Acid Generation and Metal Release in Oil Sands Froth Treatment Tailings

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Oil Sands Deposits

- oil sands deposits contain 168B barrels of proven bitumen reserves
- hosted in sands and sandstones of the Cretaceous McMurray formation
- ore comprised of:
  - bitumen (8–15% w/w)
  - water (2–5% w/w)
  - solids (80–90% w/w)
- approximately 3.4% (4800 km^2) of deposit area accessible by surface mining
  - active mining footprint > 950 km^2 (2017)

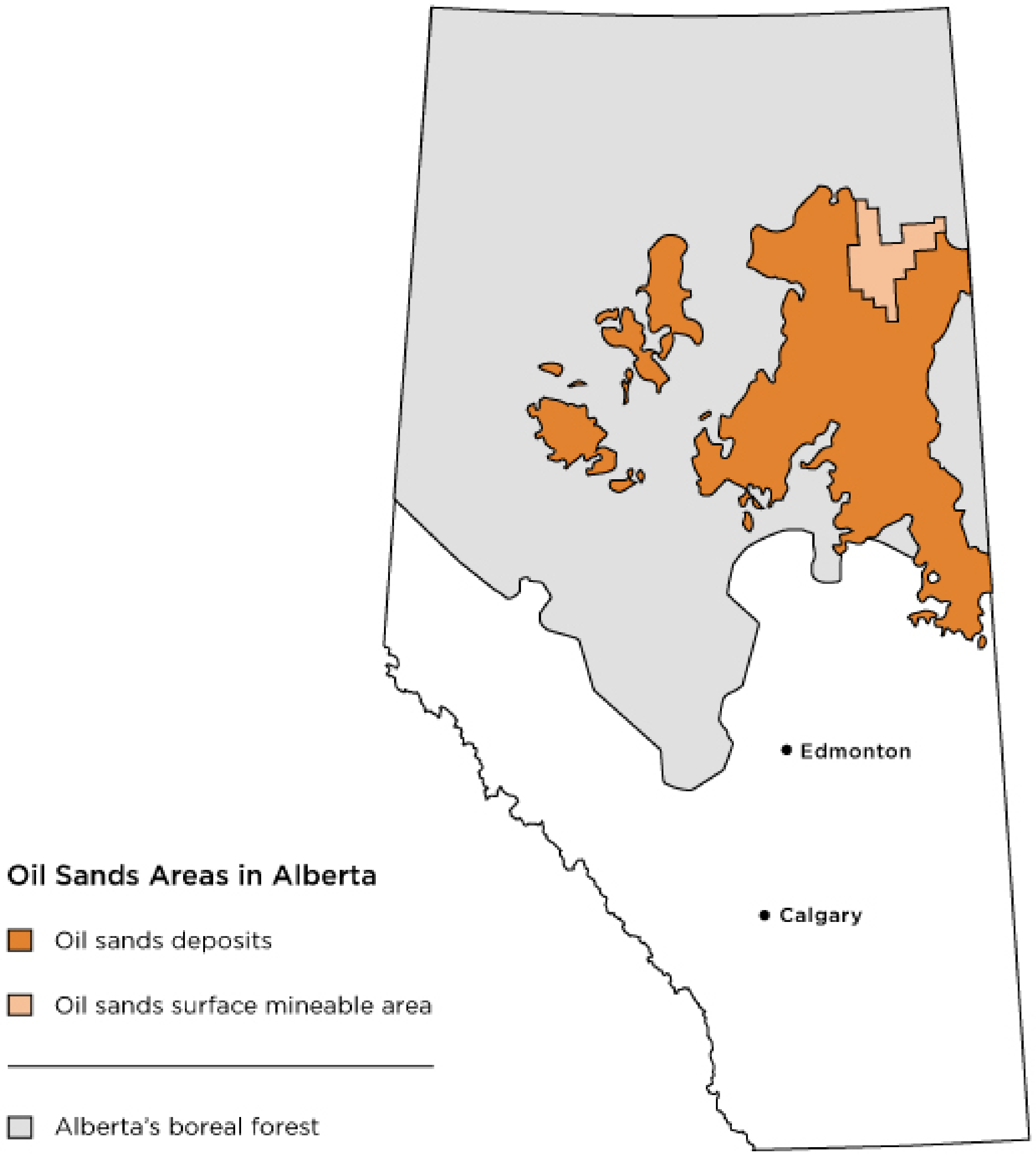

Figure: https://www.aer.ca/providing-information/by-topic/oil-sands
Data: http://osip.alberta.ca/library/Dataset/Details/27

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Source: https://www.flickr.com/photos/syncrudecanada/15738331538/

Oil Sands Ore

- contains bitumen characterized by:
    - high viscosity and density
    - high molecular weight carbon
    - low hydrogen-to-carbon ratio
    - elevated sulfur and nitrogen
- extraction and upgrading required to produce synthetic crude oil
    - diluted bitumen also exported

Surface Mining

- open pit mining used where ore is within ~100 m of surface
    - truck and shovel method
    - high recovery rates (cutoff grade ~8% w/w)
    - open pits can exceed 10 km^2
    - large water and energy requirements
    - accounts for ~50% of bitumen production

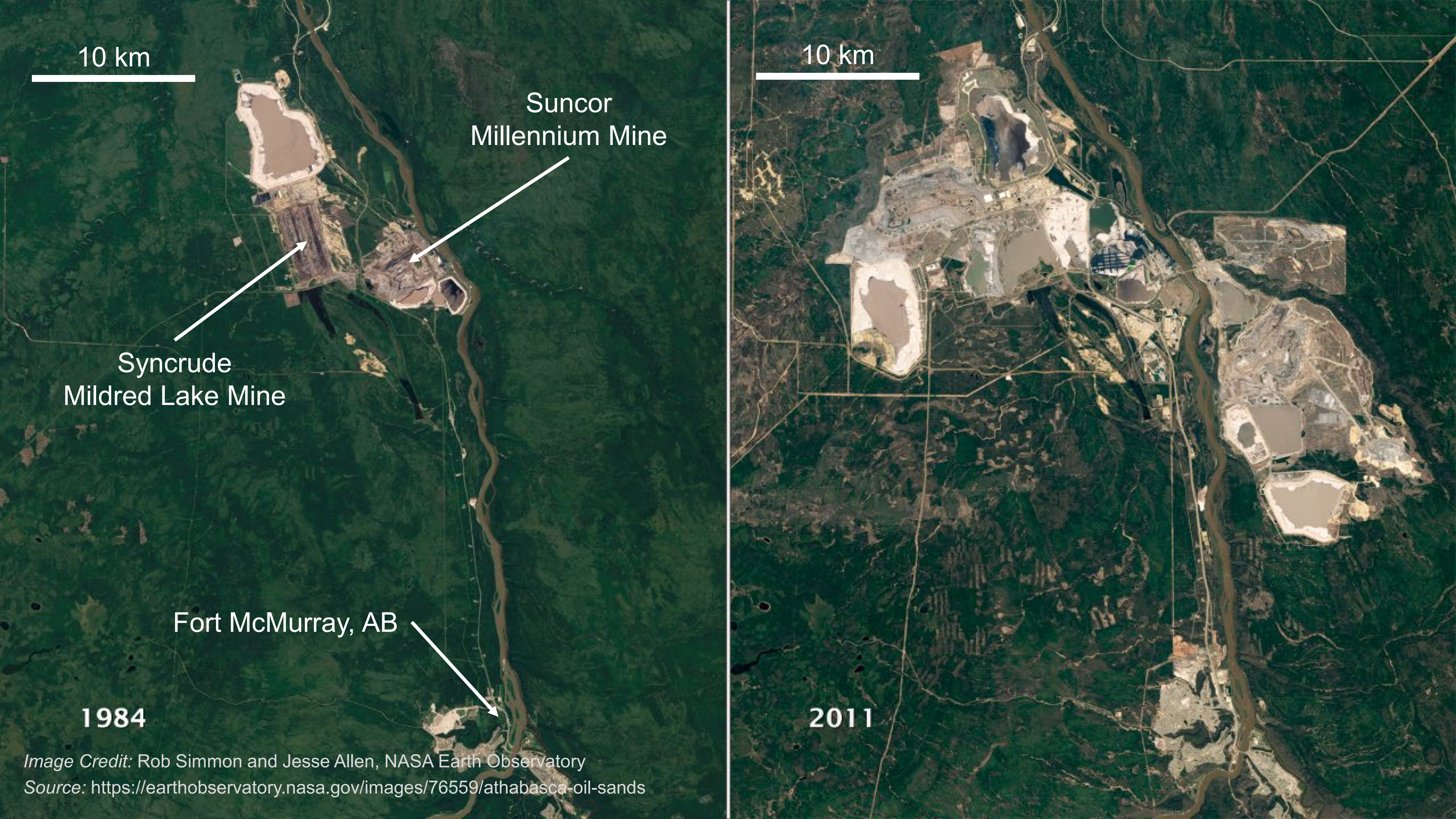
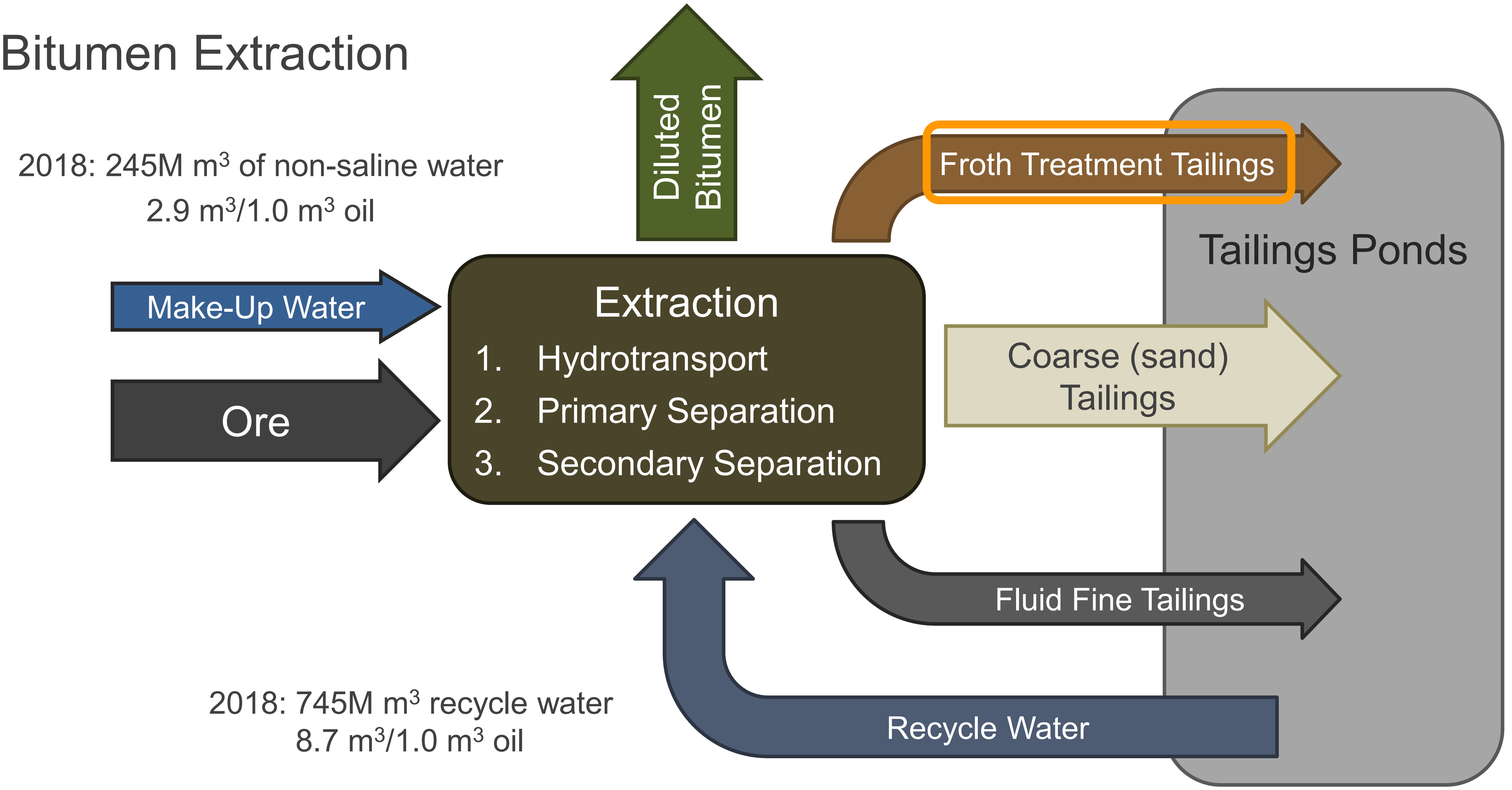


Image Credit: Rob Simmon and Jesse Allen, NASA Earth Observatory
Source: https://earthobservatory.nasa.gov/images/76559/athabasca-oil-sands

Bitumen Extraction



Data: https://aer.ca/protecting-what-matters/holding-industry-accountable/industry-performance/oil-sands-mining-water-use#summary

Figure after: Mikula (2012) *In:* Restoration and Reclamation of Boreal Ecosystems. Ch. 6, pp. 103-122.

Froth Treatment Tailings (FTT)

- produced during bitumen froth treatment
  - diluent hydrocarbons added to aerated bitumen froth lowers viscosity and liberates entrained solids
  - solids comprised of (phyllo)silicates, oxides, carbonates, and sulfides
- sub-aerial or sub-aqueous deposition within engineering tailings facilities
  - diluent recovered before hydrotransport

FTT Geochemistry

- sulfides concentrated in FTT relative to other tailings streams
  - principally pyrite and marcasite
- potential environmental concerns include:
  - acid generation
  - metal(loid) release
  - biogenic gas production
- geochemical evolution variable among mines and within deposits
  - sub-aerial versus sub-aqueous deposition
  - naphthanic versus parrafinic solvent
  - differences in ore mineralogy and processing

Plant 6 FTT Deposit

- partially water-saturated beach deposit
- located in Mildred Lake Settling Basin (MLSB)

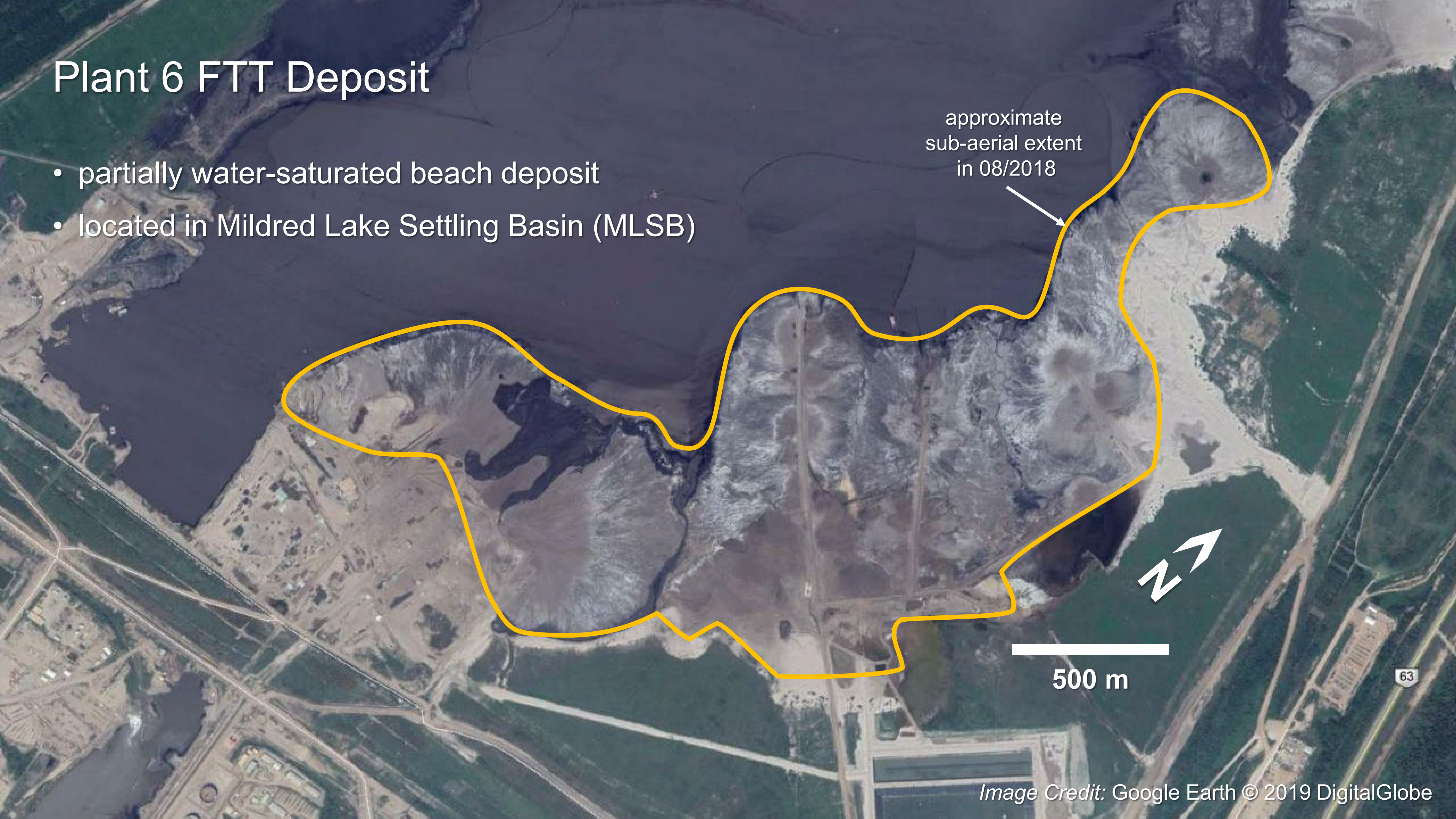
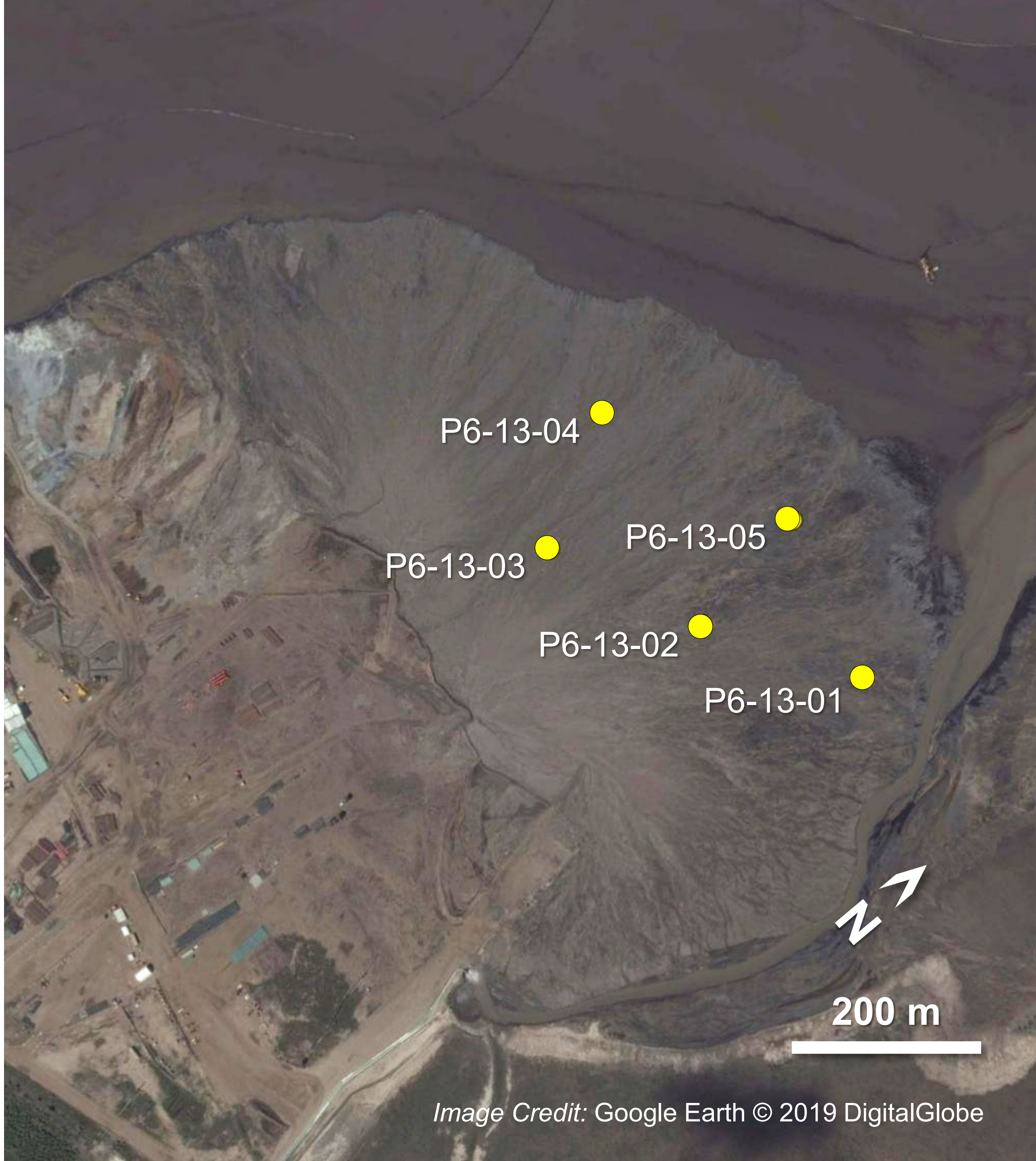


Image Credit: Google Earth © 2019 DigitalGlobe

Field Study: 2013

- purpose:
  - preliminary examination of FTT geochemistry and mineralogy
- methods:
  - auger: 0.0 – 0.3 m b.g.s. (frozen upper layer)
  - sonic coring: 1.3 – 3.3 and 3.3 – 5.3 m BGS
- analyses:
  - particle-size distribution: laser diffraction
  - mineralogy: optical, SEM, XRD
  - geochemistry: digestions, EPMA, PCA
  - ABA: modified Sobek with siderite correction



Mineralogy

- silicates + phyllosilicates dominate
- pyrite is the principal sulfide
  - marcasite also observed
  - complex sulfide textures
- carbonate content similar to sulfide content
  - siderite dominates
- weathered FTT can have large amorphous component

Mineral	Ideal formula	mean ± 1σ (wt. %)	median (wt. %)	minimum (wt. %)	maximum (wt. %)
Silicates					
Almandine	$Fe_3Al_2(SiO_4)_3$	0.76 ± 0.35	0.86	0.24	1.2
Dravite	$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$	4.4 ± 1.5	4.5	1.7	7.2
Quartz	SiO_2	57 ± 13	61	24	73
Zircon	$ZrSiO_4$	3.3 ± 1.0	3.2	0.57	4.7
Phyllosilicates					
Kaolinite	$Al_2Si_2O_5(OH)_4$	5.7 ± 9.0	2.6	0.59	39
Illite	$K_{0.65}Al_{2.0}(Al_{0.65}Si_{3.35}O_{10})(OH)_2$	2.6 ± 0.72	2.6	1.4	3.4
Illite-Smectite		6.7 ± 4.5	6.8	2.3	15
Oxides					
Anatase	TiO_2	2.4 ± 0.66	2.4	1.0	3.7
Ilmenite	$FeTiO_3$	1.3 ± 0.51	1.4	0.47	2.1
Magnetite	Fe_3O_4	0.27 ± 0.11	0.29	0.12	0.47
Rutile	TiO_2	5.4 ± 1.6	5.6	2.7	8.1
Carbonates					
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	0.82 ± 0.19	0.79	0.52	1.1
Calcite	$CaCO_3$	0.52 ± 0.53	0.35	0.23	1.8
Dolomite	$CaMg(CO_3)_2$	2.5 ± 1.8	1.9	0.46	6.7
Siderite	$FeCO_3$	6.6 ± 3.8	5.6	2.4	18
Sulfides					
Pyrite	FeS_2	6.5 ± 2.7	7.0	1.4	9.9
Marcasite	FeS_2	1.0 ± 0.47	0.95	0.25	2.1
Sulfates					
Gypsum	$CaSO_4 \cdot 2H_2O$	0.71 ± 0.40	0.56	0.25	1.1
Jarosite	$KFe_3(SO_4)_2(OH)_6$	0.22 ± 0.07	0.25	0.11	0.27

Quantification by Rietveld refinement according to:
Raudsepp and Pani (2003) MAC Short Course Vol. 3, pp. 165–180.

Source: Lindsay et al. (2019) *Appl. Geochem.* 102: 186-196. https://doi.org/10.1016/j.apgeochem.2019.02.001

Mineralogy

a–c. FTT sample in (a) transmitted ppl, (b) transmitted xpl, and (c) reflected ppl;

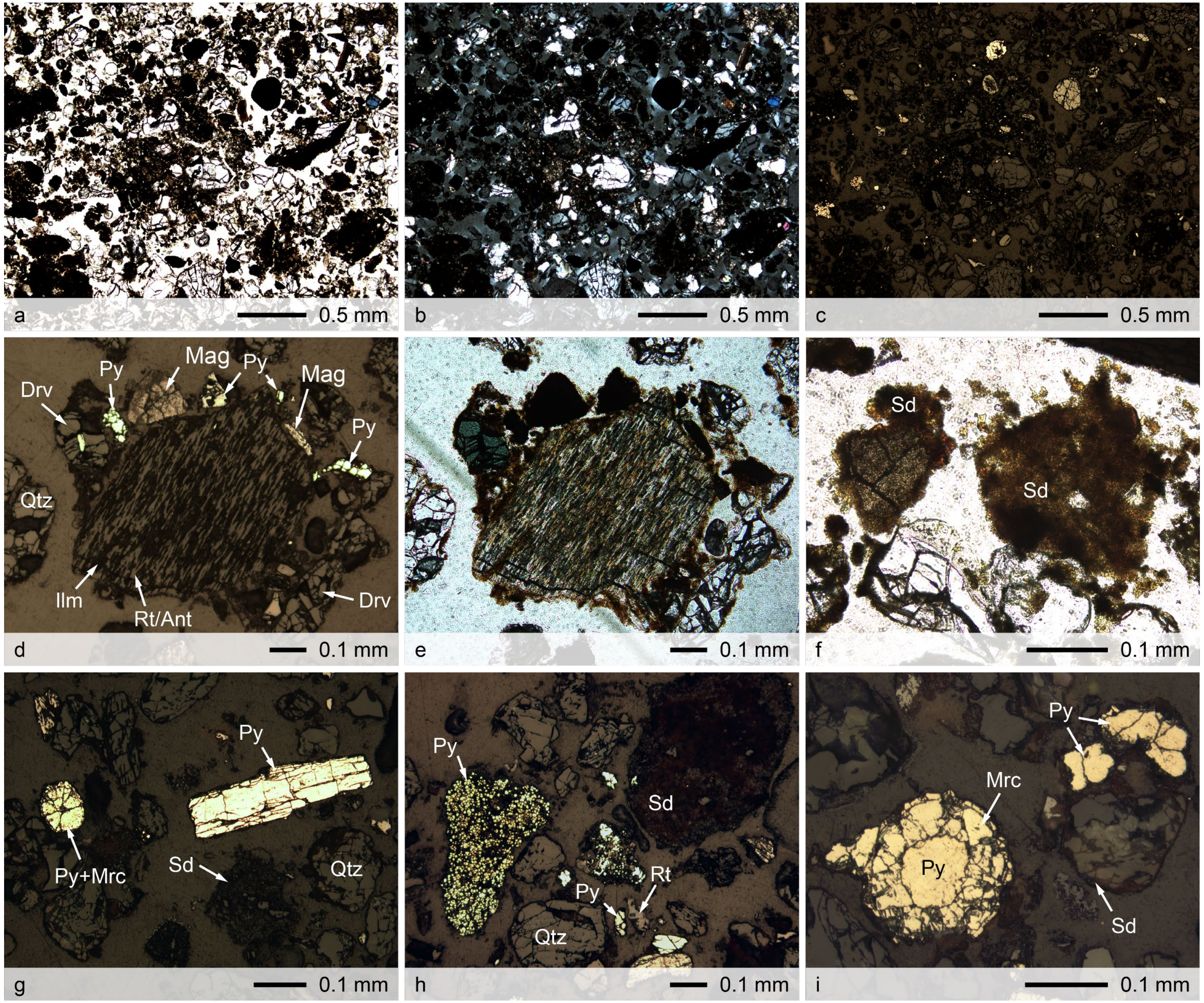
d. leucoxene textured ilmentite (Ilm) in reflected ppl with rutile (Rt) or anatase (Ant), pyrite (Py), magnetite (Mag), dravite (Drv) and quartz (Qtz);

e. siderite (Sd) in transmitted ppl (e);

f. acicular Py and marcasite (Mrc) and elongate subhedral Py with Sd and Qtz;

g–h. clustered Py framboids with discrete Mag, Sd, Rt and Qtz grains; and

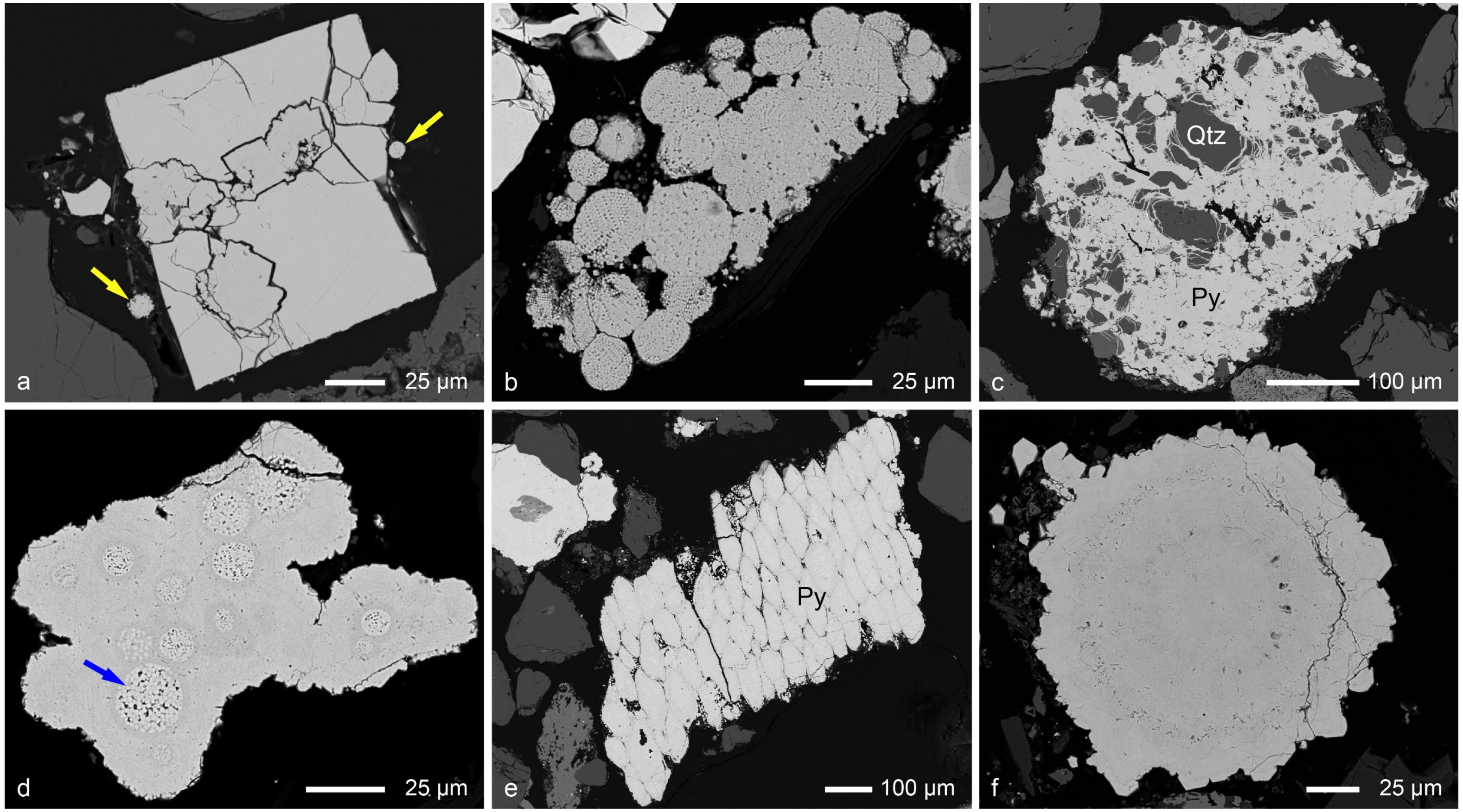
i. Mrc rim on weathered Py framboid with Sd.



Polished 30 µm thin sections.
ppl: plane polarized light
xpl: cross-polarized light

Source: Lindsay et al. (2019) *Appl. Geochem.* 102: 186-196. https://doi.org/10.1016/j.apgeochem.2019.02.001

Mineralogy



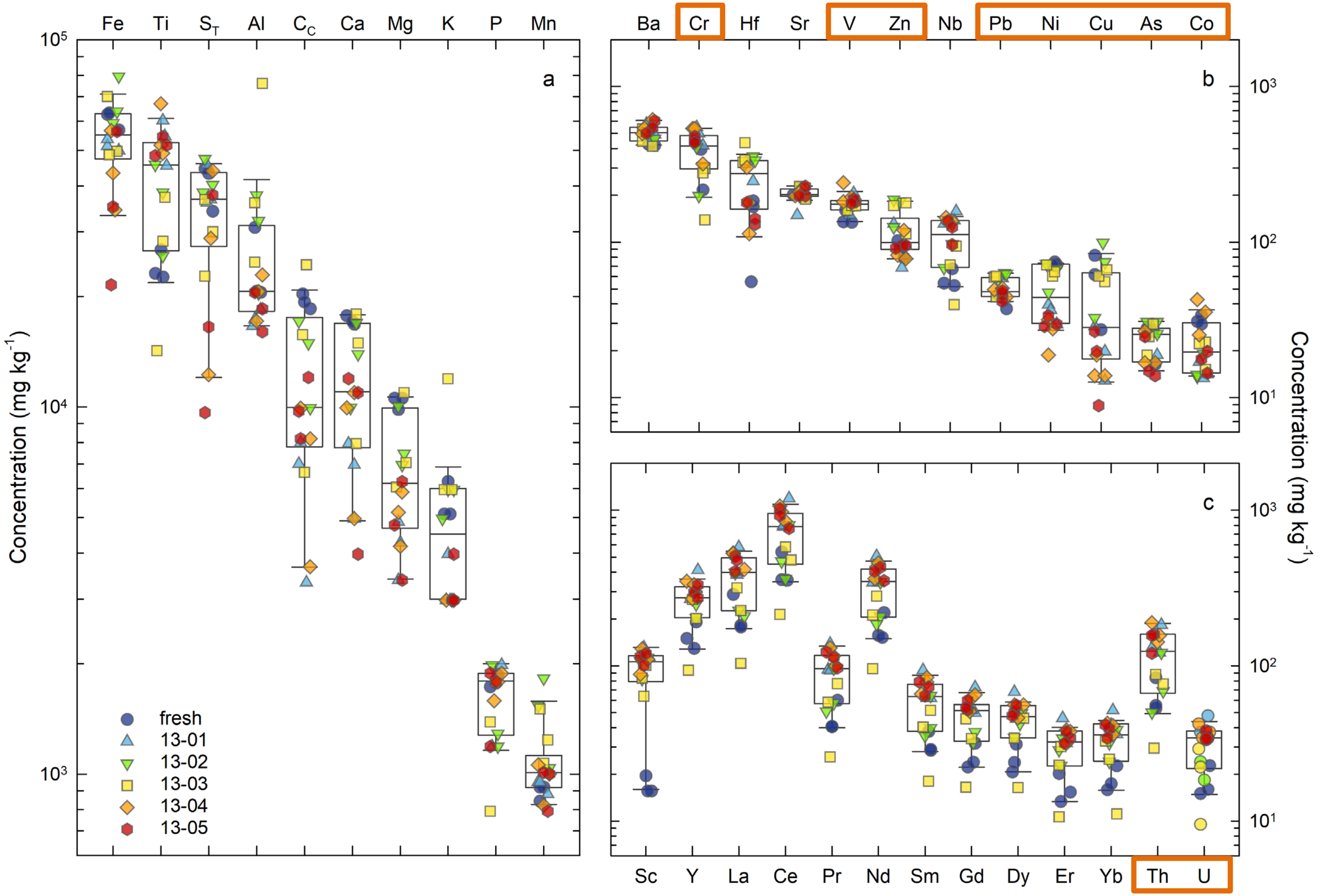
a. euhedral pyrite with discrete framboids at arrows;
b. clustered and intergrown pyrite framboids;
c. pyrite (Py) intergrowth with quartz (Qtz);
d. pyrite overgrowth on remnant framboids;
e. pyrite permineralization of organic matter; and
f. acicular radiating pyrite with marcasite.

Backscattered electron images of polished thin sections.

Source: Lindsay et al. (2019) *Appl. Geochem.* 102: 186-196. https://doi.org/10.1016/j.apgeochem.2019.02.001

Geochemistry

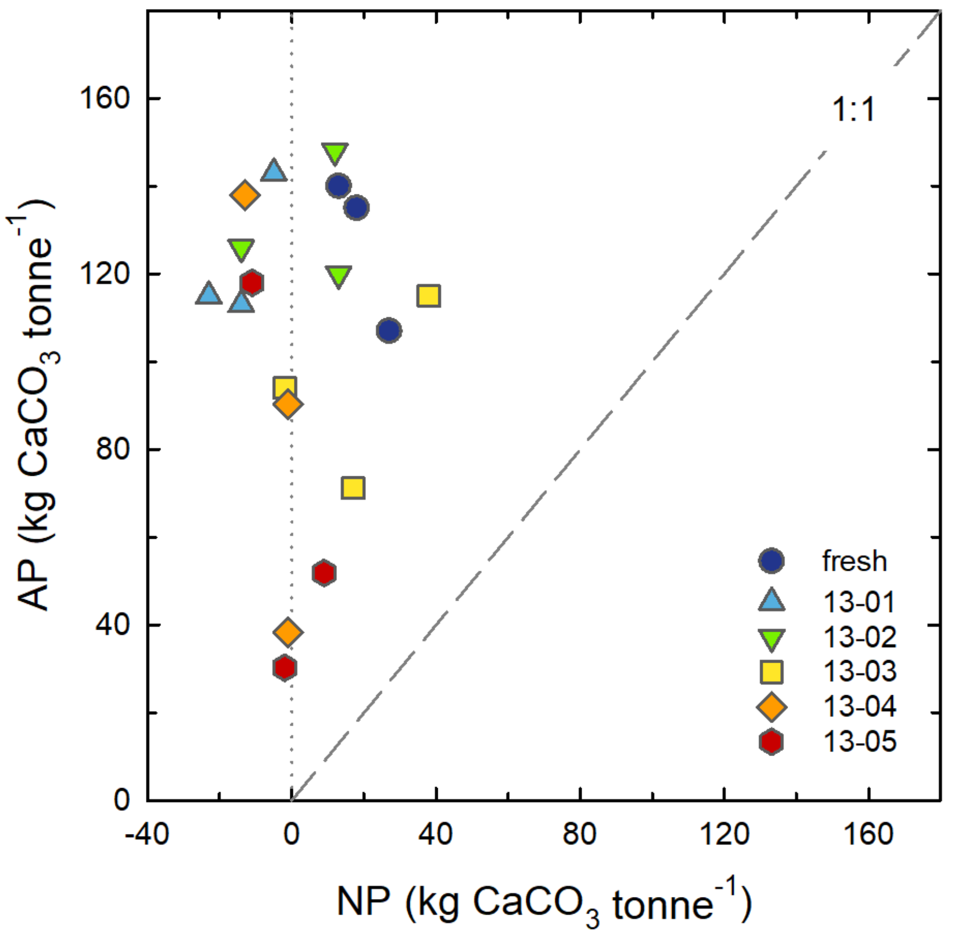
- major element composition generally reflect mineral assemblage
- pyrite contains As, Cu, Co, Fe, Mn, Ni (plus trace Se and V)
- Fe, Mn, Ni, Pb, Sr and Zn associated with carbonates
- REEs, Th and U likely associated with zircon, monazite, and xenotime
- Cr and V likely associated with multiple phases



Source: Lindsay et al. (2019) *Appl. Geochem.* 102: 186-196. https://doi.org/10.1016/j.apgeochem.2019.02.001

Acid-Base Accounting

- consistent negative net neutralization potential (NNP)
- low or negative neutralization potential (NP)
  - negative values attributed to partial dissolution of Fe(II)-bearing phases during acid addition
- potential for acid generation during oxidative weathering
  - findings consistent with mineralogical analysis



Source: Lindsay et al. (2019) *Appl. Geochem.* 102: 186-196. https://doi.org/10.1016/j.apgeochem.2019.02.001

Field Study: 2015

- purpose:
  - preliminary examination of FTT pore-water chemistry
- methods:
  - direct-push coring to refusal (< 1 to ~3 m bgs)
  - hardpan encountered at L04, L05, L06
- analyses:
  - pore-water: squeezing, chemistry
  - mineralogy: optical, SEM, XRD
  - geochemistry: digestions, XRF/XAS
  - ABA: modified Sobek with siderite correction
  - microbiology: 16S rRNA gene sequencing

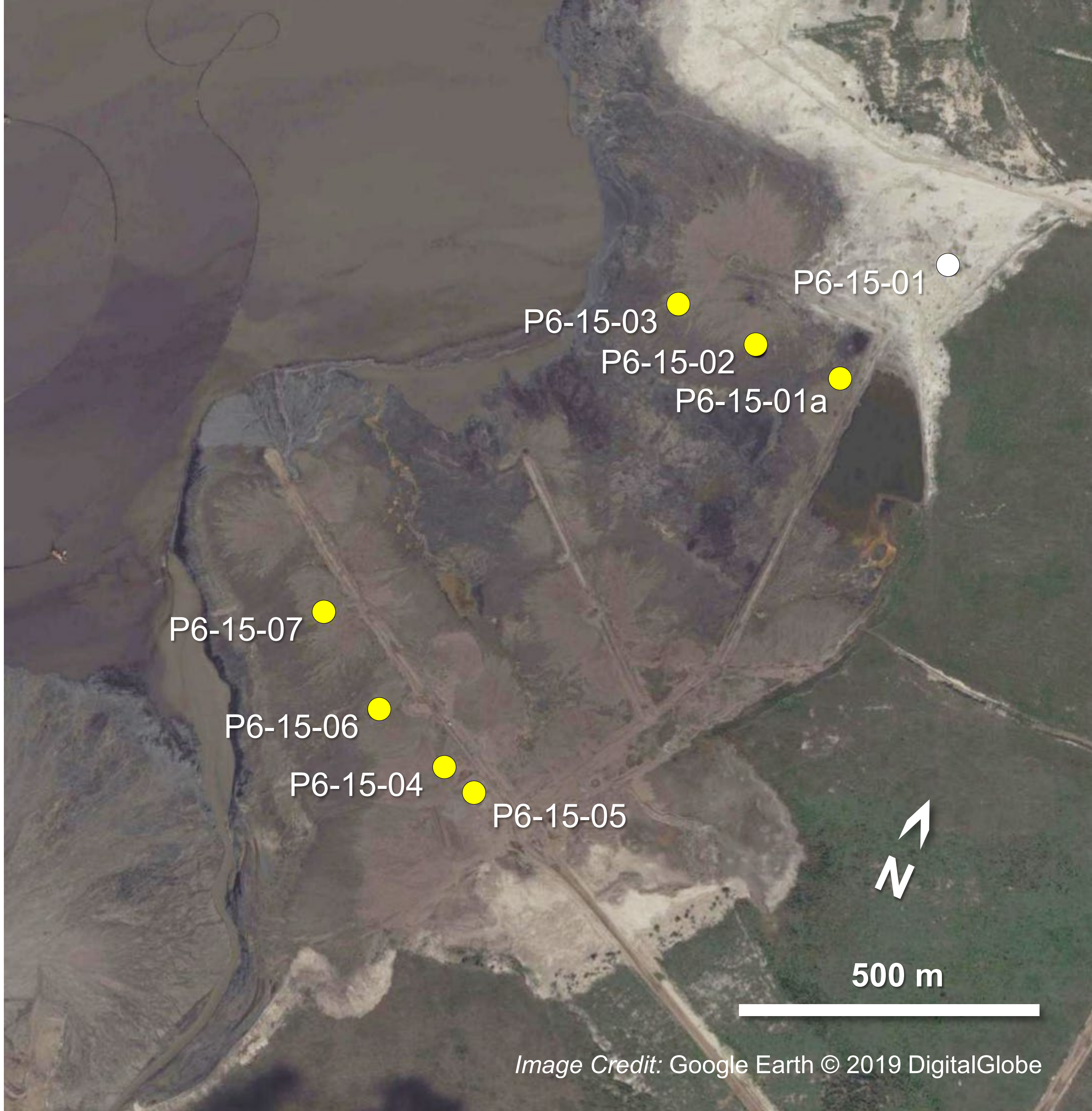
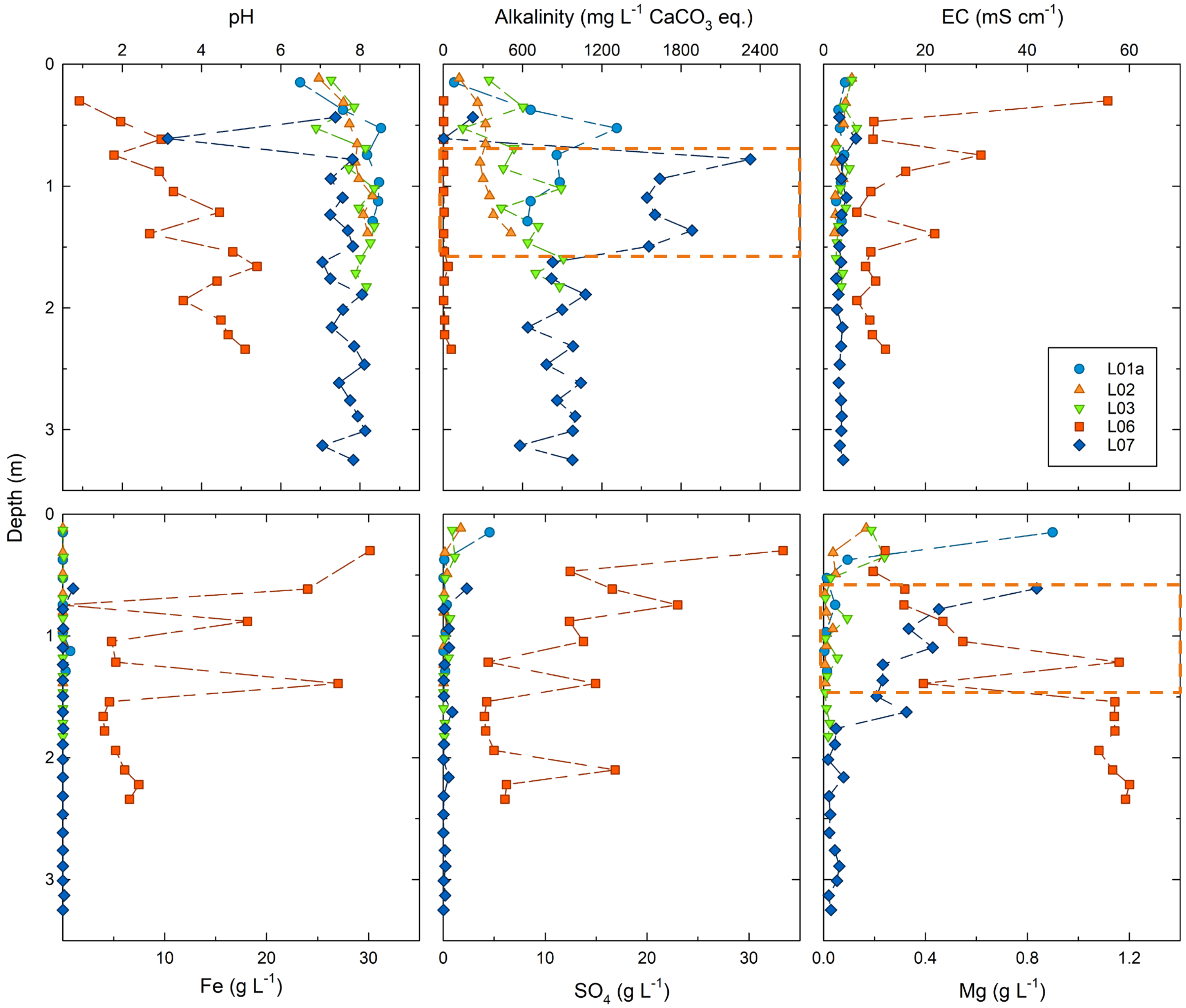


Image Credit: Google Earth © 2019 DigitalGlobe

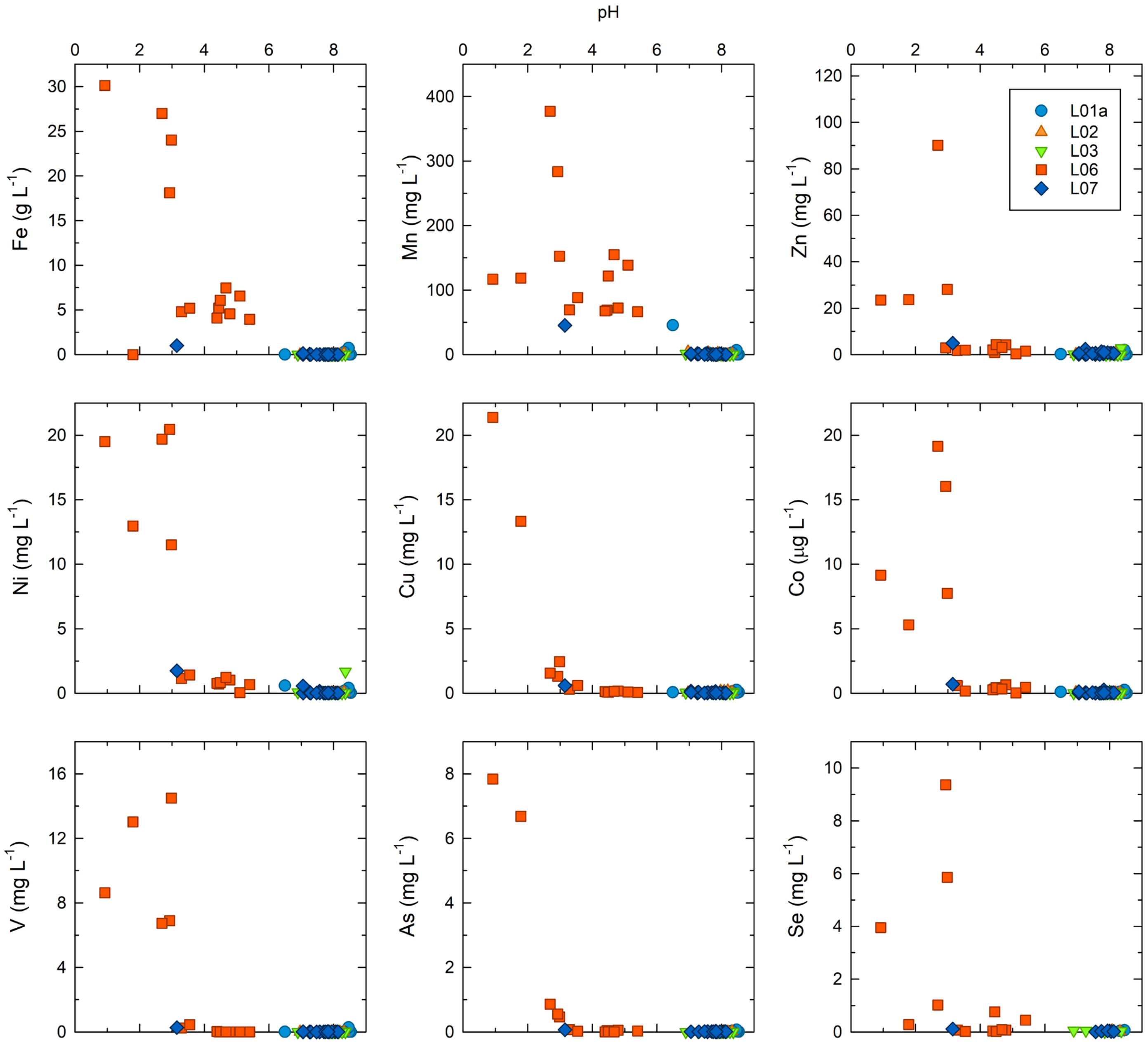
Pore-Water Chemistry

- Locations 01a–03:
  - circumneutral pH, relatively low dissolved metal concentrations
- Locations 04–05:
  - extensive hard pan (limited sample)
- Location 06:
  - acidic pH, no alkalinity, high EC and dissolved metal concentrations
- Location 07:
  - evidence of weathering front
  - Mg and alkalinity low in upper 0.5 m
  - acidic conditions likely to develop with time



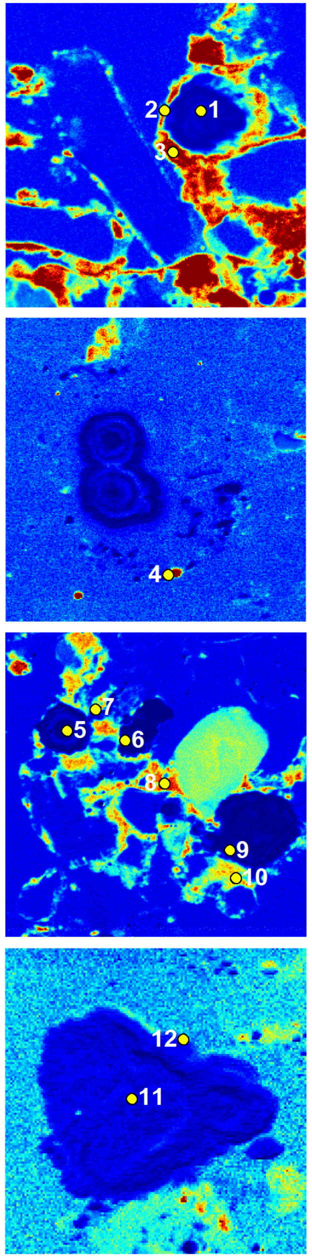
Pore-Water Chemistry

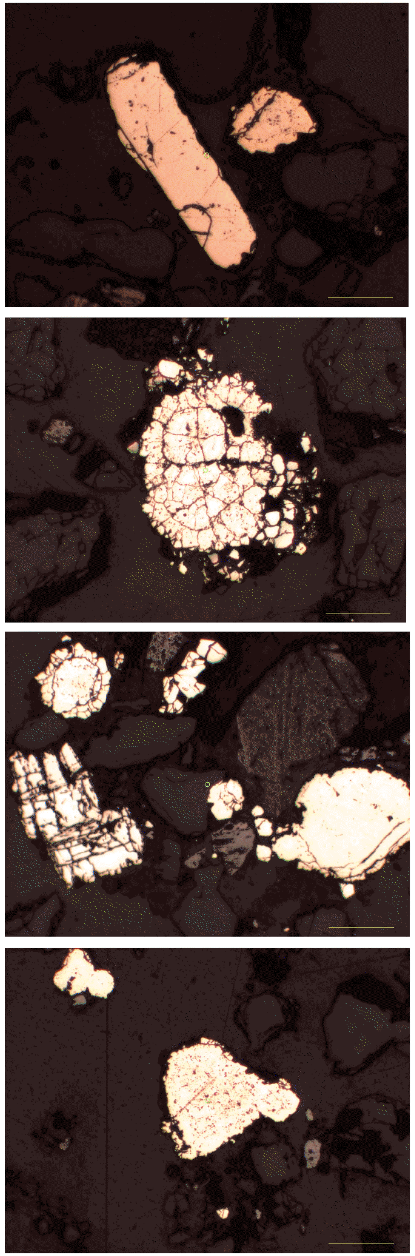
- large increase in dissolved metal(loid)s at pH < 5
  - increased solubility of metal (hydr)oxides and carbonates with decreasing pH
  - limited capacity for metal(loid) sorption

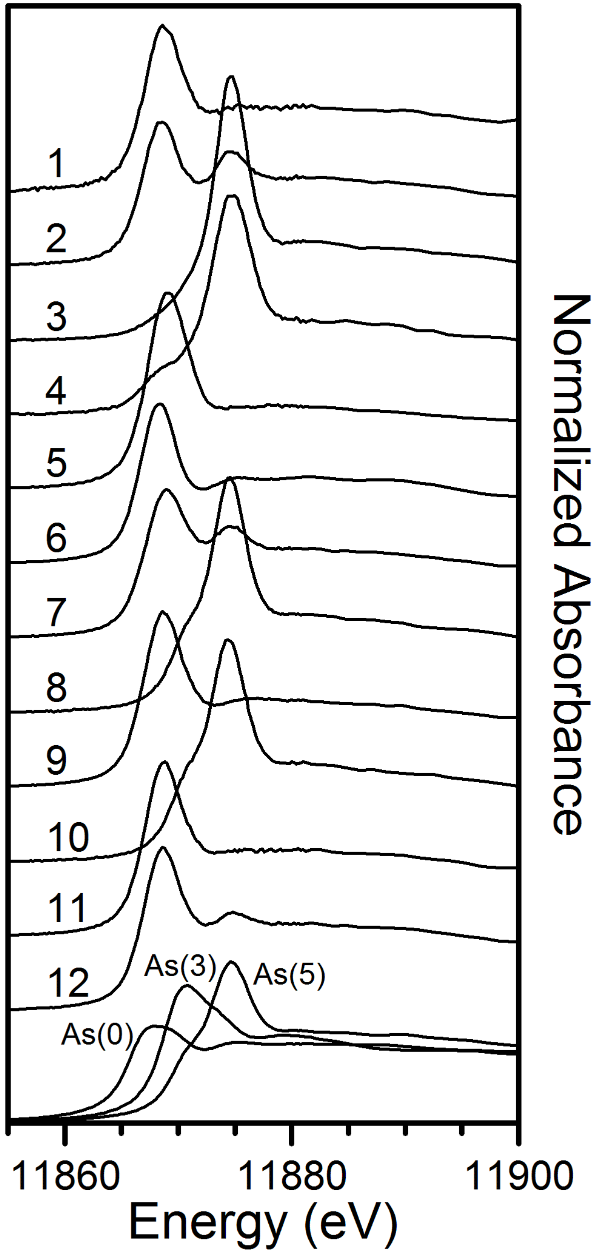


Arsenic Mobility

- As released during pyrite oxidation
- As(V) accumulation in vadose zone
  - associated with Fe(III) (oxyhydr)oxides
- long-term mobility likely controlled by:
  - pH-dependent precipitation-dissolution and sorption reactions
  - As and Fe redox cycling



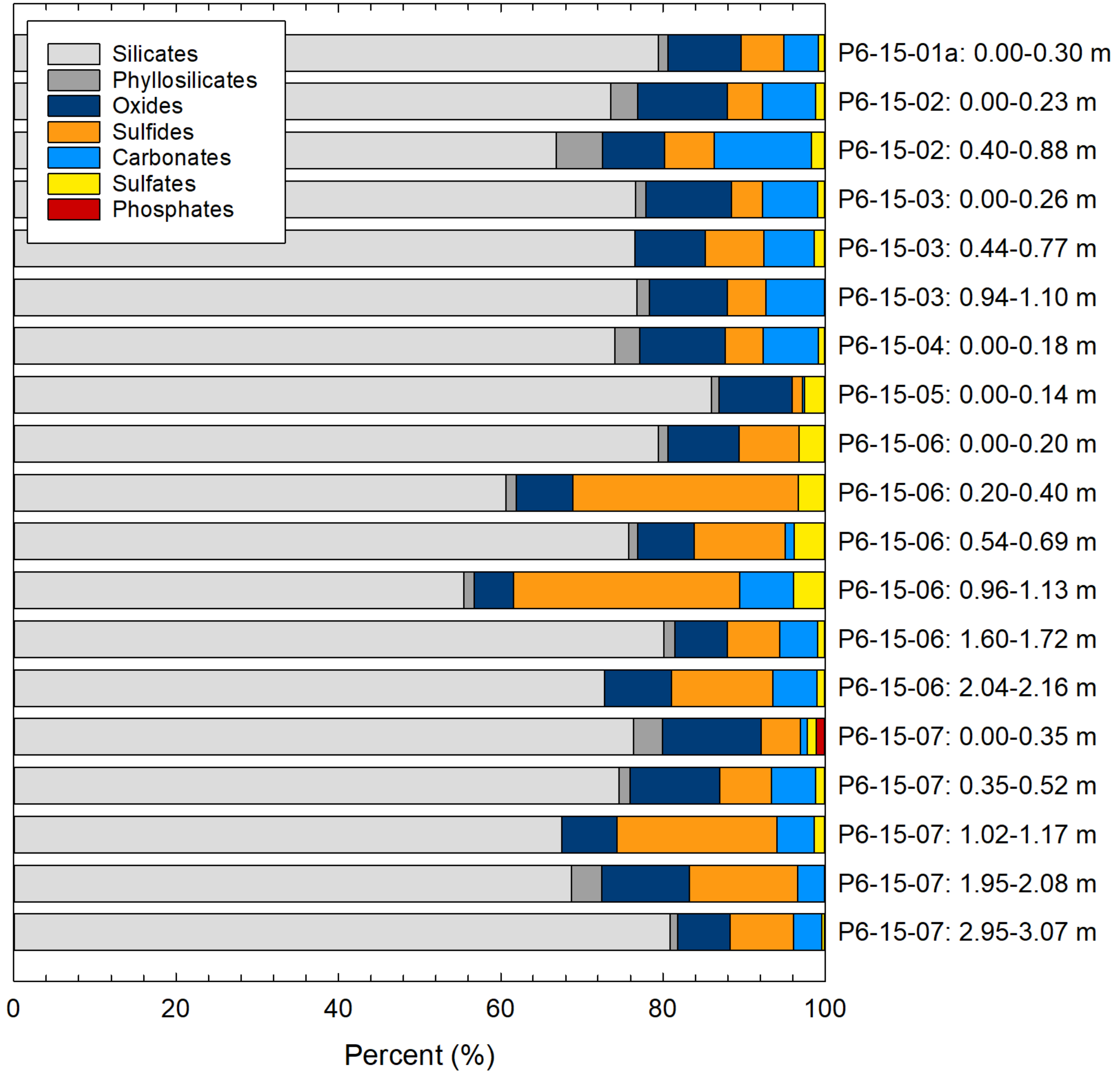




Left: synchrotron µXRF maps of As speciation.
Middle: reflected light microscope photograph.
Right: synchrotron µXANES spectra.

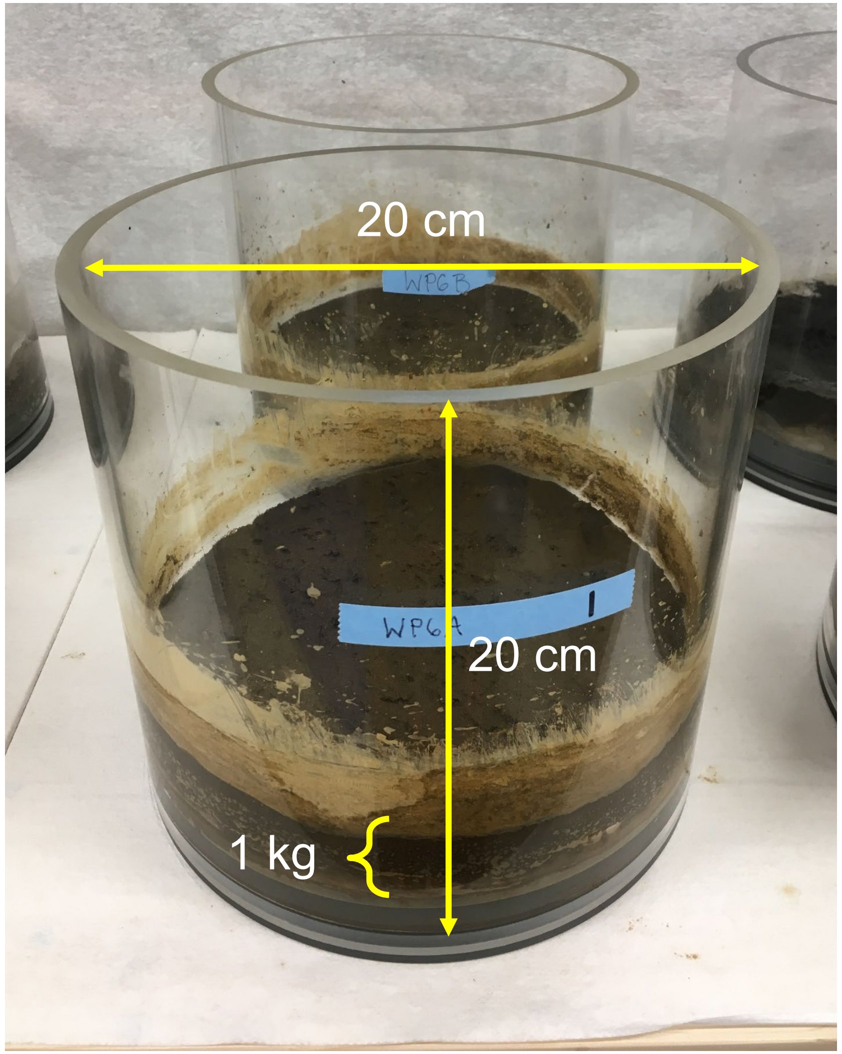
Mineralogy

- wider range of sulfide and carbonate contents than observed in 2013 study
  - sulfides: 1.3 to 27 wt. % (median 7.2 wt. %)
  - carbonates: < 1 to 15 wt. % (median 5.4 wt. %)
  - siderite accounted for 61 to 100% of carbonates
- varied degree of weathering
  - sulfides and carbonates depleted in highly weathered samples
  - jarosite and gypsum accumulation apparent
- large amorphous component in weathered tailings
  - ongoing research to identify these phases and assess their influence on metal(loid) mobility



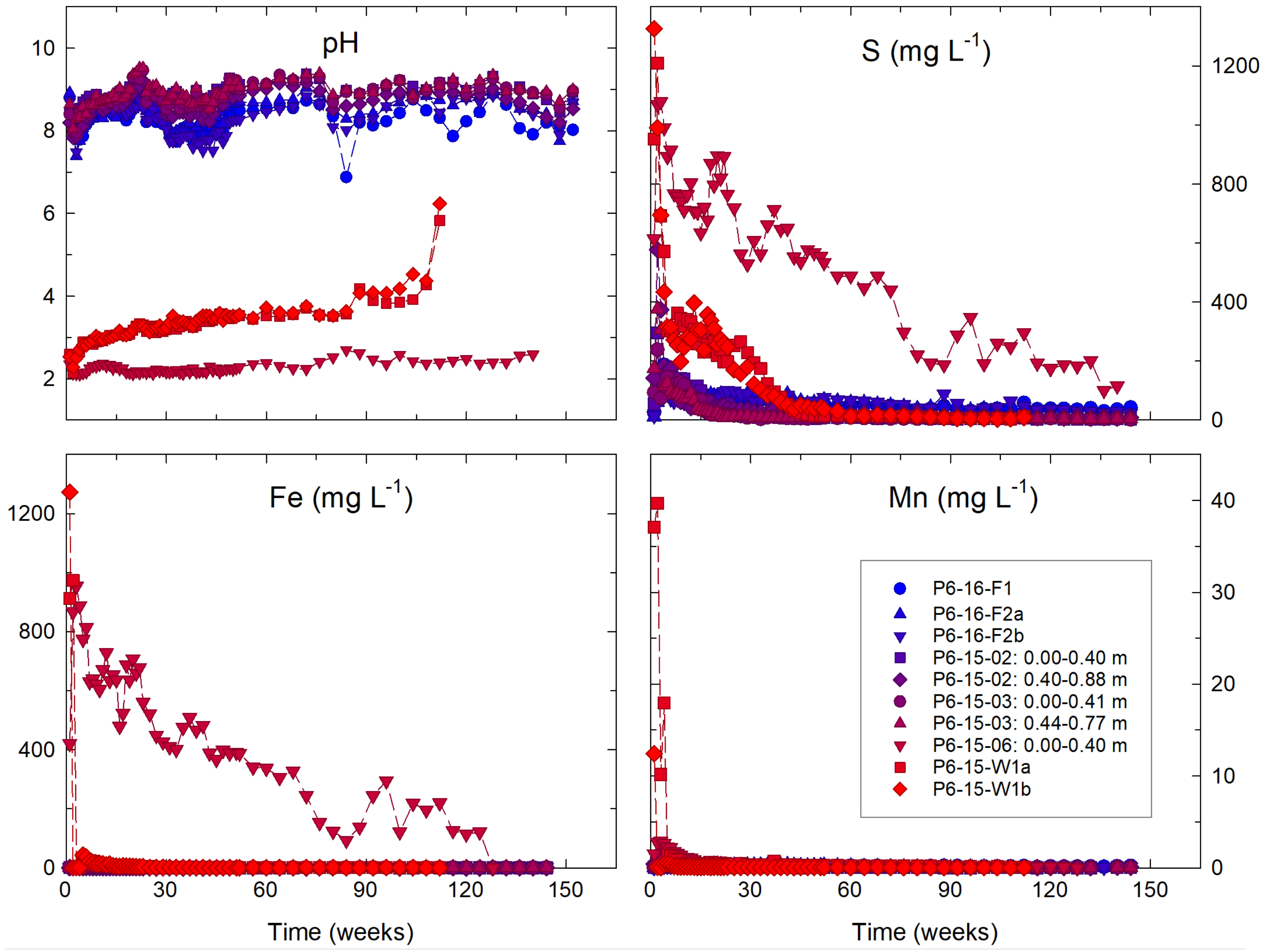
Laboratory Study: 2016–present

- purpose:
  - assess acid generation and metal leaching over time in varied samples
- methods:
  - 1 kg (eq. dry wt.) of FTT (no solvent wash) placed in each column
  - glass wool and perforated support
  - ambient lab conditions (PO_2, T, RH)
  - flushed with 1 L of DI every 7th day
- analyses:
  - chemical analysis of leachate
  - mineralogy at beginning and end



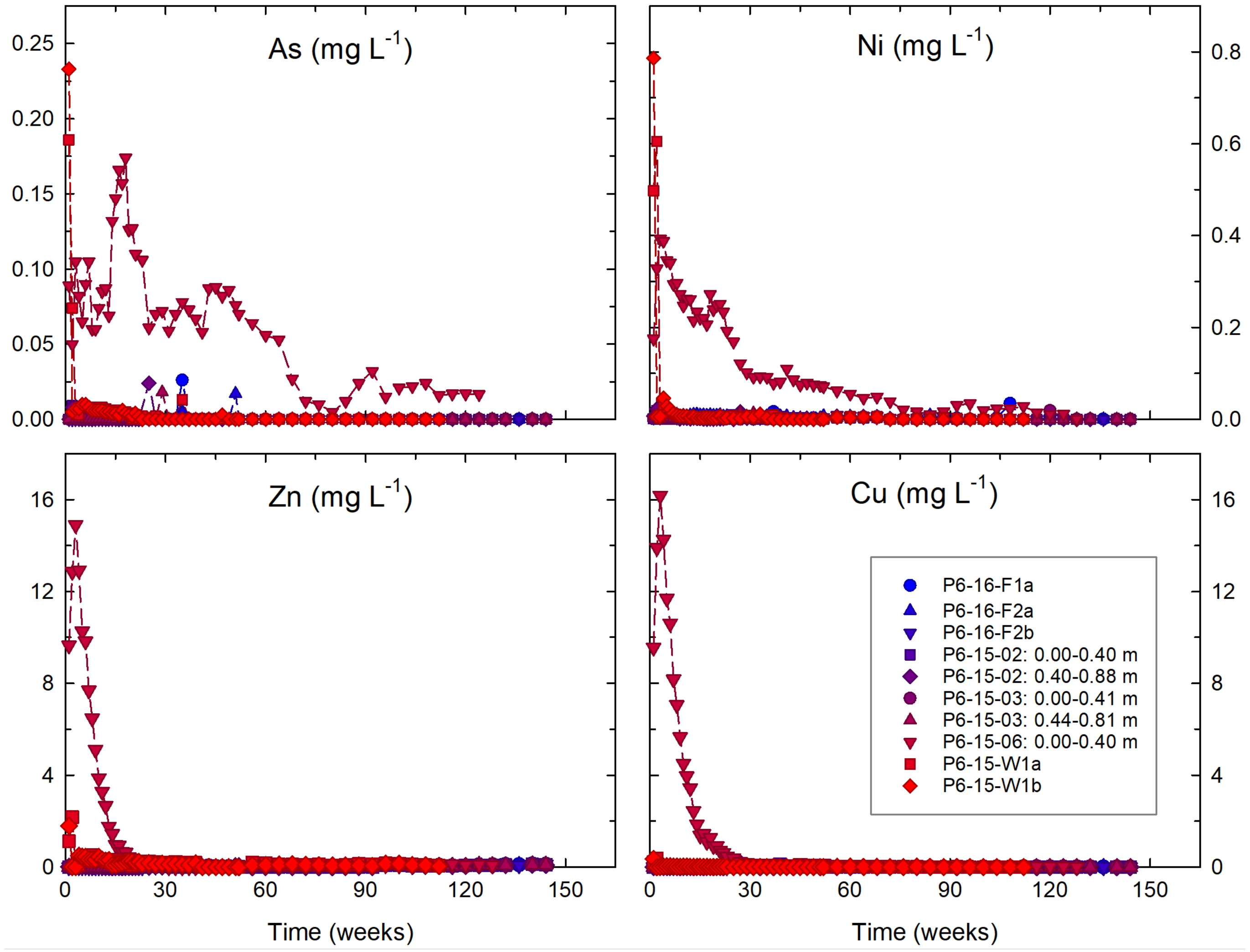
Column Drainage

- drainage pH ranges from ~2 to 9
  - weathered FTT samples generated acid for extended time
  - evidence of ongoing oxidation in fresh/non-weathered FTT samples
- ongoing S release indicative of sulfide-mineral oxidation
  - apparent in fresh FTT samples and
    - P6-16-F1, P6-16-F2a, P6-16-F2b
  - S release declining with time for P6-15-06



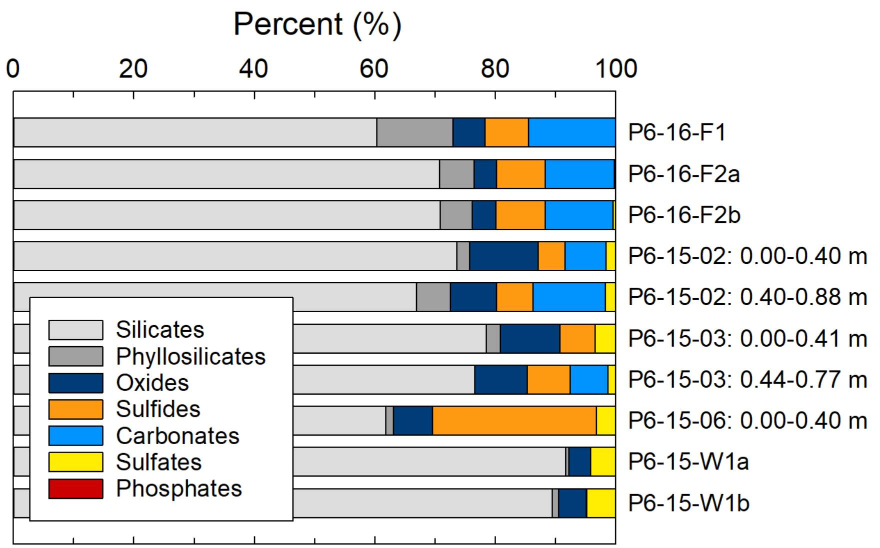
Column Drainage

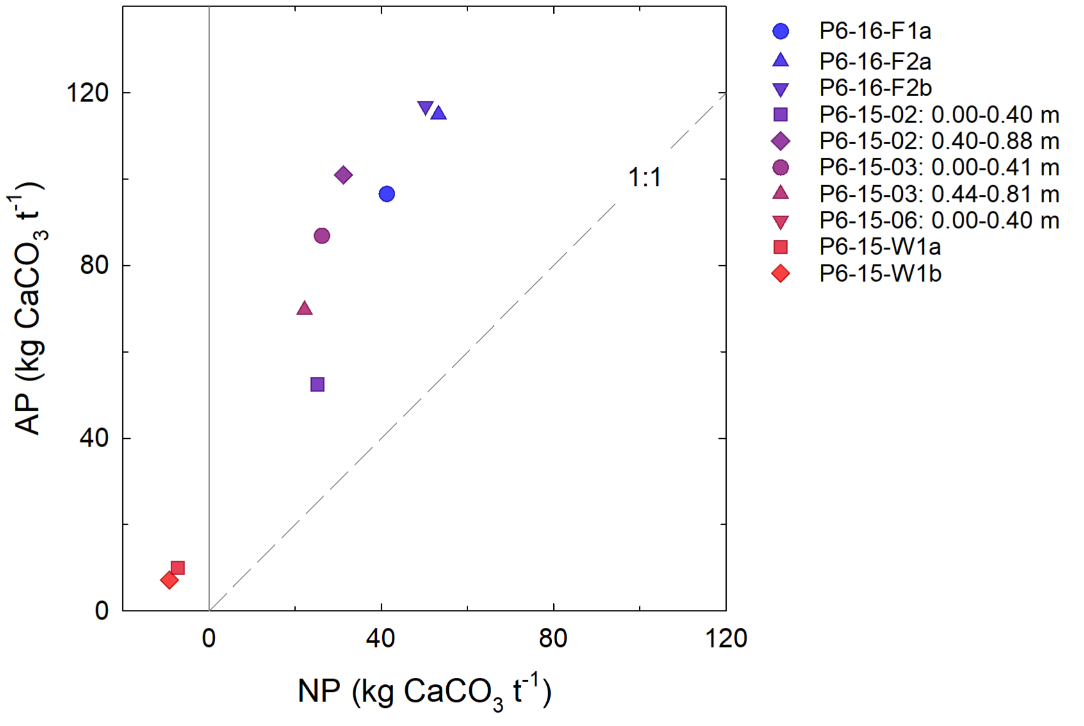
- metal(loid)s present in leachate
  - concentrations not representative of potential field conditions
- concentrations generally low in pH 7–9 leachate
  - likely due to sorption or co-precipitation reactions with Fe(III) (oxyhydr)oxides
- highest concentrations observed in FTT sample P6-15-06
  - exhibits pH < 3 and evidence of active oxidation (i.e., S release)



Column Solids

- ABA results indicate that all FTT samples are likely acid generating
- only initially weathered samples generated drainage with pH < 3
- evidence of ongoing sulfide-mineral oxidation in initially non-weathered samples
  - sustained S, Ca and Mg release
- carbonate assemblage comprised of 60 to 100% siderite
  - lower siderite content in initially non-weathered samples





Lessons Learned

- acid generation and metal leaching
  - acid rock drainage type waters can be generated
  - sulfide content and water-saturation are key variables
- acidic waters ($pH < 5$) characterized by:
  - high dissolved sulfate and iron concentrations
  - high dissolved metal(loid) concentrations (i.e., As, Se, V, Ni, Zn, Cu, Co)
- time to acid generation likely fairly long
  - organics may limit initial oxidation rates
  - metal(loid) source terms change over time
- acid generation and metal transport may be mitigated
  - sub-aqueous disposal, soil covers, etc.
  - sulfidogenesis, passive treatment, etc.

Ongoing/Future Research

- develop models of the geochemical evolution of FTT deposits
- assess efficacy of current oil sands mine reclamation strategies
- evaluate new approaches for mitigating acid generation and metal release

Funding:

NSERC CRSNG

Syncrude Securing Canada's Energy Future

Industrial Research Chair in Mine Closure Geochemistry

Field/Lab Support:

Noel Galuschik, Dr. Soumya Das, Drake Meili, Lawrence Swerhone
University of Saskatchewan

Dr. Jordan Hamilton, Dallas Heisler, Wendy Kline,
Tara Penner, Jessica Piercey
Syncrude Canada Ltd.

ConeTec Investigations