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RESEARCH ARTICLE | MAY 31 2024

ToF-SIMS spectra of historical inorganic pigments: Natural and synthetic ultramarine blues and smalt in both polarities

Special Collection: [ToF-SIMS Spectra of Historical Inorganic Pigments](#)

Caroline Bouvier  ; Sebastiaan Van Nuffel  ; Alain Brunelle  

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Surf. Sci. Spectra 31, 015006 (2024)

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- ▶ partial pressure measurement and control of process gases
- ▶ reactive sputter process control
- ▶ vacuum diagnostics
- ▶ vacuum coating process monitoring

ToF-SIMS spectra of historical inorganic pigments: Natural and synthetic ultramarine blues and smalt in both polarities

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Note: This paper is part of the 2024 Special Topic Collection on ToF-SIMS Spectra of Historical Inorganic Pigments.

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ABSTRACT

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is increasingly used to analyze cultural heritage materials because it can simultaneously detect organic and inorganic materials while mapping them on a surface. The precise identification of a pigment in a specific layer of a painting or of remaining color on a statue can inform about the technique used or the time of manufacture as well as expose possible forgeries when anachronistic ingredients are identified. Reference spectra are required to confidently identify a given pigment using ToF-SIMS. This paper focuses on four blue pigments manufactured following historical recipes: two natural ground and processed lapis lazuli pigments, one synthetic ultramarine pigment, and the blue-colored ground cobalt glass pigment smalt. The positive and negative polarity ToF-SIMS reference spectra using a Bi_3^+ primary ion species are presented. Differentiating these family of pigments is of interest as they have similar compositions but are used in very different contexts. It is particularly noteworthy that the two natural lapis lazuli pigments can be distinguished from the synthetic counterpart ultramarine using ToF-SIMS.

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Accession#: 01927, 01928, 01929, and 01930

Technique: SIMS

Specimen: Lapis Lazuli from Chile, Lapis Lazuli sky-blue, Ultramarine blue, and Smalt

Instrument: IONTOF, TOF SIMS IV

Major Species in Spectra: O, H, Al, Si, Na, Ca, K, Co, S, Cl, Fe, and C

Minor Species in Spectra: Hydrocarbon contamination

Published Spectra: 8

Spectral Category: Reference

INTRODUCTION

ToF-SIMS imaging can detect a wide range of elements, so colored minerals can be identified and mapped, given that reference spectra are available for reliable assignment. Here, we provide a ToF-SIMS spectral database for four historical blue inorganic pigments of similar composition, as they all contain some proportion of silicon oxide. As the definite chemical composition of the pigments made from ground natural lapis lazuli is subjected to the variable mineral content of the stone, two pigments from distinct

geographical origin and color shade (namely #01927 and #01928) are compared. A synthetic equivalent, commonly referred to as “ultramarine” and existing since the 19th century, is presented in comparison (#01929) as well as a blue-colored ground cobalt glass, known as smalt (#01930). For each, a list of their secondary ions is given in both polarities.

The reference materials were supplied by specialized manufacturers selling pigments reproducing historical recipes as closely as possible, such as Kremer Pigmente GmbH. Pigments were available

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as ground powder of variable particle size (a few tens of μm to $100\ \mu\text{m}$) conditioned in glass sealed vials. In paintings, pigment particles are dispersed and not dissolved, so all references were analyzed without any preparation treatment. Natural and synthetic pigments may contain impurities, and specimen compositions described below are the major components as found on the material data sheets provided by the suppliers.

A stainless-steel spatula was cleaned with propan-2-ol, and the powder was directly deposited on a $1 \times 1\ \text{mm}^2$ piece of a conductive double-sided tape (3M Electrically Conductive Adhesive Transfer Tape 9703) already fixed to a $1\ \text{cm} \times 1\ \text{cm} \times 0.125\ \text{mm}$ stainless steel plate (17-7PH, Goodfellow Cambridge Limited, UK) fitting the dimensions of the sample holder. A hand press covered with clean aluminum foil was applied onto the powder to fix it to the tape. This allowed us to minimize the risk of dust formation when operating in the analysis chamber under ultrahigh vacuum (10^{-8} to 10^{-9} hPa) while ensuring a flat surface.

All spectra were obtained on an IONTOF TOF SIMS IV equipped with a 25 keV bismuth liquid metal ion gun and an argon gas cluster ion beam (GCIB). Before all analyses, a $500 \times 500\ \mu\text{m}^2$ surface was cleaned using 1500–2000 Ar clusters with a kinetic energy of 20 keV (sputter ion dose of 2×10^{15} ions/ cm^2). Analyses were then performed on a $250 \times 250\ \mu\text{m}^2$ area centered in this larger cleaned area, rastered over 128×128 pixels using the high current bunched mode. Primary ion dose (25 keV Bi_3^+) was 4.35×10^{11} ions/ cm^2 . Surface potential was compensated and charging of the sample was compensated with low-energetic 20 eV electrons of the flood gun.

In cases where the grain size and shape prevented a large enough flat surface accessible for the analysis, delayed extraction mode included on the ToF analyzer was used since this reduces the variation in time of flight due to surface topography.¹ This was necessary for lapis lazuli sky-blue (Accession #01928), as the data obtained using bunched mode were limited in mass resolution due to topography. The imaging capabilities of the ToF-SIMS instrument were also especially useful in attributing peaks by referring to their co-localization.

Data were calibrated using sets of peaks as similar as possible for all spectra, using peaks that could be confidently identified while taking into account the mass interferences involving Al, Si, Na, K, and Ca. The lists were designed so that meaningful comparisons between datasets are possible. Calcium has a distinctive isotopic pattern ensuring confident attribution of the peaks; hence, #01927 and #01928 positive polarity data were calibrated using lists including Ca^+ , SiONa^+ , $\text{Ca}_2\text{O}_2\text{H}^+$, and $\text{Ca}_3\text{O}_3\text{H}^+$ ions. #01929 and #01930 positive polarity data were calibrated, which included Al^+ , SiONa^+ , $\text{SiO}_2\text{Na}_2^+$, and $\text{SiO}_3\text{Na}_3^+$. The negative polarity data were calibrated for #01927, #01928, and #01929 using SiO_2^- , AlSiO_4^- , $\text{AlSi}_2\text{O}_6^-$, $\text{AlSi}_3\text{O}_8^-$, and $\text{AlSi}_4\text{O}_{10}^-$, while the non-Al containing smalt #01930 was calibrated using SiO_2^- , $\text{Si}_2\text{O}_5\text{H}^-$, $\text{Si}_3\text{O}_7\text{H}^-$, $\text{Si}_4\text{O}_9\text{H}^-$, and $\text{Si}_5\text{O}_{11}\text{H}^-$. The calibration lists allowed for a good coverage of the mass range of interest for each specimen, and they are reported in the corresponding tables below. The mass calibration in the range below m/z 30 in the datasets #01928 is impacted by the low count and peak asymmetry due to the use of delayed extraction.

Figures and tables presented below contain the major peaks for both polarities. Each pigment is uniquely identified thanks to an accession number, and they are grouped according to their

composition and described in the following section. Their historical relevance is briefly described based on current literature.^{2–4} The spectrum ID# refer to that number, added with “–01” for positive spectra and with “–02” for negative spectra.

SPECIMEN DESCRIPTION (ACCESSION #01927, #01928, AND #01929)

Specimen: (Accession #01927) Lapis Lazuli from Chile (Kremer Pigmente ref. 1056038), (Accession #01928) Lapis Lazuli, sky-blue (Kremer Pigmente ref. 10562), and (Accession #01929) Ultramarine Blue (Kremer Pigmente ref. 45000)

CAS Registry #: (Accession #01927 and #01928) 57455-35-5; (Accession #01929) 101357-30-6 (57455-37-5), 1332-58-7

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: (Accession #01927 and #01928) Sodium aluminum silicate sulfurized; (Accession #01929) Silicic acid, aluminum sodium salt, sulfurized, and kaolin

Source: Kremer Pigmente GmbH

Specimen Composition: (Accession #01927 and #01928) Lazurite [$\text{Na}_6\text{Ca}_2(\text{AlSiO}_4)_6(\text{SO}_4, \text{S}_2, \text{S}_3, \text{Cl}, \text{OH})_2$] inclusions in dolomite, sodalite $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, pyrite FeS_2 ; (Accession #01929) Synthetic ultramarine, $\text{Na}_x\text{Al}_y\text{Si}_6\text{O}_{24}\text{S}_y$ ($x = 6–10$ and $y = 2–4$ depending on manufacturing process)

Form: Ground pigment powder

History and Significance: A rare, semiprecious, dark-blue stone found as inclusions in dolomite/calcite marble. Its main mineral is sulfur aluminosilicate lazurite, combined with various minerals like sodalite and pyrite. The pigment is produced from stone by grinding, sieving, and washing. It is blue to blue gray, with large irregular particles and variable quantities of colorless crystalline impurities. The rarity and complexity of the process led to ultramarine being more expensive than gold for centuries. A synthetic form has been available since the 19th century, recognizable by the distinctive shape of the particles, which are smaller. Its chemical structure is very close to lazurite, but not fully known, as discussed in the literature.² TOF-SIMS informs about the synthetic or natural origin by both the particle morphology and the spectral differences. The spectra of both natural lapis lazuli pigments are similar, while that of synthetic ultramarine are distinctive. Natural organic resins can be used in the manufacturing process, and they can be detected simultaneously as the inorganic compounds (see #01929). The sensitivity of ToF-SIMS for fluorine also proved to be of interest, as F-rich mineral can be found in natural lapis lazuli.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250\ \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto a conductive double-sided tape attached to stainless steel $1 \times 1\ \text{cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low-energy electron flood gun was used. Bias voltage between 20 and -30 V. Flood gun filament current of 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and 1×10^{-6} Pa

Pre-analysis Beam Exposure: $Ar_{1500-2000}$, 20 keV, 2×10^{15} ions/cm²

SPECIMEN DESCRIPTION (ACCESSION # 01930)

Specimen: Smalt (Kremer Pigmente ref. 10000)

CAS Registry #: 14808-60-7, 1308-06-1, 1307-96-6

Specimen Characteristics: Inhomogeneous; solid; amorphous; dielectric; inorganic compound; powder

Chemical Name: Cobalt potassium silicate glass (quartz, tricobalt tetraoxide, and cobalt monoxide)

Source: Kremer Pigmente GmbH

Specimen Composition: $CoOKSi$ (various wt. % of SiO_2 , K_2O , and CoO)²

Form: Ground pigment powder

History and Significance: It is the oldest synthetic cobalt pigment, obtained by grinding blue glass colored by cobalt oxides, in turn obtained by heating quartz in the presence of potassium carbonate and cobalt chloride. Used from the 16th to 18th centuries as a cheap alternative to lapis and azurite. It tends to turn gray in oil paints over time. Possible traces of nickel and arsenic can be present. This pigment does not contain aluminum.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu m^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto a conductive double-sided tape attached to stainless steel 1×1 cm² plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low-energy electron flood gun was used. Bias voltage between 20 and -30 V. Flood gun filament current of 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and 1×10^{-6} Pa

Pre-analysis Beam Exposure: $Ar_{1500-2000}$, 20 keV, 2×10^{15} ions/cm²

INSTRUMENT CONFIGURATION

Manufacturer and Model: IONTOF, TOF SIMS IV

Analyzer Type: Time-of-flight

Sample Rotation: No

Rotation Rate: 0 rpm

Oxygen Flood Source: None

Oxygen Flood Pressure: N/A

Other Flood Source: None

Other Flood Pressure: N/A

Unique Instrument Features Used: The analyzer was equipped with delayed extraction mode. It was used when the topography of the pigment's grains impacted the signal quality (e.g., grains of several tens of micrometers with sharp edges). The delayed extraction mode allows for an attenuation of the relative delays between secondary ions due to height differences on the surface.

Energy Acceptance Window: 20 eV

Post-acceleration Voltage: 10 000 eV

Sample Bias: 10–20 eV

Specimen Normal-to-analyzer (Θ): 0°

Ion Sources

Ion Source 1 of 2

Purpose of This Ion Source: Analysis beam

Ion Source Manufacturer: IONTOF GmbH

Ion Source Model: Liquid metal ion gun (LMIG) with bismuth cluster (25 keV)

Beam Mass Filter: Yes

Beam Species and Charge State: Bi_3^+

Beam Gating Used: Double pulsed + bunched

Additional Beam Comments: None

Beam Voltage: 25 000 eV

Net Beam Voltage (impact voltage): 25 000 eV

Ion Pulse Width: 0.8–1.2 ns

Ion Pulse Rate: 5–10 kHz

DC Beam Current: ~ 10 nA

Pulsed Beam Current: ~ 0.0004 nA

Current Measurement Method: Faraday cup

Beam Diameter: $\sim 2 \mu m$

Beam Raster Size: $250 \times 250 \mu m^2$

Raster Pixel Dimensions: 128×128

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

Ion Source 2 of 2

Purpose of This Ion Source: Sputtering beam

Ion Source Manufacturer: IONTOF GmbH

Ion Source Model: Argon gas cluster ion beam (GCIB)

Beam Mass Filter: Yes

Beam Species and Charge State: Ar_n^+ with $n = 1500-2000$

Beam Gating Used: Wien filter

Additional Beam Comments: Used as sputter gun, not analysis mode

Beam Voltage: 20 000 eV

Net Beam Voltage (impact voltage): 20 000 eV

Ion Pulse Width: N/A

Ion Pulse Rate: N/A

DC Beam Current: ~ 10 nA

Pulsed Beam Current: N/A

Current Measurement Method: Faraday cup

Beam Diameter: $\sim 50 \mu m$

Beam Raster Size: $500 \times 500 \mu m^2$

Raster Pixel Dimensions: N/A

Beam Incident Angle: 45°
Source-to-Analyzer Angle: 45°

ACKNOWLEDGMENT

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Caroline Bouvier: Investigation (lead); Writing – original draft (equal). **Sebastiaan Van Nuffel:** Investigation (equal); Writing – review & editing (equal). **Alain Brunelle:** Conceptualization (lead); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

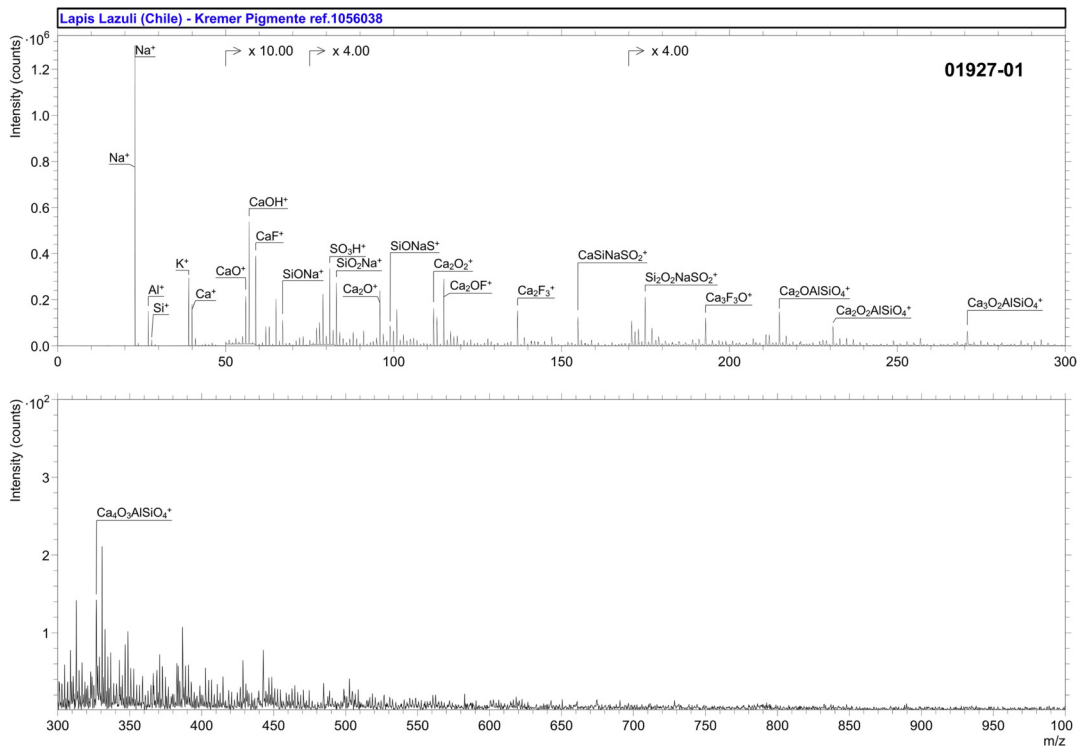
The data that support the findings of this study are available within the article and its supplementary material.

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- ⁴J. R. Barnett, S. Miller, and E. Pearce, *Opt. Laser Technol.* **38**, 445 (2006).

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01927-01	26.980 (-21.0)	Al ⁺	Lazurite, sodalite
	39.962 (-14.9)	Ca ⁺	Lazurite, dolomite
	55.956 (-15.8)	CaO ⁺	Lazurite, dolomite
	56.966 (17.4)	CaOH ⁺	Lazurite, dolomite
	58.959 (-26.0)	CaF ⁺	F-rich mineral impurity
	82.953 (-30.9)	SiO ₂ Na ⁺	Lazurite
	95.921 (11.5)	Ca ₂ O ⁺	Lazurite, dolomite
	98.938 (50.1)	SiONaS ⁺	Lazurite
	111.914 (-5.73)	Ca ₂ O ₂ ⁺	Lazurite
	112.925 (22.0)	Ca ₂ O ₂ H ⁺	Lazurite, dolomite
	114.919 (8.96)	Ca ₂ OF ⁺	F-rich mineral impurity
	136.918 (-11.6)	Ca ₂ F ₃ ⁺	F-rich mineral impurity
	154.897 (39.0)	CaSiNaSO ₂ ⁺	Lazurite
	174.891 (-21.7)	Si ₂ O ₂ NaSO ₂ ⁺	Lazurite
	214.863 (24.3)	Ca ₂ OAlSiO ₄ ⁺	Lazurite
	230.855 (9.91)	Ca ₂ O ₂ AlSiO ₄ ⁺	Lazurite
	270.824 (32.8)	Ca ₃ O ₂ AlSiO ₄ ⁺	Lazurite
	326.783 (32.0)	Ca ₄ O ₃ AlSiO ₄ ⁺	Lazurite



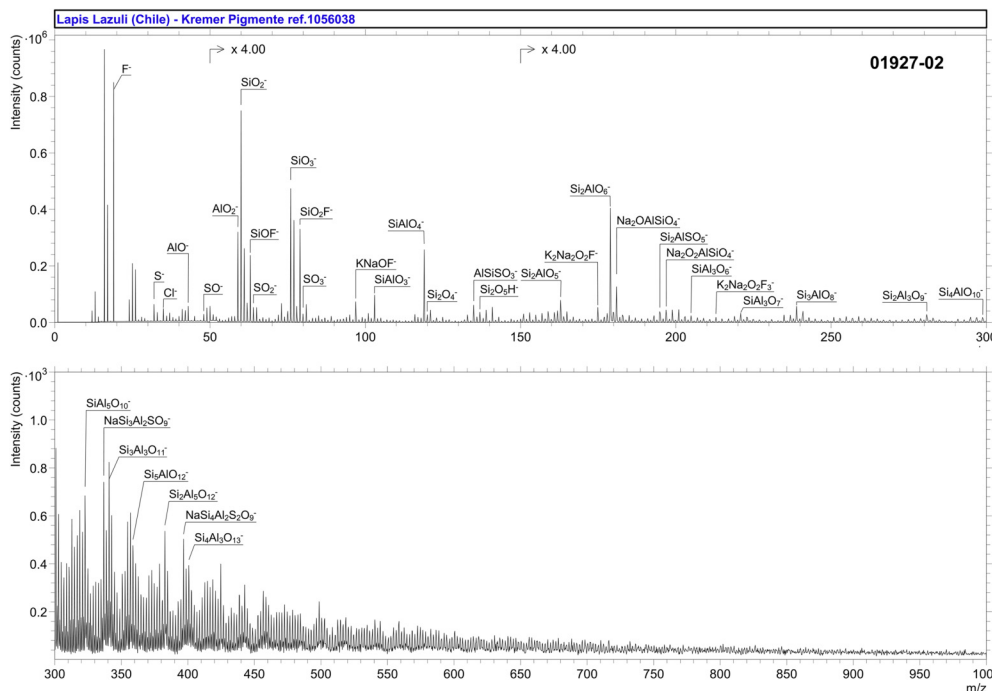
Accession #:	01927-01
Specimen:	Lapis Lazuli from Chile—Kremer Pigmente ref. 1056038—Positive polarity
Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	1700 m/ Δ m
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Al ⁺ , Ca ⁺ , SiONa ⁺ , Ca ₂ O ₂ H ⁺ , and Ca ₃ O ₃ H ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.35 $\times 10^{11}$ ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 13 nA
DC Beam Current:	10.4 nA
Beam Diameter:	~2 μ m
Beam Raster Size:	250 \times 250 μ m ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Positive
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	335 s
Comment:	Very large grains, mass resolution impacted. The sodium peak saturated.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01927-02	18.999 (-7.07)	F ⁻	Accessory mineral (ex: phlogopite)
	31.973 (17.7)	S ⁻	Lazurite
	34.970 (20.2)	Cl ⁻	Lazurite, sodalite, phlogopite
	42.977 (-3.48)	AlO ⁻	Lazurite, sodalite, phlogopite
	47.967 (-8.23)	SO ⁻	Lazurite
	58.971 (-11.9)	AlO ₂ ⁻	Lazurite, sodalite, phlogopite
	60.977 (22.6)	SiO ₂ H ⁻	Lazurite, sodalite, phlogopite
	62.971 (-2.18)	SiOF ⁻	Phlogopite
	63.964 (31.1)	SO ₂ ⁻	Lazurite
	76.974 (51.1)	SiO ₃ H ⁻	Lazurite, sodalite, phlogopite
	78.968 (23.9)	SiO ₂ F ⁻	Phlogopite
	79.960 (33.5)	SO ₃ ⁻	Lazurite
	96.950 (24.6)	KNaOF ⁻	Phlogopite
	102.946 (22.5)	SiAlO ₃ ⁻	Lazurite, sodalite, phlogopite
	118.937 (-17.5)	SiAlO ₄ ⁻	Lazurite, sodalite, phlogopite
	134.922 (17.7)	AlSiSO ₃ ⁻	Lazurite
	136.939 (14.1)	Si ₂ O ₅ H ⁻	Lazurite, sodalite, phlogopite
	162.917 (37.0)	Si ₂ AlO ₅ ⁻	Lazurite, sodalite, phlogopite
	174.898 (13.7)	K ₂ Na ₂ O ₂ F ⁻	Phlogopite
	178.904 (-6.98)	Si ₂ AlO ₆ ⁻	Lazurite, sodalite, phlogopite
	180.909 (-21.6)	Na ₂ OAlSiO ₄ ⁻	Lazurite, sodalite, phlogopite
	194.886 (18.7)	Si ₂ AlSO ₅ ⁻	Lazurite
	196.904 (-23.1)	Na ₂ O ₂ AlSiO ₄ ⁻	Lazurite, sodalite, phlogopite
	204.896 (19.3)	SiAl ₃ O ₆ ⁻	Lazurite, sodalite, phlogopite
	212.893 (2.29)	K ₂ Na ₂ O ₂ F ₃ ⁻	Phlogopite
	220.888 (7.87)	SiAl ₃ O ₇ ⁻	Lazurite, sodalite, phlogopite
	238.874 (6.40)	Si ₃ AlO ₈ ⁻	Lazurite, sodalite, phlogopite
	280.854 (4.23)	Si ₂ Al ₃ O ₉ ⁻	Lazurite, sodalite, phlogopite
	298.843 (14.1)	Si ₄ AlO ₁₀ ⁻	Lazurite, sodalite, phlogopite
	322.840 (16.3)	SiAl ₅ O ₁₀ ⁻	Lazurite, sodalite, phlogopite
	336.816 (14.8)	NaSi ₃ Al ₂ SO ₉ ⁻	Lazurite
	340.824 (10.2)	Si ₃ Al ₃ O ₁₁ ⁻	Lazurite, sodalite, phlogopite
	358.807 (3.43)	Si ₅ AlO ₁₂ ⁻	Lazurite, sodalite, phlogopite
	382.805 (9.45)	Si ₂ Al ₅ O ₁₂ ⁻	Lazurite, sodalite, phlogopite
396.762 (6.81)	NaSi ₄ Al ₂ S ₂ O ₉ ⁻	Lazurite	
400.776 (-26.6)	Si ₄ Al ₃ O ₁₃ ⁻	Lazurite, sodalite, phlogopite	

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Accession #:

01927-02

■ Specimen:

Lapis Lazuli from Chile—Kremer Pigmente ref. 1056038—Negative polarity

■ Technique:

SIMS

Instrument:

IONTOF, TOF SIMS IV

Analyzer Type:

Time-of-flight

Analyzer Mass Resolving Power:

1400 m/Δm

Mass Resolving Power Determined at:

25 D

Species Used for Mass Calibration:

Cl^- , SiO_2^- , AlSiO_4^- , $\text{AlSi}_2\text{O}_6^-$, $\text{AlSi}_3\text{O}_8^-$, and $\text{AlSi}_4\text{O}_{10}^-$

Specimen Normal-to-Analyzer:

0°

Source-to-Analyzer Angle:

45°

Primary Beam Ion Gun:

LMIG

Primary Ion Species:

Bi_3^+

Primary Ion Dose:

4.35×10^{11} ion/cm²

Primary Ion Pulse Width:

0.8–1.2 ns

Primary Ion Pulse Rate:

5 kHz

Net Beam Voltage:

25 000 eV

Pulsed Beam Current:

0.000 13 nA

DC Beam Current:

10.4 nA

Beam Diameter:

~2 μm

Beam Raster Size:

250 × 250 μm²

Beam Incident Angle:

45°

Secondary Source Polarity:

Negative

Mass Range Minimum:

0 Da

Mass Range Maximum:

3545 Da

Spectrum Dead Time Corrected:

Yes

Total Spectral Acquisition Time:

335 s

Comment:

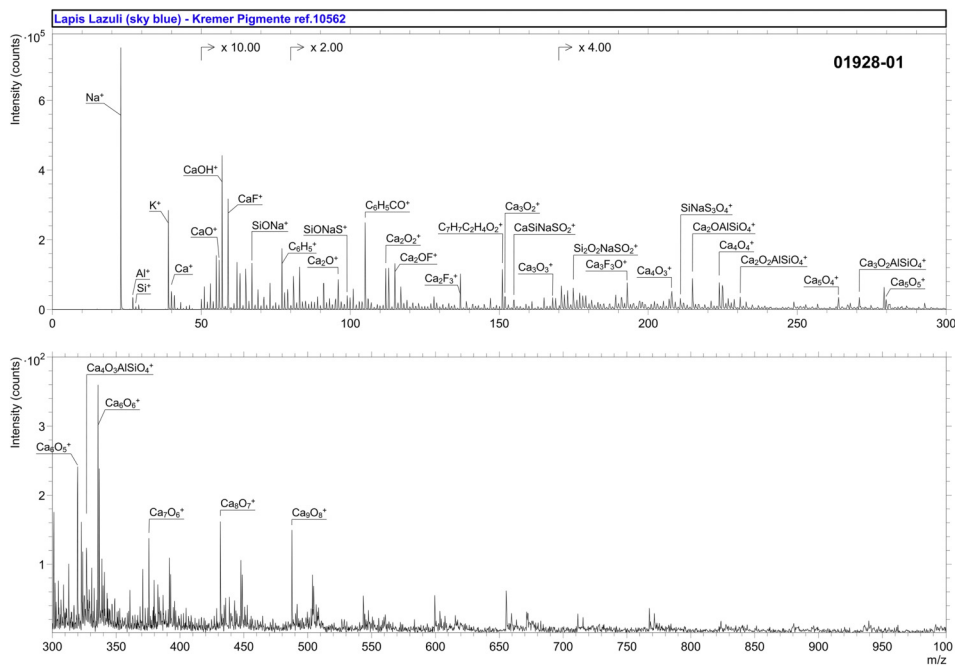
Very large grains, mass resolution impacted. Fluorine content is notably high, probably from a naturally occurring accessory mineral occurring with lazurite [like phlogopite $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$]. Assignments were refined thanks to colocalization in ion images.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01928-01	26.982 (38.4)	Al ⁺	Lazurite, sodalite
	39.960 (-52.3)	Ca ⁺	Lazurite, dolomite
	55.954 (-50.3)	CaO ⁺	Lazurite, dolomite
	56.962 (-47.8)	CaOH ⁺	Lazurite, dolomite
	58.957 (-54.9)	CaF ⁺	F-rich mineral impurity
	95.922 (29.3)	Ca ₂ O ⁺	Lazurite, dolomite
	98.936 (24.6)	SiONaS ⁺	Lazurite
	111.914 (-3.31)	Ca ₂ O ₂ ⁺	Lazurite
	112.923 (7.19)	Ca ₂ O ₂ H ⁺	Lazurite, dolomite
	114.920 (13.1)	Ca ₂ OF ⁺	F-rich mineral impurity
	136.922 (13.8)	Ca ₂ F ₃ ⁺	F-rich mineral impurity
	151.878 (10.5)	Ca ₃ O ₂ ⁺	Lazurite, dolomite
	154.895 (27.0)	CaSiNaSO ₂ ⁺	Lazurite
	167.873 (6.75)	Ca ₃ O ₃ ⁺	Lazurite, dolomite
	174.891 (-19.4)	Si ₂ O ₂ NaSO ₂ ⁺	Lazurite
	207.837 (11.7)	Ca ₄ O ₃ ⁺	Lazurite, dolomite
	210.858 (-19.3)	SiNaS ₃ O ₄ ⁺	Lazurite
	214.868 (47.3)	Ca ₂ OAlSiO ₄ ⁺	Lazurite
	223.832 (10.5)	Ca ₄ O ₄ ⁺	Lazurite, dolomite
	230.854 (4.70)	Ca ₂ O ₂ AlSiO ₄ ⁺	Lazurite
	263.798 (22.3)	Ca ₅ O ₄ ⁺	Lazurite, dolomite
	270.828 (47.4)	Ca ₃ O ₂ AlSiO ₄ ⁺	Lazurite
	279.785 (8.04)	Ca ₅ O ₅ ⁺	Lazurite, dolomite
	319.744 (-18.1)	Ca ₆ O ₅ ⁺	Lazurite, dolomite
	326.776 (10.9)	Ca ₄ O ₃ AlSiO ₄ ⁺	Lazurite
	335.746 (4.65)	Ca ₆ O ₆ ⁺	Lazurite, dolomite
	375.709 (3.73)	Ca ₇ O ₆ ⁺	Lazurite, dolomite
	431.666 (3.96)	Ca ₈ O ₇ ⁺	Lazurite, dolomite
	487.631 (17.8)	Ca ₉ O ₈ ⁺	Lazurite, dolomite

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Accession #:

01928-01

■ Specimen:

Lapis Lazuli, sky blue—Kremer Pigmente ref. 10562—Positive polarity

■ Technique:

SIMS

Instrument:

IONTOF, TOF SIMS IV

Analyzer Type:

Time-of-flight (with delayed extraction)

Analyzer Mass Resolving Power:

3400 m/Δm

Mass Resolving Power Determined at:

39 Da

Species Used for Mass Calibration:

Na⁺, Ca⁺, Na₂⁺, SiONa⁺, Ca₂O₂H⁺, Ca₃O₃H⁺, and Ca₄O₄H⁺

Specimen Normal-to-Analyzer:

0°

Source-to-Analyzer Angle:

45°

Primary Beam Ion Gun:

LMIG

Primary Ion Species:

Bi₃⁺

Primary Ion Dose:

3.28 × 10¹¹ ion/cm²

Primary Ion Pulse Width:

~100 ns

Primary Ion Pulse Rate:

6.7 kHz

Net Beam Voltage:

25 000 eV

Pulsed Beam Current:

0.000 09 nA

DC Beam Current:

14.6 nA

Beam Diameter:

400 μm

Beam Raster Size:

150 × 150 μm²

Beam Incident Angle:

45°

Secondary Source Polarity:

Positive

Mass Range Minimum:

0 Da

Mass Range Maximum:

2010 Da

Spectrum Dead Time Corrected:

Yes

Total Spectral Acquisition Time:

197 s

Comment:

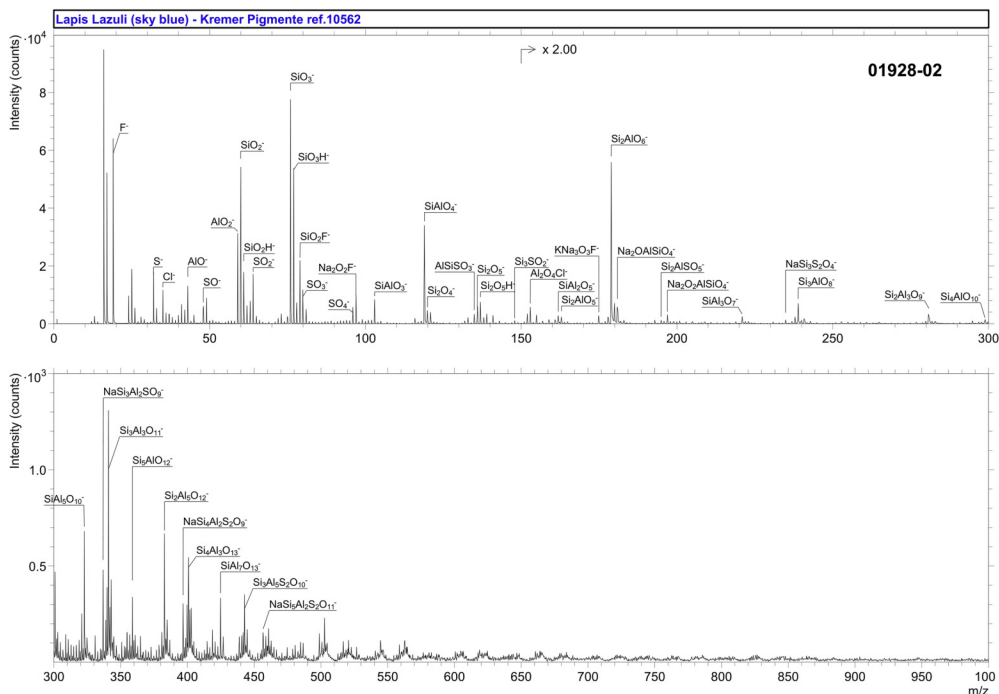
Very large grains, delayed extraction mode had to be used. The lighter the hue of lapis lazuli is, the higher is the proportion of other minerals such as dolomite. Fluorine-containing ions were identified thanks to imaging capabilities, as they were colocalized with F⁻ in the corresponding negative polarity dataset obtained on the same area.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01928-02	19.008 (-)	F ⁻	Accessory mineral (ex: phlogopite)
	31.974 (38.7)	S ⁻	Lazurite
	34.971 (31.1)	Cl ⁻	Lazurite, sodalite, phlogopite
	42.976 (-18.9)	AlO ⁻	Lazurite, sodalite, phlogopite
	47.965 (-60.1)	SO ⁻	Lazurite
	58.970 (-27.8)	AlO ₂ ⁻	Lazurite, sodalite, phlogopite
	60.972 (-51.4)	SiO ₂ H ⁻	Lazurite, sodalite, phlogopite
	63.960 (-45.6)	SO ₂ ⁻	Lazurite
	76.970 (-4.17)	SiO ₃ H ⁻	Lazurite, sodalite, phlogopite
	78.966 (-3.00)	SiO ₂ F ⁻	Phlogopite
	79.957 (-10.5)	SO ₃ ⁻	Lazurite
	95.956 (33.1)	SO ₄ ⁻	Lazurite
	96.966 (-24.9)	Na ₂ O ₂ F ⁻	Phlogopite
	102.947 (27.4)	SiAlO ₃ ⁻	Lazurite, sodalite, phlogopite
	118.941 (19.1)	SiAlO ₄ ⁻	Lazurite, sodalite, phlogopite
	134.922 (44.2)	AlSiSO ₃ ⁻	Lazurite
	136.939 (16.4)	Si ₂ O ₅ H ⁻	Lazurite, sodalite, phlogopite
	147.895 (12.3)	Si ₃ SO ₂ ⁻	Lazurite
	152.916 (22.3)	Al ₂ O ₄ Cl ⁻	Lazurite, sodalite, phlogopite
	161.918 (16.2)	SiAl ₂ O ₅ ⁻	Lazurite, sodalite, phlogopite
	162.914 (21.6)	Si ₂ AlO ₅ ⁻	Lazurite, sodalite, phlogopite
	174.912 (-28.0)	KNa ₃ O ₃ F ⁻	Phlogopite
	178.903 (-11.2)	Si ₂ AlO ₆ ⁻	Lazurite, sodalite, phlogopite
	180.910 (-15.2)	Na ₂ OAlSiO ₄ ⁻	Lazurite, sodalite, phlogopite
	194.885 (13.5)	Si ₂ AlSO ₅ ⁻	Lazurite
	196.901 (-37.5)	Na ₂ O ₂ AlSiO ₄ ⁻	Lazurite, sodalite, phlogopite
	220.884 (-11.6)	SiAl ₃ O ₇ ⁻	Lazurite, sodalite, phlogopite
	234.852 (31.7)	NaSi ₃ S ₂ O ₄ ⁻	Lazurite
	238.865 (-29.2)	Si ₃ AlO ₈ ⁻	Lazurite, sodalite, phlogopite
	280.846 (-25.9)	Si ₂ Al ₃ O ₉ ⁻	Lazurite, sodalite, phlogopite
	298.838 (-4.47)	Si ₄ AlO ₁₀ ⁻	Lazurite, sodalite, phlogopite
	322.832 (-7.14)	SiAl ₅ O ₁₀ ⁻	Lazurite, sodalite, phlogopite
	336.804 (-18.9)	NaSi ₃ Al ₂ SO ₉ ⁻	Lazurite
	340.818 (-5.18)	Si ₃ Al ₃ O ₁₁ ⁻	Lazurite, sodalite, phlogopite
	358.807 (3.36)	Si ₅ AlO ₁₂ ⁻	Lazurite, sodalite, phlogopite
	382.797 (-11.0)	Si ₂ Al ₅ O ₁₂ ⁻	Lazurite, sodalite, phlogopite
396.771 (28.0)	NaSi ₄ Al ₂ S ₂ O ₉ ⁻	Lazurite	
400.777 (-24.8)	Si ₄ Al ₃ O ₁₃ ⁻	Lazurite, sodalite, phlogopite	
424.780 (-6.23)	SiAl ₇ O ₁₃ ⁻	Lazurite, sodalite, phlogopite	
442.746 (29.9)	Si ₃ Al ₅ S ₂ O ₁₀ ⁻	Lazurite	
456.719 (-14.9)	NaSi ₅ Al ₂ S ₂ O ₁₁ ⁻	Lazurite	

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Accession #:

01928-02

■ Specimen:	Lapis Lazuli, sky blue—Kremer Pigmente ref. 10562—Negative polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV (with delayed extraction)
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	3300 m/Δm
Mass Resolving Power Determined at:	49 Da
Species Used for Mass Calibration:	SiO ₂ ⁻ , AlSiO ₄ ⁻ , AlSi ₂ O ₆ ⁻ , AlSi ₃ O ₈ ⁻ , and AlSi ₄ O ₁₀ ⁻
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	3.28 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Width:	~100 ns
Primary Ion Pulse Rate:	6.7 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 09 nA
DC Beam Current:	14.6 nA
Beam Diameter:	400 μm
Beam Raster Size:	150 × 150 μm ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Negative
Mass Range Minimum:	0 Da
Mass Range Maximum:	2022 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	197 s

Comment: Very large grains, delayed extraction mode had to be used. Fluorine content is notably high, probably from a naturally occurring accessory mineral occurring with lazurite [like phlogopite KMg₃(AlSi₃O₁₀)(F,OH)₂]. Assignments were refined thanks to colocalization in ion images.

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SPECTRAL FEATURES TABLE

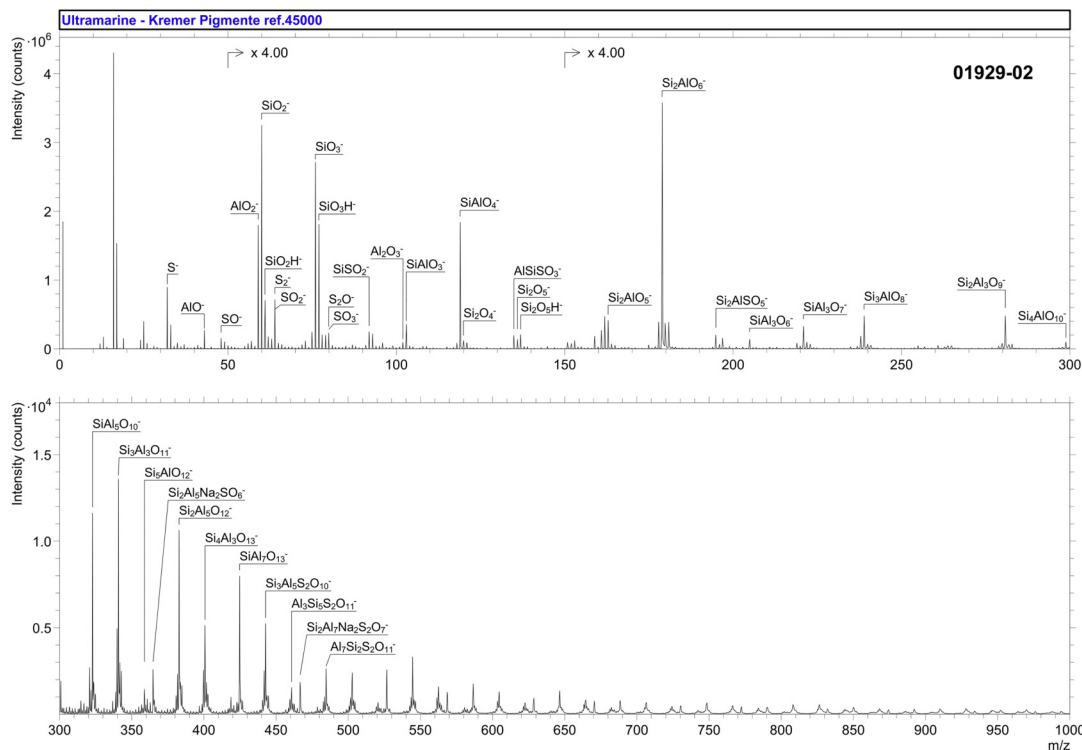
Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01929-01	26.982 (20.4)	Al ⁺	Sodium aluminum sulfosilicate
	45.979 (-3.68)	Na ₂ ⁺	Sodium aluminum sulfosilicate
	61.973 (-10.1)	Na ₂ O ⁺	Sodium aluminum sulfosilicate
	77.960 (-3.47)	Al ₂ HNa ⁺	Sodium aluminum sulfosilicate
	91.055 (-7.92)	C ₇ H ₇ ⁺	Abietic-type acid from colophony
	93.942 (-7.25)	SiONaAl ⁺	Sodium aluminum sulfosilicate
	94.936 (-16.6)	Si ₂ ONa ⁺	Sodium aluminum sulfosilicate
	100.941 (31.2)	SiAlNa ₂ ⁺	Sodium aluminum sulfosilicate
	104.949 (-17.7)	Na ₂ O ₂ Al ⁺	Sodium aluminum sulfosilicate
	105.071 (10.7)	C ₈ H ₉ ⁺	Abietic-type acid from colophony
	105.945 (-7.18)	Na ₂ O ₂ Si ⁺	Sodium aluminum sulfosilicate
	109.926 (28.5)	Na ₂ S ₂ ⁺	Sodium aluminum sulfosilicate
	115.052 (-21.6)	C ₉ H ₇ ⁺	Abietic-type acid from colophony
	121.923 (23.1)	NaKSiO ₂ ⁺	Sodium aluminum sulfosilicate
	128.059 (-23.7)	C ₁₀ H ₈ ⁺	Abietic-type acid from colophony
	128.936 (4.33)	SiNa ₃ O ₂ ⁺	Sodium aluminum sulfosilicate
	132.910 (-24.4)	Na ₃ S ₂ ⁺	-/Sodium aluminum sulfosilicate/-
	141.066 (-30.8)	C ₁₁ H ₉ ⁺	Abietic-type acid from colophony
	144.933 (14.9)	SiNa ₃ O ₃ ⁺	Sodium aluminum sulfosilicate
	148.926 (25.7)	SiNa ₂ AlO ₃ ⁺	Sodium aluminum sulfosilicate
	160.907 (18.2)	Si ₂ Na ₂ AlO ₂ ⁺	Sodium aluminum sulfosilicate
	164.918 (5.34)	SiNa ₂ AlO ₄ ⁺	Sodium aluminum sulfosilicate
	165.066 (-23.3)	C ₁₃ H ₉ ⁺	Abietic-type acid from colophony
	176.884 (14.2)	Si ₂ Na ₂ AlSO ⁺	Sodium aluminum sulfosilicate
	204.882 (30.1)	Si ₂ Na ₂ AlSiO ₃ ⁺	Sodium aluminum sulfosilicate
	227.174 (-25.0)	C ₁₇ H ₂₃ ⁺	Abietic acid fragment (M—C ₃ H ₇ O ₂)
	246.842 (10.0)	Si ₂ Na ₂ Al ₃ SO ₂ ⁺	Sodium aluminum sulfosilicate
	255.187 (49.0)	C ₁₈ H ₂₃ O ⁺	Abietic acid fragment (M—C ₂ H ₇ O)
	271.213 (26.0)	C ₁₉ H ₂₇ O ⁺	Abietic acid fragment (M—CH ₂ O)
	311.229 (-16.6)	C ₂₀ H ₃₁ ONaH ⁺	Resin acid soap
	327.229 (-7.99)	C ₂₂ H ₃₁ O ₂ ⁺	Abietic-type ester
	348.784 (-8.34)	Si ₂ Al ₅ Na ₂ SO ₅ ⁺	Sodium aluminum sulfosilicate
366.266 (28.9)	C ₂₅ H ₃₄ O ₂ ⁺	Abietic-type ester	
413.274 (13.1)	C ₂₆ H ₃₇ O ₄ ⁺	Abietic-type ester	
450.733 (34.5)	Si ₂ Al ₇ Na ₂ S ₂ O ₆ ⁺	Sodium aluminum sulfosilicate	

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01929-02	31.972 (-18.9)	S ⁻	Sodium aluminum sulfosilicate
	42.976 (-26.1)	AlO ⁻	Aluminosilicate
	47.966 (-22.7)	SO ⁻	Sodium aluminum sulfosilicate
	58.971 (-15.0)	AlO ₂ ⁻	Aluminosilicate
	60.974 (-13.3)	SiO ₂ H ⁻	Aluminosilicate
	63.946 (19.5)	S ₂ ⁻	Sodium aluminum sulfosilicate
	63.962 (-6.30)	SO ₂ ⁻	Sodium aluminum sulfosilicate
	76.974 (48.1)	SiO ₃ H ⁻	Aluminosilicate
	79.943 (37.5)	S ₂ O ⁻	Sodium aluminum sulfosilicate
	91.938 (-15.6)	SiSO ₂ ⁻	Sodium aluminum sulfosilicate
	101.946 (-20.6)	Al ₂ O ₃ ⁻	Aluminosilicate
	102.943 (-10.9)	SiAlO ₃ ⁻	Aluminosilicate
	118.938 (-9.51)	SiAlO ₄ ⁻	Aluminosilicate
	134.916 (4.25)	AlSiSO ₃ ⁻	Sodium aluminum sulfosilicate
	136.935 (-11.9)	Si ₂ O ₅ H ⁻	Aluminosilicate
	162.910 (-5.94)	Si ₂ AlO ₅ ⁻	Aluminosilicate
	178.907 (6.72)	Si ₂ AlO ₆ ⁻	Aluminosilicate
	194.886 (19.0)	Si ₂ AlSO ₅ ⁻	Sodium aluminum sulfosilicate
	204.886 (-25.0)	SiAl ₃ O ₆ ⁻	Aluminosilicate
	220.881 (-26.2)	SiAl ₃ O ₇ ⁻	Aluminosilicate
	238.876 (15.1)	Si ₃ AlO ₈ ⁻	Aluminosilicate
	280.849 (-15.9)	Si ₂ Al ₃ O ₉ ⁻	Aluminosilicate
	298.843 (14.3)	Si ₄ AlO ₁₀ ⁻	Aluminosilicate
	322.826 (-26.3)	SiAl ₅ O ₁₀ ⁻	Aluminosilicate
	340.814 (-17.7)	Si ₃ Al ₃ O ₁₁ ⁻	Aluminosilicate
	358.802 (-11.6)	Si ₅ AlO ₁₂ ⁻	Aluminosilicate
	364.790 (18.3)	Si ₂ Al ₅ Na ₂ SO ₆ ⁻	Sodium aluminum sulfosilicate
	382.793 (-24.5)	Si ₂ Al ₅ O ₁₂ ⁻	Aluminosilicate
	400.779 (-20.3)	Si ₄ Al ₃ O ₁₃ ⁻	Aluminosilicate
	424.763 (-44.3)	SiAl ₇ O ₁₃ ⁻	Aluminosilicate
442.727 (-12.6)	Si ₃ Al ₅ S ₂ O ₁₀ ⁻	Sodium aluminum sulfosilicate	
460.724 (13.5)	Al ₃ Si ₅ S ₂ O ₁₁ ⁻	Sodium aluminum sulfosilicate	
466.718 (10.6)	Si ₂ Al ₇ Na ₂ S ₂ O ₇ ⁻	Sodium aluminum sulfosilicate	
484.707 (-12.5)	Al ₇ Si ₂ S ₂ O ₁₁ ⁻	Sodium aluminum sulfosilicate	

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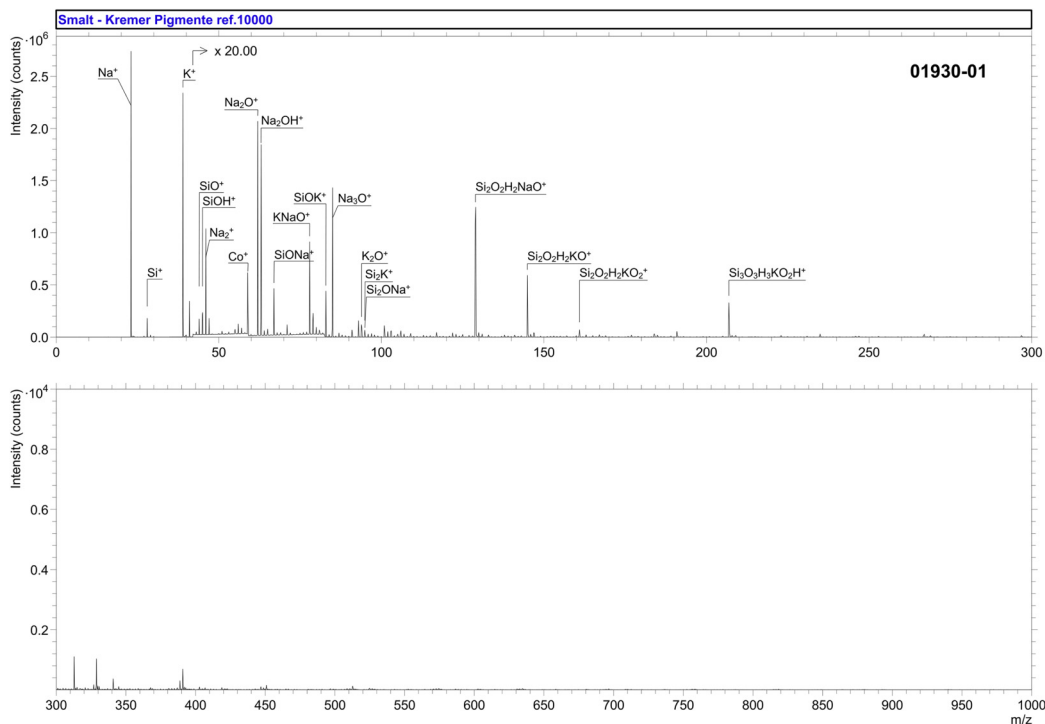


Accession #:	01929-02
Specimen:	Ultramarine Blue—Kremer Pigmente ref. 45000—Negative polarity
Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2700 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	SiO ₂ ⁻ , AlSiO ₄ ⁻ , AlSi ₂ O ₆ ⁻ , AlSi ₃ O ₈ ⁻ , AlSi ₄ O ₁₀ ⁻ , and AlSi ₅ O ₁₂ ⁻
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.37 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 15 nA
DC Beam Current:	14.7 nA
Beam Diameter:	400 μm
Beam Raster Size:	250 × 250 μm ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Negative
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	293 s
Comment:	Delayed extraction mode used in addition to refine peak assignment. Data shown are standard mode.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01930-01	43.971 (-4.75)	SiO ⁺	CoOKSi
	44.979 (-8.83)	SiOH ⁺	CoOKSi
	45.978 (-0.44)	Na ₂ ⁺	—
	58.932 (-6.22)	Co ⁺	CoOKSi
	61.952 (-11.8)	Na ₂ O ⁺	—
	62.982 (3.14)	Na ₂ OH ⁺	—
	77.951 (35.6)	KNaO ⁺	—
	82.937 (18.5)	SiOK ⁺	CoOKSi
	84.965 (14.3)	Na ₃ O ⁺	—
	93.921 (-10.8)	K ₂ O ⁺	CoOKSi
	94.915 (-20.6)	Si ₂ K ⁺	CoOKSi
	94.937 (-8.95)	Si ₂ ONa ⁺	—
	128.948 (35.9)	(SiOH) ₂ NaO ⁺	—
	144.923 (38.9)	(SiOH) ₂ KO ⁺	CoOKSi
	160.908 (-25.1)	(SiOH) ₂ KO ₂ ⁺	CoOKSi
	206.902 (10.6)	(SiOH) ₃ KO ₂ H ⁺	CoOKSi



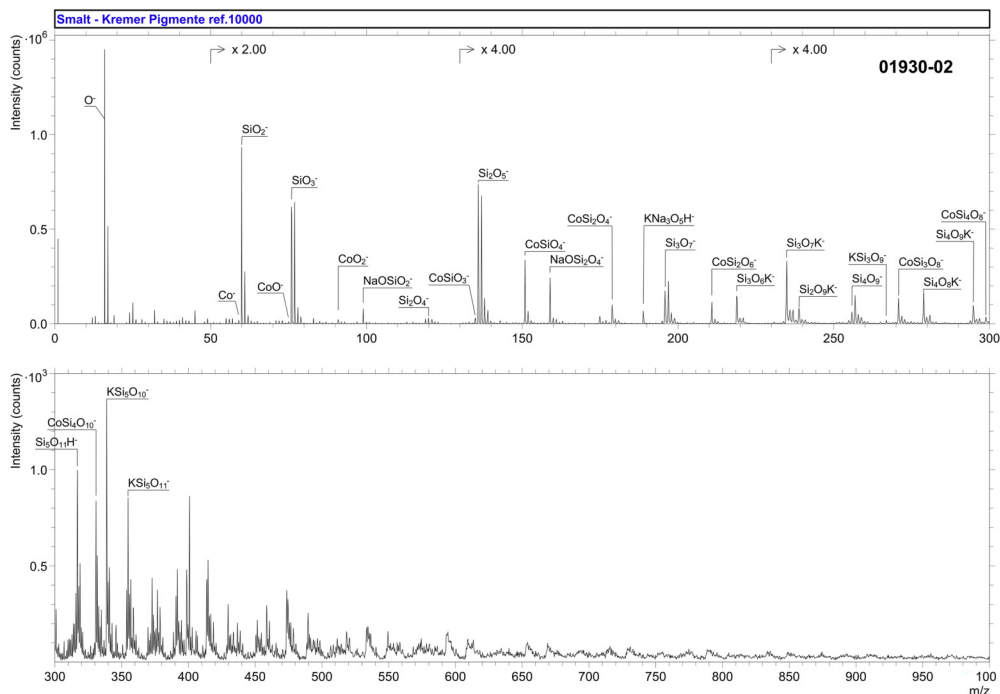
Accession #:	01930-01
■ Specimen:	Small—Kremer Pigmente ref. 10000—Positive polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	1700 m/Δm
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Al ⁺ , ⁴¹ K ⁺ , Na ₂ ⁺ , SiONa ⁺ , SiO ₂ Na ₂ ⁺ and SiO ₃ Na ₃ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.37 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 15 nA
DC Beam Current:	14.7 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Positive
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	293 s
Comment:	Large grains, mass resolution impacted. High sodium content, likely from the glass. Above m/z 200 attribution is not given, as many possibilities exist due to the mass interferences between K and NaO.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01930-02	58.935 (26.1)	Co ⁻	CoOKSi
	74.929 (7.03)	CoO ⁻	CoOKSi
	90.923 (-9.67)	CoO ₂ ⁻	CoOKSi
	98.951 (6.97)	NaOSiO ₂ ⁻	CoOKSi
	106.920 (16.6)	CoO ₃ ⁻	CoOKSi
	134.898 (12.0)	CoSiO ₃ ⁻	CoOKSi
	150.888 (-16.3)	CoSiO ₄ ⁻	CoOKSi
	158.915 (-26.2)	NaSi ₂ O ₅ ⁻	—
	178.878 (58.5)	CoSi ₂ O ₄ ⁻	CoOKSi
	188.924 (43.5)	KNa ₃ O ₅ H ⁻	—
	195.892 (-20.1)	Si ₃ O ₇ ⁻	CoOKSi
	210.855 (-11.8)	CoSi ₂ O ₆ ⁻	CoOKSi
	218.869 (19.8)	Si ₃ O ₆ K ⁻	CoOKSi
	234.867 (31.1)	Si ₃ O ₇ K ⁻	CoOKSi
	238.877 (19.7)	Si ₂ O ₉ K ⁻	CoOKSi
	255.860 (-10.1)	Si ₄ O ₉ ⁻	CoOKSi
	266.846 (-12.1)	KSi ₃ O ₉ ⁻	CoOKSi
	270.821 (-9.66)	CoSi ₃ O ₈ ⁻	CoOKSi
	278.837 (20.2)	Si ₄ O ₈ K ⁻	CoOKSi
	294.830 (14.0)	Si ₄ O ₉ K ⁻	CoOKSi
	316.834 (-9.30)	Si ₅ O ₁₁ H ⁻	CoOKSi
	330.782 (-25.8)	CoSi ₄ O ₁₀ ⁻	CoOKSi
	338.802 (10.7)	KSi ₅ O ₁₀ ⁻	CoOKSi
354.787 (-12.3)	KSi ₅ O ₁₁ ⁻	CoOKSi	

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Accession #:

01930-02

<p>■ Specimen: ■ Technique: Instrument: Analyzer Type: Analyzer Mass Resolving Power: Mass Resolving Power Determined at: Species Used for Mass Calibration: Specimen Normal-to-Analyzer: Source-to-Analyzer Angle: Primary Beam Ion Gun: Primary Ion Species: Primary Ion Dose: Primary Ion Pulse Width: Primary Ion Pulse Rate: Net Beam Voltage: Pulsed Beam Current: DC Beam Current: Beam Diameter: Beam Raster Size: Beam Incident Angle: Secondary Source Polarity: Mass Range Minimum: Mass Range Maximum: Spectrum Dead Time Corrected: Total Spectral Acquisition Time:</p>	<p>Smalt—Kremer Pigmente ref. 10000—Negative polarity SIMS IONTOF, TOF SIMS IV Time-of-flight 1500 m/Δm 25 Da Cl⁻, SiO₂⁻, Si₂O₅H⁻, Si₃O₇H⁻, Si₄O₉H⁻, and Si₅O₁₁H⁻ 0° 45° LMIG Bi₃⁺ 4.37 × 10¹¹ ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 15 nA 14.7 nA ~2 μm 250 × 250 μm² 45° Negative 0 Da 3540 Da Yes 308 s</p>
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Comment: Very large grains, mass resolution impacted. Co containing ions were identified thanks to the images, with colocalization with the Co⁺ and Co⁻ ions. The absence of aluminum oxide is notable, and this avoids to misattribute some peaks to aluminosilicate compounds.

03 June 2024 13:41:47

SPECTRAL FEATURES TABLE (peaks appearing in all spectra—Positive Polarity)

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
All	22.99 (–)	Na ⁺	Lapis lazuli, Synthetic ultramarine, Smalt
...	27.98 (27.4)	Si ⁺	Lapis lazuli, Synthetic ultramarine, Smalt
...	38.96 (29.9)	K ⁺	Lapis lazuli, Synthetic ultramarine, Smalt
...	66.96 (7.03)	SiONa ⁺	Lapis lazuli, Synthetic ultramarine, Smalt

(Mean absolute deviation values are given for the mass deviations, except for sodium as the peaks were saturated).

03 June 2024 13:41:47

SPECTRAL FEATURES TABLE (peaks appearing in all spectra—Negative Polarity)

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
All	59.97 (15.8)	SiO ₂ [–]	Lapis lazuli, Synthetic ultramarine, Smalt
...	75.97 (34.3)	SiO ₃ [–]	Lapis lazuli, Synthetic ultramarine, Smalt
...	119.94 (8.45)	Si ₂ O ₄ [–]	Lapis lazuli, Synthetic ultramarine, Smalt
...	135.93 (14.0)	Si ₂ O ₅ [–]	Lapis lazuli, Synthetic ultramarine, Smalt

(Mean absolute deviation values are given for the mass deviations.)