

# From lapis lazuli to synthetic ultramarines: a $\mu$ -Raman spectroscopy investigation on the history and development of “the Most Perfect” Color

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**Abstract** – Natural ultramarine has been one of the most precious blue pigments employed in the past in the artifacts. It is typically obtained by crushing and grinding the lapis lazuli rock and selectively extracting the blue mineral lazurite. Since the early 19<sup>th</sup> century, when the synthetic version was produced, the use of this much less expensive material became widespread, and synthetic ultramarine blue replaced the natural one in painting palettes. The present study is conducted as a preliminary  $\mu$ -Raman investigation for creating a comprehensive and detailed database of the ultramarine pigments, both natural and synthetic, employed over the centuries until today.

## I. INTRODUCTION

Lazurite mineral is responsible for the blue color of lapis lazuli. The IMA Commission lately redefined it on New Minerals, Nomenclature and Classification (CNMNC) with the idealized formula  $\text{Na}_7\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)(\text{S}_3)\cdot\text{H}_2\text{O}$  [1]. It is a member of the aluminosilicate group with the same structure as sodalite ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ ) [2]. It comprises interconnected  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra joined to form a three-dimensional framework with anions and cations located inside the large central cavities, commonly designated as  $\beta$ -cages hosting large cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ), additional anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{S}^{3-}$ , etc.) and neutral molecules ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ) [2]. The location of the chromophores within the sodalite  $\beta$ -cages accounts for the pigment stability to air and heat, despite the highly unstable nature of di- and tri-sulphur radical anions. Sodalite-type compounds with different additional anions ( $\text{CO}_3^{3-}$ ,  $\text{HCOO}^-$ ,  $\text{AlF}_6^{3-}$ ,  $\text{OH}^-$ ) have also been synthesized. Lazurite's color is attributed to sulfur polyanions trapped in the  $\beta$ -cages, being the trisulfur radical ( $\text{S}^{3-}$ ) mainly responsible for the blue color. Contributions from disulfur ( $\text{S}^{2-}$ ) and tetrasulfur ( $\text{S}^{4-}$ ) radicals can shift the color towards yellow or red,

respectively [3]. Thus, the proportion of different sulfur species is regarded as one of the decisive factors influencing the final aspect of the pigment [2]. Natural lazurite occurs in association with other minerals like calcite ( $\text{CaCO}_3$ ), pyrite ( $\text{FeS}_2$ ), diopside ( $\text{CaMgSi}_2\text{O}_6$ ), wollastonite ( $\text{CaSiO}_3$ ), forsterite ( $\text{Mg}_2\text{SiO}_4$ ), phlogopite ( $\text{K}(\text{Mg},\text{Fe},\text{Mn})_3\text{Si}_3\text{AlO}_{16}(\text{F}(\text{OH}))_2$ ), muscovite ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ), and other sodalite group members such as nosean ( $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}(\text{SO}_4)\cdot\text{H}_2\text{O}$ ) and h aüyne ( $\text{Na}_3\text{CaSi}_3\text{Al}_3\text{O}_{12}(\text{SO}_4)$ ), depending on the geographical origin of the rock [4].

In the traditional method of producing pigment from lapis lazuli, as outlined by Cennini [4, 5], these minerals are removed by a lengthy purification process which, when repeated several times, results in several grades of pigment, each less saturated in color than the one before. The last, crudest, grade is typically referred to as ultramarine ash [4]. Ultramarine was a very expensive and precious blue pigment extensively used in Europe throughout medieval paintings [3]. This precious pigment took on an iconographic value, and it was reserved for the robes of only the most prominent figures, such as Christ and the Virgin Mary, in religious scenes [3, 6]. In 1828, a synthetic version of the ultramarine blue pigment was first obtained using a chemical process involving both calcination and oxidation steps [7, 8]. Owing a similar composition to lazurite, the use of its synthetic analog,  $\text{Na}_{6-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$ , quickly spread across Europe during the 19<sup>th</sup> century, replacing the natural one in many of its applications since it was cheaper and easier to produce but maintaining the appreciated bright blue aspect. Recently, new synthetic routes have been proposed based on fly ash as an alternative to kaolin [8] or employing aluminum sulphate as both the aluminum and sulphur source [8]. Thenceforth, the identification and discrimination between natural and synthetic ultramarine pigments are relevant to the analysis of works of art, with particularly interesting applications in authentication issues and/or for detecting

unknown subsequent restoration interventions [3].

To this end,  $\mu$ -Raman spectroscopy was chosen in this study due to its exceptional ability to predict and discover the compositional properties of inorganic materials (e.g., crystalline phases and their transitions), as well as of organic materials or functional groups. The peculiarity of this technique consists in its non-destructive and repeatability character and its high sensitivity, also for portable instrumentations, a characteristic highly desirable for field tests of precious ancient relics [6].

## II. MATERIALS AND METHODS

### A. Materials

Five samples were analyzed in this preliminary study. Among them, three samples, two gemstones (LPS1 and LPS2) and one rock fragment (LPS3) of lapis lazuli come from the Mineral and Gem collection of the Messina University (Messina, Italy) (Figure 1).

The other two samples (ULM1 and ULM2) are synthetic blue ultramarine pigments commercially available (Figure 2).

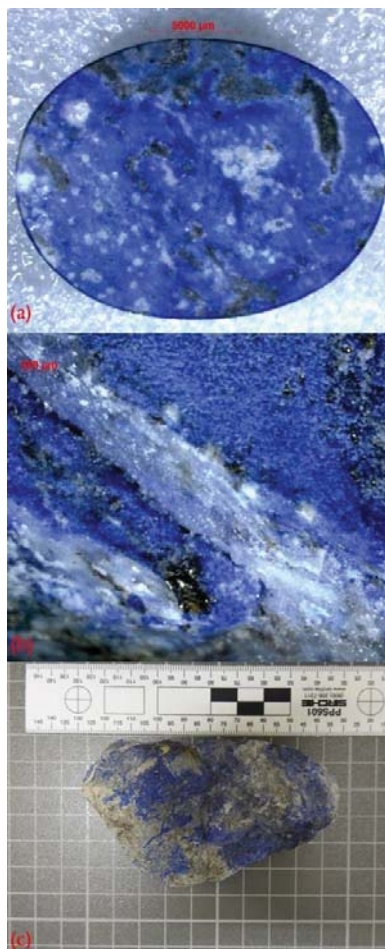


Fig. 1: Studied gemstones and rock fragment: LPS1 (a), particular of LPS2 (b), and LPS3 (c)

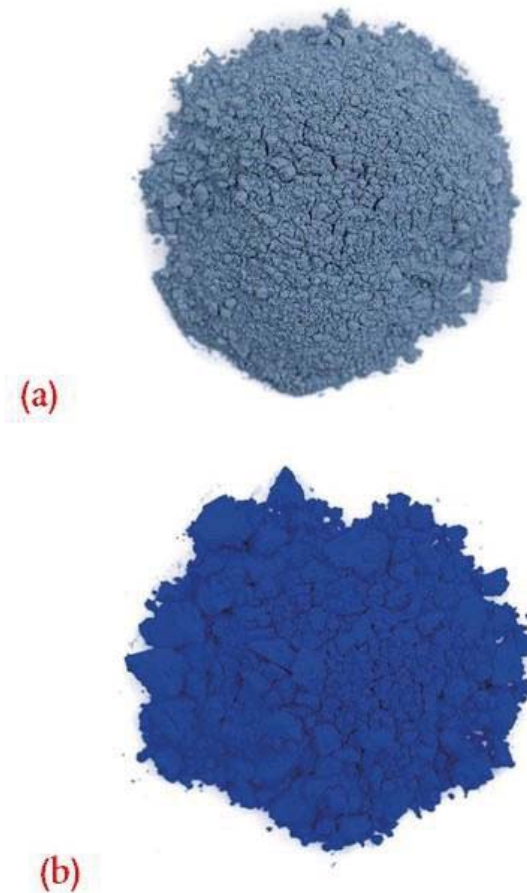


Fig. 2: Studied pigments: ULM1 (a), and ULM2 (b)

An indicative description of these samples is provided in Table 1.

Table 1. Natural and synthetic samples employed in this study.

Sample ID	Type	Origin
LPS1	Gemstone	Natural
LPS2	Gemstone	Natural
LPS3	Rock fragment	Natural
ULM1	Powdered pigment	Synthetic
ULM2	Powdered pigment	Synthetic

### B. Methods

$\mu$ -Raman measurements were collected by a portable “BTR111MiniRam™” (BW&TEK Inc.) spectrometer, working with a 785 nm (diode laser) excitation wavelength and a thermoelectric cooled charge-coupled device (CCD) detector. The system was equipped with a BAC151B

Raman microscope. The laser spot was focused on the mineral surface through a 40x objective, which guaranteed a working distance of 3.98 mm and a laser beam spot size of 50  $\mu\text{m}$ . The maximum power at the samples was  $\sim 90$  mW. Spectra were registered between 60 and 3150  $\text{cm}^{-1}$ , with an acquisition time of 40 s and a resolution of 8  $\text{cm}^{-1}$ , by accumulating 32 scans in order to increase the signal-to-noise ratio.

### III. RESULTS AND DISCUSSION

Figure 3(a) shows the  $\mu$ -Raman spectra of the natural lazurite in samples LPS1, LPS2, and LPS3. It is worth noting that natural lazurites are characterized by a non-

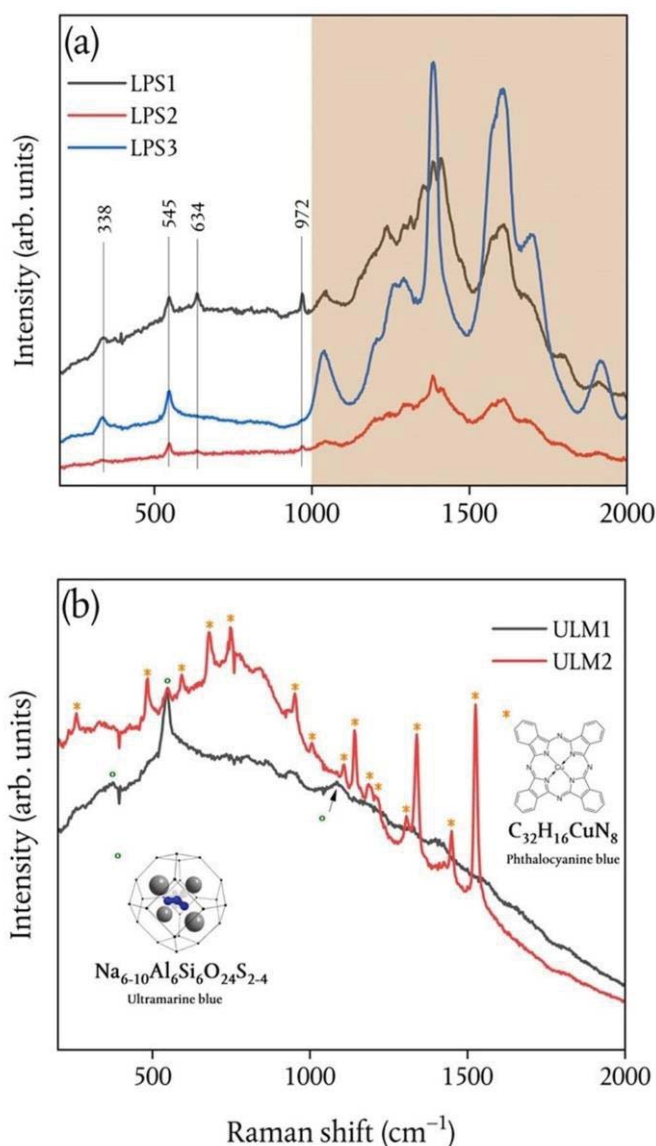


Fig. 3:  $\mu$ -Raman spectra of the investigated natural samples (a) and synthetic samples (b)

ideal chemical composition, which implies a substantial complexity of their Raman spectra [2,3]. An overall inspection of Figure 3(a) reveals that  $\mu$ -Raman profiles appear quite similar for the samples LPS1 and LPS2. The detected  $\mu$ -Raman profiles revealed the fundamental peak of  $\text{S}^{3-}$  chromophore (at ca. 545  $\text{cm}^{-1}$  – symmetric stretching  $\nu_1$ ) [2,4]. The detected peak at ca. 338  $\text{cm}^{-1}$  can be assigned to the presence of amounts of the  $\text{S}^{4-}$  anions in all investigated natural lazurites [2], whereas the peaks at ca. 634  $\text{cm}^{-1}$  and 972  $\text{cm}^{-1}$ , detected in the samples LPS1 and LPS2, can be assigned to the presence of  $\text{SO}_4^{2-}$  anions [2, 9]. Figure 3(a) also shows a strong luminescence in the 1000 – 2000  $\text{cm}^{-1}$  spectral region. It can be due to transition elements in the monoclinic pyroxene mineral diopside ( $\text{CaMgSi}_2\text{O}_6$ ), as well as to the gemstone treatments, including heating, bleaching, surface coating, and more [2, 3]. Figure 3(b) shows the Raman spectra of the synthetic and commercial ultramarines blue (samples ULM1 and ULM2). The detected  $\mu$ -Raman profile of the sample ULM1 revealed, as a main feature, a high-intense peak centered at ca. 545  $\text{cm}^{-1}$  and assigned to the  $\text{S}^{3-}$  chromophore symmetric stretching  $\nu_1$  [2]. The other two weak peaks are detected at ca. 335  $\text{cm}^{-1}$  and 1090  $\text{cm}^{-1}$  and are assigned, respectively, to the  $\text{S}^{4-}$  symmetric stretching  $\nu_1$  and  $\text{S}^{3-}$  overtone ( $2 \times \nu_1$ ) [2]. The overall inspection of the Raman profile of the sample ULM2 revealed a complex spectrum. The peak centered at ca. 545  $\text{cm}^{-1}$  is still detected and indicates the ultramarine blue presence [2, 4]. The peaks centered at ca. 257, 480, 592, 678, 750, 950, 1010, 1112, 1142, 1186, 1218, 1310, 1336, 1448, and 1526  $\text{cm}^{-1}$  belong to the phthalocyanine blue [10].

### IV. CONCLUSIONS

This study allowed initiation for characterizing and discriminating the natural and synthetic ultramarines. The preliminary information obtained is in good agreement with literature and, in particular, suggests the peculiar characteristic pattern of luminescence bands, emerging in the zone between 1000 and 2000  $\text{cm}^{-1}$ , as typical of the natural lazurites [10], then allowing a clear differentiation from synthetic ultramarines. Also of note is that the presence of these characteristic luminescence/vibronic features not only indicates that a particular ultramarine pigment is derived from a natural source but, more significantly, may be indicative of its particular geological origin [11]. Raman spectroscopy is therefore useful to provide preliminary information on the origin of these materials based on their above-mentioned luminescence pattern [12, 13].

Raman spectroscopy also confirms its role as an ideal method for the examination of gemstones and pigments. Thanks to the ability of microscopically examining small details, Raman can distinguish not only real versus artificial materials, but can also provide basic information on their origin [14, 15]. Its strength is the possibility in obtaining in a very short time the identification of a

mineral species or even gemstone variety [16]. It needs therefore to be added that Raman spectroscopy is also particularly able to determine the content and chemical state (oxidation and binding) of sulphur (chromophore) in synthetic ultramarines [17, 18]. In addition to that, a hypothesis of a means of distinguishing the natural from the artificial variety of the ultramarine pigment is put forward. More precisely, it is based on the fact that, while the spectral features obtainable from the natural pigment vary considerably, those of the artificial pigment are always identical and easily reproducible, since they correspond exclusively to those characteristics of synthetic ultramarine [19].

This study therefore becomes significant in recognizing synthetic and commercial ultramarines, with promising forensic applications in contrasting forgery and fraud criminal offences due to the non-destructive, repeatability, and high sensitivity character of the  $\mu$ -Raman spectroscopy method. This is highlighted by examples taken in this study, which provide a focus for current and future applications and developments [20-23].

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