

Soft X-ray Absorption Spectroscopy and Imaging of Sulfur in Lapis Lazuli

Marc S. Walton¹, Alessa A. Gambardella², and Catherine M. Schmidt Patterson²

¹ Northwestern University/Art Institute of Chicago Center for Scientific Studies in the Arts (NU-ACCESS), Evanston, IL, USA.

² Getty Conservation Institute, Los Angeles, CA, USA.

Since antiquity, lapis lazuli has been highly valued across many cultures for its bright blue color. Due to the material's significance, there has long been interest in understanding its color variations and determining its geographic origin, whether used as the processed pigment ultramarine in painted works of art (e.g. paintings and manuscripts) or the raw lapis lazuli stone in cultural heritage objects (e.g. jewelry and inlaid decorations). While the most well-known source of lapis lazuli is Afghanistan, there are several other sources, including sites in Tajikistan, Iran, Russia, Canada, and Chile. Naturally occurring lapis lazuli contains the blue mineral lazurite ($\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4, \text{S}_3, \text{S}_2, \text{Cl}, \text{OH})_2$) with a variety of accessory minerals that are common to many of the known geological deposits—e.g. hauyne ($\text{Na}_3\text{Ca}(\text{Si}_3\text{Al}_3)\text{O}_{12}(\text{SO}_4)$), pyrite (FeS_2), calcium carbonate (CaCO_3), and diopside ($\text{MgCaSi}_2\text{O}_6$). Much of the current research on the provenance of lapis lazuli has focused on the spectroscopic characteristics, the composition, and the overall distribution of the accessory minerals within the whole rock [1-4]. For example, work in our laboratory has shown that diopside inclusions in lapis lazuli sometimes have a fluorescent response to infrared wavelengths which may be characteristic of the geological deposit [5]. One challenge with basing provenance on the composition and distribution of accessory minerals is that the accessory minerals are mostly removed during the production of the ultramarine pigment, a process that requires crushing, sorting, and soaking the rock in an alkaline solution. Thus, a technique that focuses on *in-situ* analysis of the lazurite mineral alone, which remains chemically unaltered during this intensive processing, is desirable. Expanding on our previous work, this study therefore focuses on the lazurite component of lapis lazuli.

Lazurite is a member of the sodalite group that is defined by its aluminosilicate cage structure. According to literature, the characteristic blue color of the lazurite is due to the presence of polysulfide anions trapped within the cage at the time of the rock formation via contact metamorphism. Furthermore, the overall intensity of the blue color is thought to be due to both the total amount of polysulfide and how this polysulfide anion is coupled to the surrounding molecular framework [2]. Here we investigate the sulfur speciation within the aluminosilicate cage of lazurite—using a diverse sample set of both lapis lazuli and ultramarine pigments from many origins including Afghanistan, Russia, and Chile—as a potential means for identifying a geological fingerprint.

Sulfur x-ray absorption near edge structure (XANES) spectroscopy was performed on the samples using the newly developed soft X-ray Beamline (14-3) at the Stanford Synchrotron Radiation Lightsource (SSRL). S K-edge XANES has previously been used to study the origins of color in lazurite [6]. As is shown in Figure 1, the S K-edge spectrum collected on a sample originating in Afghanistan and Tajikistan (blue and green traces respectively). All of the spectra share a strong peak at 2483 eV that may be assigned to sulfate (SO_4^{4-}) in the lazurite structure. However, at lower energies notable differences in each spectrum may be observed in the position and shape of the pre-edge peaks. The pre-edge features are of particular interest to this study since they are associated with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) species centered around ~2473 eV and the polysulfide (S_x^{2-}) at ~2469 eV [6]. These data allow sulfate,

polysulfide, and thiosulfate species, and their distributions within a sample as is shown in Figure 1b, to be characterized, which facilitates comparisons of these species between geologically diverse sources. As a whole, our work not only contributes to a deeper understanding of lapis lazuli but also illustrates the potential of soft X-ray analysis for cultural heritage research.

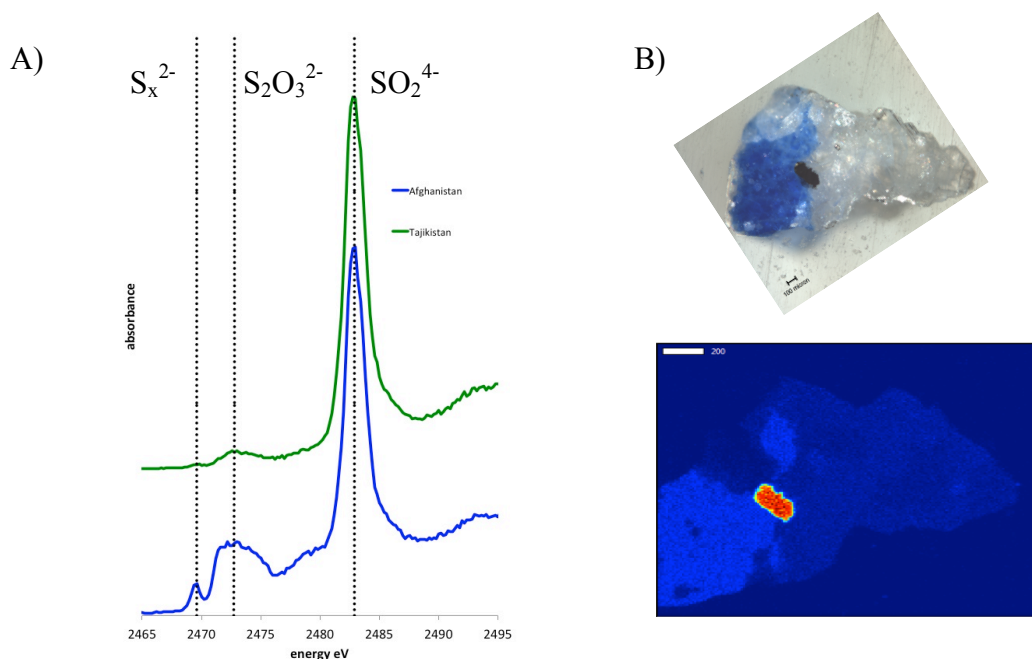


Figure 1. A) Two S K-edge spectra of lapis lazuli from different geographic locations: the Pamir Mountains in Tajikistan, and Badakshan in Afghanistan. Note that the spectra are offset from each other for easier viewing. B) A sample from Tajikistan and the corresponding XRF distribution map of sulfur.

References

- [1] Re, A., et al., *New markers to identify the provenance of lapis lazuli: trace elements in pyrite by means of micro-PIXE*. Applied Physics A, 2013. **111**(1): p. 69-74.
- [2] Aleksandrov, S.M. and V.G. Senin, *Genesis and composition of lazurite in magnesian skarns*. Geochemistry International, 2006. **44**(10): p. 976-988.
- [3] Lo Giudice, A., et al., *Multitechnique characterization of lapis lazuli for provenance study*. Analytical and Bioanalytical Chemistry, 2009. **395**(7): p. 2211-2217.
- [4] Favaro, M., et al., *Characterization of lapis lazuli and corresponding purified pigments for a provenance study of ultramarine pigments used in works of art*. Analytical and Bioanalytical Chemistry, 2012. **402**(6): p. 2195-2208.
- [5] Schmidt, C.M., M.S. Walton, and K. Trentelman, *Characterization of Lapis Lazuli Pigments Using a Multitechnique Analytical Approach: Implications for Identification and Geological Provenancing*. Analytical Chemistry, 2009. **81**(20): p. 8513-8518.
- [6] Fleet, M.E., et al., *Chemical State of Sulfur in Natural and Synthetic Lazurite by S K-edge XANES and X-ray Photoelectron Spectroscopy*. The Canadian Mineralogist, 2005. **43**: p. 1589-1603.