# Carbonation of Serpentine for Safe, Effective and Permanent $CO_2$ Sequestration*

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# Overview

- What is mineral carbonation?
- Advantages and disadvantages of mineral carbonation
- Progress in mineral carbonation R&D
- The “direct” method for olivine/serpentine carbonation
- The ORNL method for olivine/serpentine carbonation
- A plot twist!
- Conclusion

# What is Mineral Carbonation?

Mineral carbonation is a promising technology for reducing $CO_2$ emissions from fossil fuel-fired power plants, cement factories, and steel mills. It involves reacting $CO_2$ with non-carbonate (predominantly silicate) minerals to form one or more (usually solid) carbonate compounds. The process mimics natural weathering of silicate minerals to form carbonate minerals such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), and siderite ($FeCO_3$).

# Advantages of Mineral Carbonation Compared to Alternative Methods for Wide-Scale $CO_2$ Sequestration

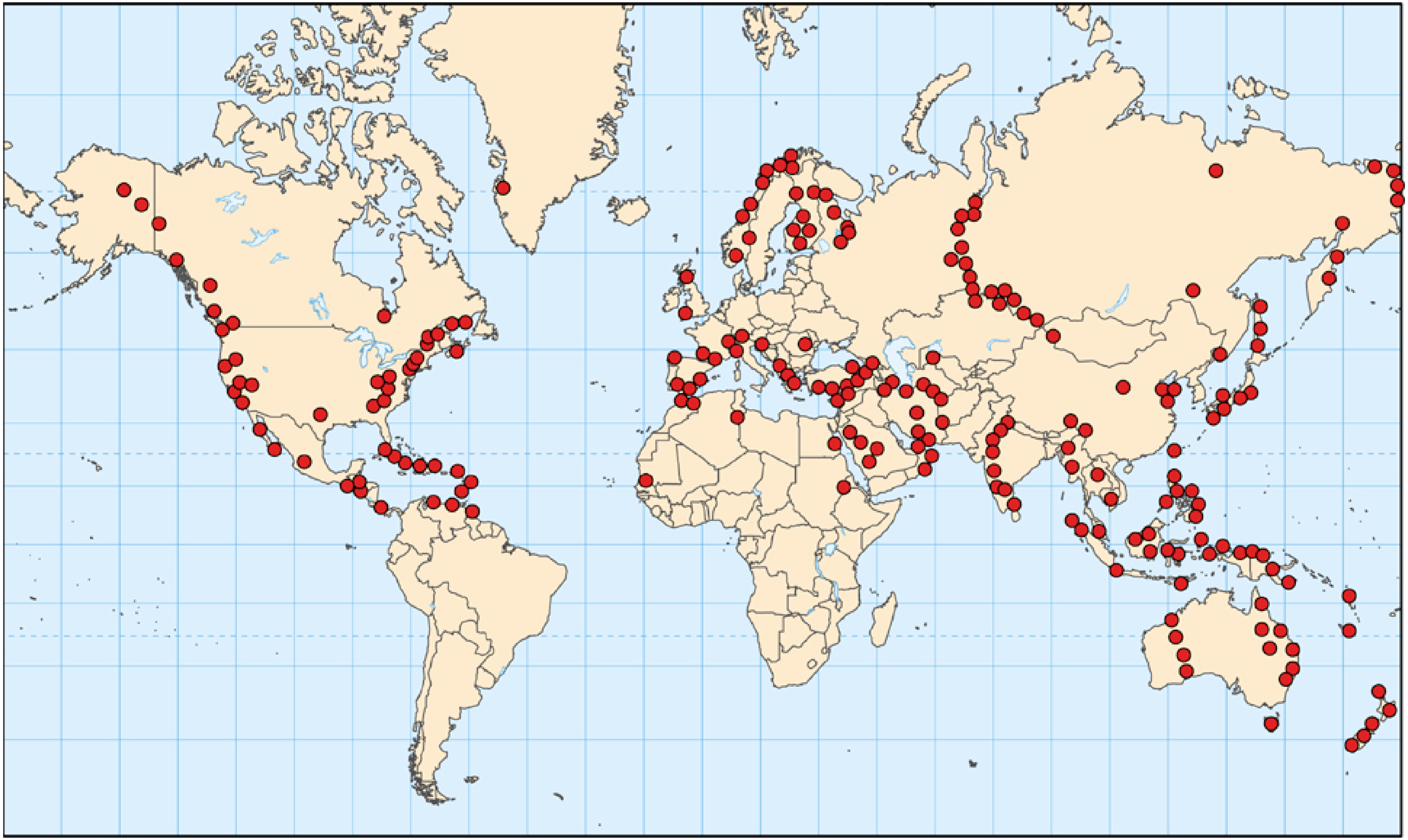
- In mineral carbonation technologies, natural and anthropogenic silicates are rapidly converted to carbonates by reaction with $CO_2$ under controlled environmental conditions.
- Mineral carbonation pathways are exothermic.
- The carbonate compounds formed in mineral carbonation technologies are thermodynamically stable, environmentally benign, and weakly soluble in meteoric water.

# Advantages of Mineral Carbonation Compared to Alternative Methods for Wide-Scale $CO_2$ Sequestration *(continued)*

- Regardless of the particular end use or disposal scheme selected for the solid products of mineral carbonation, the reacted $CO_2$ will remain tightly bound in the crystallographic structures of the carbonates—immobilized for an indefinite period of time.
- A large reduction in the *total* volume of the primary reactants in mineral carbonation (the silicate feedstock + $CO_2$) is automatically achieved because the $CO_2$-bearing solids produced are >1000x more dense than gaseous $CO_2$ at STP (standard temperature and pressure – 25°C, 1 atm).

# Advantages of Mineral Carbonation Compared to Alternative Methods for Wide-Scale $CO_2$ Sequestration *(continued)*

- The raw materials required for mineral carbonation (dunites, serpentinites, and basalts) are widely available in the U.S. and many foreign countries.
- If serpentine is used as the silicate feedstock, magnetite, chromite and water are co-produced with magnesite.



Worldwide distribution of serpentine-rich rocks (modified from Ziock, 2000).

# Disadvantages of Mineral Carbonation

- Mining/rock excavation is expensive, environmentally intrusive, and unappealing to the general public.
- There are unwarranted concerns about the health hazards of serpentine asbestos (chrysotile).
- Mineral carbonation reactions are very sluggish at ambient temperature and pressure.
- To date, it has not been demonstrated that the solid products of carbonation have any significant commercial value.

# Progress in Mineral Carbonation R&D

| Year(s) | Investigator(s) | Contribution(s) |
|---|---|---|
| 1990 | Seifritz | Proposed the concept |
| 1995 | Lackner et al. | Seminal paper |
| 1995-1997 | Lackner, Butt, Wendt et al. | Important research on olivine/serpentine carbonation |
| 1998 | Walters, Guthrie, McKelvy et al. | MSWG, "direct" method for olivine/serpentine carbonation |
| 2003 | Blencoe et al. | ORNL method for olivine/serpentine carbonation |

# Comparison of the "Direct" and ORNL Methods for Olivine/Serpentine Carbonation

## *"Direct" Method*

$$\mathbf{Mg_3Si_2O_5(OH)_4 + 3CO_2(aq) \rightarrow 3MgCO_3(\downarrow) + 2SiO_2(\downarrow) + 2H_2O(liq)}$$

*T*: 155°C, *P*: 185 bars, serpentine heat pretreatment (dehydroxylation) is required, a single stream of mixed $MgCO_3$ and $SiO_2$ gel is produced

## *ORNL Method*

$$\mathbf{Mg_3Si_2O_5(OH)_4 + 2OH^- + 3H_2O(liq) \rightarrow 3Mg(OH)_2(\downarrow) + 2SiO(OH)_3^-,} \quad \mathbf{(1)}$$

$$\mathbf{2SiO(OH)_3^- + 2CO_2(aq) \rightarrow 2HCO_3^- + 2SiO_2(\downarrow) + 2H_2O(liq)} \quad \mathbf{(2)}$$

$$\mathbf{2Mg(OH)_2 + 2HCO_3^- \rightarrow 2MgCO_3(\downarrow) + 2OH^- + 2H_2O(liq)} \quad \mathbf{(3)}$$

$$\mathbf{Mg(OH)_2 + CO_2(gas) \rightarrow MgCO_3(\downarrow) + H_2O(liq)} \quad \mathbf{(4)}$$

Net reaction: $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$

*T*: ≤ 200°C, *P*: ≤ 15 bars, no serpentine heat pretreatment is required, separate streams of $MgCO_3$ and $SiO_2$ gel are produced

# Particular Advantages of the “Direct” Olivine/Serpentine Carbonation Process

- Olivine and (dehydroxylated) serpentine are carbonated in a single processing step.
- Extensive carbonation is achieved quickly at a very low processing temperature (155°C).

# Particular Advantages of the ORNL Olivine/Serpentine Carbonation Process

- No heat pretreatment or extreme grinding of the olivine/serpentine feedstock is required.
- All reactions proceed rapidly at temperatures between 25 and 200°C, and pressures ≤15 bars.
- The "rock solvent" (caustic soda, NaOH) is consumed in step 1 of the process, and entirely regenerated in step 3.
- Separate streams of silica gel and magnesite are produced; consequently, each substance has commercial value.
  In contrast, the "direct" method generates a stream of intimately mixed magnesite and silica gel, which is a waste material due to the economic impracticality of post-process separation.
- It may be possible to separate $CO_2$ from flue gas in step 2 of the process.

# Energy Penalties Avoided by Using the ORNL Olivine/Serpentine Carbonation Process

- Enthalpy increments of the reactants and products of serpentine dehydroxylation at 600ºC: 18.0 $kJ \cdot mol^{-1}$
- Enthalpy of serpentine dehydroxylation at 600ºC: 139.2 $kJ \cdot mol^{-1}$
- Compression of $CO_2$ (~15 bars for the ORNL process versus ~185 bars for the "direct" carbonation method): 3.5 $kJ \cdot mol^{-1}$
- Total energy savings using the ORNL process: $18.0 + 139.2 + 3 \times 3.5 = 167.7$ $kJ \cdot mol^{-1}$

# Potential Commercial Uses of the Silica and Magnesite Produced by the ORNL Olivine/Serpentine Carbonation Process

- **Silica**: silica-based desiccants, silica brick, silicon carbide, various types of glass, and elemental silicon (the foundation material for numerous semiconducting electronic devices)
- **Magnesite**: magnesite cement, magnesia, and magnesium metal (!)

# Technical Challenges for the ORNL Olivine/Serpentine Carbonation Process

The main technical challenges for the ORNL olivine/serpentine carbonation process arise from three needs: (i) to separate residual $OH^-$ from $SiO(OH)_3^-$ in step 1, (ii) to separate $HCO_3^-$ from silica gel in step 2, and (iii) to recreate a concentrated aqueous solution of caustic soda in step 3. Potential processing procedures for achieving these aims include:

| | |
|---|---|
| **Step 1** | precipitating solid NaOH by boiling off water, and separating the solid caustic from the $SiO(OH)_3^-$-enriched liquid |
| **Step 2** | gently centrifuging the aqueous solution to physically segregate the silica gel from the $HCO_3^-$-rich liquid |
| **Step 3** | boiling off water to elevate the concentration of $OH^-$ |

# Advantages of Using the New ORNL Process to Produce Magnesium from Olivine/Serpentine "Ore"

- No $CO_2$ is vented to the atmosphere during chemical processing!
- Producing magnesium from olivine and serpentine reduces the need to use carbonate rocks as sources of the metal.
- If mining olivine and serpentine globally results in a lower market price for magnesium, that could quickly lead to greater use of the metal in building automobiles and aircraft. Increasing the quantities of lightweight metals in the structural components of automobiles and aircraft would enhance fuel efficiency and (therefore) lower the amounts of $CO_2$ emitted per mile of travel.
- Olivine and serpentine can be mined for magnesium production <u>and</u> $CO_2$ sequestration, the amount of rock used for each purpose being dictated by market conditions.

# Magnesium Production
## Summary of Current Producers

| Company | Production Process | Raw Material |
|---|---|---|
| Noranda | Electrolysis | Serpentine |
| Magcorp | Electrolysis | Natural Brine |
| Norsk Hydro- Canada | Electrolysis | Magnesite |
| Norsk Hydro- Norway | Electrolysis | $MgCl_2$ |
| Dead Sea Magnesium | Electrolysis | Carnallite |
| Avisma | Electrolysis | Carnallite |
| Solikamsk | Electrolysis | Carnallite |
| Northwest Alloys | Thermal Reduction | Dolomite |
| Timminco | Thermal Reduction | Dolomite |
| Pechiney | Thermal Reduction | Dolomite |
| Rima | Thermal Reduction | Dolomite |
| Chinese Producers | Pidgeon | Dolomite |

# Conclusion

The pioneers of mineral carbonation R&D were right all along!

- Klaus Lackner
- Darryl Butt
- Chris Wendt
- George Guthrie
- Fraser Goff
- Rich Walters
- Bill O'Connor
- Steve Gerdemann
- Mike McKelvy

Mineral carbonation has the potential to be a widely deployed, "value-added" technology for sequestering huge masses of $CO_2$.