurities in the ultramarine samples, because these are very low in abundance and their S *K*-edge peaks are located at somewhat higher energies [22]. To our knowledge, a similar pre-peak feature has not been observed previously for S *K*-edge XANES spectra [18,22], or for XANES spectra of other materials containing radical anions for that matter. This is not unexpected given the unusual stereochemical setting for the reduced sulfur species in the ultramarine cage which stabilizes an anomalously high concentration of polysulfide radical anions. More generally, pre-peaks are also uncommon in *K*-edge XANES spectra of ligand atoms, except where interaction with a transition metal is involved; e.g., the strong pre-peak in Cl *K*-edge XANES of titanium–TEMPO complexes is attributed to transition to unoccupied molecular orbitals formed by interaction of Cl 3*p* and Ti 3*d* orbitals [26].

Due to the presence of the pre-peak, S *K*-edge XANES spectra may be used to obtain an independent estimate of the proportion of cage sites occupied by the polysulfide radical anion in ultramarine blue pigments. For this purpose, it is assumed that S_3^- is the dominant radical anion species and that the area of the pre-peak defined by the Gaussian component A in the deconvoluted spectrum (Fig. 3) represents the absorption by the sulfur atom associated most closely with the extra electron, and the absorption by the two other sulfur atoms of the S_3^- cluster contributes to component B. Then the total area of the deconvoluted spectrum associated with the polysulfide radical anion is approximately 3xA. This estimate is independent of the actual extra-electron density as long as residence life times are relatively long compared with absorption events. There is uncertainty associated with possible difference in the absorption cross sections of the three sulfur atoms of S_3^- and the contribution of multiple scattering to components D and E. For the ultramarine blue pigments we assume that all of component D is multiple scattering and the proportion of sulfate in component E is given by the above spectrum subtraction method. With the added assumption that all of the cage sites are occupied by sulfur species, the occupancy of the polysulfide radical anion S_3^- is 33% in 4501 (intense ultramarine blue color) and 22% in 4504 (dark blue color). These estimates are in reasonable agreement with proportions of 43% [6] and 16% [12], respectively, obtained from calibrated EPR spectra for these two pigments.

The relationship between the intensity of blue coloration and proportion of total reduced sulfide (or sulfate) is not fully quantitative for the synthetic ultramarine pigments (Fig. 2) and is not directly transferable to lazurite and other sodalite-structure materials as well. This is well illustrated by comparing the S *K*-edge XANES spectra for lazurite from Afghanistan [15] and spectrum 4 of pigment 4504 (Figs. 2B, 4). Both of these XANES spectra are dominated by sulfate, yet lazurite is deep royal blue [15] and the calcined pigment is powder blue. On the other hand, the lazurite spectrum has a well defined pre-peak (Fig. 4), indicating about 1% occupancy of the cage sites by the polysulfide radical anion S_3^-, whereas the spectrum of the treated ultramarine has a very weak pre-peak, consistent with the difference in coloration of the two samples.

On an absolute basis, smaller amounts of the chromophore are required for a strong coloration in the mineral compared with synthetic ultramarines. This discrepancy may be related to the greater degree of crystal perfection of the natural product and more efficient coupling of the chromophore with the aluminosilicate framework. Powder X-ray diffraction patterns suggest that the present ultramarine pigments have poorly organized crystal structures, and their crystallinity does not significantly improve with heat treatments of short duration. We suggest that change in composition of cage constituents is effected by diffusion rather than recrystallization, with neutral sulfur and oxygen molecules being the most mobile and, at the very least, hopping between adjacent cages. Three different S_3^- radical anions were detected in the EPR study of Arieli et al. [12], all having open configurations and in relative amounts dependent on preparation conditions, particularly heat treatment. Given these points, the intensification of the strong blue color of ultramarine pigments on heating to high temperature in a closed system could be related more to annealing of the aluminosilicate framework than to continued reaction of the reduced sulfur species.

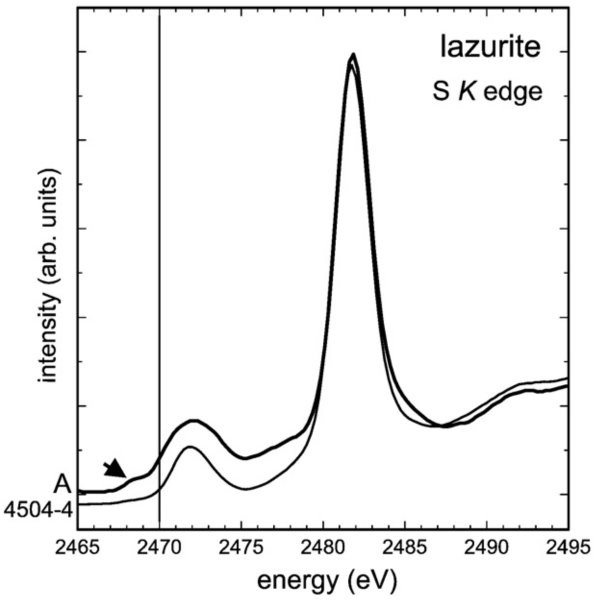

Fig. 4. Sulfur *K*-edge XANES spectrum for lazurite from Afghanistan (A) [15], compared with spectrum for experiment 4504-4 (Table 1; highlighted in Fig. 2B): arrow locates weak pre-peak associated with S_3^-; spectra recorded by fluorescence yield.

5. Conclusions

Sulfur *K*-edge XANES spectra provide an independent estimate of the proportion of cage sites occupied by the polysulfide radical anion S_3^- in ultramarine blue pigments. The XANES spectrum for the S_3^- chromophore is characterized by a pre-peak at about 2468.0 eV, which reflects the presence of the unpaired electron. The area of the pre-peak decreases systematically with decrease in reduced sulfur species and intensity of the blue coloration and increase in sulfate for ultramarine pigments and their heat-treated products. 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.

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