Tailings and Mineral Carbonation: The Potential for Atmospheric CO$_2$ Sequestration

H. Andrew Rollo
Lorax Environmental Services Ltd.

Heather. E. Jamieson
Department of Geological Sciences and Geological Engineering
Queen's University

Claudine A. Lee
Dillon Consulting Ltd.

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<u>Overview</u>

- Carbon Dioxide Sequestration

- History of Investigations

- Ekati Diamond Mine (location, geology, processing)

- Mineralogy

- Water Chemistry

- Modeling Results

- Estimates of annual CO_2 sequestration

- Conclusions and Implications

CO$_2$ Sequestration

Geological Storage

– Injection directly into geological formations (oil fields, coal seams, exhausted natural gas reservoirs)

– Currently used by oil industry to help increase oil recovery

– Leakage due to fracturing decreases storage efficiency

Ocean Storage

– Injection directly into deep ocean (> 1000 m)

– Ocean eventually equilibrates with atmosphere and releases excess CO$_2$

– Poorly understood biological effects of ocean CO$_2$ storage

Organic Storage

– Uptake of atmospheric CO$_2$ by trees and plants

– Release of stored CO$_2$ when plant matter burns or decomposes

Mineral Storage (Mineral Carbonation)

– Reaction of CO$_2$ with Mg-silicate minerals to form carbonates

– Considered one of the only permanent options for storing atmospheric CO$_2$

– Energy intensive due to pretreatment requirements of mineral reactant

__Mineral Carbonation__

Olivine (forsterite)

$$Mg_2SiO_4 + 2CO_2 = 2MgCO_3 + SiO_2 + 95 \text{ kJ/mol}$$

Serpentine

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 = 3MgCO_3 + 2SiO_2 + 2H_2O + 64 \text{ kJ/mol}$$

History of Investigations

Rollo (2003)
- Define the components of the mineral-water system within the processed kimberlite containment facility at Ekati Diamond Mine
- Determine the minerals and processes controlling observed water chemistry in the processed kimberlite containment facility

Lee (2005)
- Conducted laboratory experiments to replicate process plant discharge chemistry and identify if processed kimberlite material may sequester CO_2

Ekati Diamond Mine
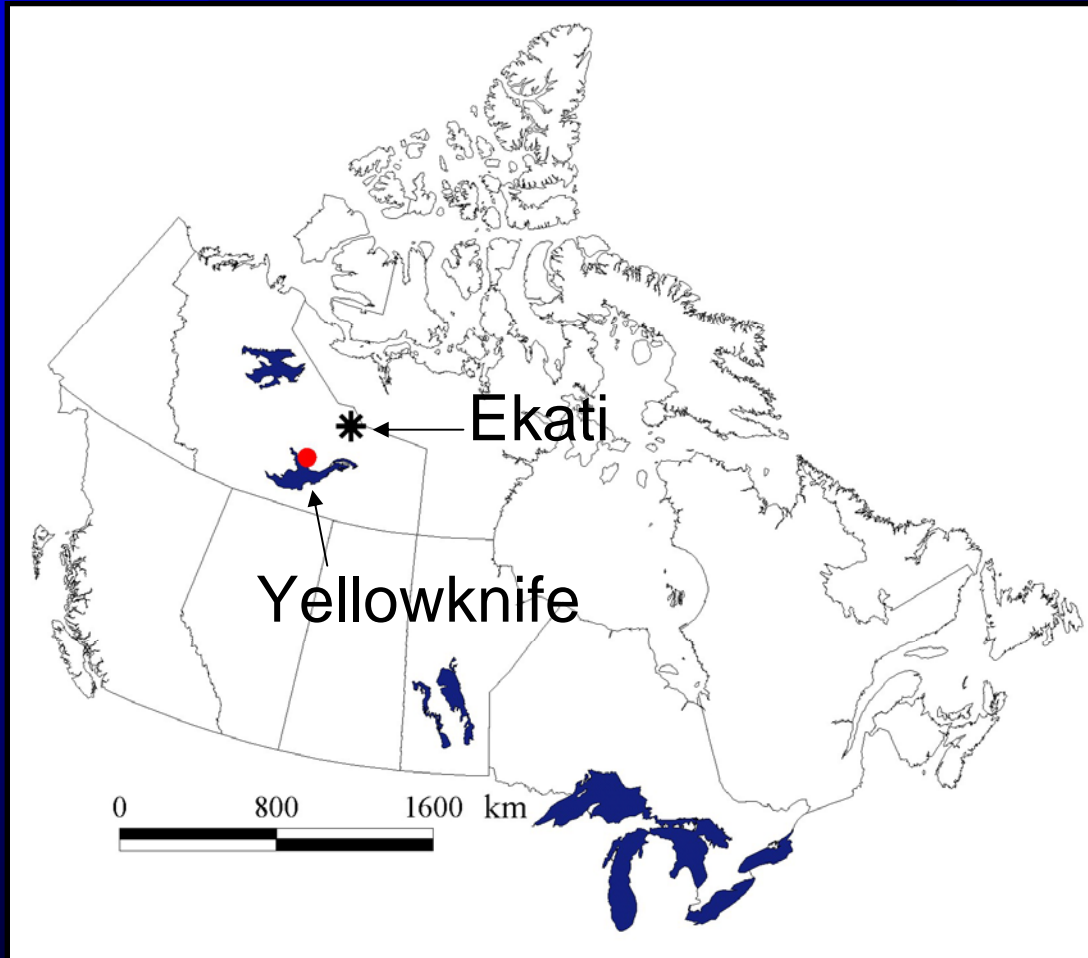
Located approximately 300 km northeast of Yellowknife within the Lac De Gras Kimberlite field

Ekati Diamond Mine

- Approximately 11 kimberlite pipes over 17 year mine life

- Combination of open pit and underground mining

- 13,000 – 16,000 wet tonnes of kimberlite processed daily

- 30,000 – 40,000 m^3 water used in the ore processing

    - 60% – 70% is recycled within the processing plant

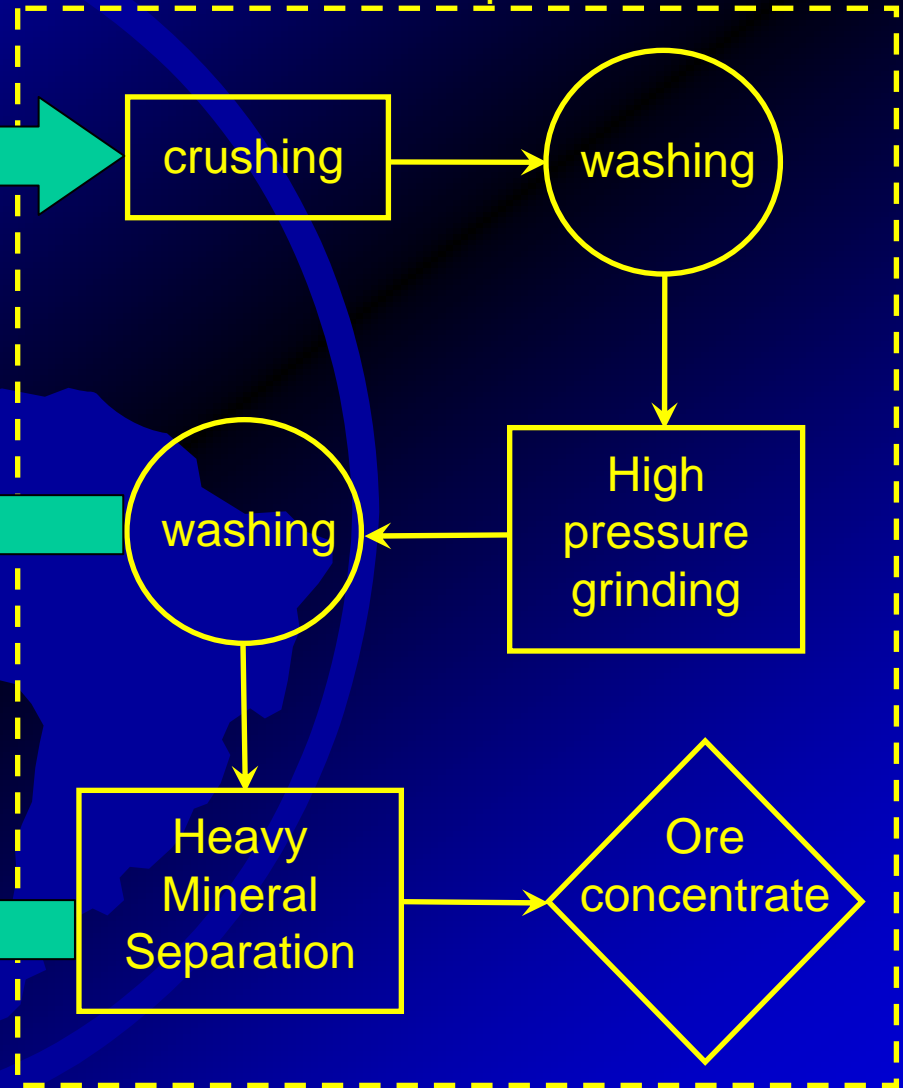   - Remainder (30% - 40%) is reclaimed from tailings storage facility
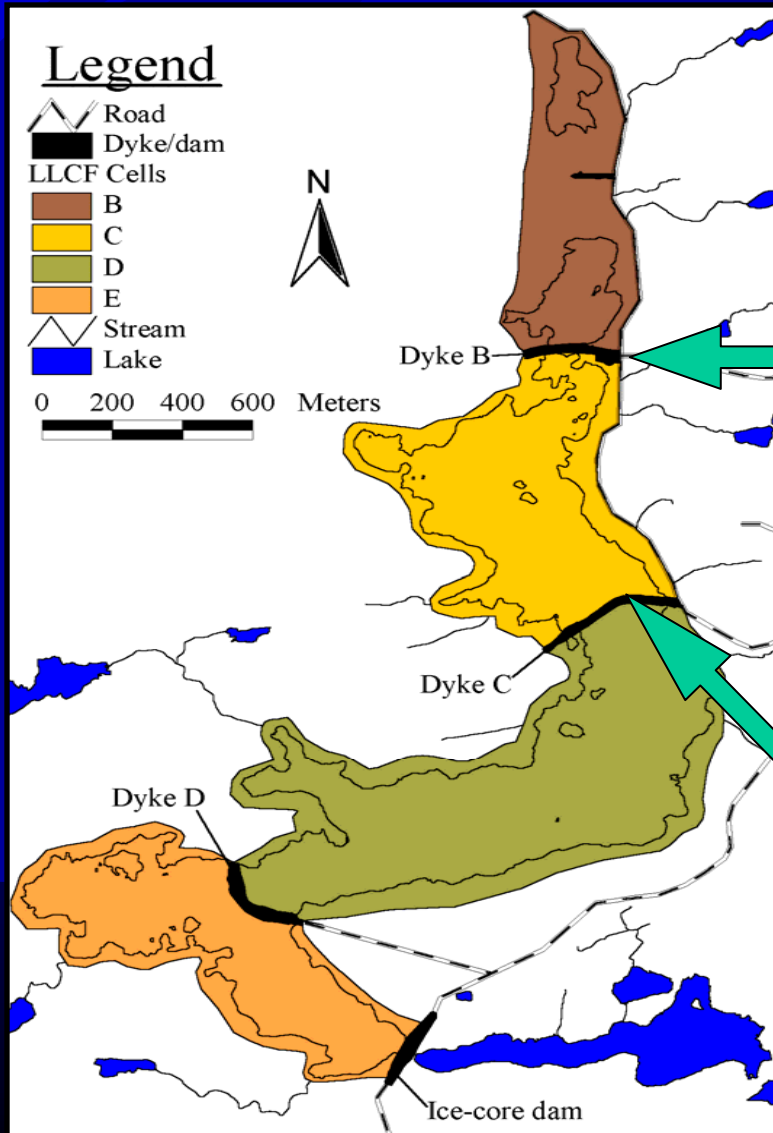
Ore processing

Kimberlite Ore

Processed kimberlite fines (< 0.5 mm)

Coarse kimberlite reject material (0.5 to 8 mm)

Process plant

crushing → washing → High pressure grinding → washing → Heavy Mineral Separation → Ore concentrate

Processed Kimberlite Fines Storage Facility

Legend

- Road
- Dyke/dam
- LLCF Cells
  - B
  - C
  - D
  - E
- Stream
- Lake

N

0 200 400 600 Meters

Dyke B

Dyke C

Dyke D

Ice-core dam

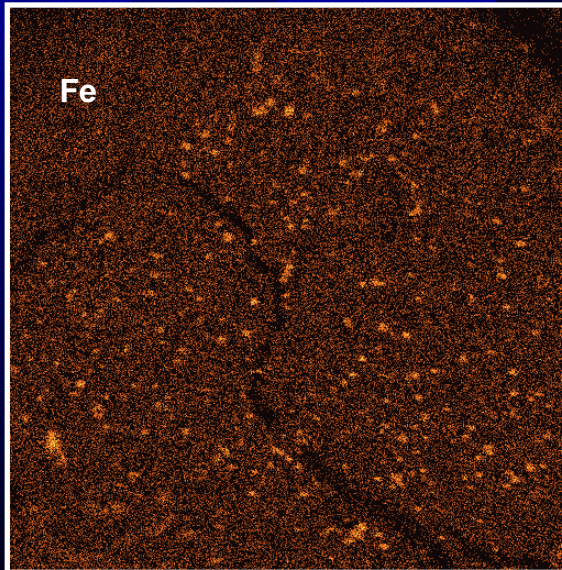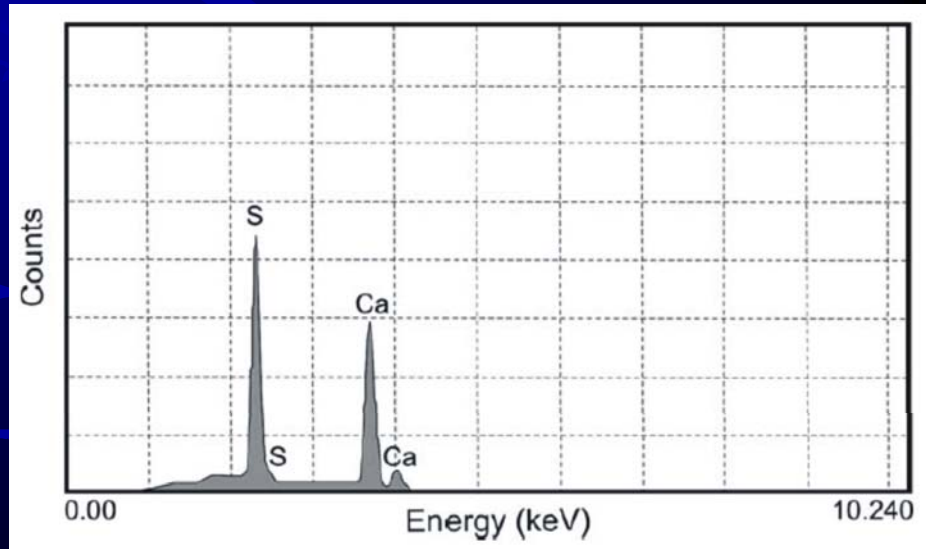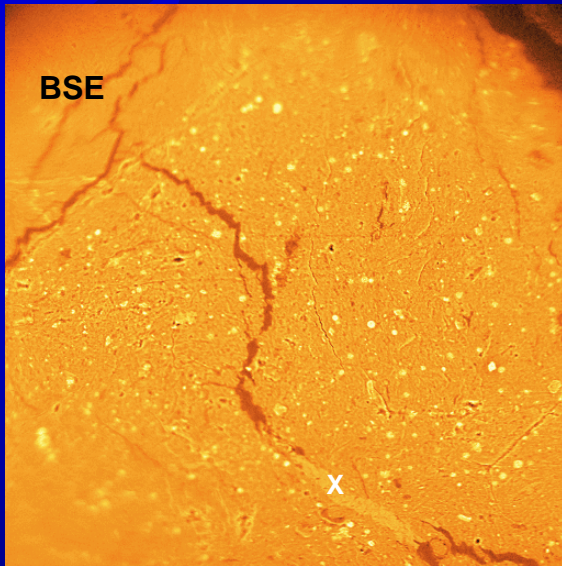Process plant discharge

Water-reclaim barge

Kimberlite Mineralogy

- Kimberlite ore is composed predominantly of serpentine and olivine (> 50%)

- Mud xenoclasts common

- Other minerals include:
    - Phlogopite
    - Pyroxene
    - Garnet
    - Calcite
    - pyrite and Ca-sulphates (restricted to mud xenoclasts)
    - Clay minerals (saponite)

- Mineralogy of processed kimberlite fines is essentially identical to unprocessed kimberlite ore (minus Ca-sulphate)

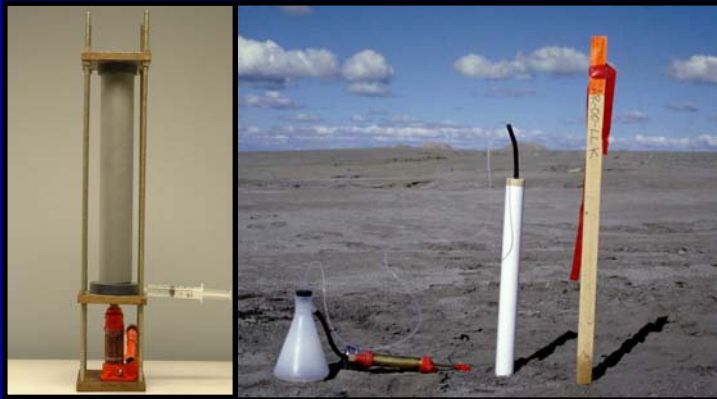- Significant amounts of Fe-oxides absent from any samples collected

Kimberlite Ore
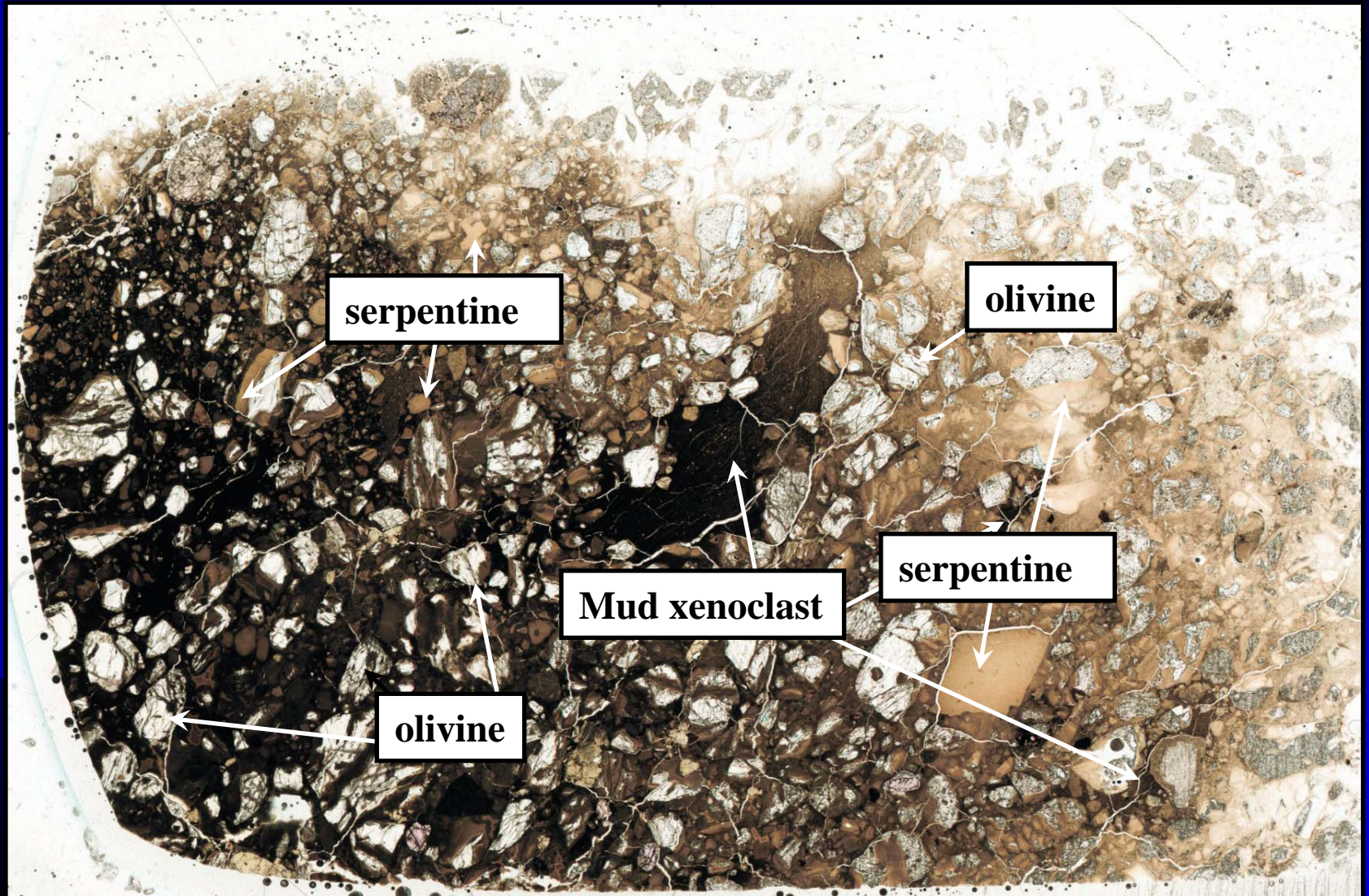
Mudstone: Sulphides and Sulphates
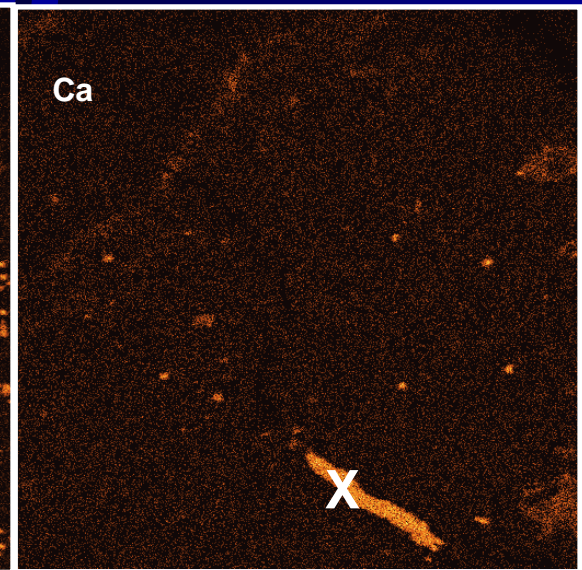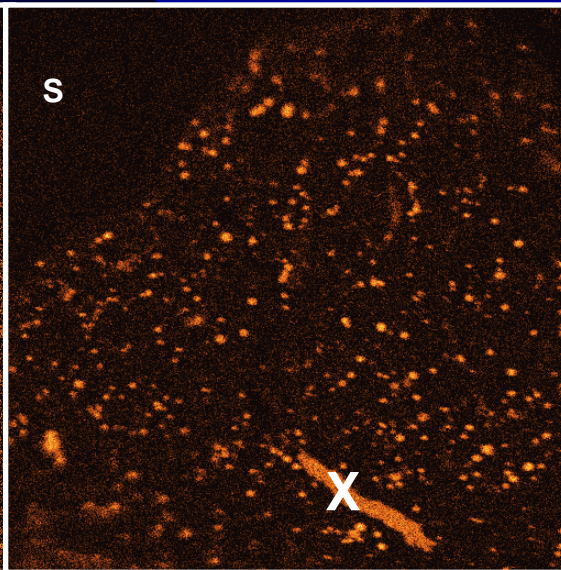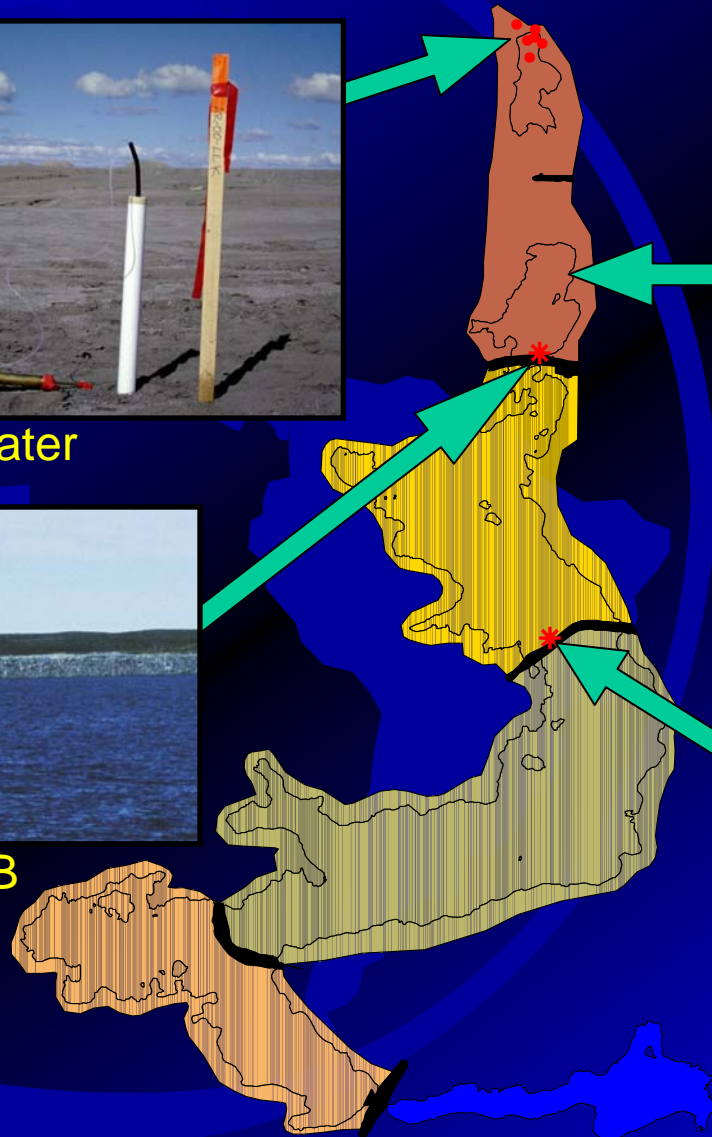
Water Samples

Pore-water

Process plant discharge

Dyke B

water-reclaim barge

Dyke C

Water Chemistry

- Approximately 90 water samples collected
- Water chemistry dominated by:
    - SO_4 (90 – 1600 mg/L)
    - Alkalinity (40 – 60 mg $CaCO_3$/L)
    - Mg (30 – 330 mg/L)
    - Ca (20 – 190 mg/L)
    - K (20 – 60 mg/L)
    - Na (8 – 15 mg/L)
    - Cl (5 – 30 mg/L)
    - Si (2 – 6 mg/L)
- pH 7 – 9
- Fe very low (< 0.5 mg/L)
- Trace metal concentrations are generally low

Saturation Indices

|	Pore-water	Discharge	Dyke B	Reclaim
Chrysotile	-1.42	-0.57	-0.21	-5.99
Forsterite	-7.31	-6.50	-6.26	-10.12
Enstatite	-2.72	-2.46	-2.51	-4.45
Diopside	-3.93	-3.59	-3.53	-7.41
Gypsum	-0.78	-1.94	-2.14	-2.32
Saponite	~3.8	~3.5	~2.6	~-3.3
Calcite	-0.17	-0.05	-0.19	-1.02
Magnesite	-0.35	-0.10	-0.36	-1.25
$CO_{2(g)}$	-3.30	-3.59	-3.73	-3.23

MgO-SiO$_2$-Al$_2$O$_3$-H$_2$O System (12°C)
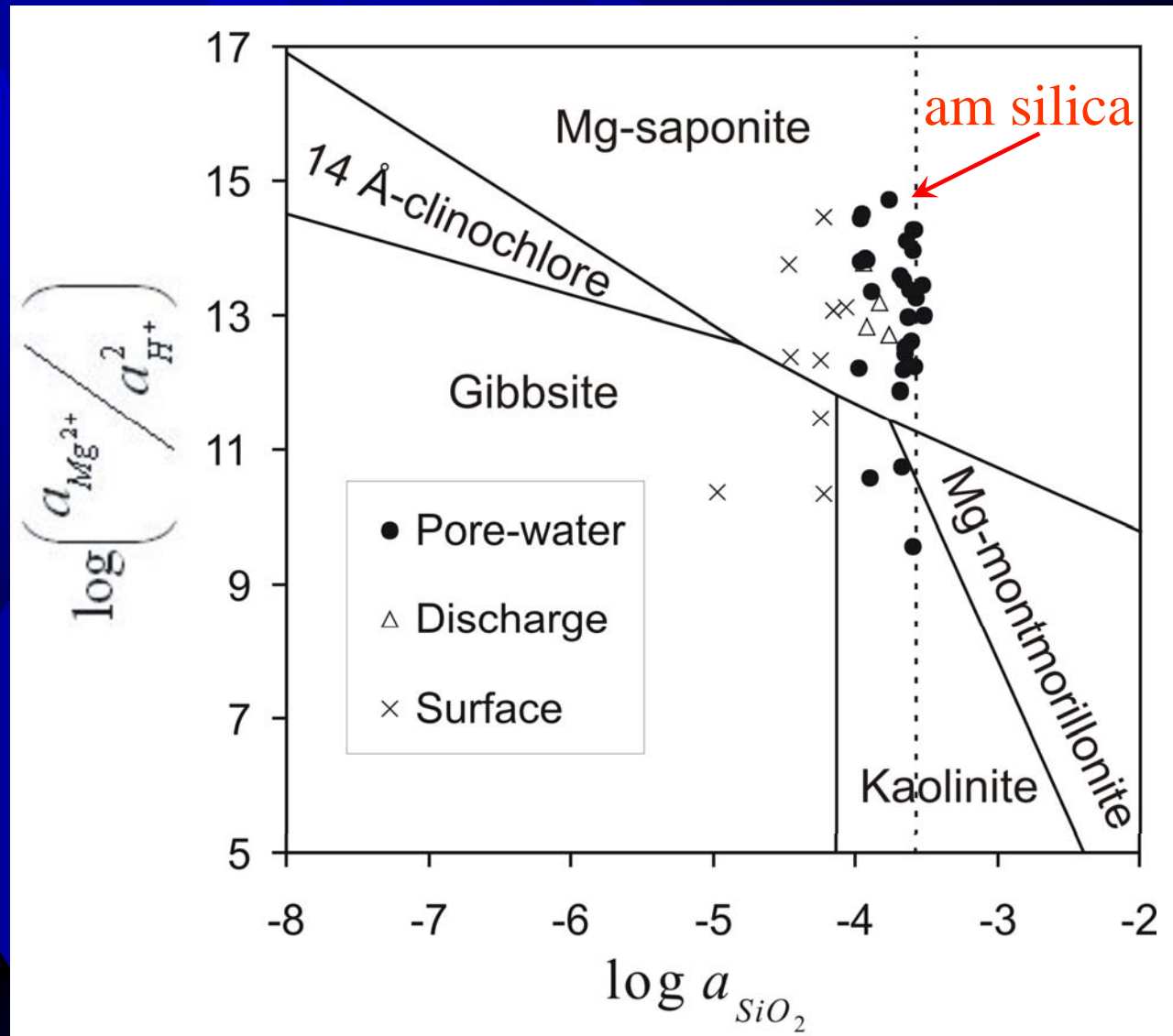
Inverse Modeling

- Mass-balance approach to determine a set a phase transfers responsible for the change in chemistry between two water samples along the same flow path

- Requires initial and final water composition plus knowledge of the mineralogy along the flow path

- Calculations conducted using PHREEQC

Water Flow Path

Process Plant

Reclaim barge
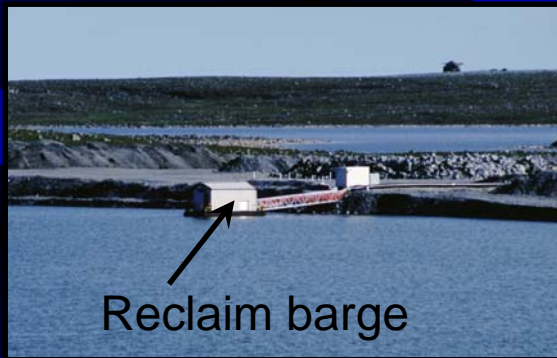
Inverse Model: Solution Chemistry

	Reclaim	Discharge
Sample Date	04-Jul-02	09-Jul-02
Temperature (°C)	16.35	20.25
pH	8.08	7.74
DO	9.99	7.84
Alkalinity (mg/L CaCO$_3$)	43.6	59.6
Ca	17.8	54.1
Fe	0.005	0.018
K	33.7	81.2
Mg	30.5	90.2
Na	12.3	22.5
Si	2.00	4.9
Cl	43	55
SO$_4$	118	472

Inverse Model: Mineralogy

Mineral	Formula
Magnesite	$MgCO_3$
Chrysotile	$Mg_3Si_2O_5(OH)_4$
CO$_2$(g)	CO_2
Forsterite	Mg_2SiO_4
Gypsum	$CaSO_4 \cdot 2H_2O$
Halite	$NaCl$
Saponite-Ca	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Saponite-K	$K_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Saponite-Mg	$Mg_{3.165}Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Saponite-Na	$Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Am. Silica	SiO_2
Fayalite	Fe_2SiO_4
Pyrite	FeS_2

Inverse Model: Scenarios

Four scenarios were modeled:

Scenario 1: Gypsum was included as main source of dissolved SO_4 and the increase in Fe was considered negligible (Fe omitted)

Scenario 2: Similar to 1, except fayalite was included as source of dissolved Fe

Scenario 3: Similar to scenario 1, except pyrite was included as source of dissolved Fe

Scenario 4: Assumed that pyrite was sole source of dissolved SO_4 (gypsum omitted)

All models generated using scenario 4 required precipitation of large amounts of Chrysotile!

Inverse Model: Results (mol/kg solution)

Mineral	Scenario 1	Scenario 2	Scenario 3
Chrysotile	5.959	5.954	5.875
$CO_2(g)$	17.88	17.86	17.63
Forsterite	--	--	--
Gypsum	0.003954	0.004151	0.004147
Halite	0.0006	0.0006	0.0006
Magnesite	-17.88	-17.86	-17.63
Am. Silica	-11.92	-11.91	-11.75
Saponite-Ca	-0.01789	-0.01908	-0.01907
Saponite-Mg	0.01500	0.01495	0.01493
Saponite-K	0.003012	0.004247	0.004239
Saponite-Na	-0.0001234	-0.0001106	-0.0001048
Fayalite	NI	0.0000001261	NI
Pyrite	NI	NI	0.000000252

Inverse Model: Results

Mineral	1	2	3	Ratio
Chrysotile	5.959	5.954	5.875	1
$CO_2(g)$	17.88	17.86	17.63	3
Magnesite	-17.88	-17.86	-17.63	3
Am. Silica	-11.92	-11.91	-11.75	2

$$1Mg_3Si_2O_5(OH)_4 + 3CO_2 = 3MgCO_3 + 2SiO_2 + 2H_2O$$

CO$_2$ Sequestration Experiments (Lee 2005)

- Conducted to replicate process plant discharge water chemistry in laboratory

- Seven experiments run for varying times with varying charges of kimberlite material

- Initial solution chemistry similar to process plant reclaim

- Solute concentrations increased linearly towards process plant discharge water chemistry

- Inverse modeling results suggest dissolution of Mg-silicates and CO$_2$ and precipitation of amorphous SiO$_2$ and carbonate

Lee (2005) Experimental Results
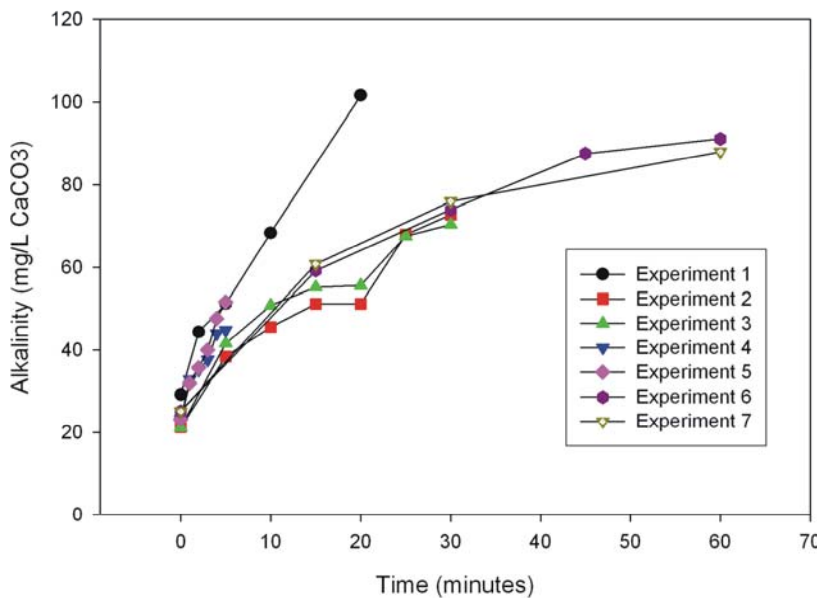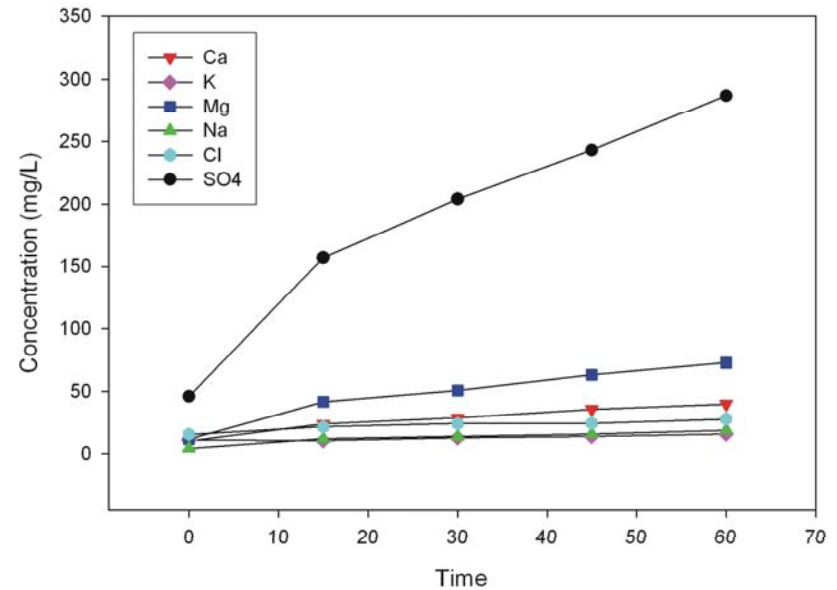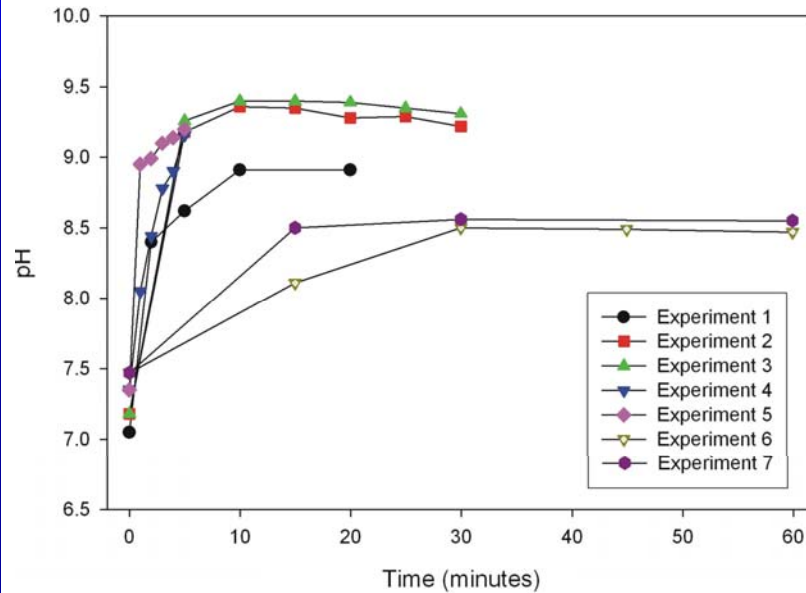
Discharge (n=9; 2000 – 2003)

pH	8.38
Alkalinity	64.2 mg $CaCO_3$/L
Ca	25.7 mg/L
K	64.1 mg/L
Mg	49.8 mg/L
Na	15.3 mg/L
Cl	30.8 mg/L
SO_4	212 mg/L

Mineral Carbonation: Evidence

- Inorganic carbon content increases from ore to fines
  - ore = 1.40 %; processed kimberlite = 2.38 %
- Saturation indices of magnesite and amorphous SiO_2 near saturation

CO$_2$ Sequestration Potential

- Daily water use in process plant = 30,000 m^3 to 40,000 m^3
  - 9,000 m^3 to 16,000 m^3 (30% to 40%) reclaimed from containment facility

- 9 Mkg and 16 Mkg solution discharged daily (ρ = 1000 kg/m^3)

- CO$_2$ mole transfer = 17.88 mol/kg = 0.787 kg CO$_2$/kg solution

- 7,000 tonnes to 12,000 tonnes CO$_2$ sequestered daily

- 2.6 to 4.6 Mt CO$_2$ may be sequestered passively per year

Conclusions and Implications

- Results suggest that CO_2 sequestration (mineral carbonation) is occurring passively during ore processing at Ekati

- Processing of kimberlite ore (grinding) provides an energy efficient way of pretreating Mg-silicate material for mineral carbonation (no additional energy is required)

- Ore processing at mines with ultramafic host rocks has potential to partially offset CO_2 emissions

- Existing tailings at ultramafic deposits may be viable source materials for CO_2 sequestration by mineral carbonation (waste becomes product)