Understanding the Suspended Solids in the Inland Empire Brine Line

SAWPA Workshop

December 20, 2011

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Trussell Technologies, Inc.

Presentation Overview

- Review Previous Workshop Findings
- Current Solids Characterization
- Historical Data Analysis
- Next Steps

PREVIOUS WORKSHOP REVIEW

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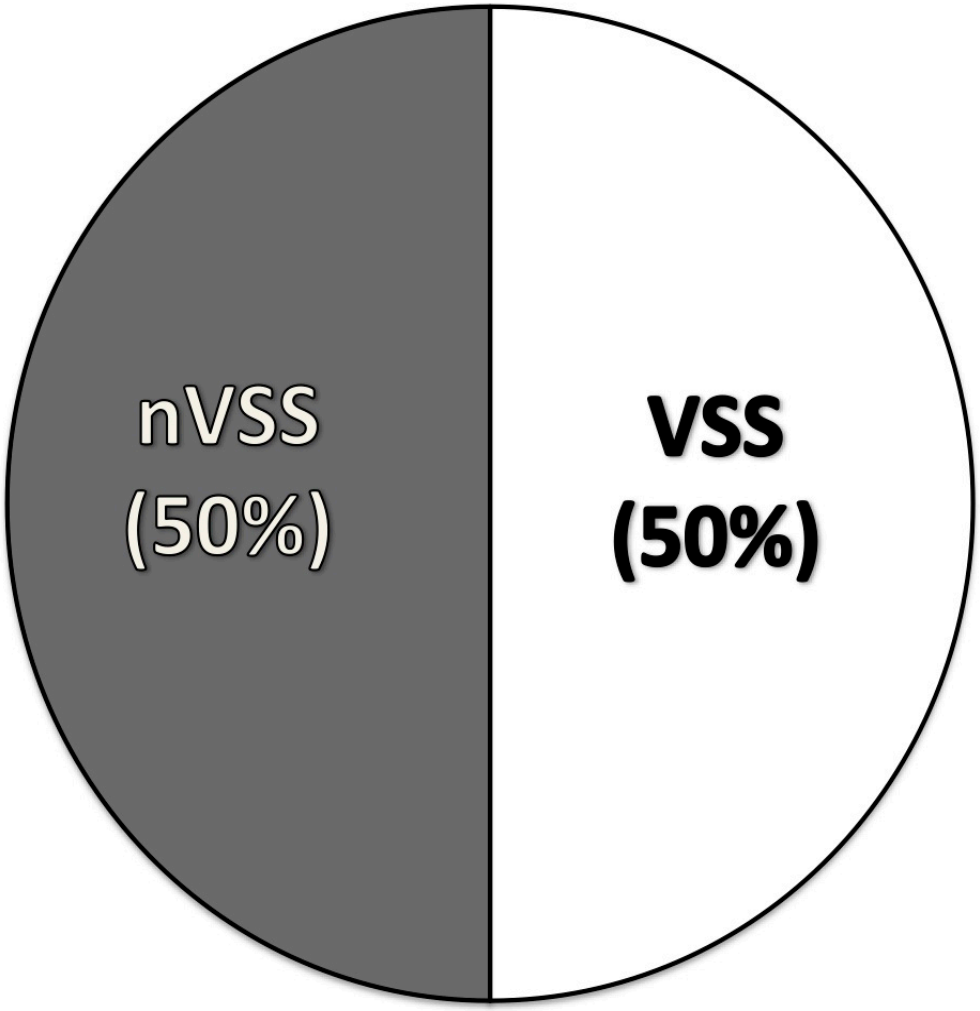
Back in September

- Directly measured POC (two samples)
  - Suggested more organics then previously observed by indirect measurements (TOC – DOC)
- Characterized crystalline structures of inorganics (XRD + ICP)
  - Amorphous Calcium Phosphate (ACP) & Calcite bulk of inorganics
- Large fraction of VSS remained unknown
  - Water?
  - Ratio of TOC to organic solids?
  - Other inorganic volatilization?

Estimate of Solids Breakdown



Applies only to September TT Samples

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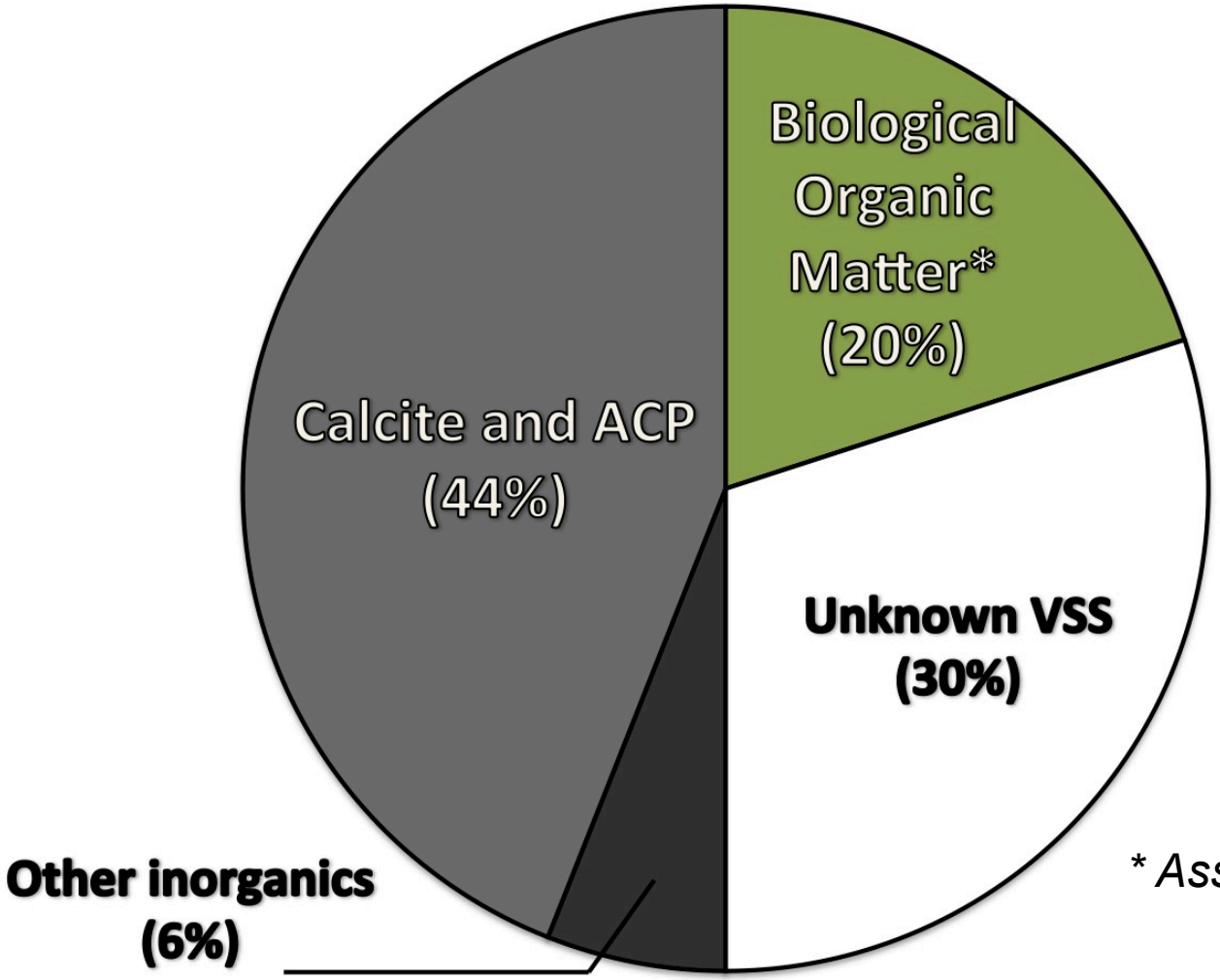
Estimate of Solids Breakdown



Applies only to September TT Samples

** Assumes BOM = 2 x POC*

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Next Steps from September

- Continue to quantify the solids make-up
  - Two months of sampling to improve understanding of variability in solids over time
  - XRD, ICP, TSS/VSS, optimize POC measurements
- Explain more of unknown fractions
  - Unknown nVSS ➔ SEM-EDX
  - Unknown VSS ➔ TGA and organics characterization
- Characterization of the organics
  - FTIR, EEM, HPC, fluorescence microscopy

CHARACTERIZATION OF SOLIDS TODAY

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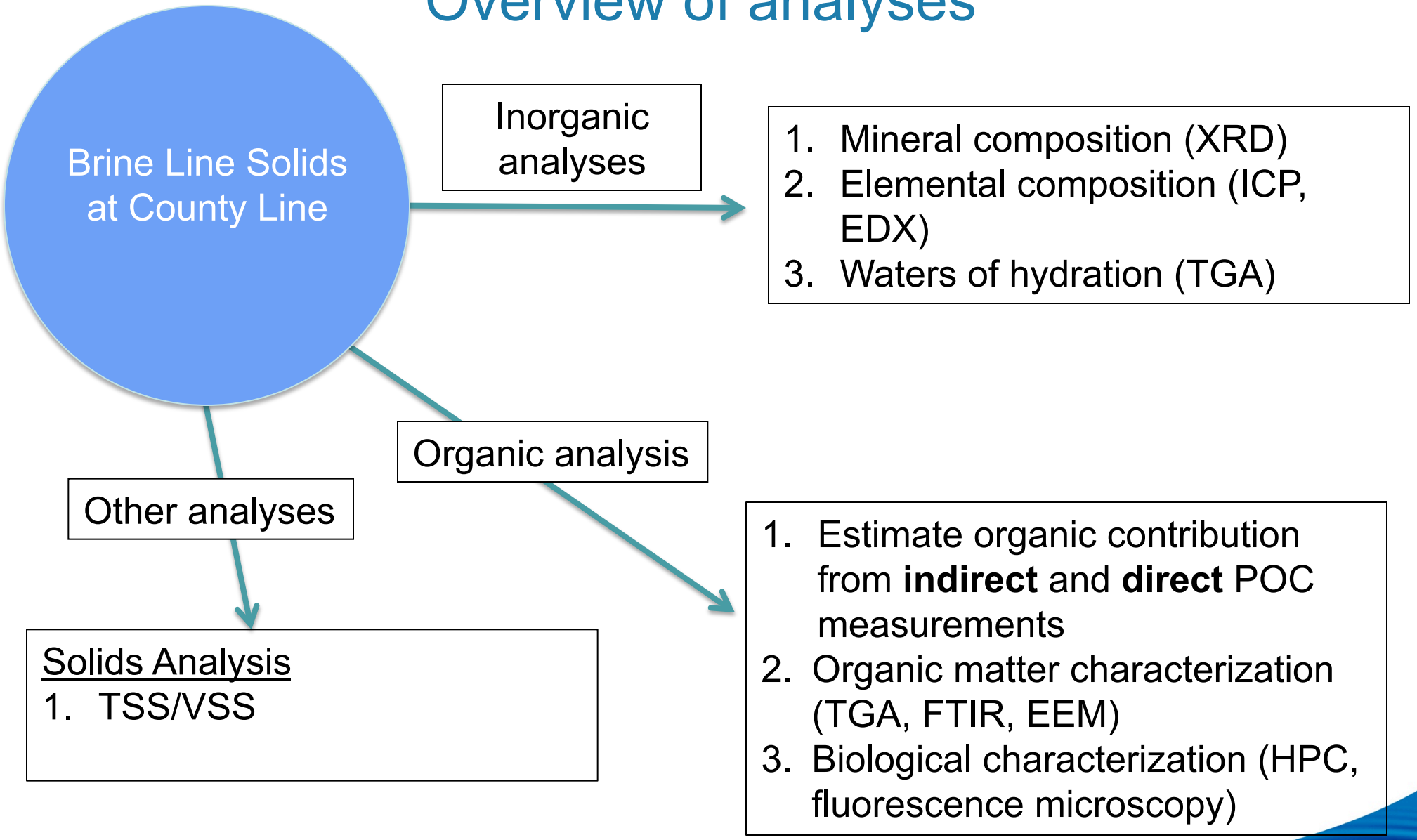
Overview of analyses



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DETERMINING THE MAKEUP OF THE INORGANICS

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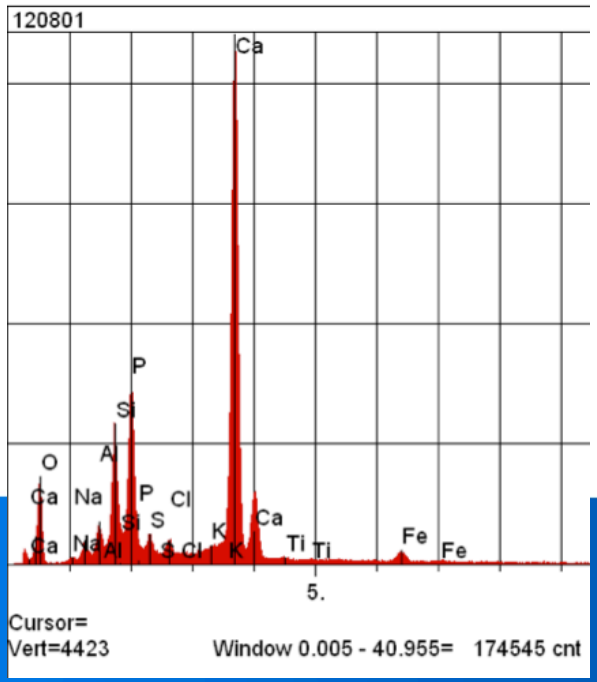
Elemental analyses verifies predominance of Ca

- Elemental Analysis:
  - Babcock & MWH: ICP of redissolved solids
  - Camet Labs: EDX of solids
- Conclusions:
  - Ca is predominant mineral
  - P is high
  - Si is also significant



Sludge results

	EDX % of mass	ICP g/Kg
Ca	62.2%	125
P	15.1%	50
Si	9.4%	25
Fe	3.8%	5
Al	2.2%	-
Mg	1.4%	8
S	1.3%	9
K	1.1%	3
Na	0.7%	8

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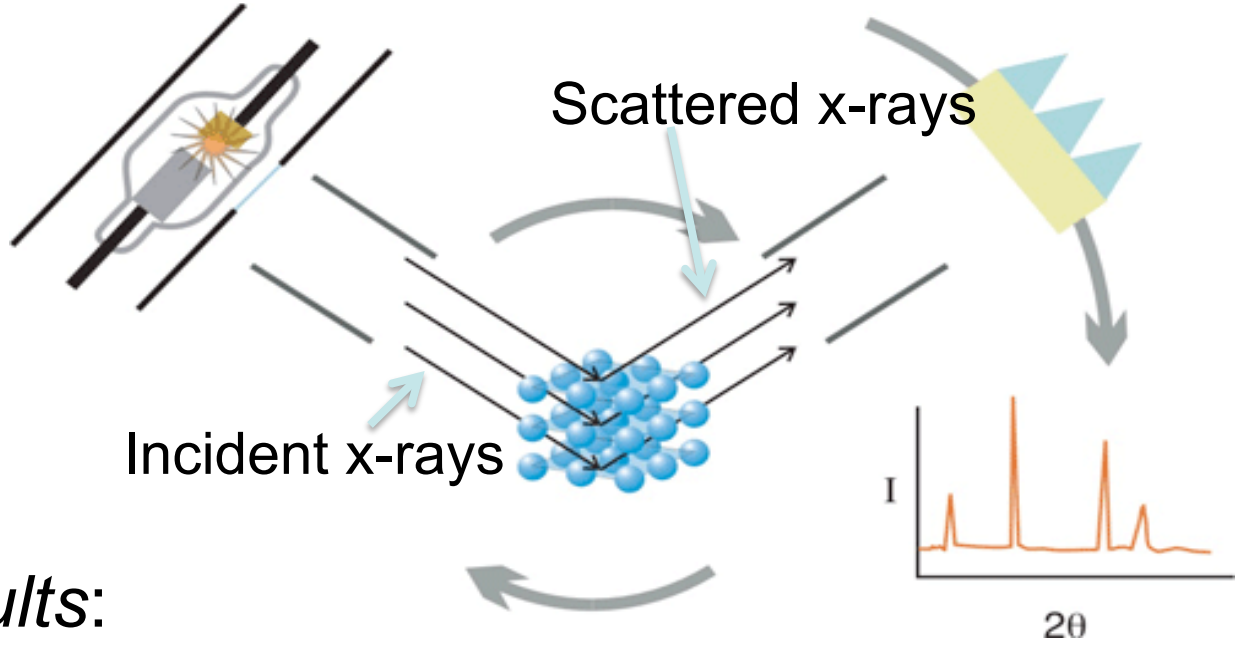
Mineral Identification: X-Ray Diffraction (XRD)

- Identifies samples based on their crystalline structure



Previous results:

- $CaCO_3$ + amorphous calcium phosphate (ACP) = ~80-90% of minerals
- SiO_2 (1-2%)

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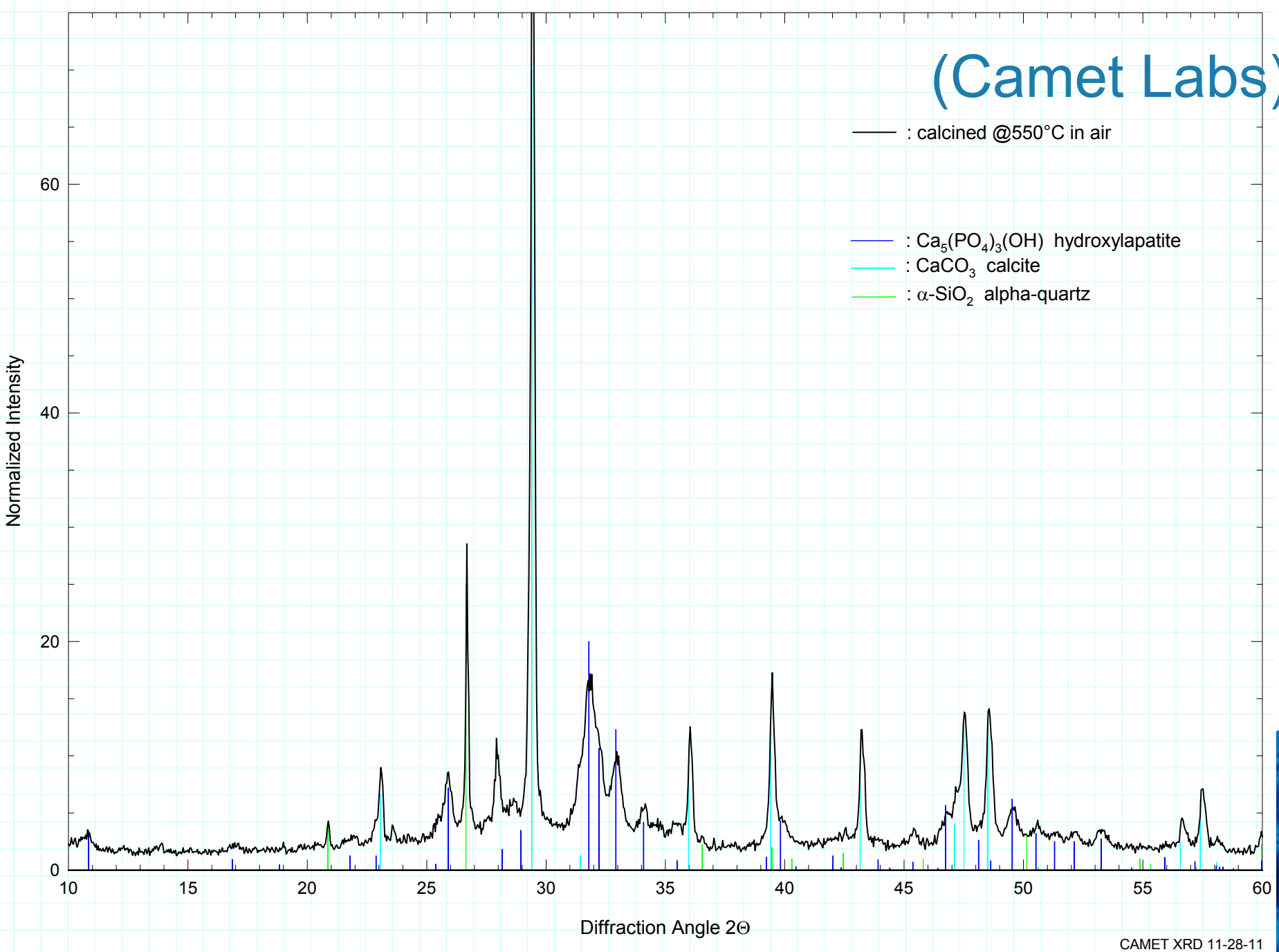
Example of recent XRD result

(Camet Labs)



Example of recent XRD result

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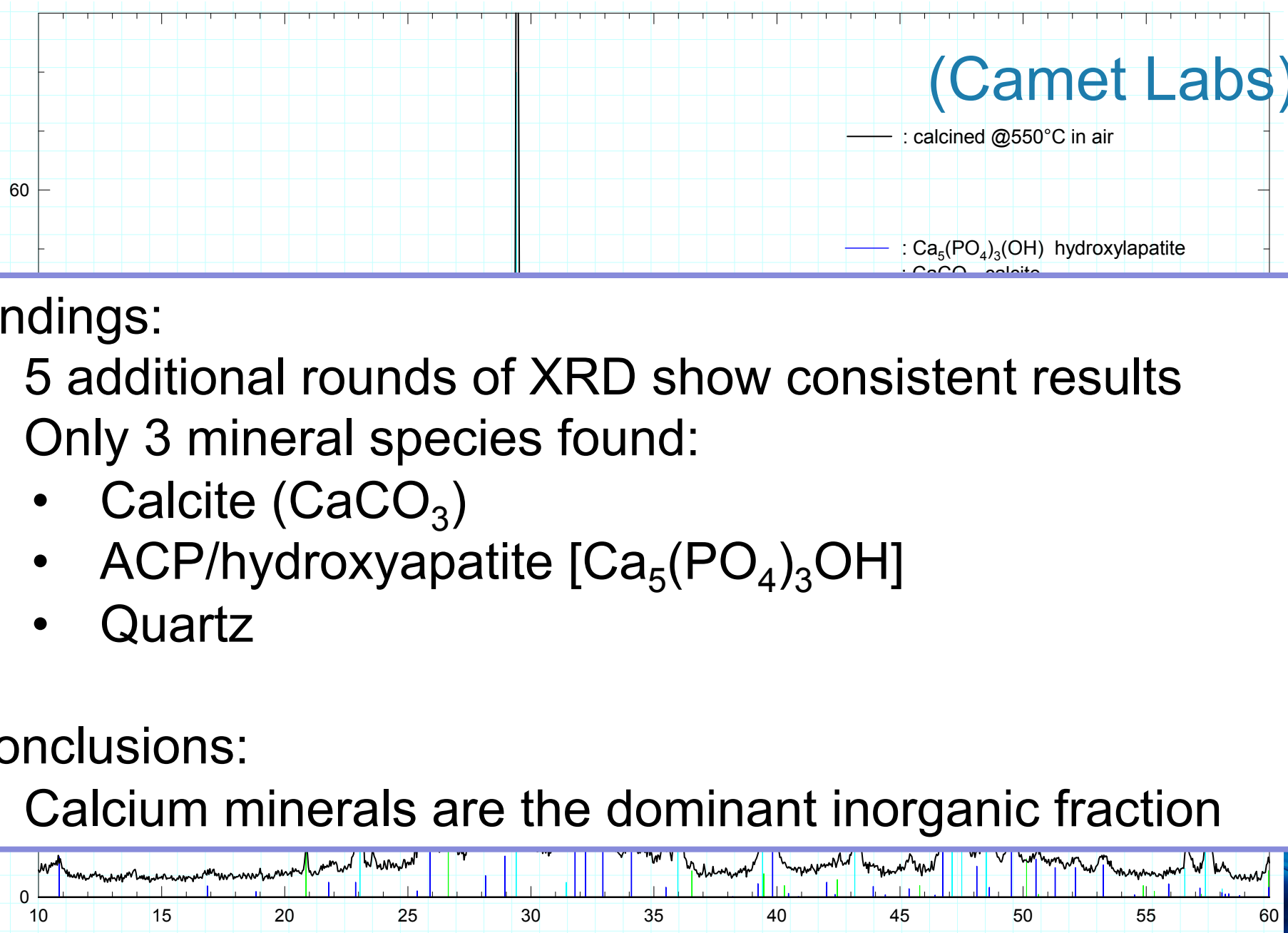


Findings:

- 5 additional rounds of XRD show consistent results
- Only 3 mineral species found:
  - Calcite ($CaCO_3$)
  - ACP/hydroxyapatite [$Ca_5(PO_4)_3OH$]
  - Quartz

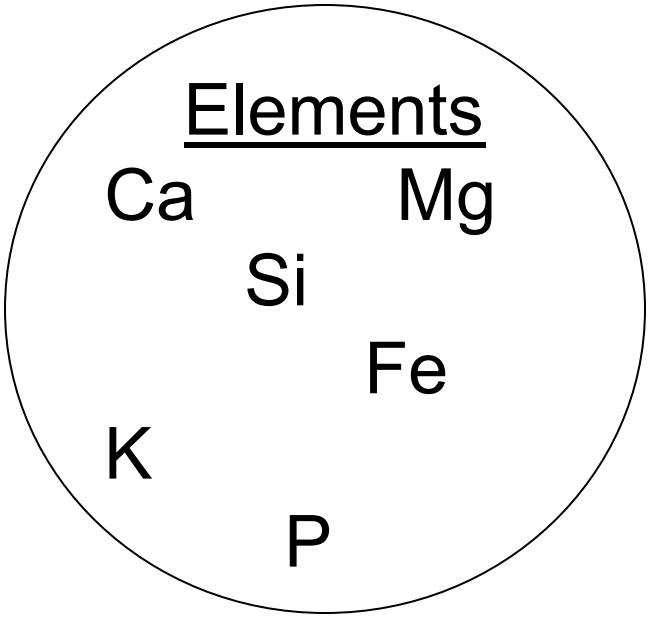
Conclusions:

- Calcium minerals are the dominant inorganic fraction

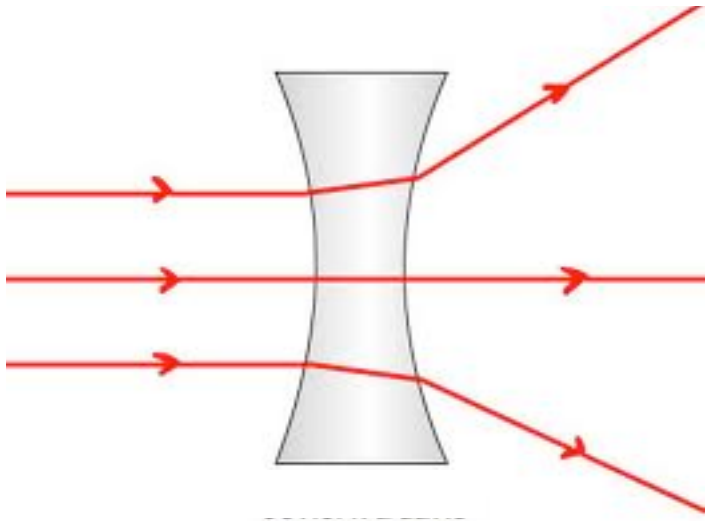
XRD shows calcium minerals dominate

- Next question: *how much* is present?
  - XRD: only semi-quantitative info on mineral fraction
- 2-step process

1. Elemental Analysis (ICP, SEM-EDX)



2. Mineral Analysis (XRD)



Maximum Mineral Fraction (Calculated)

Calcite: 45%

ACP: 37%

SiO2: 12%

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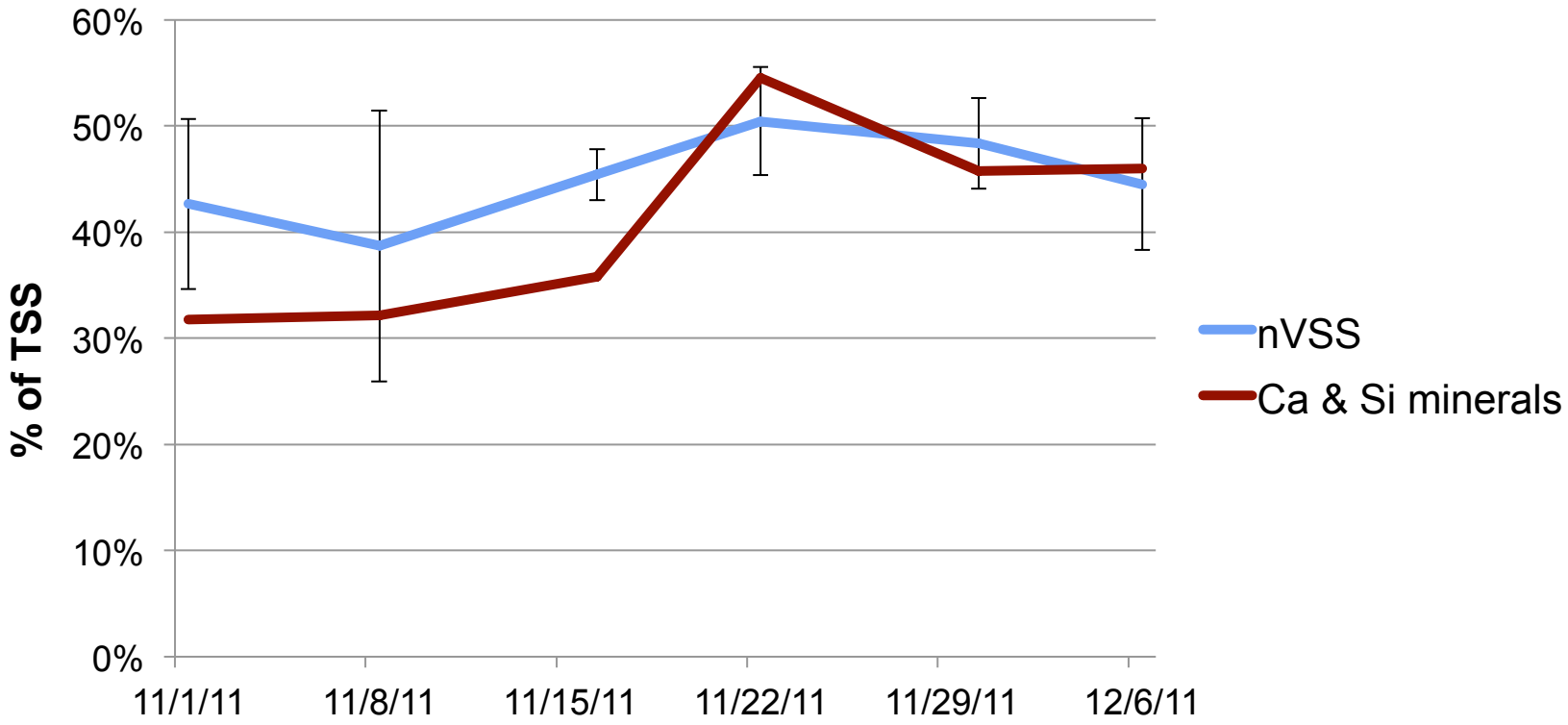
Inorganics - Summary

- Conclusions: same answer as last time
- Ca + Si minerals: >90% of nVSS (41 of 45%)



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DETERMINING THE AMOUNT AND COMPOSITION OF ORGANICS

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What is the organic material?

- Biological organic matter?
  - *Initial hypothesis for solids formed in line*

- Testing for presence of biological material
  - Bacterial cell culture: heterotrophic plate counts (HPC)
  - Fluorescence microscopy
  - Chemical analyses: Fourier-transform infrared analysis (FTIR), excitation-emission matrix (EEM)
  - Physical assays: thermogravimetric analysis (TGA)

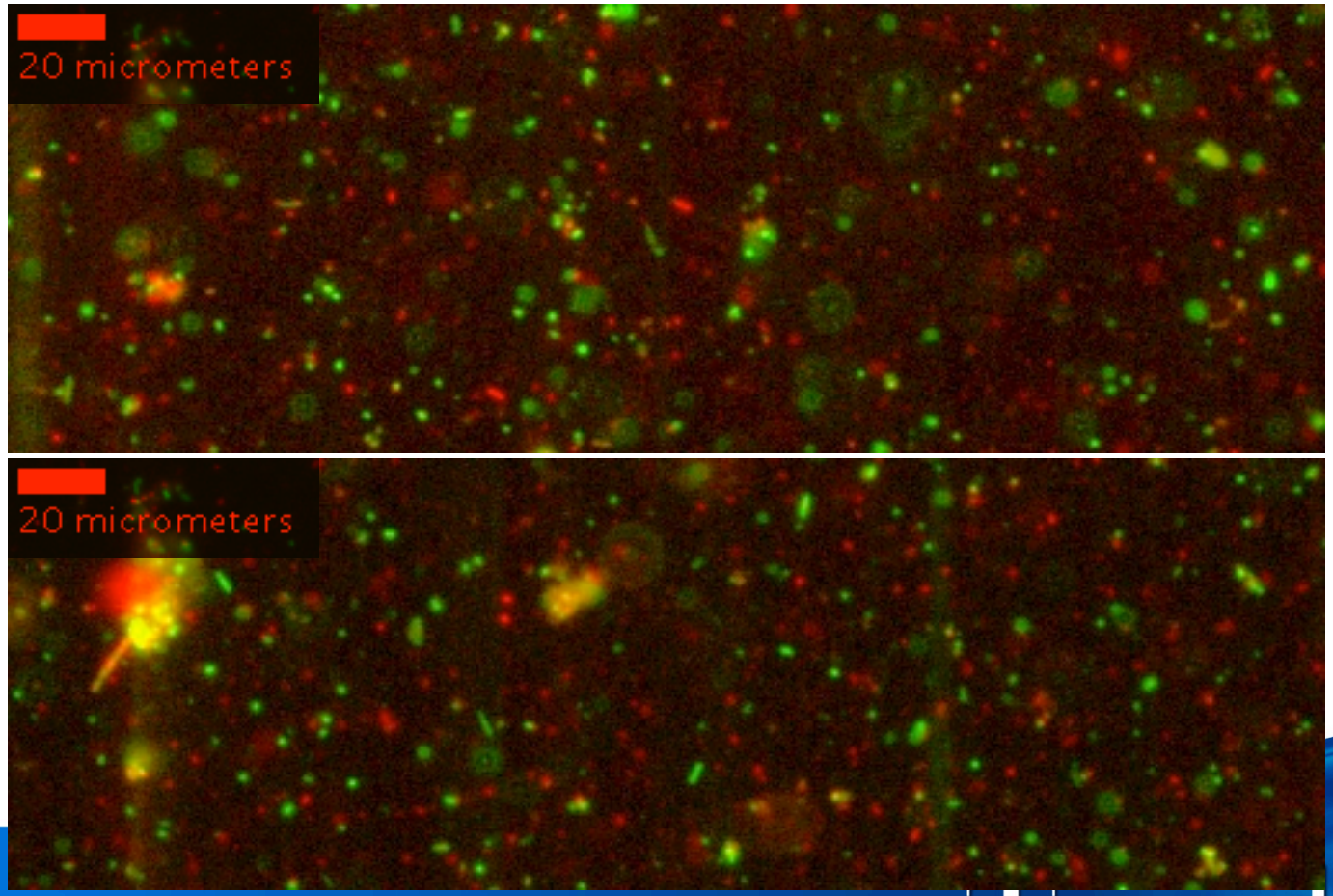
HPC suggests low biological content

- Culturable heterotrophs account for ~0.3% of the TSS mass

- Limitations of HPC:
  - Only measures culturable heterotrophs
  - Selects for certain bacterial types over others (aerobic vs. anaerobic)

Microscopy supports low biological estimates

- Method: microscopic analysis of live/dead bacteria
  - Green dye: living bacteria
  - Red dye: dead bacteria



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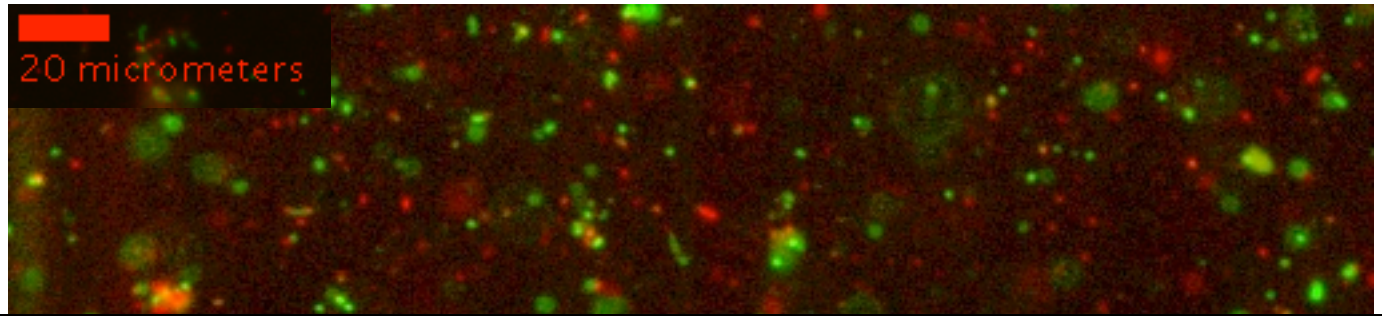
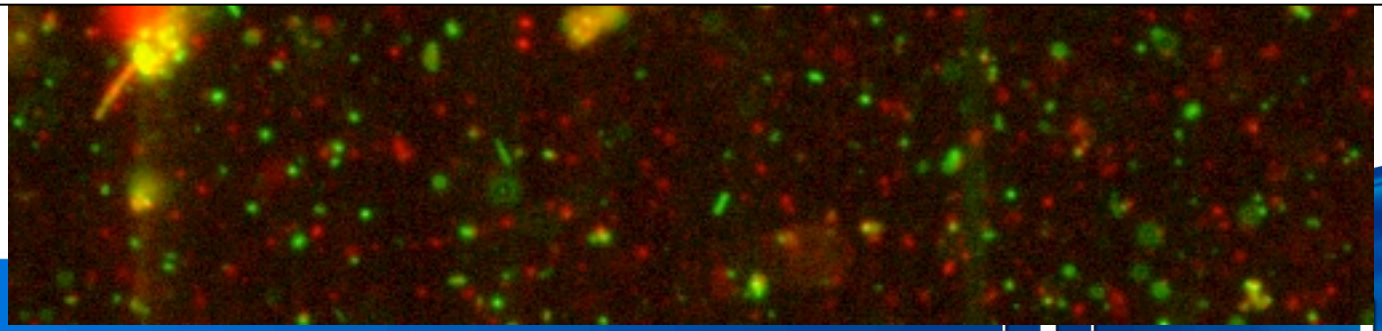


Mass concentration of bacteria still small (~1%)

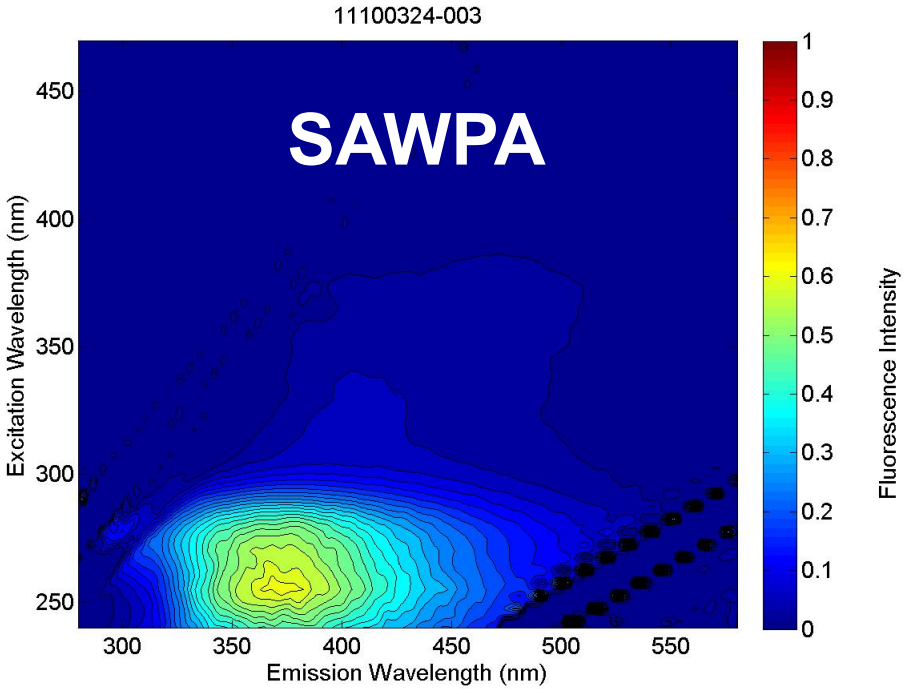
(note: based on one sampling date)

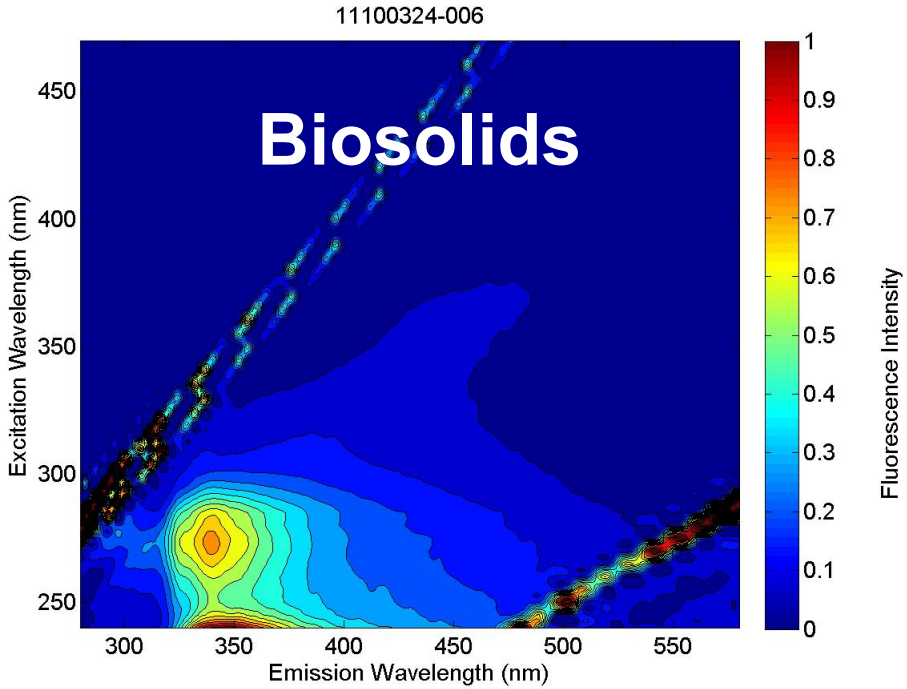


Chemical analyses support biological estimates

- FTIR (Fourier-Transfer Infrared) Results
  - Low bio content based on comparison with biological control
  - Side note: potential match with fossil material ($CaCO_3$ and HA)?

- Excitation-emission matrix (EEM) results
  - SAWPA solids show *different profile* than biological control

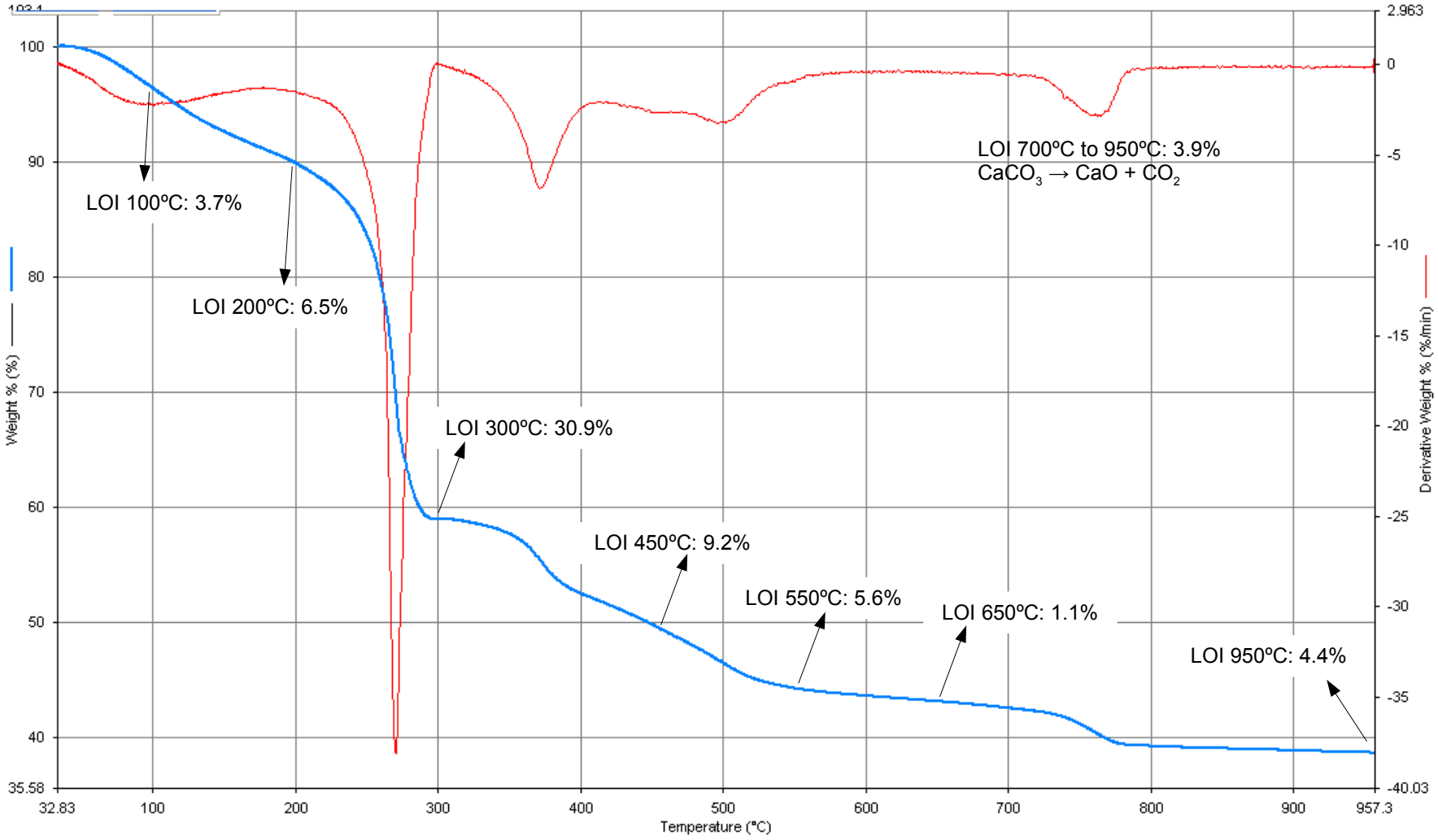




If it’s not biological organic matter, then what is it?

Thermogravimetric Analysis (TGA)

Continuous measurement of mass change with temp



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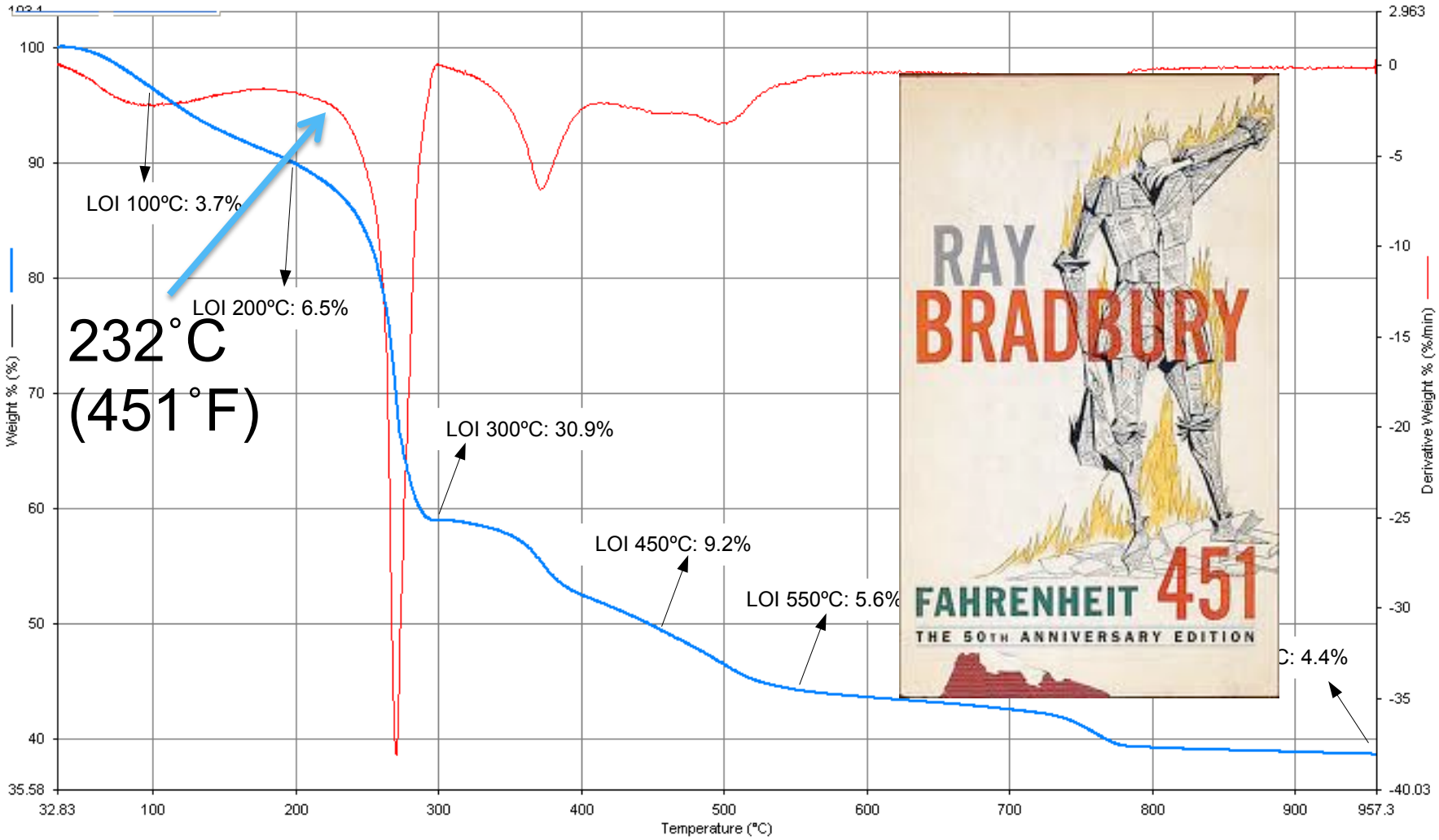
TGA suggests new organic candidate



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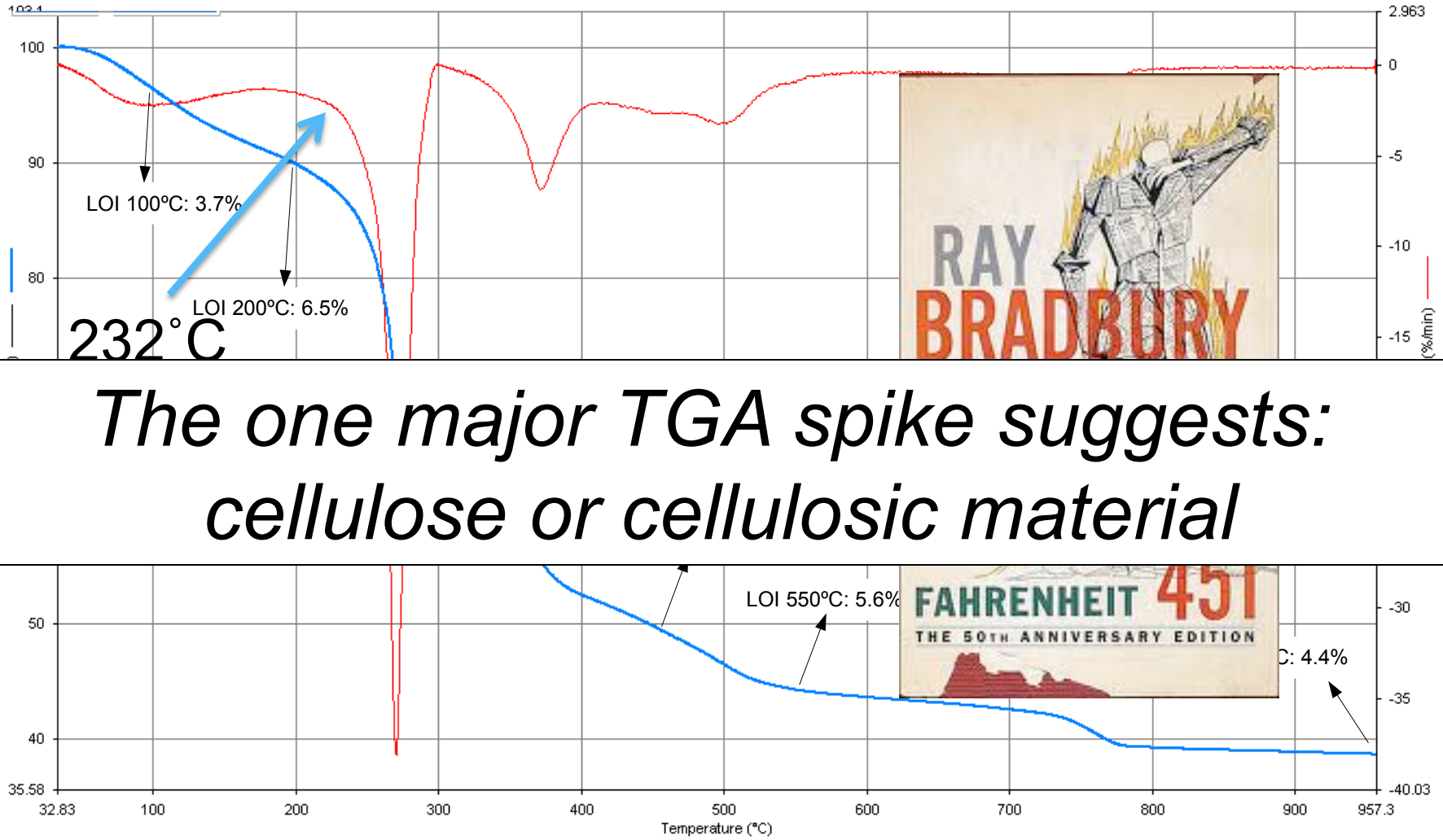

The one major TGA spike suggests: cellulose or cellulosic material

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Is cellulose a reasonable candidate?

- Visual inspection: Wet solids

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Is cellulose a reasonable candidate?

- Dried solids

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Is cellulose a reasonable candidate?

- Dried solids: A closer look

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Is cellulose a reasonable candidate?

- Dried and ground solids

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Is cellulose a reasonable candidate?

- Dried and ground solids: A closer look

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Is cellulose a reasonable candidate?

- Dried and ground solids: A closer look

Cellulose hypothesis passes the visual inspection

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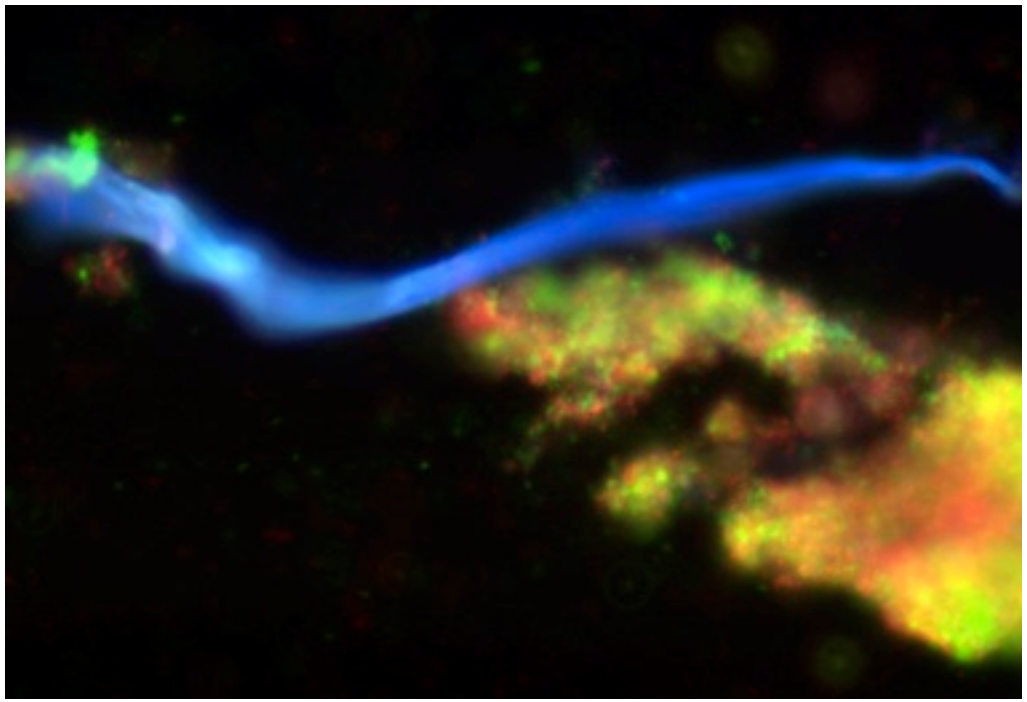
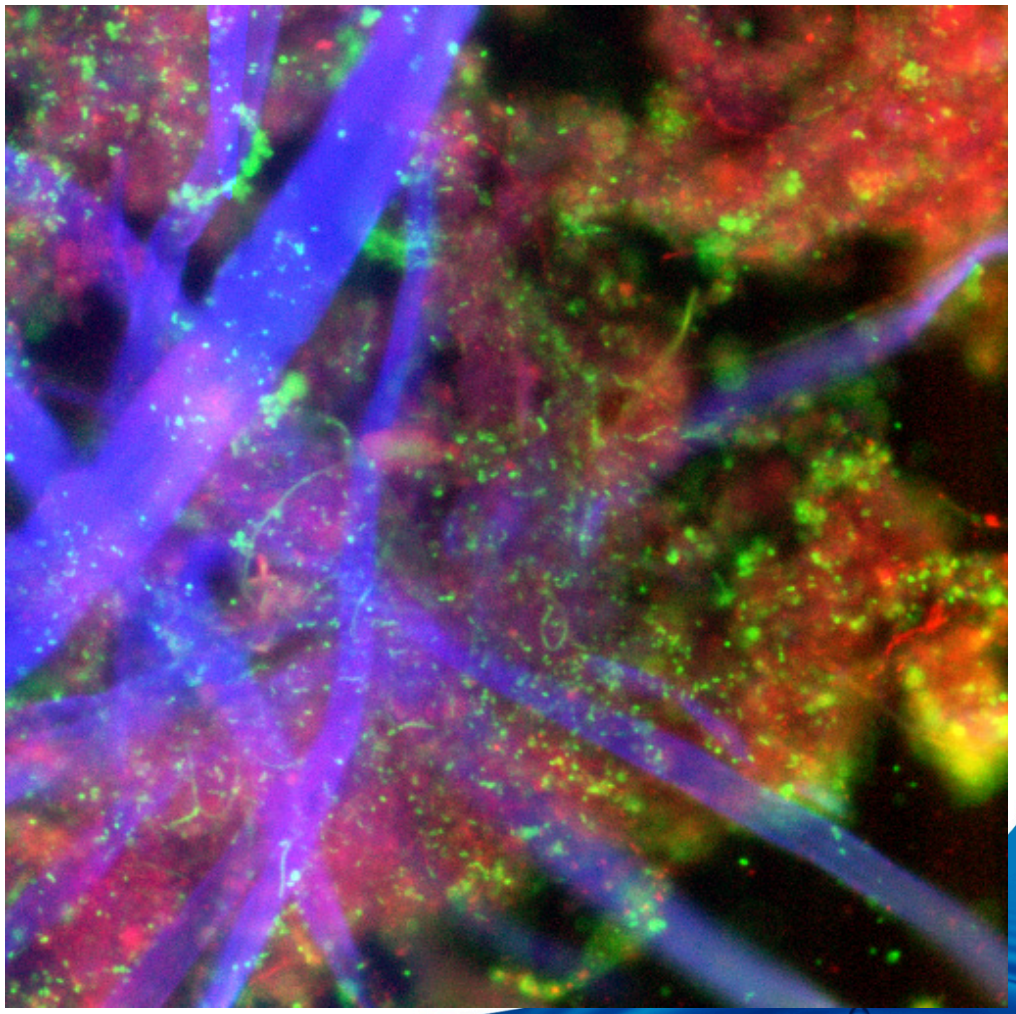
Is cellulose a reasonable candidate?

- From the FTIR report:
  - Peak in all 3 SAWPA samples may indicate presence of "*cellulose or other polymeric carbohydrate material…wood, paper, cellophane, and cellulose derivatives*"

Is cellulose a reasonable candidate?

- Fluorescence Microscopy
  - Cellulose = blue
  - Live cells = green
  - Dead cells = red





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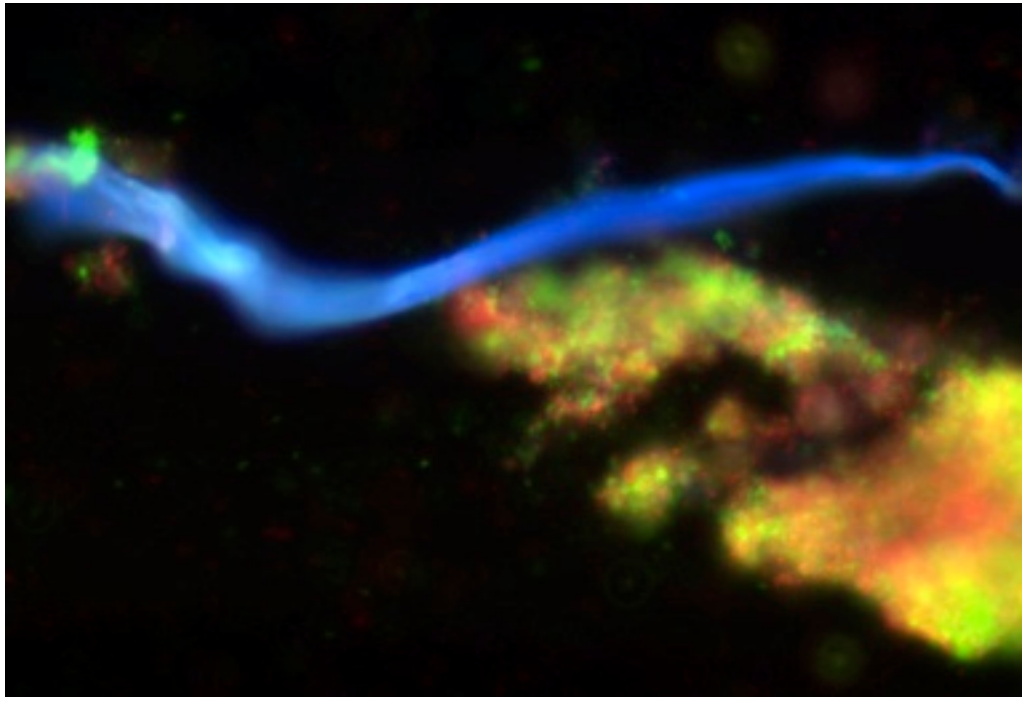

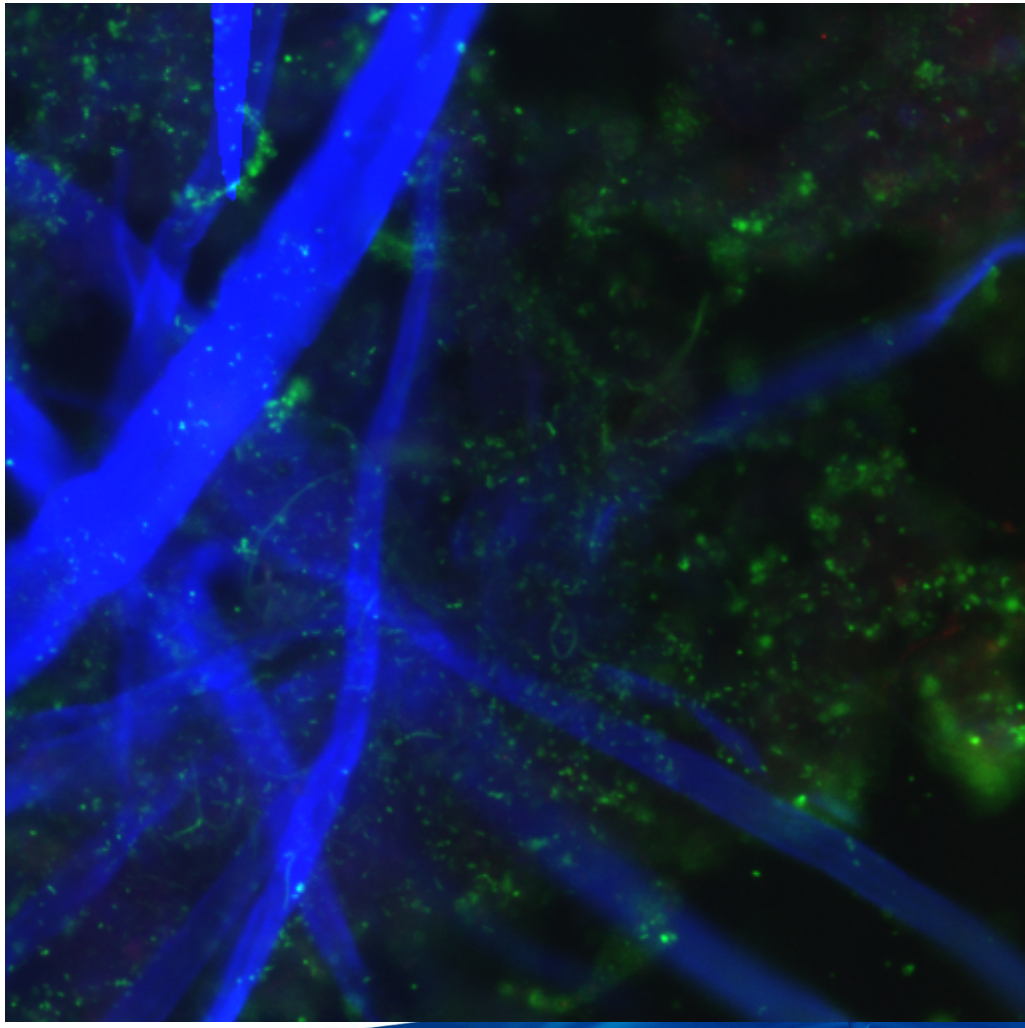

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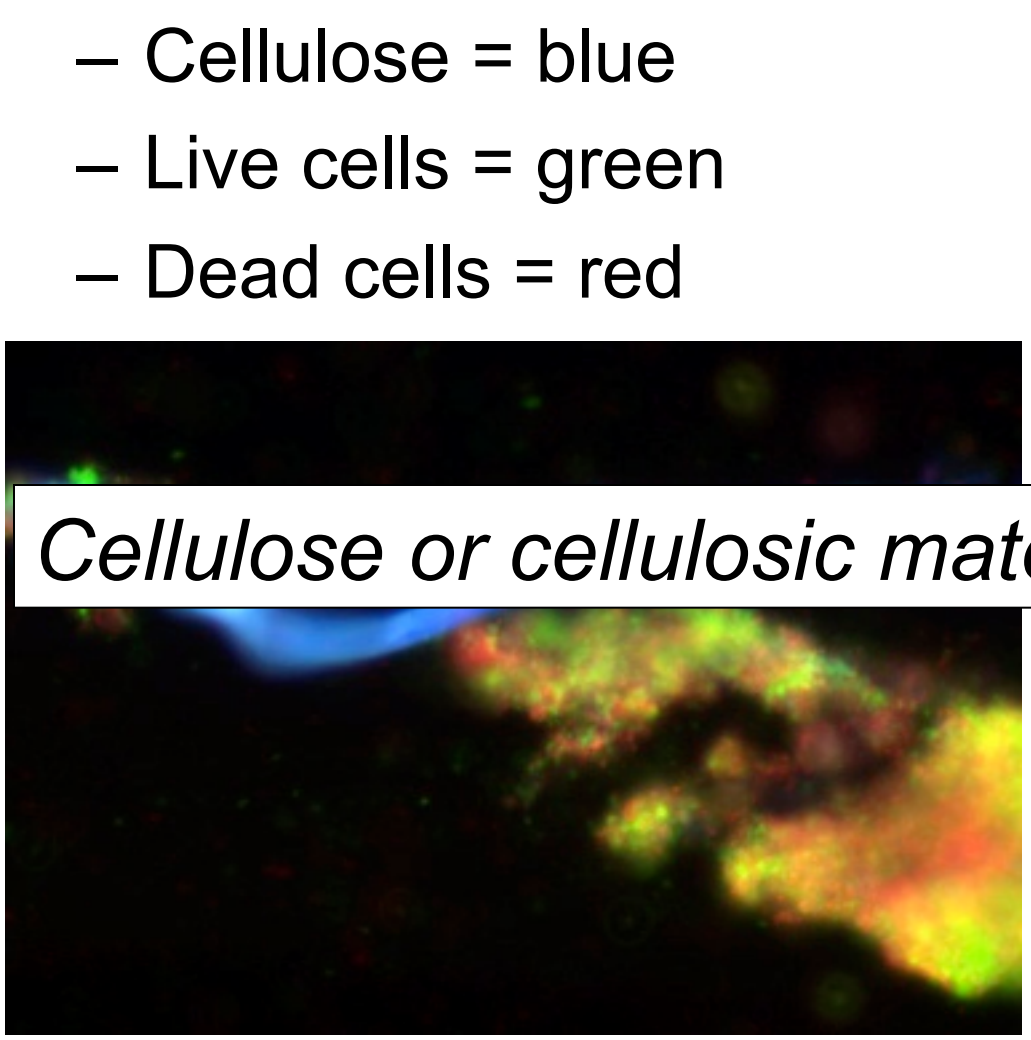

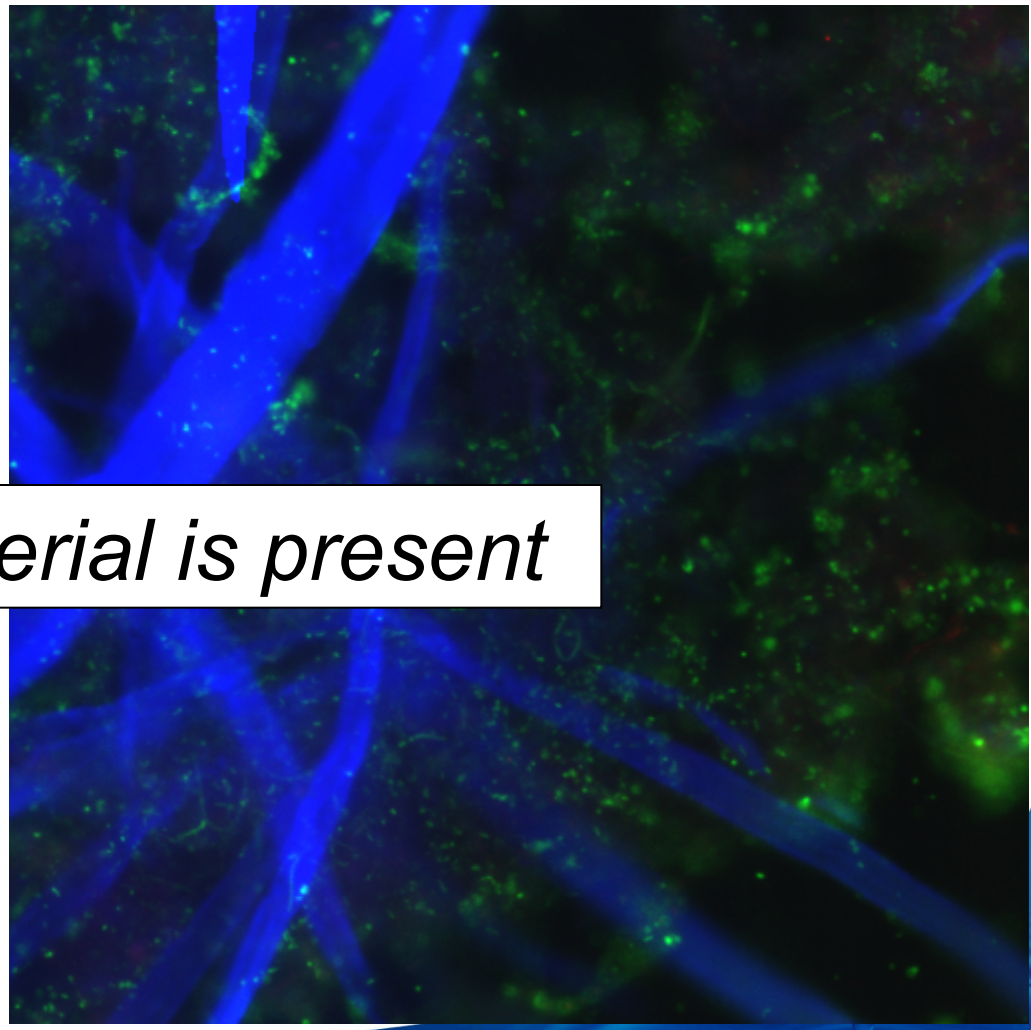

Cellulose or cellulosic material is present

How much cellulose is there?

- **From TGA analysis**, we can quantify the amount of cellulosic material from the spike

Cellulosic Material:

Avg: 34% of TSS

4 samples: 31-37%

Other VSS:

Avg: 22% of TSS

4 samples: 19-23%

Organic Carbon Analysis

- What fraction of the solids is organic?
- Particulate organic carbon (POC) → organic matter
- Indirect POC
  - Measure raw sample (TOC)
  - Measure filtered liquid (DOC)
  - POC = TOC - DOC
- Direct POC



  - Measure the TOC of the suspended solids (POC = TOC_{ss})
- Previous results: Direct POC (TT) > Indirect POC

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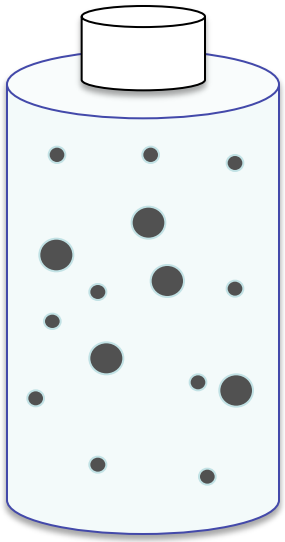
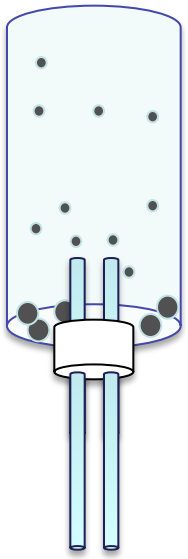
Limitation of OC Liquid Suspensions

Well-mixed suspension of brine line sample



TOC Sample Vial



Large particulates may settle or become clogged in instrument tubing: Need another method

Organic Carbon Analysis

Direct POC (Babcock soil instrument)

- Detects significantly more OC than direct POC (TT), indirect POC (TT, BL)
- *Best method for POC measurement*

Findings

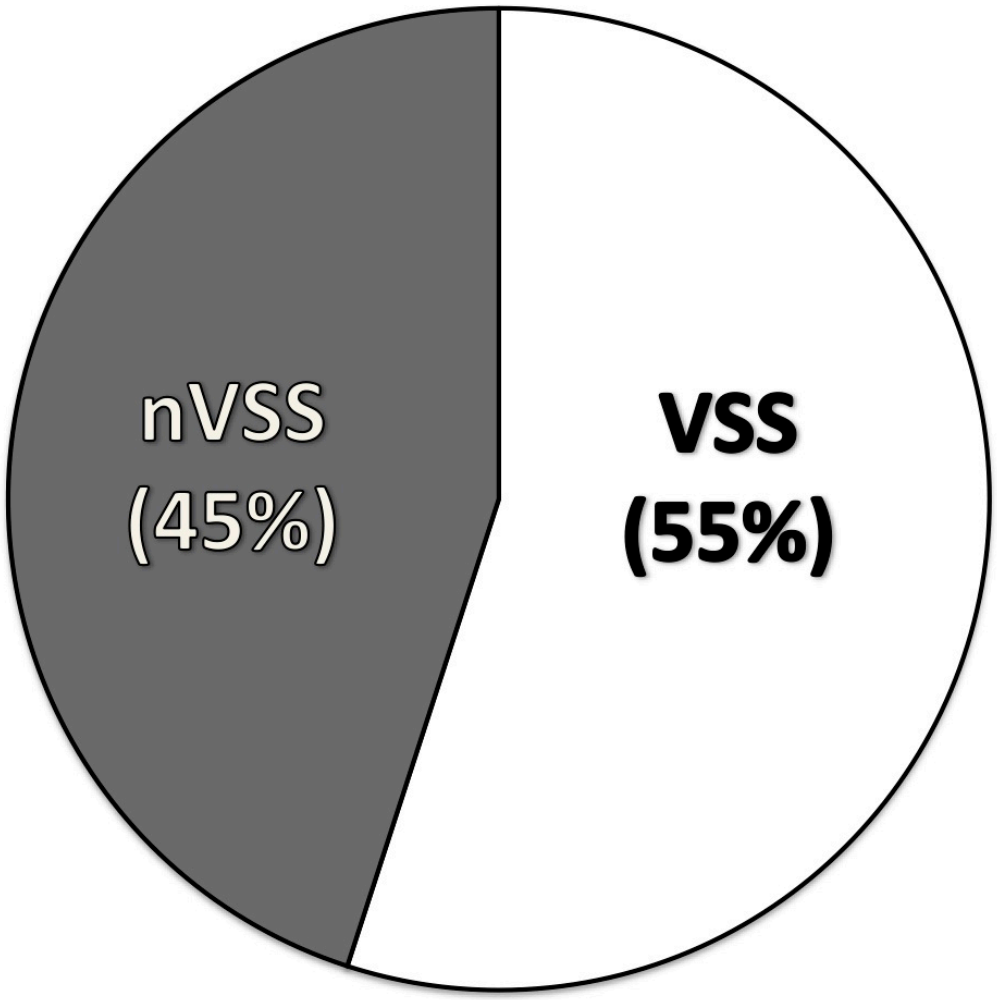
- Significantly more OC in SAWPA solids than previously thought
- POC accounts for 23% of TSS (2 samples tested)
  - 2/3 is Cellulose; 1/3 is bio-organic matter
- Converting this to total mass
  - Cellulose = 34% of TSS (TGA) (assumes OC/SS = 44%)
  - Bio-organic matter = 13% of TSS (assumes OC/SS = 60%)
- Organic mass now explains most of VSS

Organics Summary

- Organic content higher than previously thought
- Most of organic mass is cellulose-like material
- Biological contribution is low: HPC, FTIR, microscopy, EEM
- Previous hypotheses:
  - Biological material
  - Organic precipitates
  - Organic particulates discharged into Brine Line

SUMMING IT ALL TOGETHER
INORGANICS + ORGANICS

Estimate of TSS Breakdown*



nVSS = non-VSS = inorganic fraction

*Based on 6-sample avg. of TSS, VSS data

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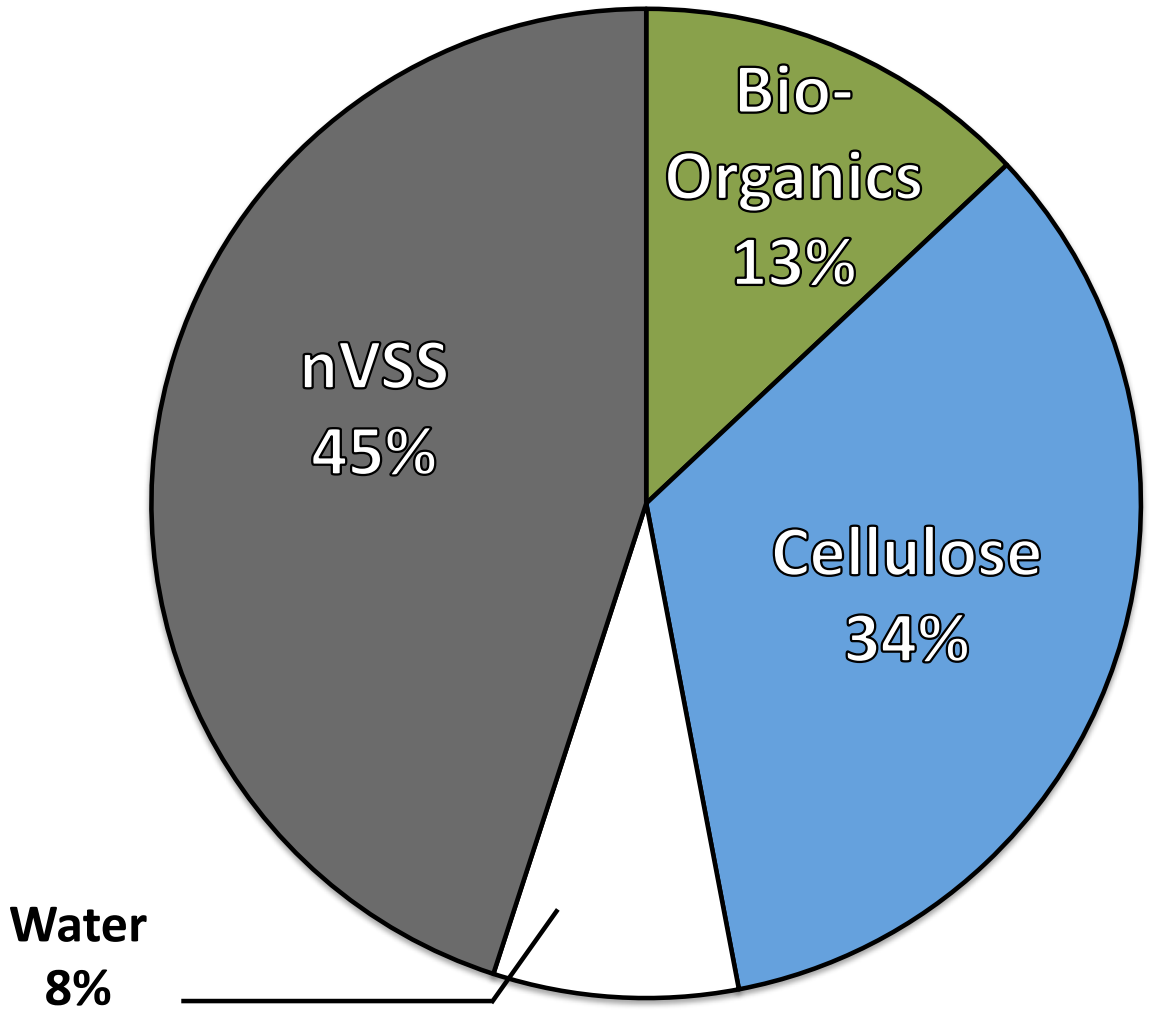
Add in what we learned about VSS



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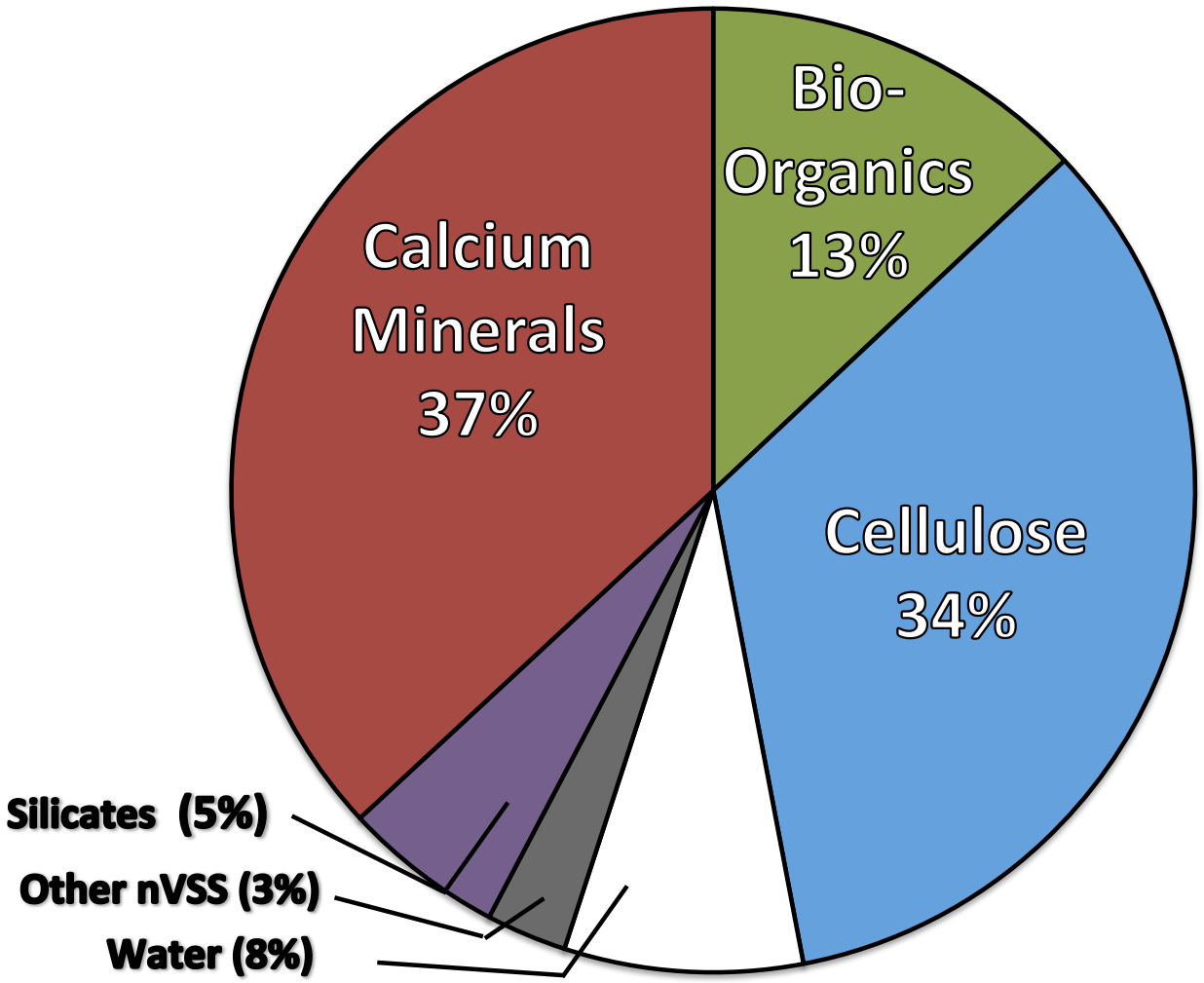
Putting It All Together



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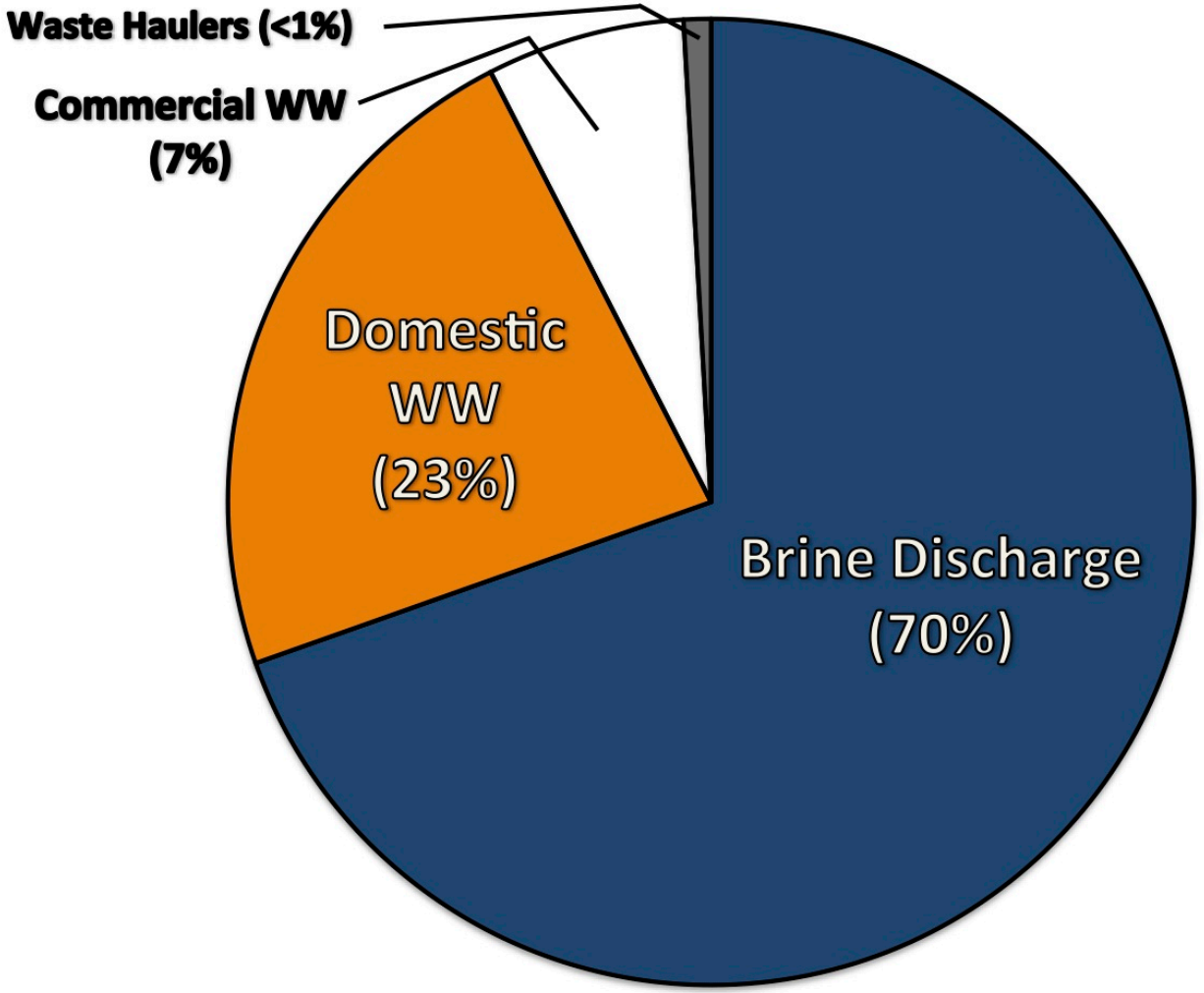
UNDERSTANDING THE PROBLEM: *A LOOK AT HISTORICAL DATA*

What goes *into* the Brine Line*



Breakdown by Flow

** Represents data from Aug 2010 to Aug 2011*

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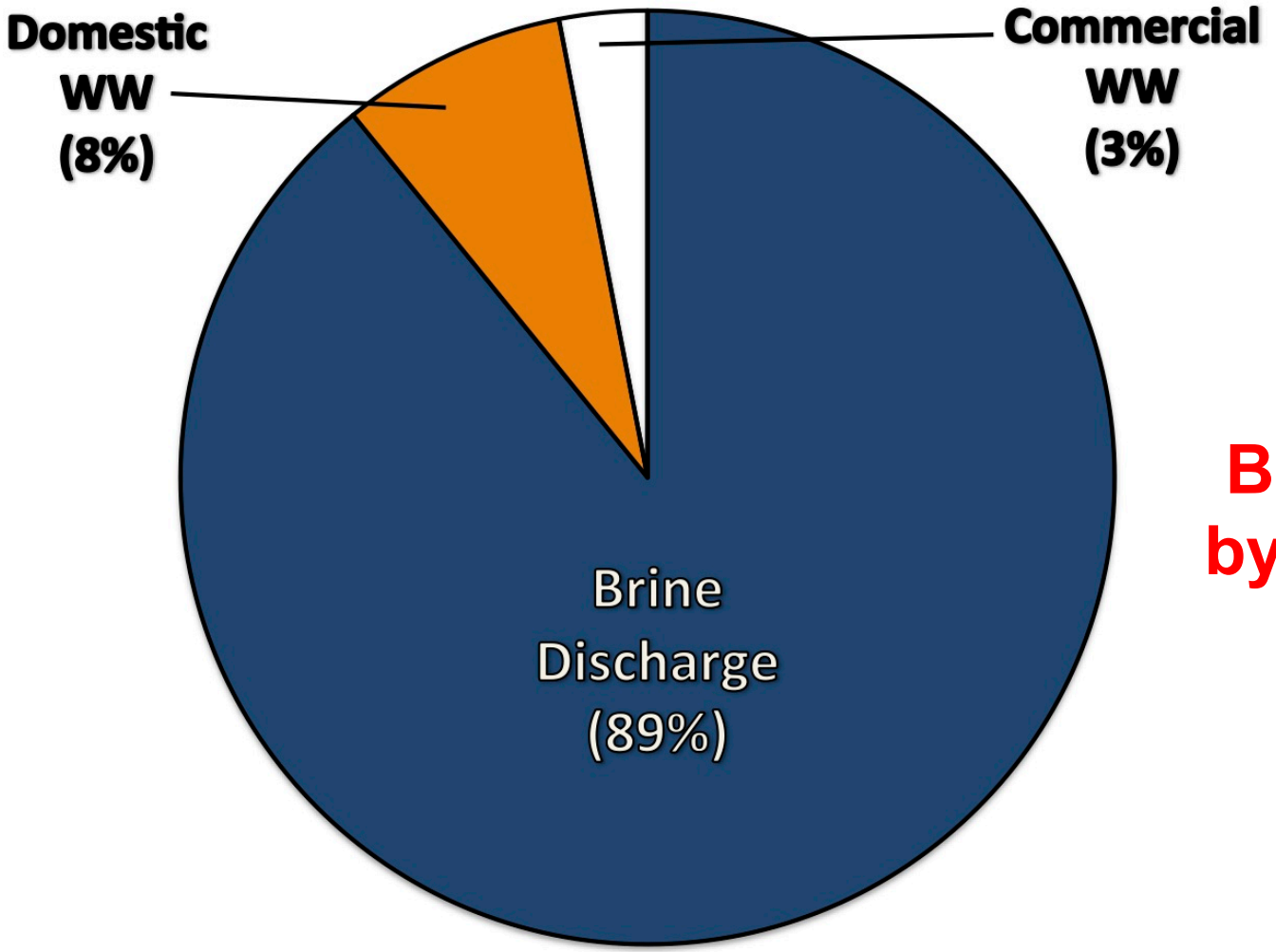
What goes *into* the Brine Line*



Breakdown by Hardness

** Represents data from Aug 2010 to Aug 2011*

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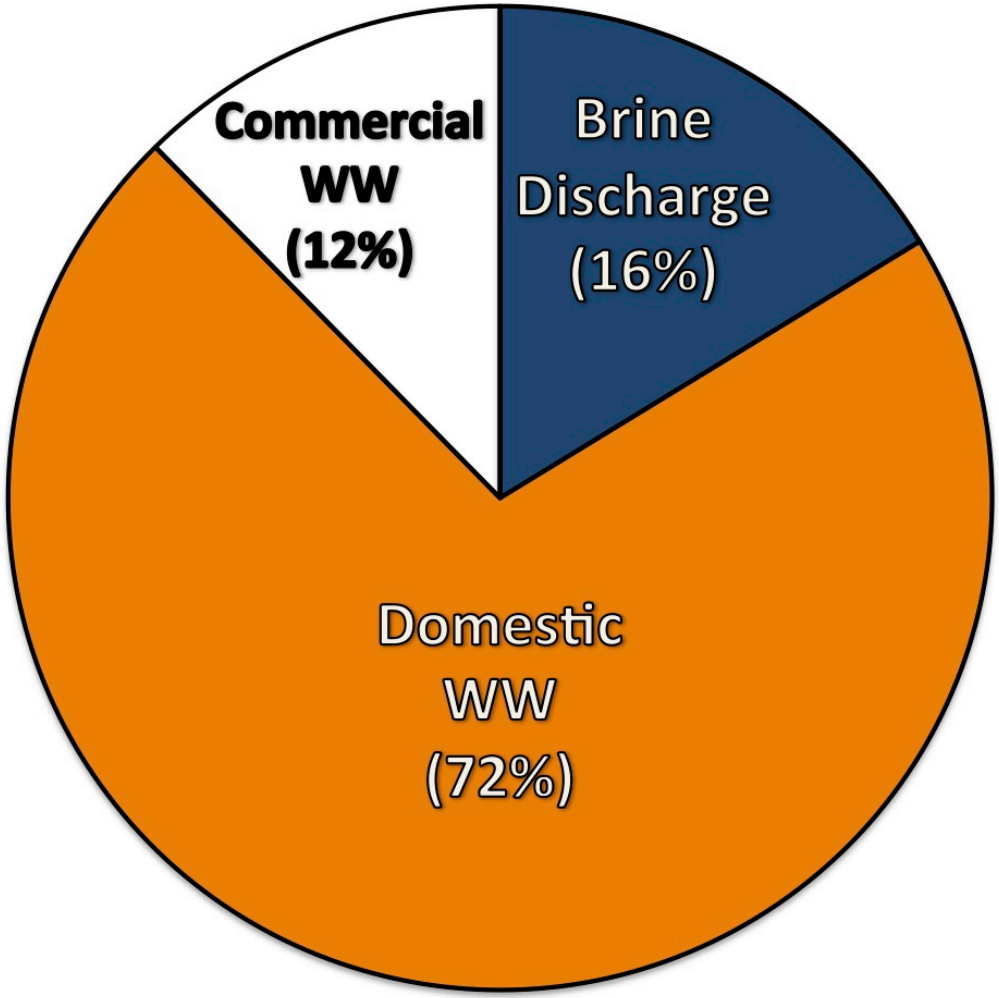
What goes *into* the Brine Line*



Breakdown by TSS Load

** Represents data from Aug 2010 to Aug 2011*

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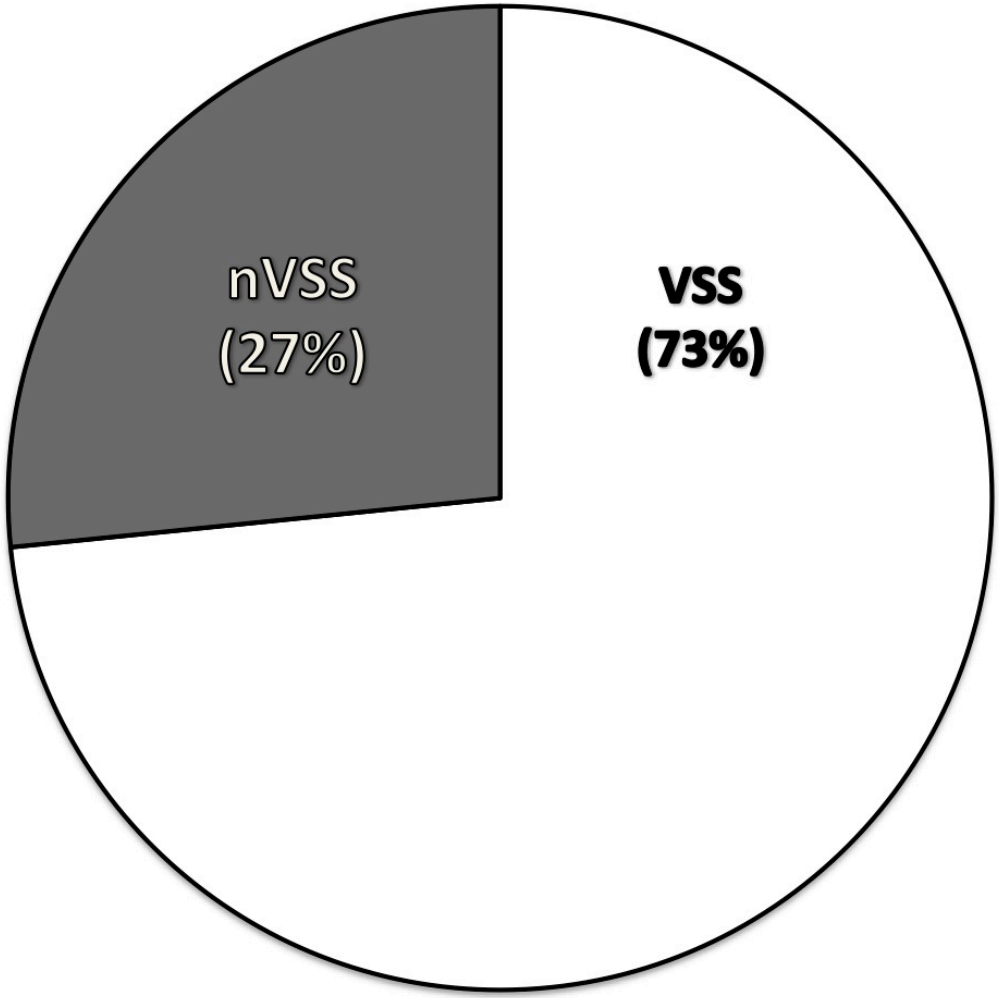
What goes *into* the Brine Line*



Breakdown By Suspended Solids Source

** Represents data from Aug 2010 to Aug 2011*

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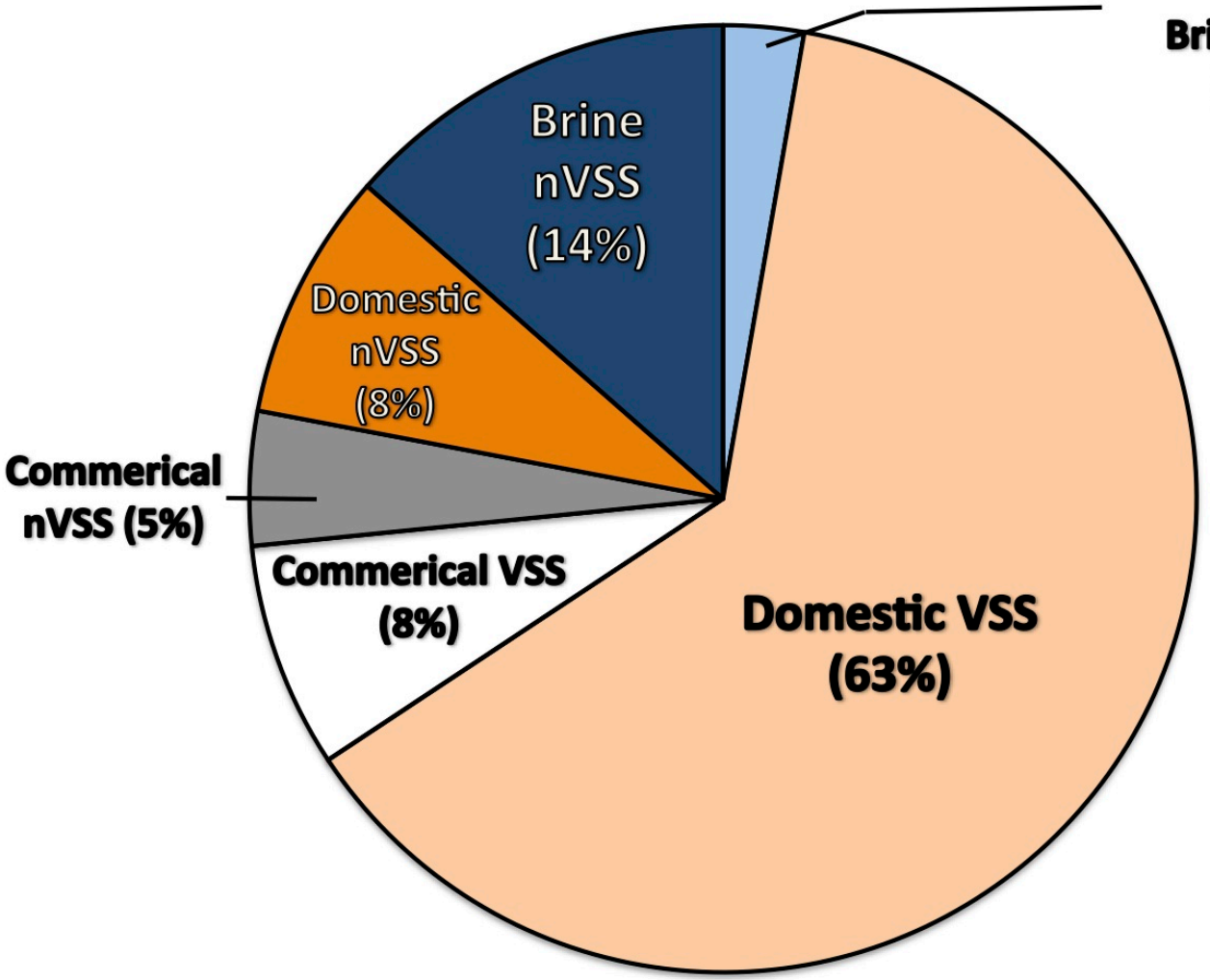
What goes *into* the Brine Line*



Breakdown By Suspended Solids Source

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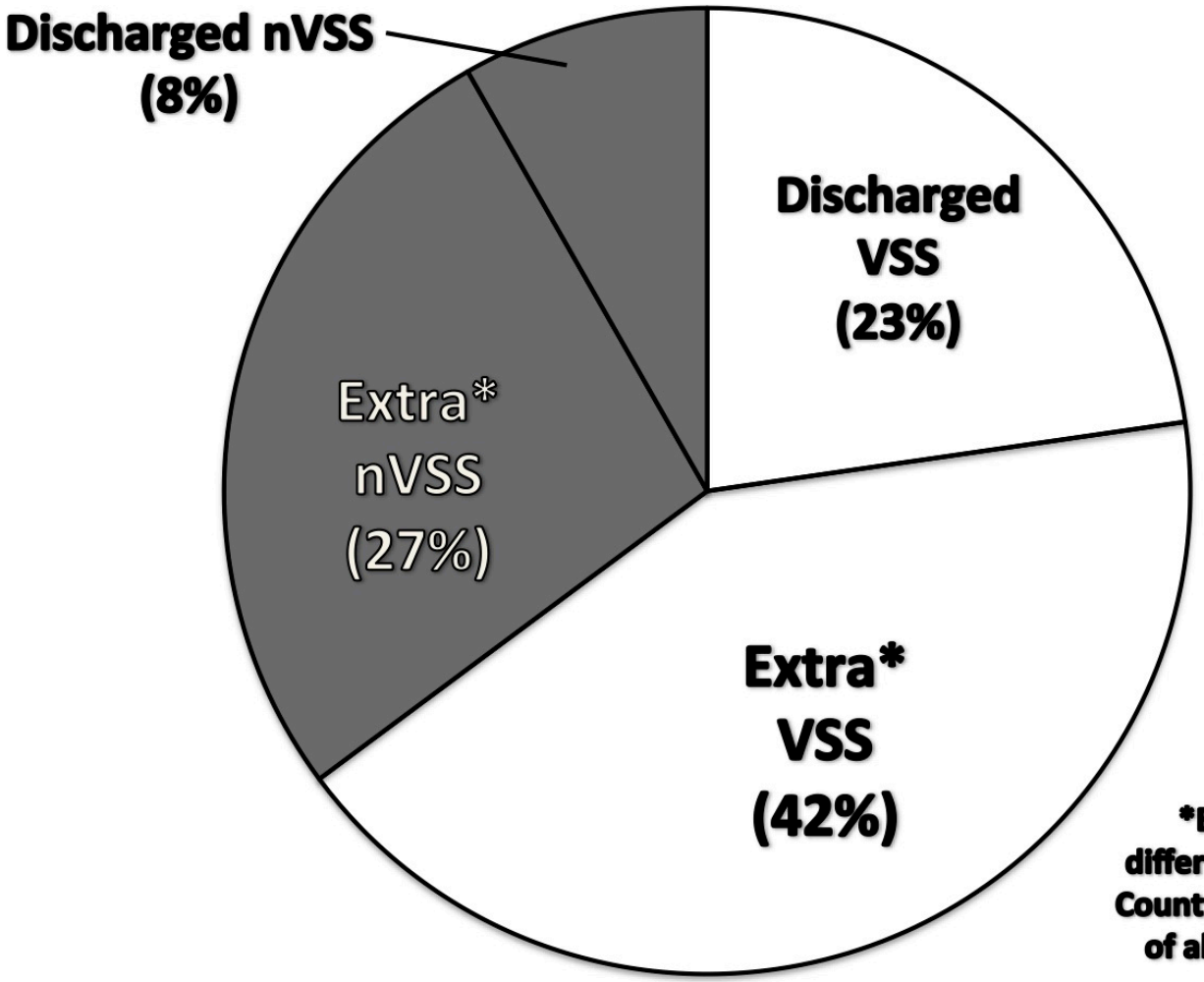
What *comes out* of the Brine Line*



Note:
Change in VSS/TSS from 73% to 65%

***Extra is the difference between County Line and sum of all dischargers**

** Represents data from Aug 2010 to Aug 2011*

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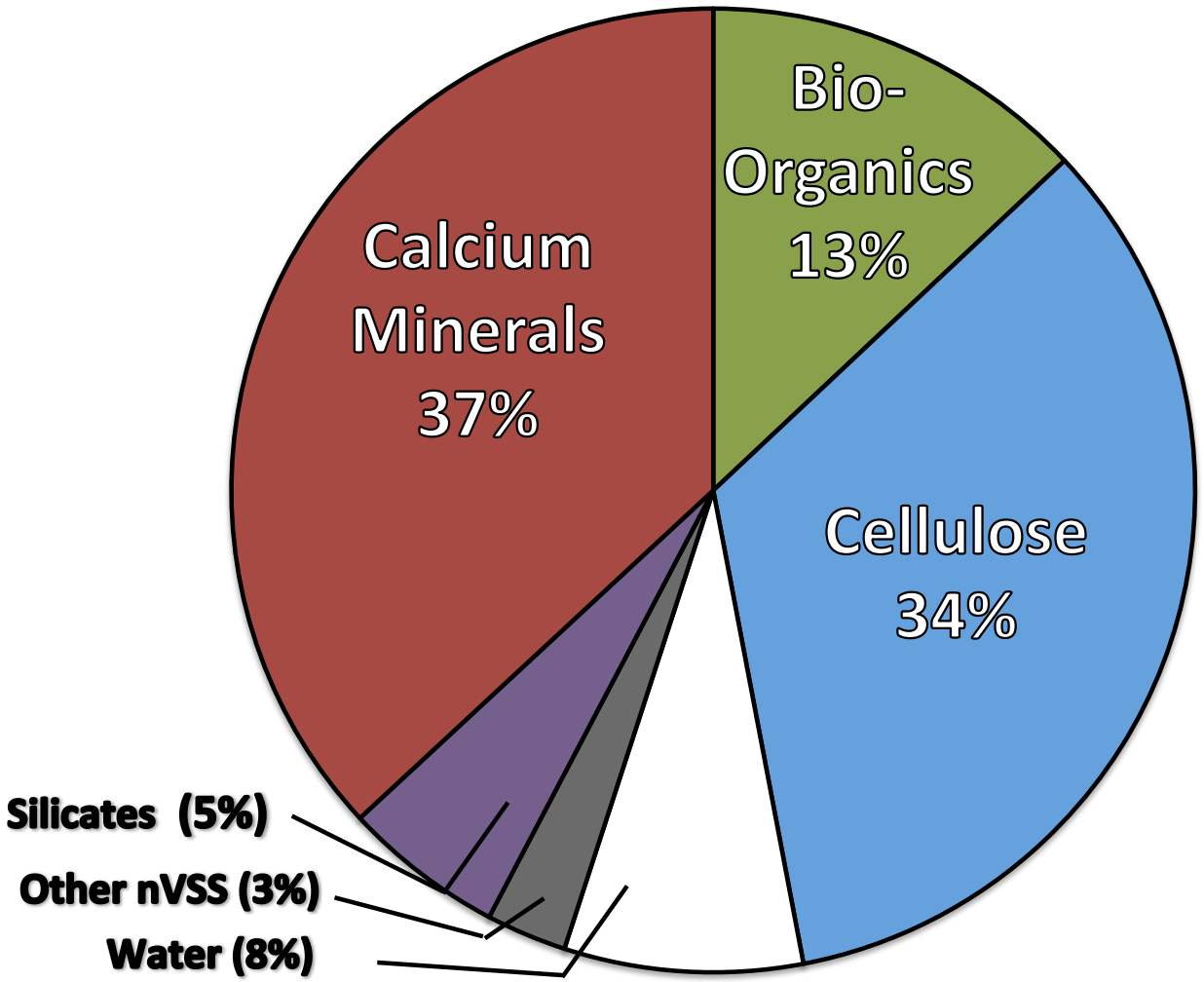
Current Estimate of Solids Breakdown



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What can be done to control solids formation?

- **Cellulose:** mostly inert and not likely to form in the line
- **Biological organic matter:** control options not feasible
- **Calcite & ACP:** changes in pH may help control formation
- **Data:** Possibility for increasing data accuracy by increasing collection frequency

NEXT STEPS

Next Steps: Solids Formation Control

1. Assess pH Reduction Strategy
   a. Conduct Survey of discharger practice
      1) pH before/after adjustment
      2) Caustic use
   b. Conduct Bench-scale study
      1) Solids @ Co. line,
      2) Upstream blends
   c. Assess potential
2. Continue *special* direct POC measurements, include discharger survey
3. Continue *routine* TOC and Ca measurements for dischargers