The Composition and Formation Mechanism of a Banded Scale in Clay Pipe Sewers

David Jenkins
Professor Emeritus
Environmental Engineering
University of California
Berkeley

Prepared for
Mr. Joe Parker
National Clay Pipe Institute - Southern California
PO BOX 549, 23835 Temescal Canyon Rd.,
Corona, CA 91718, USA

February 16, 2009

The Problem

At several locations in the sewerage systems of communities tributary to the Orange County Sanitation District wastewater treatment plants a ‘whitish scale’ formed on the pipe surface above the ‘water’ level. In some locations the scale was of a thickness that caused concern over its influence on the flow capacity of the sewer.

Objectives

The objectives of this study were to determine the chemical nature of the scale, to provide an explanation of the mechanism by which it forms and to recommend methods for its removal and prevention.

Method of Investigation

The following materials and information were provided:

1. Several pieces of scale taken from sewers in Costa Mesa by Mr. Joe Parker, National Clay Pipe Institute (NCPI).

2. Photographs taken from TV inspections of Costa Mesa sewer lines experiencing the scaling problem (Appendix 1).

3. Laboratory reports on the gross chemical composition by E.S. Babcock and Sons Inc. (Babcock) and West Coast Analytical Services Inc. (West Coast) (Appendix 2).

Closer visual examination of the scale samples revealed that they had a banded structure with whitish (major) and black (minor) layers (Appendix 3). Material was removed from each layer of the scale by scraping the individual layers with a scalpel and a knife point. An intact scale sample and the powdered materials scraped from each layer were sent to R.J. Lee Group (Lee) for analysis by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) and by X-ray diffraction (XRD). SEM/EDS analysis provides information on the overall morphology and the elemental composition of solids (Appendix 4). XRD analysis yields information on the crystalline nature of solids (Appendix 4).

Results

TV inspection of the sewers showed that the scale was present only above the sewage level and it was heaviest at, and close to, the manholes.

The analyses by Babcock and West Coast suggested that the scale was a solid containing major amounts of calcium (Ca), magnesium (Mg) and manganese (Mn). When the scale was treated with dilute hydrochloric acid it fizzed. This suggested that carbonate minerals were present in the scale.

SEM/EDS analysis showed that the whitish layer was composed primarily of calcium carbonate with trace amounts of magnesium and sulfur. The black layer was primarily manganese with some calcium and/or iron and other trace elements. XRD analysis showed that the whitish layer contained major amounts of the calcium carbonate mineral aragonite and minor amounts of the calcium carbonate mineral calcite. The black layer contained major amounts of the manganese mineral todokorite (or possibly the mineral calcium buserite) and the calcium carbonate mineral, calcite. Minor amounts of the silica mineral, quartz, were also present. The Lee report was sent to Professor Alain Manceau, University of Grenoble, France - one of the world's leading experts on manganese minerals and the interpretation of XRD spectra of minerals. Prof. Manceau's conclusion was that the XRD spectra were typical of a two-layer hydrate form of buserite.

Interpretation of Results

The laboratory analytical results, the field observations and the visual appearance of the scale suggest that it is being formed from groundwater that seasonally leaks into the sewer/manhole system. The following scenario is proposed:

(i). In the areas where the affected sewers are located, the groundwater level fluctuates with season, being high enough to inundate the sewer system during the wet season but leaving the sewer system 'high and dry' during the dry season.

(ii). Due to biological activity in the soil the groundwater is both devoid of oxygen (anaerobic) and has a high dissolved carbon dioxide concentration. The high dissolved carbon dioxide concentration lowers the groundwater pH compared to what it would be if the groundwater were exposed to the surface atmosphere (such as in a sewer).. At this low pH the groundwater dissolves carbonate minerals in the soil, thereby increasing its calcium and magnesium concentrations. The anaerobic conditions also ensure that any iron or manganese salts present in the groundwater are in their reduced forms (ferrous and manganous) rather than in their oxidized forms (ferric and manganic). Ferrous and manganous salts are much more soluble than the equivalent ferric and manganic salts.

(iii). When the groundwater level rises during the wet season, the groundwater infiltrates the sewer and manholes where it encounters an oxygenated (aerobic), lower carbon dioxide-content atmosphere. The infiltrated groundwater pH increases. This causes precipitation of calcium carbonate (the whitish scale).

(iv). Sewer infiltration by groundwater ceases during the dry season when the groundwater levels subside. The scale on the sewer surface becomes aerobic and over time communities of microorganisms capable of oxidizing ferrous iron to ferric iron and manganous salts to manganic salts become established on the surface of the precipitated calcium carbonate. Since the oxidized iron and manganese salts are less soluble than their ferrous and manganous counterparts, precipitation of ferric and manganic-containing minerals takes place (the black layer).

Field observations support this mechanism of scale formation as follows:

(i). Scale never forms below the high water (sewage) level in the sewer.

This is explained by the fact that the sewage flow dilutes the infiltrated groundwater flow so that the solubilities of any calcium, ferric or manganic salts are not be exceeded.

(ii). The amount of scale formed in different regions of the sewer is not identical. The scale was most prominent at locations proximate to a manhole.

This can be explained because the since the manhole structures are the most likely parts of the sewer system that would allow groundwater infiltration. As the infiltrated groundwater flows along the interior sewer surface, away from the manhole, it becomes less and less saturated with the scale forming salts (because they have already precipitated). Thus precipitation ceases and there is no more scale formation.

(iii). The scale has a banded structure consisting of alternating layers of whitish calcium carbonate and a black manganic oxide mineral.

The banded structure of the scale is explained by the seasonal variation of the groundwater level. Successive layers of scale are laid down as the groundwater rises and falls during the wet (high groundwater) and dry (low groundwater) seasons. The whitish calcium carbonate precipitates first because its precipitation relies solely on the pH change encountered when the groundwater is exposed to the lower carbon dioxide content of the sewer atmosphere. The manganic oxide precipitation occurs later because it requires the development of a microbial community capable of oxidizing the manganous salts in the infiltrated ground water to manganic salts.

Resolution of the Scaling Problem

Two types of action may be needed:

(i). Remove the existing scale. This is only required if the scale is serious enough to restrict existing and future anticipated sewage flows.

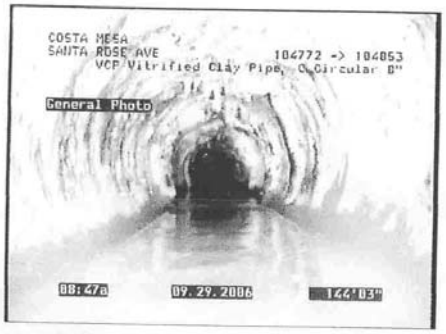
(ii). Prevent further scaling from occurring. The manhole structures should be sealed and made watertight to groundwater infiltration. The City of Costa Mesa has already taken this action. It would be interesting to determine whether this action provided a remedy to the scaling problem.

Appendix 1.

Photographs of Scale in Costa Mesa Sewers

Inspection photos

City:	Street:	Date:	section number:	PSR:
COSTA MESA	SANTA ROSE AVE	20060929	4	



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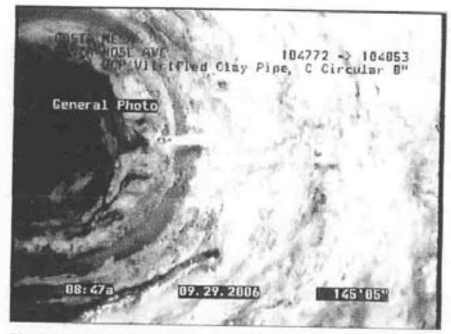

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Photo: 30a, Tape/Media No.: 002, 00:00:00
257.33FT, Manhole

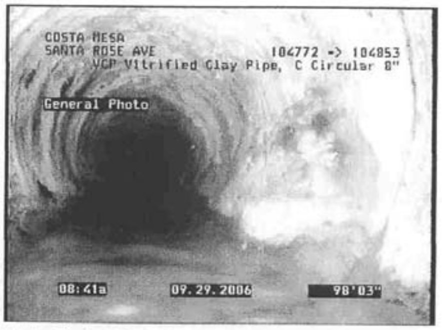
Photo: 30b, Tape/Media No.: 002, 00:00:00
257.33FT, Manhole

The Environmental Protection Specialists

National Plant Services, Inc
1461 Harbor Ave
Long Beach, Ca 90813
Tel: 800-445-3614, Fax: 562-495-1528

Inspection photos

City:	Street:	Date:	section number:	PSR:
COSTA MESA	SANTA ROSE AVE	20060929	4	



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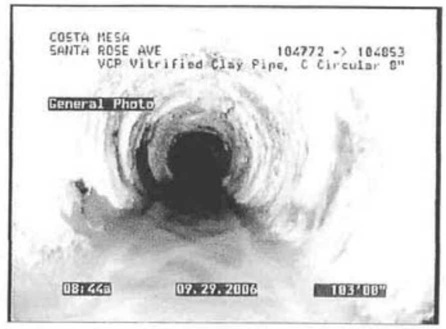

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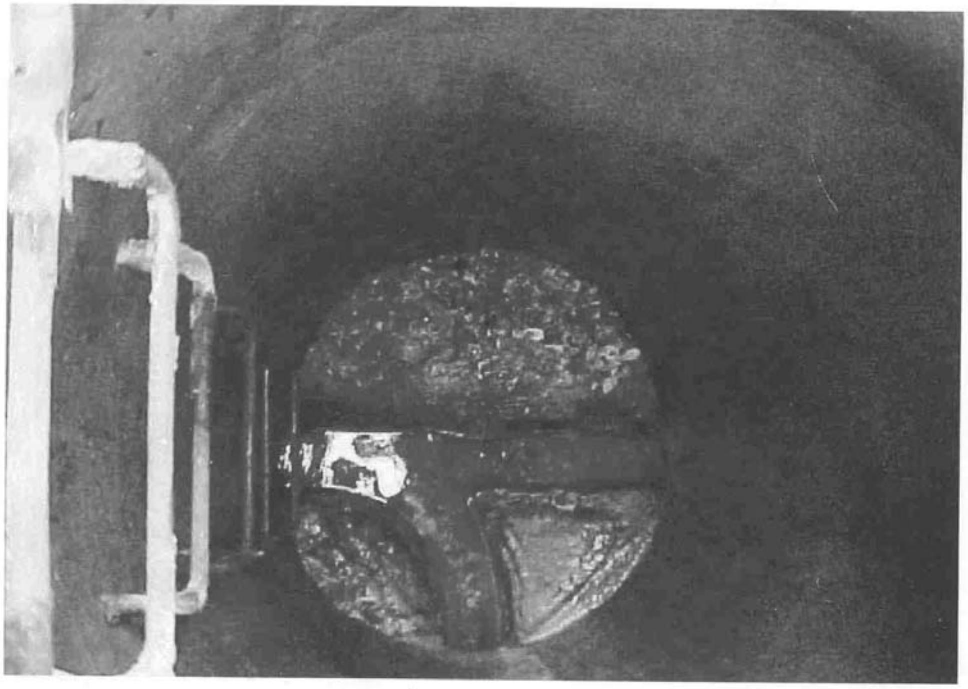
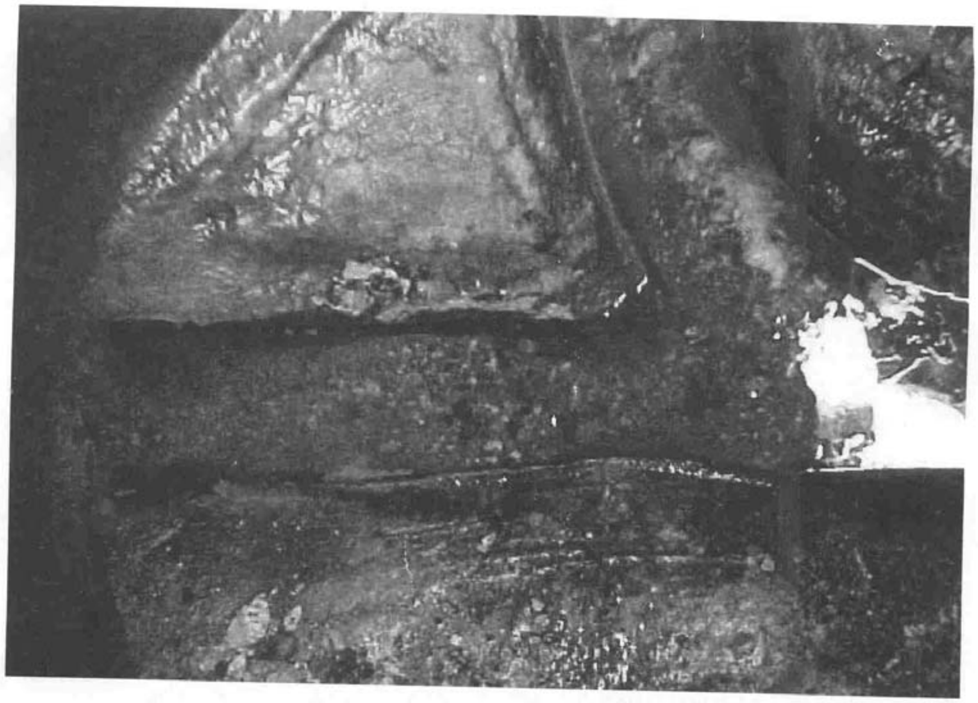




Appendix 2.

Laboratory Reports of E. S. Babcock and Sons Inc. and West Coast Analytical Service.

E.S. BABCOCK & SONS, INC.
Established 1906

(1)

NELAP #02101CA ELAP#1156
6100 Quail Valley Court Riverside, CA 92507-0704
P.O. Box 432 Riverside, CA 92502-0432
PH (951) 653-3351 FAX (951) 653-1662
www.babcocklabs.com

Client Name: National Clay Pipe Institute
Contact: Joe Parker
Address: P.O. Box 549
Corona, CA 92878

Report Date: 06-Feb-2007

Project Name: No Project
Project Number: No Project

Work Order Number: A7A2194
Received on Ice (Y/N): No Temp: 18 °C

Laboratory Reference Number
A7A2194-01

Sample Description	Matrix	Sampled Date/Time	Received Date/Time
Costa Mesa Sewer Effluent Sample	Liquid	01/18/07 00:00	01/25/07 12:18

Analyte(s)	Result	RDL	Units	Method	Analysis Date	Analyst	Fla
Cations							
Calcium	80	2.5	mg/L	EPA 200.7	02/01/07 13:52	lmt	
Magnesium	19	2.5	mg/L	EPA 200.7	02/01/07 13:52	lmt	
Metals and Metalloids							
Aluminum	970	250	ug/L	EPA 200.7	02/01/07 13:53	lmt	
Iron	470	120	ug/L	EPA 200.7	02/01/07 13:53	lmt	
Manganese	ND	25	ug/L	EPA 200.8	02/01/07 21:29	krv	N_RLm
Total Silica	26	12	mg/L	EPA 200.7	02/01/07 13:52	lmt	

Ca 80/20 4
Mg 19/12 ~1.5

ACCREDITED IN ACCORDANCE WITH nelac

E.S. BABCOCK & SONS, INC.
Established 1906

NELAP #02101CA ELAP#1156
6100 Quail Valley Court Riverside, CA 92507-0704
P.O. Box 432 Riverside, CA 92502-0432
PH (951) 653-3351 FAX (951) 653-1662
www.babcocklabs.com

2

Client Name: National Clay Pipe Institute
Contact: Joe Parker
Address: P.O. Box 549
Corona, CA 92878

Report Date: 06-Feb-2007

Analytical Report:
Project Name: No Project
Project Number: No Project

Work Order Number: A7A2194

Received on Ice (Y/N): No Temp: 18 °C

Laboratory Reference Number
A7A2194-02

Sample Description	Matrix	Sampled Date/Time	Received Date/Time
Costa Mesa Sewer Solid Sample	Solid	01/18/07 00:00	01/25/07 12:18

Analyte(s)	Result	RDL	Units	Method	Analysis Date	Analyst	Fla
Cations							
Calcium	350000	2000	mg/kg	EPA 6010B	02/01/07 16:13	ICP	
Magnesium	7100	200	mg/kg	EPA 6010B	01/30/07 18:25	lmt	
Metals and Metalloids; EPA SW846 Series							
Aluminum	210	20	mg/kg	EPA 6010B	01/30/07 18:26	lmt	
Iron	260	20	mg/kg	EPA 6010B	01/30/07 18:26	lmt	
Manganese	9100	500	mg/kg	EPA 6020	02/02/07 14:03	la	
Total Silica	ND	500	mg/kg	EPA 6010B	01/30/07 18:25	lmt	
Aggregate Soil Properties							
Loss on Ignition (as Volatile Solids)	3.3	0.1	%	SM 2540G	02/02/07 14:25	aec	

(3)

WEST COAST ANALYTICAL SERVICE, INC.

Orange County Sanitation District
Attn: Dan Tremblay

Job No: 92126
December 18, 2006

Anions by EPA 300.0
Ion Chromatography-Suppressed Conductivity

Column:	Dionex AS9-SC/AG9-SC
Eluent:	2 mM Na2CO3, 0.75 mM NaHCO3
Flow:	2.0 mL/min
Injection:	300 µL
Detection:	Suppressed Conductivity

Cannot analyze for HCO_3^-, CO_3^{2-} with this eluent

Solid

The sample was broken into smaller pieces and extracted in duplicate at 1g to 20 mL half-strength eluent with sonication for 15 minutes. The sample was then diluted by 1:10 for analysis with water (final dilution factor = 200). A blank and matrix spike were prepared in the same manner. Detection limits are adjusted for the dilution factor.

Sample ID: Method Blank

Analyte	µg/g	Detection Limit
Chloride	1.1	0.4
Nitrate	ND	0.4
Sulfate	ND	0.4

Date Analyzed: 12-12-06

Sample ID: LIMS Sample Number 983388 AD HOC IRVINE SEWER

Analyte	µg/g	Detection Limit
Chloride	10	4
Nitrate	6	4
Sulfate	934	4

? CO_3^{2-} HCO_3^{2-}

Date Analyzed: 12-12-06

Calibration Summary

Sample ID: 1 PPM Reference Standard

Analyte	Result	% Rec	% Rec Limits
Chloride	0.93	93	90 - 110
Nitrate	0.93	93	90 - 110
Sulfate	0.96	96	90 - 110

Standard Curves (n = 5) $r^2 > 0.999$ for all anions.

WCAS

WEST COAST ANALYTICAL SERVICE, INC.

Orange County Sanitation District
Attn: Dan Tremblay

Job No: 92126
December 18, 2006

Selected Metals by SOP 7040, Rev 8
Quantitative Analysis Report
Inductively Coupled Plasma-Mass Spectrometry

Parts Per Million (µg/g)

Sample ID	Calcium	Magnesium	Potassium	Sodium
LIMS Sample Number 983388 AD HOC IRVINE SEWER	326000	3060	34	430
Detection Limit:	6	2	3	2

Date Analyzed: 12-12-06

Quality Control Summary

Sample: LIMS Sample Number 983388 AD HOC IRVINE SEWER

Analyte	Sample Result	Duplicate Result	Average Result	Sample RPD	Spike Conc	Spike Result	Spike % Rec
Calcium	326000	316000	321000	3.1	1890	325000	NR
Magnesium	3060	2910	2985	5	1890	4550	NR
Potassium	33.7	34.5	34.1	2.3	1890	2160	112
Sodium	430	409	419.5	5	1890	1970	82

Date Analyzed: 12-12-06
NR - Not Reported; sample concentration is larger than spike.

Sample: Laboratory Fortified Blank

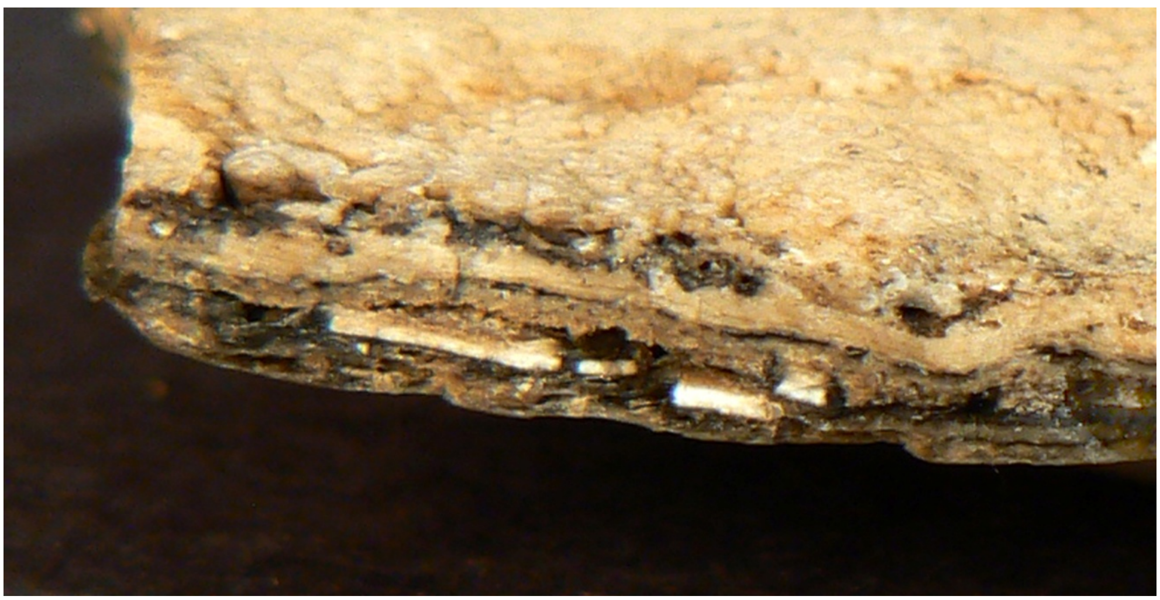
Analyte	Blank Result	Spike Conc	Spike Result	Spike % Rec
Calcium	4.7	2000	1760	88
Magnesium	1.5	2000	1890	94
Potassium	1.9	2000	1950	97
Sodium	ND	2000	1620	81

Date Analyzed: 12-12-06

WCAS

Appendix 3.

Photographs of Scale Showing its Banded Structure



Appendix 4.

SEM/EDS and XRD Analytical Reports

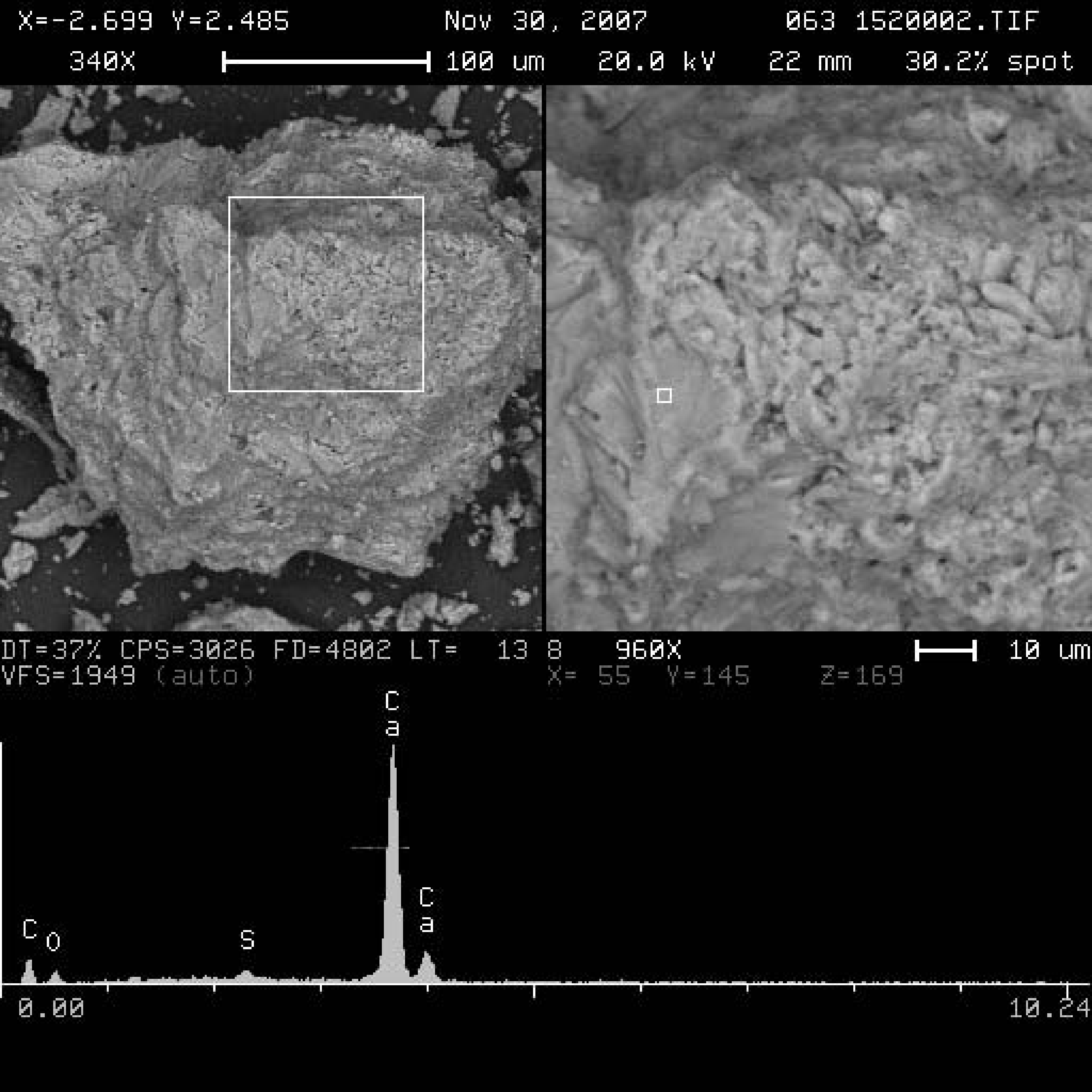
SEM/EDS Analytical Reports

0631520 -
white particles

0631521 -
black particles.

XRD Analytical Report

TEH711217.pdf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960X
10 um
VFS=1949 (auto)
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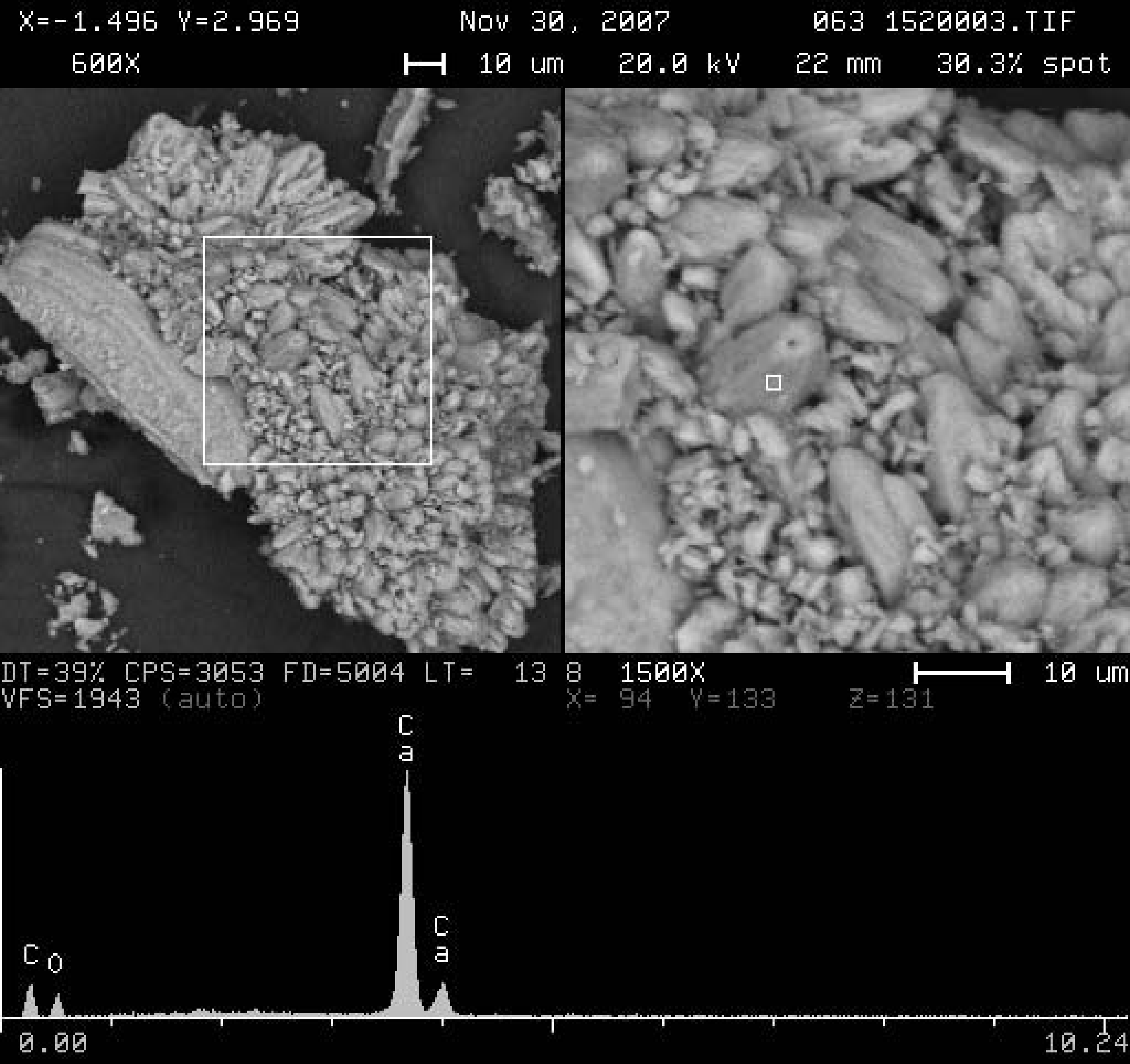
Ca
Ca
C
O
S
0.00
10.24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1500X
10 um
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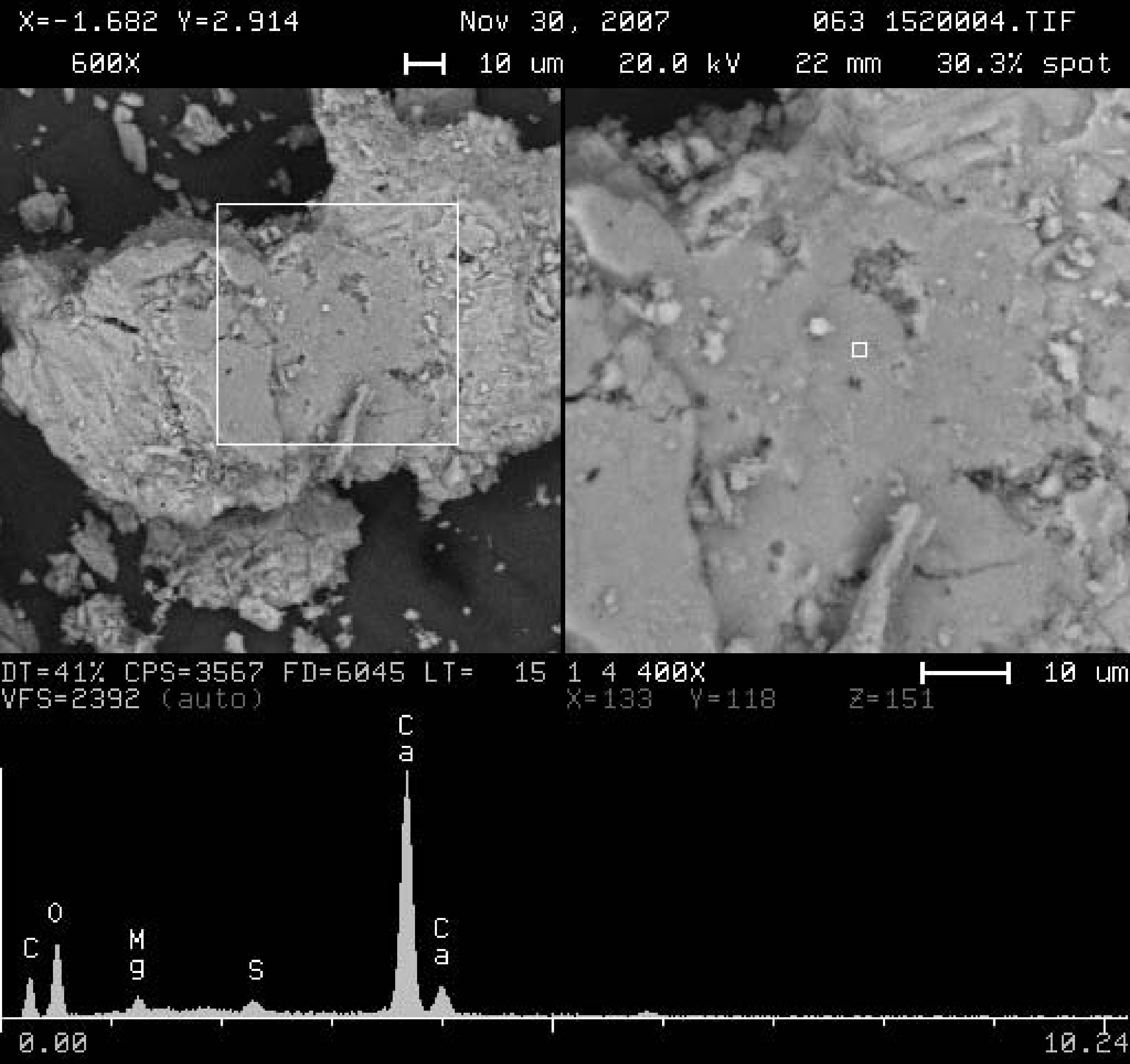
Ca
Ca
C
O
0.00
10.24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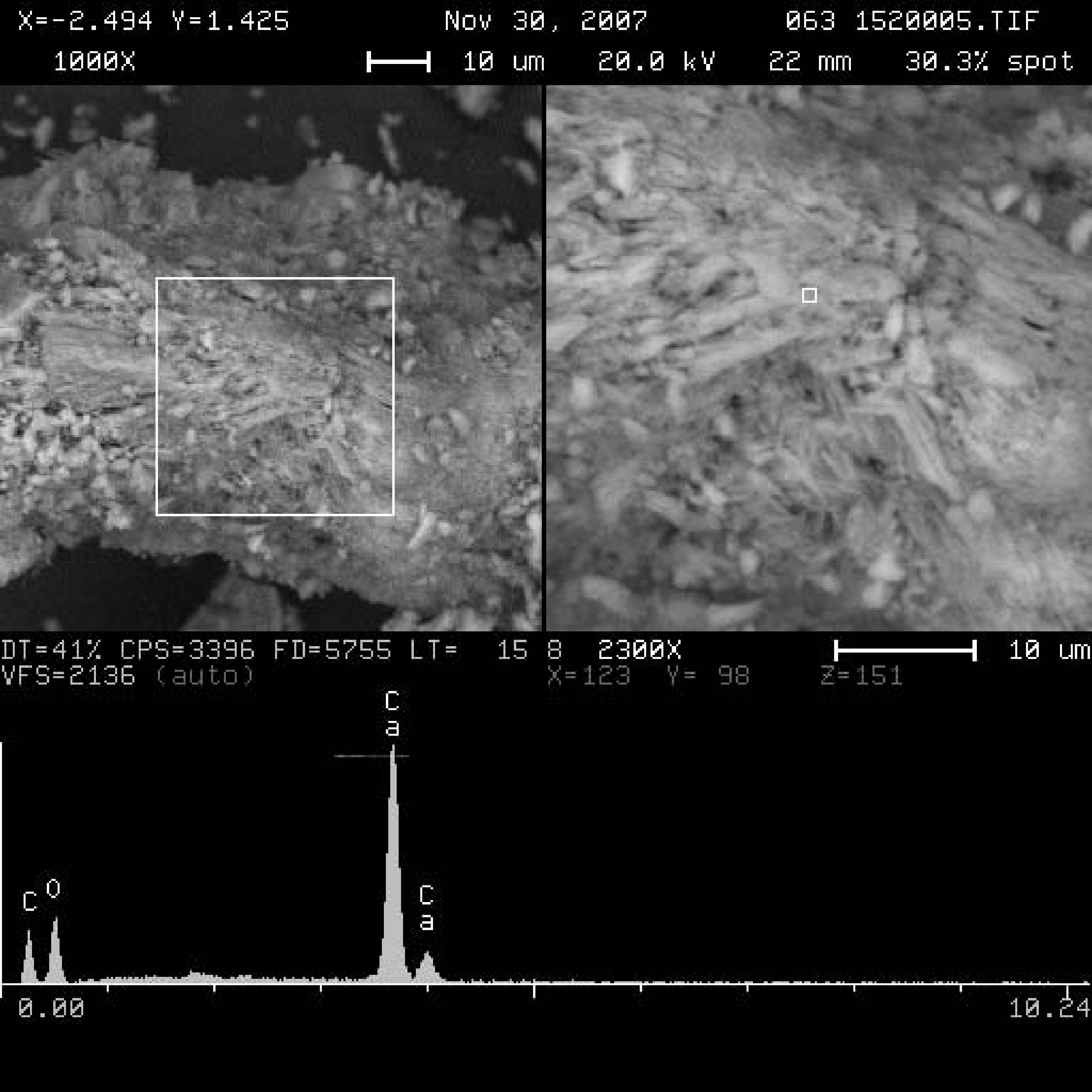
Ca
C
O
Mg
S
Ca
0.00
10.24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O
Ca
Ca
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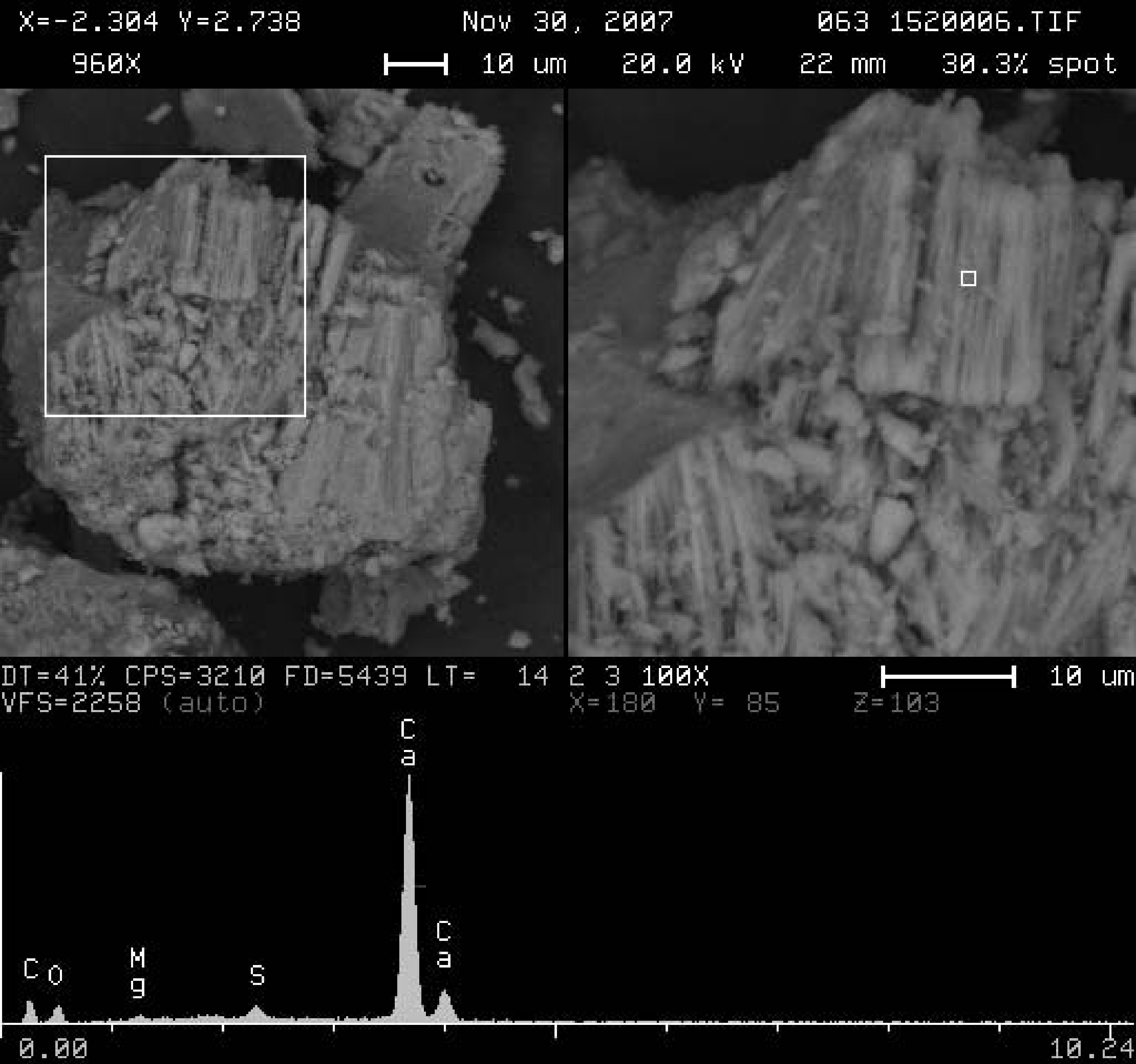
10.24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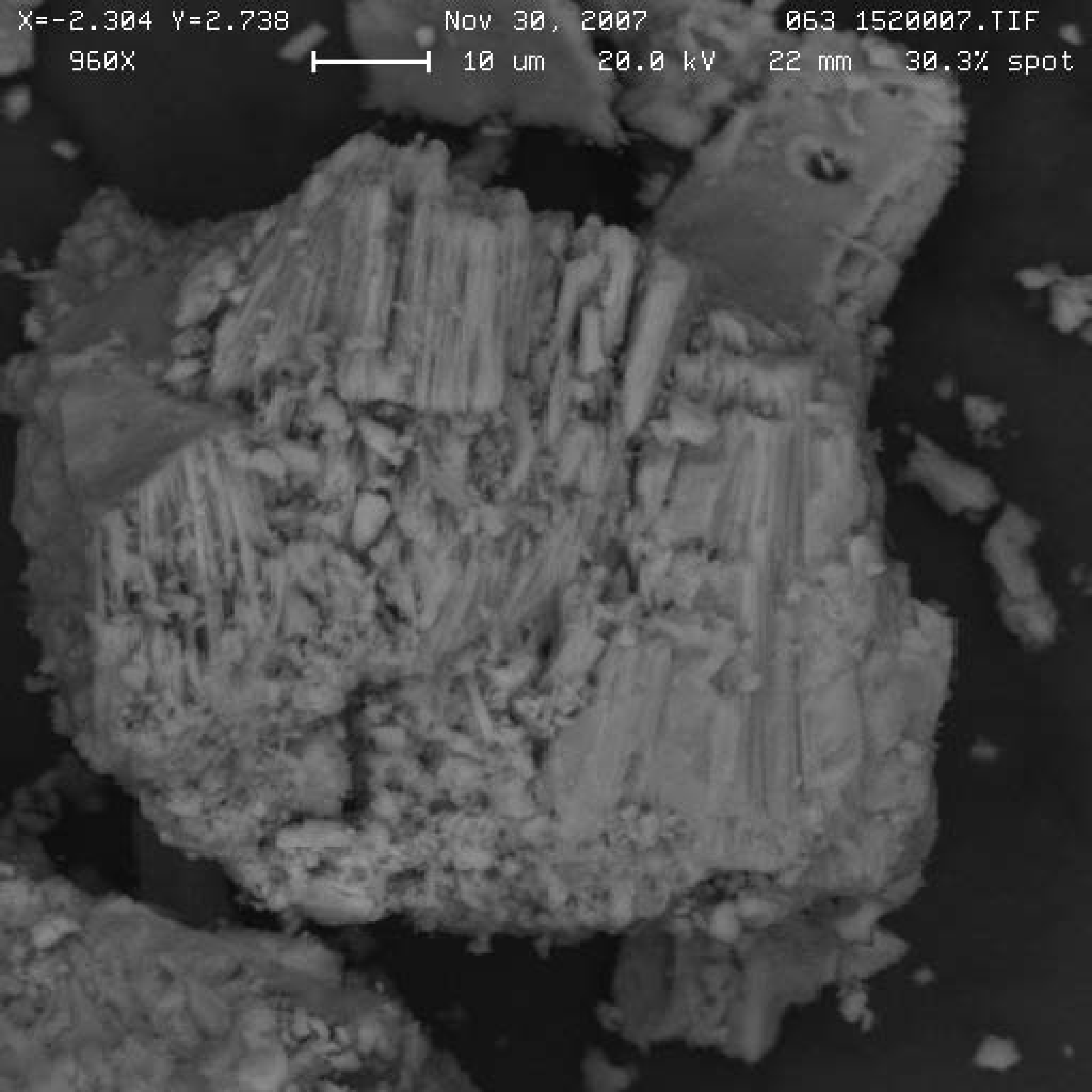
Ca
Ca
C
O
Mg
S
0.00
10.24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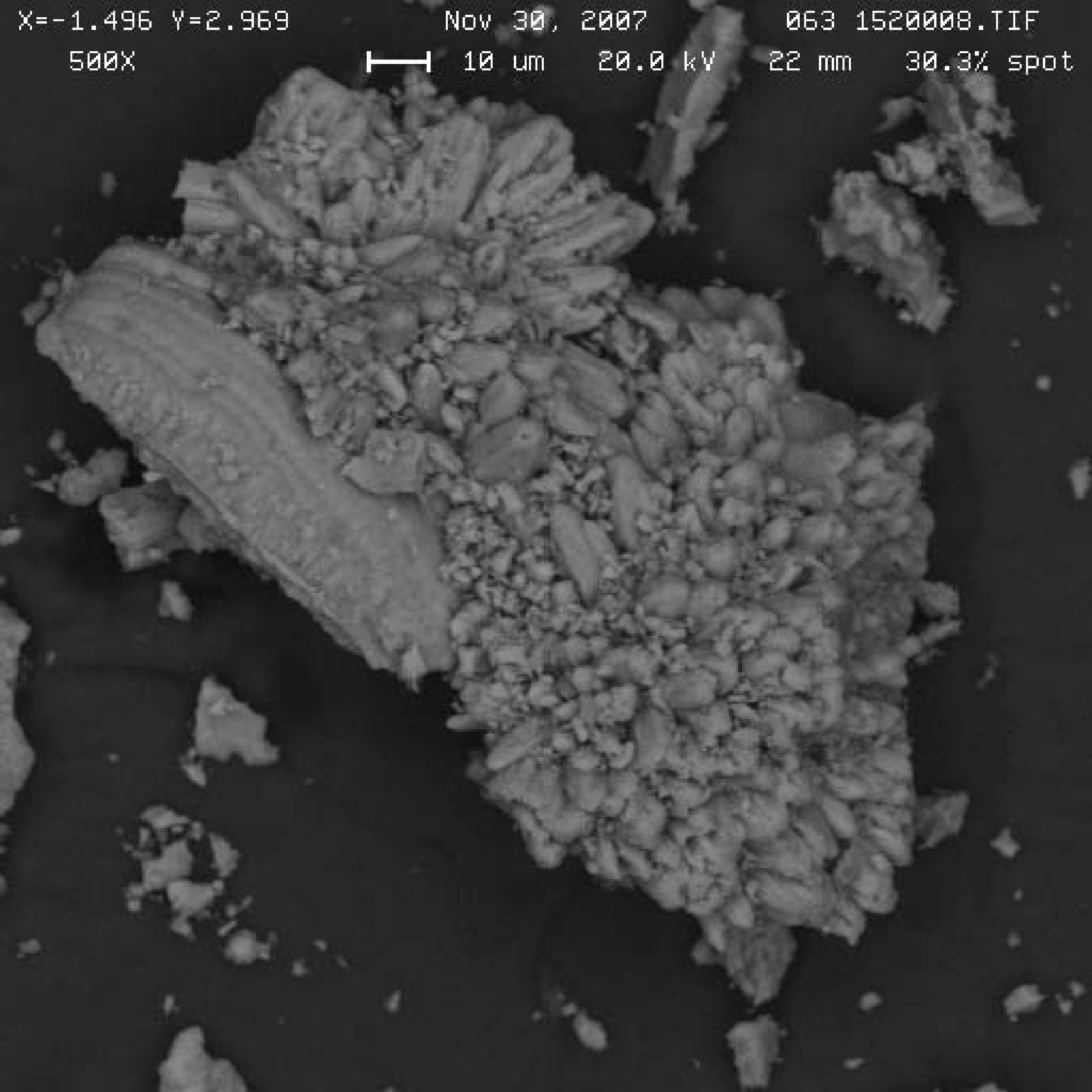
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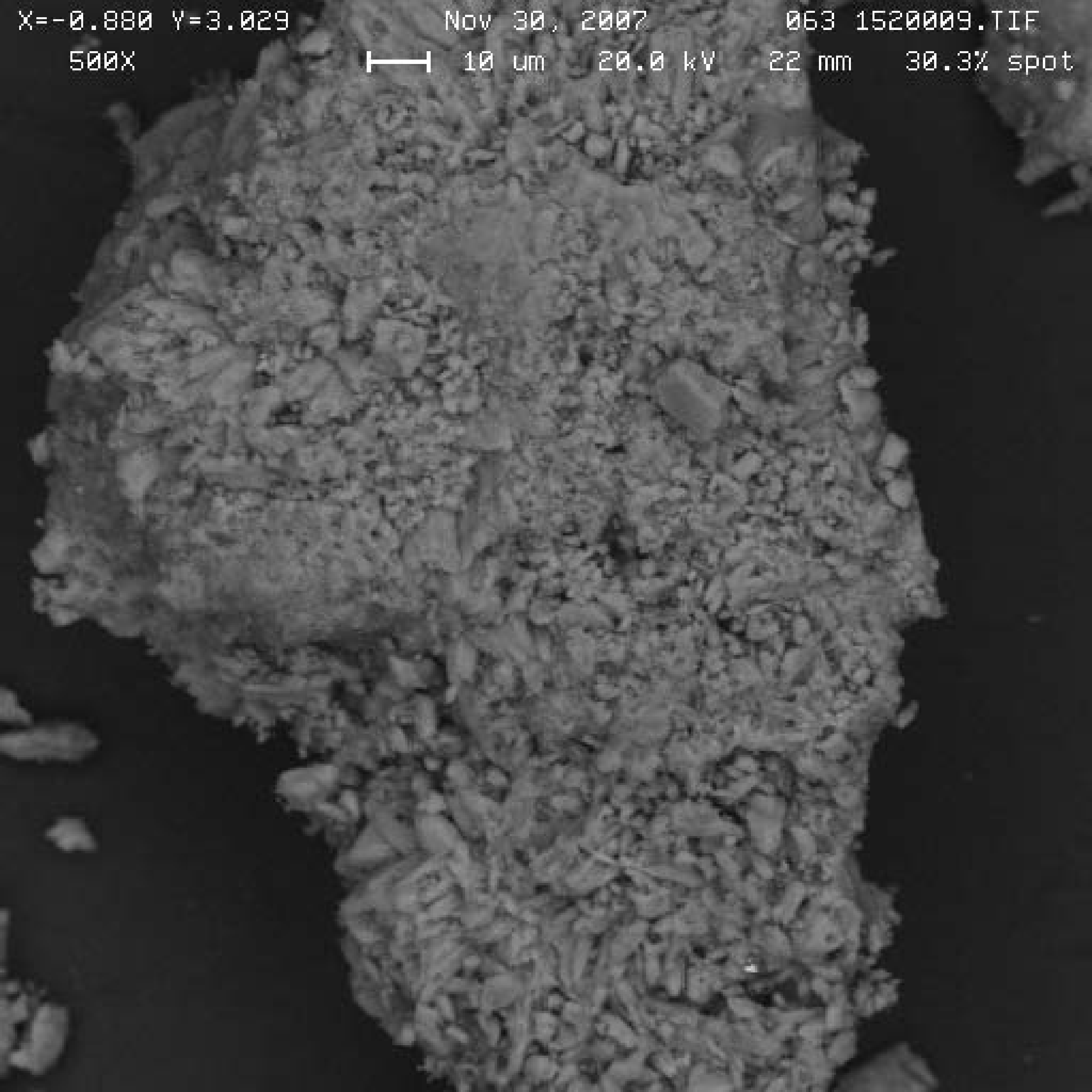
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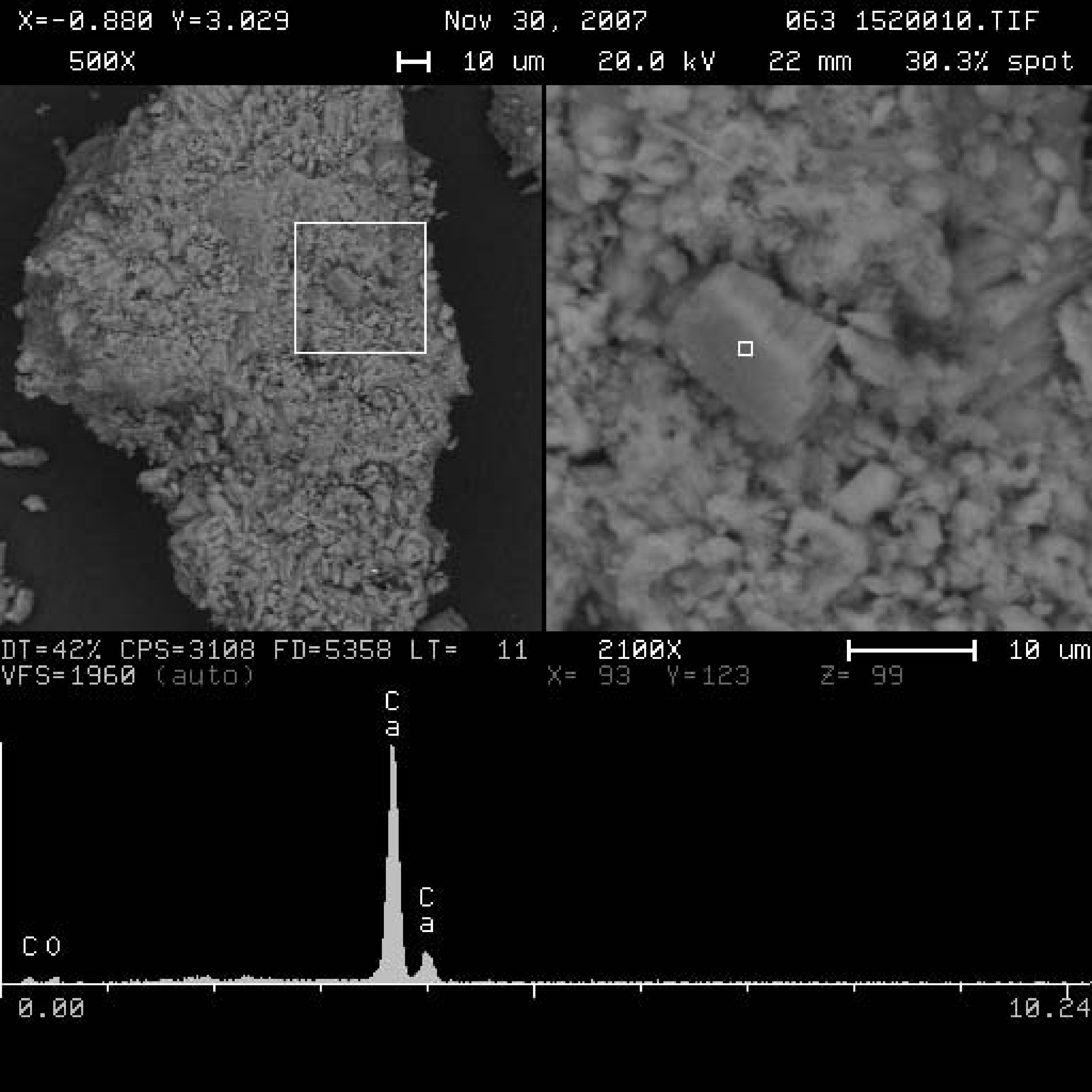
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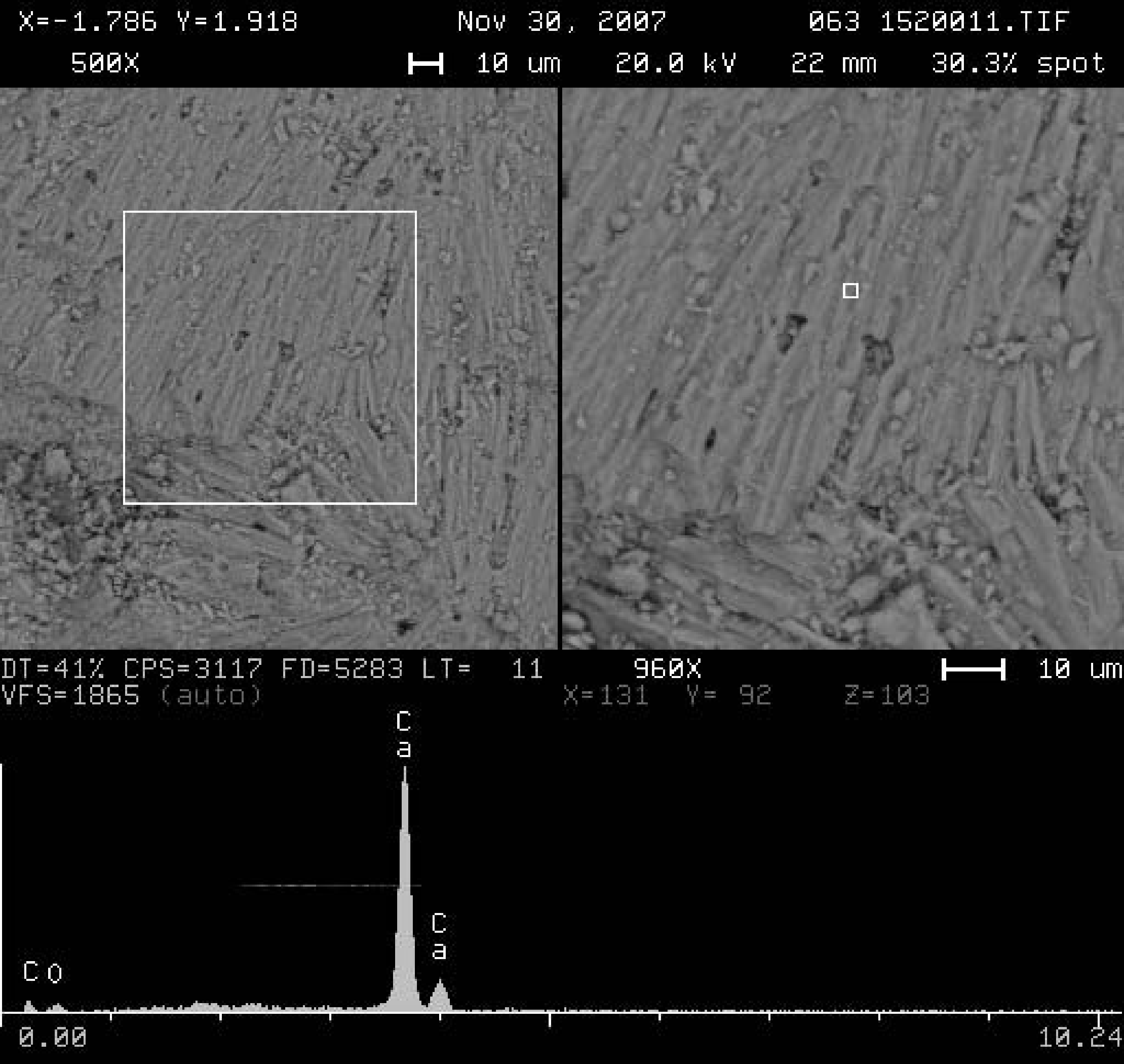
Ca
Ca
C O
0.00
10.24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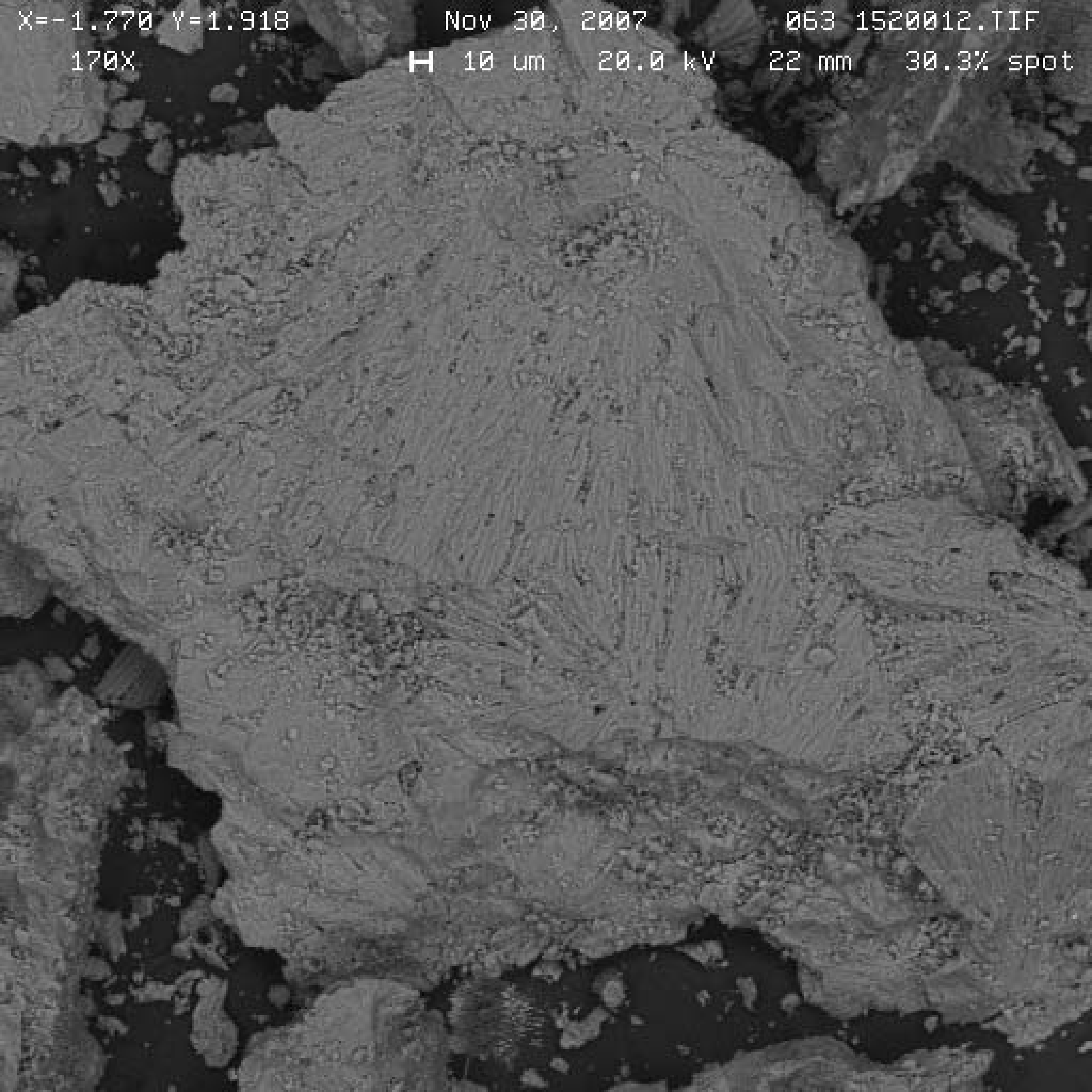
C
O
0.00
10.24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20.0 kV
22 mm
30.3% spot

RJ LeeGroup, Inc.
350 Hochberg Road, Monroeville, PA 15146
Tel: (724) 325-1776 | Fax: (724) 733-1799

LABORATORY REPORT

David Jenkins & Associates		Report Date:	12/12/2007
11 Yale Circle		Samples Received:	12/4/2007
Kensington, CA 94708-1015		RJ Lee Group Job No.:	TEH711217
ATTENTION:	Dr. David Jenkins	Client Job No.:	N/A
Telephone:	(510)527-0672	Purchase Order No.:	N/A

ANALYSIS: X-ray diffraction (XRD) for crystalline phases

A portion of each sample was ground and mounted into a small XRD holder for analysis. The sample was run on a PANalytical X'Pert Pro diffractometer using copper radiation.

Client Sample No.: Material - Outer White Layer
RJ Lee Group Sample No.: 0631520

Phase	Composition	Concentration
Aragonite	$CaCO_3$	Major
Calcite	$CaCO_3$	Minor

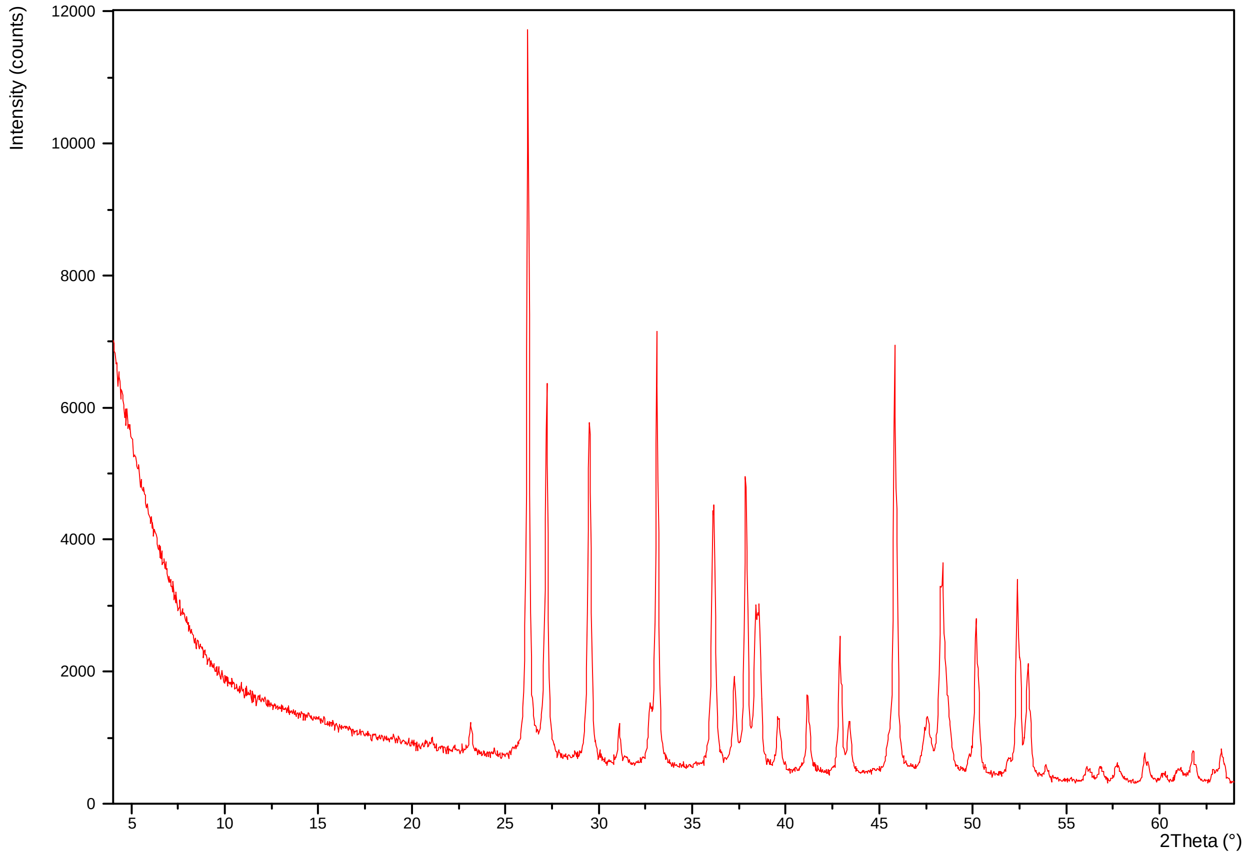

Figure 1 –X-ray diffraction pattern of the sample 0631520, labeled "Material – Outer White Layer", with degrees 2θ along the x-axis and intensity (counts) along the y-axis.

Client Sample No.: Material – Inner Black Layer
RJ Lee Group Sample No.: 0631521

Phase	Composition	Concentration
Todorokite*	$(Na,Ca,K)_2(Mn^{4+},Mn^{3+})_6O_{12} \cdot 3\text{-}4.5H_2O$	Major
Calcite	$CaCO_3$	Major
Quartz	SiO_2	Trace

* This phase is extremely poorly crystalline and it may also include a Ca-buserite (expanded or hydrated birnessite δ-MnO_2), Mn-oxide phase.

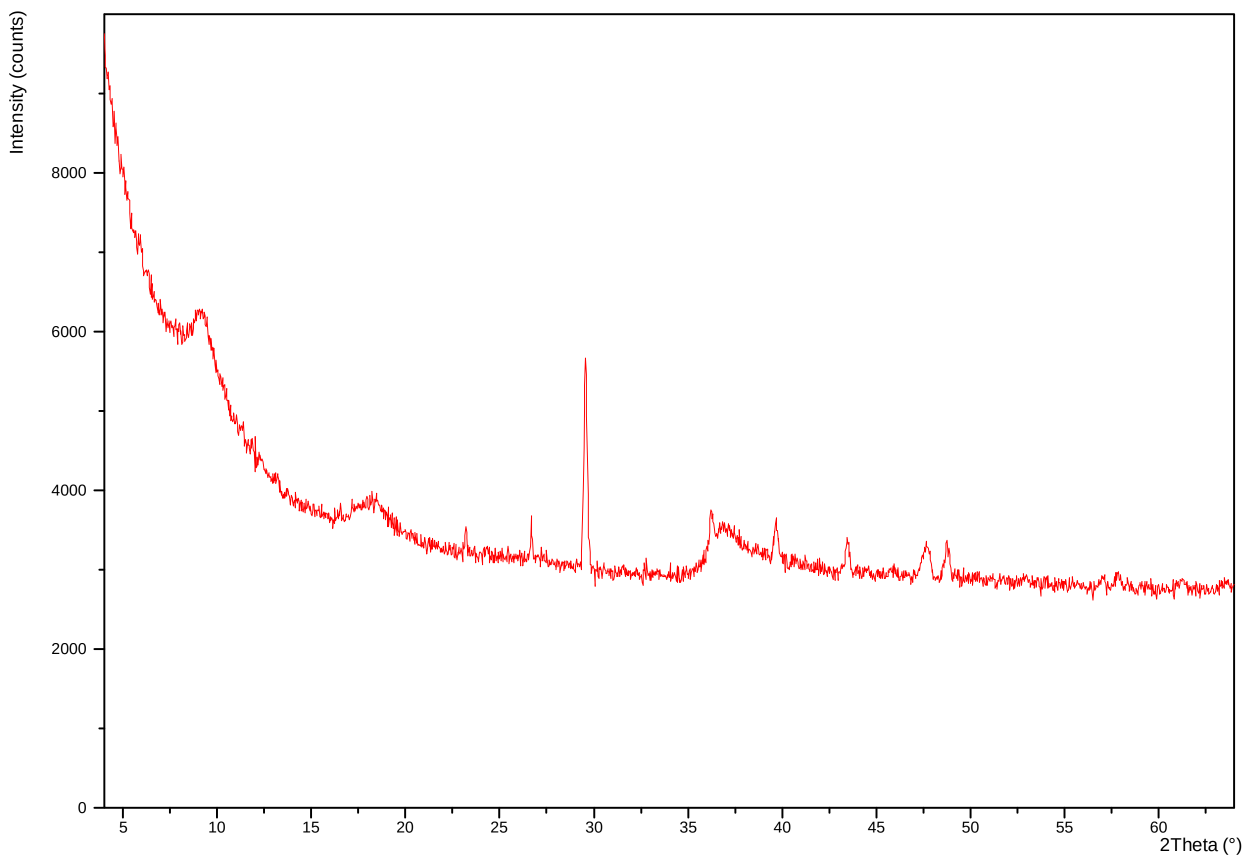

Figure 2 –X-ray diffraction pattern of the sample 0631521, labeled “Material – Inner Black Layer”, with degrees 2θ along the x-axis and intensity (counts) along the y-axis.

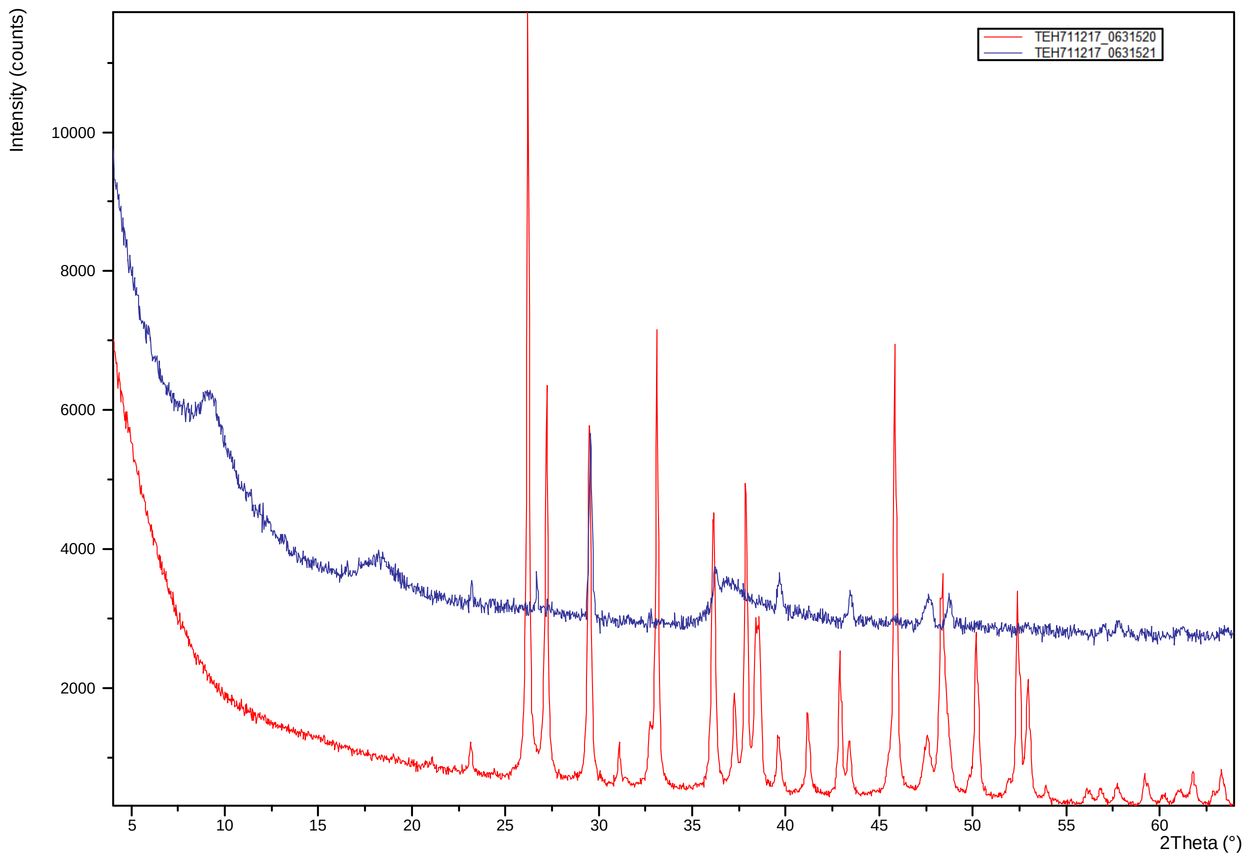

Figure 3 - Overlay plot of the diffractograms for the "Outer White Layer" (red) and the "Inner Black Layer" (blue) samples, with degrees 2θ along the x-axis and intensity (counts) along the y-axis.

Authorized Signature ________________ Date 12/12/07

Christina L. Lopano, Ph.D.
Scientist, X-ray Diffraction Group