HydroEQ

Challenges with High Carbon, Complex Sulphur Speciation Mine Wastes

Adapting ML/ARD Geochemical Characterization Methods for Canada's Oil Sands

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December 2025

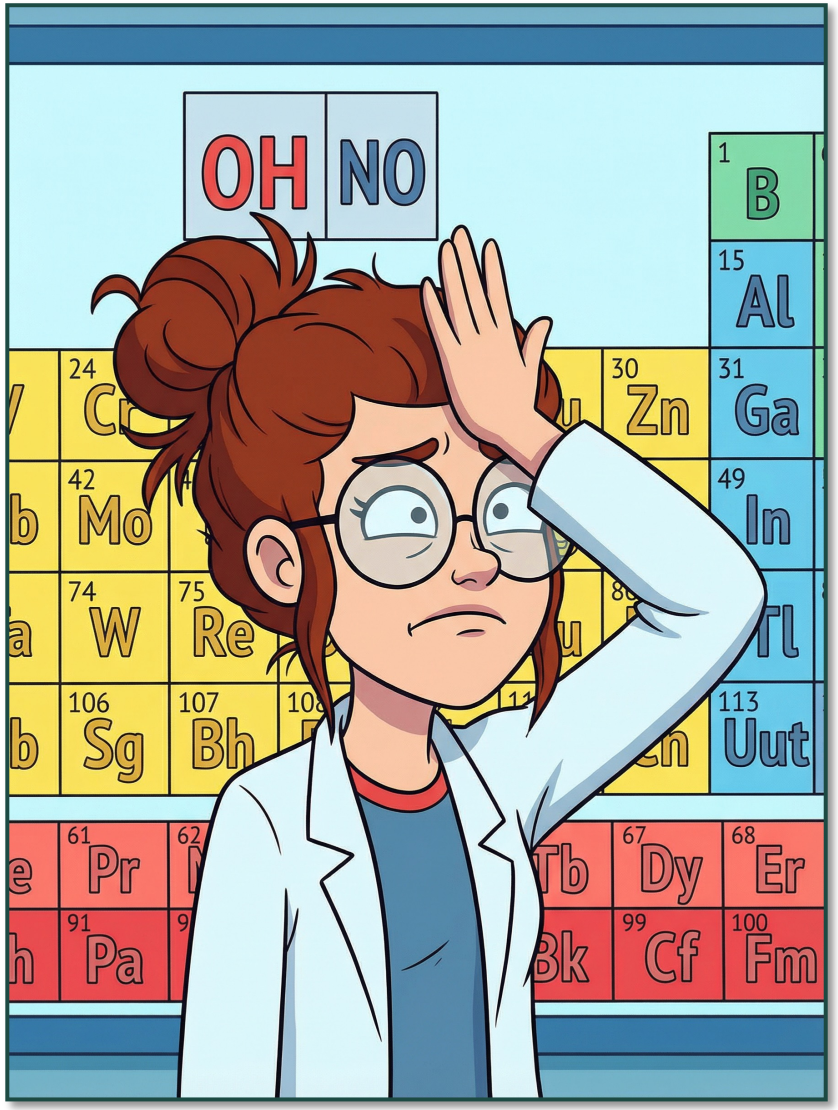
What makes a “challenging” geochemical characterization program?

1. Complex sulphur speciation and 2. High amorphous content
   - Inaccuracies in quantification using standard methods
   - “Mystery” phases – what is it?

3. Complex neutralizing potential
   - Mixed-metal carbonates (notably iron and manganese)

4. Organic carbon
   - Can interfere with sample analysis
   - How does it affect contact water quality over time?

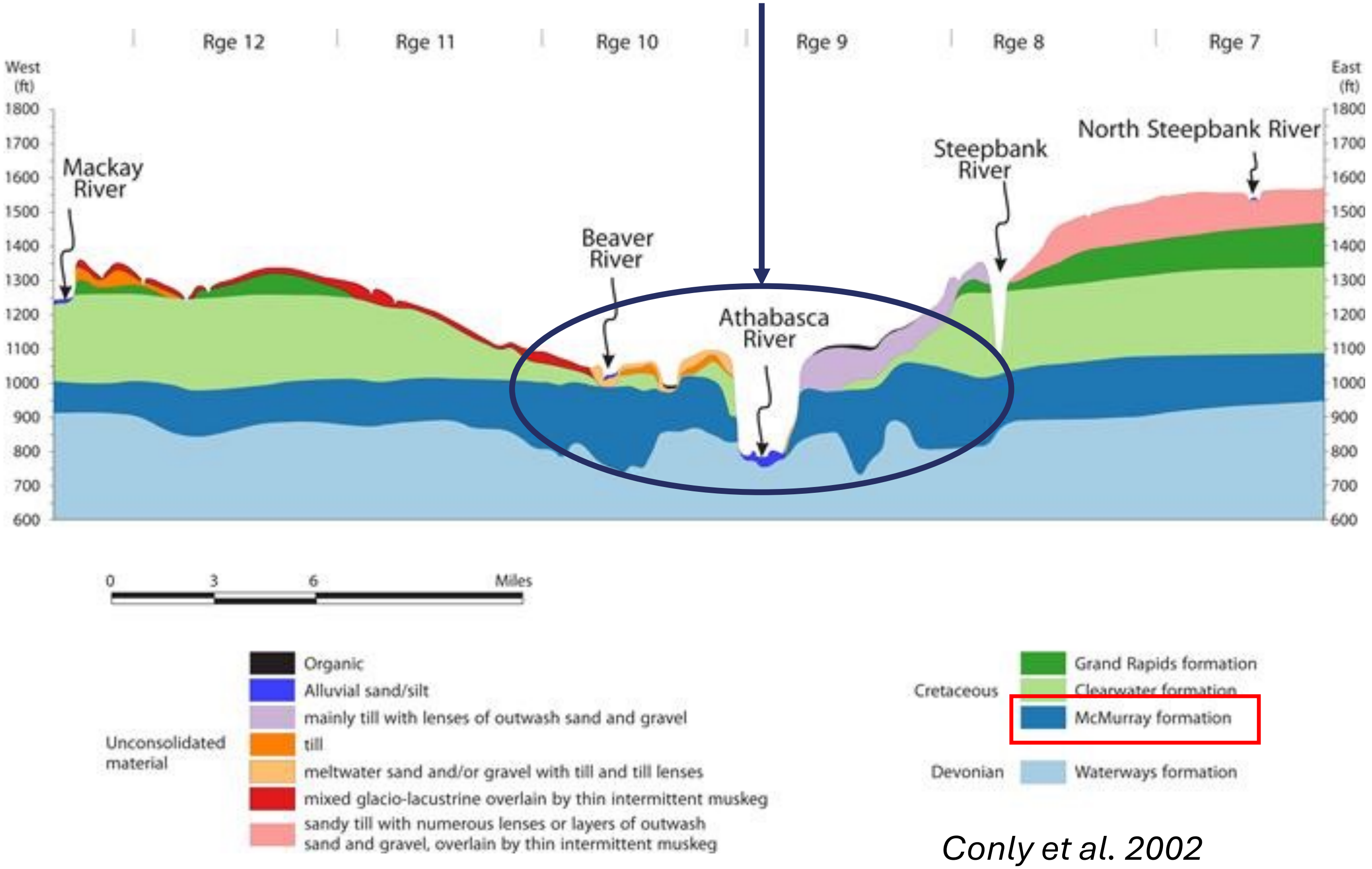
Oil Sands mine waste streams typically pose most or all of these challenges



Oil Sands Mining

- Truck and shovel operations (minimal blasting)
- Waste streams include:
    - Overburden
    - Interburden (mine rock equivalent)
    - **Tailings (multiple streams)**
    - Petroleum coke
- Mines are massive

Bitumen associated with the McMurray Formation (dark blue layer), the "Mineable Oil Sands Region" surrounds the Athabasca River between Fort McMurray and Fort McKay where ore is <100 m from surface

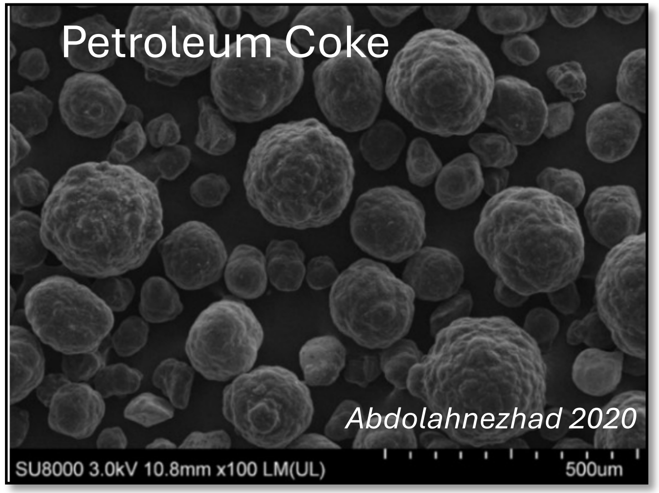


Conly et al. 2002

Organics

- Oil Sands:
  - Diluent/Solvent
  - Bitumen
  - Coal fragments
  - Petroleum coke

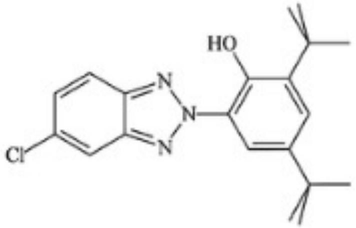
Photo: https://www.alberta.ca/oil-sands-facts-and-statistics



Abdolahnezhad 2020

Peng et al 2024

- Coal/Metal/Diamond Mines:
  - Flotation and Blasting reagents
  - Cyanide degradation compounds
  - Organic polymers
  - Residual coal fragments
  - PAHs and phenol compounds
  - Humic and fulvic acids



Organics

Challenges and Solutions

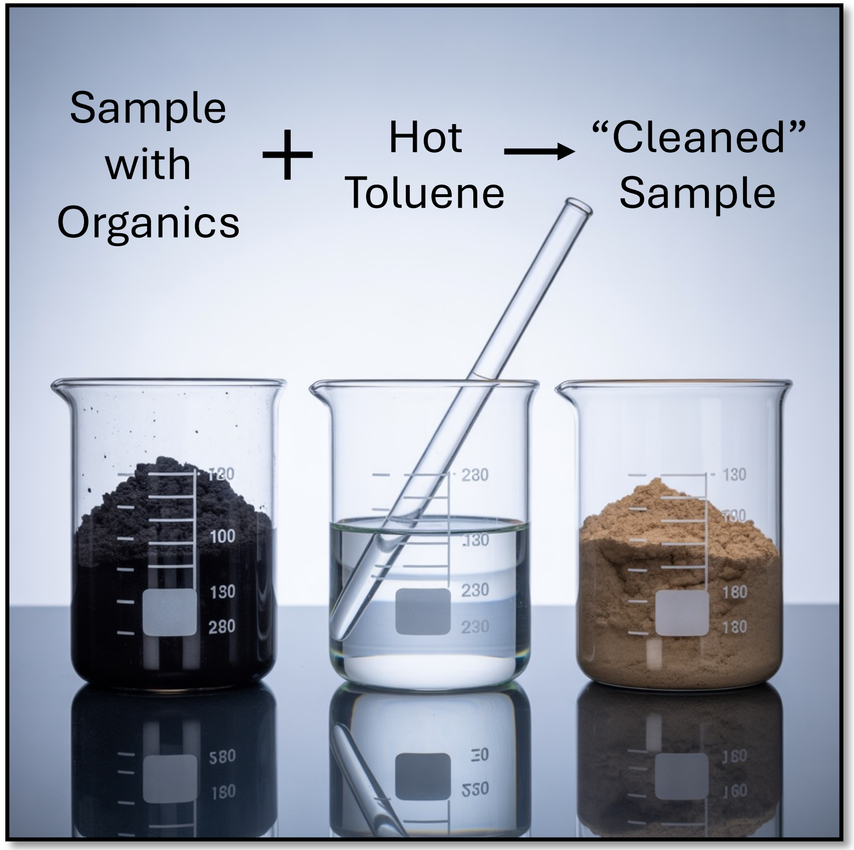
Challenge: Static Test Failures

- Standard ML/ARD static test methods require samples to be dried, homogenized, and crushed to a fine pulp. Some organics interfere with this:
  - Drying (time and fumes)
  - Homogenization and splitting (riffle splitter)
  - Pulping (paste instead of powder)
- Many standard static test methods are water-based, and some organics make samples **hydrophobic**

Bitumen from Bitmount, 1940s. Source: https://history.alberta.ca/energyheritage/sands/origins/the-geology- oil-sands/the-composition-of-oil-sands.aspx

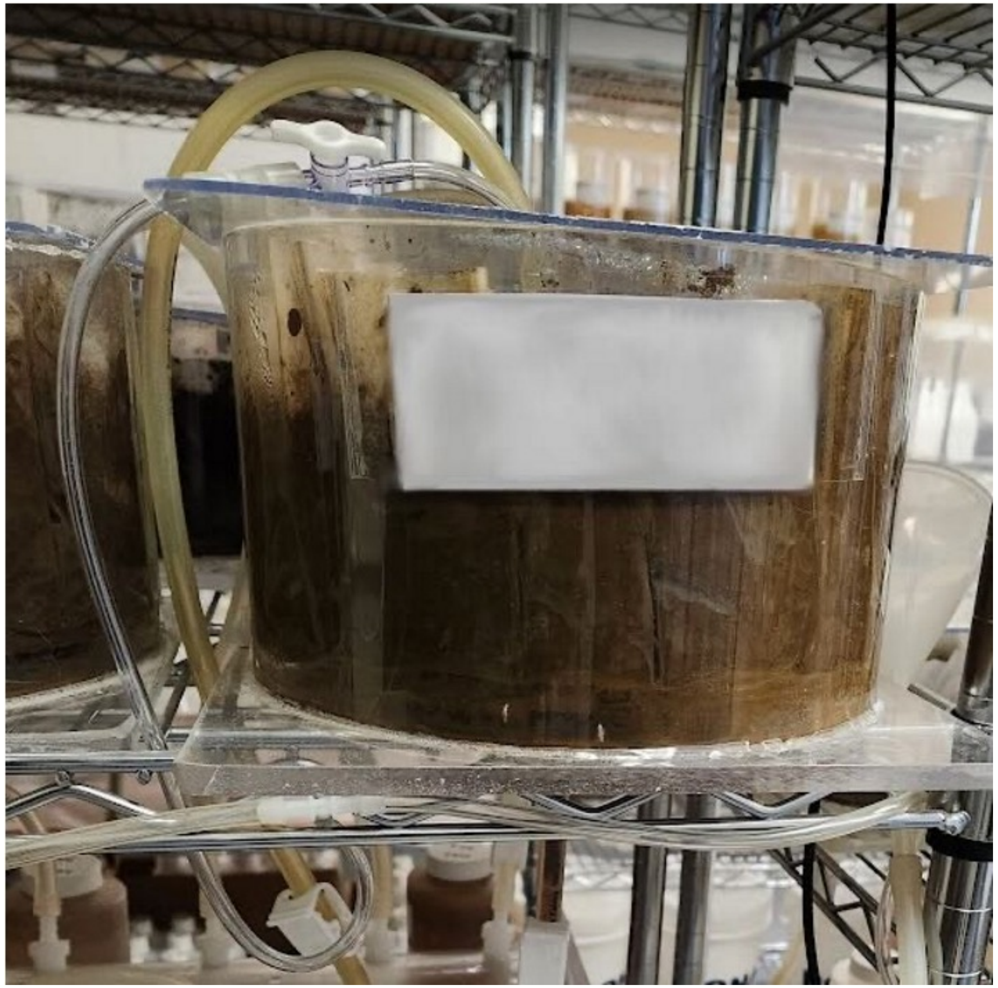
Solution: Toluene Wash

- Remove solvent-soluble organics that interfere with static tests with toluene wash
- This mitigates most issues with static tests (previous slide)
  - Sample prep delay/failure
  - Low-temperature static tests
- Note, not all organics are removed, but the ones that remain don't typically interfere with static analysis



Challenge: Understanding Kinetics – Waste with Organics

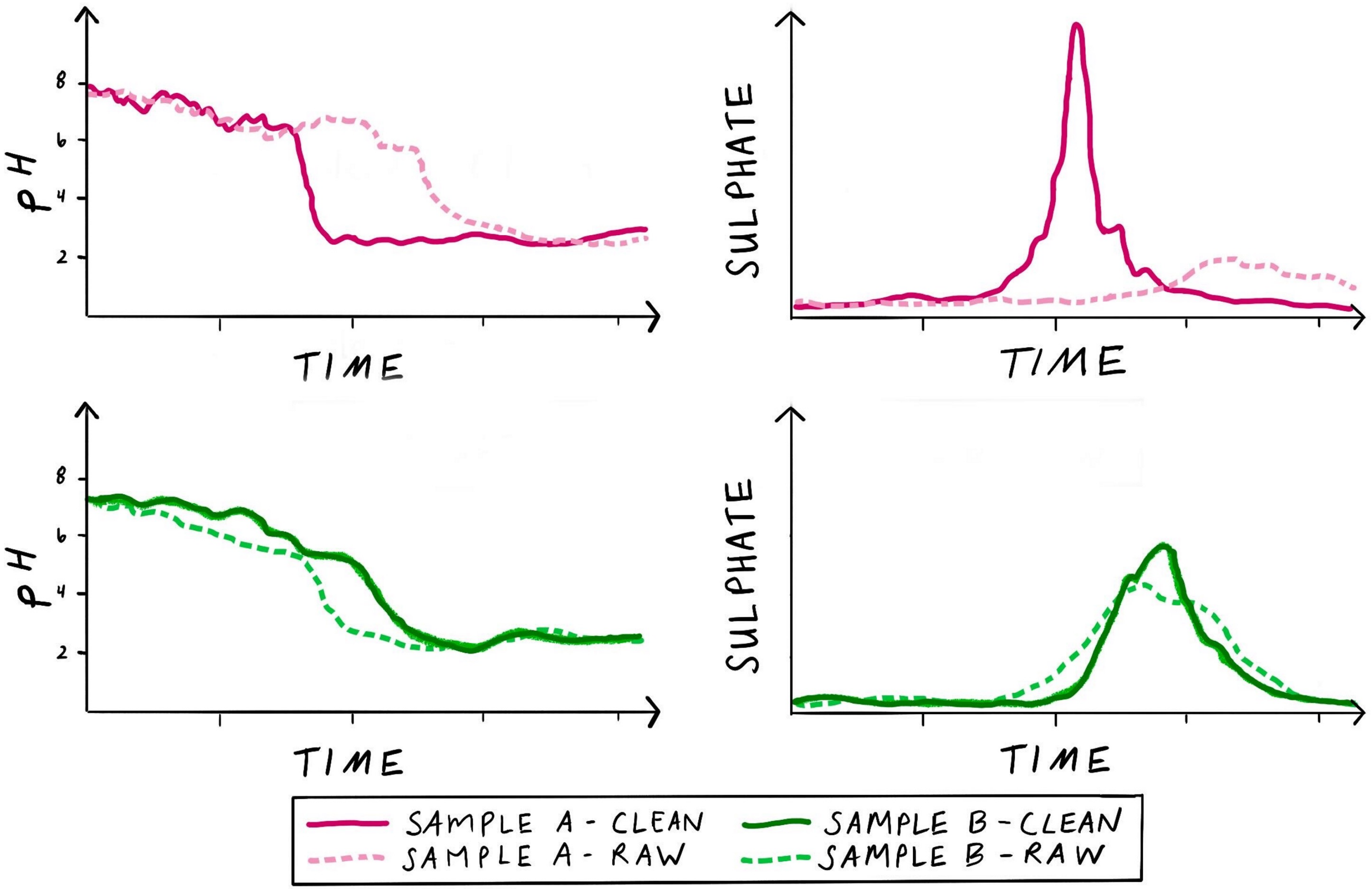
- Kinetic tests are typically run to confirm acid generation potential, understand loading rates, etc.
- In removing organics:
  - How well do test results represent field conditions?
  - Could sample preparation (e.g. toluene wash) affect the results?



Solution: Paired Tests

- Run paired tests with toluene-washed (“clean”) and unaltered (“raw”) samples:
  - Distinguish influence of organics and sample prep on kinetics (e.g. timing to acid onset, loading rates)
- Why do a “clean” kinetic test at all?
  - Bridge between static tests and raw kinetic
  - Raw tests fail more often
  - Understand potential affects of sample prep

EXAMPLE: pH and Sulphate in two Clean/Raw Humidity Cell Test Pairs



Organics can affect on time to acidic pH (or not)

Organics can affect loading (magnitude, duration, accumulation) (or not)

Note: cartoons approximate general trends observed; do not represent actual sample data.

Challenge: Mineralogy with Organics

- X-Ray Diffraction (XRD) methods are a part of standard geochemical programs to characterize bulk mineralogy
  - But – XRD cannot recognize organics. They are not crystalline and do not diffract
- Scanning-electron microscope (SEM) methods, including the automated SEM methods, are often the next step after XRD when we need more information on mineralogy
  - But – organics are invisible to the SEM with typical sample prep, SEM detectors cannot distinguish organics from the “background” epoxy resin of the grain mount

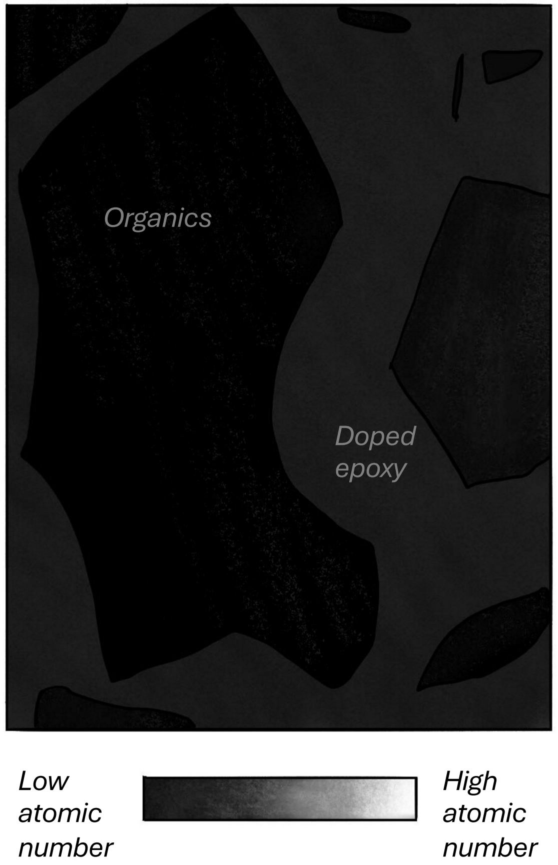
Background: Automated SEM Mineralogy Methods

- Automated SEM methods (e.g., TIMA, QEMSCAN, MLA) were originally developed for resource / metallurgical programs, adapted in the past 10-15 years for environmental samples
- Used when we want quantitative mineralogy with information on textures, mineral chemistry, and mineral relationships.
- TIMA and QEMSCAN are often available at commercial labs in Canada.

Solution: Carbonaceous Prep Method for TIMA

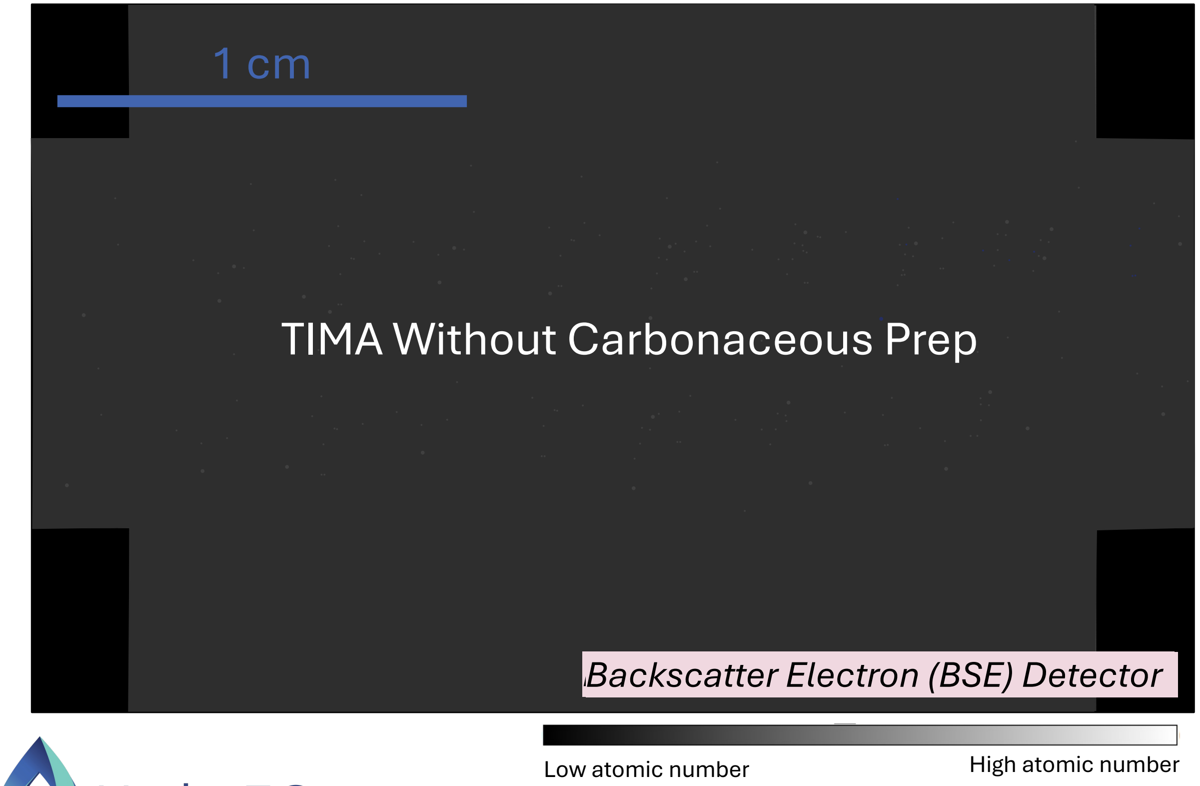
- We have worked with SGS Canada (Burnaby) mineralogists over the past six years to adapt automated SEM mineralogy sample prep and analysis methods to samples with organics
- Latest innovation: “**Carbonaceous Prep**” TIMA - an adapted sample mount prep method to efficiently distinguish background epoxy and organic sample particles.

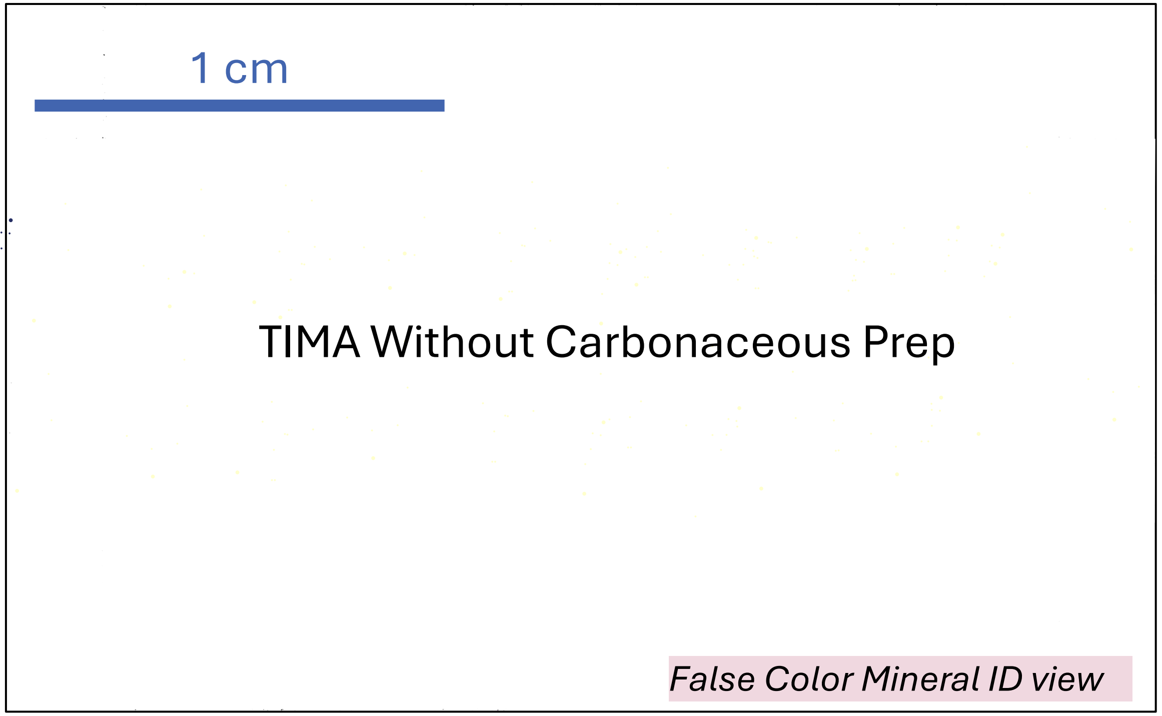
Cartoon: SEM Backscatter Electron Detector



Example: TIMA, No Carbonaceous Prep Method

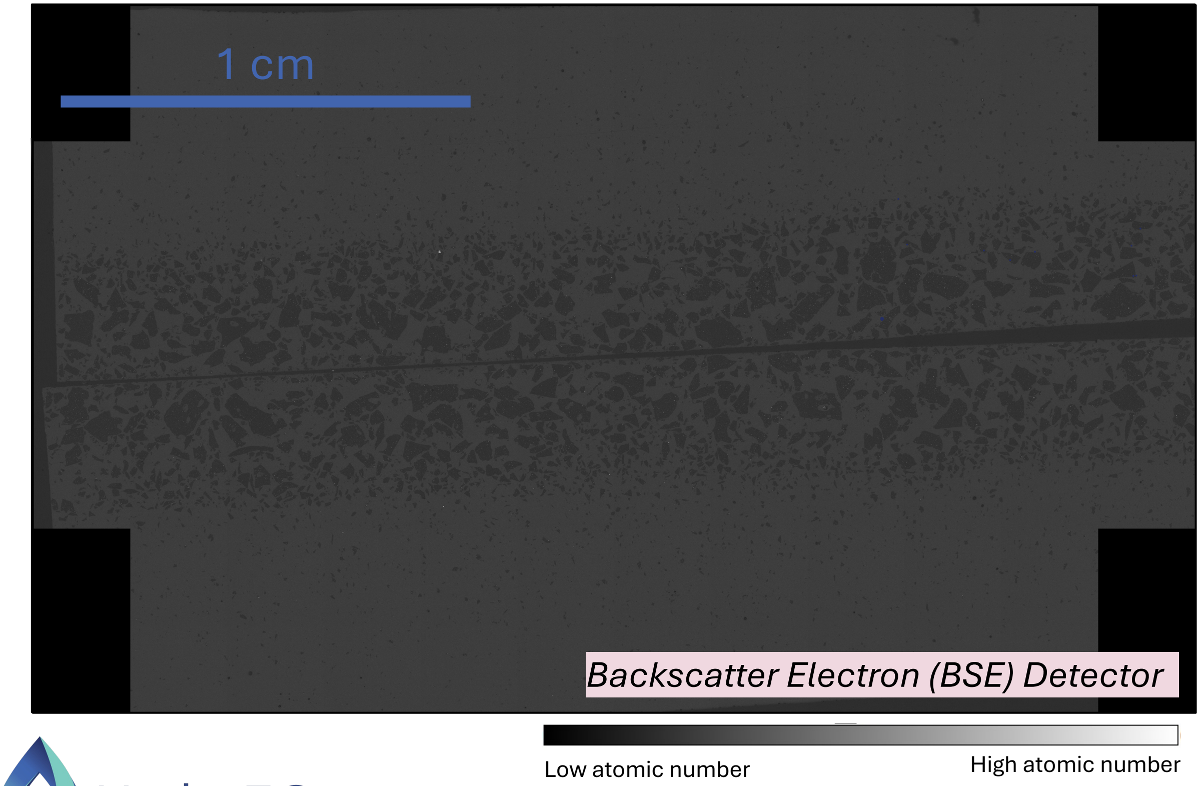
- Example: NO CARBONACEOUS PREP, high TOC sample
  - Left: standard epoxy background and carbonaceous grains (BSE)
  - Right: mineral ID after background subtraction



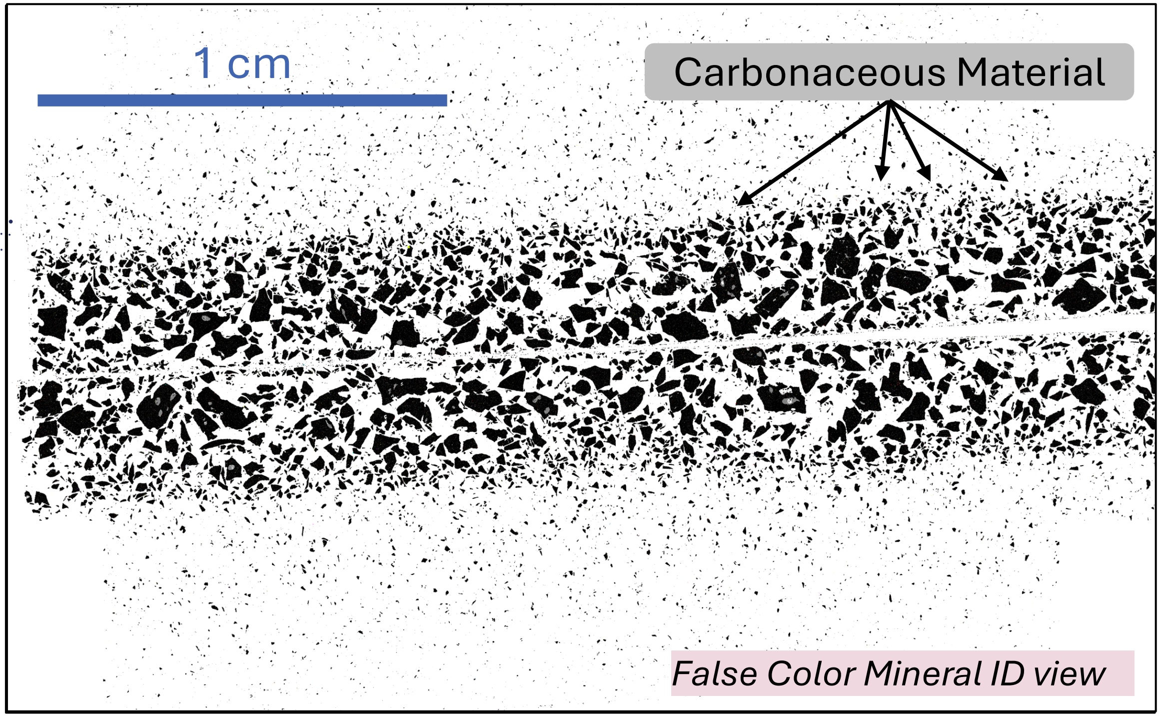


Example: TIMA Carbonaceous Prep Method

- Example: Carbonaceous Prep, high TOC sample
  - Left: carbonaceous prep mount and carbonaceous grains (BSE)
  - Right: mineral ID after background subtraction



Backscatter Electron (BSE) Detector

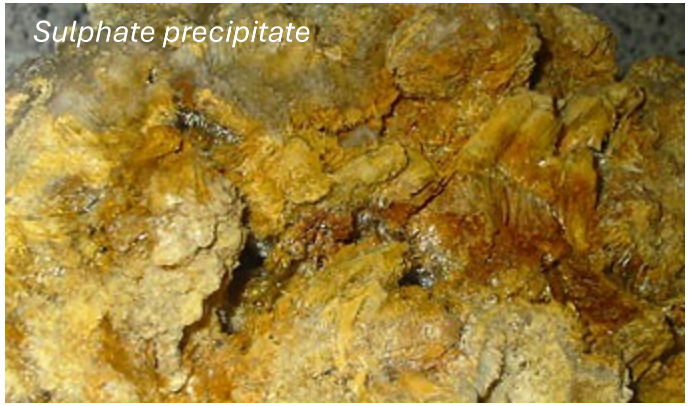


False Color Mineral ID view

High Amorphous Content

Challenges and Solutions

Challenge: Detecting and Distinguishing Amorphous Phases



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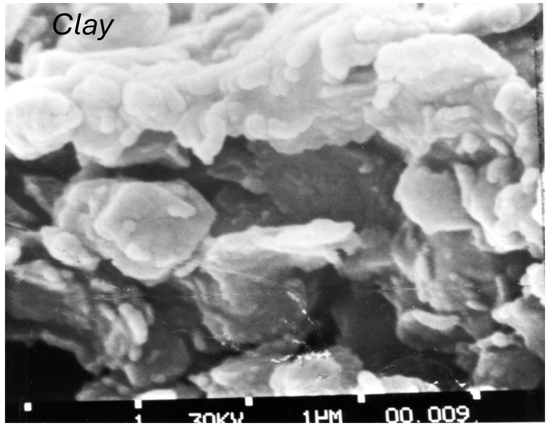

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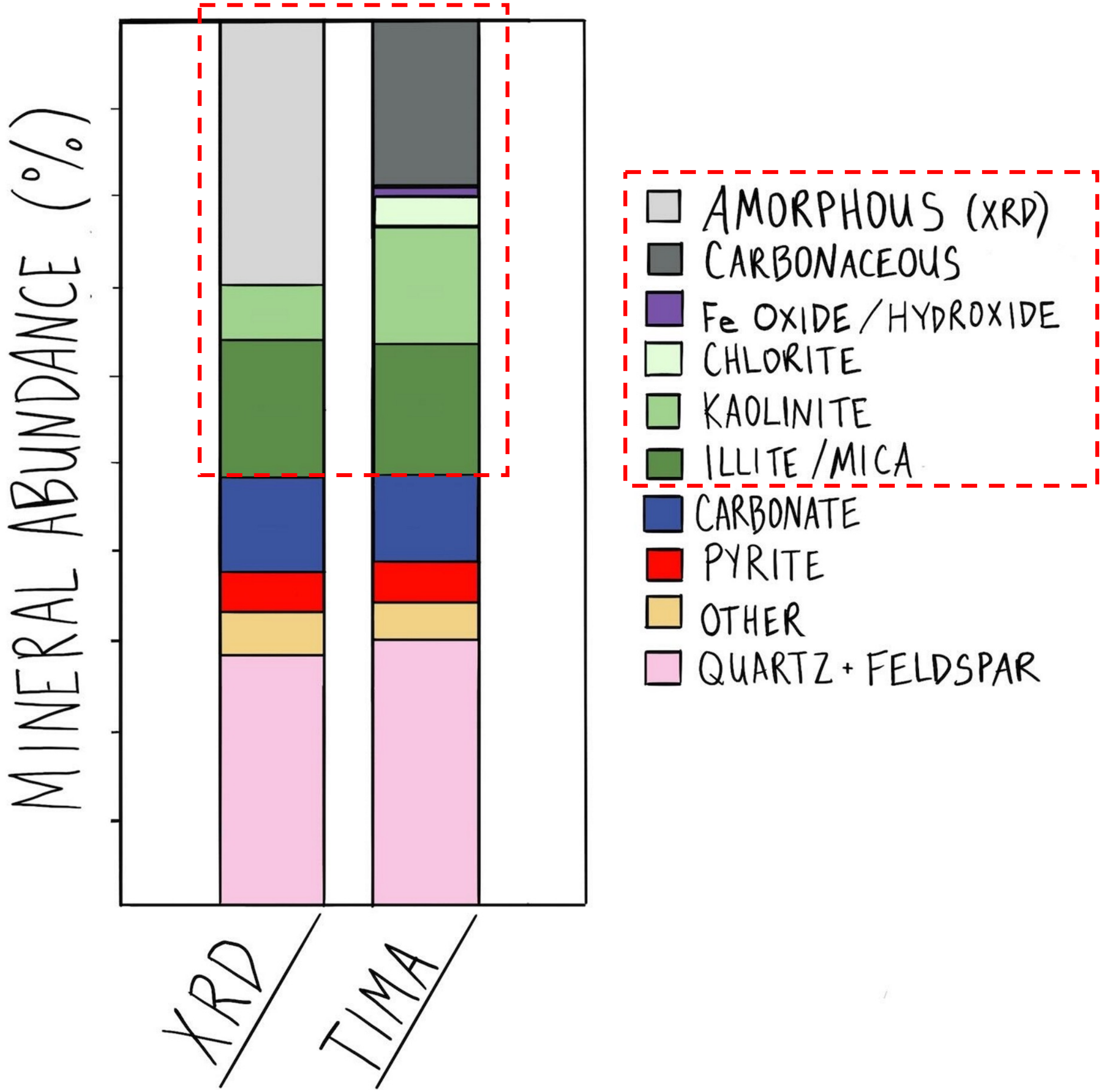
https://en.wikipedia.org/wiki/Bituminous_coal#/media/File:Primary_coking_coal_20180405_154027_1.jpg

- “Amorphous” = insufficiently crystalline for detection using common powder XRD methods.
  - E.g.: secondary weathering products (poorly crystalline sulphates, oxyhydroxides), all organics, some phyllosilicates/clays
- “Amorphous content” can be reported for Rietveld XRD, but results:
  - Are qualitative (at best)
  - Don’t identify or distinguish different “amorphous” phases
- How can we understand the potential effect of “amorphous” phases on ML/ARD if we don’t know what they are?

Solution: TIMA Quantitative Mineral ID

- TIMA can usually provide quantitative bulk mineralogy even where XRD “amorphous” content is high
  - “Carbonaceous prep” for samples with organics
- Example: sample with high amorphous content, organics, and phyllosilicates
  - Multiple “amorphous” phases that TIMA better differentiates and detects



Note: cartoons approximate general trends observed; do not represent actual sample data.

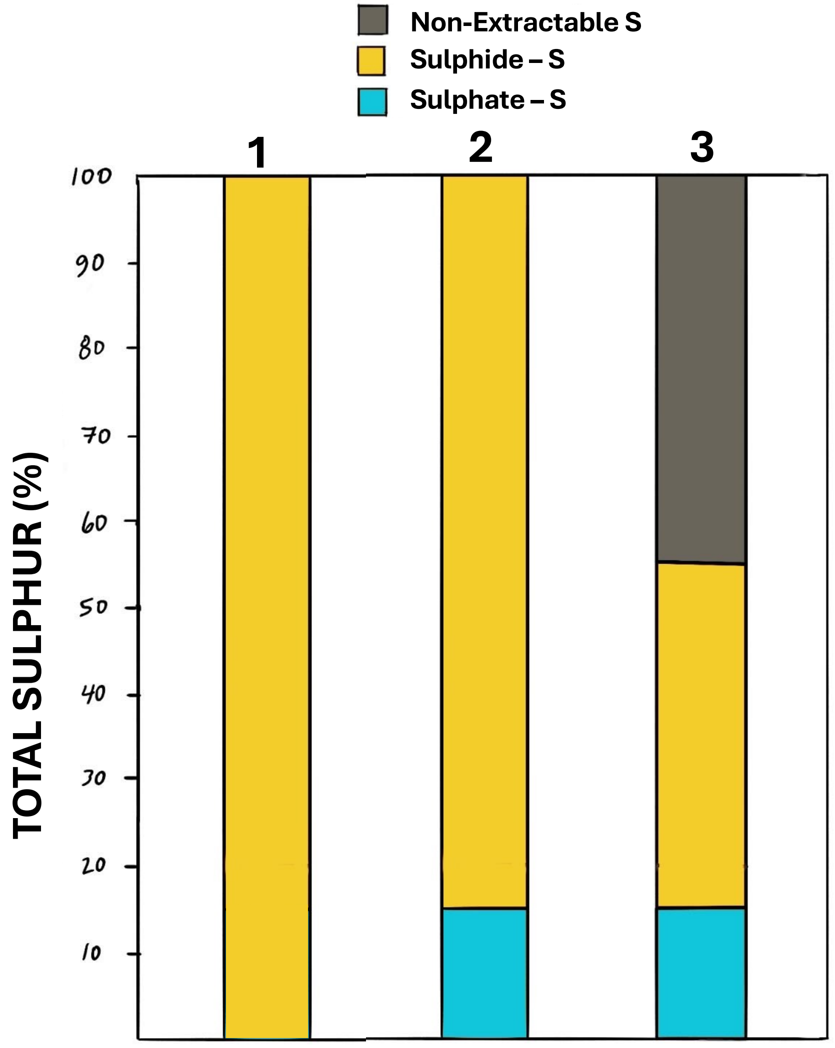
Sulphur

Challenges and Solutions

Challenge: ABA Sulphur Species

- Acid potential (AP) is typically assumed to come only from sulphide minerals and calculated using the following data:
    1. Total Sulphur (when all sulphur is sulphide)
    2. Total Sulphur – Sulphate
    3. Measured using a sulphide leach method
- When sulphide is measured, you can end up with a group of "mystery sulphur phases" (called non-extractable)
    - What are they and how do they contribute to ML/ARD?
- Also note, in our experience:
    - When organics are present, 1 & 2 **overestimate sulphide.**
    - The sulphide leach method (3) can **underestimate sulphide**

Three Common Acid-Base Accounting (ABA) Sulphur Species Methods



$S_{Sulphide} = S_{Total}$

$S_{Sulphide} = S_{Total} - S_{Sulphate}$

$S_{Non-Extractable} = S_{Total} - S_{Sulphate} - S_{Sulphide}$

Solution: TIMA – Sulphur Deportment

- Use the TIMA carbonaceous prep method to better identify and quantify sulphur species
- Examples:
  1. Low - Mid TOC
  2. Very High TOC

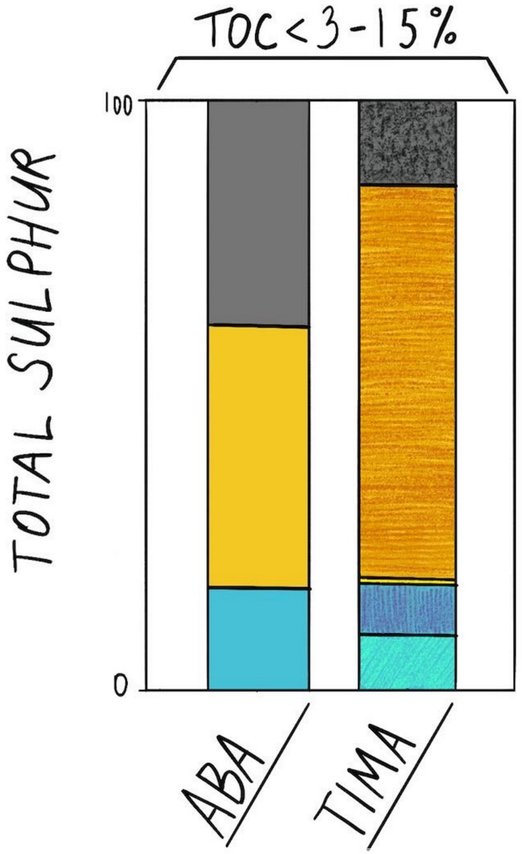
Note: ABA = Acid-Base Accounting

ABA
- ■ NON-EXTRACTABLE S
- ■ SULPHIDE S
- ■ SULPHATE S

TIMA
- ■ CARBONACEOUS
- ■ PYRITE
- ■ OTHER SULPHIDES
- ■ Fe/OTHER SULPHATE
- ■ GYPSUM

Example 1

Example 2



Note: cartoons approximate general trends observed; do not represent actual sample data.

Complex Neutralization Potential

Challenges and Solutions

Challenge: Carbonate Differentiation

- Only calcium (Ca) and magnesium (Mg) components of carbonate minerals contribute to neutralization
  - Iron (Fe) and manganese (Mn) components of carbonate minerals are not net neutralizing
- Standard methods:
  - Total inorganic carbon (TIC) analysis will overestimate carbonate neutralization potential (NP) where Fe / Mn carbonates are abundant
  - XRD cannot detect mixed metal carbonate cation chemistry (e.g., actual proportions of Fe, Mn, Ca, and Mg) and is qualitative

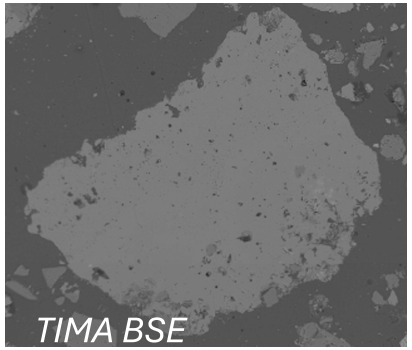
Solution: TIMA Carbonate Chemistry

- Use TIMA to quantify mixed metal carbonate minerals and collect data on their chemical composition
- Calculate mineralogical carbonate NP from net-neutralizing carbonate components (Ca and Mg) to better:
  - Estimate carbonate neutralization potential (NP)
  - Contextualize Modified Sobek bulk NP and role of silicate NP

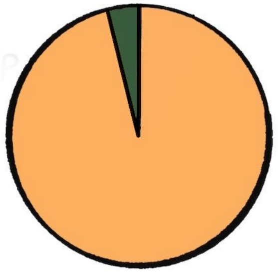
🟧 Ca+Mg
🟩 Fe+Mn

CALCITE

Ideal formula: $CaCO_3$

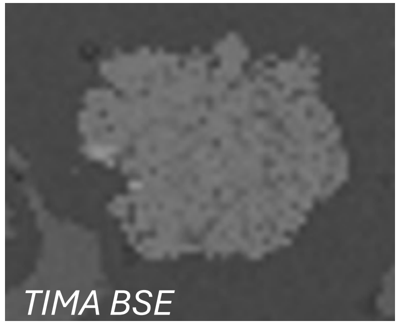


TIMA Cation Chemistry

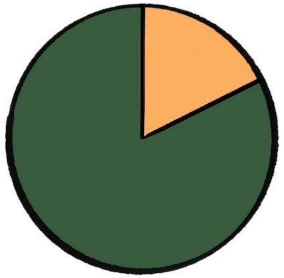


SIDERITE

Ideal formula: $FeCO_3$



TIMA Cation Chemistry

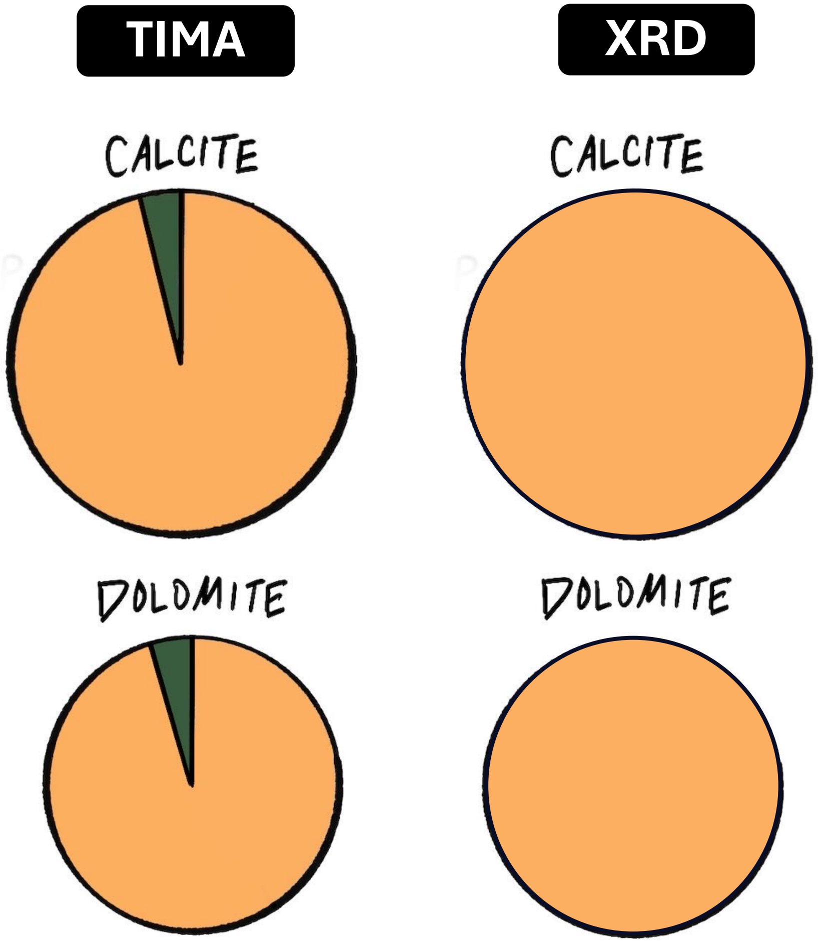


Note: cartoons approximate general observed trends

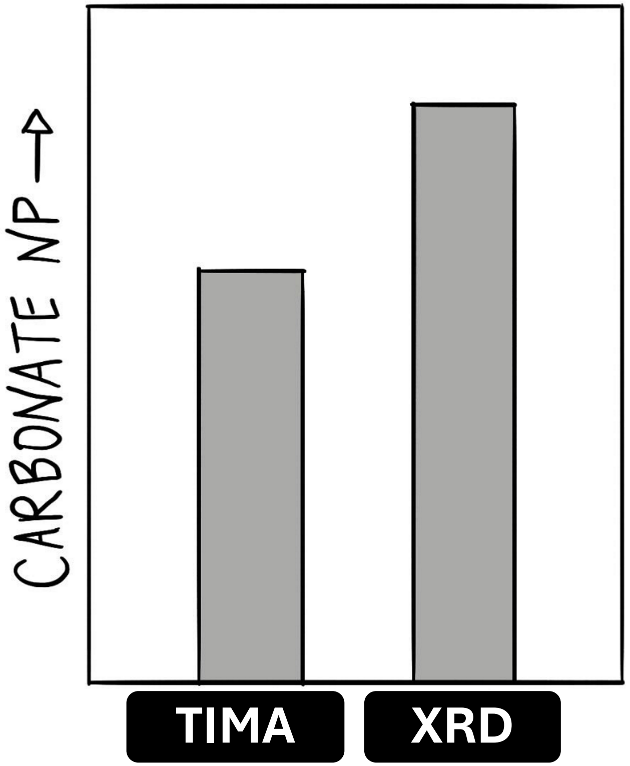
TIMA and XRD Calculated Carbonate NP

- Example: Abundant calcite and dolomite with some Fe/Mn.
- XRD Carbonate NP can over or underestimate effective NP when carbonate mineral composition contains mixed cations that are different from the ideal mineral formulas

CATION CHEMISTRY



CALCULATED CARBONATE NP



XRD cation chemistry is calculated using standard mineral definitions

Summary

Summary

- Typical ML/ARD characterization methods require refinement for some materials with complex sulphur speciation, organic carbon, amorphous content, and/or complex neutralization potential
- There are ways to successfully adapt ML/ARD methods to materials with these challenges

Considerations in Applying Adapted Methods

- Current adaptations rely heavily on TIMA mineralogy.
  - More expensive than standard geochemical tests
  - Best results require **specialized resources** and time (e.g., end-user knowledge, skilled mineralogists, iterative QAQC and design)
  - Often *more accurate* but can be *less precise* than static tests, depending on particle size distribution.
- The workflow described herein (toluene wash → static testing → TIMA) adds logistical challenges (multiple labs and sample tracking) and increases turn-around times compared to the standard program

Next Steps – the Work Continues

- Quantifying sulphide – some preliminary work on adapting the standard sulphide leach test method is showing promise
- Organics – developing guidelines for sample handling and analysis based on organic compound group and concentration
- Investigating proxies and relationship factors to address the following:
  - Program costs and slow turnaround times
  - While the adapted methods described herein increase accuracy, they are not practical in the application of operational segregation or other operational needs where timely data is needed

Acknowledgements

- Thank you to our collaborators:
  - Current and former colleagues who have contributed to this work: Kate Smith, David Dockman, and Barbara Petrunic
  - Laboratory collaborators:
    - Logan Jameson and Lain Glossop, mineralogists at SGS Canada
    - Prab Bhatia, Said Zeinab, Ivy Rajan, and their team at Global ARD Testing Services

Summary

Challenge		**Issue**	**Main Solution**
Organics	Sample Prep and Static analysis	• hard to dry, homogenize, pulp, hydrophobicity, migration under vacuum • Water-based, low-temperature static tests and NAG pH do not work properly for samples with solvent-soluble organics	Toluene wash
	Grains invisible using standard grain mounts under SEM	• Can't distinguish organic grains from epoxy mount	Carbonaceous prep method for TIMA
	Unknown composition in organic phases	• Will they weather, and if so, will they release COPCs to contact water?	TIMA with carbonaceous prep
High Amorphous Content	High amorphous content	• Inaccurate bulk mineralogy by XRD • What makes up the amorphous phase and how could it impact WQ?	TIMA
Sulphur	Complex sulphur speciation	• Inaccurate results by leach methods • Sulphide concentrations often below XRD detection limits and organic phases not detected by XRD.	TIMA with carbonaceous prep, reconciled with total sulphur
	Substantial "non-extractable" component	• What is it? How could it affect WQ?	TIMA with carbonaceous prep, reconciled with total sulphur
	Sulphate phases	• Using ABA cannot distinguish between very low and high solubility phases, or phases associated with acid release, which affects WQ. • With XRD, can identify some phases if concentrations are high enough and they are crystalline, but miss nuances (metals hosted in secondary sulphates)	TIMA reconciled with total sulphur
Complex Neutralization Potential	Complex carbonate mineralogy	• Standard tests don't fully quantify the amount of Fe/Mn in the mineral, which affects its neutralization efficiency	TIMA
	Unreliable detection of phyllosilicates	• Bulk mineralogy by XRD often inaccurate for phyllosilicates that can contribute to neutralization potential.	TIMA with carbonaceous prep

Note: mentions of "TIMA" refer to analyses that are assay reconciled to whole rock analysis bulk chemistry, total sulphur, and total carbon. Not all automated mineralogy laboratories automatically assay reconcile results.