Carbon Dioxide Sequestration:

Aqueous Mineral Carbonation Studies Using Olivine and Serpentine

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Aqueous Mineral Carbonation

- DOE Mineral Carbonation Study Group
  - Albany Research Center
  - Arizona State University
  - Los Alamos National Laboratory
  - National Energy Technology Laboratory
  - Science Applications International Corp.

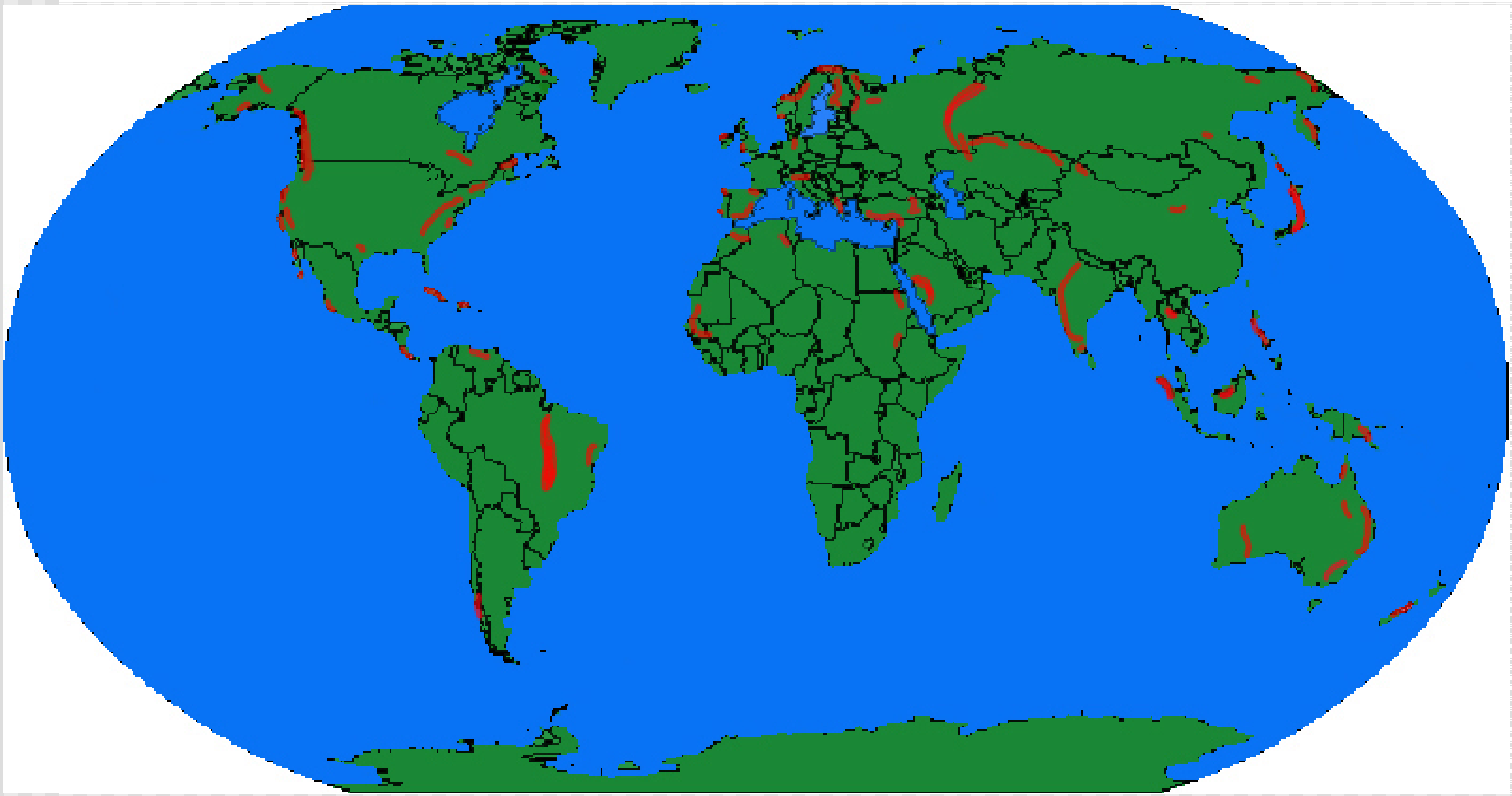
Aqueous Mineral Carbonation

- **Means to reduce greenhouse gas emissions from fossil-fuel-fired power plants**
- **Conversion of gaseous CO_2 to solid carbonate**
- **Process occurs in nature**
  - Chemical weathering
  - Biological activity
    - Corals
    - Coccoliths
- **Several candidate minerals and/or waste materials**
  - Magnesium silicates
  - Calcium silicates
  - Asbestos wastes
  - Iron and steel slags
  - Coal fly ash

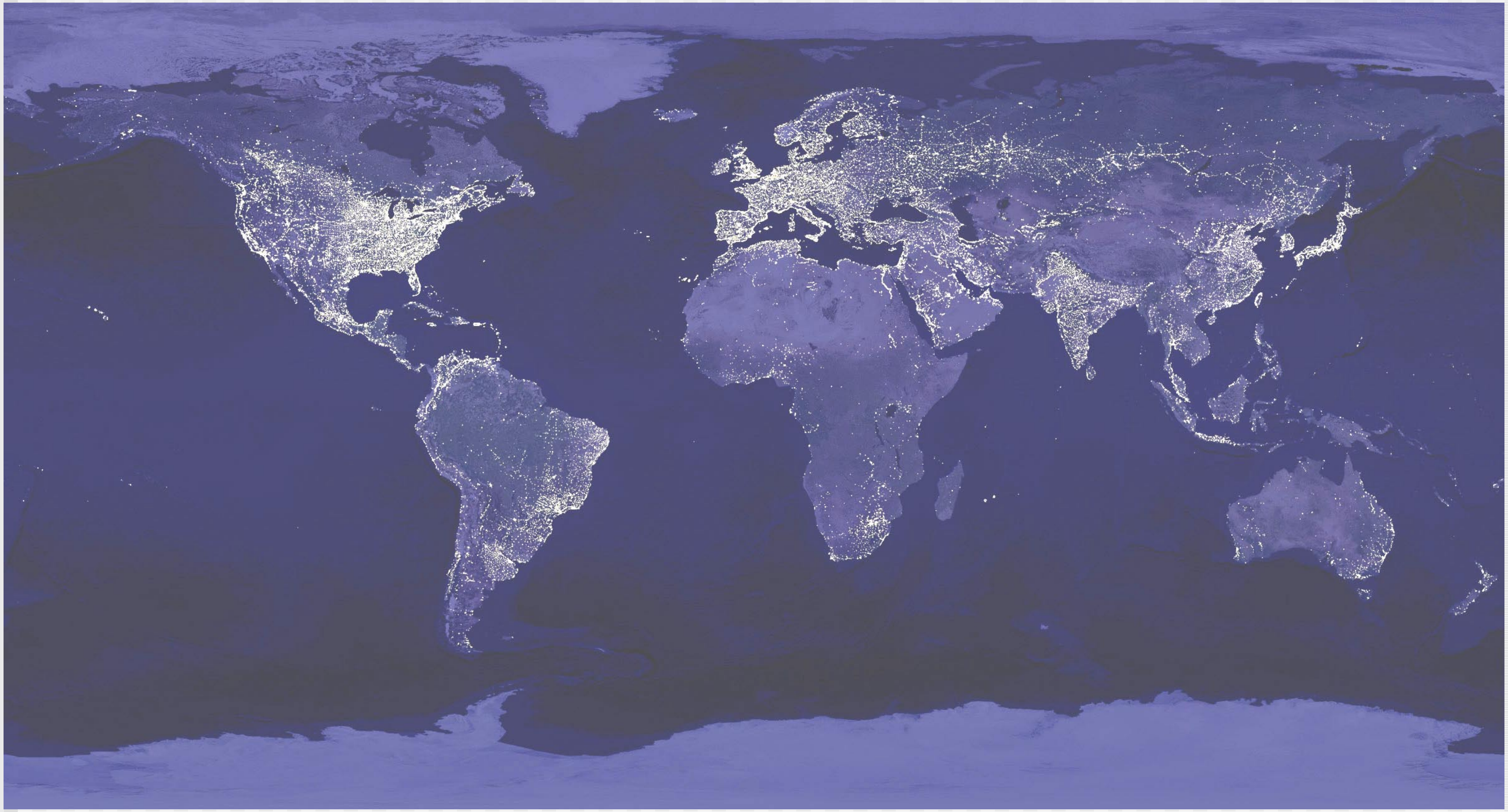
Aqueous Mineral Carbonation

- **Only magnesium silicates (ultramafics) occur in sufficient supply to make significant impact**
- **Long term stability**
  - Carbonates are thermodynamically favored
  - No legacy issues
  - Naturally occurring products
- **Abundant supply of ultramafic rock**
- **Potential to produce value-added byproducts**
- **Utilization/remediation of wastes**
- **Compatible with advanced and current power systems**

Global Ultramafic Sequences



Global High Density Power Consumption



Materials Characterization

- **Olivine: forsterite-fayalite series (Mg_2SiO_4- Fe_2SiO_4)**
  - (MgO) = 45-50 wt pct (actual)
  - (Iron oxides) = 6-10 wt pct
    - Fe^{+2}: Fe^{+3} = 2.0-2.5
  - **Ore grade olivine may contain alteration products**
    - Serpentine [$Mg_3Si_2O_5(OH)_4$]
    - Talc [$Mg_3Si_4O_{10}(OH)_2$]

- **Serpentine: antigorite (below), lizardite, chrysotile (asbestos) [$Mg_3Si_2O_5(OH)_4$]**
  - (MgO) = 38-45 wt pct (actual)
  - (Iron oxides) = 5-8 wt pct
    - Fe^{+2}: Fe^{+3} = 1.5-2.0 (magnetite)
  - **Olivine alteration (eq. 1a & 1b)**
  - **Heat pretreatment necessary to remove water (~13 wt pct)**

$$4Mg_2SiO_4 + 4H_2O + 2CO_2 \rightarrow 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3 \quad (1a)$$

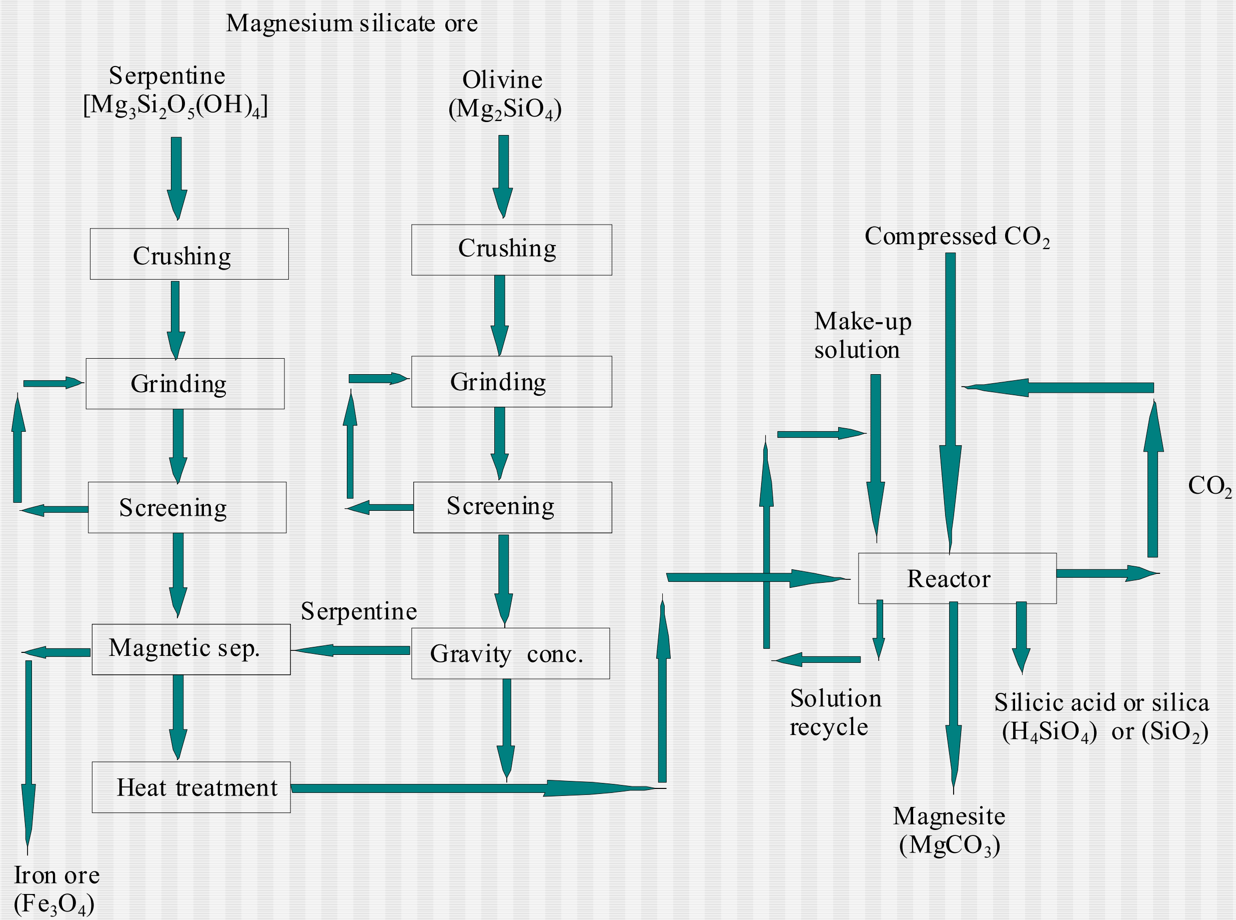
$$3Mg_2SiO_4 + 4H_2O + SiO_2 \rightarrow 2Mg_3Si_2O_5(OH)_4 \quad (1b)$$

Active Olivine and Serpentine Quarries

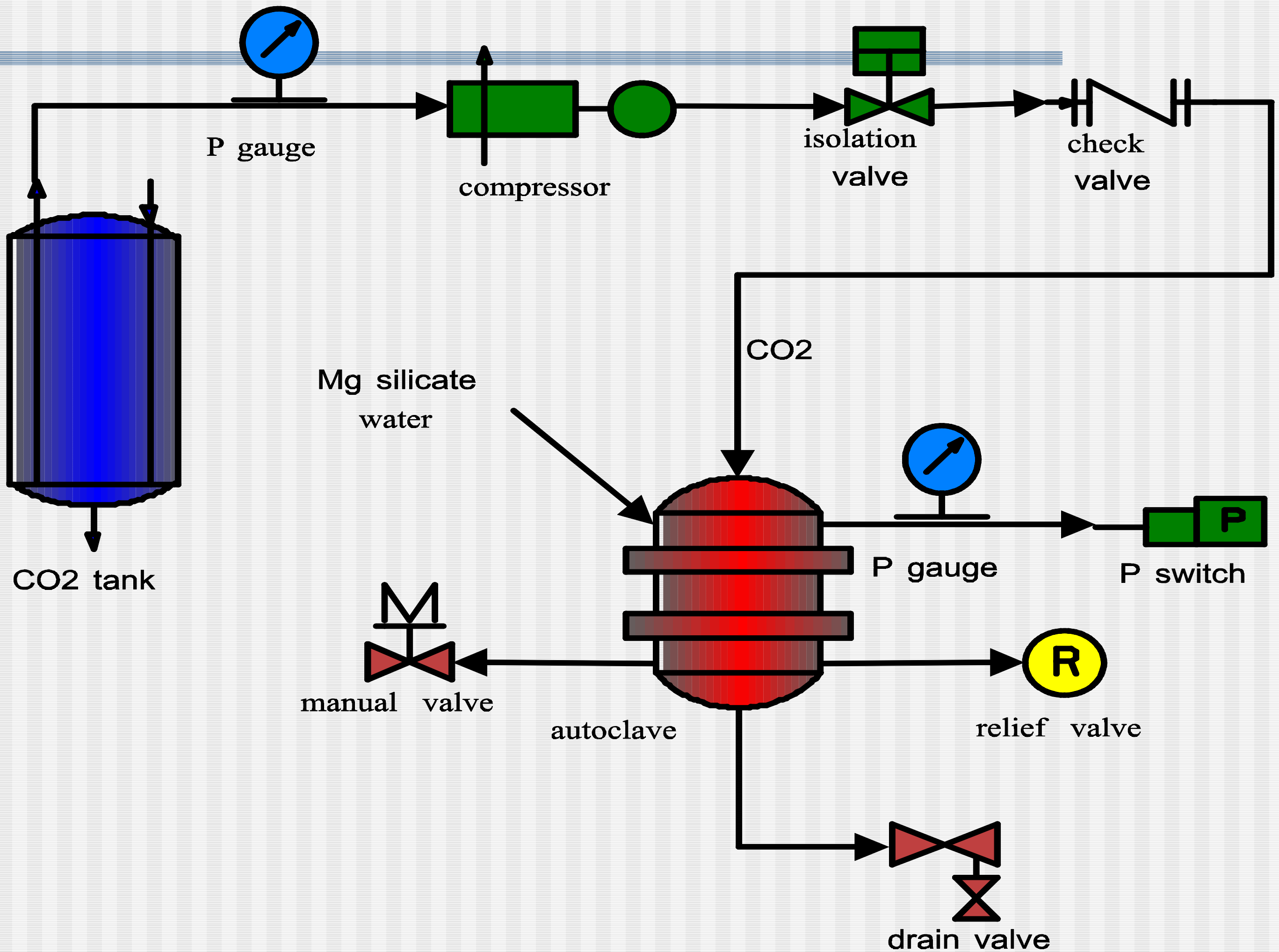
- **Olivine a common industrial mineral**
  - Refractories
  - Foundry sand
- **Major deposits**
  - Twin Sisters dunite, WA (below)
  - Norway
  - Japan
- **Massive local occurrences of unaltered dunite**
  - Twin Sisters estimated at 200 billion tons
- **Global resource undetermined**

- **Serpentine mines common**
  - Road base & asphalt (PA quarry below)
  - Flux for iron ore sintering (Australia)
  - Additional capacity necessary
- **Scale consistent with requirements**
  - 1 GW power plant – 30-40 kt/day
- **Mining cost estimates – $4-5/ton**
- **Work index [-200 mesh (75 µm)]**
  - Serpentine – 10.7 kWh/ton
  - Limestone – 11.6 kWh/ton
- **Must address chrysotile**

Magnesium Silicate Process Flow Diagram



Laboratory-Scale System



Solution Chemistry and Theoretical Reactions

- Carbonic Acid System
  - Distilled water
    - pH from ~5.0 to 5.5
    - (CO_2) = <0.1 g/liter initially
  - Carbonic acid formation and dissociation (eq. 2)
  - H^+ ion hydrolyzes Mg silicate (eq. 3)
  - Mg^{+2} cation reacts with bicarbonate ion to form solid carbonate and H^+ ion (eq. 4)

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (2)$$

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{+2} + H_4SiO_4 \quad (3)$$

$$Mg^{+2} + HCO_3^- \rightarrow MgCO_3 + H^+ \quad (4)$$

Modified Solution Chemistry and Theoretical Reactions

- Bicarbonate/Salt System
  - 0.64 *M* $NaHCO_3$, 1 *M* NaCl
    - ph from ~7.8-8.0 (in situ pH?)
    - (CO_2) = ~22 g/liter initially
    - (Na) = ~33 g/liter
    - (Cl) = ~34 g/liter
  - Modified reaction sequence (eq. 5)
  - Regeneration of bicarbonate (eq. 6)
  - Complexing ions may = increased solubility (eq. 7)

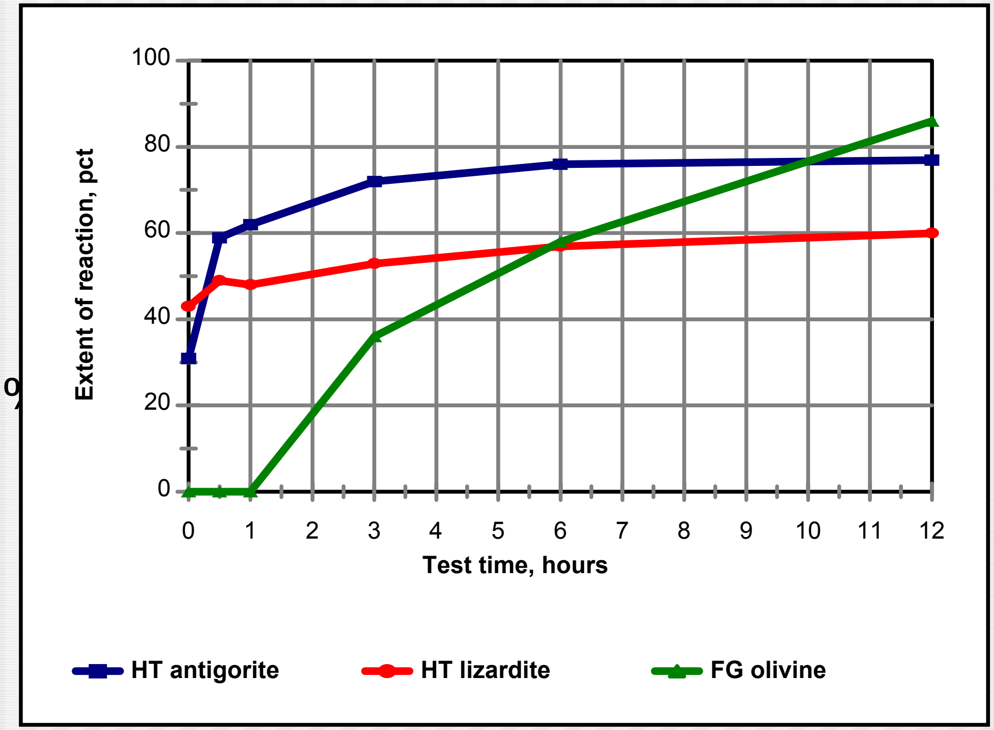
$$Mg_2SiO_4 + 2HCO_3^- \rightarrow 2MgCO_3 + SiO_2 + 2OH^- \quad (5)$$

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (6)$$

$$Mg^{+2} + 2Cl^- \rightarrow MgCl_2 \text{ or } MgCl_3^- \text{ or } MgCl_4^{-2} \text{ etc.} \quad (7)$$

Mineral Carbonation: Reaction Kinetics

- **Time series on 3 minerals**
  - Heat treated antigorite
  - Heat treated lizardite
  - Foundry grade olivine
- **Constant conditions**
  - T=155ºC; P_{CO2}=150 atm; 15% solids; 1,000 rpm
  - Times: 0, 0.5, 1, 3, 6, 12 hr
- **Olivine reactivity much lower**



Mineral Carbonation: Reactivity

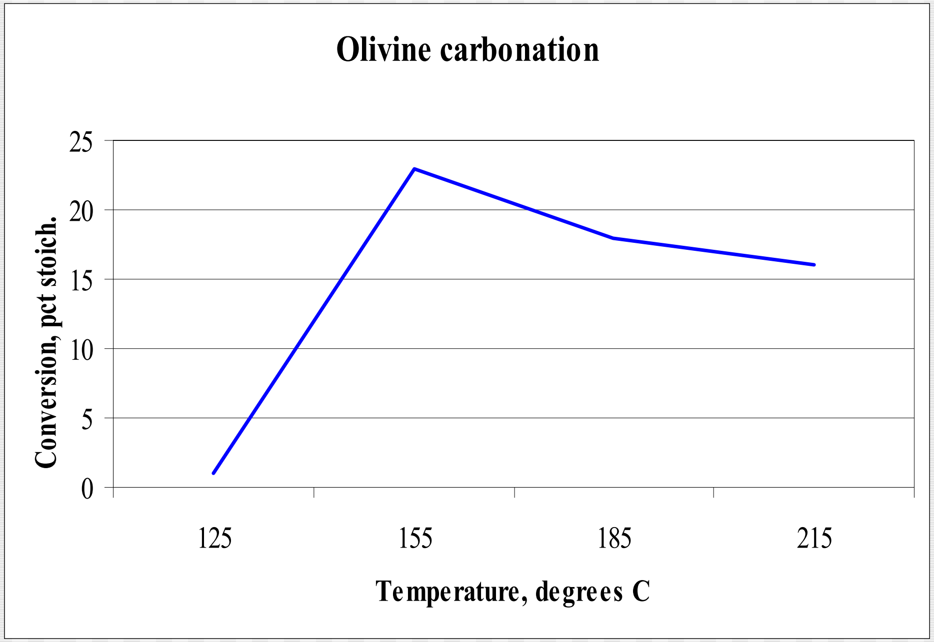
- Relative surface areas
  - Antigorite (-75 µm): 8.5 m^2/g; heat treated: 18.7 m^2/g
  - Lizardite (-75 µm): 32.3 m^2/g; heat treated: 10.8 m^2/g
  - Olivine (-75 µm): 4.6 m^2/g
- Reaction rates (best results for 1 hour carbonation tests)
  - Antigorite (heat treated): 0.012 $g/m^2/h$
  - Lizardite (heat treated): 0.011 $g/m^2/h$
  - Olivine (reground in 1 *M* NaOH, 1 *M* NaCl): 0.013 $g/m^2/h$
- Enhanced olivine reactivity (1 h, 155°C, P_{CO2}=150 atm)
  - Olivine only: 0% conversion
  - Olivine spiked with 5% Fe_3O_4: 3% conversion
  - Olivine spiked with 5% MgO: 17% conversion (of olivine)
  - Olivine reground in 1 *M* NaOH, 1 *M* NaCl: 20% conversion
    - Chemical pretreatment during size reduction shows promise

Mineral Carbonation: Reactivity

- Effects of Mg^{2+} concentration
  - Additions of $MgCl_2$ to bicarbonate solution
    - 0.12 M $MgCl_2$
      - 15% increase on heat-treated serpentine
      - Limited improvement on olivine
  - Recycled carbonation solutions
    - Poor results for short-term carbonation tests
    - Fully successful long-term tests (12-24 hours)
- Additions of highly soluble Mg (solid MgO) appear more effective than solution modifications (for olivine)
  - Surface phenomenon?
    - Surfactants
    - Metal catalysts (Co, Ni)

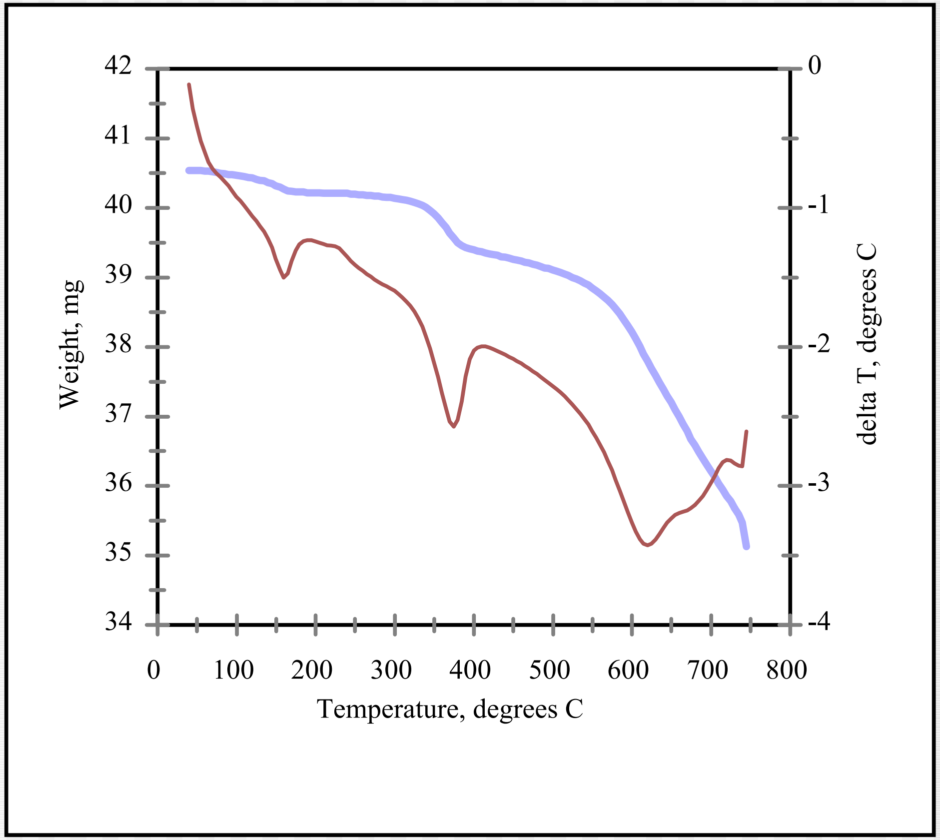
Mineral Carbonation: Low P_{CO2} (20 atm) Tests

- Antigorite (heat treated)
  - ~39% carbonated (1 h, 155°C)
  - ~22% carbonated (1 h, 50°C)
- Lizardite (heat treated)
  - ~51% carbonated (1 h, 155°C)
  - ~39% carbonated (1 h, 50°C)
- Olivine
  - Temperature series, 6 hours (see graph)



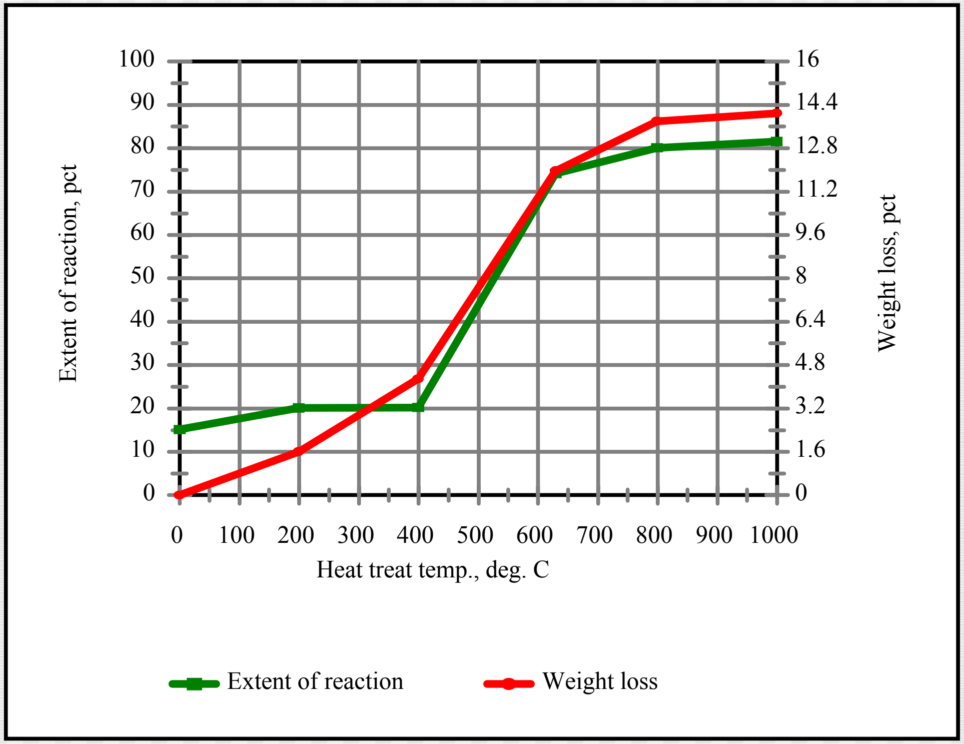
Serpentine Heat Treatment

- **Thermal Analysis (antigorite)**
  - Three separate endotherms
    - Desorption of adsorbed water at 160C
    - Evolution of water of crystallization (dehydration) at 374C (brucite?)
    - Dehydroxylation (evolution of constitutional water) at 614C
    - Exotherm above 700C – forsterite crystallization
- **Must remove chemically bound water to promote carbonation**
- **Serpentine converted to forsterite and a metastable silicate**
- **Oxidation of iron appears to passivate the serpentine**
  - Nonoxidizing atmosphere
  - Magnetic separation



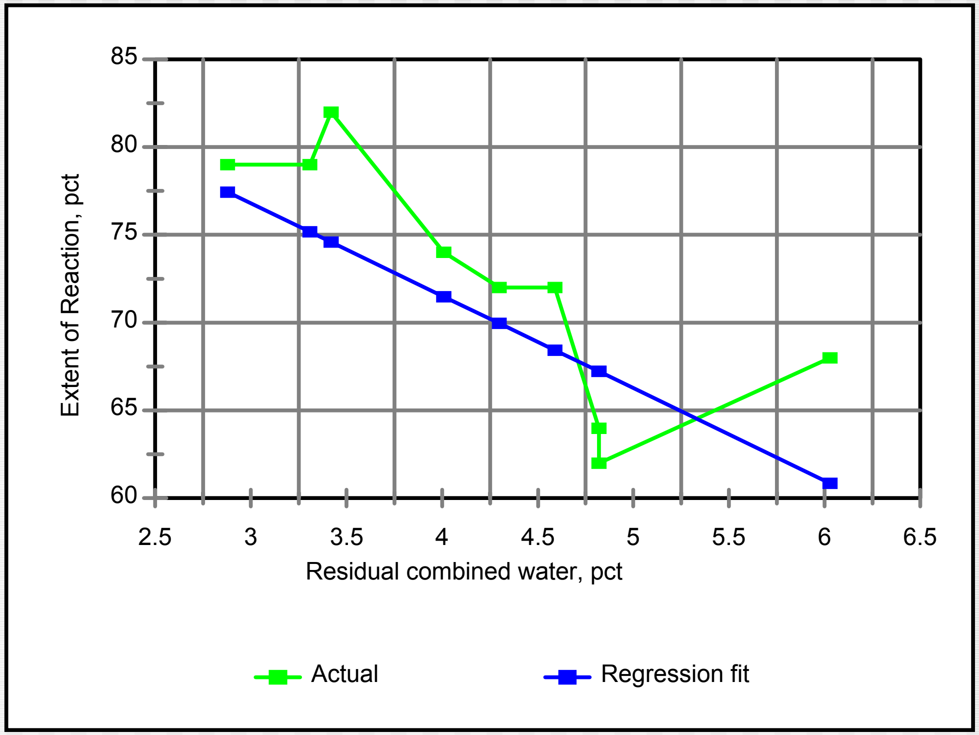
Serpentine Heat Treatment

- **Weight loss directly related to carbonation**
  - ~12% weight loss optimal for this ore
  - Carbonation near constant above 650 C – formation of forsterite
- **Optimal heat treatment temperature 600-650ºC (metastable silicate)**
- **Energy cost: ~200 kW· h/ton**
  - Potential for energy recovery
  - Feasibility unlikely
  - Investigating alternate routes to activate serpentine
  - Re-emphasis on olivine



Serpentine Heat Treatment

- Residual combined water
  - Impacts carbonation
  - Linear relationship
- Must remove water from serpentine
- Loss on Ignition (LOI)
  - Indicator for reactivity
  - Normalized results

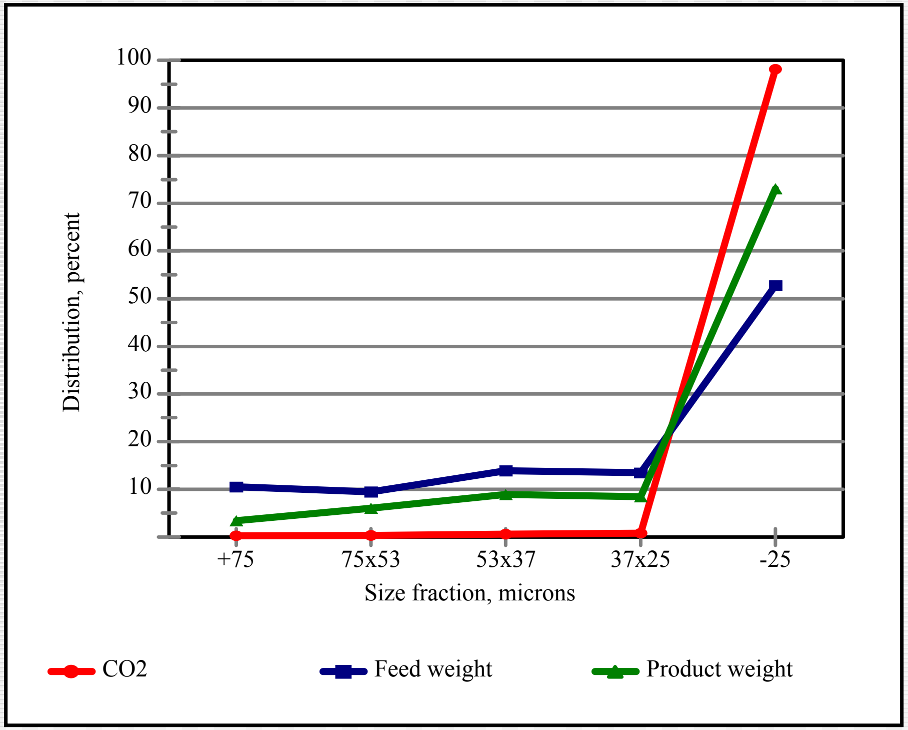


General Characteristics: Solid Products

- **Olivine carbonation**
  - Tests with ~80% conversion to the carbonate
    - (CO_2) = ~30 wt pct
    - (free SiO_2) = 25-30 wt pct
    - (MgO) = ~35 wt pct
    - ($MgCO_3$) = ~65 wt pct (calculated)
  - XRD analyses
    - Magnesite ($MgCO_3$)
    - No silica pattern (amorphous SiO_2)
    - Residual olivine (forsterite) and enstatite
- **Heat treated serpentine carbonation**
  - Tests with ~80% conversion to the carbonate
    - (CO_2) = ~30 wt pct
    - (free SiO_2) = 25-30 wt pct
    - (MgO) = ~35 wt pct
    - ($MgCO_3$) = ~65 wt pct (calculated)
  - XRD analyses
    - Magnesite ($MgCO_3$)
    - No silica pattern (amorphous SiO_2)
    - Residual olivine (forsterite)
    - No chrysotile

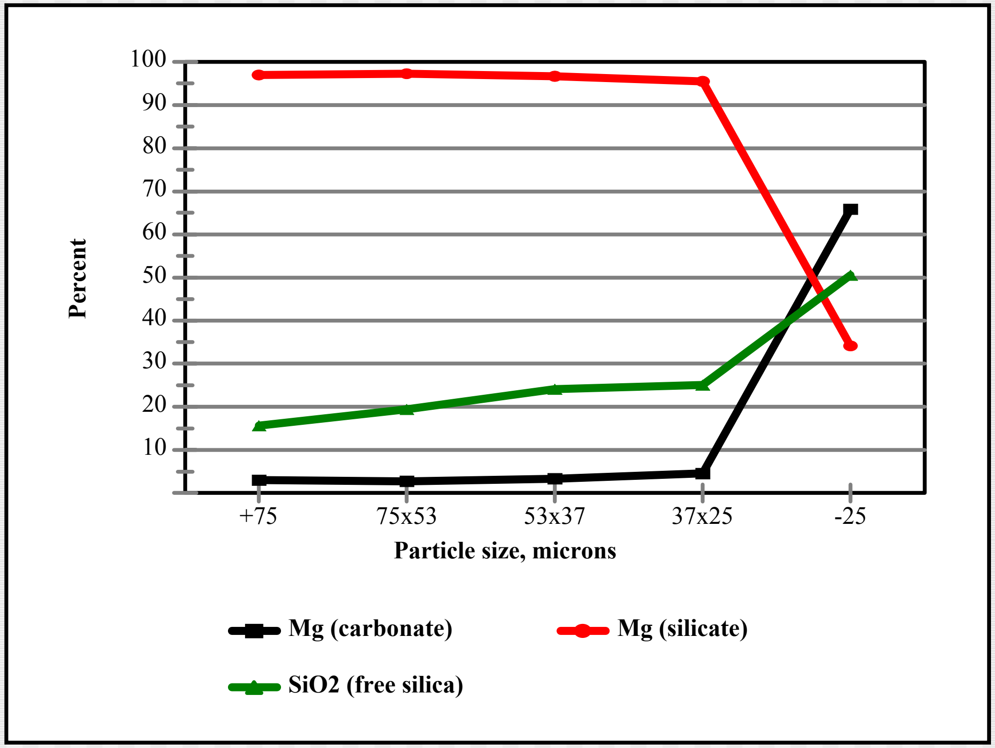
Solid Product Characterization

- **Several key questions**
  - Solid-state vs aqueous?
  - Surface controlled?
  - Diffusion limited?
  - Passive layers or coatings?
  - Fate of silica?
  - Morphology of magnesite product?
  - Toxicity of magnesite product?
- **Typical particle size analysis**
  - Some size reduction apparent
  - -25 micron fraction: 27 wt pct CO_2
    - 98% of all CO_2 in total product
  - Recent analyses suggest magnesite occurs as –10 micron agglomerates

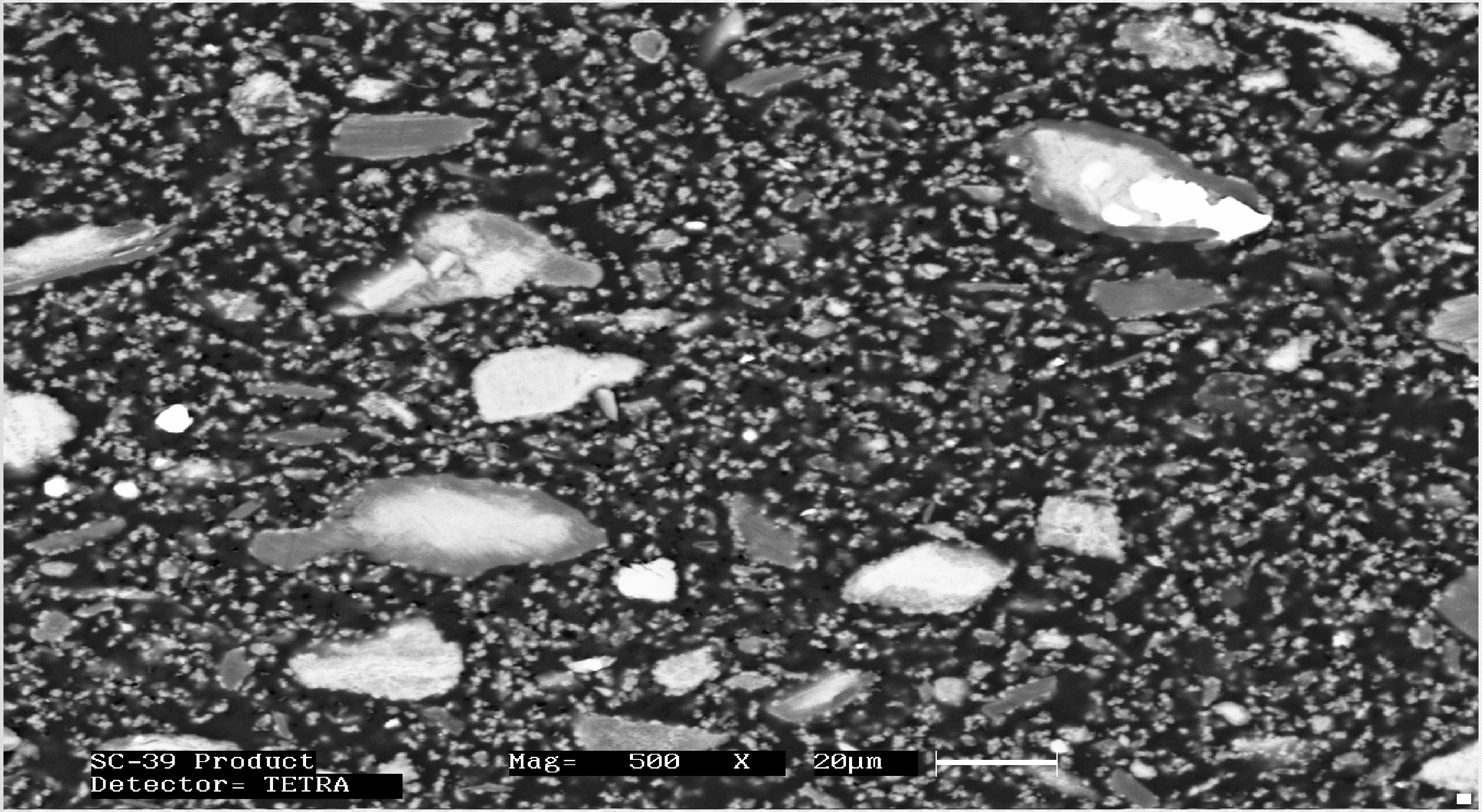


Solid Product Characterization

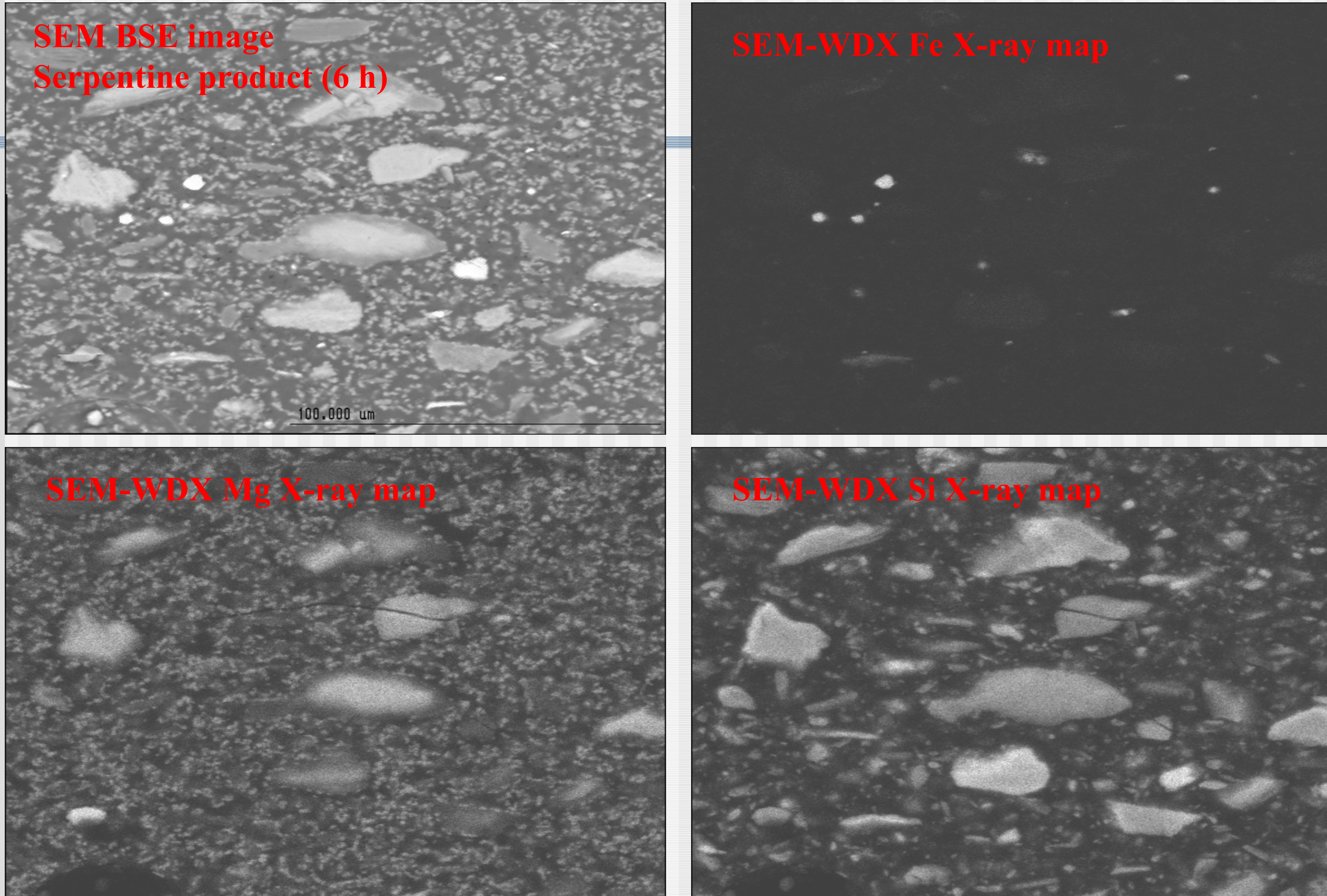
- **Calculated phase concentrations by size fraction**
- **Assumptions**
  - All CO_2 occurs as $MgCO_3$
  - Excess MgO occurs as Mg_2SiO_4
  - Excess SiO_2 occurs as free silica
- **Potential for coarse silicate recycle by hydrocylcone separation of product**
- **Increase attritioning to remove silica-rich rims**



Heat Treated Serpentine Reaction Products



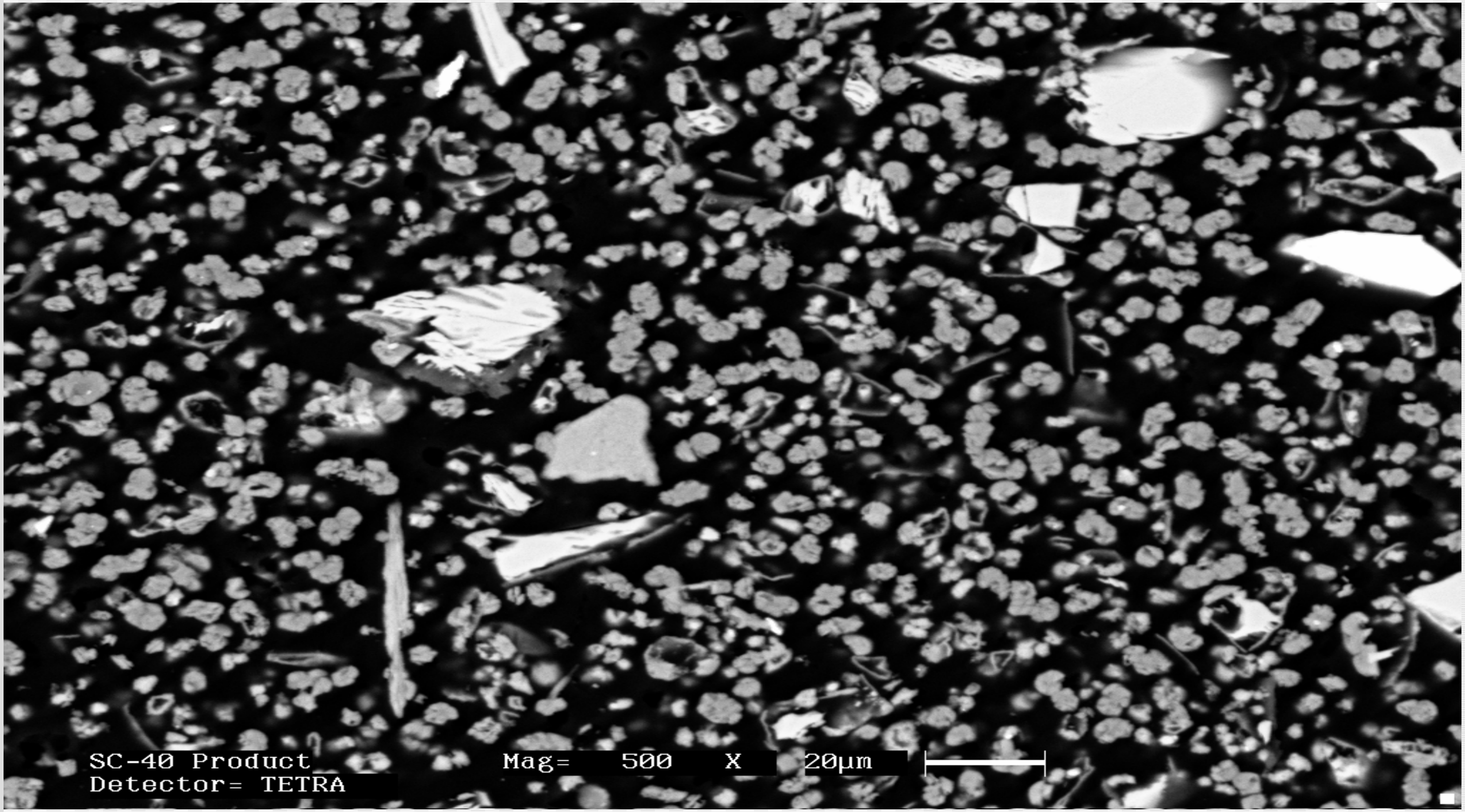
Serpentine Reaction Products



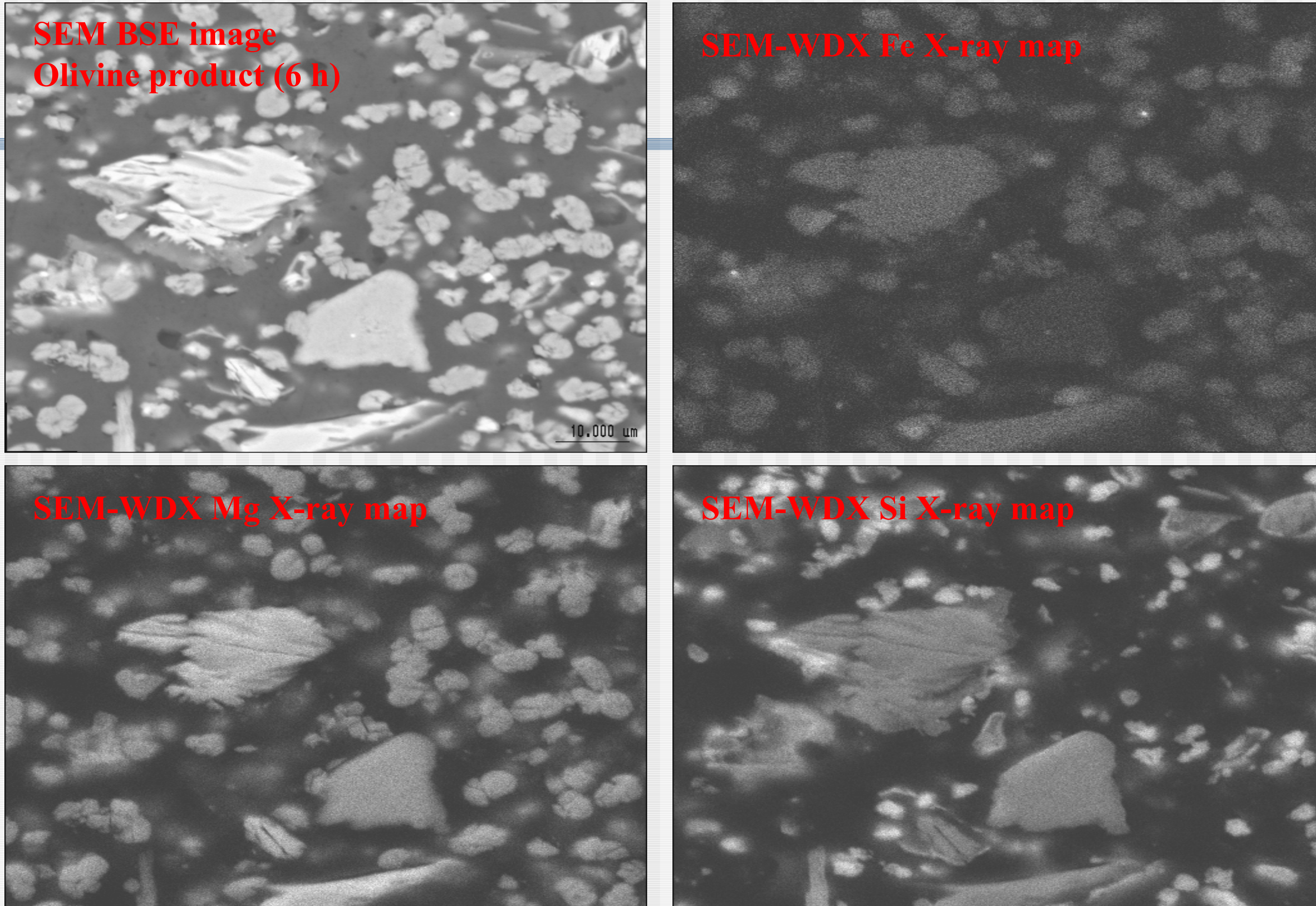
Solid Product Characterization

- Apparent two stage reaction path
  - Dissolution into aqueous phase
  - Carbonate precipitation (not solid-state)
- Dissolution is likely surface controlled
  - Particle size tests
    - Extent of reaction increases with decrease in particle size
    - -200 mesh (75 microns) target size
    - -400 mesh (37 microns) slightly better
- Silica enriched zones
  - May form passive layer on partially reacted silicate
  - Reaction may be diffusion limited

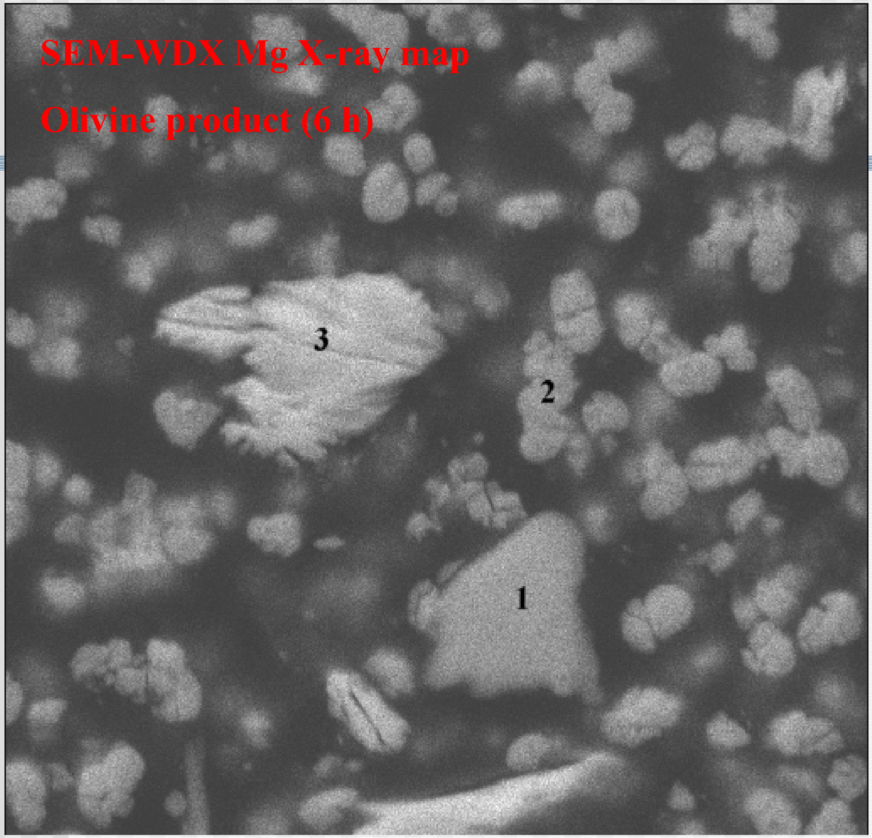
Olivine Reaction Products

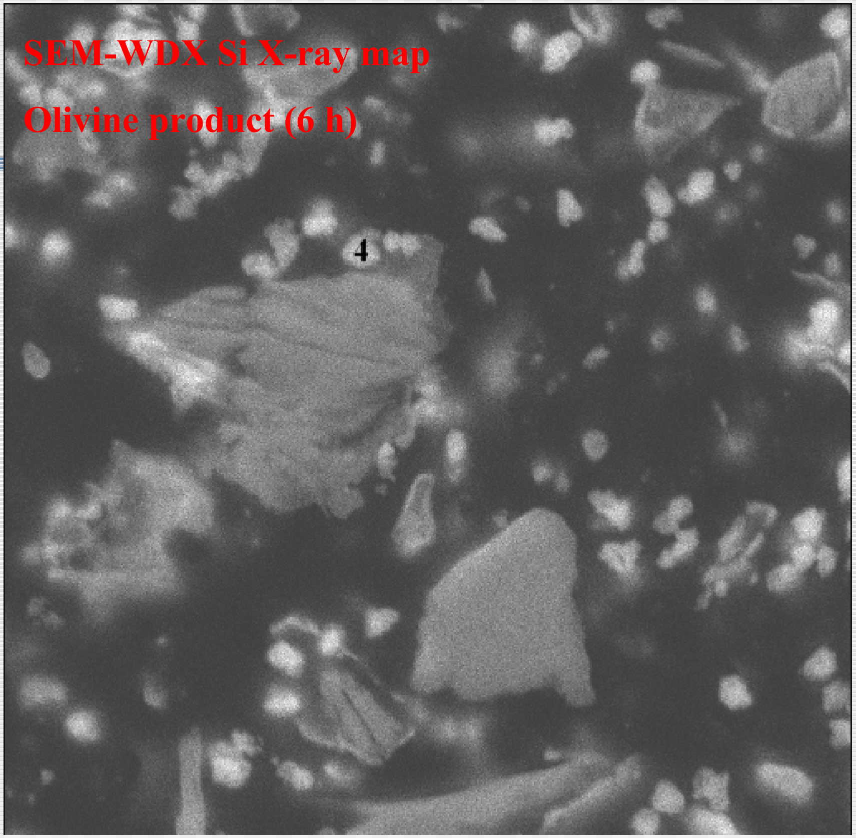


Olivine Reaction Products



Olivine Reaction Products





	Atomic percent			
Point	C	Mg	Si	Mg/Si
1	3	20	13	1.5
2	26	17	1	17
3	3	25	12	2.1
4	6	1	26	0.04

Minus 10 micron particles include:
(1) high silica fragments - attrition of Mg depleted grains (?)
(2) rounded particles (primarily magnesium carbonate) - agglomerates of much finer nuclei (precipitate)

Solid Product Characterization

- **Silica-rich particles in minus 10 micron fraction**
  - Silicate particles become silica enriched with Mg^{2+} removal
  - Fines formed by attrition or exfoliation of coarser particles
  - Means to encourage silica nucleation
- **Magnesium carbonate particles in minus 10 micron fraction**
  - Apparent precipitation product
  - Agglomerates of much finer particles
  - 10 microns appears to be upper size limit
    - Particle size appears independent of test time
    - Agitation phenomena (?)
- **Solid product passes EPA TCLP**

General Characteristics: Product Solutions

- Carbonic Acid System (H_2CO_3)
  - Tests with ~80% conversion to the carbonate (24 h)
    - pH increases to ~6.8 to 7.2
    - (CO_2) = 0.5-1.0 g/liter
    - (Mg) = ~0.1 g/liter
    - (Si) = ~0.2 g/liter
- Lower (CO_2), thus lower [CO_2] retards the reaction rate

- Bicarbonate System ($NaHCO_3$ & NaCl)
  - Tests with ~80% conversion to the carbonate (0.5 - 3 h)
    - pH increases slightly to ~7.9 to 8.1
    - (CO_2) = 19-22 g/liter
    - (Mg) = ~0.05 g/liter
    - (Si) = ~0.02 g/liter
    - (Na) = ~32 g/liter
    - (Cl) = ~35 g/liter
- Buffered solution –recyclable with make-up
- Bicarbonate CO_2 carrier

Summary and Conclusions

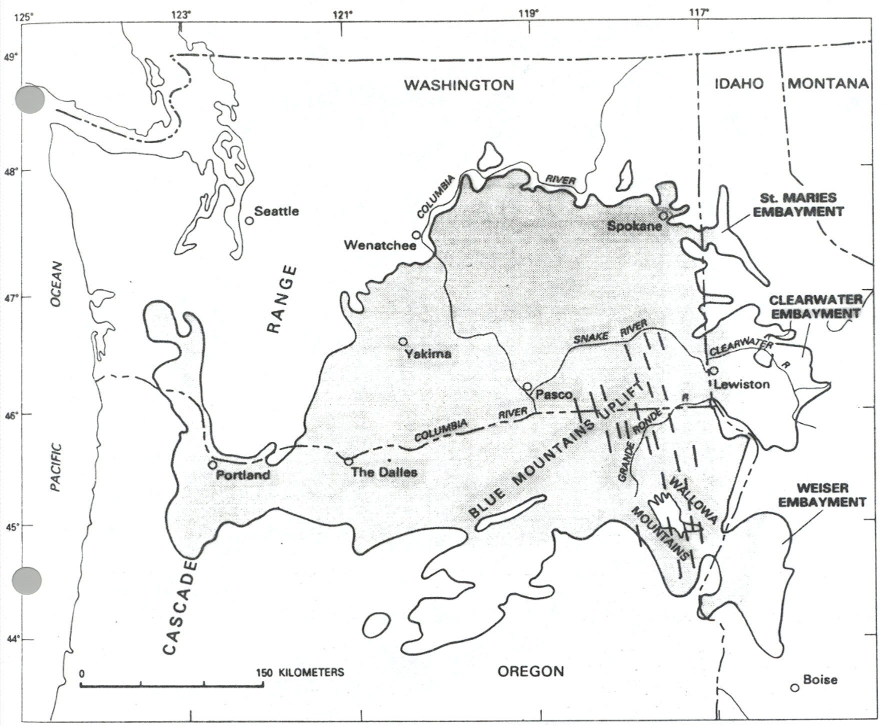
- **Both olivine and serpentine are amenable to direct carbonation**
  - Reaction time reduced from >24 hours to ~1 hour
  - Conversion of the Mg silicate to the Mg carbonate:
    - Up to ~80% efficiency achieved in 1 hour @ P_{CO_2} = 150 atm, T = 155°C
    - Up to ~50% efficiency achieved in 1 hour @ P_{CO_2} = 20 atm, T = 155°C
    - Up to ~40% efficiency achieved in 1 hour @ P_{CO_2} = 20 atm, T = 50°C
- **Heat pretreatment activates serpentine (meta-stable silicate?)**
  - Removal of water:
    - Creates defects in crystal lattice (pseudo-amorphous)
    - Increases dissolution rate by decreasing activation energy?
- **Heat pretreatment/carbonation appears to destroy chrysotile**
- **Solid product non-hazardous based on EPA TCLP**
- **Process improvements**
  - Potential carbonation conditions: 20 atm @ 50°C (heat-treated serpentine)
  - Solids concentration to 30% demonstrated
  - Particle size increased to –200 mesh (-75 µm)

Continuing Studies

- **Feasibility study, including engineering and economic evaluations of flow-type reactors**
- **Bench and pilot-scale testing**
- **Development of geochemical model (LANL)**
- **Investigate mineral pretreatment options**
- **Investigate by-products and beneficial product uses**
  - Iron concentrates
  - Liming agents
  - Hydrophilic silica
- **Apply ex-situ studies to in-situ (geologic) sequestration**
  - CO_2 injection into deep brine aquifers in ultramafic sequences
    - Abundant mineral reactant (contrary to sedimentary sequences)
    - Columbia River Basalt Group

Geologic Sequestration: CRBG

- Columbia River Basalt Group
  - Area: ~200,000 km^2
  - Mass: over 300,000 km^3
  - Total thickness: over 1 km in places
  - Numerous flows
    - Unique opportunity for gas injection
- Fossil-fuel-fired power plants (near geographic center)
  - 0.5 GW coal-fired plant
  - 0.8 GW natural gas plants (two 0.5 GW plants under construction)
    - ~2.3 GW generating capacity
    - ~35 ktons/day CO_2 emissions



Approximate area of CRBG (GSA Bulletin, 97, 11, November, 1986).

CRBG

- Stratigraphic column (GSA Bulletin, 97,11, November, 1986)
- Erosional unconformities at interflow contacts
  - High porosity zones
    - Shallow fresh water aquifers
    - Deep brine aquifers
      - CO_2 injection
- Basalt mineralogy
  - High mineral trapping potential
  - Up to 25 wt pct combined CaO, FeO and MgO

Series		Group	Sub-group	Formation	Member	K-Ar age (m. y.)	Magnetic polarity
MIOCENE	Upper Miocene	Columbia River Basalt	Yakima Basalt Subgroup	Saddle Mountains Basalt	Lower Monumental Member	6[2]	N
					Erosional unconformity		
					Ice Harbor Member		
					Basalt of Goose Island	8.5[2]	N
					Basalt of Martindale	8.5[2]	R
					Basalt of Basin City	8.5[2]	N
					Erosional unconformity		
					Buford Member		R
					Elephant Mountain Member	10.5[2]	N, T
	Middle Miocene				Erosional unconformity		
					Pomona Member	12[2]	R
					Erosional unconformity		
					Esquatzel Member		
					Erosional unconformity		
					Weissenfels Ridge Member		
					Basalt of Slippery Creek		N
					Basalt of Lewiston Orchards		N
					Asotin Member		N
					Local erosional unconformity		
					Wilbur Creek Member		N
					Umatilla Member		N
					Local erosional unconformity		
				Wanapum Basalt	Priest Rapids Member		R3
					Roza Member		R3 T
					Frenchman Springs Member		N
					Eckler Mountain Member		
					Basalt of Shumaker Creek		N2
					Basalt of Dodge		N2
					Basalt of Robinette Mountain		N2
	Lower Miocene			Grande Ronde Basalt		14-16.5[3]	N2
							R2
			Picture Gorge Basalt -?-?-		(Basalt of Dayville / Basalt of Monument Mountain / Basalt of Twickenham)[1]	(14.6-15.8)[1,3]	N1
							R1
				Imnaha Basalt			R1
							T
							R0 ?

CRBG

- Idealized cross section through flow in CRBG (GSA Bulletin, 97, 11, November, 1986)
- Vesicular top (formed by gas evolution during emplacement)
  - "Flow-top breccia"
    - High porosity (~30%, compared to ~12% for typical sandstone aquifer)
    - High permeability (20 darcy compared to 100 millidarcy for typical oil reservoir)
- Pillow basalts at base of section
  - Add to "porous zone"
- Basal colonnade of low porosity/permeability ("cap")