Sulfur K-edge XANES of Lazurite: Toward Determining the Provenance of Lapis Lazuli

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Abstract

Lazurite, the blue mineral found in lapis lazuli, may be a marker for the identification of provenance. Sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES) of lazurite from lapis lazuli of various locations, such as Afghanistan, Russia, Chile, the USA, Iran, Tajikistan, and Myanmar, is described. The XANES spectra reveal that several different sulfur chemistries exist within lazurite, attributed to contributions from multiple sulfur species. A peak at 2482.5 eV is attributed to sulfate; an envelope of peaks between 2470 and 2475 eV is attributed to polysulfide radicals, polysulfide dianions, neutral sulfur, and/or thiosulfate; and a peak at 2469.1 eV is attributed to the trisulfur and/or disulfur radical(s). Also, a peak of unknown origin arises at 2466.3 eV in several spectra. The spectral profile for the envelope of peaks (2470 to 2475 eV) varies between samples and in some instances, within a sample. Most notably, the studied samples from Chile display two distinct peaks near 2471.7 and 2473.5 eV with a local minimum at 2472.5 eV, unlike the most commonly observed pattern—that typically observed for samples from Afghanistan—with a single maximum intensity near 2472.5 eV. Other more subtle variations in this energy range also correlate with provenance at varying degrees.

Keywords: lapis lazuli; lazurite; ultramarine; XANES; sulfur; provenance

1.1 Introduction

Sought for its intense blue color, the semi-precious stone lapis lazuli has been highly valued since at least the 5th millennium B.C.E.^{1,2}, when it was formed into ornaments, jewelry, and seals³⁻⁵. Later, from the 7th century C.E., lapis lazuli was ground into a pigment (known as ultramarine) which continues to be a common painting material to this day^{4,6,7}. As one of the most desired and expensive artists' materials throughout history, there has long been interest in determining the provenance of natural lapis lazuli. It is commonly believed that the Sar-e-Sang deposit within the Badakhshan region of modern Afghanistan was the sole source of the rock in antiquity^{1,2,7,8}. However, more recent investigations have revealed several other potential sources of lapis lazuli within the Badakhshan province itself and in the greater Pamir mountains, which also could have been mined in the past^{8,9}. On a broader geographical scale, sources in Siberia near Lake Baikal, as well as sources in Chile and California, may account for contemporary trade and exploitation of this semi-precious stone⁸.

Lapis lazuli is composed of a suite of common minerals: pyrite (FeS₂), calcite (CaCO₃), diopside (MgCaSi₂O₆), wollastonite (CaSiO₃), and aluminosilicates of the sodalite group¹. Most notable among the sodalite group minerals is lazurite, the mineral responsible for the valued blue color of lapis lazuli (see Figure 1a)^{10,11}. The formula of lazurite has been described in many ways in the literature^{F1}—but may be approximated by (Na,Ca)₈(Al₆Si₆O₂₄)(SO₄,S,Cl)₂^{1,14}—where the cations and anions are trapped within an aluminosilicate framework. The lazurite anion composition is intermediate between two other members of the sodalite group, chloride-containing sodalite (Na₈(Al₆Si₆O₂₄)(Cl₂)) and sulfate-containing nosean (Na₈(Al₆Si₆O₂₄)(SO₄·H₂O))¹³. The most similar sodalite group member to lazurite is haüyne ((Na,Ca)₄₋₈(Al₆Si₆O₂₄)(SO₄,S,Cl)₁₋₂)¹³, and lazurite is often considered as a sulfide-rich haüyne⁸.

Much of the recent research on the provenance of lapis lazuli has focused on studying the presence and distribution of the minerals accessory to lazurite—including pyrite, calcite, diopside, and wollastonite—and their trace element chemistry with a variety of techniques¹⁵⁻²². Many of the accessory minerals, however, may be partially removed during the processing of lapis lazuli into the ultramarine pigment, lending motivation to the study of the blue-colored lazurite; pigment processing typically involves collecting blue lazurite particles that are washed from kneading the ground rock in wax within a dilute solution of potassium carbonate²³. To date, provenance studies of the lazurite phase of lapis lazuli have included investigating variation in the elemental composition^{16,21}, trace element distribution²¹, carbon dioxide content²⁴, and sulfur isotope ratios²⁵.

Here we examine the provenance of lapis lazuli—prior to studying processed materials such as pigments—by focusing specifically on the sulfur speciation within lazurite. Although the mechanism is not well understood, the variation in the color of lazurite is thought to arise from altered ratios of the sulfur species, with the blue color attributed to the trisulfur radical (S₃[•]) and deviations from

^{F1} Additional representations of the composition include e.g. the 'ideal' (Na₆Ca₂(Al₆Si₆O₂₄)S₂)¹⁰; the broader (Na,Ca)₈(Al,Si)₁₂O₂₄(S,SO₄)¹²; to the more inclusive Na₆Ca₂(Al₆Si₆O₂₄)(SO₄,S,S₂,S₃,Cl,OH)₂¹³

blue a result of disulfur (S_2^-) and tetrasulfur (S_4^-) radical species respectively contributing yellow and red to the overall color of lazurite²⁶⁻³⁸. While many researchers have demonstrated via a variety of measurements the existence and stabilized presence of the disulfur and trisulfur species within the lazurite structure, the actual occurrence of a tetrasulfur radical is less understood³⁵. Supported in part by the knowledge that the trisulfur radical is unstable in solution²⁷, the production of these sulfur species in general is proposed to occur during the rock formation^{29,30} rather than being already present in the geological environment. Following formation, the resulting aluminosilicate framework is inaccessible and does not support diffusion of the sulfur species^{29,30}. Together, these observations suggest that sulfur speciation within lazurite is defined upon its formation. Such geological conditions may, in turn, explain the variation in the color of the mineral and/or relate to geographical provenance.

This study explores the extent to which the sulfur speciation—and by inference geological formation conditions and geographical provenance—is measurable by sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES). Sensitive to the formal oxidation state and coordination chemistry of sulfur³⁹, sulfur K-edge XANES is ideal for probing the sulfur chemistry of lazurite and has been previously employed in lazurite studies by Tauson *et al.*⁴⁰, Fleet *et al.*^{41,42}, and Goettlicher *et al.*¹⁴. Because of the sensitivity of XANES to transitions from all of the present sulfur species, resultant data strongly complements recent multi-technique studies of lapis lazuli and ultramarine^{15-22,24-34,37-38,40}. The technique is also particularly attractive for use in the field of cultural heritage as it is non-destructive and requires little to no sampling; however, it requires a helium (or vacuum) chamber with fixed incident beam and detector geometries, limiting the size/shape of objects that can be examined *in-situ*. Using sulfur K-edge XANES, variation of the sulfur environment within the aluminosilicate framework of lazurite is studied on thirty-eight samples from diverse geographical locations. Reporting on identifiable differences observed within the lazurite spectra, we provide the most comprehensive sulfur K-edge XANES study of lazurite to date.

1.2 Materials and methods

1.2.1 Sample collection and preparation

Lapis lazuli rock was obtained from several institutions for which a provenance was recorded at the time of specimen collection (34 specimens in total, Table 1); 4 specimens of unknown provenance were also examined. Most specimens were sampled and mounted in methyl methacrylate resin or epoxy resin (Technovit 2000 LC or Beuhler Epothin epoxy resin) and polished to expose the sample. Sample surfaces were dry-polished using Micro-mesh polishing papers from coarsest to finest grit and cleaned of residue with a soft buffing pad, which is a typical approach in conservation science and geochemistry (making the approach applicable for extension to paint samples). Specimens obtained from The Field Museum of Natural History were not sampled but rather analyzed directly on a polished face of the rock. All mounted samples were examined under visible light (crossed polarizing filters) and by ultraviolet fluorescence (Leica DM4000 microscope, Diagnostic Instruments ‘Flex’ camera) prior to XANES measurements. An example image of a lapis lazuli specimen and a prepared sample, along with a microscope image of an exposed surface, is presented in Figure 1a.

Reference powders were used as-received. Precipitated sulfur powder (S_8); sodium bisulfite, granular, mixed with sodium metabisulfite ($NaHSO_3$, with $Na_2S_2O_5$); and sodium thiosulfate pentahydrate, crystal ($Na_2S_2O_3 \cdot 5H_2O$) were obtained from Baker Chemicals. Sodium sulfite (Na_2SO_3) was obtained from Lauder Chemical. Ammonium sulfamate (98 %) ($NH_4SO_3NH_2$); sodium hydrosulfite ($Na_2S_2O_4$); sodium sulfate decahydrate, crystal ($Na_2SO_4 \cdot 10H_2O$); and tin(II)sulfide ($Sn(II)S$) were obtained from Sigma Aldrich. Additional reference samples were acquired from rock specimens of gypsum (Mexico) and pyrite (Zacatecas, Mexico) from Ward’s Natural Science Establishment, Inc. Lastly, samples were obtained from rock specimens of sodalite (CIT-6314, Ontario, Canada) and haüyne (H-2518, Albano, Rome, Italy) from the California Institute of Technology. All reference materials were prepared in Technovit 2000 LC as described above.

1.2.2 Synchrotron-based measurements

At the Stanford Synchrotron Radiation Lightsource (SSRL), XANES spectra and X-ray fluorescence (XRF) maps were collected using beam line 14-3. Within a helium chamber, samples were mounted at 45° to both the incident X-ray beam and the detector. X-ray incident energies were selected using a Si (111) double crystal monochromator. The X-ray beam was focused to a size of approximately $5 \times 5 \mu m$ using Kirkpatrick-Baez mirrors imaging a secondary source at the front of the experimental hutch. The flux in the focused spot was approximately 2×10^{10} photons s^{-1} . A vortex silicon drift detector (Hitachi USA High Technologies) was used to monitor the fluorescence signal for all measurements.

X-ray fluorescence maps were acquired for Al, Si, and S with an incident X-ray energy of 2500 eV while rastering the X-ray beam across the samples using step sizes from 25 to 50 μm . These maps were used to locate the sample and target the beam onto lazurite phases for XANES analysis. Spectra were collected at the sulfur K-edge with energies swept from 2460 to 2540 eV (with an energy resolution of 0.2 eV from 2460 to 2500 eV and 2 eV from 2500 to 2540 eV) in fluorescence mode. Approximately 10 spectra were obtained at different positions on each sample (Table 1). In addition, radiation damage was monitored on a few samples by acquiring several spectra at a fixed position; no substantial changes were observed in the spectra nor was sulfate reduced to sulfite (i.e. a decrease and increase in the sulfate peak and sulfite peak, respectively, was not apparent), indicating the samples were stable on the timescale of our experiment. Spectra were also obtained for the reference materials (a total of 51 spectra on 13 reference samples).

General data processing was performed with SixPack software using standard procedures⁴³, including minor smoothing of some spectra and normalizing the intensity of the pre-edge to 0 AU and the post-edge to 1 AU. The reference spectra of gypsum and haiyue were used for energy calibration, setting the value of the sulfate peak to 2482.5 eV, as referenced in the ESRF database⁴⁴. The averaged spectra per sample were utilized to improve the signal to noise ratio and allow the overall variation in spectral shape between samples to be examined, while minimizing the influence of spectral intensity from spectrum to spectrum; the individual (non-averaged) spectra from each sample and the corresponding Principal Component Analysis (PCA) performed on these spectral data are shown in Supporting Information (SI-1 and SI-2, respectively). Furthermore, the number of possible contributions from, and coordinations of, sulfur species, as will be discussed below, complicates the potential of assisting comparisons with peak fitting. We direct the reader to a report by Manceau *et al.*⁴⁵ for information on the complexities of fitting peaks in sulfur K-edge XANES spectra.

1.3 Results and Discussion

The XANES spectrum of lazurite typically displays four distinct features. As shown in the average XANES spectrum of all samples in Figure 1b, there is a major peak centered at 2482.5 eV (feature 1), a broad envelope of peaks between 2470 and 2475 eV (feature 2), a minor peak at 2469.1 eV (feature 3), and an occasional minor peak at 2466.3 eV (feature 4, inset image). At the lower energies (features 2-4), a second derivative of the spectrum (solid trace, Figure 1c) shows that feature 2 is composed of multiple peaks, the most distinguishable at 2470.9, 2471.7, 2472.5, 2473.5, and 2474.1 eV (labeled A-E).

Common to all lazurite spectra is the peak at 2482.5 eV (feature 1, Figure 1b), associated with S^{6+} of sulfate (SO_4^{2-}) in sulfate-containing reference materials (Figure 2) and the lazurite structure^{14,40}. Observed in all individual lazurite spectra acquired in this study, this feature displays a consistent shape (always with highest intensity, which varies some between spectra). As a consequence, this peak will not be considered in the following discussion as a diagnostic marker of provenance, although its constant presence indicates that sulfate is an important component of the overall chemistry for all lazurite samples. Also common to all lazurite spectra is a subtle baseline feature between 2475 and 2480 eV at the rising edge (Figure 1b). This feature may be attributed to multiple scattering events⁴¹ as well as contributions from sodium sulfite near 2478 eV⁴⁴ and Figure 2) and/or the trisulfur radical between 2475 and 2477 eV, as observed in a simulated spectrum by Pascal and coworkers (see discussion below)⁴⁶.

Over the remaining energies, from 2465 to 2475 eV, the spectral shape observed in Figure 1b is not consistent between spectra, although features are always present. Rather, notable variation is observed from sample to sample, implying different observable sulfur chemistries. The average spectra from each of the 38 lazurite samples were visually grouped based on major identifiable differences in spectral shape, ignoring overall intensity, as exhibited in Figure 3 (a-e); those spectra dissimilar to others are shown in Figure 3f. Comparing the data in these groups to the peak positions ascribed to features 2-4 in Figure 1c allows the observed variation between groups—and its relation to provenance—to be described.

While comparing the average spectra of each sample allows the determination of gross differences in the spectral pattern of the lazurite samples, and the regions from which they come, such averages may mask variations that exist at the level of the individual specimen. Figure 4 illustrates individual spectra from representative samples from this dataset displaying both low and high variability within a sample. With the exception of noise variation, it should be noted that most samples display fairly low variability. The spectral profiles in the low in-sample variability example, RA1 (Figure 4a), are fairly consistent for each spectrum; such low variability was commonly observed across samples from all regions. High in-sample variability, on the other hand, was less frequently observed, but again, from all regions. An example of such is demonstrated by RNT11 in Figure 4b, where more than one spectral pattern was detected. Instances of in-sample variability may in itself provide a unique signature for a region, however, many more than 10 spectra per sample would be needed to investigate this potential. Individual spectra from the remaining samples are given in the Supporting Information (SI-1). In-sample variability is easily visualized by Principal Component Analysis (PCA) performed on all of the (individual, non-averaged) spectral data also shown in the Supporting Information (SI-2). Compared to the average spectra, the PCA results provide no further guidance for clustering the samples into groups; in general, the PCA analysis supports the visual clustering, as described in SI-2.

1.3.1 Geographical Variation

Returning to Figure 3, the spectral profiles shown in Group 1 (Figure 3a) represent those most commonly observed within this dataset, hence the similarity of each spectrum to the average spectrum in Figure 1b. The profiles are characterized by the distinct peak at 2472.5 eV, fairly symmetrical envelope (2470 to 2475 eV), and relatively intense peak at 2469.1 eV. Of the samples exhibiting this spectral shape, four (lower most traces: RAF, RAT16, RJ, and RA5) show much lower overall intensities with respect to sulfate, which may point to a lower overall reduced sulfur content; interestingly, the sulfate peaks of these samples have the highest intensities of all the samples (see Supporting Information for an example, SI-3). The distinction may constitute a separate, though related, grouping if the relation of the envelope species to sulfate is dependent upon geological environment.

Most (nine of fourteen) of the samples from Afghanistan fall within Group 1 (blue traces, Figure 3a), suggesting that this pattern will most likely be observed for a sample from Afghanistan; a similar pattern was observed in work by Goettlicher *et al.* on lazurite¹⁴.

This chemistry, however, is not exclusive to Afghanistan: similar spectra are also observed from samples from the USA (one of five samples, RUH, pink trace), Russia (one of four samples, RRF, green trace, also observed by Goettlicher ¹⁴), and Tajikistan (the only sample, RJ, orange trace). The last of these in particular is unsurprising as Tajikistan may not be geographically distinguishable from Afghanistan: the known source of lapis lazuli in Tajikistan is the Pamir Mountains, which extend into Badakhshan, the source of the samples from Afghanistan. Indeed, the grouping of the sample from Tajikistan with those from Afghanistan may indicate that the sulfur chemistry is common to samples from a broad Badakhshan geographical region. Because Afghanistan is the only region with such a high percentage of its total samples displaying this spectrum, it may be hypothesized that samples RNT11 and RNT6, which have no recorded provenance but share similar spectral profiles to others in Group 1 (grey traces, Figure 3a), also originate from Afghanistan or the broader Badakhshan region.

Representing many fewer spectra is Group 2 (Figure 3b). While similar to Group 1 with relatively intense peaks at 2469.1 and 2472.5 eV, the spectra of Group 2 also have strong contributions at 2470.9, 2471.7, 2473.5, and 2474.1 eV, resulting in a flattened profile across the envelope. To our knowledge, this spectral shape has not previously been reported for lazurite.

Of the samples in Group 2, two are from Afghanistan and one is from Iran (blue and purple traces, respectively, Figure 3b). This flattened profile may stem from minor geographical differences. Of the samples for which the specific mine location is known (those provided by GeoVision, Inc., Table 1), RAM5 (Group 2) originates from a different mine from RAJD (Group 1). With respect to the remaining sample, Iran is not only highly disputed as a source of lapis lazuli ⁹ (i.e. the record of RIF2 having an Iranian source may be inaccurate due to human error when the stone was collected) but, if the source exists, it would be closer to Afghanistan geographically than any other well-known lapis lazuli source. These results reveal that the XANES profiles of both Groups 1 and 2, and the chemistries they represent, may be indicative of the broader Badakhshan region with the samples originating primarily from Afghanistan, Tajikistan, or (possibly) Iran.

The spectral profile exhibited by those samples in Group 3 (Figure 3c) is the most unique and has not previously been reported for lazurite. Rather than containing a maximum intensity near 2472.5 eV like Group 1, the spectra have a local minimum at this energy. The envelopes of each sample in Group 3 instead contain two local maxima near 2471.7 and 2473.5 eV. Further, a shoulder within the envelope at 2470.9 eV is frequently observed along with a peak at 2469.1 eV at relatively low intensity compared to the spectra in Group 1 and 2. Lastly, a peak at 2466.3 eV (see inset, Figure 1b) is present in all spectra in Group 3 unlike its more sporadic appearance in the spectra of other samples.

Notably, all seven spectra of samples from Chile (red traces, Figure 3c) fall within Group 3. In addition, a sample from an unknown location (RNT17, grey trace) displays a very similar spectral shape to that of samples from Chile, especially RCT9 and RCF7. Taken together, these data imply that lazurite in Chilean lapis lazuli will typically produce a XANES spectrum of the shape presented in Figure 3c, and suggests that RNT17 is from Chile. These data strengthen previous observations that the mineralogy of lapis lazuli from Chile is distinguishable from that from other regions, containing potassium-poor lazurite ²¹ and the accessory mineral wollastonite (CaSiO_3) rather than diopside ($\text{MgCaSi}_2\text{O}_6$) ^{17,F2}; the related unique XANES profile suggests that the chemistry of formation, and thus the sulfur speciation within the lazurite aluminosilicate framework, is also different from that found in other locations around the globe.

Easily distinguished from those already described, the spectra in Group 4 (Figure 3d) have a maximum intensity near 2472.9-2473.1, which is slightly higher in energy than that of Group 1, producing a more asymmetrical appearance of the envelope overall. Also, the peak at the maximum is broader and more rounded, consistent with additional contributions near both 2472.5 and 2473.5 eV. Much like Groups 1 and 2, however, a fairly strong contribution at 2469.1 eV relative to the envelope is observed. Further, like Group 1, there appear to be variations in overall intensity, with that of RRH (Russia, green trace) much lower than the others. Lastly, the profiles have a distinct shoulder at 2470.9 eV, most prominent in RMT (Myanmar, black trace) and RRT (Russia, green trace), which may signify a slightly different chemistry and perhaps define a sub-group. The majority of spectra from Russian samples (three of four) fall within this group, implying a relation of this spectral shape to samples from Russia. As with the other groups, however, samples from other locations occasionally display this spectral shape—one from Afghanistan (RAF, blue trace), one from Iran (RIF4, purple trace), and one from Myanmar (RMT, black trace)—suggestive of similar chemistries.

The spectra in Group 5 (Figure 3e) appear to be intermediate between Groups 1, 3, and 4. For instance, all show a maximum at 2472.7 eV (the maxima of Groups 1 and 4 are at 2472.5 and 2473.0 ± 0.1 eV, respectively), a distinct shoulder at 2470.9 eV of variable intensity (similar to the spectra in Group 4), and a weak peak at 2469.1 eV (most similar to those in Group 3). These distinctions together demonstrate the complexity of defining common spectral profiles for a heterogeneous mineral. It is noteworthy, however, that the spectra of Group 5 represent three of the five samples from the USA, and most significantly, the three samples specifically from California, suggesting a relation between this intermediate chemistry and the formation conditions of Californian lapis lazuli.

^{F2} Environmental SEM-EDS analysis (FEI-Phillips XL30 ESEM-FEG/Oxford INCA EDS) of the samples from Chile and RNT17, all sharing comparable XANES profiles, reveals similarly low magnesium content, implying mineralogy like those previously reported.

Finally, there exist a few spectra presented in Figure 3f that are not well-described by these five groups nor are they all similar to one another. Of the spectra, RUT8-1 (the USA, pink trace) and RAT17 (Afghanistan, blue trace) are most similar to one another whereas RAH (Afghanistan, blue trace) and RN1 (unknown provenance, grey trace) have different shapes, none displaying a strong correlation between shape and region.

Overall, the variation observed from the averaged spectra in Figure 3 reveals potential correlations of the sulfur XANES spectral shape to geographical origin for samples of lapis lazuli, with particular shapes favored by samples of a given region. Such correlations are strongest for samples from Chile and Afghanistan, while those from other regions appear to be less robust. Strongly supported by the number of specimens examined, samples from Afghanistan and Chile most often display spectral shapes categorized as Groups 1 or 2 and Group 3, respectively. Similarly, although to a lesser extent, a majority of samples from Russia and the USA are categorized as Groups 4 and 5, respectively. Such correlation between the spectral profile and geographical region of a sample implies that certain geological conditions are favored in particular regions producing the different observed chemistries of these samples.

1.3.2 Peak Assignments

To better understand the relation of sulfur chemistry to provenance, and its potential relation to geological conditions of formation, it is necessary to determine which species are contributing to the peaks within the lazurite spectra observed in the groups described above. Because the lazurite aluminosilicate framework is thought to contain a variety of possible sulfur species and chemical environments, the peaks contributing to the spectra in Figure 3 may arise from several different sulfur transitions (sulfur K-edge pre-edge absorptions are attributed to electronic transitions from the sulfur 1s orbital to unoccupied p-type molecular orbitals, influenced by both oxidation state and coordination⁴⁷). Previous lazurite studies have proposed probable sulfur species, including contributions from polysulfides (S_x^{2-}), polysulfide radicals ($S_x^{\cdot-}$), and other sulfur species (e.g. monosulfide, sulfite, thiosulfate, and elemental sulfur)^{14,40-42}. Proposed XANES peak assignments for these species are summarized in the Supporting Information (SI-4).

Related, Pascal and coworkers⁴⁶ recently reported simulations of sulfur K-edge spectra using density functional theory (DFT) driven calculations for poly-sulfur species, the details of which are also summarized in SI-4; the calibration of these values were made relative to the report's reference of the work by Fleet and coworkers. Most significantly, Pascal *et al.* demonstrate that the number of sulfur atoms and the location of the atoms within the molecule (i.e. terminal or internal) play a significant role in the position and number of peaks in the resulting XANES spectrum regardless of charge state, revealing that assignments are more complex than a single peak per sulfur species and vice versa. XANES is also sensitive to coordination, further complicating possible peak positions for a given species. Extrapolating from the literature assignments and experimentally determined peak assignments from reference materials (Figure 2), we propose the species contributions listed in Table 2 for the spectral features observed in natural lazurite.

The simplest variation observed in the spectra of Figure 3 is that of the peak at 2469.1 eV, assigned to either the trisulfur radical ($S_3^{\cdot-}$) and/or the disulfur radical ($S_2^{\cdot-}$) (Table 2). This peak is attributed by Fleet to the sulfur atom associated with the extra electron⁴¹. Pascal and coworkers ascribe this peak in the simulated spectrum of $S_3^{\cdot-}$ to the 1s to π^* transition in the terminal sulfur atoms; this peak is also present in the simulated spectrum of $S_2^{\cdot-}$ ⁴⁶. In the lazurite spectra of Figure 3, the intensity of the peak at 2469.1 eV with respect to the envelope (2470 to 2475 eV) is either relatively high, as seen in the spectra of Groups 1, 2, and 4 (Figures 3a, 3b, and 3d), or relatively low, as seen in the spectra of Groups 3 and 5 (Figures 3c and 3e), suggesting that the latter groups—those containing the majority of spectra from Chile and the USA—have less contribution from $S_3^{\cdot-}/S_2^{\cdot-}$ relative to other sulfur species than other groups.

The peaks within the envelope can also be described in part by $S_3^{\cdot-}$ and $S_2^{\cdot-}$. The simulations of Pascal *et al.* suggest that $S_3^{\cdot-}$ contributes to experimental peaks near 2471.7, 2473.5, and 2474.1 eV, while $S_2^{\cdot-}$ contributes to peaks near 2471.7 and 2472.5 eV (Table 2). In the simulated spectrum of $S_3^{\cdot-}$, a peak at 2471.8 eV is ascribed to the 1s to π^* transition of the internal sulfur atom and is significantly higher in intensity than that at 2469.1 eV, consistent with the general spectral patterns observed in Figure 3; the peak at 2469.1 eV is proposed to be weaker due to valence electronic screening of the 1s core electron, the availability of only one π^* orbital, and the contribution of two transitions to the peak near 2471.7 eV⁴⁶. Similarly, Fleet *et al.* suggests contributions from the other two sulfur atoms of $S_3^{\cdot-}$ to a peak at 2471.4 eV, also at a higher intensity than the peak at 2469.1 eV⁴¹. Intermediate in intensity between these two peaks are the simulated peaks at 2473.5 and 2474.0 eV (see SI-4 for proposed transitions), again consistent with the general shape of the lazurite spectra⁴⁶. In contrast, however, the simulated results for $S_2^{\cdot-}$ reveal nearly equal intensities of the peak at 2469.1 and that near 2471.7 eV, both of which are more intense than that at 2472.5 eV⁴⁶. Consequently, based on the relative intensities proposed by Pascal *et al.*, any contribution of $S_2^{\cdot-}$ at 2471.7 and 2472.5 eV in the experimental data shown here, therefore, must be minor for the peak at 2469.1 eV to retain its relative intensity to the envelope. The contributions from $S_3^{\cdot-}$ at its respective peaks, on the other hand, are consistent with the general shape of any lazurite spectrum in Figure 3.

Although the proposed assignments and relative intensities of $S_3^{\cdot-}$ match well with the overall spectral shape of the lazurite spectra, it is necessary that other species also contribute to the peaks at 2473.5 and 2474.1 eV as the intensities at these energies are generally equal to or higher than that at 2471.7 eV in the spectra of Figure 3, unlike those proposed in the simulated spectrum. Most notably, the spectra of Groups 3, 4, and 5 (Figures 3c, 3d, and 3e) show the most intense peaks at 2473.5 eV relative to those at 2471.7 and 2474.1 eV implying that $S_3^{\cdot-}$ cannot solely be responsible. Other species proposed in the literature (SI-4) near 2473.5 eV are the

tetrasulfur dianion (S_4^{2-}) and tetrasulfur radical ($S_4^{\cdot-}$), and near 2474.1 eV are the trisulfur dianion (S_3^{2-}) and tetrasulfur radical ($S_4^{\cdot-}$), any of which may contribute at varying degrees to all of the spectra. Another distinguishing aspect among the spectra is the contribution at 2472.5 eV. While there exists a clear maximum at this energy for Group 1 (Figure 3a), there is a local minimum observed in Group 3 (Figure 3c). From the proposed literature, the only polysulfide species near this energy are $S_2^{\cdot-}$ (at 2472.5 eV) and $S_4^{\cdot-}$ (at 2472.9). As just discussed, the presence of the former cannot solely give rise to the experimentally-observed relative intensity. The presence of the latter, on the other hand, is disputed³⁵. The presence and absence of this peak may be attributed to variations in neutral sulfur, as the reference sulfur, S_8 , in this report contains a peak very near 2472.5 eV (Figure 2), consistent with reported energies^{44,46}. As a result, it may be inferred that lazurite from Chile, those with spectra in Group 3 (Figure 3c), contain less neutral sulfur relative to other species than that from other regions.

The remaining peak in the envelope to be assigned is that at 2470.9 eV. Unlike the other peaks in Table 2, there is no obvious assignment either from the literature nor reference materials for this feature. The closest, relevant assignments come from the simulated spectra⁴⁶ of S_3^{2-} , $S_4^{\cdot-}$, and S_4^{2-} . Because the relative intensities of the peaks for each of these species can reasonably be proposed to occur within the envelope, further proposals regarding which species may be more favorable for this peak cannot be made. In general, however, variation in the relative intensity of this peak is observed among the spectra in Figure 3, having most prominent contributions in the spectra of Group 2 (Figure 3b) and the upper two spectra of Group 4 (RMT and RRT, Figure 3d).

Remaining differences in the spectral shapes of the envelope may be described by the minor contributions from the species previously discussed or other sulfur species at the energies shown in Table 2, for instance, thiosulfate^{35,40}, which may contribute to the envelope at 2471.7 eV⁴⁴, the exact energy of the lazurite feature that may also result from $S_3^{\cdot-}$; in Figure 2, our reference material from thiosulfate displays a similar peak at 2472.1 eV. It should be noted that the contribution of the mineral pyrite, with a peak at 2472.1 eV (consistent with the ESRF database⁴⁴) in Figure 2, to each lazurite spectrum is assumed here to be negligible because it typically overwhelms any lazurite spectrum to which it contributes, as was observed in a handful of spectra collected from suspected phases of lazurite (see SI-5a and SI-5b for comparison).

A final peak observed to vary among the spectra of lazurite is that observed at 2466.3 eV (feature 4, inset Figure 1b). To our knowledge, this peak has not previously been reported for lazurite, although a similar pre-edge peak has been observed in both the spectrum of hackmanite¹⁴ and that of synthetic silicate glasses^{48,49}. Hackmanite, $(Na_8(AlSiO_4)_6Cl_{2-y-z}(S_x^{2-})_y\Box_z)$, is similar to lazurite and contains XANES features much like features 2 and 3 in Figure 1b, however, shifted to higher energies¹⁴. Despite this, feature 4 is observed at the same energy in both minerals, implying that the sulfur species, or environment, responsible for this peak is different from that for the other peaks. As mentioned earlier, this peak only consistently appears in the spectra of Group 3 (Figure 3c), further emphasizing the unique chemistry of lazurite from Chile.

1.3.3 Uncommon Spectrum

Not represented by the averaged data in Figure 3, a unique spectrum exemplified in SI-5c was detected in five samples, RUT8, RAH, RCH, RCT9, and RCT7. The spectrum displays very prominent peaks near 2466.3, 2471.7, 2473.5, and 2474.1 eV. Of note, this spectral pattern shows not only a very weak peak at 2469.1 eV ($S_3^{\cdot-}$ and/or $S_2^{\cdot-}$) but also a prominent peak at 2466.3 eV (unknown species), suggesting that the presence of these polysulfide radicals is independent of the species responsible for the peak at 2466.3 eV. In addition, given the very low intensity of the peak at 2469.1 eV relative to the peak near 2471.7 eV, this spectrum provides evidence for the presence of thiosulfate (Figure 2), the reference spectrum of which is re-shown in SI-5d for comparison; other possible minor contributions at 2471.7 eV may include $S_2^{\cdot-}$, S_3^{2-} , and/or the disulfur dianion (S_2^{2-}). From the narrow FWHM, it can be inferred that this peak is not, for instance, a result of pyrite contributions at 2472.1 eV. While only detected in five samples, this spectral pattern occurred more than once in RAH and RUT8; in the case of RUT8, in which the spectrum was most frequently observed, the average plotted in Figure 3f was performed solely on the remaining spectra (denoted RUT8-1). Furthermore, the samples in which this spectrum was observed were collected from three separate regions (the USA, Afghanistan, and Chile) and three different institutions. Because of the reproducibility of the spectrum, we infer that it is a true spectral pattern, but notably, one that does not become apparent when data from each sample is averaged. Consequently, this pattern (and corresponding chemistry) is likely less common than those shown in Figure 3.

Despite the complexity of assigning species, the data support the presence of the trisulfur radical and suggest higher contributions of the trisulfur radical relative to the disulfur radical in the lazurite spectra. In addition, the varying spectral profiles indicate variation in the sulfur speciation that may involve the di-, tri-, and tetra- sulfur dianions and radicals along with neutral sulfur and thiosulfate. With a grasp of the contributing sulfur chemistries, the relation of the variation in these chemistries with geography is better understood and suggests differences in geological environments.

1.4 Conclusions

The data presented in this study emphasize the need to characterize the heterogeneity within lazurite. Such heterogeneity is not surprising given the number of possible sulfur species—and the number of possible XANES features contributed by each species—within the envelope and the complex interdependencies they each may have with one another. Understanding the heterogeneous nature

of lazurite will ultimately help describe the geological conditions of formation and possibly the cause of color variation of this mineral. The study of lazurite with sulfur K-edge XANES demonstrates that sulfur chemistry of lazurite is not only variable but measurable and that the observed pre-edge variations potentially correlate to the region from which the lapis lazuli originated.

Consistent with previous reports, all averaged XANES spectra of lazurite show a peak at 2469.1 eV indicative of the presence of the trisulfur radical, of which the relative contribution appears to be higher than that of the disulfur radical, consistent with the attributions of the former to the blue color. In general, most spectra also have maxima near 2472.5 eV, most likely a result of the neutral sulfur species S_8 , but with subtle variation pointing to differences in origin. The spectral variation observed between samples further suggests narrower geographical regions as suggested by the three notable pre-edge patterns observed for samples from Afghanistan—a high intensity profile with a maximum at 2472.5 eV, a low intensity profile with a maximum at 2472.5 eV, and a flattened profile. As compared to those from other regions, the XANES spectra of samples from Chile display the most consistent and diagnostic spectral profile, with relatively significant contributions near 2471.7 and 2473.5 eV from likely the trisulfur radical and either the tetrasulfur dianion and/or the tetrasulfur radical, respectively. The distinction of samples from Chile using sulfur speciation extends similar distinguishing observations with respect to overall mineralogy^{17,21}, implying a unique geological environment at Chilean deposits. Finally, a distinct occasional spectral pattern may provide evidence for the presence of thiosulfate within lazurite or a related lazurite-like mineral.

Although inherent heterogeneity, and the necessary reliance on the accuracy of provenance documentation, may complicate analyses and interpretation for natural minerals such as lapis lazuli, the results presented here show the promise of K-edge XANES for aiding our geological understanding of lapis lazuli formation and in turn, how such formation relates to questions of provenance. An improved understanding of the natural variation of sulfur chemistry in lazurite also provides an avenue to elucidating the chemical modification that lazurite may undergo when processed into ultramarine blue pigments, and ultimately describing the provenance, color, and stability of those pigments in works of art.

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Table 1. Details concerning each sample from lapis lazuli specimens. In the “Sample” column, the first letter refers to rock (R); the second letter refers to the region: Afghanistan (A), Chile (C), Russia (R), the USA (U), Tajikistan (J), Iran (I), Myanmar (M), or Unknown (N); and the remaining characters are unique identifiers to the samples.

Sample	# of XANES spectra	Specimen identifier/ Accession number	Region	Additional information	Provider*
RA1	11	--	Afghanistan	--	1
RA2	10	--	Afghanistan	--	1
RA3	10	RAWI 18609	Afghanistan	--	2
RA4	10	RAWI 18610	Afghanistan	--	2
RA5	11	--	Afghanistan	--	1
RAH	14	HM91015	Afghanistan	--	3
RAF	6	FM13105	Afghanistan	--	4
RAT8	10	CIT8860	Afghanistan	Badakhshan	5
RAT16	11	CIT16826	Afghanistan	Sar-e-Sang, Kosha Valley, Badakhshan Province	5
RAT17	11	CIT17477	Afghanistan	Sar-e-Sang mining district	5
RAM4	12	--	Afghanistan	Mine 4	1
RAM5	12	--	Afghanistan	Mine 5	1
RAJD	11	--	Afghanistan	Mine Jan Dook	1
RADZ	11	--	Afghanistan	Mine Dare Zo	1
RCF2	5	FM2653	Chile	--	4
RCF7	3	FM7950	Chile	--	4
RCH	11	HM138939	Chile	--	3
RCT2	13	CIT2251B	Chile	Andes of Ovalle	5
RCT8	10	CIT8861	Chile	Andes of Ovalle	5
RCT9	10	CIT9349	Chile	Andes of Ovalle	5
RCT7	10	H750	Chile	Andes of Ovalle, Coquimbo	5
RR1	10	Siber1	Russia	--	2
RRH	11	HM110624	Russia	--	3
RRF	6	FM2649	Russia	Siberia	4
RRT	10	H3125	Russia	Transbaikalia, Siberia	5
RUT2	10	CIT2250	USA	San Antonio Canyon, San Gabriel Mountains, Los Angeles County	5
RUT8	11	CIT8301	USA	Nevada, Clark Co?	5
RUT15	10	CIT15577	USA	San Antonio Canyon, San Bernardino County, California	5
RUT3	8	H34	USA	Cascade Canyon, San Bernardino County, California	5
RUH	8	HM106245	USA	Colorado	3
RJ	10	--	Tajikistan	--	1
RIF4	5	FM4882	Iran	--	4
RIF2	6	FM2657	Iran	--	4
RMT	11	CIT16500	Myanmar	Daltaw, Mogok	5
RNT17	10	CIT17966	Unknown	--	5
RNT11	10	CIT11358	Unknown	(Chile?)	5
RNT6	11	CIT6505	Unknown	--	5
RN1	10	--	Unknown	--	2

* 1. Gary Bowersox, GeoVision Inc. (Honolulu, HI); 2. Getty Conservation Institute reference collection (Los Angeles, CA); 3. Mineralogical Museum, Harvard University (Cambridge, MA); 4. The Field Museum of Natural History (Chicago, IL) 5. Professor George Rossman, California Institute of Technology, Caltech Mineral Collection (Pasadena, CA).

Table 2. Possible contributing species to the XANES spectra of lazurite at the energies within parentheses.

Feature	Peak position (from Figure 1), eV	Possible contributing species
1	2482.5	Sulfate (2482.5 eV)
--	2475 to 2480	Multiple scattering events Na_2SO_3 (2478.0 eV)* $\text{S}_3^{\cdot-}$ (2474 to 2477 eV)
2E	2474.1	$\text{S}_4^{\cdot-}$ (2474.1 eV) S_3^{2-} (2474.0 eV) $\text{S}_3^{\cdot-}$ (2474.0 eV)
2D	2473.5	S_4^{2-} (2473.5 eV) $\text{S}_4^{\cdot-}$ (2473.5 eV) $\text{S}_3^{\cdot-}$ (2473.5 eV)
2C	2472.5	$\text{S}_4^{\cdot-}$ (2472.9 eV) S (2472.5 eV)* $\text{S}_2^{\cdot-}$ (2472.5 eV)
2B	2471.7	S_3^{2-} (2471.9 eV) $\text{S}_3^{\cdot-}$ (2471.8 eV), broad $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2471.7 eV)* S_2^{2-} (2471.5 eV) $\text{S}_2^{\cdot-}$ (2471.5 eV) S_4^{2-} (2471.3 eV) $\text{S}_4^{\cdot-}$ (2471.3 eV)
2A	2470.9	S_4^{2-} (2471.3 eV) $\text{S}_4^{\cdot-}$ (2471.3 eV) S_3^{2-} (2470.4 eV) $\text{S}_4^{\cdot-}$ (2470.2 eV), shoulder
3	2469.1	$\text{S}_3^{\cdot-}$ (2469.1 eV) $\text{S}_2^{\cdot-}$ (2469.0 eV)
4	2466.3	unknown

* Species for which energies were taken from the ESRF database [44]; all other energies are from the lazurite XANES literature [41, 46].

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Figure captions for:

Sulfur K-edge XANES of Lazurite: Toward Determining the Provenance of Lapis Lazuli

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Figure 1. (a) Clockwise, photographs of whole rock, mounted sample, and polished sample (under microscope). (b) Averaged XANES spectrum of all sample spectra (39 samples in total; each sample spectrum is the average of the individual spectra acquired on such sample) from lazurite in lapis lazuli specimens; inset shows details of lower energy portion of the spectrum. (c) Second derivative (solid curve) of averaged spectrum (dashed curve).

Figure 2. XANES spectra of sulfur-containing reference materials. All were acquired from purchased powders except those marked with an asterisk. All spectra are offset for clarity.

Figure 3. For each lazurite sample, the averaged XANES spectrum of all individual spectra for samples from Afghanistan (blue), Chile (red), Russia (green), the USA (pink), Tajikistan (orange), Iran (purple), Myanmar (black), and unknown locations (grey) grouped by common spectral shape in the energy range of 2465 to 2475 eV. The vertical dashed lines correspond to those energies marked in Figure 1c. All spectra are offset for clarity. Refer to Table 1 for details concerning each sample and the number of spectra included in each average.

Figure 4. Examples of individual spectra showing (a) low spectral variability (RA1) and (b) high spectral variability (RNT11). All spectra are offset for clarity.

SI-1. Individual spectra taken at different positions on each sample, offset for clarity

SI-2. (a) Bivariate score plot of principal component 4 versus principal component 2 from Principal Component Analysis (PCA) performed on the first derivative of all individual spectra ranging from 2460.2 eV to 2475.2 eV labeled by region for samples from Afghanistan (blue As), Chile (red Cs), the USA (green Us), Russia (pink Rs), Tajikistan (maroon Ts), Myanmar (magenta Ms), Iran (orange Is) and unknown locations (yellow and green Ns) showing general clustering of samples by region while also showing that similarities exist in some regions by the (partial) overlapping of these clusters. (b) Upper portion of the same score plot labeled with sample details displaying examples of in-sample variability. Both plots were produced use the Unscrambler software suite (with cross validation).

SI-3. XANES spectra of RA5 (solid trace) with relatively high intensity sulfate peak (at 2482.5 eV) and low intensity pre-edge features (2465 to 2475 eV) and RA2 (dashed trace) with relatively low intensity sulfate peak and high intensity pre-edge features.

SI-4. Literature peak assignments proposed for XANES spectra of lazurite. Energies have been corrected for differences in calibration and calibrated to the ESRF sulfate peak position.⁴⁴

SI-5. Example XANES spectra of (a) pyrite reference material, (b) occasional pyrite-contribution with lazurite, (c) occasional unique spectral pattern observed from lazurite, and (d) thiosulfate reference material. All spectra are offset for clarity.