

XRF Elemental Analysis for Prediction of Clay-related Process Variables in Oil Sands

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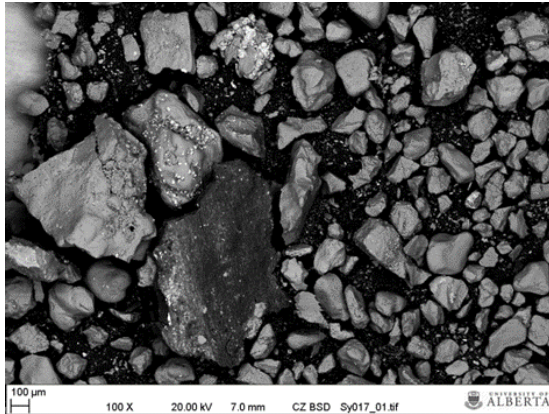
Clays, Fines, and Clay Minerals

- Clays – Mineral solids with particle sizes $\leq 2 \mu\text{m}$
- Fines – Mineral solids with particle sizes $\leq 44 \mu\text{m}$
- Clay Minerals – Hydrous aluminosilicates with layered structures

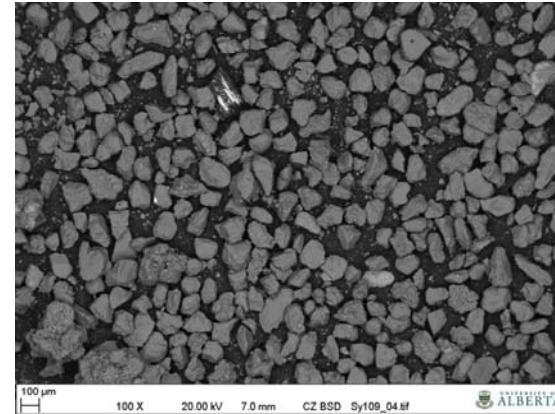
Major Clay Minerals in Oil Sands

- **Kaolinite**, kaolinite-smectite mixed layer clays
- **Illite**, degraded illite, illite-smectite mixed layer clays
- Smectite (montmorillonite)
- Chlorite

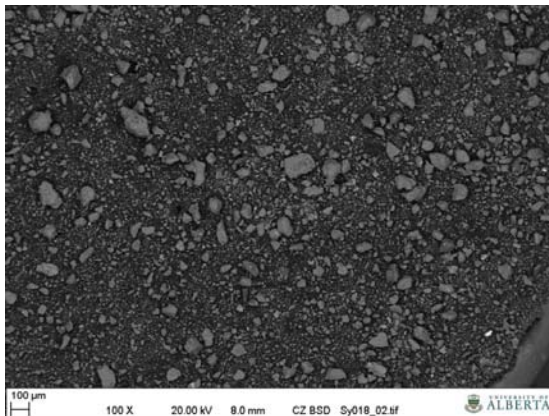
Grain Size Distribution of Oil Sands Solids (SEM)



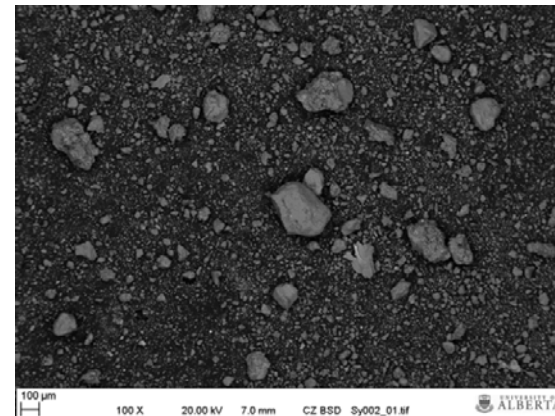
high grade estuarine ore



high grade marine ore



estuarine waste



marine channel
interburden

Oil Sands Samples Used in this Study

Sample ID	Ore Type / Description	Bitumen (wt%)	Water (wt%)	Solid (wt%)	Fines (wt%)	Clay (wt%)	MBI (meq/100g)
Sy001	Medium Grade Estuarine (with Minor Marine)	10.98	2.60	86.17	19.83	5.25	0.6
Sy002	Marine Channel Interburden	5.00	10.12	84.80	50.72	10.73	1.4
Sy003	Marine Channel	5.55	10.69	83.68	42.27	10.55	1.7
Sy004	Multi Bench Estuarine & Marine Ore	9.34	5.03	85.46	23.39	7.07	0.9
Sy005	High Grade Estuarine Ore	11.06	3.26	85.24	27.62	6.92	0.4
Sy006	Marine Ore; Burrowed	10.05	4.54	84.98	17.24	5.85	0.5
Sy013	Estuarine Ore	7.81	8.86	83.43	48.19	12.11	1.7
Sy015	Estuarine Ore	12.82	4.25	82.57	15.96	3.90	0.3
Sy016	Estuarine Ore	5.91	10.50	83.71	48.04	10.28	1.7
Sy017	Estuarine Ore	13.84	4.16	82.22	10.21	2.50	0.2
Sy018	Estuarine Waste	4.49	8.48	87.20	60.30	12.63	2.2
Sy019	Marine Ore	12.46	5.28	82.37	14.82	4.80	0.5

Mineralogical Composition (XRD)

Sample ID	Qtz	Ksp	Pla	Cal	Dol	Sid	Anh	Pyr	Kao	Ill	Chl	Sme	M-L	Total Clay
Sy001	85	5	1	0	1	0	0	0	5	3	0	0	0	8
Sy002	66	3	1	2	3	1	0	1	15	8	0	0	0	23
Sy003	67	1	1	2	2	0	0	1	17	9	0	0	0	26
Sy004	89	3	0	0	0	0	0	0	5	3	0	0	0	8
Sy005	87	6	0	0	0	0	0	0	6	1	0	0	0	7
Sy006	88	2	0	0	0	0	0	0	7	3	0	0	0	10
Sy013	74	3	1	0	0	1	0	0	10	11	0	0	0	21
Sy015	90	1	0	0	0	0	0	0	7	2	0	0	0	9
Sy016	71	4	1	0	0	0	0	0	11	13	0	0	0	24
Sy017	93	1	0	0	0	0	2	0	4	0	0	0	0	4
Sy018	72	1	0	0	0	1	0	0	13	13	0	0	0	26
Sy019	92	2	0	0	0	0	0	0	3	2	1	0	0	6

Chemical Formulae of Minerals

Class	Mineral Name	Chemical Formula
Detrital Silicate	Quartz	SiO_2
	K-feldspar	KAlSi_3O_8
	Plagioclase	$(\text{Na}, \text{Ca})\text{AlSi}_3\text{O}_8$
Carbonate	Calcite	CaCO_3
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$
	Siderite	FeCO_3
Sulfate	Anhydrite	CaSO_4
Sulfide	Pyrite	FeS_2
Clay Mineral	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	Illite	$\text{K}_{0.6}(\text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$
	Chlorite	$(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg}, \text{Fe})_3(\text{OH})_6$
	Montmorillonite (smectite)	$(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

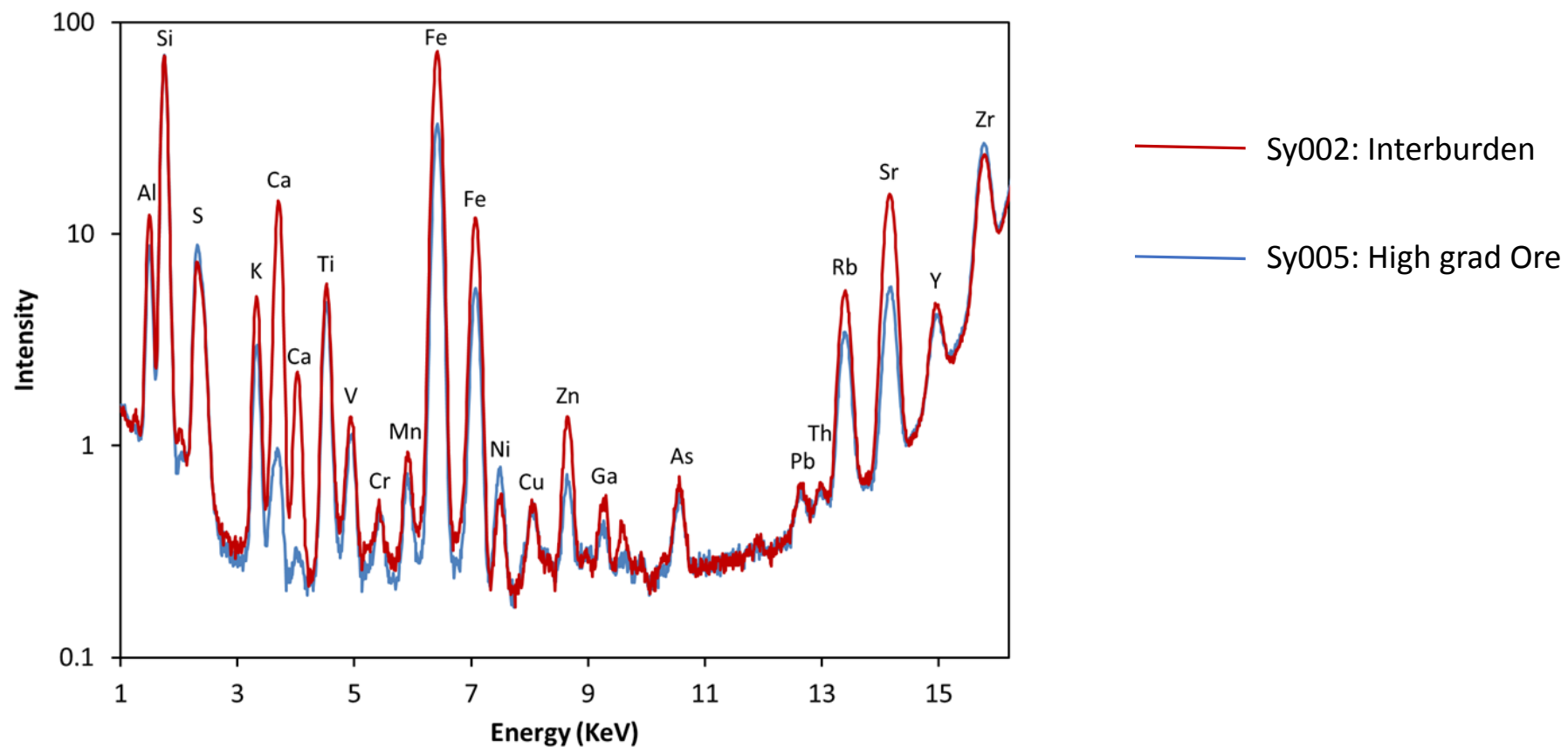
X-ray Fluorescence Spectrometry (XRF)

- Rapid measurement of elemental composition
- Up to 31 elements detected in oil sands by ED-XRF spectrometer
- Potentially useful for both oil sands ore and tailings

Oil Sand Elements Measured by XRF

detected										easily detected													
1a												0											
1 H	IIa																						2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne						
11 Na	12 Mg	IIIb	IVb	Vb	Vib	VIII		Ib		IIb	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar							
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra	89-103	104 Rf	105 Ha	106 Sg																		
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	71 Yb	72 Lu									
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw									

ED-XRF Spectra of Oil Sands Samples



Process Variables Examined

Process Variables	Description	Comments
Bitumen Content	weight percent of bitumen	high grade, good processability
Fines Content	weight percent of fines ($< 44 \mu\text{m}$)	high fines content, poor processability correlated to clay content
Clay Content	weight percent of clay-size fraction ($< 2 \mu\text{m}$)	composed mainly of clay minerals
Kaolinite/illite	mass ratio of kaolinite to illite	kaolinite/illite > 2 ?
Total Clay	sum of clay minerals in weight percent	sometimes used interchangeably with clay content
Methylene Blue Index (MBI)	amount of methylene blue adsorbed (meq/100 g)	surface reactivity of clay minerals used commonly in oil sand industry

Principal Component Analysis: Peak Area of Elements Measured by XRF

Factor 1: Al, S, K, Ti, Zn, Ga, Pb, Th, Rb, and Y



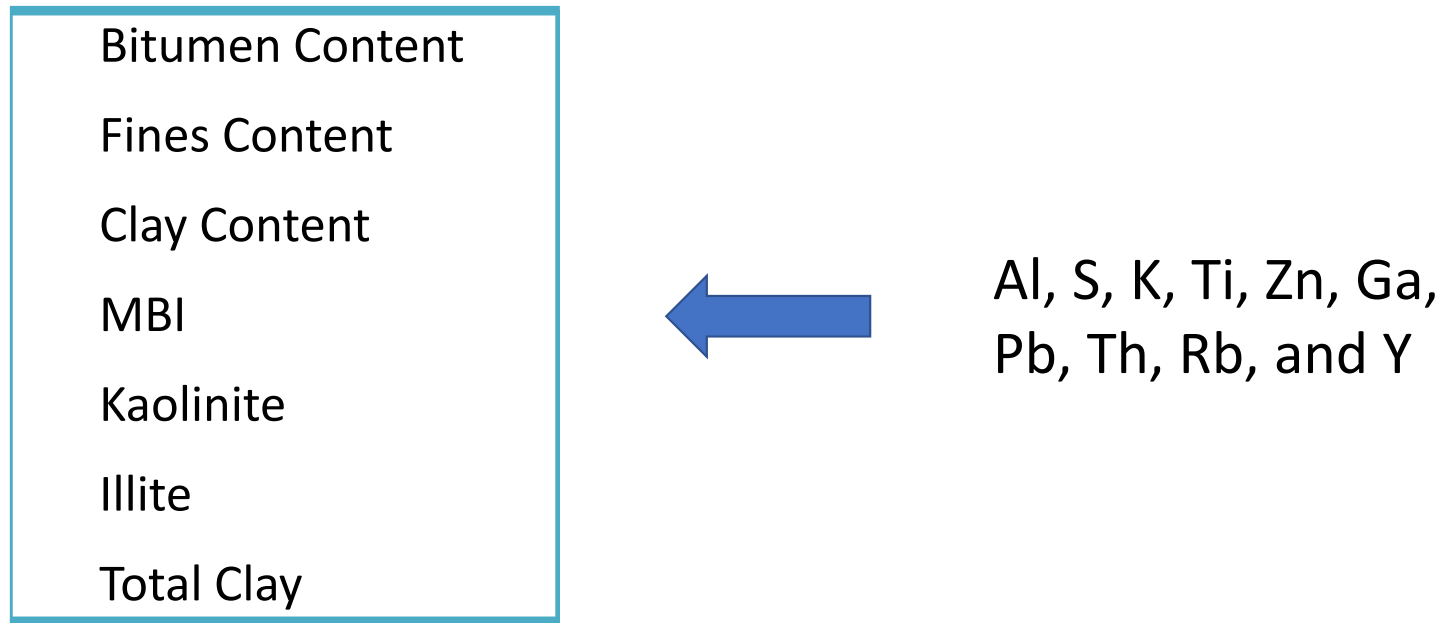
Clay indicator?

Factor 2: Mg, Ca, Sr, and Ba

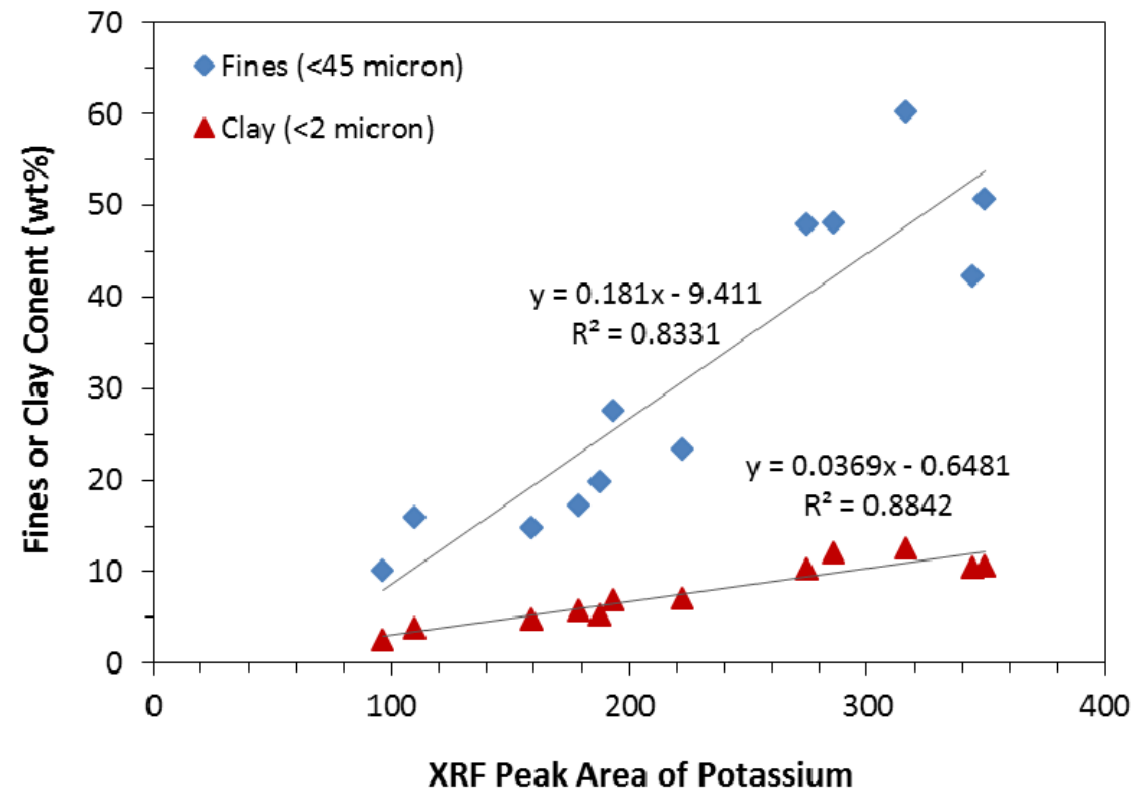


Carbonates?

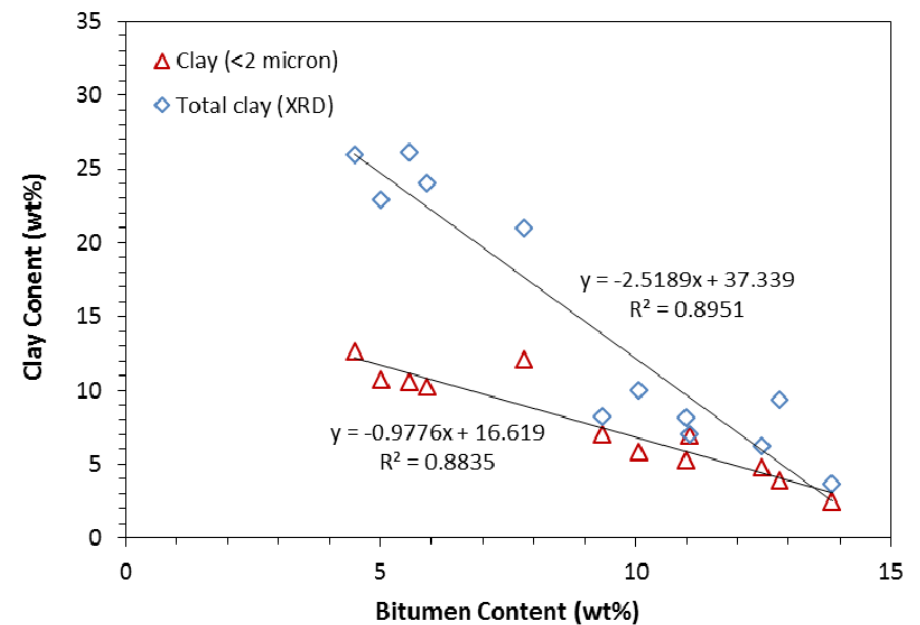
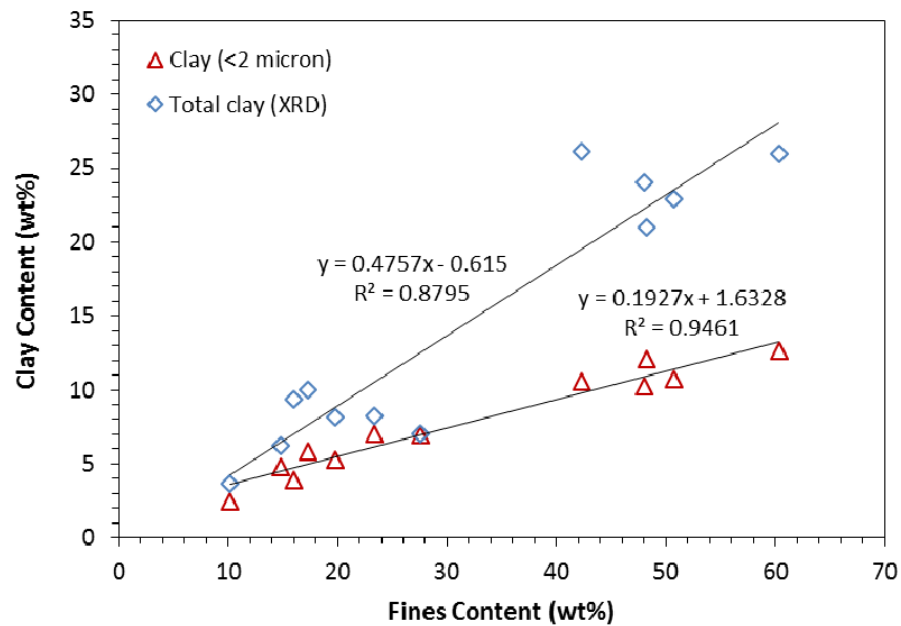
Correlations between Process Variables and Individual Elements



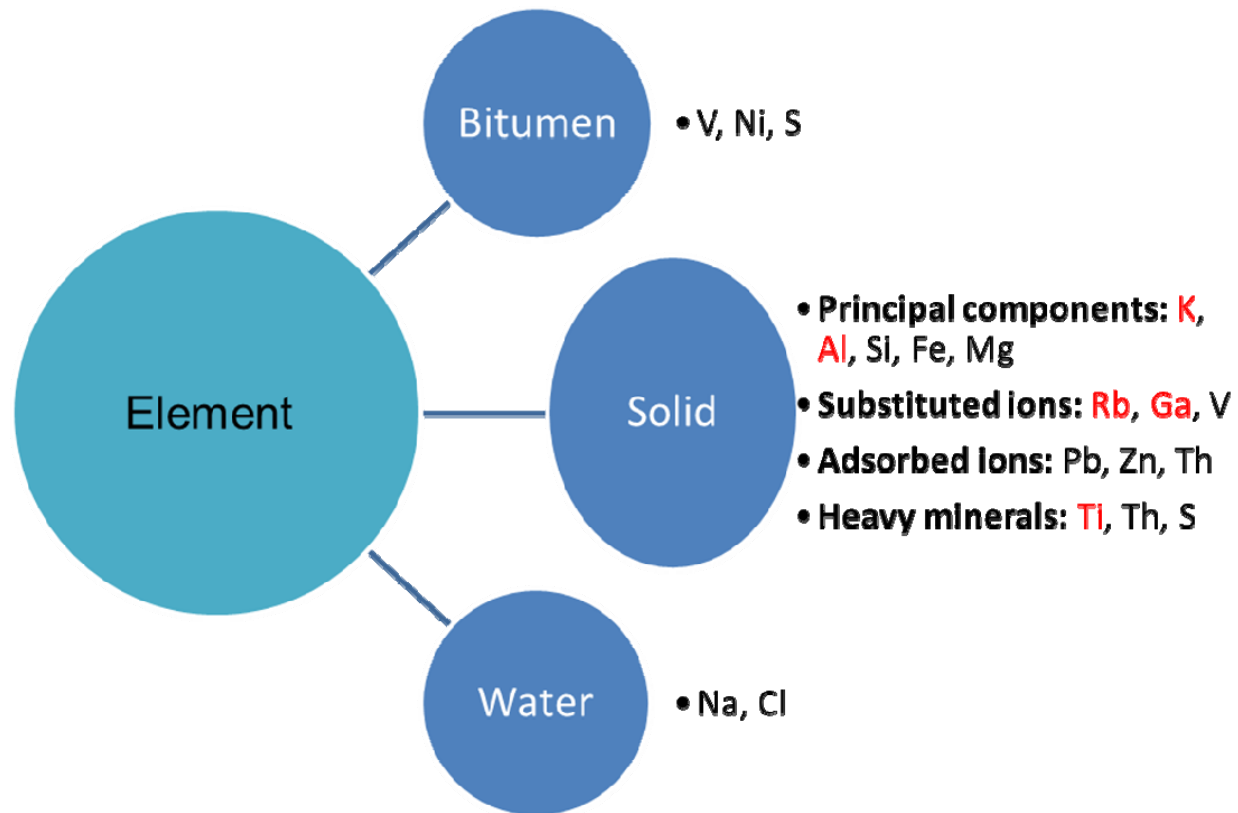
Correlations of Fines and Clay Content with K



Inter-relationships between Process Variables

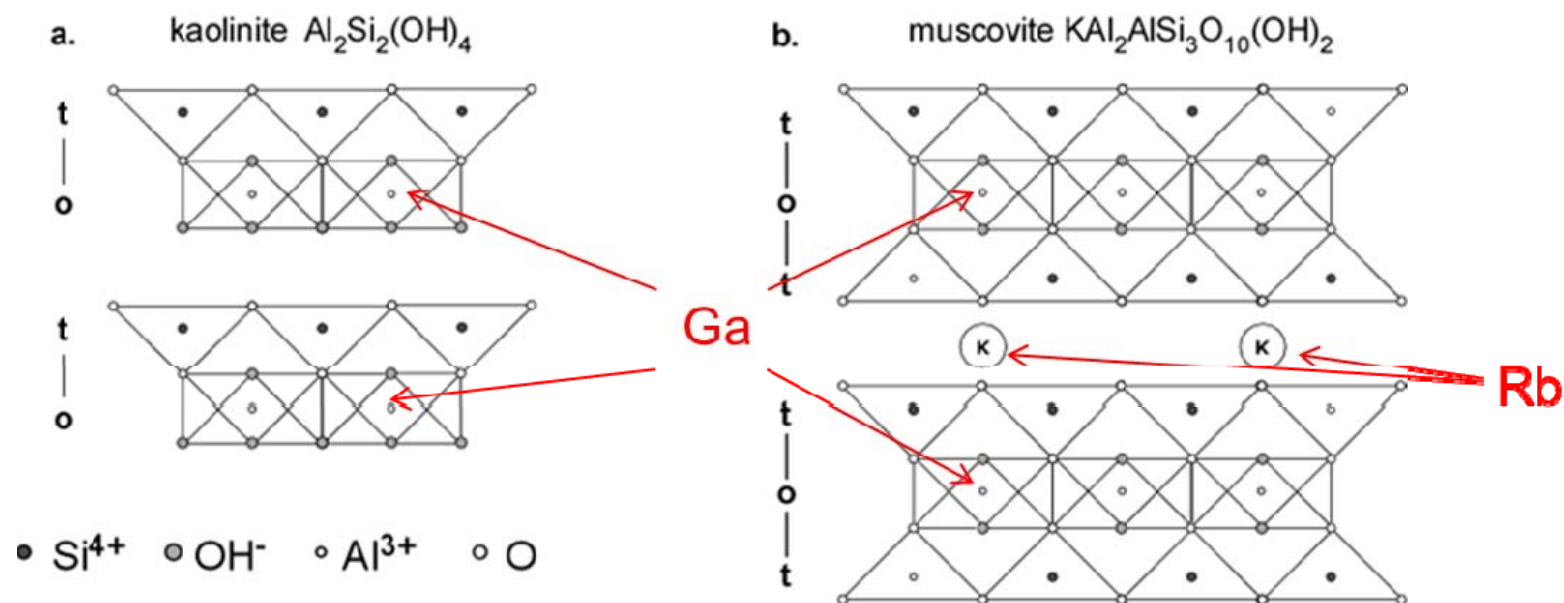


Elemental Distribution in Oil Sands

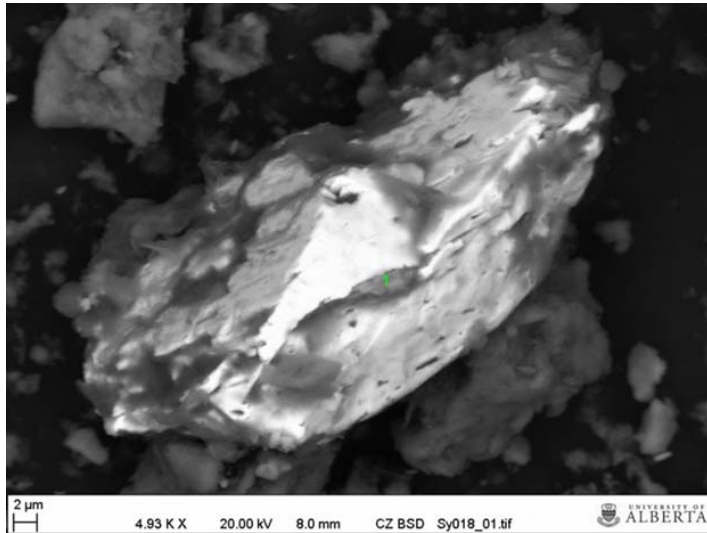


Isomorphous Substitution in Clay Structures

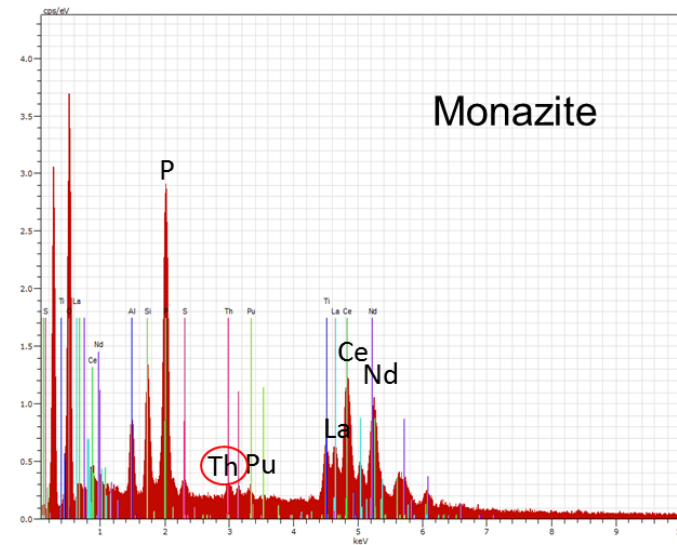
- **Ga** – substitute for Al in silicate minerals.
- **Rb** – substitutes for K in silicate minerals.



Thorium-bearing Mineral in Oil Sands

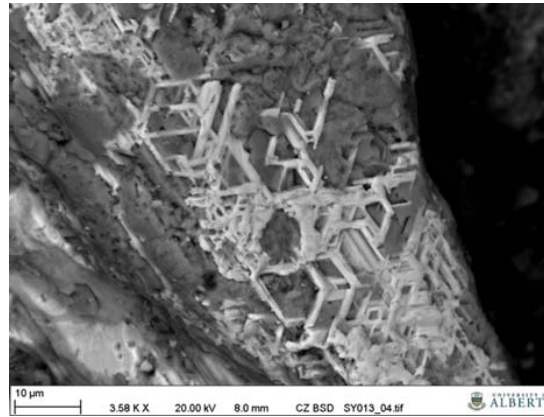
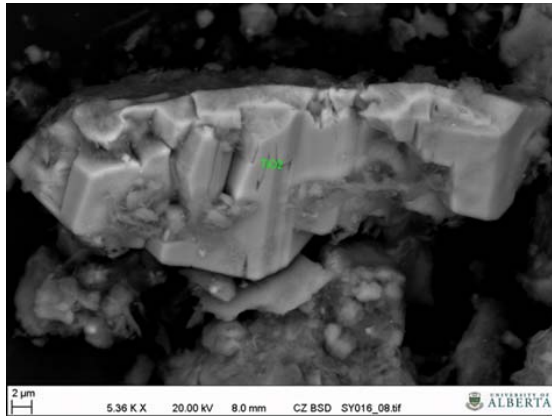


Monazite found in oil sands
(Ce, Nd, La, **Th**, Pu)PO₄

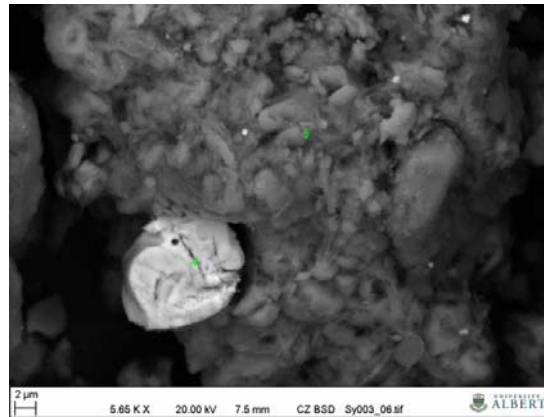
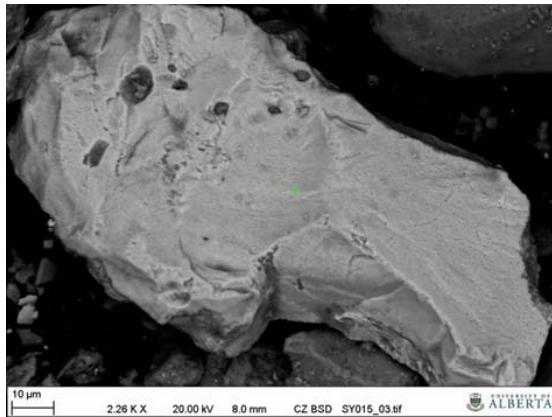


EDX spectrum of monazite

Ti-bearing Minerals in Oil Sands



Titanium oxide (TiO_2)



Titanium iron oxide

Multiple Regression Models for Process Variables

Bitumen Content

Fines Content

Clay Content

MBI

Kaolinite

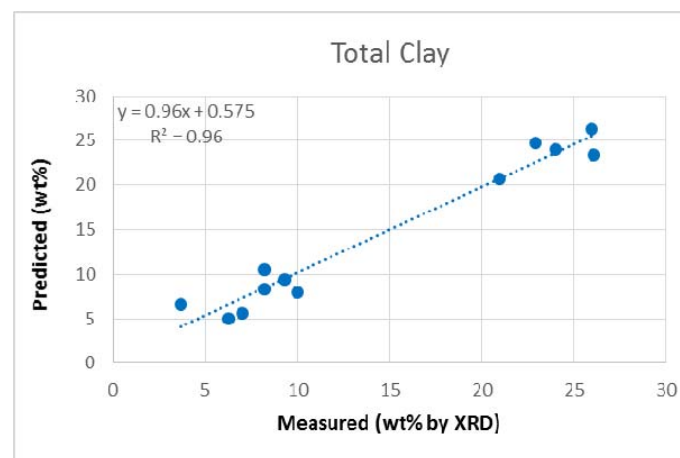
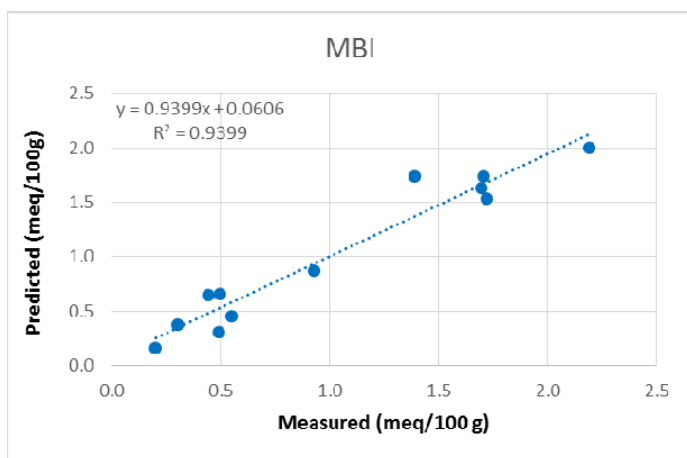
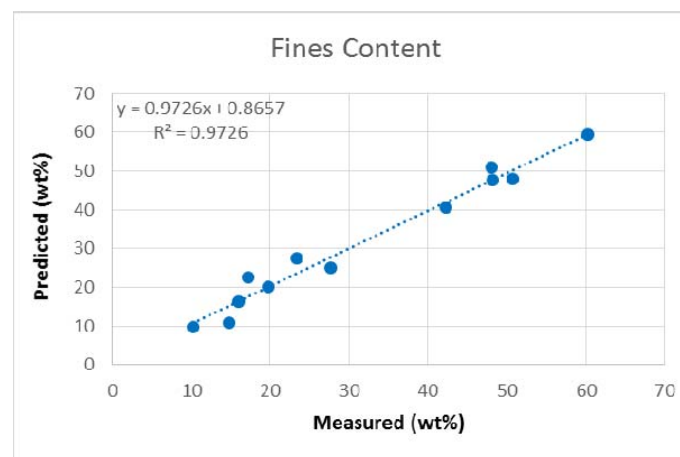
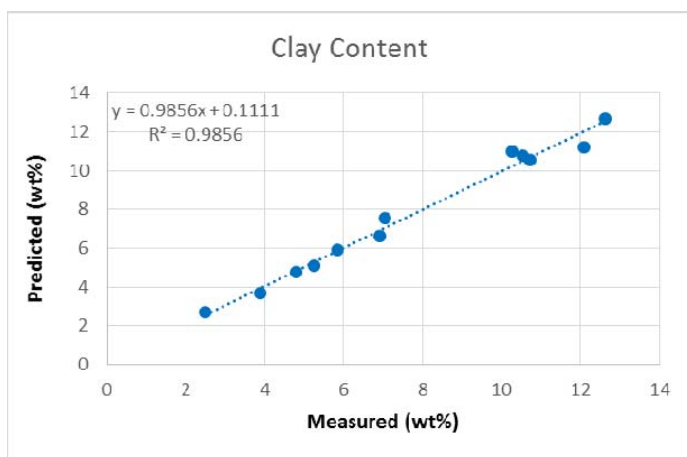
Illite

Total Clay

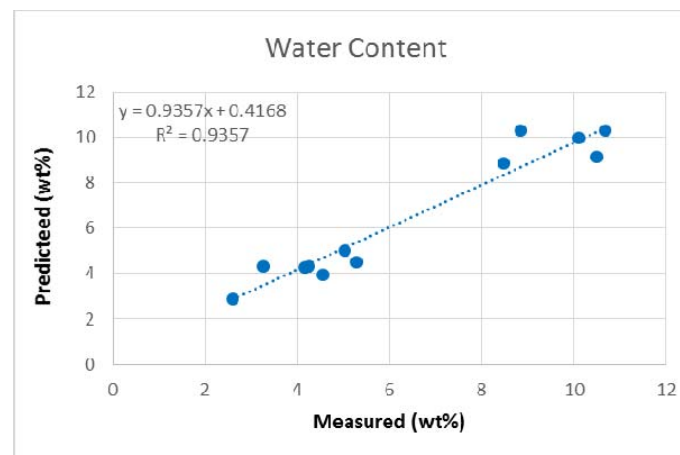
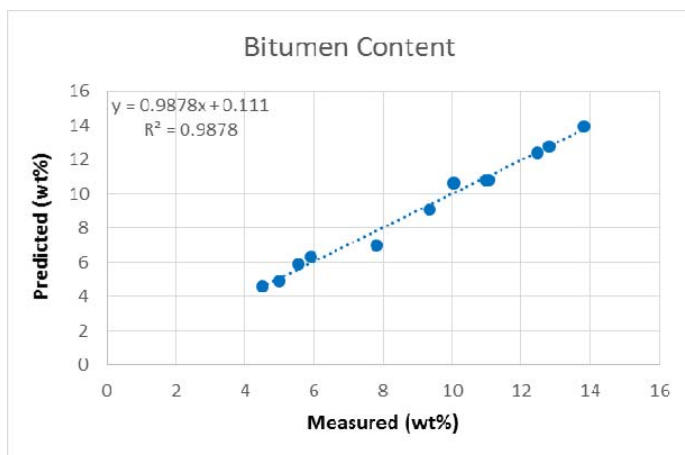
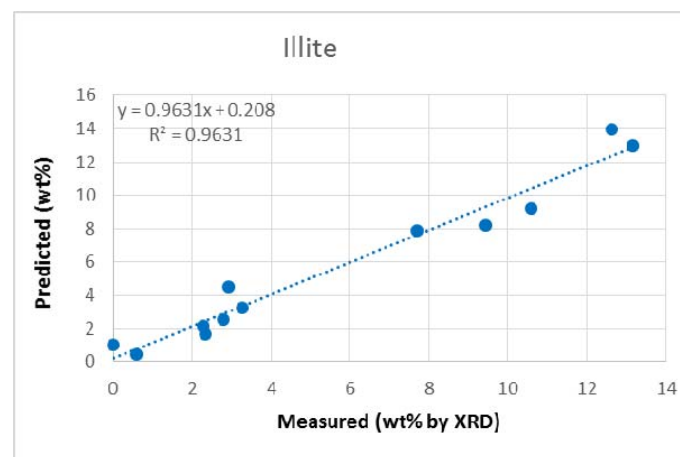
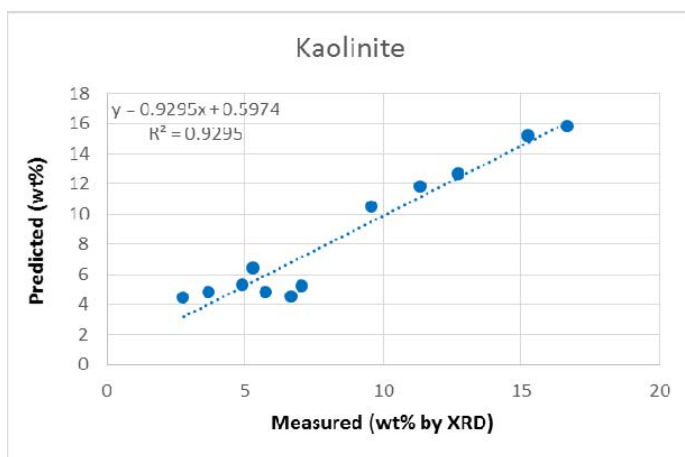


**Multiple Regression
Models including three
or more elements**

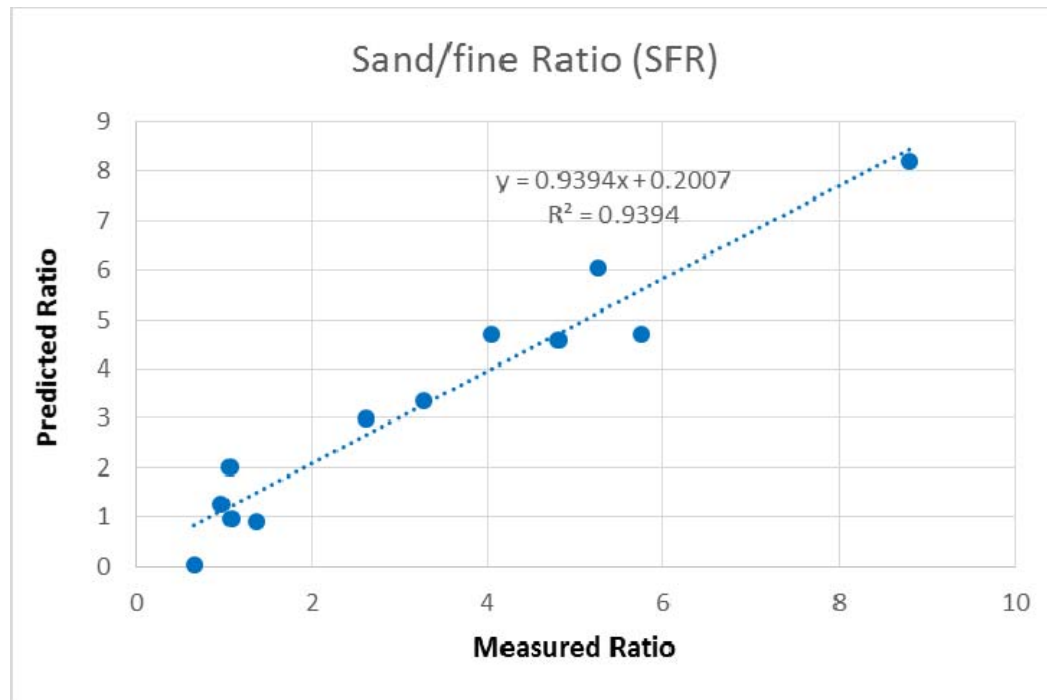
Process Variables: Predicted vs. Measured



Process Variables: Predicted vs. Measured



Prediction of Sand/fine Ratio (SFR)



Summary

- XRF can provide rapid measurement of elemental compositions.
- Some elements can be used as clay indicators in oil sands.
- Clay-related process variables can be predicted using multiple regression models based on XRF analysis.
 - Geochemical investigation is necessary to develop clay models.
 - Models are site specific.
- The method have a potential application in oil sands tailings.
- This work has been filed for a US provisional patent.