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Structure and mineralogy of hydrophilic and biwettable sub-2μm clay aggregates in commercial bitumen froth analyzed at the nanometer scale

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54th Annual Clay Minerals Society Conference, Edmonton, Alberta, June 5-8, 2017

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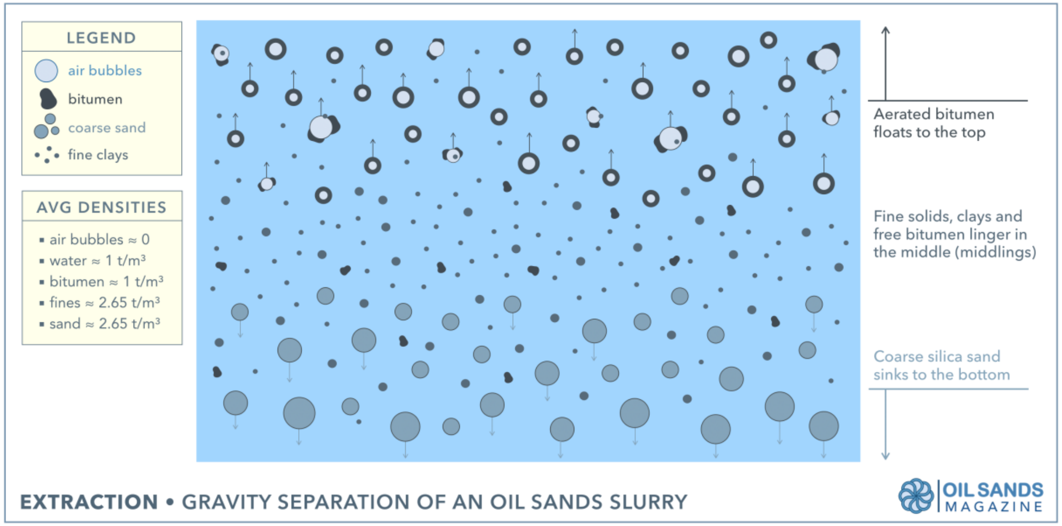
OUTLINE FOR THE TALK

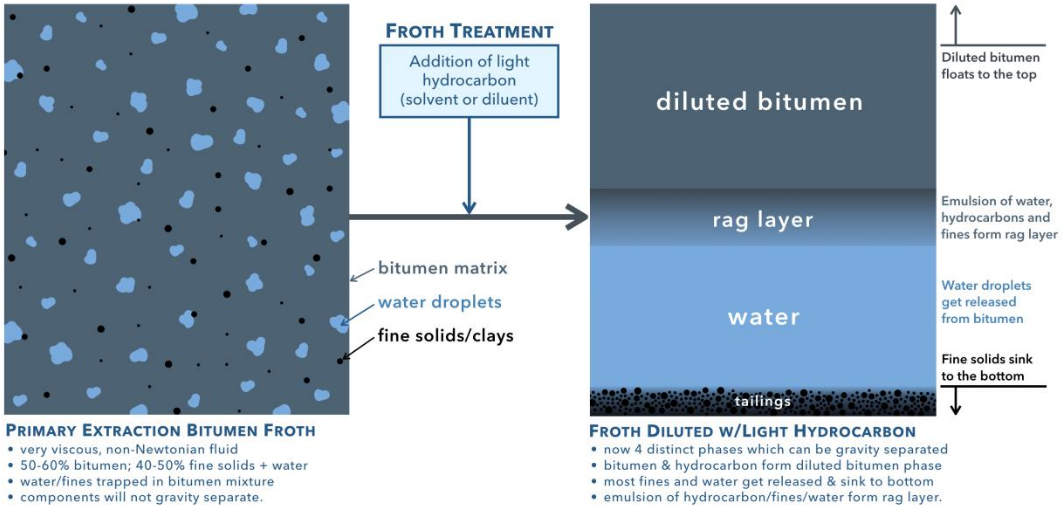
- Bitumen extraction
- Previous Work: contaminant solids in solvent-diluted bitumen
- Present Work: contaminant solids in bitumen froth
  - Quantitative Separation: size and wettability
  - Mineralogy
  - Wettability characteristics of sub-2μm mineral aggregates
  - Ultrafine clay minerals: distribution and organic coating
- Summary

Bitumen Extraction and Froth Treatment

1. Aqueous Flotation of Bitumen Froth



2. Froth Treatment

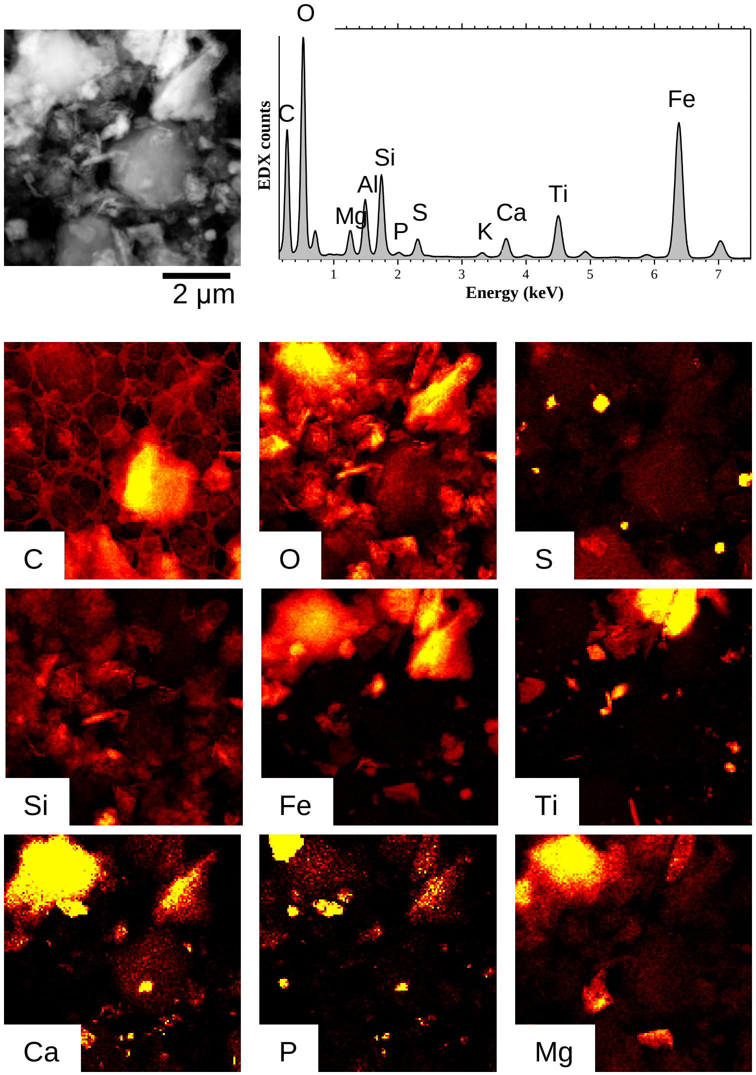


Previous work: Contaminant Solids in Solvent-diluted Bitumen

phase	concentration (wt %)	abbreviation	phase	chemical formula
QTZ + SIL	7.05 (0.14)	QTZ	quartz	SiO_2
ILL	12.61 (0.02)	ILL	Illite	$K_{0.8}Al_2(Al_{0.8}Si_{3.2})O_{10}(OH)_2$
KAO	18.34 (0.64)	KAO	kaolinite	$Al_2Si_2O_5(OH)_4$
CHL	0.57 (1.53)	CHL	chlorite	$(Mg_{2.5}Fe_{2.5}Al)\ (AlSi_3)O_{10}(OH)_8$
PYR	11.33 (0.02)	CAL	calcite	$CaCO_3$
SID + AFE	23.32 (0.25)	DOL	dolomite	$CaMg(CO_3)_2$
DOL + CAL + ANK	2.83 (0.16)	ANK	ankerite	$CaFe_{2/3}Mg_{1/3}(CO_3)_2$
RUT + ANA	3.40 (0.01)	SID	siderite	$FeCO_3$
ZIR	0.00 (0.01)	PYR	pyrite	FeS_2
GYP	0.005 (0.001)	ZIR	zircon	$ZrSiO_4$
BAS	0.005 (0.001)	RUT	rutile	TiO_2
ANO	0.005(0.001)	ANA	anatase	TiO_2
SAN	0.005 (0.001)	ILM	ilmenite	$FeTiO_3$
APA	1.24 (0.01)	LEP	lepidocrocite	$FeO(OH)$
ORC	11.42 (0.52)	GYP	gypsum	$CaSO_4{\cdot}H_2O$
clay minerals (ILL + KAO + CHL)	31.51 (0.44)	BAS	bassanite	$CaSO_4{\cdot}0.5H_2O$
heavy minerals (SID + PYR + ZIR + RUT + ANA + ILM + LEP)	38.10 (0.24)	ANO	anorthite	$CaAl_2Si_2O_8$
total mass accounted for	92.16 (0.10)	SAN	sanidine	$KAlSi_3O_8$
		APA	apatite	$Ca_5(PO_4)_3(OH)$
		ORC	amorphous organic carbon	$C_{1.00}$
		SIL	amorphous silica	SiO_2
		AFE	amorphous Fe oxide-hydroxide	$Fe(OH)_3$ or $FeO(OH)H_2O$

Couillard, M.; Mercier, P.H.J. *Energy and Fuels* **2016**, 30, 5513-5524.

Heterogeneity of Oil Sands Fine Solids



Energy-dispersive X-ray spectroscopy (EDX) maps confirm the presence of the minerals whose abundances are determined by a recently developed quantitative phase analysis methodology.

Three major sources of carbon are identified in the residual solids:
carbonate minerals,
micron-sized carbon-rich particles, and
organic carbon intermixed with clay.

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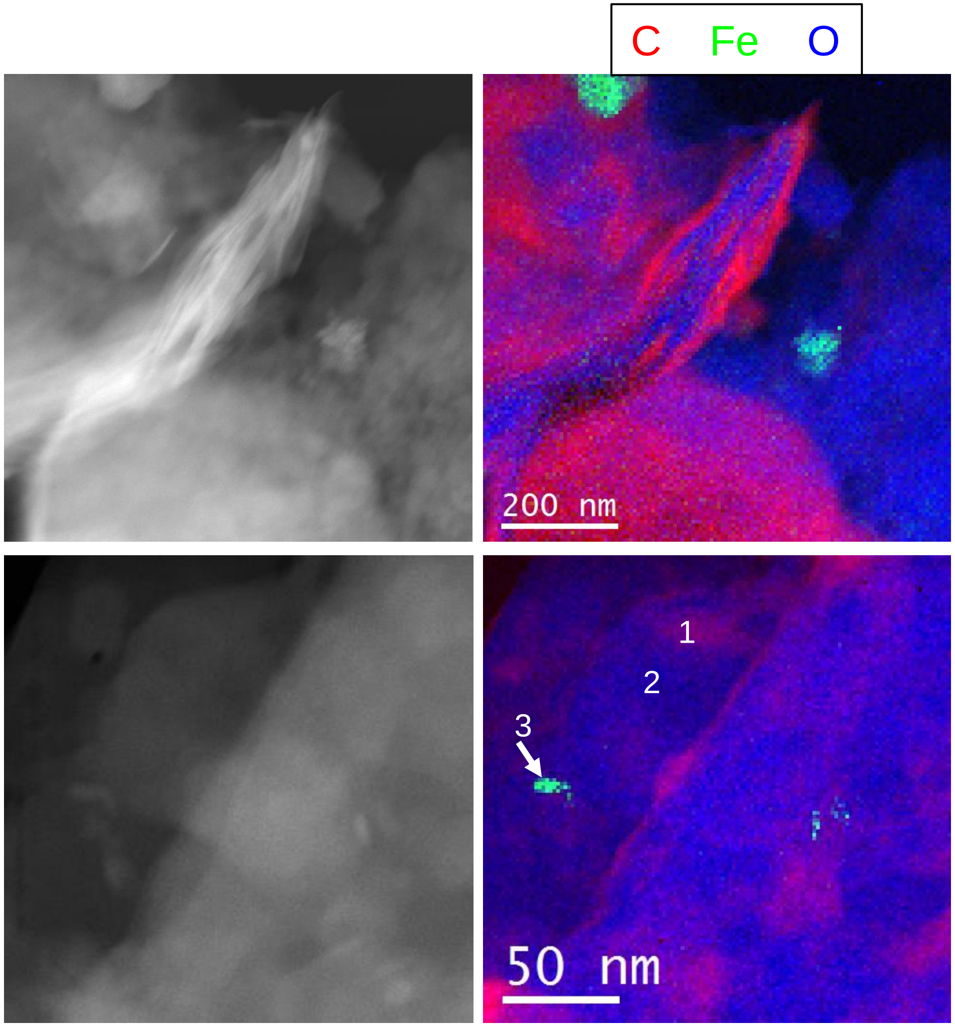
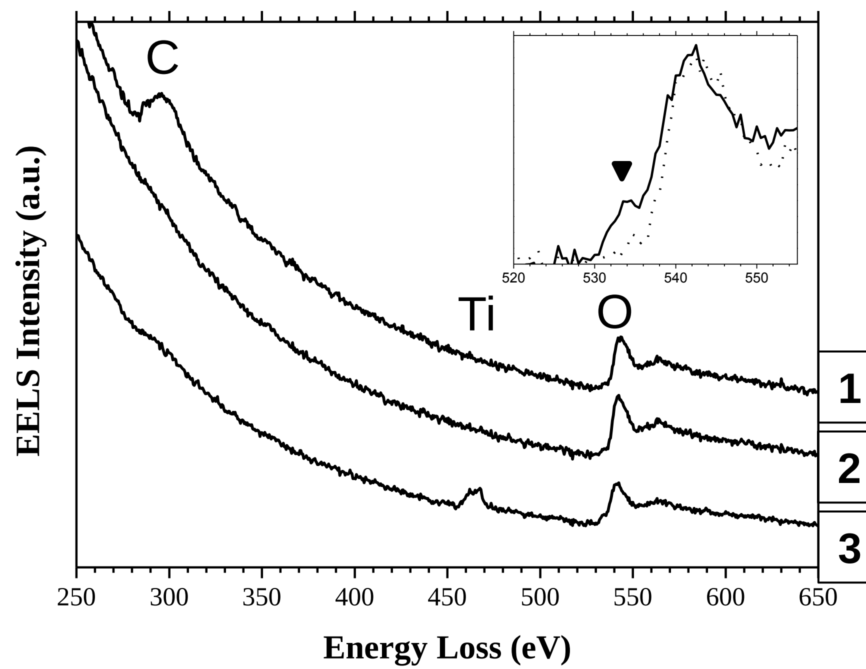
Intermixing of carbon and ultrafine clay minerals



As confirmed by electron energy-loss spectroscopy, the ultrafine clay minerals are partially covered with C, with some metal-bearing nanoparticles dispersed on their surfaces.



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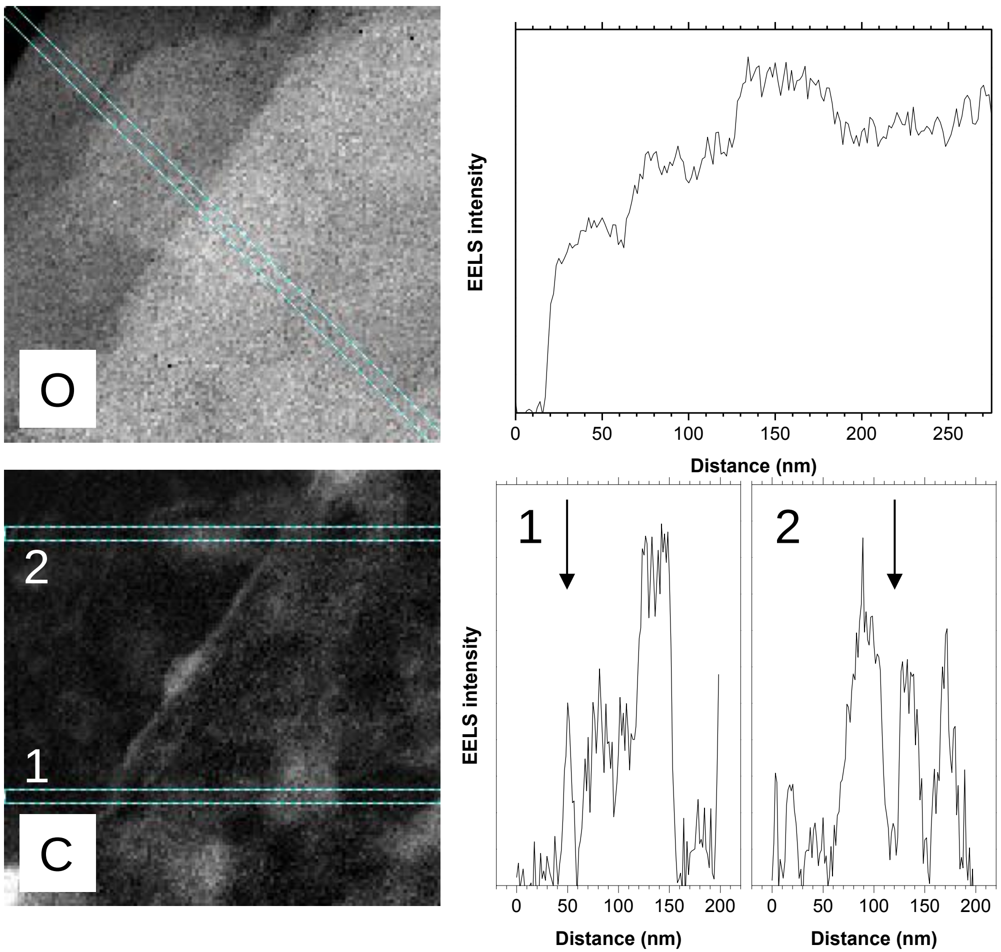
Patchy organic coating of clay surfaces



The organic coating appears to be "patchy", with some nanometre scale carbon features in EELS maps, and some exposed regions on the clay surfaces.

The analysis also confirms that the carbon is on the surface of the clay minerals, and not incorporated in the lattice.

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Contaminant Solids in Solvent-diluted Bitumen

- The analysis reveals the complexity and heterogeneity of the fine solids present in a diluted bitumen.
- Carbon is found in three major sources:
  - Carbonate minerals
  - Micrometer-sized carbon rich particles
  - organic carbon intermixed with clay minerals
- A non-uniform organic coating has been observed on ultrafine clays
  - Carbon features of only a few nanometers have been observed
  - Some regions of the clay surfaces remain exposed

HERE:
In bitumen froth, prior to Naphthenic Froth Treatment, can we identify these same types of solids? In particular, what is the wettability character of sub-2μm particles?

This is important as sub-2μm particles may contribute to emulsion stabilization in NFT processes.

Present work: Contaminant Solids in bitumen froth

- Quantitative mineralogy and direct observation of sub-2μm mineral aggregates.
- Comparison of hydrophilic and biwettable mineral aggregates
- Surface characteristics of biwettable and hydrophilic ultrafine clay minerals.

Application of Stoke's law to isolate sub-2μm solids

Jackson's Book, Eq. 3.7, p.127:

$$t_{min} = \frac{63.0 * 10^8 * n * log_{10}\frac{R}{S}}{N_m^2 * D_u^2 * \Delta s}$$

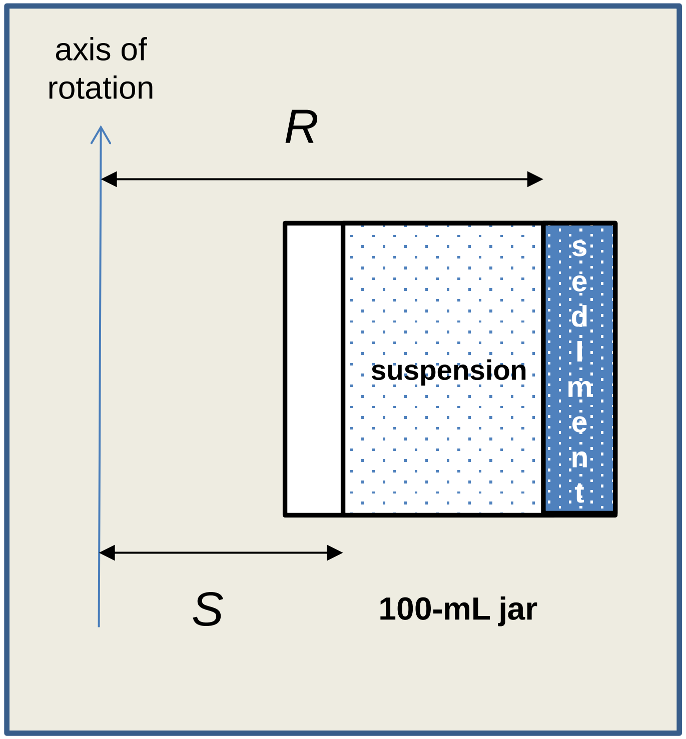
$$N_m^2 = rpm\ centrifuge$$

$$D_u^2 = particle\ diameter\ in\ microns$$

$\Delta s = difference\ in\ specific\ gravity\ between$
$solvated\ particle\ and\ the\ suspension\ liquid$ (in g/cm³)

$\frac{R}{S} = ratio\ of\ distance\ from\ top\ of\ sediment\ to\ centre\ of\ centrifuge\ (R)$
$to\ that\ of\ top\ of\ suspension\ to\ centre\ of\ centrifuge\ (S)$

$n = viscosity\ of\ liquid\ in\ poises\ based\ on\ temperature$ (in poise)

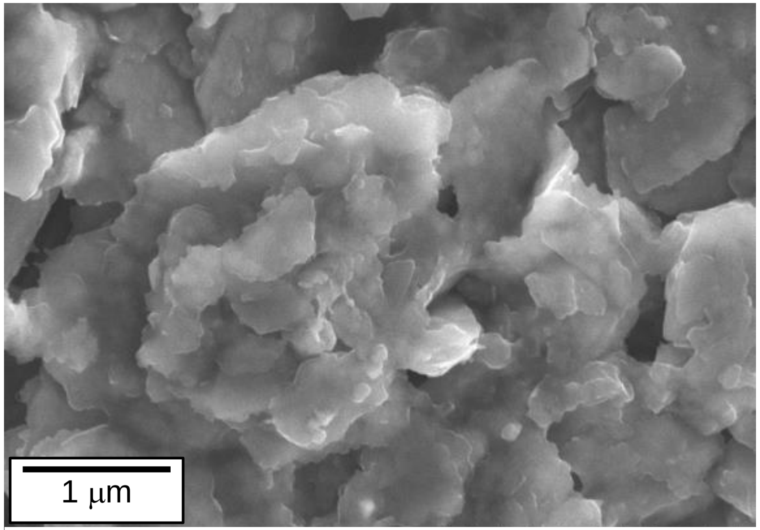


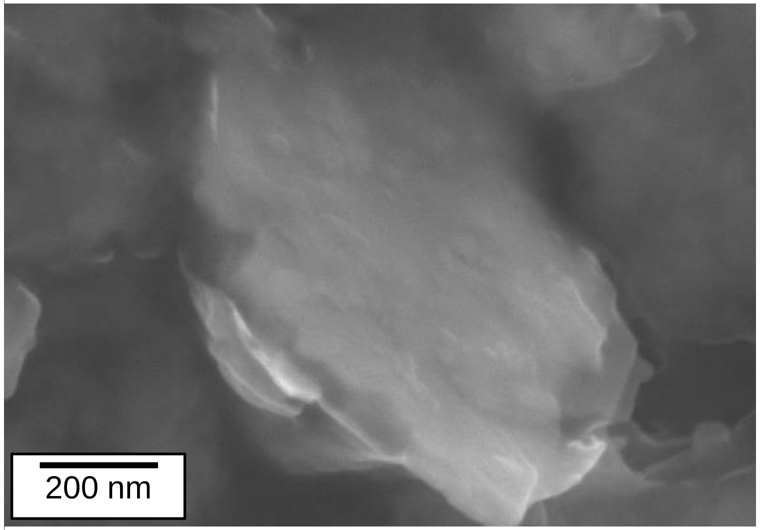
For siliceous rock like oil sands, a particle density ρ_p of 2.65 kg/m³ is adequate for all diameters down to 0.2 μm. A specific gravity of 2.5 kg/m³ is appropriate for siliceous particles in the size range of 0.2 μm. In the <0.2 μm fraction the specific gravity in heavy liquids falls to about 2.2 kg/m³. Water has a density of 0.998 kg/m³ at 20 °C.

Sub-2μm Contaminant Solids in Bitumen Froth

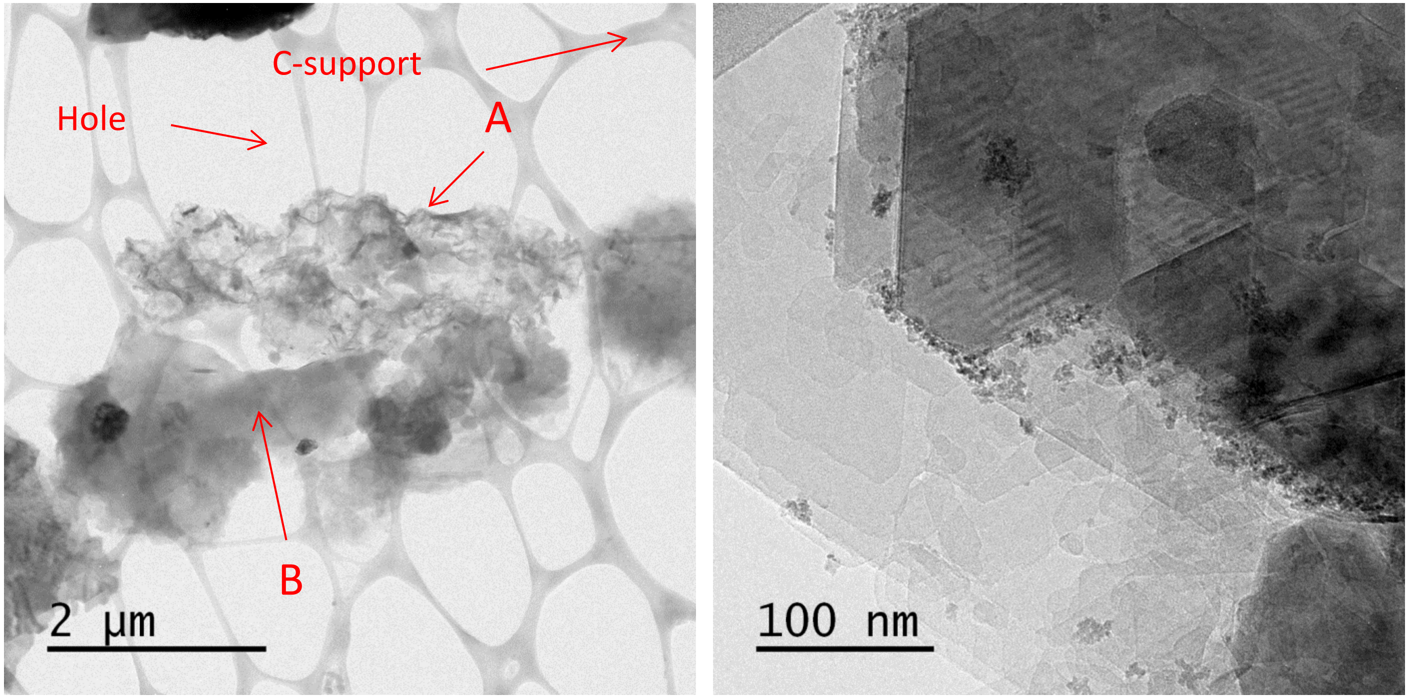
Variable pressure SEM

(direct imaging of sample, *i.e.* no coating applied on the specimen imaged here)





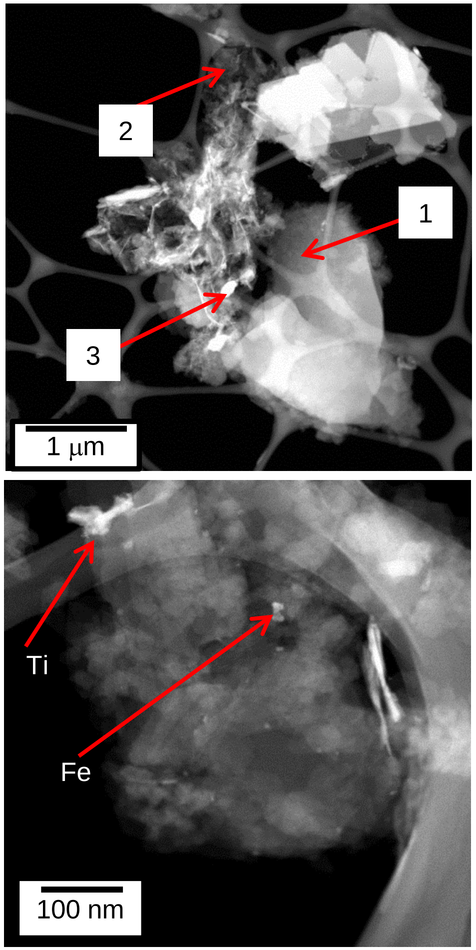
Sub-2μm Mineral Aggregate

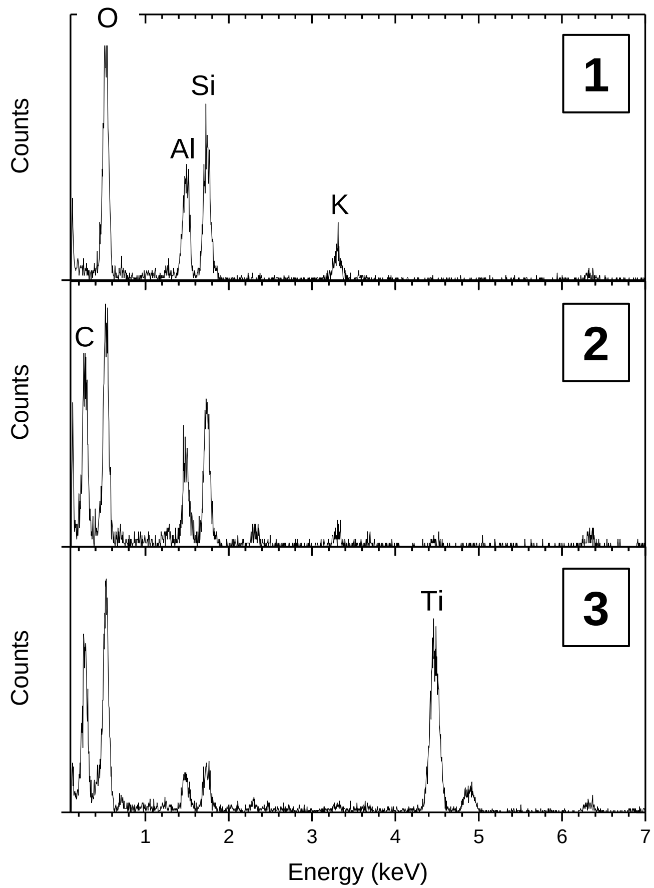


TEM

Two distinct clay aggregates are observed: randomly oriented platelets (region A), and large ordered stacks (region B). As visible on higher resolution images, the large ordered stacks (region B), also have ultrafine clay platelets stacked face-to-face on their surfaces. Nanometer-scale metal-bearing particles are also found dispersed on the clay surfaces, and accumulate preferentially at steps.

Sub-2μm Mineral Aggregate





EDX spectra acquired over a hole in the support, indicate that clay minerals in region 2 contains significant amount of C, whereas no C signal is detected in region 1.

These results suggest that region 2 corresponds to organo-clay aggregates.

Bright features in the images correspond to metal-bearing nanoparticles, containing Ti as confirmed by EDX in region 3, but also Fe and Ca in other instances.

ADF-STEM-EDX (ADF = annular dark-field)

Separation of froth F1 by wettability (WET) followed by clay-ultrafines (CUF) separation

combined techniques (WET+CUF) applied for 1st time

Froth F1 →

WET

HPS
~50–55 wt% per total solids

IS
~10–15 wt% per total solids

ORS
~35 wt% per total solids

HSCS
<1 wt% per total solids

CUF

HPS → wt% per total solids*

CS	77(6)
CC	6.9(2)
UF	5.7(4)

ORS → wt% per total solids*

CS	86(5)
CC	8.4(1.6)
UF	5.2(7)

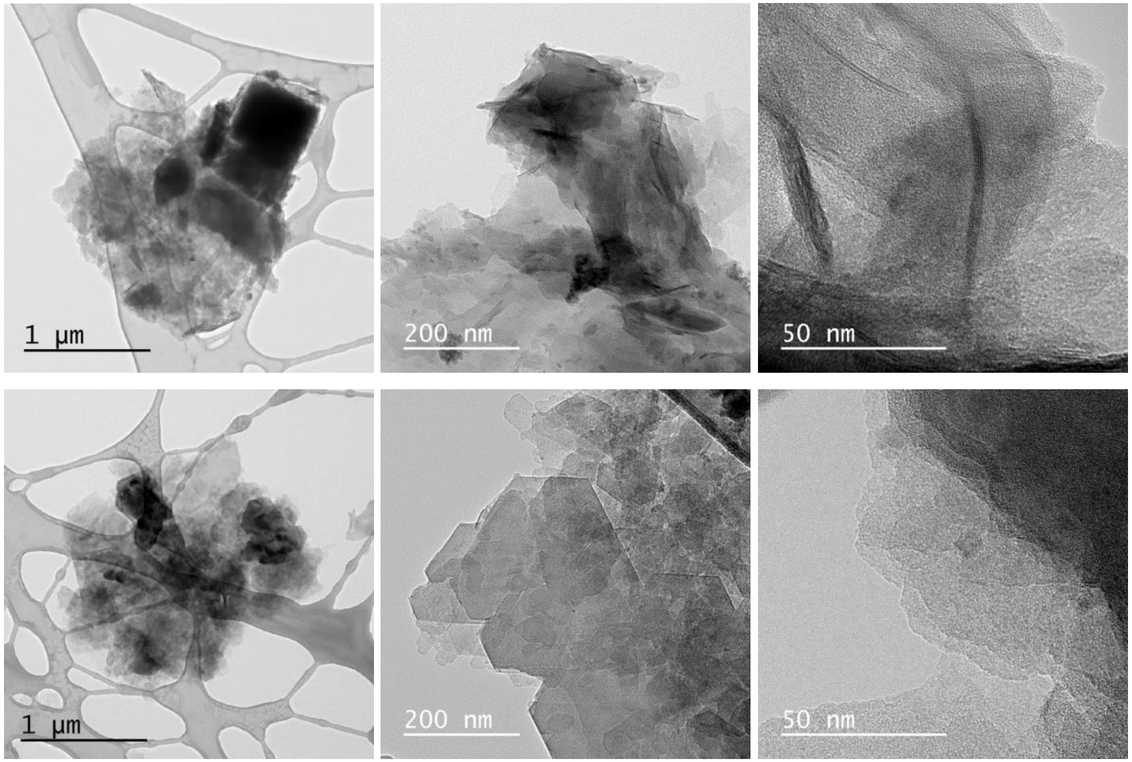
* Numbers in parenthesis refer to the last digit(s) and represent 1σ standard uncertainty errors.

Hydrophilic (HPS) and Biwettable (ORS) Sub-2μm Aggregates

TEM

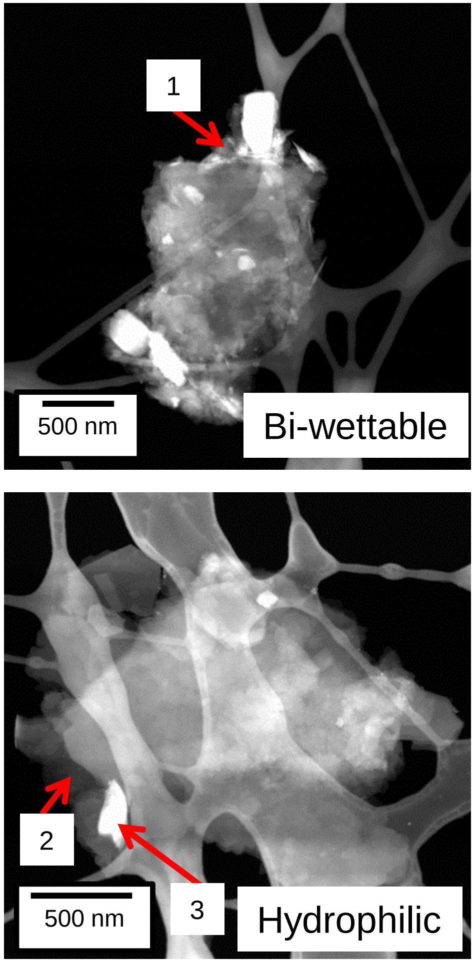
Biwettable (ORS)

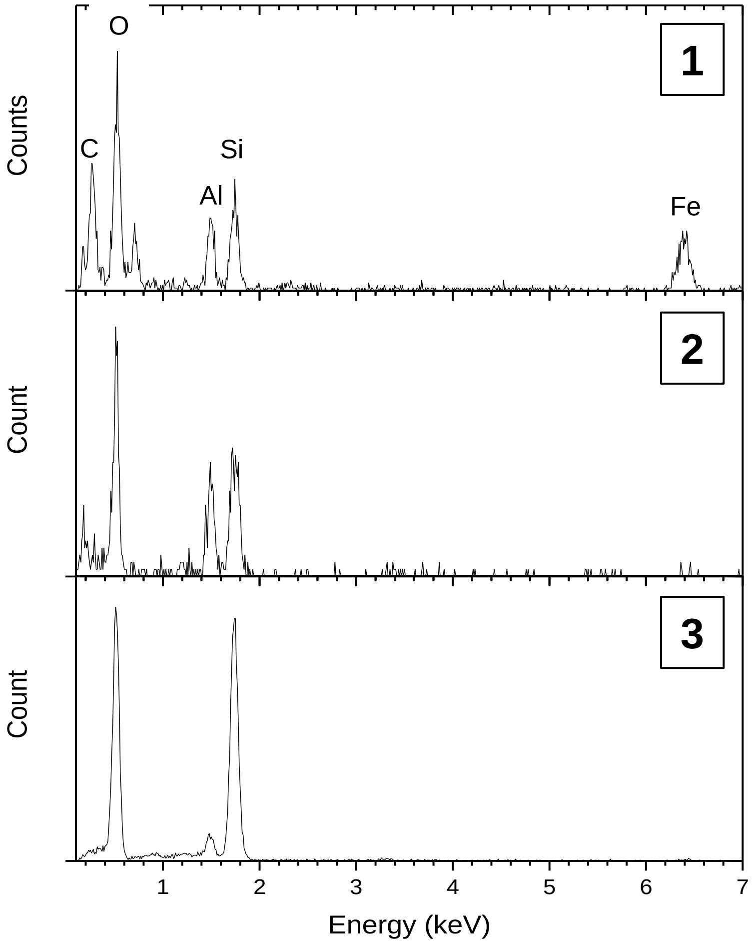
Hydrophilic (HPS)



At low magnifications, mineral aggregates for both ORS and HPS fractions appear qualitatively fairly similar. Clear differences, are revealed at higher magnifications: ORS aggregates contains mainly randomly oriented clay platelets, whereas HPS clay platelets are predominantly found in an ordered face-to-face stacking. Some ORS platelets have thickness of only a few atomic planes.

Hydrophilic (HPS) and Biwettable (ORS) Sub-2μm Aggregates





EDX confirms the presence of Fe, Ti, and Ca bearing minerals. Silica particles are also detected, and are found predominantly in the HPS fraction due to its hydrophilic characteristics.

A strong carbon signal is observed for the ORS, whereas no clear carbon signal is detected for the HPS.

ADF-STEM-EDX (ADF = annular dark-field)

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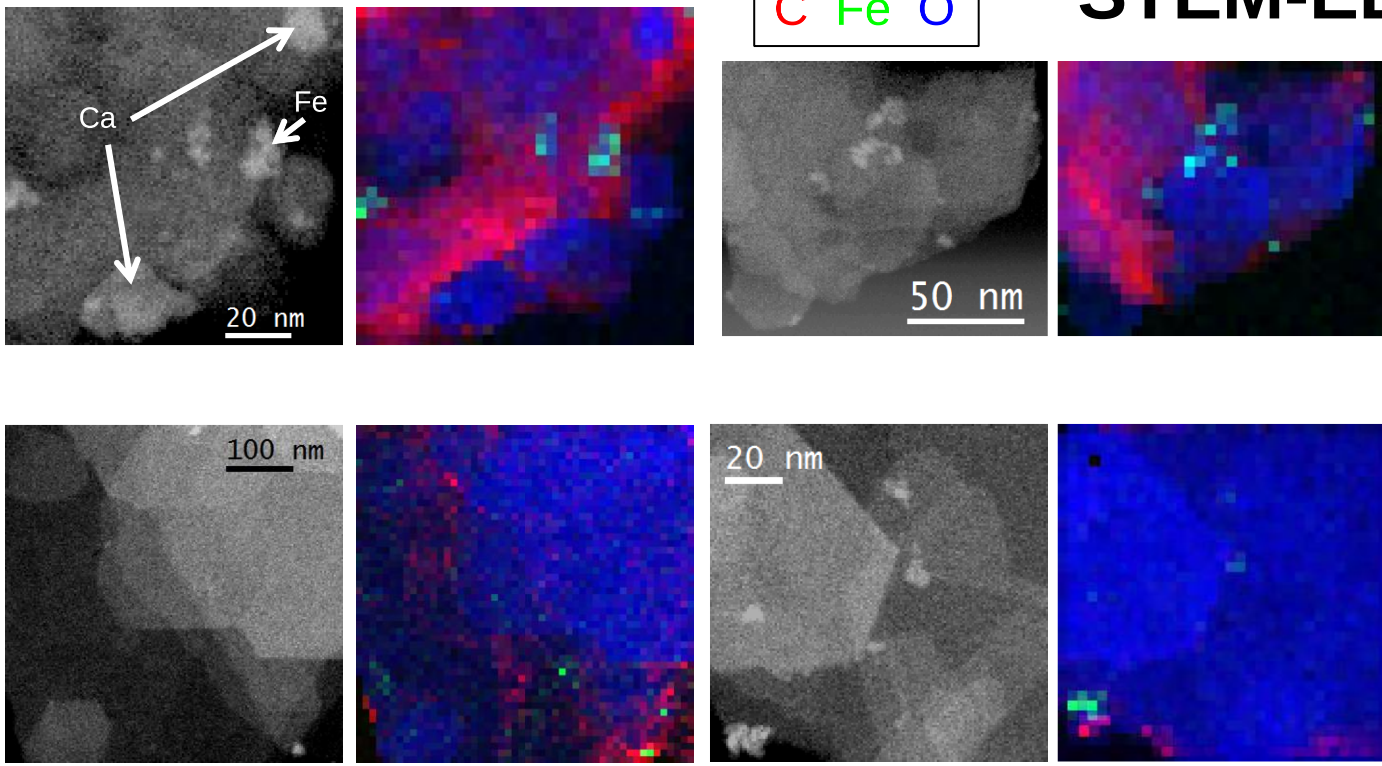
Organic coating on clay mineral particles at the nanometer scale

STEM-EELS

C Fe O

Biwettable (ORS)

Hydrophilic (HPS)



Carbon maps were acquired using spatially-resolved EELS analysis to compare the organic coatings of clay minerals found in ORS and HPS. Significant amount of C is detected on ORS ultrafine clays, and the coating appears to be non-uniform at the nanometer-scale.

=> This is similar to our previous work on solids in solvent-diluted bitumen product.

Summary

In summary, we have analyzed with nanometer precision the structure and composition of sub-2µm heterogeneous mineral aggregates present in a commercial bitumen froth, with an emphasis on the role of determining the wettability characteristics of clay particle surfaces.

- Separation of the bitumen froth by wettability (WET) first, followed by clay-ultrafines (CUF) separation, enabled isolation of sub-2μm mineral aggregates (coarse clays) with distinct wettability characteristics.
- We observed that coarse clays from hydrophilic solids (HPS) contain mainly orderly stacked clay platelets, whereas biwettable solids (ORS) comprise aggregates with randomly oriented clay platelets.
- In contrast to hydrophilic solids (HPS), an organic coating is revealed on the sub-2μm mineral aggregates from the biwettable (ORS) fraction, and is found to be inhomogeneous at the nanometer scale.

Acknowledgements

The authors thank Syncrude for financial support and permission to publish this work.

This work was performed under the High Efficiency Mining program in place at the NRC.

Questions, comments, discussion?

Thank you

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