Aqueous mineral carbonation and CO_2 reactions in basalts for forming mineral carbonates

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- Present day atmospheric concentration of CO_2 ~ 320 ppm

- Environmentally safe permissible upper limit ~ 450 ppm

- Global CO_2 concentration risen by 25% over last 200 Yrs.

- Excess usage of Fossil Fuels
- To meet ever growing Energy Demands–
  - **Increase in atmospheric accumulation of CO_2**
  - **Triggering perceptible changes in Climate--**
    - **Melting of Polar Ice Caps**
    - **Recession of Glaciers**
    - **Slow but inexorable rise in Sea Levels**

What is Carbon Sequestration?

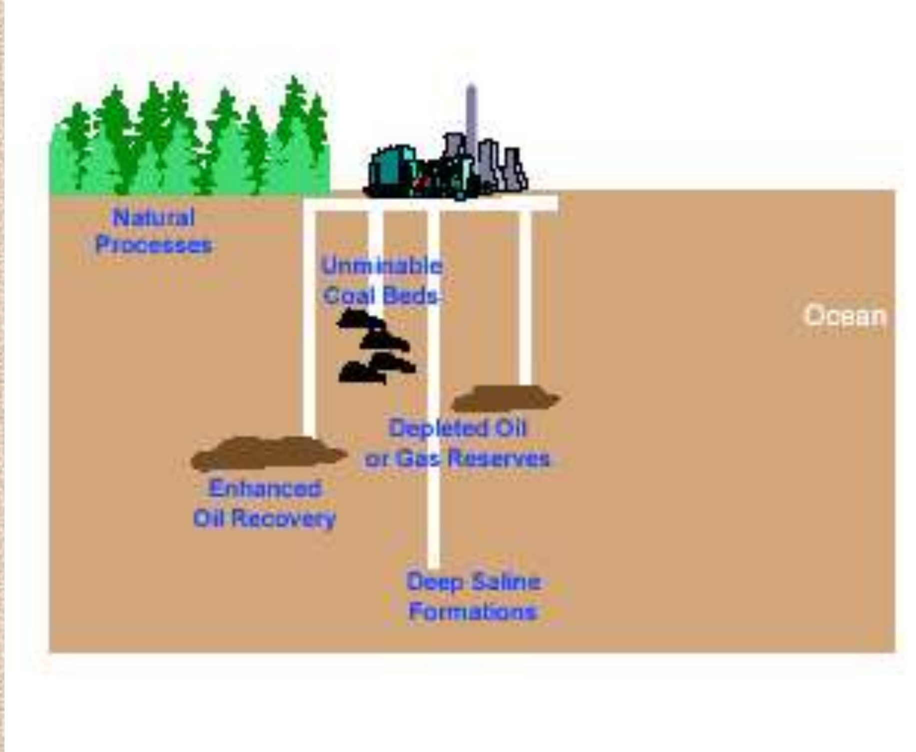
Capture and storage of CO_2 and other Greenhouse Gases that would otherwise be emitted to the atmosphere

Capture can occur:

- at the point of emission when absorbed from air.

Storage locations include:

- underground reservoirs.
- dissolved in deep oceans.
- converted to solid material.
- trees, grasses, soils, or algae

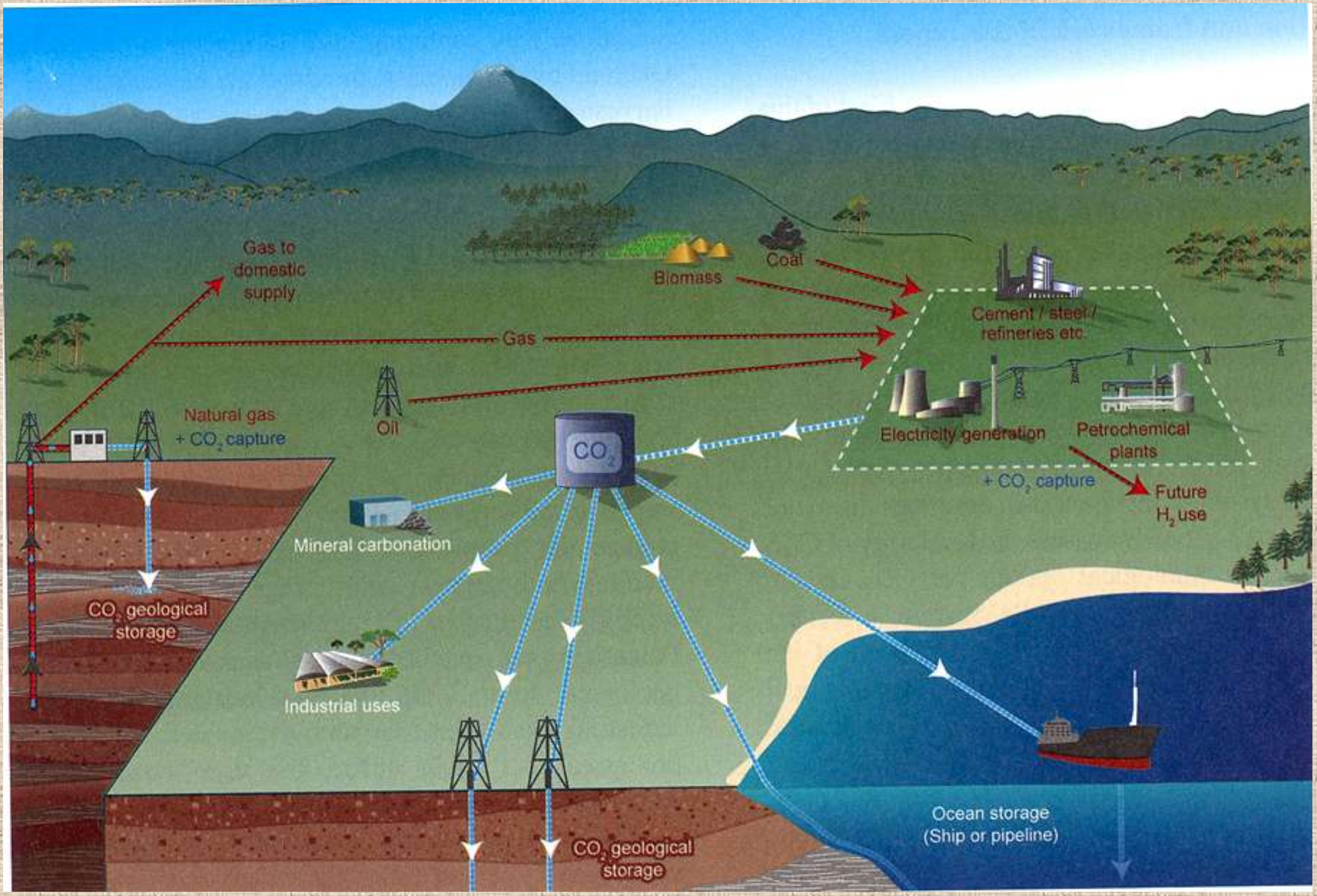


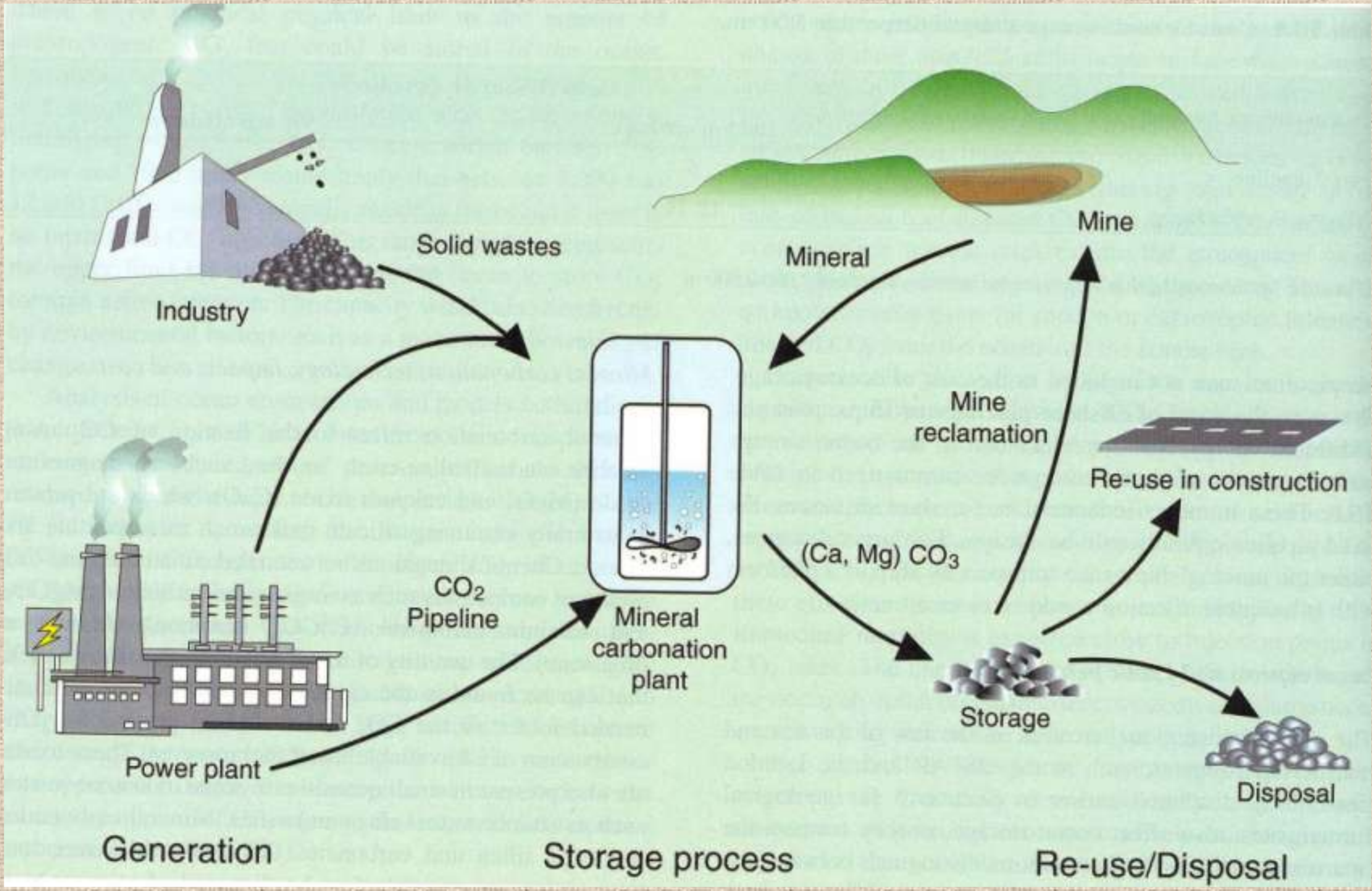
Storage Options- Geological (Best)--

- Capacity & security for sequestering large quantity of CO_2 with economic benefits.

Potential Storage Sites--

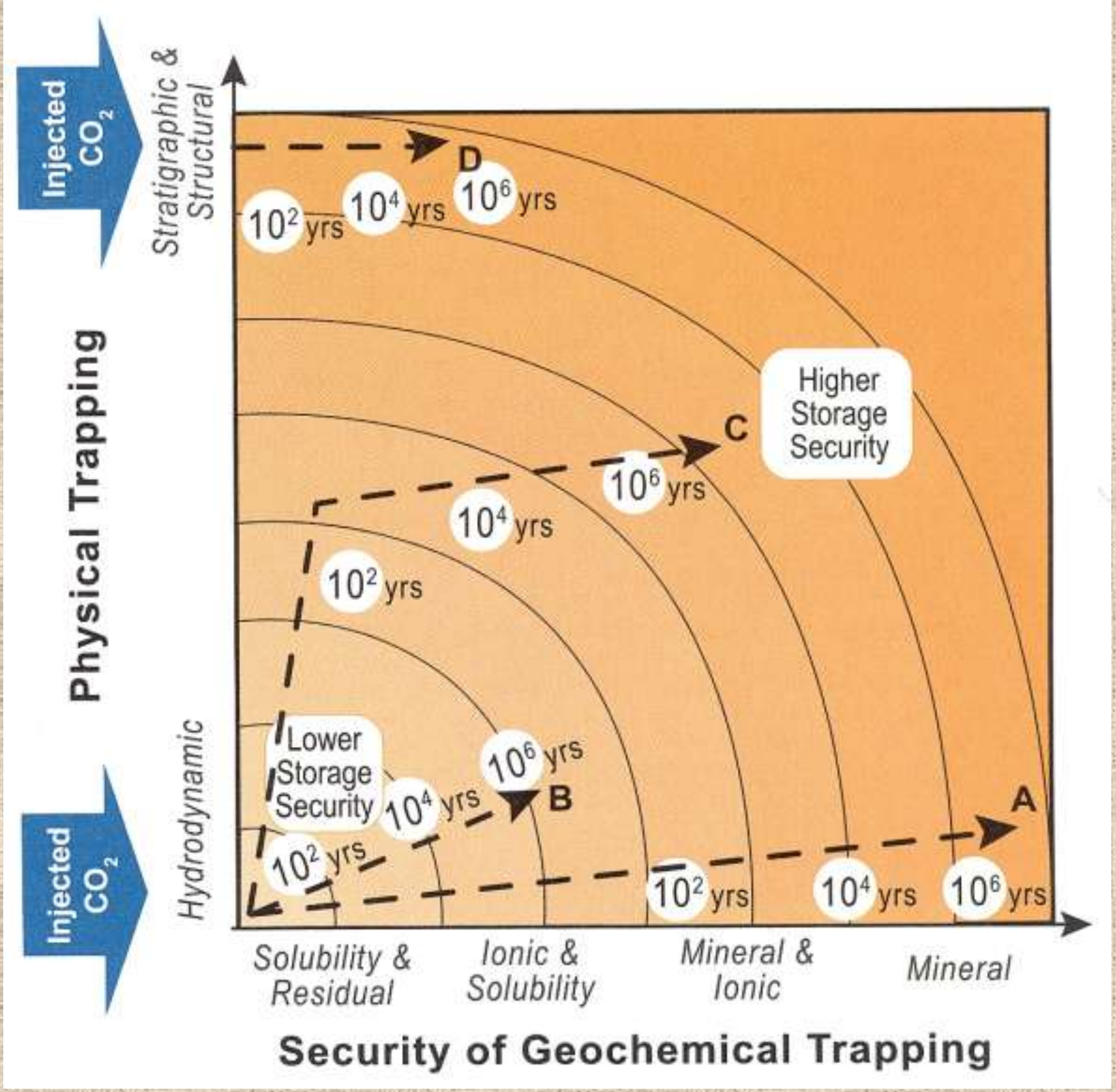
- Deep Saline Aquifers
- Basic/Ultrabasic Rock Formations (CFB, LC,GSB)
- Oil and Gas Fields (EOR)
- Abandoned Coal Mines (CBM)


Gas to domestic supply
Biomass
Coal
Cement / steel / refineries etc.
Gas
Oil
Natural gas + CO_2 capture
CO_2
Electricity generation
Petrochemical plants
+ CO_2 capture
Future H_2 use
Mineral carbonation
CO_2 geological storage
Industrial uses
Ocean storage (Ship or pipeline)
CO_2 geological storage

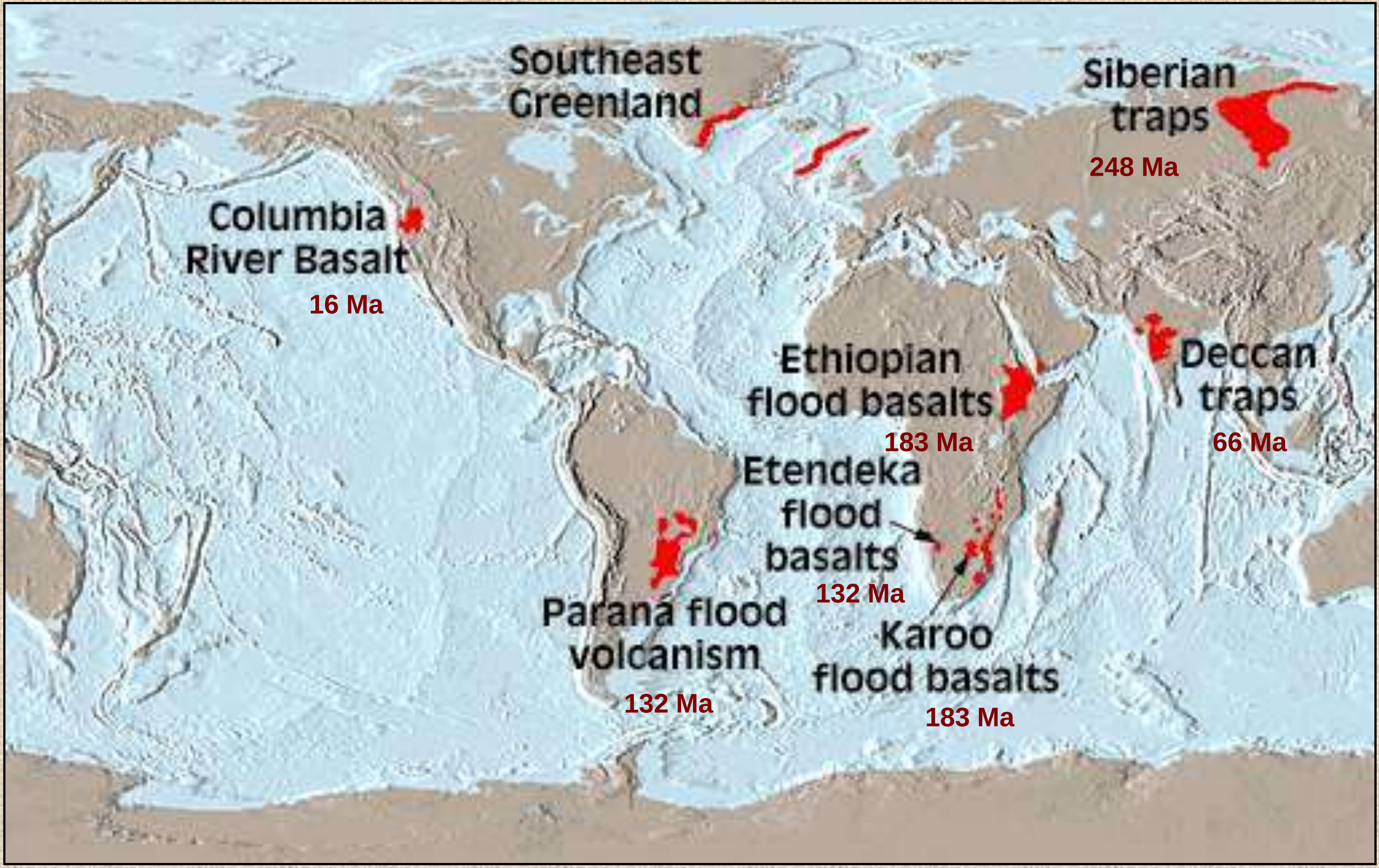


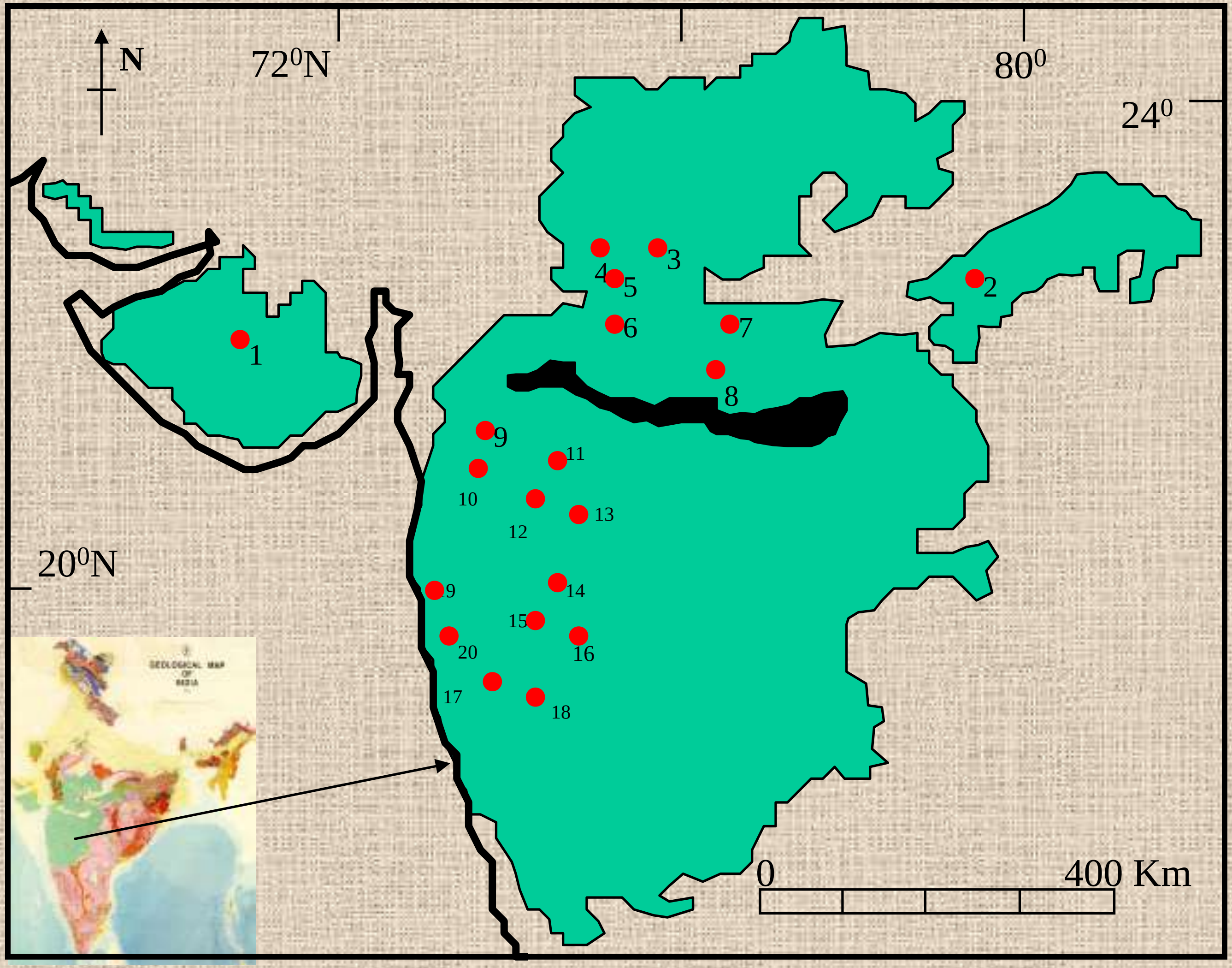
Solid wastes
Industry
Mineral
Mine
Mine reclamation
Re-use in construction
(Ca, Mg) CO_3
CO_2 Pipeline
Mineral carbonation plant
Storage
Power plant
Disposal
Generation
Storage process
Re-use/Disposal

- **Geological sequestration of CO_2 to be a practicable large scale disposal option, the injected CO_2 must remain safely underground for geological time scales.**
- **Best achieved by *Mineral Trapping*, allowing the natural buffering processes sufficient time to reduce the global atmospheric CO_2 levels to environmentally safe and acceptable levels.**


Injected CO2
Stratigraphic & Structural
D
10² yrs
10⁴ yrs
10⁶ yrs
Physical Trapping
Higher Storage Security
C
10⁶ yrs
10⁴ yrs
10² yrs
Hydrodynamic
Injected CO2
Lower Storage Security
10⁶ yrs
10⁴ yrs
B
10² yrs
A
10² yrs
10⁴ yrs
10⁶ yrs
Solubility & Residual
Ionic & Solubility
Mineral & Ionic
Mineral
Security of Geochemical Trapping

Flood basalts cover more than 1 million km^2 of the Earth's surface





Generalised Geology Map of Deccan Volcanic Province,India (Modified after Richa Sahu et. al. 2003)

Why Deccan Flood Basalt Province ?

- Large and continuous aerial extent (500,000 Sq. Km.)
- Number of sequential basalt flows (av. >10)
- Favorable structural and interflow features.
- Reactive Fe-Mg-Ca and Na-rich silicate mineral assemblages
- Underlain at places by Mesozoic Sediments (SST)
- -- suggesting that the DVP can be a potential deep underground storage reservoir for CO_2

  -- (to be proved by pilot scale studies)

Objectives

- To carryout laboratory scale aqueous mineral carbonation experiments under simulated conditions, using basalt-picrite, water and CO_2 (reactants) aimed at mineral carbonation and document the nature of carbonates (products).

- To document the reaction kinetics under varied P, T, pH conditions between CO_2, the primary silicate minerals in basalts namely olivine, pyroxene and plagioclase (reactants) and the secondary carbonates, serpentine and clay (products) and estimate the rate and extent of mineral carbonation.

Rationale

- Study: Knowledge base on how CO_2 reacts (its reaction kinetics as a function of T,P, porosity/permeability) through low to high-T experiments to better understand the dissolution kinetics & affinity of Ca/Mg/Fe-silicates for forming the secondary carbonates.

- Computing rate of carbonate mineral formation in basalt flows requires: (a) Solution conc. of Ca/ Mg/ Fe required to precipitate stable carbonates and (b) the concentration of dissolved CO_2.

Deccan Basalt Province

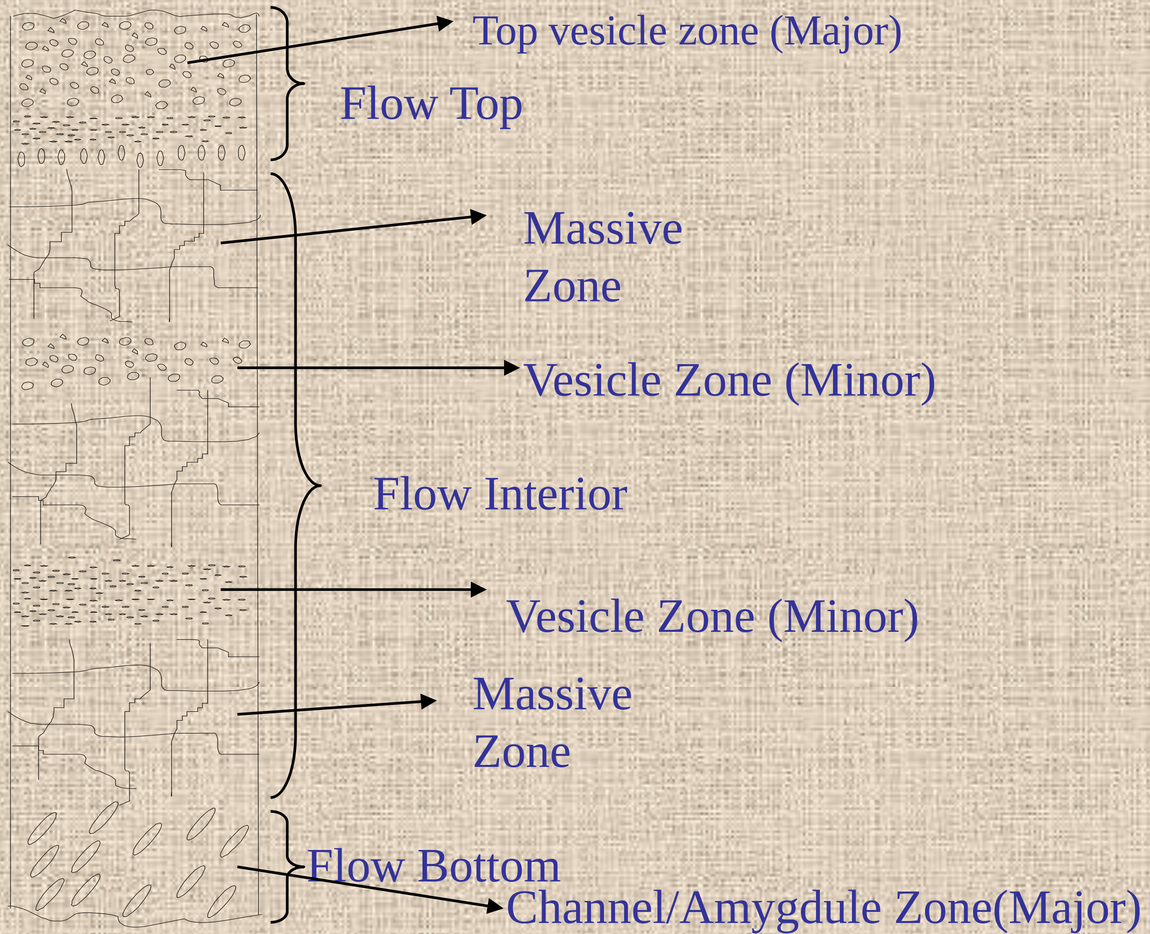
Favorable megascopic features in DVP

Intertrapeans between basalt flows, Igatpuri (Ma)

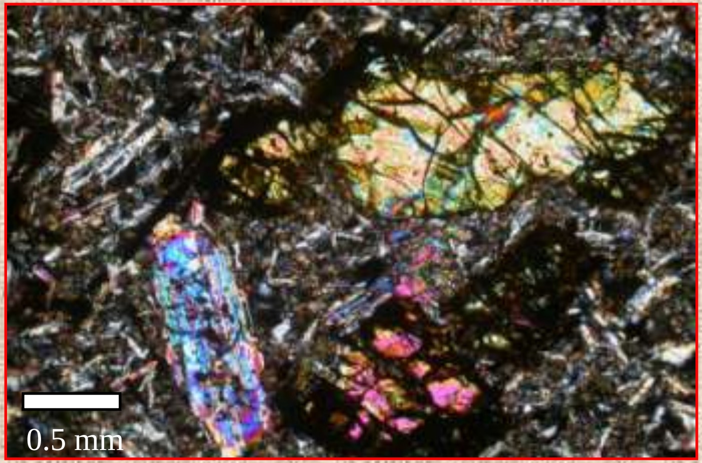
Pipe vesicles in basalts, Igatpuri (Ma)

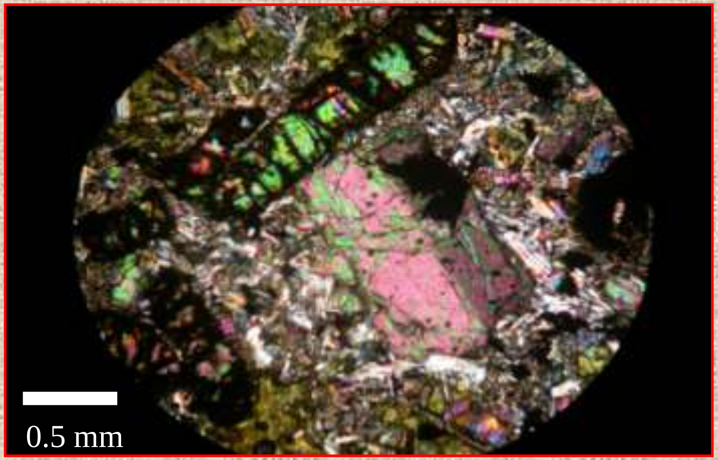
Amygdular basalt, Igatpuri (Ma)

Interflow Features in a Basalt Flow Unit at Kalsubai Hill (Ma)

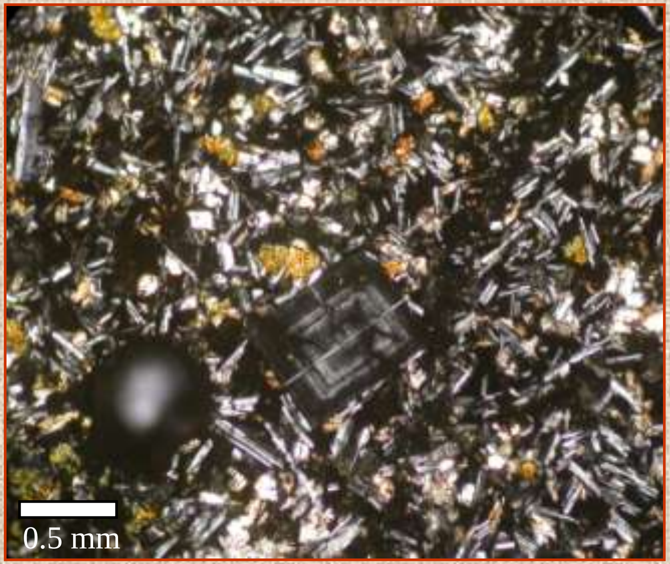


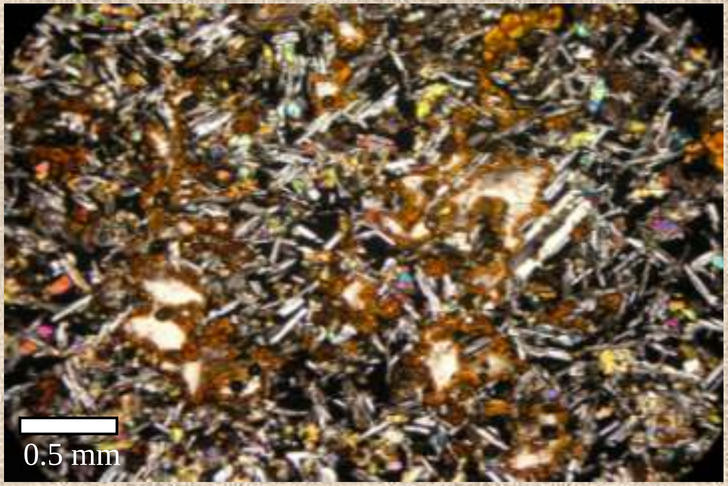
Mineralogy of Picrites





Mineralogy of Tholeiites





Simulation studies

- Preliminary Aq.Experiments using Picrite (Igatpuri Formation) & CO_2 (@100^0 C, 60 bars CO_2 pressure) for 5 months—in 3 steps

- CO_2 dissolved in an Aq.phase (CO_2+H_2O—H_2CO_3
- Fe/Mg/Ca leaching facilitated by protons (Fe/Mg/Ca-silicates(s)+2H+(aq) $(Fe/Mg/Ca)^{2+}$(aq)+SiO_2+H_2O
- Fe/Mg/Ca bearing sec. carbonates formed $(Ca/Mg)^2$+(aq)--(Ca/Mg) CO_3(s)+H^+(aq).

- A general mineralization reaction scheme is:

$$CO_2\ (g) \rightleftarrows Kh\ CO_2\ (aq)\ (1)$$

$$CO_2\ (aq) + H_2O \rightleftarrows K1\ HCO_3^- + H^+\ (2)$$

Where Kh=Henry's constant; K1=Equilibrium constant. Pressurization with CO_2 (g) produces Carbonic acid (CO_2 (aq)), bicarbonate anions and H^+ via reactions (1 & 2) lowering the solution pH.

Causative exothermic mineral reactions

- $2Mg_2SiO_4$(Ol) + $2H_2O$ $\longrightarrow$ $Mg_3SiO_5(OH)_4$ (Serp) + $MgCO_3$ (Mag).
- $CaAl_2Si_2O_8$(Plag)+$2H_2O$ + CO_2 $\longrightarrow$ $CaCO_3$(Cc)+$AlSi_2O_5$(OH) (Clay).

Both the above reactions are exothermic hence they releasing lot of heat energy during this process which can be trapped to generate electricity on a small scale.

Computing the rate of carbonate mineral formation in the basalt flows requires:

- solution conc. of Ca, Mg, Fe and Mn required to precipitate stable carbonates
- release rate of Ca, Mg, Fe & Mn from the basalt
- the concentration of dissolved CO_2.

In-situ mineral carbonation

- $CaO+CO_2 \longrightarrow CaCO_3$+179 kJ/mole.
  $MgO+CO_2 \longrightarrow MgCO_3$+118kJ/mole.

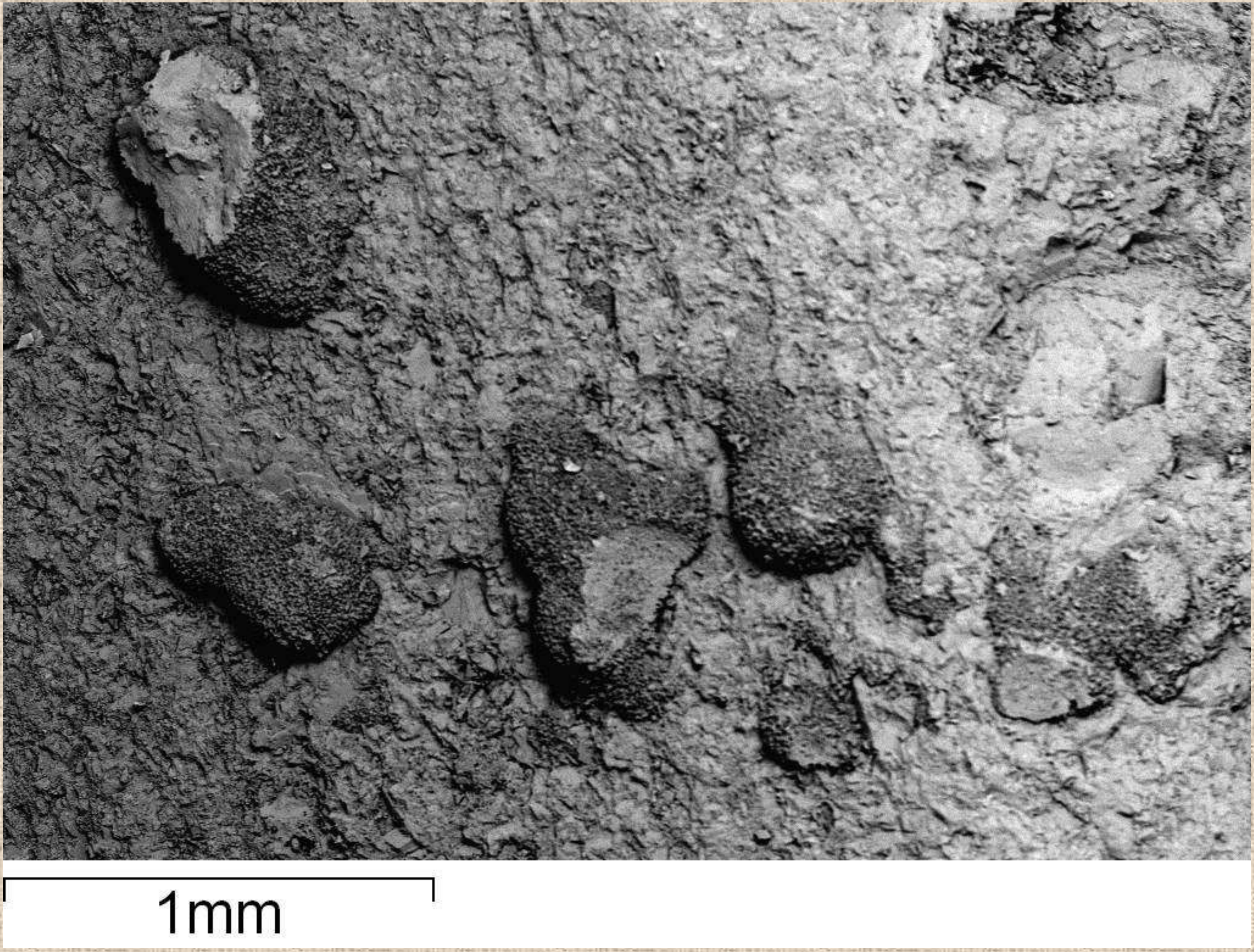
- Carbonation reaction is thermodynamically favored –carbonates are at lower energy state—CO_2.

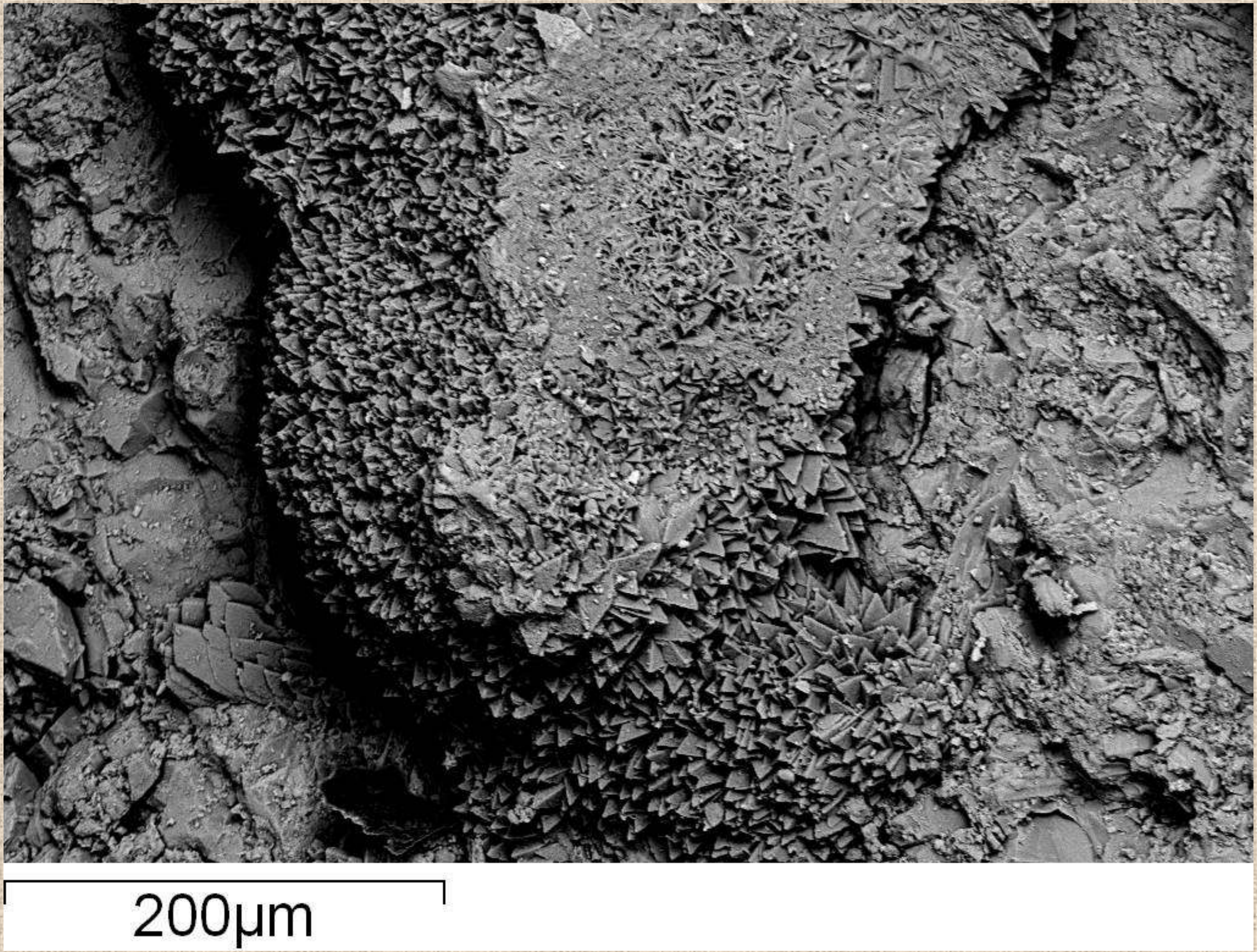
- $Mg_2SiO_4+2CO_2 \longrightarrow 2MgCO_3+SiO_2$+95kJ/mole.
  140 gms 88gms 168gms 60gms

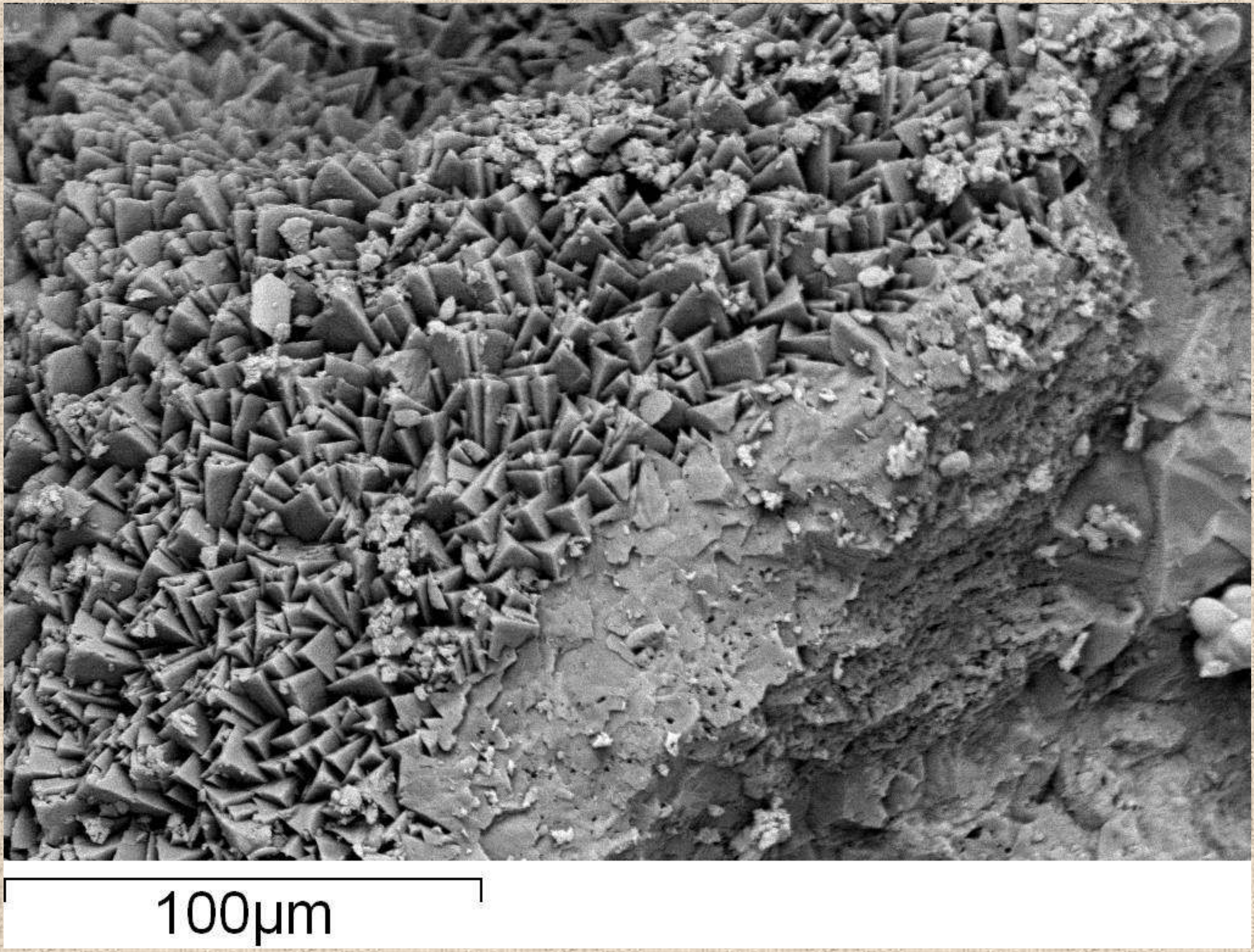
- $2Mg_2SiO_4+CO_2(g)+H_2O \longrightarrow Mg_3Si_2O_5(OH)_4+MgCO_3$+16.5 Kcal
  280gms 44gms 36gms 276gms 84gms

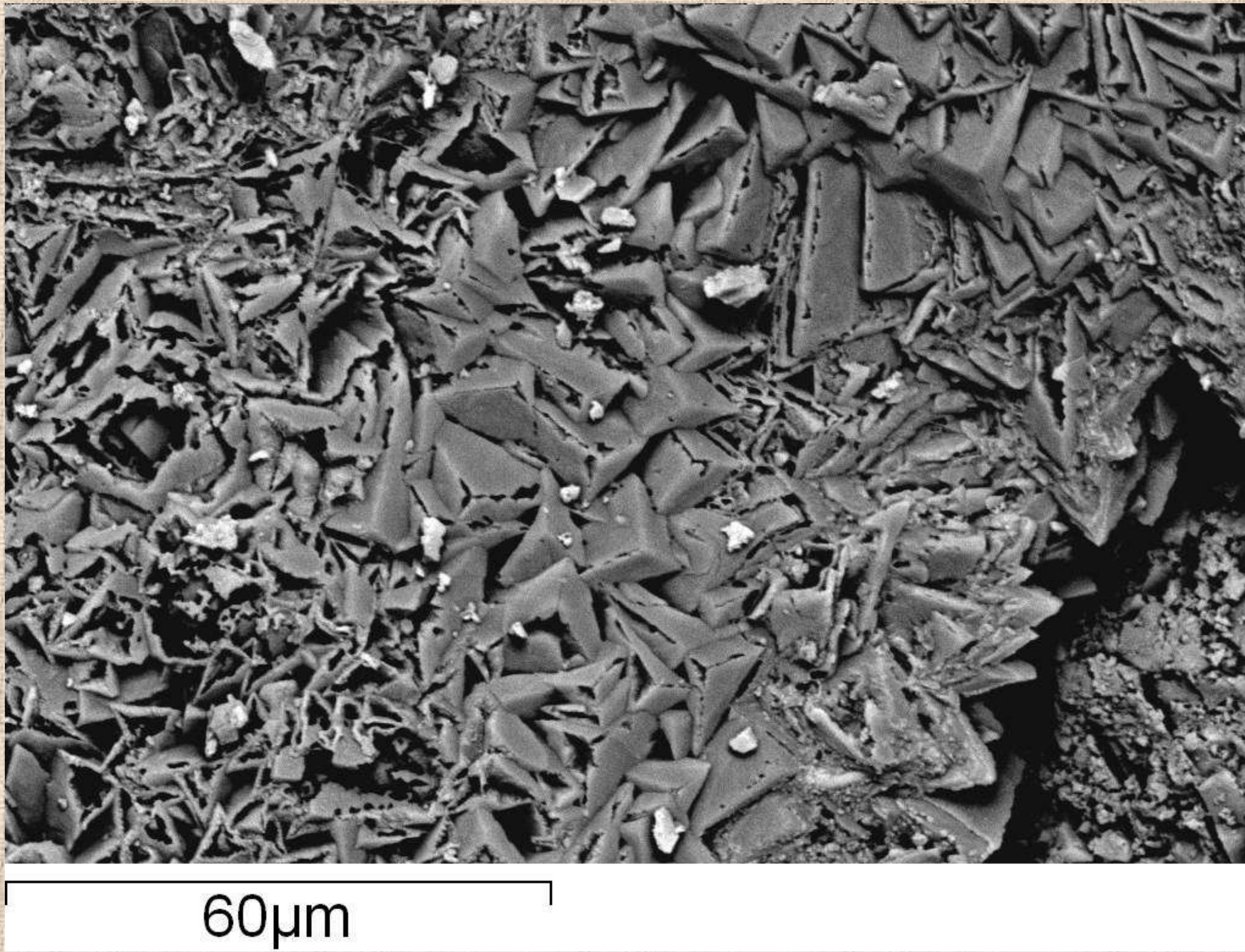
Laboratory Simulated Mineral Carbonation

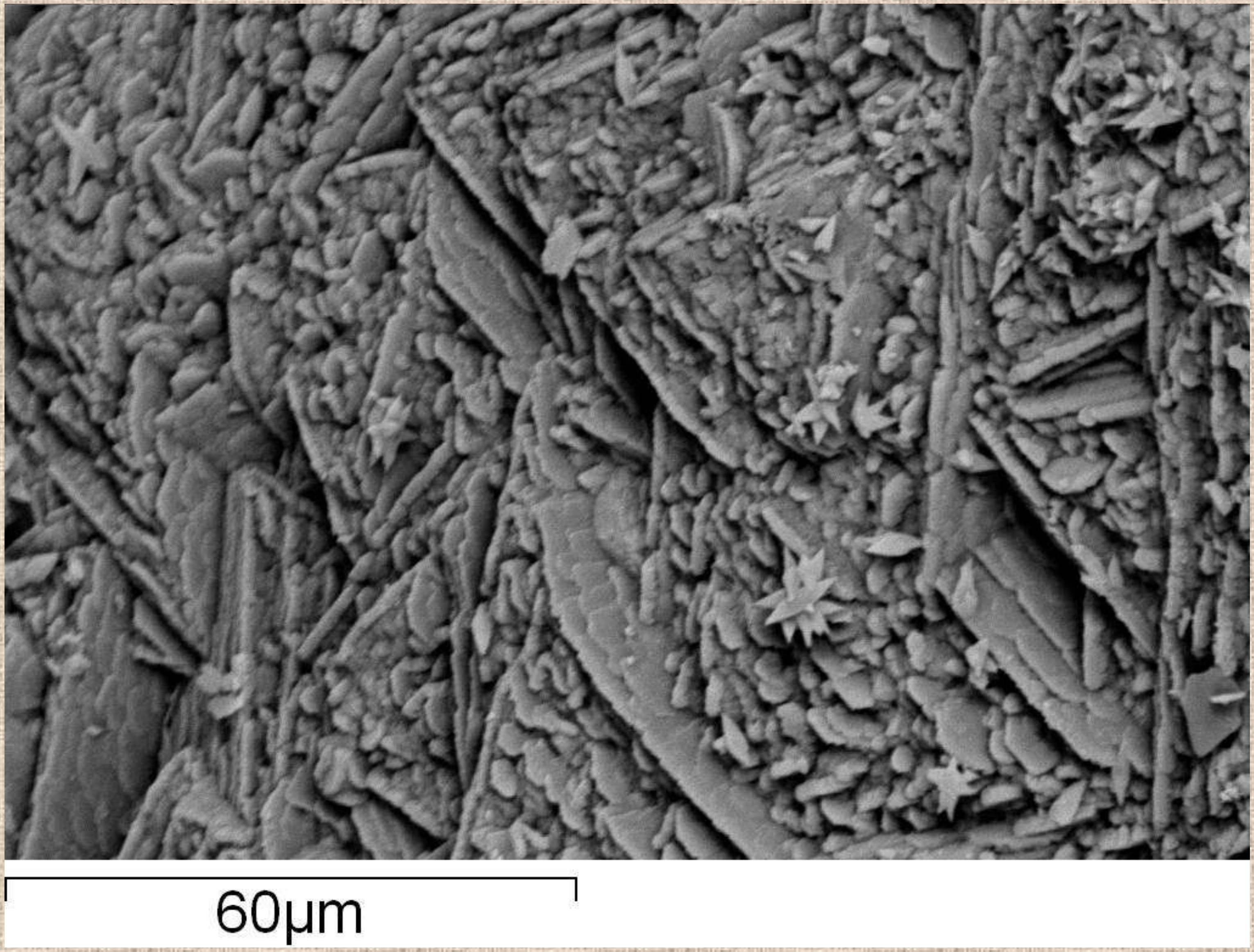
Secondary Ca/Mg/Fe carbonates formed by reacting CO_2 and Picrite (Western DVP)


1mm

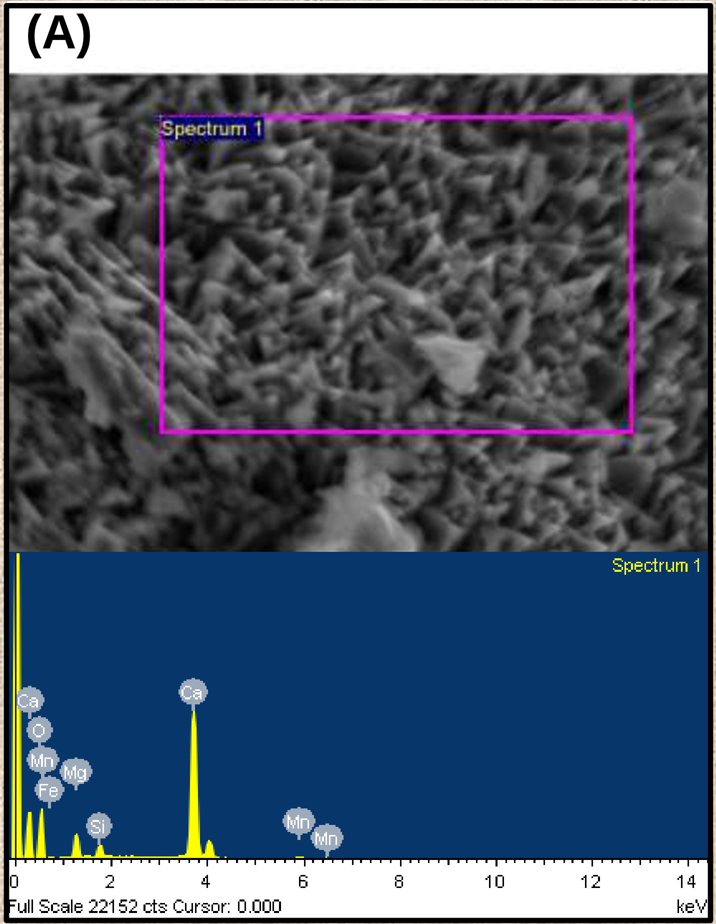

200μm

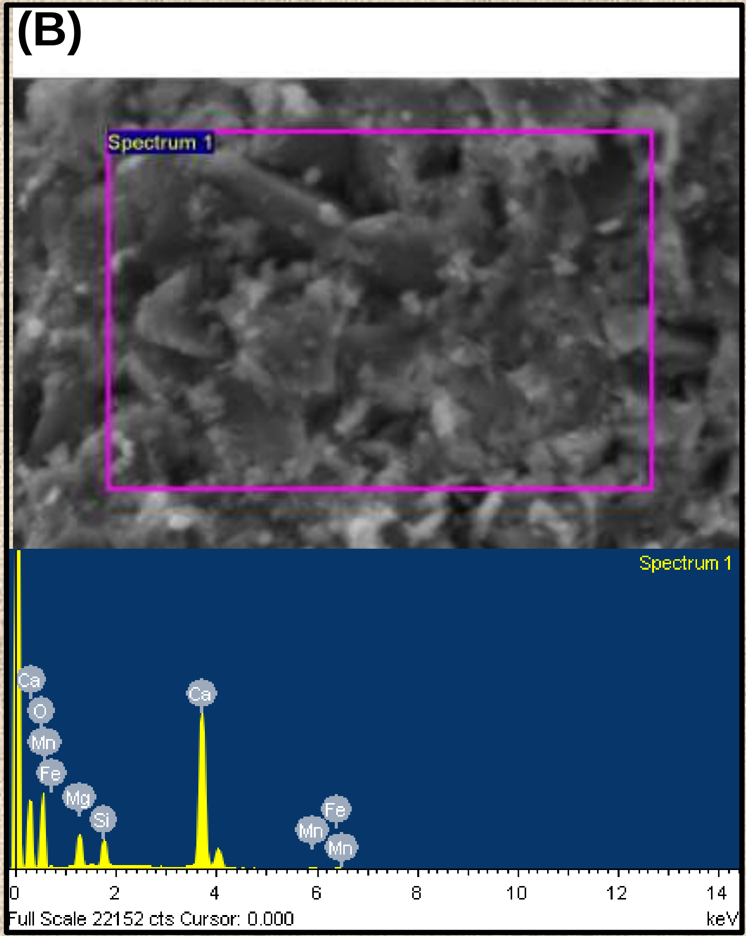

100µm


60µm

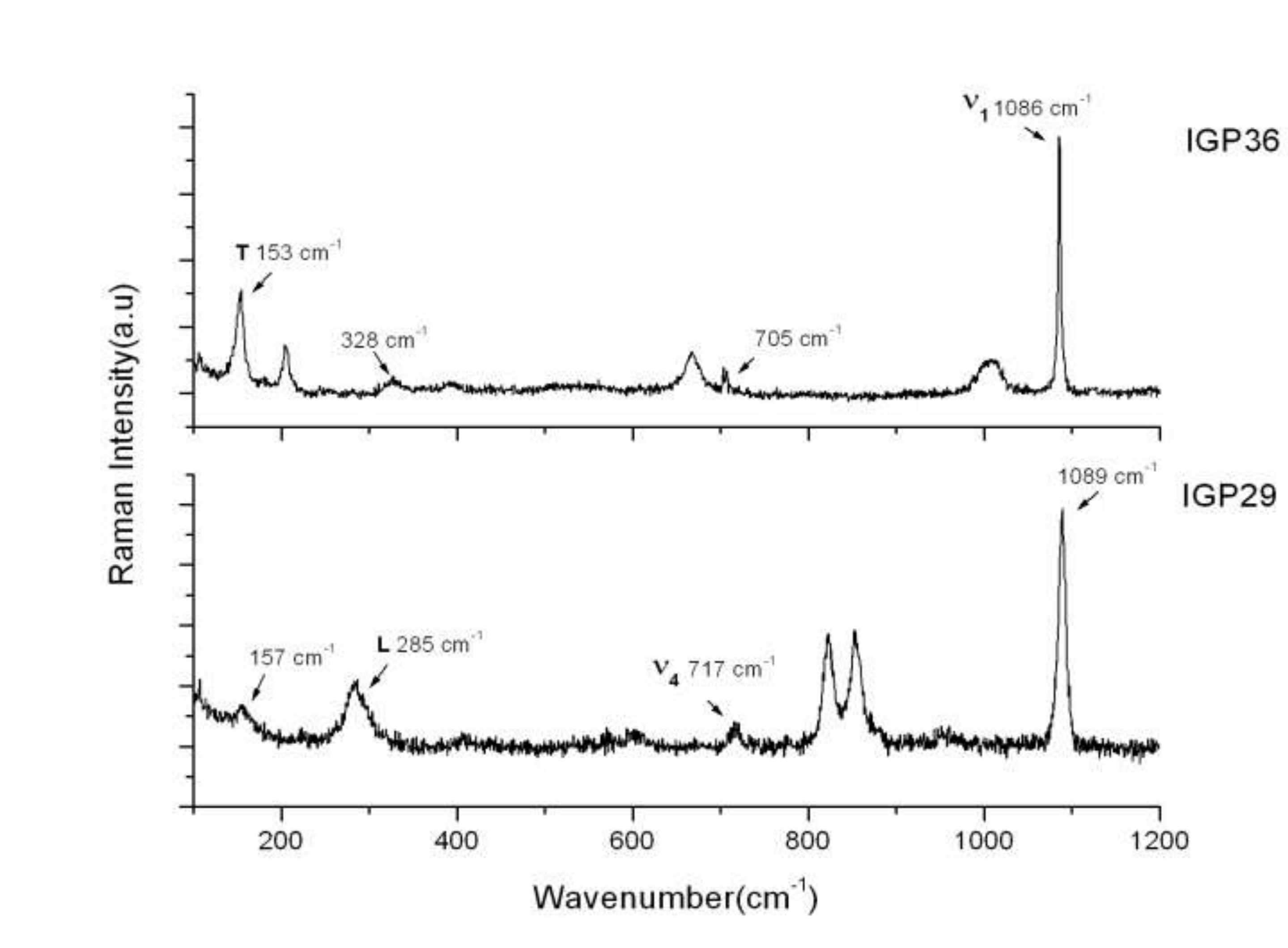

60µm

EDS Spectrum

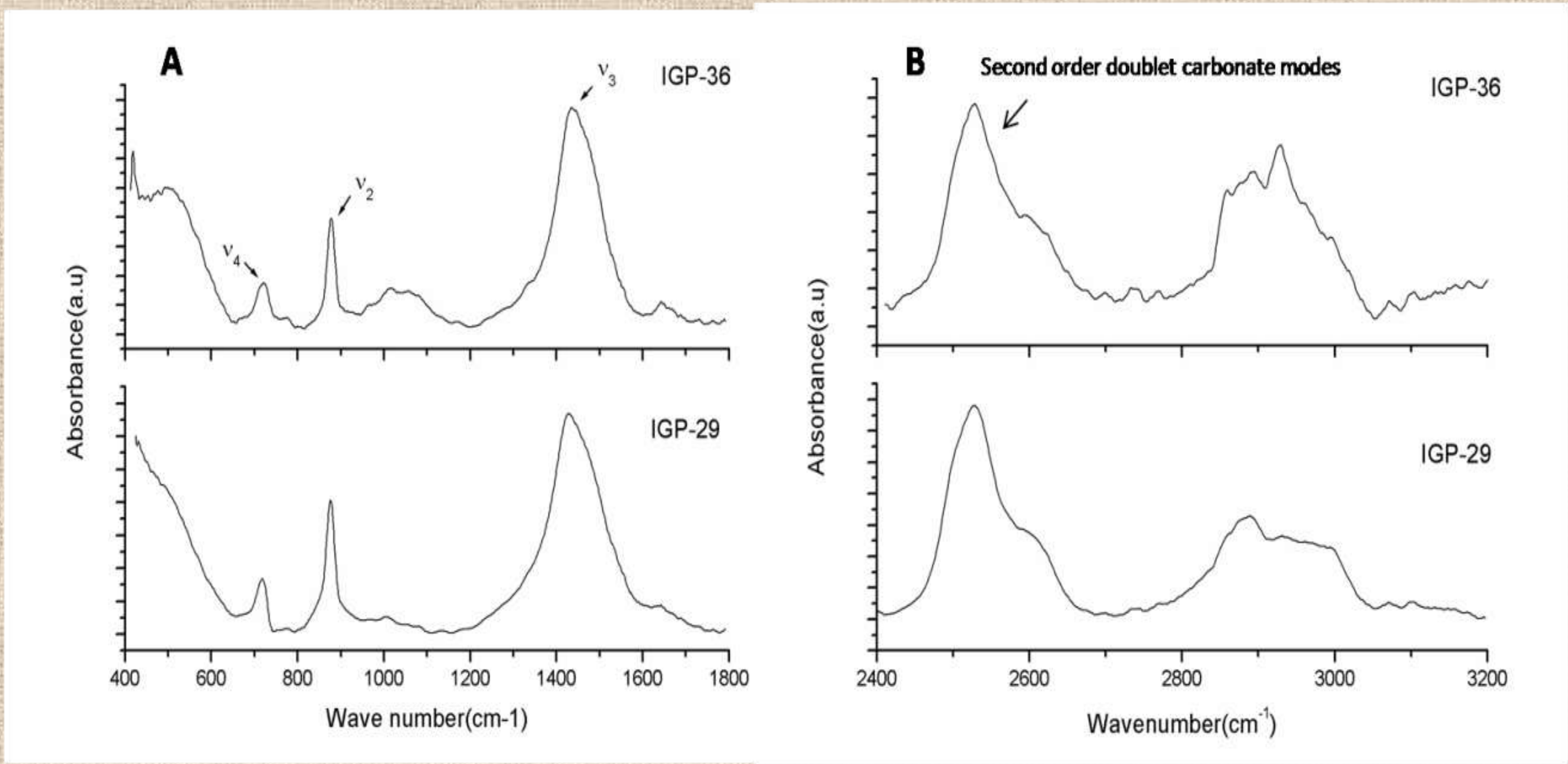




Raman spectra of secondary carbonates



FTIR spectra of secondary carbonates



Thank you