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RESEARCH ARTICLE | JUNE 06 2024

Tof-SIMS spectra of historical inorganic pigments: Calcium white pigments in both polarities

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

Caroline Bouvier  ; Sebastiaan Van Nuffel  ; Alain Brunelle  



Surf. Sci. Spectra 31, 015007 (2024)

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- ▶ analysis of neutral and radical species



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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: Calcium white pigments 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 database focuses on six white pigments made from calcium-rich natural or synthesized materials, prepared following traditional processes. Such pigments are frequently found in the preparation layers, namely, “ground,” separating the support from the observable paint layers, and providing a smooth surface to hold the paint on while preventing its absorption by the substrate. Differentiating between these pigments is helpful to better describe the painting practice. Here, ToF-SIMS reference spectra using a Bi_3^+ primary ion species are presented for both polarities.

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Accession #: 01931, 01932, 01933, 01934, 01935, 01936

Technique: SIMS

Specimen: Alba Albula, Bianco San Giovanni, Eggshell white, Dolomite, Anhydrite plaster, Natural alabaster

Instrument: IONTOF, TOF SIMS IV

Major Species in Spectra: O, H, Si, S, Al, C, Ca, Na, Mg, K, P, Cl

Minor Species in Spectra: Hydrocarbon contamination

Published Spectra: 12

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 six white pigments made of calcium-rich materials. Such materials are likely to be present in historical paintings and painted objects, especially in the deeper layers, commonly referred to as “ground” or “preparation” layers. Their structure and composition depends on the time and place in art history.

The reference materials were supplied by specialized manufacturers selling pigments reproducing historical recipes as closely as

possible, such as Kremer Pigmente GmbH, Masters Pigments, Laverdure, and Sennelier. Pigments were available as finely ground powder of variable particle size (between one and a few tens of μm) 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 conductive double-sided tape (3M Electrically Conductive Adhesive Transfer

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Tape 9703) already fixed to a 1 cm × 1 cm × 0.125 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} – 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 2×10^{15} ions/cm²). 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 Bi₃⁺) was 4.35×10^{11} ions/cm². Surface potential was compensated and charging of the sample was compensated with the low-energy 20 eV electrons of the flood gun.

All positive polarity data were calibrated using the same set of peaks appearing in all spectra, namely, Na⁺ at m/z 22.99, Ca⁺ at m/z 39.96, Ca₂O⁺ at m/z 95.92, Ca₃O₂⁺ at m/z 151.88, Ca₄O₃⁺ at m/z 207.83, Ca₅O₄⁺ at m/z 263.79, and Ca₆O₅⁺ at m/z 319.75. All negative polarity data were calibrated using combinations of the following ions: Cl[−] at m/z 34.97, CaO[−] at m/z 55.96, CaO₂H[−] at m/z 72.96, Ca₂O₃H[−] at m/z 128.92, and Ca₃O₄H[−] at m/z 184.88. These calibration lists allowed for an adequate coverage of the mass range of interest, and the calcium containing calibration ions could be verified using their isotopic pattern. The actual calibration set for each individual dataset can be found in the associated table.

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 the current literature.^{1–5} The Spectrum ID# refers to that number, added with “−01” for positive spectra and with “−02” for negative spectra.

SPECIMEN DESCRIPTION (ACCESSION # 01931)

Specimen: Alba Albula, warm white chalk from Albula, Switzerland (Kremer Pigmente ref. 11283)

CAS Registry #: 471-34-1

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Calcium carbonate

Source: Kremer Pigmente GmbH

Specimen Composition: CaCO₃

Form: Ground pigment powder

History and Significance: White earths derived directly from calcite-rich clay sediments are one of the oldest pigments. They are often found in the preparation layer applied to the substrate of a painting. This white pigment with a beige hue is made by ground stones naturally found in the Albula mountain pass (Switzerland). It is likely to contain other minerals than calcite.

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 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 2.35A. Residual surface potential was compensated before analysis.

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 # 01932)

Specimen: Bianco San Giovanni (Kremer Pigmente ref. 11415)

CAS Registry #: 471-34-1 and 1305-62-0-1

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Calcium carbonate with calcium hydroxide

Source: Kremer Pigmente GmbH

Specimen Composition: CaCO₃ + Ca(OH)₂

Form: Ground pigment powder

History and Significance: White pigment prepared according to Cennino Cennini's recipe. Mainly composed of hydrated lime that was slowly dried and very finely ground (well below $150 \mu\text{m}$ for instance).

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 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 2.35 A. Residual surface potential was compensated before analysis.

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 # 01933)

Specimen: Eggshell White (Kremer Pigmente ref. 11410)

CAS Registry #: Unknown

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Ground eggshell

Source: Kremer Pigmente GmbH

Specimen Composition: CaCO₃, MgCO₃, Ca₃(PO₄)₂, proteins from the shell

Form: Ground pigment powder

History and Significance: Finely ground eggshell is an easily accessible source of white pigment in a workshop and is frequently mentioned in preparations. The material has been classified as an inorganic pigment in this paper, as it mainly consists of calcium and magnesium carbonates. It is, however, worth noticing that some fragments originating from the peptide backbone of proteins, naturally found in the eggshell structure, can be detected using ToF-SIMS in this pigment.

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 × 250 μm²

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto 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 2.35 A. Residual surface potential was compensated before analysis.

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 × 10¹⁵ ions/cm²

SPECIMEN DESCRIPTION (ACCESSION # 01934)

Specimen: Dolomite 10 μ (Kremer Pigmente ref. 58740)

CAS Registry #: 16389-88-1

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Natural calcium-magnesium carbonate

Source: Kremer Pigmente GmbH

Specimen Composition: CaMg(CO₃)₂

Form: Ground pigment powder

History and Significance: White CaMg(CO₃)₂-rich white sediments or minerals are often found in the preparation layer applied to the substrate of a painting.

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 × 250 μm²

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto 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 2.35 A. Residual surface potential was compensated before analysis.

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 × 10¹⁵ ions/cm²

SPECIMEN DESCRIPTION (ACCESSION # 01935, 01936)

Specimen: (Accession #01935) Anhydrite plaster, burnt gypsum (Kremer Pigmente ref. 58320), (Accession #01936) Natural alabaster plaster (Kremer Pigmente ref. 58340).

CAS Registry #: 7778-18-9

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: (Accession #01935) Calcium sulfate anhydrite, (Accession #01936) Calcium sulfate dihydrate + calcium sulfate alpha hemihydrate

Source: Kremer Pigmente GmbH

Specimen Composition: (Accession #01935) CaSO₄, (Accession #01936) CaSO₄·1/2H₂O (n = 1/2, 2)

Form: Ground pigment powder

History and Significance: Natural plasters are found in many paint mixtures as a filler to lighten a color or as a preparation material. Characterizing gypsum is important to understand the structure of a painted artwork. Natural gypsum contains strontium inclusions.

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 × 250 μm²

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto 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 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 × 10¹⁵ 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: None

Energy Acceptance Window: 20 eV

Post-acceleration Voltage: 10 000 eV
Sample Bias: 10–20 eV
Specimen Normal-to-Analyzer (Θ_e): 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: Bi₃⁺
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: ~2 μm
Beam Raster Size: 250 × 250 μm²
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: 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 ns
Ion Pulse Rate: N/A
DC Beam Current: ~10 nA
Pulsed Beam Current: N/A
Current Measurement Method: Faraday cup

Beam Diameter: ~50 μm
Beam Raster Size: 500 × 500 μm²
Raster Pixel Dimensions: N/A
Beam Incident Angle: 45°
Source-to-Analyzer Angle: 45°

ACKNOWLEDGMENTS

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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 (lead). **Sebastiaan Van Nuffel:** Investigation (equal); Writing – review & editing (lead). **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.

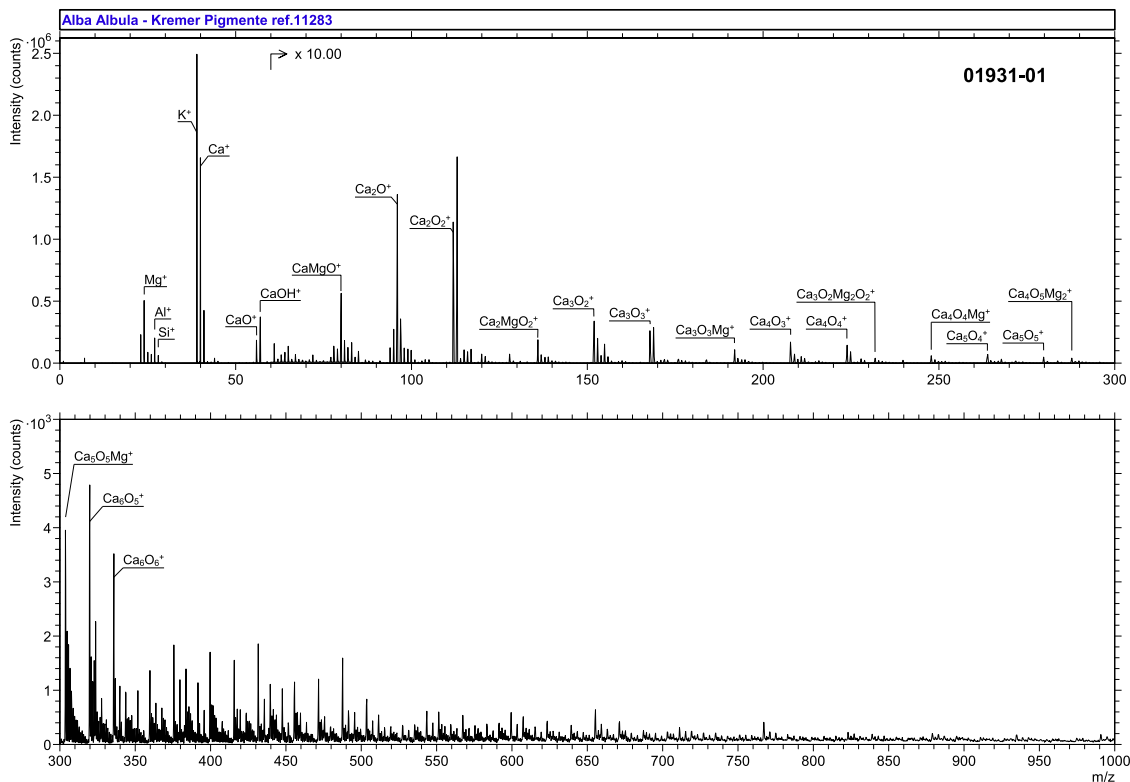
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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01931-01	23.984 (-42.8)	Mg ⁺	-
	26.980 (-30.0)	Al ⁺	Clay
	27.975 (-33.7)	Si ⁺	Clay
	38.965 (52.6)	K ⁺	-
	79.945 (38.0)	CaMgO ⁺	-
	135.900 (3.30)	Ca ₂ MgO ₂ ⁺	-
	191.858 (4.51)	Ca ₃ O ₂ MgO ⁺	-
	231.833 (-17.0)	Ca ₃ O ₂ (MgO) ₂ ⁺	-
	247.816 (5.49)	Ca ₄ O ₃ MgO ⁺	-
	287.796 (5.88)	Ca ₄ O ₃ (MgO) ₂ ⁺	CaCO ₃
	303.773 (3.81)	Ca ₅ O ₄ MgO ⁺	CaCO ₃

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Accession #:

01931-01

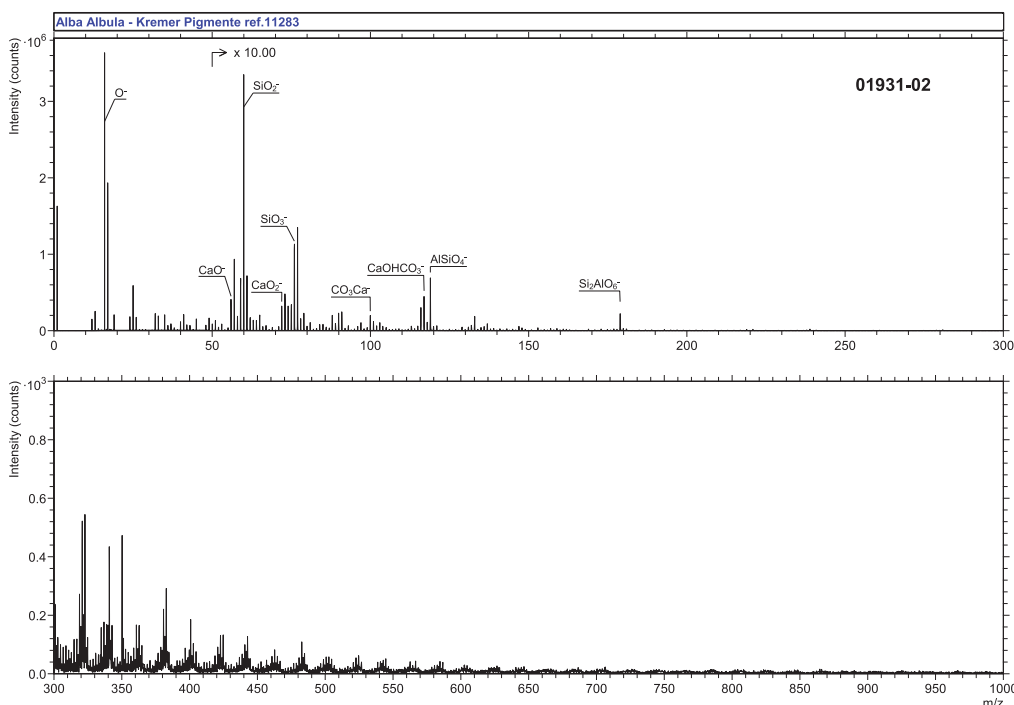
<p> Specimen: Technique: Instrument: Analyzer Type: Analyzer Mass Resolving Power: Mass Resolving Power Determined at: Species Used for Mass Calibration: Specimen Normal-to-Analyzer: Source-to-Analyzer Angle: Primary Beam Ion Gun: Primary Ion Species: Primary Ion Dose: Primary Ion Pulse Width: Primary 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> Alba Albula – Kremer Pigmente ref. 11283 – Positive polarity SIMS IONTOF, TOF SIMS IV Time-of-flight 2500 m/Δm 27 Da $\text{Na}^+, \text{Ca}^+, \text{CaO}^+, \text{Ca}_2\text{O}^+, \text{Ca}_3\text{O}_2^+, \text{Ca}_4\text{O}_3^+, \text{Ca}_5\text{O}_4^+, \text{Ca}_6\text{O}_5^+$ 0° 45° LMIG Bi_3^+ 4.34×10^{11} ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 21 nA 14.6 nA ~2 μm 250 × 250 μm² 45° Positive 0 Da 3545 Da Yes 210 s </p>
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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01931-02	15.995 (-8.90)	O ⁻	-
	63.961 (-16.7)	SO ₂ ⁻	-
	75.966 (43.5)	SiO ₃ ⁻	Clay
	79.959 (16.3)	SO ₃ ⁻	-
	99.946 (-14.8)	CaCO ₃ ⁻	CaCO ₃
	116.948 (-17.9)	CaOHCO ₃ ⁻	CaCO ₃
	118.938 (-1.81)	AlSiO ₄ ⁻	Clay
	178.907 (6.51)	Si ₂ AlO ₆ ⁻	Clay

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Accession #:

01931-02

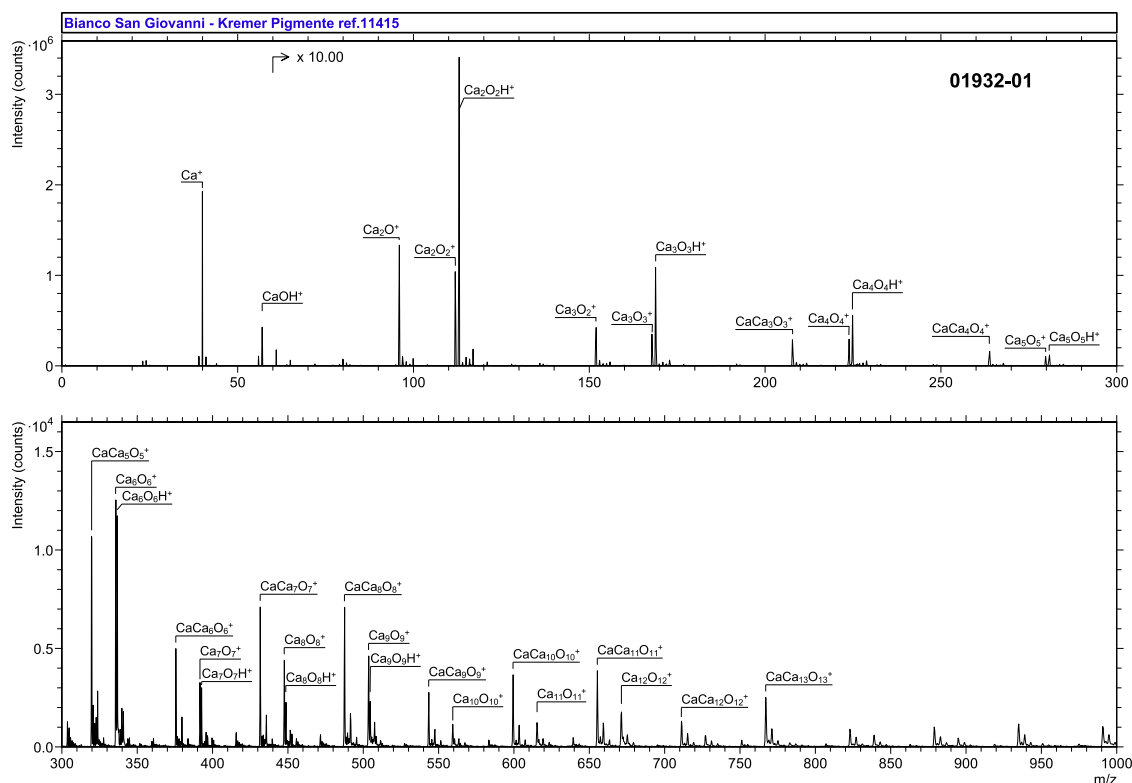
■ Specimen:	Alba Albula – Kremer Pigmente ref. 11283 – Negative polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2400 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , CaO ⁻ , Ca ₂ O ₃ H ⁻
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.34 × 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 21 nA
DC Beam Current:	14.6 nA
Beam Diameter:	~2 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:	210 s
Comment:	The peak at <i>m/z</i> 59.98 could be attributed to CO ₃ ⁻ along with a near isobaric interference from SiO ₂ ⁻ , thanks to the ion images.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01932-01	39.962 (4.34)	Ca ⁺	Ca(OH) ₂
	56.965 (3.08)	CaOH ⁺	Ca(OH) ₂
	95.920 (6.66)	Ca ₂ O ⁺	Ca(OH) ₂
	111.916 (16.7)	Ca ₂ O ₂ ⁺	Ca(OH) ₂
	112.925 (24.1)	Ca ₂ O ₂ H ⁺	Ca(OH) ₂
	151.878 (3.21)	Ca ₃ O ₂ ⁺	Ca(OH) ₂
	167.873 (4.08)	Ca ₃ O ₃ ⁺	Ca(OH) ₂
	168.881 (6.44)	Ca ₃ O ₃ H ⁺	Ca(OH) ₂
	207.833 (−6.07)	Ca ₄ O ₃ ⁺	Ca(OH) ₂
	223.829 (−1.46)	Ca ₄ O ₄ ⁺	Ca(OH) ₂
	224.838 (1.07)	Ca ₄ O ₄ H ⁺	Ca(OH) ₂
	263.789 (−10.4)	Ca ₅ O ₄ ⁺	Ca(OH) ₂
	279.784 (−10.1)	Ca ₅ O ₅ ⁺	Ca(OH) ₂
	280.794 (−2.46)	Ca ₅ O ₅ H ⁺	Ca(OH) ₂
	319.744 (−18.9)	Ca ₆ O ₅ ⁺	Ca(OH) ₂

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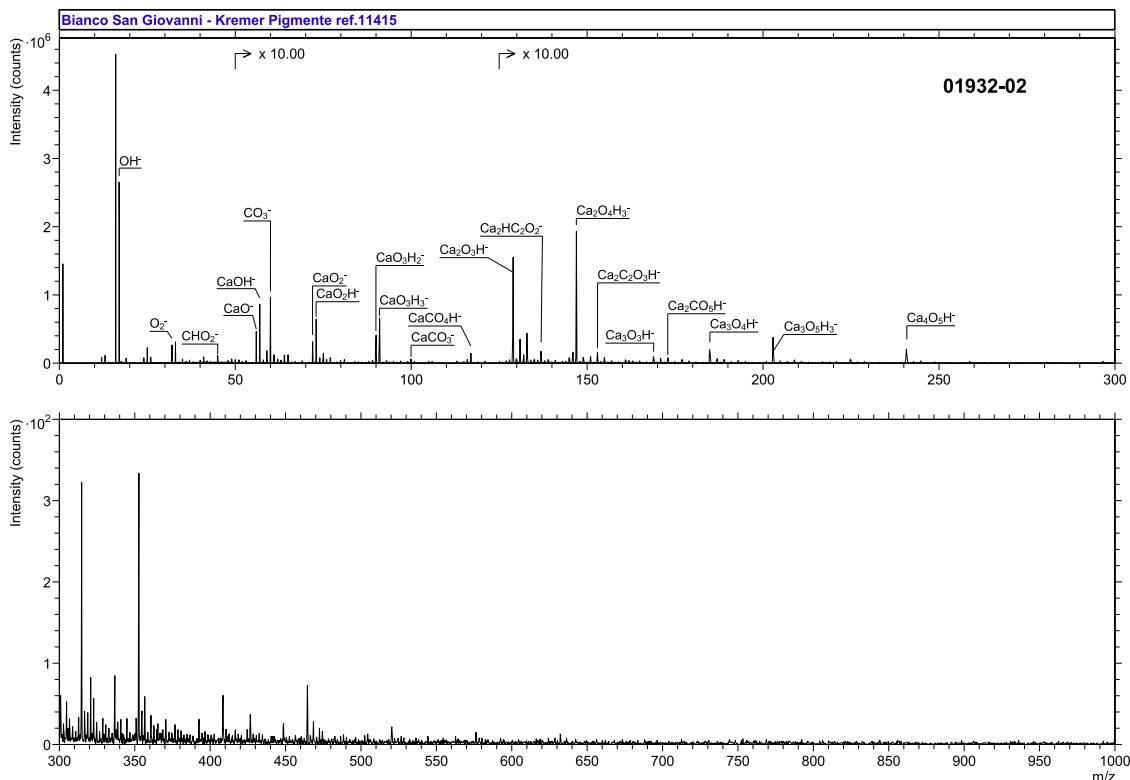
Accession #:	01932-01
■ Specimen:	Bianco San Giovanni – Kremer Pigmente ref. 11415 – Positive polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2900 m/Δm
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Na^+ , Ca^+ , CaO^+ , Ca_2O^+ , Ca_3O_2^+ , Ca_4O_3^+ , Ca_5O_4^+ , Ca_6O_5^+
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 16 nA
DC Beam Current:	15.7 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:	250 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01932-02	44.999 (8.89)	CO ₂ H ⁻	CaCO ₃
	56.966 (3.55)	CaOH ⁻	CaCO ₃ /Ca(OH) ₂
	59.986 (17.2)	CO ₃ ⁻	CaCO ₃
	72.964 (40.0)	(CaO)OH ⁻	Ca(OH) ₂
	89.965 (13.5)	(CaO)(OH) ₂ ⁻	Ca(OH) ₂
	90.974 (23.7)	(CaOH)(OH) ₂ ⁻	Ca(OH) ₂
	99.949 (6.77)	CaCO ₃ ⁻	CaCO ₃ /Ca(OH) ₂
	115.940 (-27.8)	(CaO)CO ₃ ⁻	CaCO ₃ /Ca(OH) ₂
	116.951 (-1.12)	(CaOH)CO ₃ ⁻	CaCO ₃ /Ca(OH) ₂
	128.921 (17.1)	(CaO) ₂ (OH) ⁻	Ca(OH) ₂
	136.928 (30.0)	Ca ₂ H(CO) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
	146.929 (2.06)	H(CaO) ₂ (OH) ₂ ⁻	Ca(OH) ₂
	152.921 (16.3)	Ca ₂ OH(CO) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
	168.888 (43.6)	Ca ₃ O ₃ H ⁻	Ca(OH) ₂
	172.911 (15.0)	(CaO) ₂ CO ₃ H ⁻	CaCO ₃ /Ca(OH) ₂
	184.878 (11.3)	(CaO) ₃ (OH) ⁻	Ca(OH) ₂
	202.885 (-4.64)	H(CaO) ₃ (OH) ₂ ⁻	Ca(OH) ₂
240.832 (-6.09)	(CaO) ₄ (OH) ⁻	Ca(OH) ₂	

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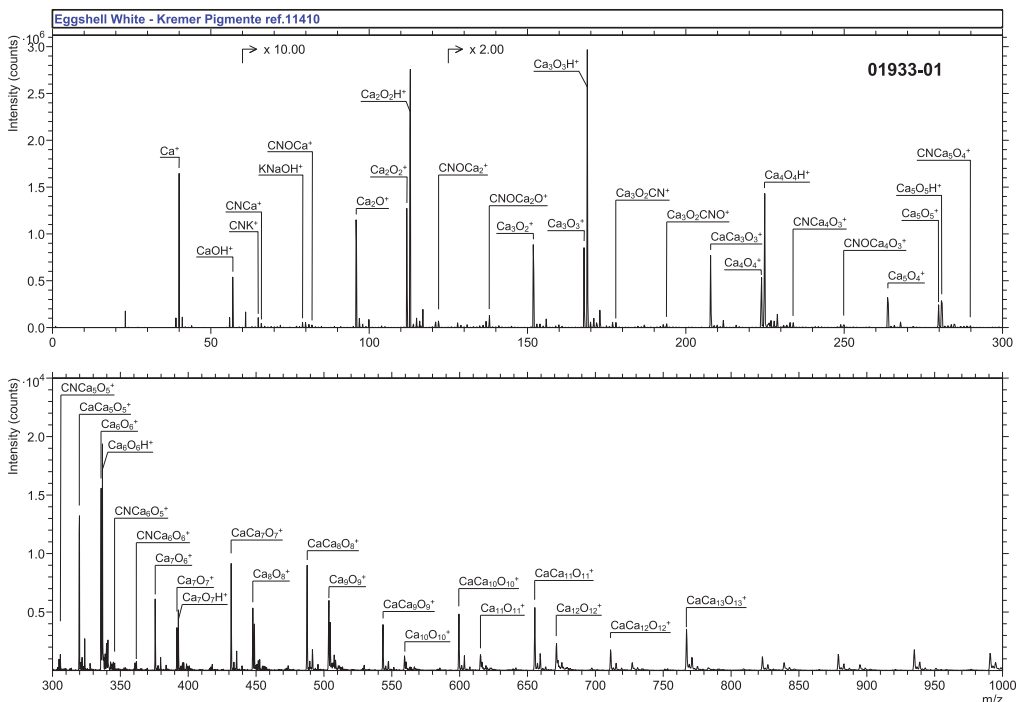
Accession #:	01932-02
Specimen:	Bianco San Giovanni – Kremer Pigmente ref. 11415 – Negative polarity
Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2500 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , CaO ⁻ , Ca ₂ O ₃ H ⁻ , Ca ₃ O ₄ H ⁻
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.37 × 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 16 nA
DC Beam Current:	15.7 nA
Beam Diameter:	~2 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:	250 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01933-01	64.970 (64.6)	(CN)K ⁺	Eggshell proteins
	65.967 (28.2)	(CN)Ca ⁺	Eggshell proteins/CaCO ₃
	78.958 (27.7)	KNaOH ⁺	Eggshell materials
	121.927 (32.1)	(CN)Ca ₂ O ⁺	Eggshell proteins/CaCO ₃
	137.922 (28.8)	(CNO)Ca ₂ O ⁺	Eggshell proteins/CaCO ₃
	177.888 (46.0)	(CN)Ca ₃ O ₂ ⁺	Eggshell proteins/CaCO ₃
	193.881 (32.2)	(CNO)Ca ₃ O ₂ ⁺	Eggshell proteins/CaCO ₃
	233.846 (36.2)	(CN)Ca ₄ O ₃ ⁺	Eggshell proteins/CaCO ₃
	249.842 (38.2)	(CNO)Ca ₄ O ₃ ⁺	Eggshell proteins/CaCO ₃
	289.807 (39.6)	(CN)Ca ₅ O ₄ ⁺	Eggshell proteins/CaCO ₃
	305.799 (29.6)	(CNO)Ca ₅ O ₄ ⁺	Eggshell proteins/CaCO ₃
	345.762 (28.3)	(CN)Ca ₆ O ₅ ⁺	Eggshell proteins/CaCO ₃
	361.755 (21.6)	(CNO)Ca ₆ O ₅ ⁺	Eggshell proteins/CaCO ₃

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Accession #:

01933-01

<p>■ Specimen:</p> <p>■ Technique:</p> <p>Instrument:</p> <p>Analyzer Type:</p> <p>Analyzer Mass Resolving Power:</p> <p>Mass Resolving Power Determined at:</p> <p>Species Used for Mass Calibration:</p> <p>Specimen Normal-to-Analyzer:</p> <p>Source-to-Analyzer Angle:</p> <p>Primary Beam Ion Gun:</p> <p>Primary Ion Species:</p> <p>Primary Ion Dose:</p> <p>Primary Ion Pulse Width:</p> <p>Primary Ion Pulse Rate:</p> <p>Net Beam Voltage:</p> <p>Pulsed Beam Current:</p> <p>DC Beam Current:</p> <p>Beam Diameter:</p> <p>Beam Raster Size:</p> <p>Beam Incident Angle:</p> <p>Secondary Source Polarity:</p> <p>Mass Range Minimum:</p> <p>Mass Range Maximum:</p> <p>Spectrum Dead Time Corrected:</p> <p>Total Spectral Acquisition Time:</p> <p>Comment:</p>	<p>Eggshell White – Kremer Pigmente ref. 11410 – Positive polarity</p> <p>SIMS</p> <p>IONTOF, TOF SIMS IV</p> <p>Time-of-flight</p> <p>2100 m/Δm</p> <p>27 Da</p> <p>Na^+, Ca^+, CaO^+, Ca_2O^+, Ca_3O_2^+, Ca_4O_3^+, Ca_5O_4^+, Ca_6O_5^+</p> <p>0°</p> <p>45°</p> <p>LMIG</p> <p>Bi_3^+</p> <p>4.37×10^{11} ion/cm²</p> <p>0.8–1.2 ns</p> <p>5 kHz</p> <p>25 000 eV</p> <p>0.000 16 nA</p> <p>15.7 nA</p> <p>~2 μm</p> <p>250 × 250 μm²</p> <p>45°</p> <p>Positive</p> <p>0 Da</p> <p>3545 Da</p> <p>Yes</p> <p>250 s</p>
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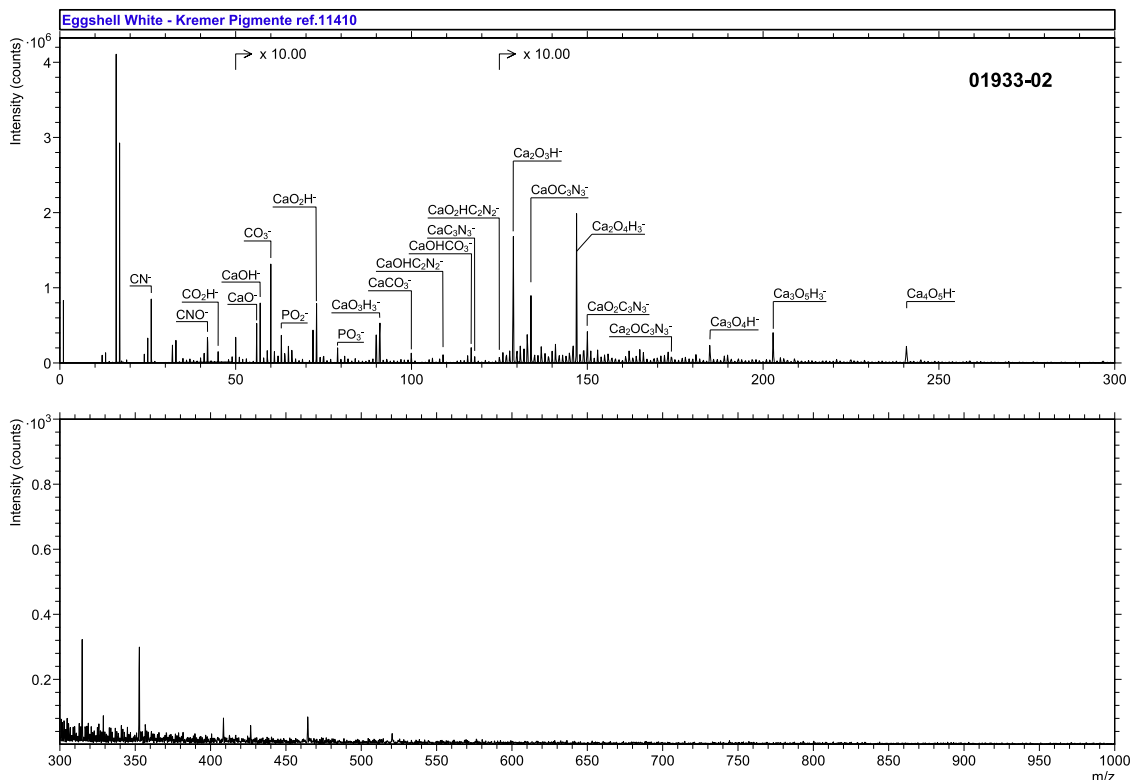
Peaks attributed to $(\text{CNO})\text{Ca}_x\text{O}_y^+$ are detected for this material. Additional series of peaks are detected, with lower intensity. They can be attributed to $\text{PO}_2(\text{CaO})_n^+$ and $\text{CNNa}(\text{CaO})_n^+$ with $n = 2-6$ and are likely from the eggshell materials.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01933-02	26.005 (56.4)	CN ⁻	Eggshell proteins
	42.001 (48.5)	CNO ⁻	Eggshell proteins
	44.999 (26.2)	CO ₂ H ⁻	CaCO ₃ /Eggshell materials
	56.965 (-7.63)	CaOH ⁻	CaCO ₃
	59.987 (27.8)	CO ₃ ⁻	Eggshell materials
	62.966 (28.1)	PO ₂ ⁻	Eggshell materials/Ca ₃ (PO ₄) ₂
	66.002 (51.4)	C ₃ NO ⁻	Eggshell proteins
	72.964 (45.1)	CaO ₂ H ⁻	CaCO ₃ /Ca(OH) ₂
	78.963 (52.2)	PO ₃ ⁻	Eggshell materials/Ca ₃ (PO ₄) ₂
	89.966 (24.8)	(CaO)(OH) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
	90.974 (23.8)	(CaOH)(OH) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
	99.953 (46.2)	CaCO ₃ ⁻	CaCO ₃
	108.974 (14.3)	CaOH(CN) ₂ ⁻	Eggshell proteins/CaCO ₃
	115.946 (23.2)	CaOCO ₃ ⁻	CaCO ₃
	116.953 (19.7)	CaOHCO ₃ ⁻	CaCO ₃
	117.974 (9.87)	Ca(CN) ₃ ⁻	Eggshell proteins/CaCO ₃
	124.970 (20.6)	CaO ₂ H(CN) ₂ ⁻	Eggshell proteins/CaCO ₃
	128.920 (9.25)	(CaO) ₂ (OH) ⁻	CaCO ₃ /Ca(OH) ₂
	133.970 (14.9)	CaOC ₃ N ₃ ⁻	Eggshell proteins/CaCO ₃
	146.931 (14.2)	H(CaO) ₂ (OH) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
	149.968 (35.4)	CaO ₂ C ₃ N ₃ ⁻	Eggshell proteins/CaCO ₃
	173.938 (43.7)	Ca ₂ OC ₃ N ₃ ⁻	Eggshell proteins/CaCO ₃
	184.881 (25.6)	Ca ₃ O ₄ H ⁻	CaCO ₃ /Ca(OH) ₂
	202.889 (-2.97)	H(CaO) ₃ (OH) ₂ ⁻	CaCO ₃ /Ca(OH) ₂
240.832 (-6.39)	Ca ₄ O ₅ H ⁻	CaCO ₃	

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Accession #:

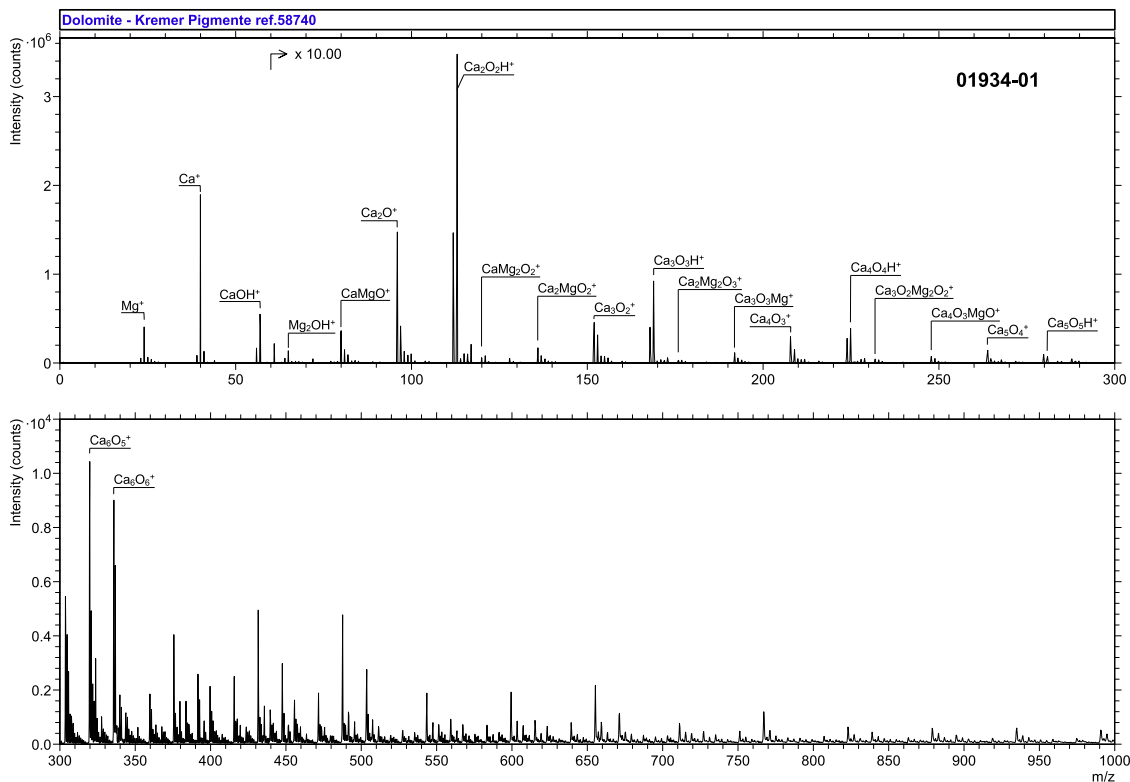
01933-02

Specimen:	Eggshell White – Kremer Pigmente ref. 11410 – Negative polarity
Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2000 $m/\Delta m$
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl^- , CaO^- , $\text{Ca}_2\text{O}_3\text{H}^-$, $\text{Ca}_3\text{O}_4\text{H}^-$
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi_3^+
Primary Ion Dose:	4.37×10^{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 16 nA
DC Beam Current:	15.7 nA
Beam Diameter:	$\sim 2 \mu\text{m}$
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$
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:	250 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01934-01	23.983 (-51.8)	Mg ⁺	CaMg(CO ₃) ₂
	64.973 (11.2)	Mg ₂ OH ⁺	CaMg(CO ₃) ₂
	79.946 (52.6)	CaMgO ⁺	CaMg(CO ₃) ₂
	119.922 (3.37)	CaMg ₂ O ₂ ⁺	CaMg(CO ₃) ₂
	135.902 (16.8)	Ca ₂ MgO ₂ ⁺	CaMg(CO ₃) ₂
	175.880 (-1.49)	Ca ₂ Mg ₂ O ₃ ⁺	CaMg(CO ₃) ₂
	191.860 (16.7)	Ca ₃ O ₂ MgO ⁺	CaMg(CO ₃) ₂
	231.838 (4.73)	Ca ₃ O ₂ (MgO) ₂ ⁺	CaMg(CO ₃) ₂
	247.818 (12.9)	Ca ₄ O ₃ MgO ⁺	CaMg(CO ₃) ₂

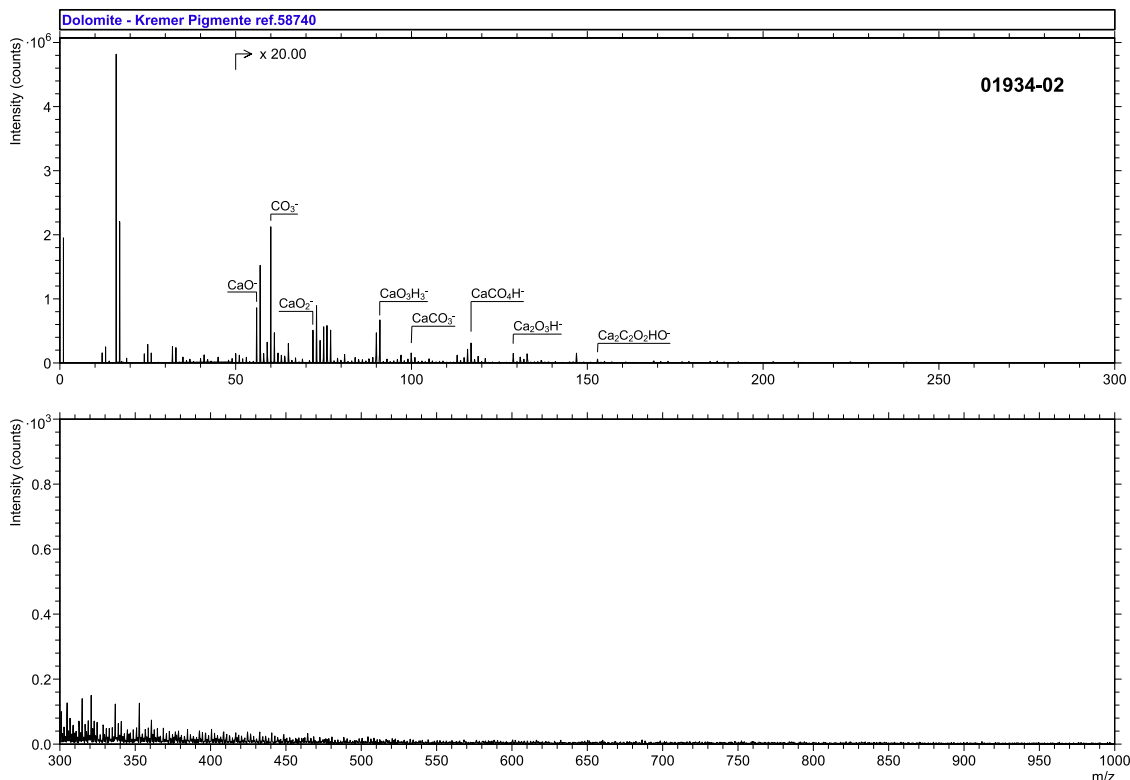


Accession #:	01934-01
■ Specimen:	Dolomite 10 μ – Kremer Pigmente ref. 58740 – Positive polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2500 m/ Δ m
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Na ⁺ , Ca ⁺ , CaO ⁺ , Ca ₂ O ⁺ , Ca ₃ O ₂ ⁺ , Ca ₄ O ₃ ⁺ , Ca ₅ O ₄ ⁺ , Ca ₆ O ₅ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	B ₁₃ ⁺
Primary Ion Dose:	4.37 $\times 10^{11}$ 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 16 nA
DC Beam Current:	15.7 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:	283 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01934-02	59.983 (-31.5)	CO_3^-	$\text{CaMg}(\text{CO}_3)_2$
	90.974 (28.0)	$(\text{CaOH})(\text{OH})_2^-$	$\text{CaMg}(\text{CO}_3)_2$
	99.944 (-35.3)	CaCO_3^-	$\text{CaMg}(\text{CO}_3)_2$
	116.947 (-31.3)	CaHCO_4^-	$\text{CaMg}(\text{CO}_3)_2$
	128.914 (-30.0)	$(\text{CaO})_2(\text{OH})^-$	$\text{CaMg}(\text{CO}_3)_2$
	136.921 (-15.0)	$\text{Ca}_2\text{H}(\text{CO})_2^-$	$\text{CaMg}(\text{CO}_3)_2$
	152.911 (-47.2)	$\text{Ca}_2\text{OH}(\text{CO})_2$	$\text{CaMg}(\text{CO}_3)_2$



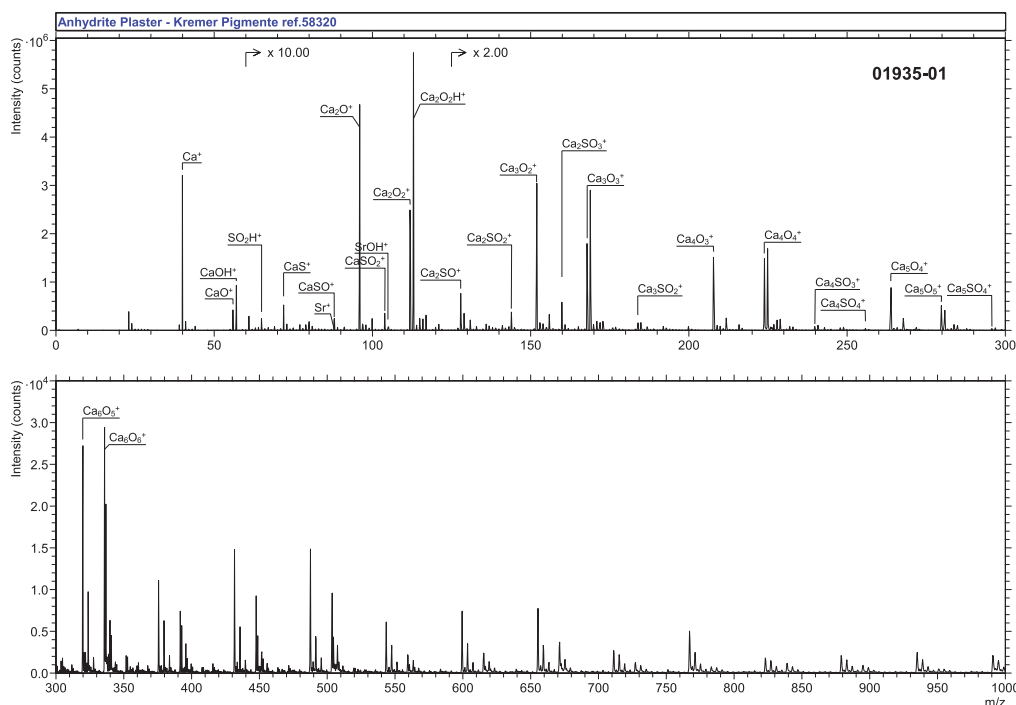
Accession #:	01934-02
■ Specimen:	Dolomite 10 μ – Kremer Pigmente ref. 58740 – Negative polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2000 m/ Δ m
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , CaO ⁻ , Ca ₂ 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:	4.37 × 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 16 nA
DC Beam Current:	15.7 nA
Beam Diameter:	~2 μ m
Beam Raster Size:	250 × 250 μ m 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:	283 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01935-01	64.971 (20.3)	SO ₂ H ⁺	CaSO ₄
	71.935 (15.5)	CaS ⁺	CaSO ₄
	87.904 (-8.75)	Sr ⁺	Natural impurities
	87.929 (3.63)	CaSO ⁺	CaSO ₄
	103.924 (3.64)	CaSO ₂ ⁺	CaSO ₄
	104.909 (7.02)	SrOH ⁺	Natural impurities
	127.895 (29.5)	Ca ₂ SO ⁺	CaSO ₄
	143.887 (2.22)	Ca ₂ SO ₂ ⁺	CaSO ₄
	159.882 (9.09)	Ca ₂ SO ₃ ⁺	CaSO ₄
	183.853 (21.2)	Ca ₃ SO ₂ ⁺	CaSO ₄
	239.813 (26.4)	Ca ₄ SO ₃ ⁺	CaSO ₄
	255.801 (-2.38)	Ca ₄ SO ₄ ⁺	CaSO ₄
	295.770 (20.1)	Ca ₅ SO ₄ ⁺	CaSO ₄

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Accession #:

01935-01

■ Specimen:	Anhydrite plaster, burnt gypsum – Kremer Pigmente ref. 58320 – Positive polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2600 m/Δm
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Na ⁺ , Ca ⁺ , CaO ⁺ , Ca ₂ O ₂ ⁺ , Ca ₃ O ₃ ⁺ , Ca ₄ O ₃ ⁺ , Ca ₅ O ₄ ⁺ , Ca ₆ O ₅ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Pulse Width:	4.34 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Rate:	0.8–1.2 ns
Net Beam Voltage:	5 kHz
Pulsed Beam Current:	25 000 eV
DC Beam Current:	0.000 21 nA
Beam Diameter:	14.6 nA
Beam Raster Size:	~2 μm
Beam Incident Angle:	250 × 250 μm ²
Secondary Source Polarity:	45°
Mass Range Minimum:	Positive
Mass Range Maximum:	0 Da
Spectrum Dead Time Corrected:	3545 Da
Total Spectral Acquisition Time:	Yes
Comment:	210 s

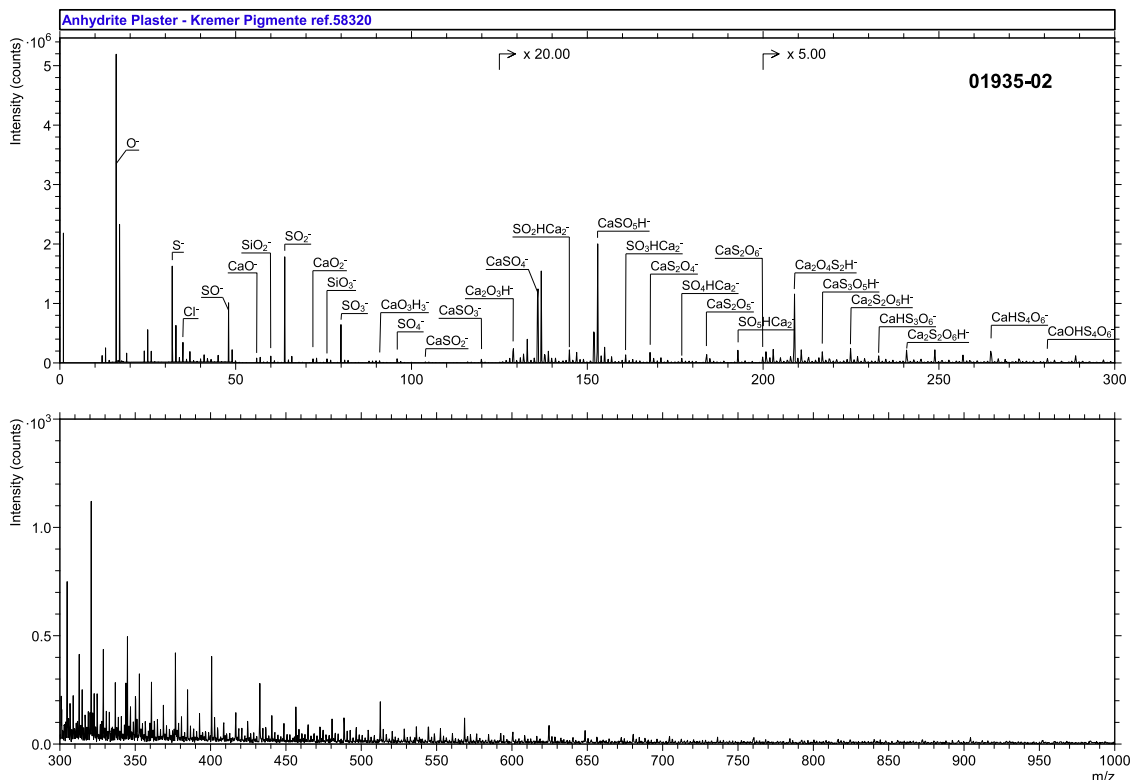
The detection of strontium in both gypsum samples is noteworthy, as it is an element found in natural gypsum.⁵ Anhydrite and gypsum share almost identical ToF-SIMS spectra.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01935-02	15.995 (-14.9)	O ⁻	-
	31.972 (-6.76)	S ⁻	-
	34.968 (-34.1)	Cl ⁻	Natural impurities
	47.965 (-45.3)	SO ⁻	CaSO ₄
	59.965 (-32.2)	SiO ₂ ⁻	Natural impurities
	63.964 (31.0)	SO ₂ ⁻	CaSO ₄
	75.965 (42.2)	SiO ₃ ⁻	Natural impurities
	79.956 (-11.7)	SO ₃ ⁻	CaSO ₄
	90.967 (-38.5)	CaO ₃ H ₃ ⁻	CaSO ₄
	95.948 (-39.7)	SO ₄ ⁻	CaSO ₄
	103.926 (9.26)	CaSO ₂ ⁻	CaSO ₄
	119.917 (-21.2)	CaSO ₃ ⁻	CaSO ₄
	128.919 (3.63)	Ca ₂ O ₃ H ⁻	CaSO ₄
	135.910 (-33.0)	CaSO ₄ ⁻	CaSO ₄
	144.898 (15.9)	SO ₂ HCa ₂ ⁻	CaSO ₄
	152.915 (-16.9)	CaSO ₅ H ⁻	CaSO ₄
	160.896 (32.2)	SO ₃ HCa ₂ ⁻	CaSO ₄
	167.882 (-27.5)	CaS ₂ O ₄ ⁻	CaSO ₄
	176.891 (32.2)	SO ₄ HCa ₂ ⁻	CaSO ₄
	183.876 (-30.1)	CaS ₂ O ₅ ⁻	CaSO ₄
	192.875 (-25.2)	SO ₅ HCa ₂ ⁻	CaSO ₄
	199.870 (-31.6)	CaS ₂ O ₆ ⁻	CaSO ₄
	208.865 (34.6)	Ca ₂ S ₂ O ₄ H ⁻	CaSO ₄
	216.859 (-11.1)	CaHS ₃ O ₅ ⁻	CaSO ₄
	224.848 (-16.8)	Ca ₂ S ₂ O ₅ H ⁻	CaSO ₄
	232.851 (-24.9)	CaHS ₃ O ₆ ⁻	CaSO ₄
240.837 (-41.3)	Ca ₂ S ₂ O ₆ H ⁻	CaSO ₄	
264.821 (-28.9)	CaHS ₄ O ₆ ⁻	CaSO ₄	
280.820 (-14.4)	CaOHS ₄ O ₆ ⁻	CaSO ₄	

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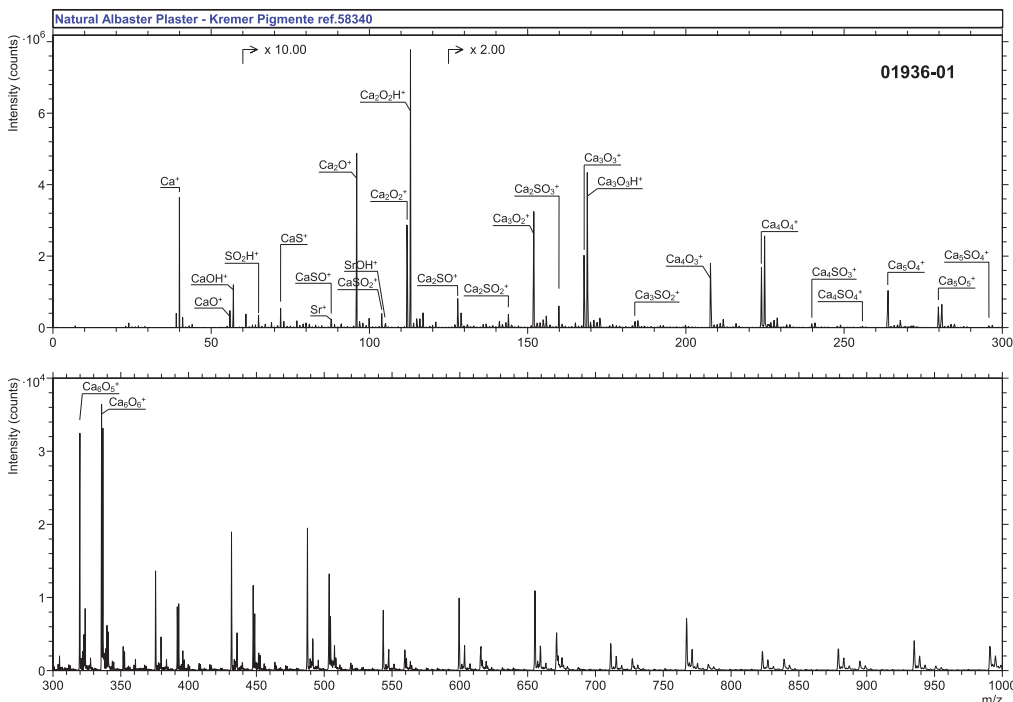
Accession #:	01935-02
■ Specimen:	Anhydrite plaster, burnt gypsum – Kremer Pigmente ref. 58320 – Negative polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2400 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , CaO ₂ H ⁻ , Ca ₂ 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:	4.34 × 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 21 nA
DC Beam Current:	14.6 nA
Beam Diameter:	~2 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:	210 s
Comment:	Anhydrite and gypsum share almost identical ToF-SIMS spectra.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01936-01	64.970 (14.3)	SO ₂ H ⁺	CaSO ₄
	71.935 (12.3)	CaS ⁺	CaSO ₄
	87.906 (12.5)	Sr ⁺	Natural impurities
	87.929 (-3.64)	CaSO ⁺	CaSO ₄
	103.923 (-11.6)	CaSO ₂ ⁺	CaSO ₄
	104.910 (20.7)	SrOH ⁺	Natural impurities
	127.895 (25.8)	Ca ₂ SO ⁺	CaSO ₄
	143.887 (1.37)	Ca ₂ SO ₂ ⁺	CaSO ₄
	159.884 (13.4)	Ca ₂ SO ₃ ⁺	CaSO ₄
	183.853 (20.5)	Ca ₃ SO ₂ ⁺	CaSO ₄
	239.812 (20.2)	Ca ₄ SO ₃ ⁺	CaSO ₄
	255.806 (16.8)	Ca ₄ SO ₄ ⁺	CaSO ₄
	295.772 (26.6)	Ca ₅ SO ₄ ⁺	CaSO ₄

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Accession #:

01936-01

■ Specimen:	Natural alabaster plaster – Kremer Pigmente ref. 58340 – Positive 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:	27 Da
Species Used for Mass Calibration:	Na ⁺ , Ca ⁺ , CaO ⁺ , Ca ₂ O ⁺ , Ca ₃ O ₂ ⁺ , Ca ₄ O ₃ ⁺ , Ca ₅ O ₄ ⁺ , Ca ₆ O ₅ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.34 × 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 21 nA
DC Beam Current:	14.6 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:	210 s

Comment:

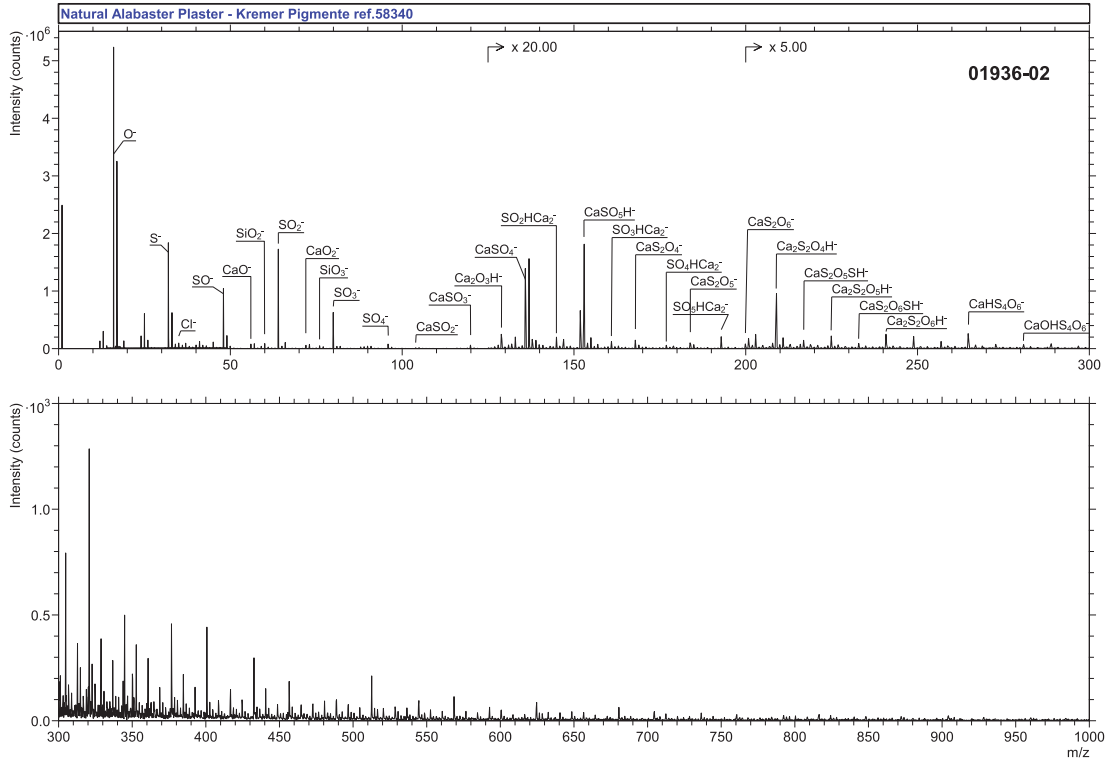
The detection of strontium in both gypsum samples is noteworthy, as it is an element found in natural gypsum.⁶ Anhydrite and gypsum share almost identical ToF-SIMS spectra.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01936-02	15.995 (-7.16)	O ⁻	-
	31.972 (-25.2)	S ⁻	-
	34.968 (-44.1)	Cl ⁻	Natural impurities
	47.965 (-47.8)	SO ⁻	CaSO ₄
	59.966 (-27.1)	SiO ₂ ⁻	Natural impurities
	63.963 (15.6)	SO ₂ ⁻	CaSO ₄
	75.965 (30.0)	SiO ₃ ⁻	Natural impurities
	79.955 (-25.7)	SO ₃ ⁻	CaSO ₄
	90.968 (-33.0)	CaO ₃ H ₃ ⁻	CaSO ₄
	95.948 (-41.0)	SO ₄ ⁻	CaSO ₄
	103.923 (-19.5)	CaSO ₂ ⁻	CaSO ₄
	119.916 (-29.8)	CaSO ₃ ⁻	CaSO ₄
	128.918 (-1.46)	Ca ₂ O ₃ H ⁻	CaSO ₄
	135.909 (-39.0)	CaSO ₄ ⁻	CaSO ₄
	144.896 (5.45)	SO ₂ HCa ₂ ⁻	CaSO ₄
	152.915 (-15.2)	CaSO ₅ H ⁻	CaSO ₄
	160.896 (35.5)	SO ₃ HCa ₂ ⁻	CaSO ₄
	167.880 (-38.4)	CaS ₂ O ₄ ⁻	CaSO ₄
	176.888 (13.6)	SO ₄ HCa ₂ ⁻	CaSO ₄
	183.874 (-38.3)	CaS ₂ O ₅ ⁻	CaSO ₄
	192.875 (-21.5)	SO ₅ HCa ₂ ⁻	CaSO ₄
	199.871 (-24.0)	CaS ₂ O ₆ ⁻	CaSO ₄
	208.862 (22.0)	Ca ₂ S ₂ O ₄ H ⁻	CaSO ₄
	216.858 (-15.6)	CaHS ₃ O ₅ ⁻	CaSO ₄
	224.853 (1.88)	Ca ₂ S ₂ O ₅ H ⁻	CaSO ₄
	232.851 (-18.6)	CaHS ₃ O ₆ ⁻	CaSO ₄
240.841 (-22.0)	Ca ₂ S ₂ O ₆ H ⁻	CaSO ₄	
264.822 (-24.7)	CaHS ₄ O ₆ ⁻	CaSO ₄	
280.820 (3.40)	CaOHS ₄ O ₆ ⁻	CaSO ₄	

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Accession #:	01936-02
■ Specimen:	Natural alabaster plaster – Kremer Pigmente ref. 58340 – Negative polarity
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2400 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , CaO ₂ H ⁻ , Ca ₂ 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:	4.34 × 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 21 nA
DC Beam Current:	14.6 nA
Beam Diameter:	~2 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:	210 s
Comment:	Anhydrite and gypsum share almost identical ToF-SIMS spectra.

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

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
All	39.96 (13.4)	Ca ⁺	All white pigments containing calcium
	56.94 (8.77)	CaOH ⁺	All white pigments containing calcium
	95.92 (11.0)	Ca ₂ O ⁺	All white pigments containing calcium
	111.92 (13.4)	Ca ₂ O ₂ ⁺	All white pigments containing calcium
	112.93 (13.4)	Ca ₂ O ₂ H ⁺	All white pigments containing calcium
	151.879 (13.1)	Ca ₃ O ₂ ⁺	All white pigments containing calcium
	167.874 (7.62)	Ca ₃ O ₃ ⁺	All white pigments containing calcium
	168.882 (11.1)	Ca ₃ O ₃ H ⁺	All white pigments containing calcium
	207.836 (7.75)	Ca ₄ O ₃ ⁺	All white pigments containing calcium
	223.831 (11.3)	Ca ₄ O ₄ ⁺	All white pigments containing calcium
	224.84 (11.7)	Ca ₄ O ₄ H ⁺	All white pigments containing calcium
	263.79 (11.3)	Ca ₅ O ₄ ⁺	All white pigments containing calcium
	279.79 (9.29)	Ca ₅ O ₅ ⁺	All white pigments containing calcium
	280.79 (12.0)	Ca ₅ O ₅ H ⁺	All white pigments containing calcium
	319.75 (6.54)	Ca ₆ O ₅ ⁺	All white pigments containing calcium
	335.74 (13.3)	Ca ₆ O ₆ ⁺	All white pigments containing calcium
	336.75 (12.1)	Ca ₆ O ₆ H ⁺	All white pigments containing calcium
375.71 (5.43)	Ca ₇ O ₆ ⁺	All white pigments containing calcium	
391.73 (2.18)	Ca ₇ O ₇ ⁺	All white pigments containing calcium	
392.72 (21.1)	Ca ₇ O ₇ H ⁺	All white pigments containing calcium	

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

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

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
All	55.96 (11.0)	CaO ⁻	All white pigments containing calcium
	71.96 (20.9)	CaO ₂ ⁻	All white pigments containing calcium

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