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CO_2 Sequestration

Experimental CO_2-Brine-Limestone Interaction at Elevated Temperature and Pressure: Implications for the Geologic Sequestration of CO_2 in Deep Saline Brines

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Multi-Agency Collaboration

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  - National Energy Technology Laboratory
  - U.S. Geological Survey
    - » Eastern Energy Resources Team
    - » Western Coastal & Marine Geology Team

Outline

- Geochemistry of CO_2 Sequestration
  - Theoretical reactions in a limestone matrix
    - CO_2 saturated-brine-mineral reactions (calcite, dolomite)
    - Examples of ionic trapping of CO_2
  - Experimental reactions in a limestone matrix
    - Solubility of CO_2 in a natural brine alone and in the presence of rocks from the Leadville Limestone at 21° and 120°C
    - Reactions between a natural brine and limestone in the presence and absence of supercritical CO_2 at 21° and 120°C
      - Address a specific brine disposal problem in a carbonate aquifer located in SW Colorado
    - Reactions between an aquifer brine and limestone in the presence and absence of supercritical CO_2 at 21° and 120°C
      - Address the ionic trapping of CO_2 in a carbonate aquifer in general

Experimental geochemical approach

- Obtain some understanding of the process of geologic sequestration of CO_2 through direct observation of geochemical reactions between supercritical CO_2 and potential aquifer fluids and host formation rocks.

Aqueous reactions of carbon dioxide:

- **Solubility: Anhydrous to aqueous form of CO_2**

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

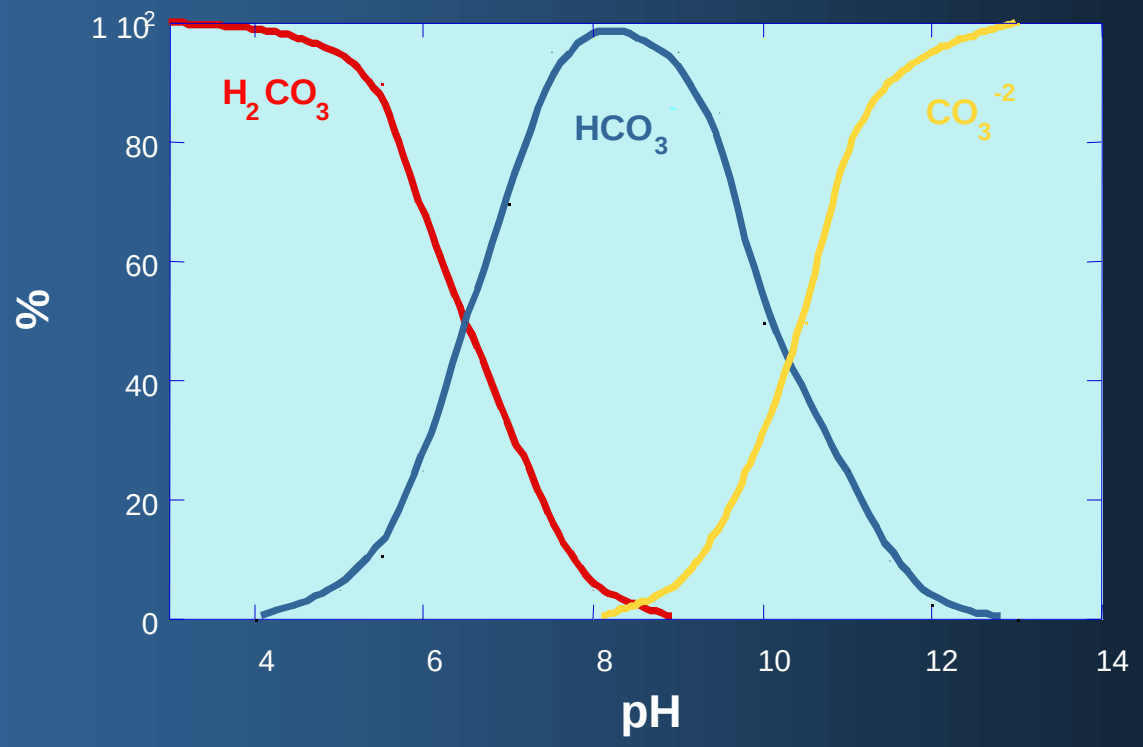
- **Dissociation of carbonic acid**

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$$

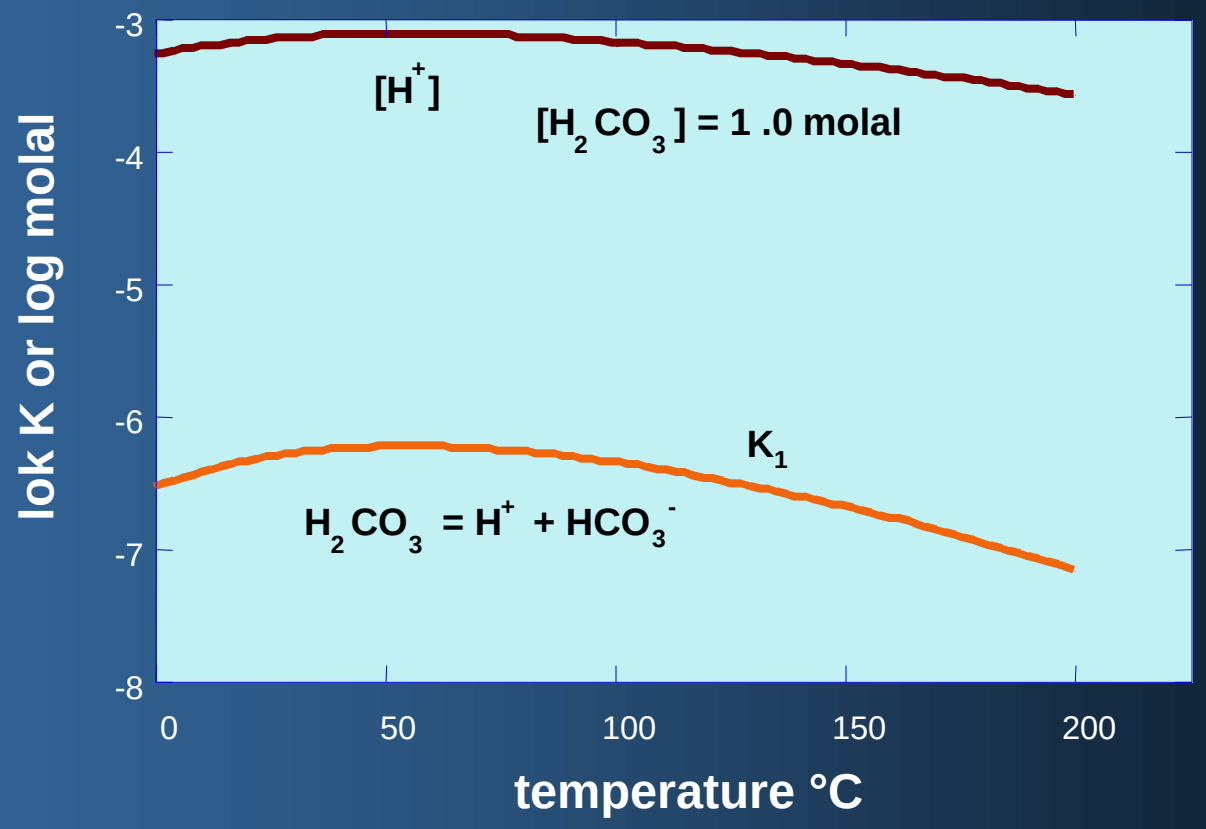
- **Dissociation of bicarbonate**

$$HCO_3^- \Leftrightarrow CO_3^{-2} + H^+$$

Idealized carbonate speciation



Carbonic acid dissociation (K_1)



Geochemistry of CO_2 storage: Trapping mechanisms

- Solubility Trapping → H_2CO_3 aqueous
  - CO_2 gas + H_2O
- Ionic Trapping → HCO_3^- aqueous, CO_3^{-2} aqueous
  - H_2CO_3 aqueous + base
  - HCO_3^- aqueous + base
- Mineral Trapping → $MeCO_3$ (solid)
  - CO_3^{-2} aqueous + Me^{+2}

Adapted From W.D.Gunter

Aqueous reactions in a limestone matrix: ionic trapping of CO_2 in water

- $CO_2 + H_2O \quad H_2CO_3$ **(Anhydrous to aqueous form of CO_2)**
- $H_2CO_3 \quad HCO_3^- + H^+ \uparrow$ **(Dissociation of carbonic acid)**

- <u>Calcite dissolution due to acidity (low pH)</u>

1. $\downarrow CO_3^{-2} + H^+ \quad HCO_3^-$

or $\downarrow CO_3^{-2} + CO_2 + H_2O \quad 2HCO_3^-$

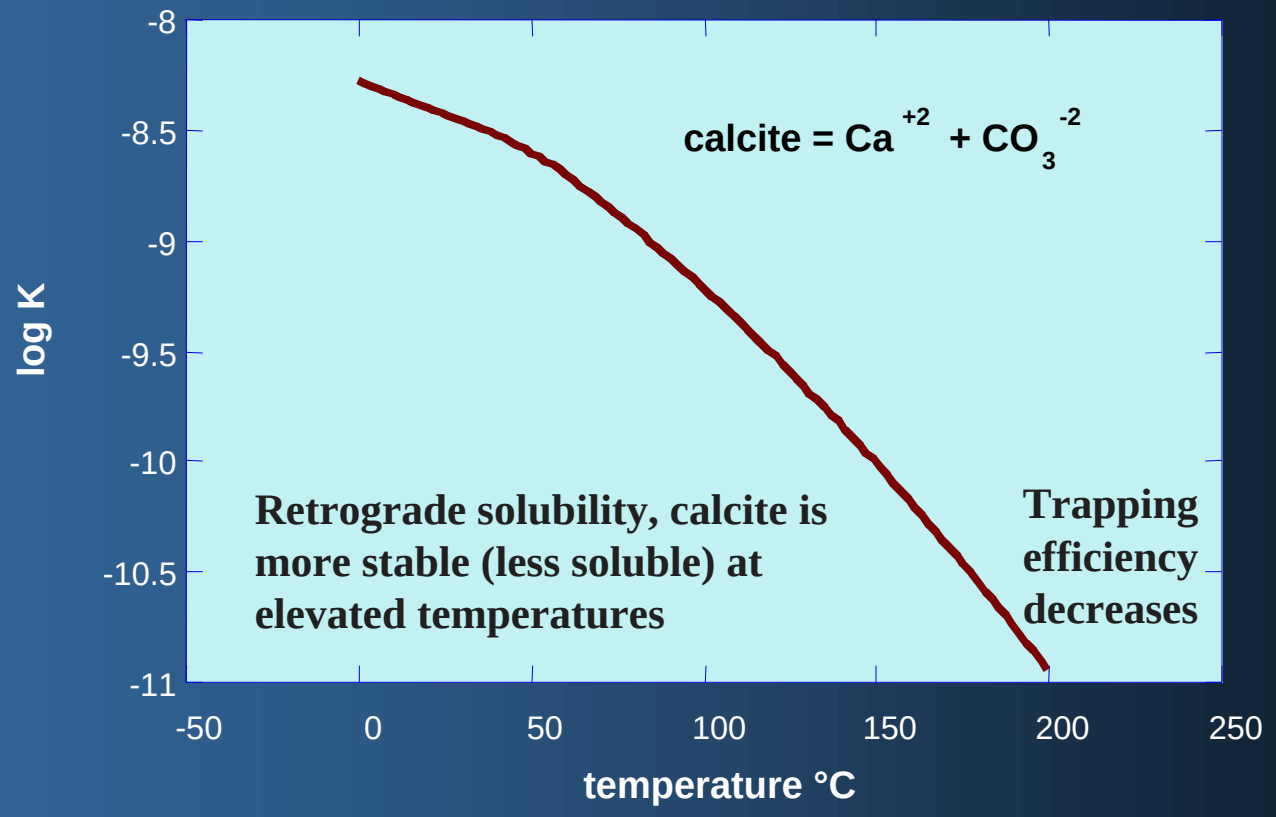
2. $\downarrow CaCO_3 \quad Ca^{+2} + CO_3^{-2} \uparrow$ Retrograde solubility

3. Net reaction: $CaCO_3 + CO_2 + H_2O \quad Ca^{+2} + 2HCO_3^-$

- Proceeds until saturation with calcite occurs ($IAP/K_{SP} = 1$)

$$\Delta G_r^0 = -RT \ln\left(\frac{Q}{K_{sp}}\right) = 0 \qquad Q = K_{IAP} = \gamma m_{Ca^{+2}} \; \gamma m_{CO_3^{-2}}$$

Calcite Dissolution



More aqueous reactions in a limestone matrix: ionic trapping of CO_2 in water

- Dolomite/siderite dissolution due to acidity (low pH)

Dolomite: $CaMg(CO_3)_2 + 2CO_2 + H_2O \quad Ca^{+2} + Mg^{+2} + 4HCO_3^-$

Siderite: $Fe(CO_3) + CO_2 + H_2O \quad Fe^{+2} + 2HCO_3^-$

- Proceeds until saturation occurs (IAP/KSP = 1)

$$\Delta G_r^0 = -RT \ln\left(\frac{Q}{K_{sp}}\right) = 0$$

$$Q_{dolomite} = K_{IAP} = \gamma m_{Ca^{+2}} \; \gamma m_{Mg^{+2}} \; \gamma m^2_{CO_3^{-2}}$$

$$Q_{siderite} = K_{IAP} = \gamma m_{Fe^{+2}} \; \gamma m_{CO_3^{-2}}$$

Summary: Carbonate geochemistry in a limestone formation

Solids		Aqueous	
calcite		Ca^{+2}	
	Dissolve →		
dolomite		Ca^{+2}/Mg^{+2}	$+HCO_3^-$
	Precipitate ←		
siderite		Fe^{+2}	

Porosity →

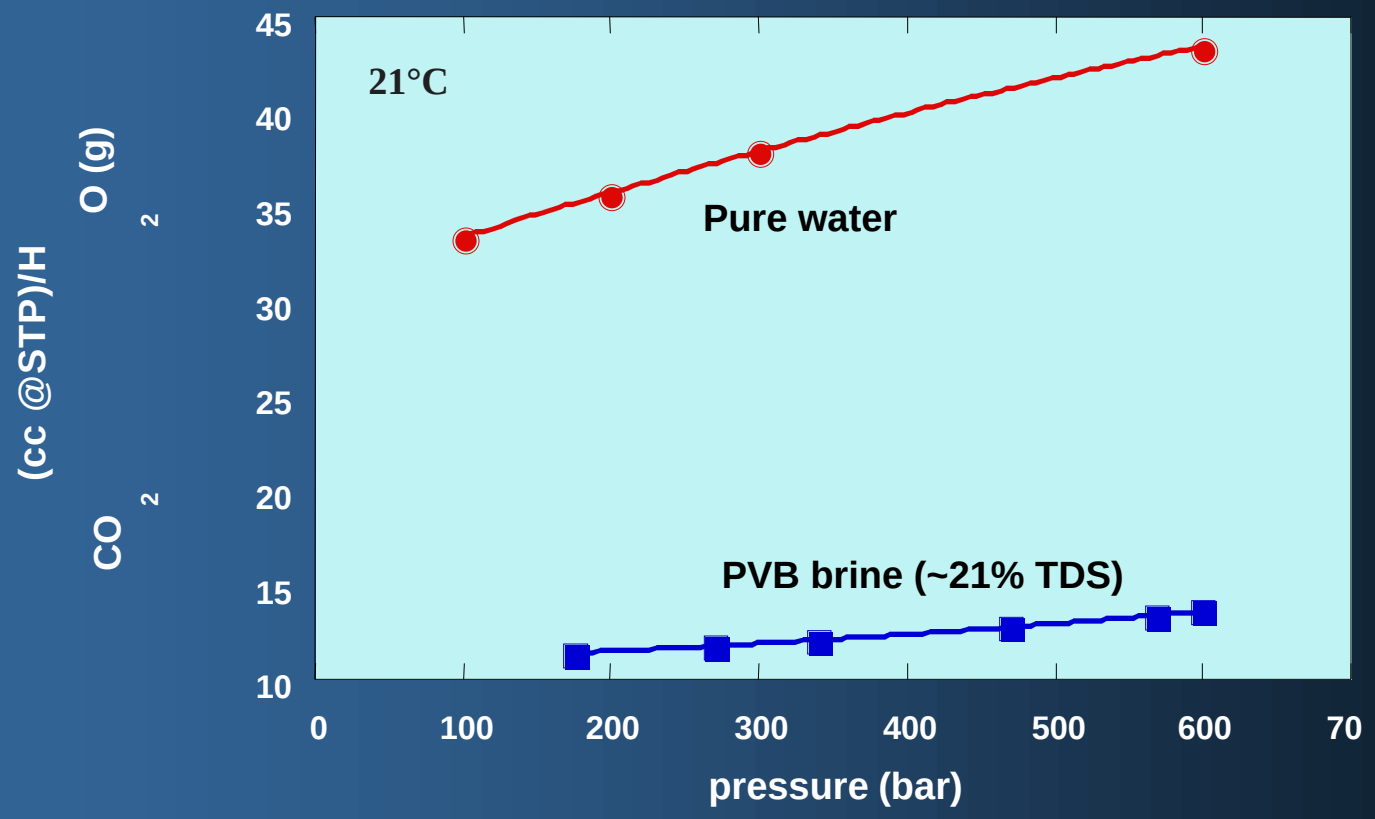
→ P_{CO2}

Experimental study: Goals

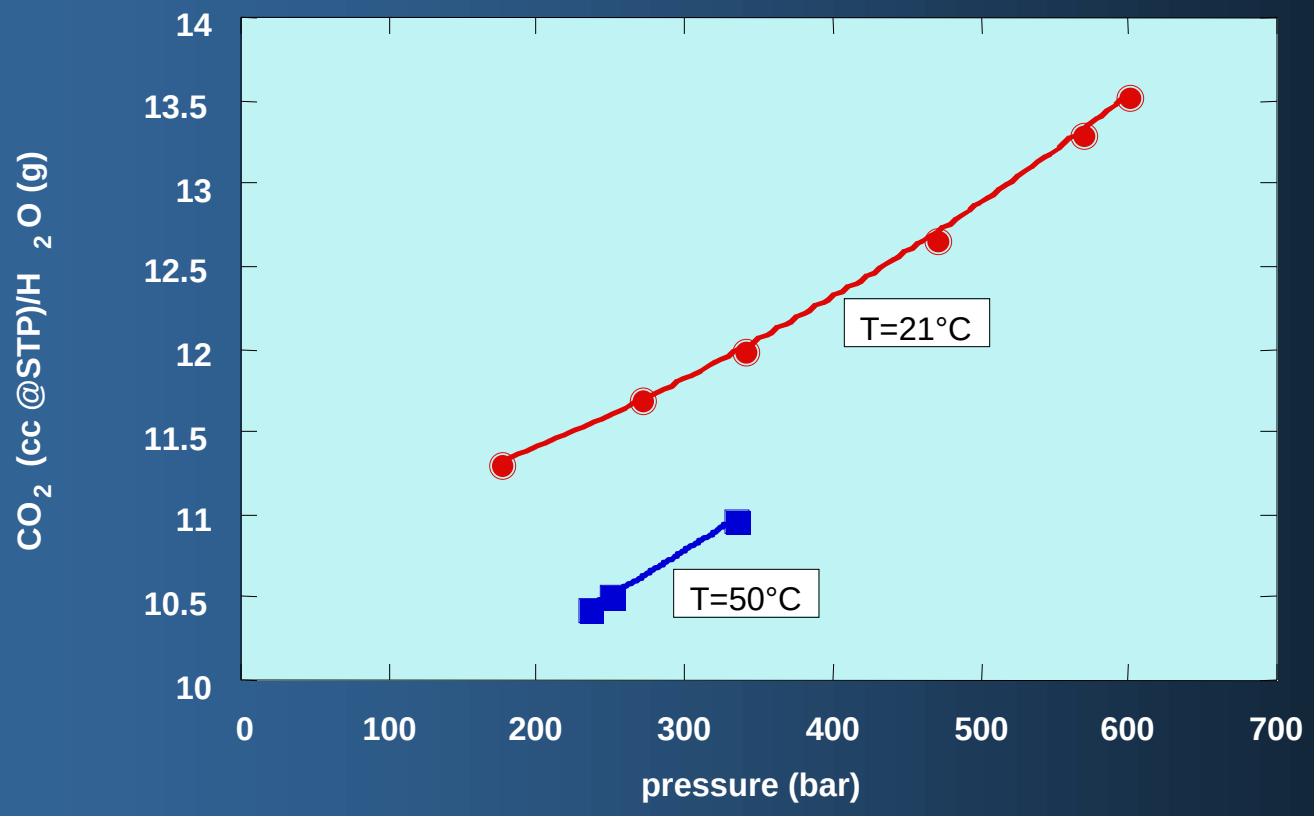
- Explore experimentally the geochemical reactions that might provide the fixation of CO_2 via mineral dissolution and precipitation.

- Provide fundamental experimental data for thermodynamic models of CO_2 sequestration in saline aquifers

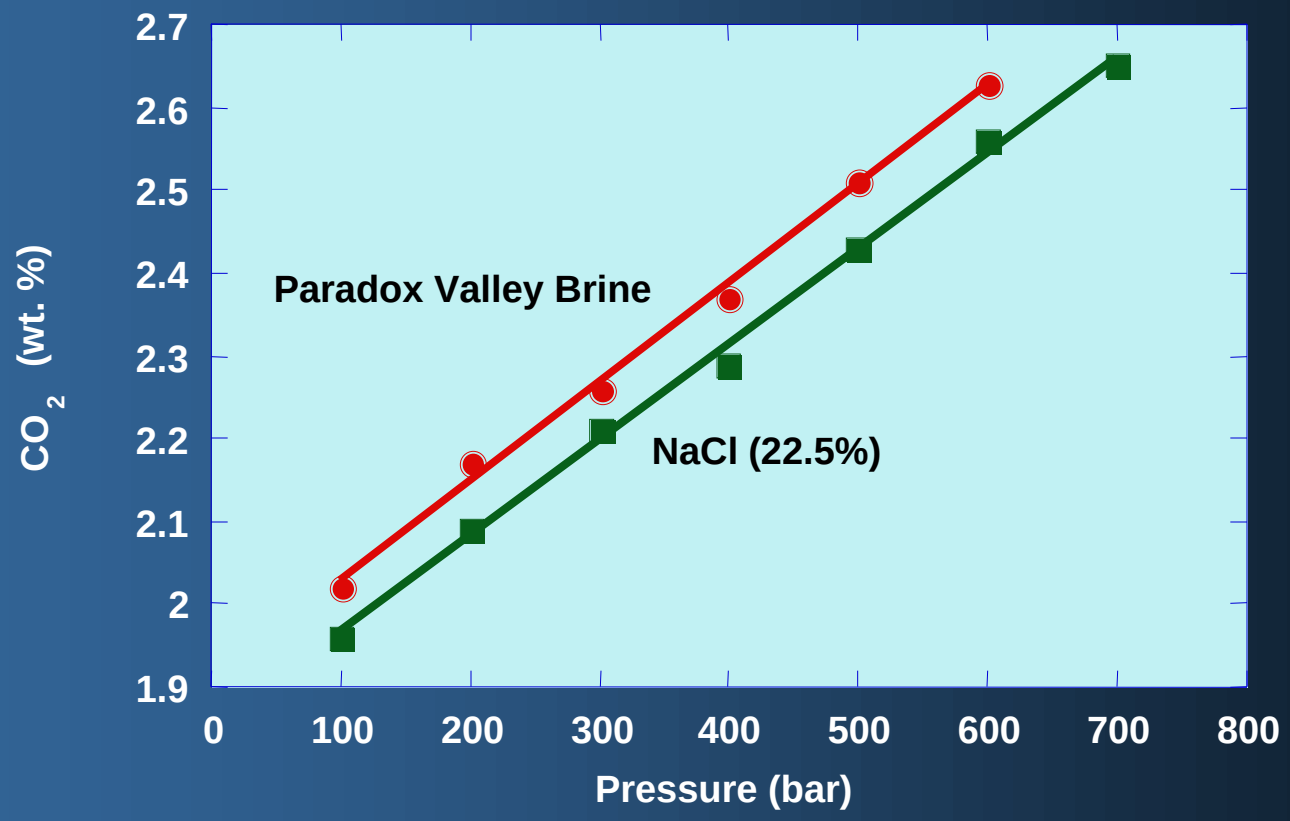
Solubility of CO_2 in pure water relative to Paradox Valley Brine



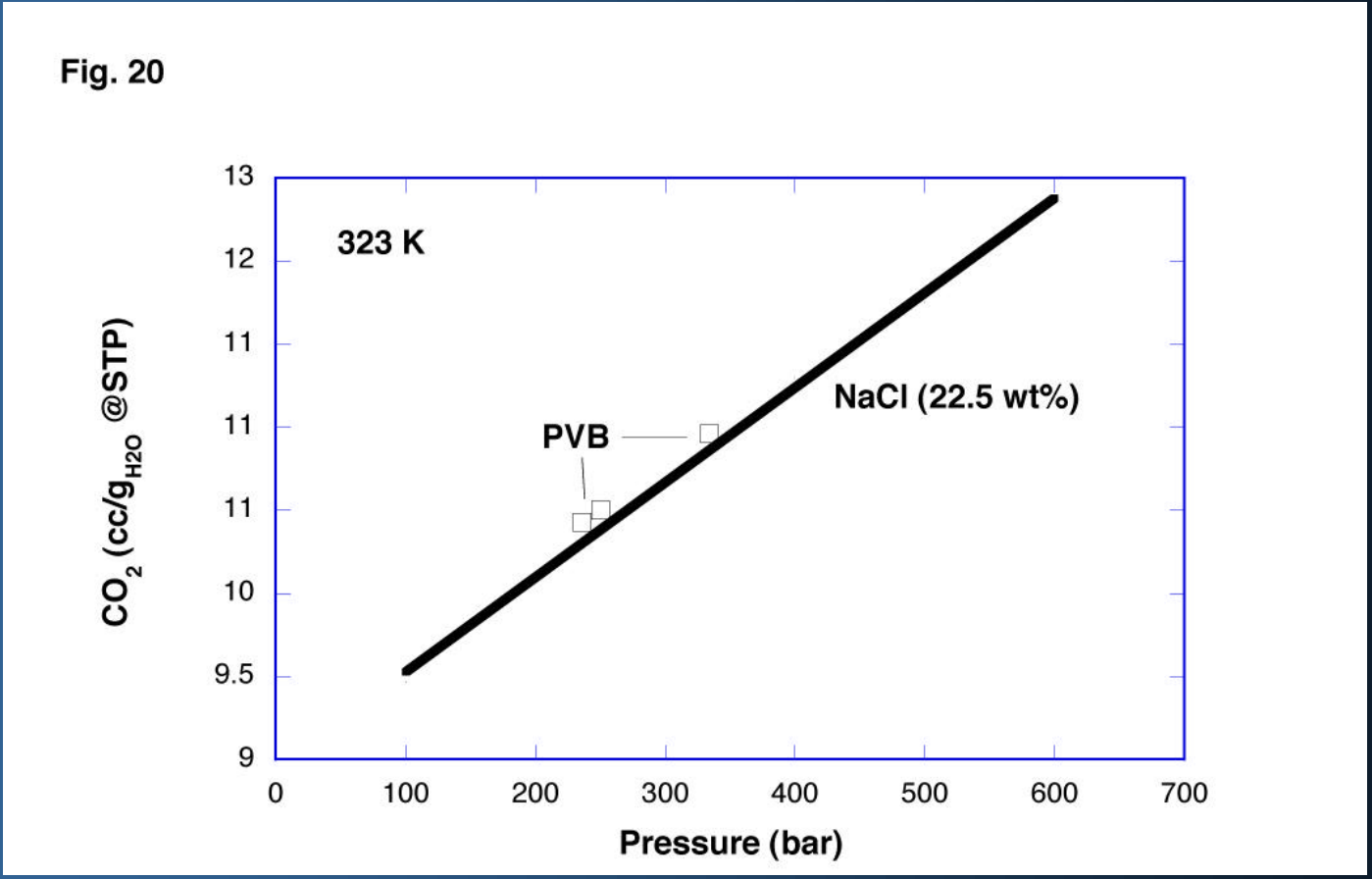
Solubility of CO_2 in Paradox Valley Brine at 21° and 50°C



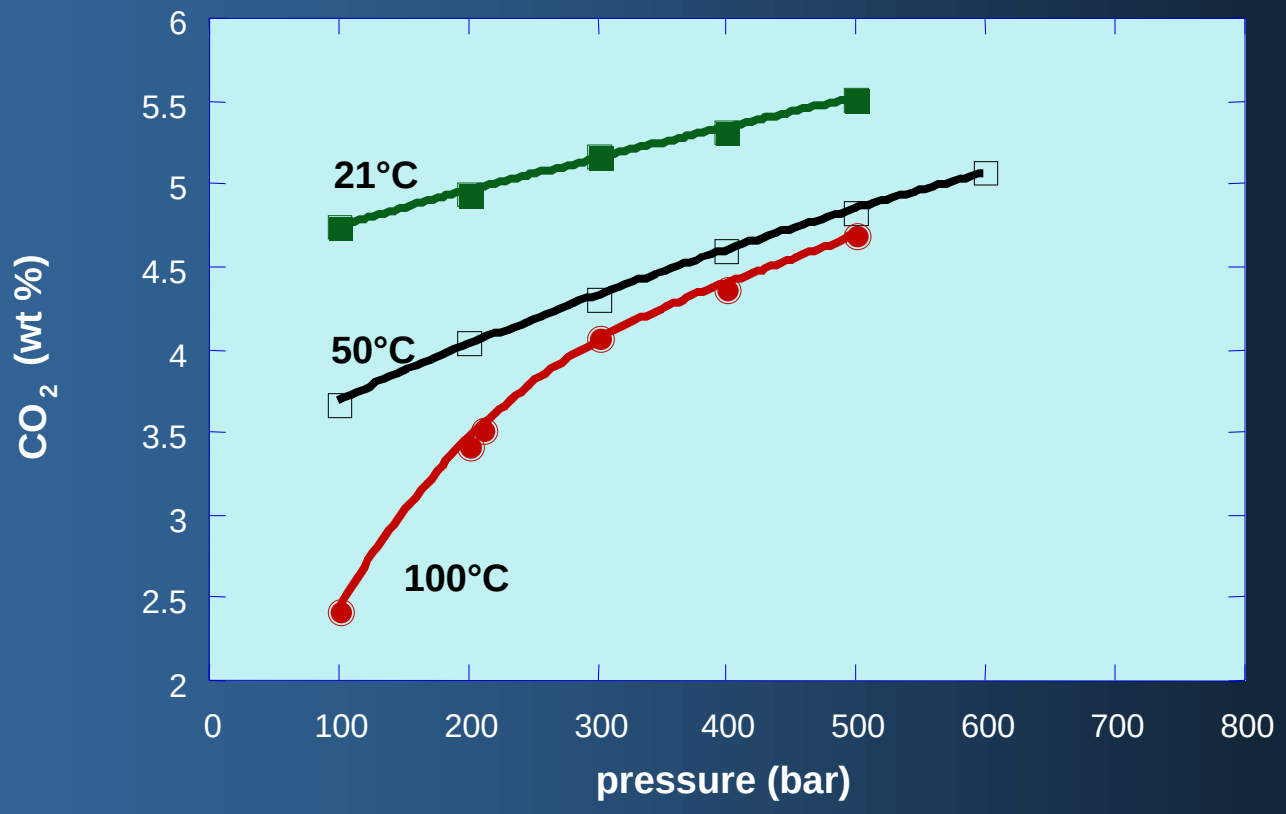
CO_2 Solubility in Paradox Valley Brine and equivalent ionic strength sodium chloride at ambient temperature (21°C)



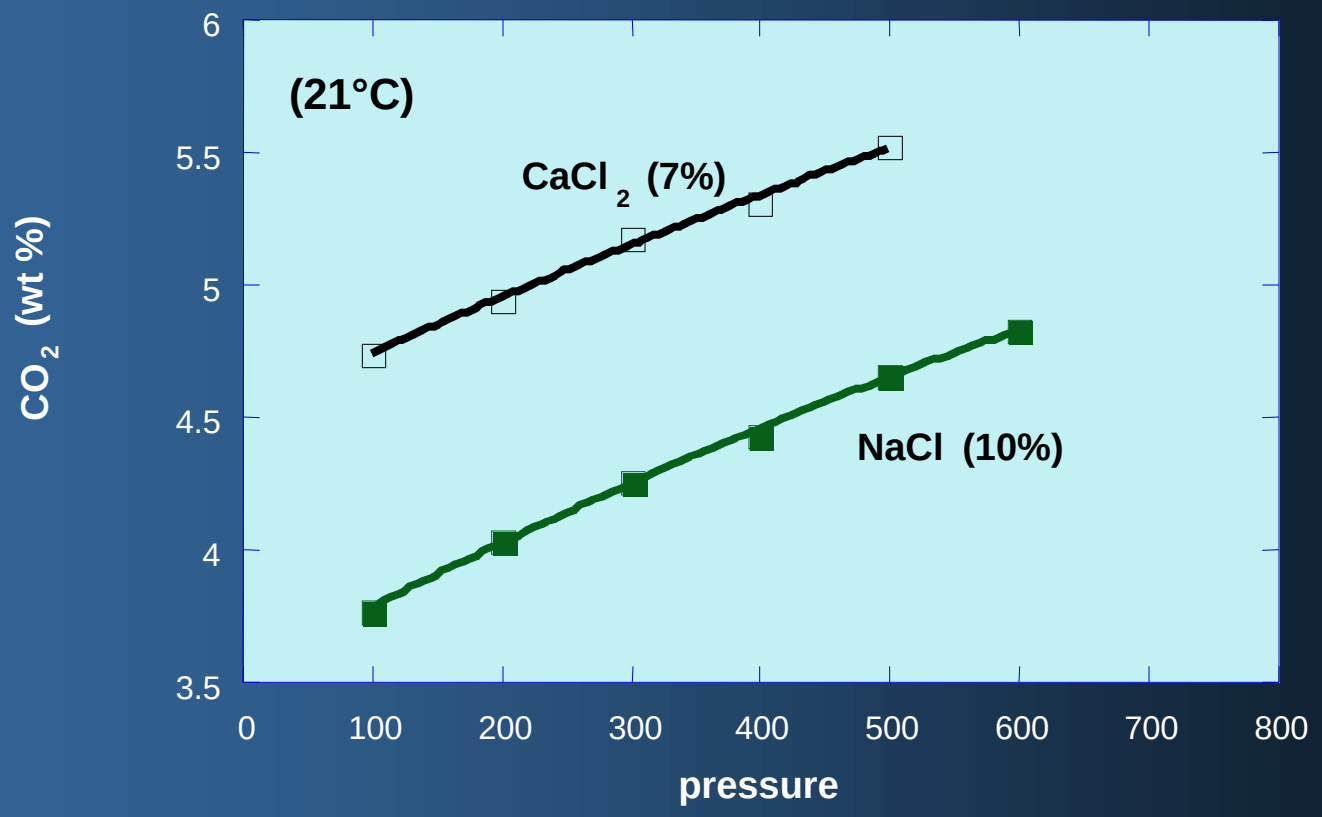
Comparison of the solubility of CO_2 in Paradox Valley Brine and NaCl at an equivalent ionic strength at 50°C.



Solubility of CO_2 in $CaCl_2$ (7%) isotherms



Isotherms of CO_2 solubility in NaCl vs. $CaCl_2$ at equivalent ionic strength (I = 1.9)



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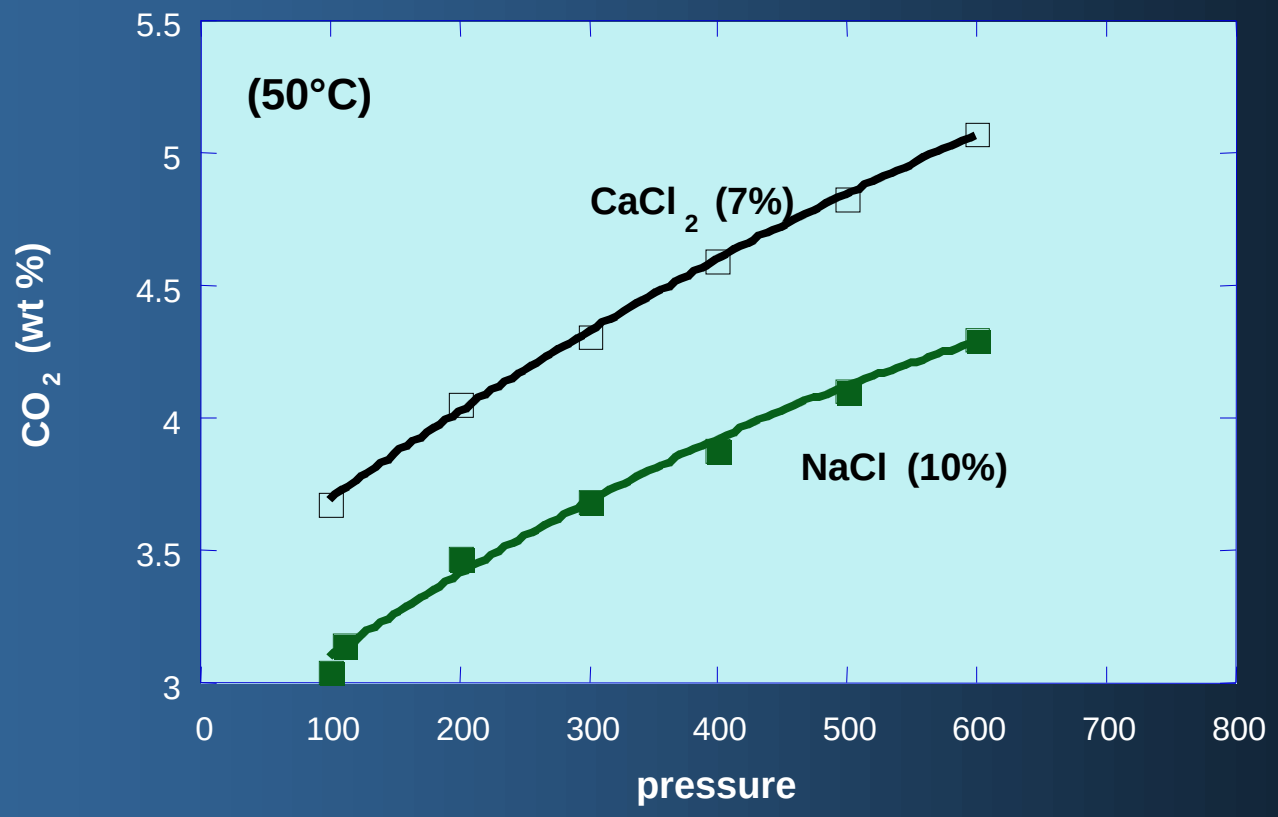
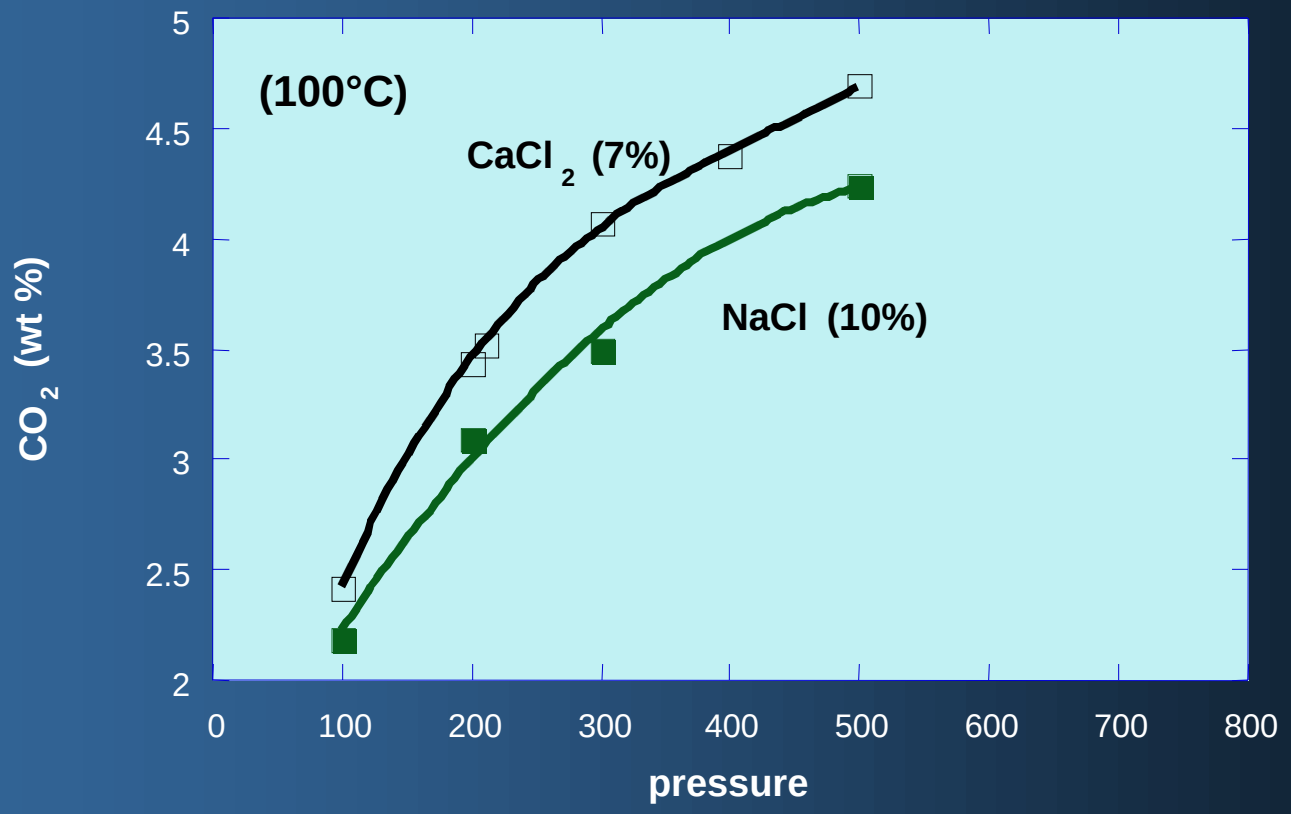
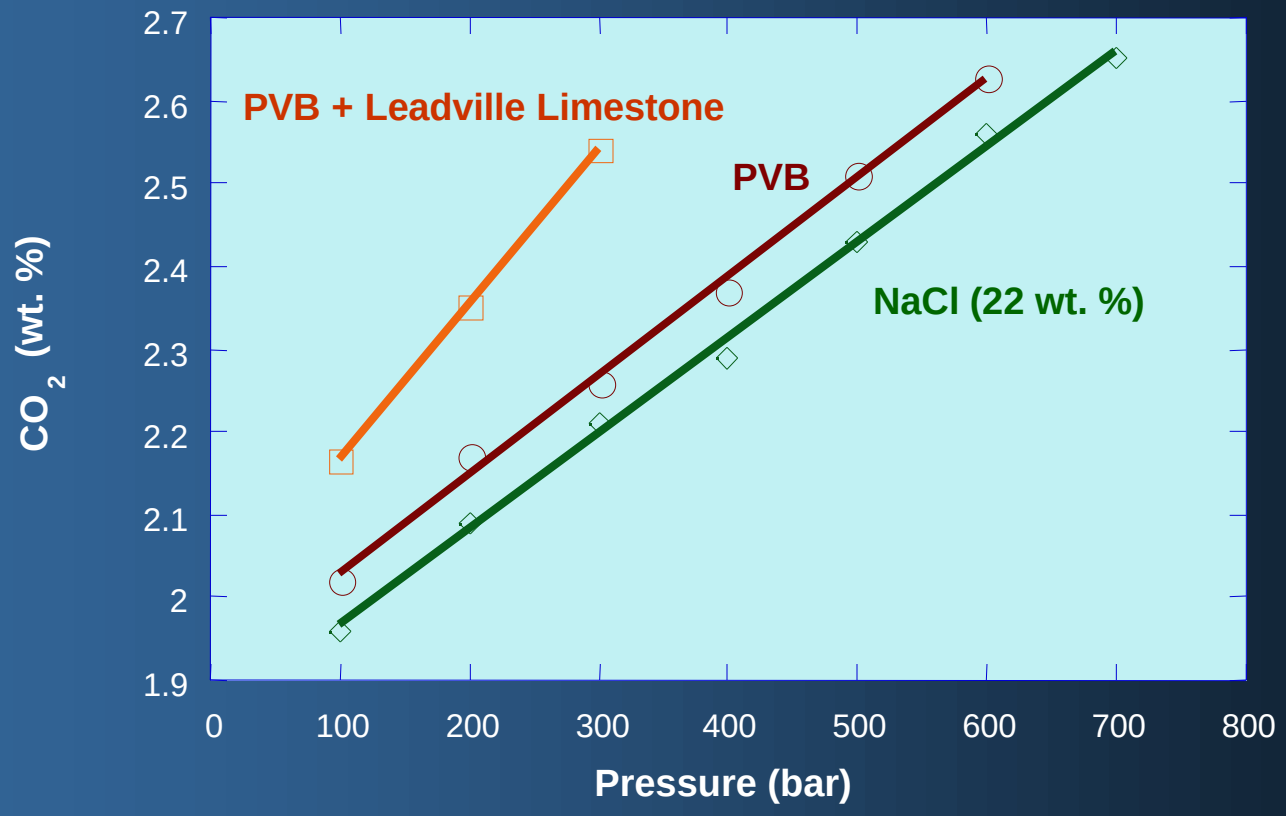


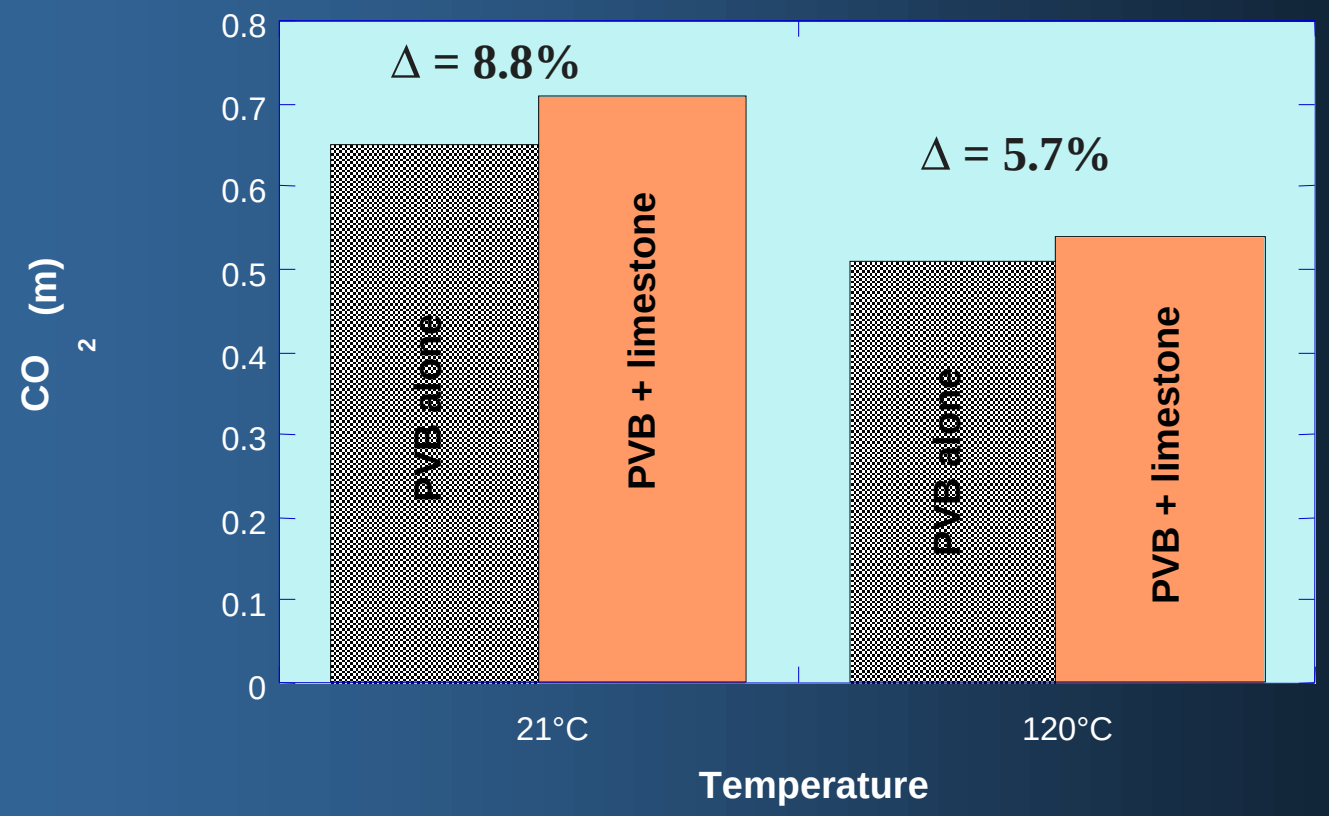
Isotherms of CO_2 solubility in NaCl vs. $CaCl_2$ at equivalent ionic strength (I = 1.9)



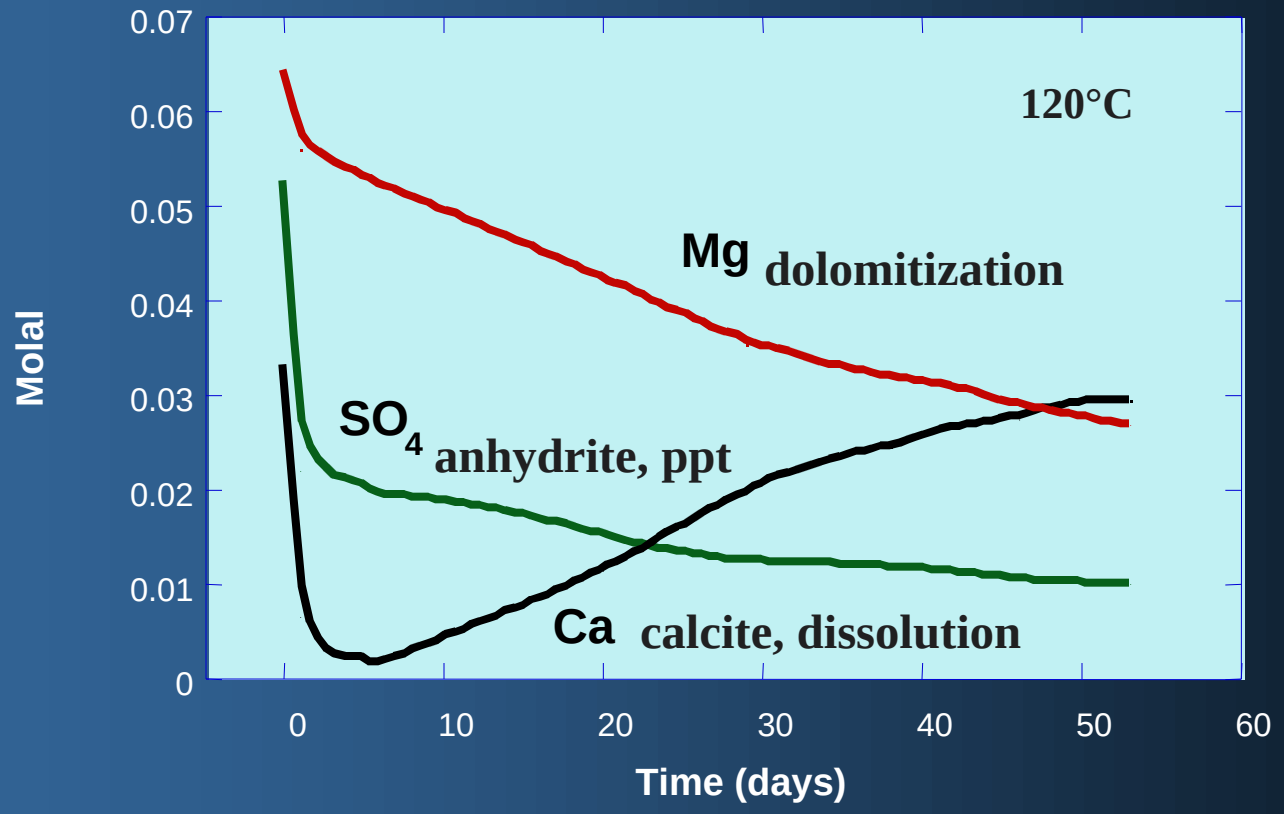
The relative solubility of CO_2 in NaCl (22%) and PVB alone and in the presence of rocks from the Leadville Limestone at 21°C



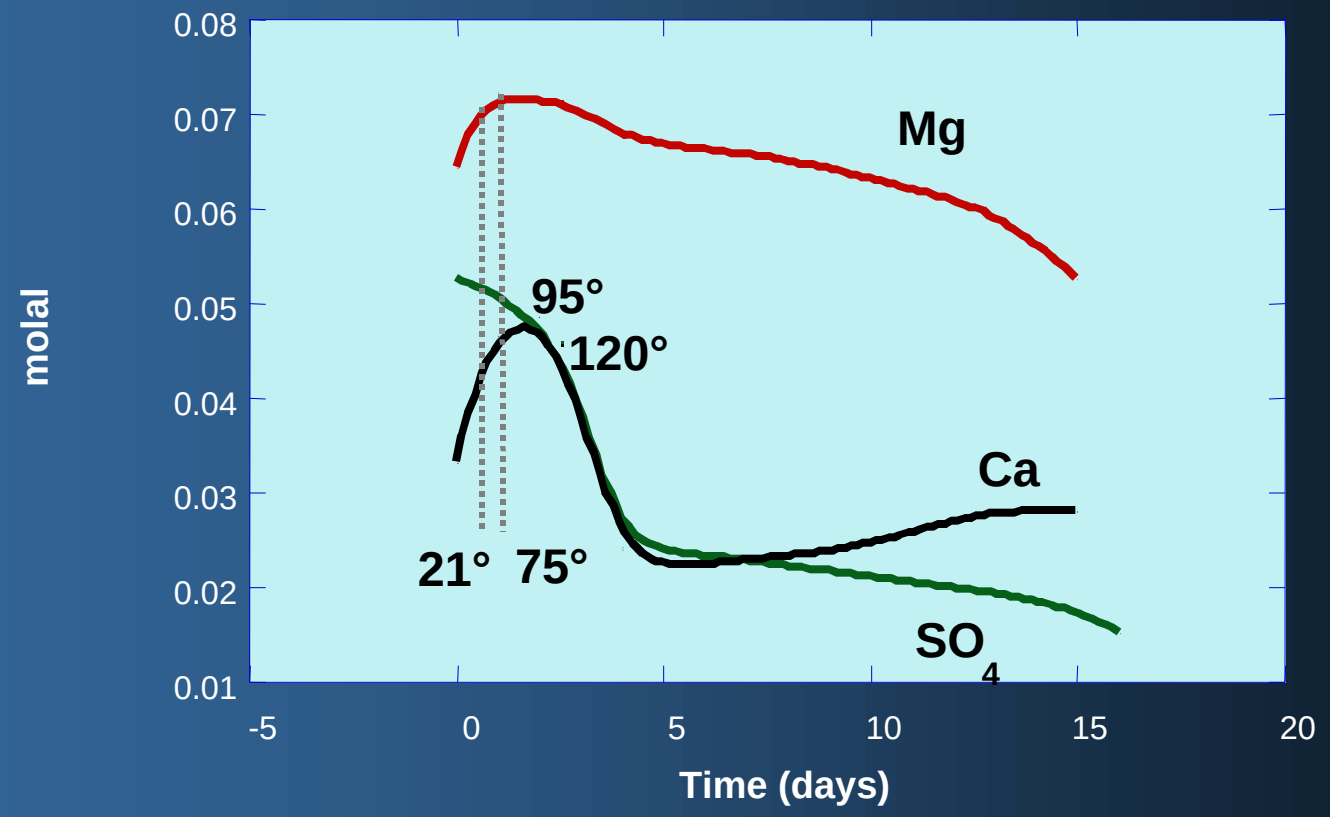
The relative solubility of CO_2 in PVB brine alone and in the presence of rocks from the Leadville Limestone at 120°C, 200 bar.



Compositional changes in PVB during reaction with rocks from the Leadville Limestone in the presence of supercritical CO_2



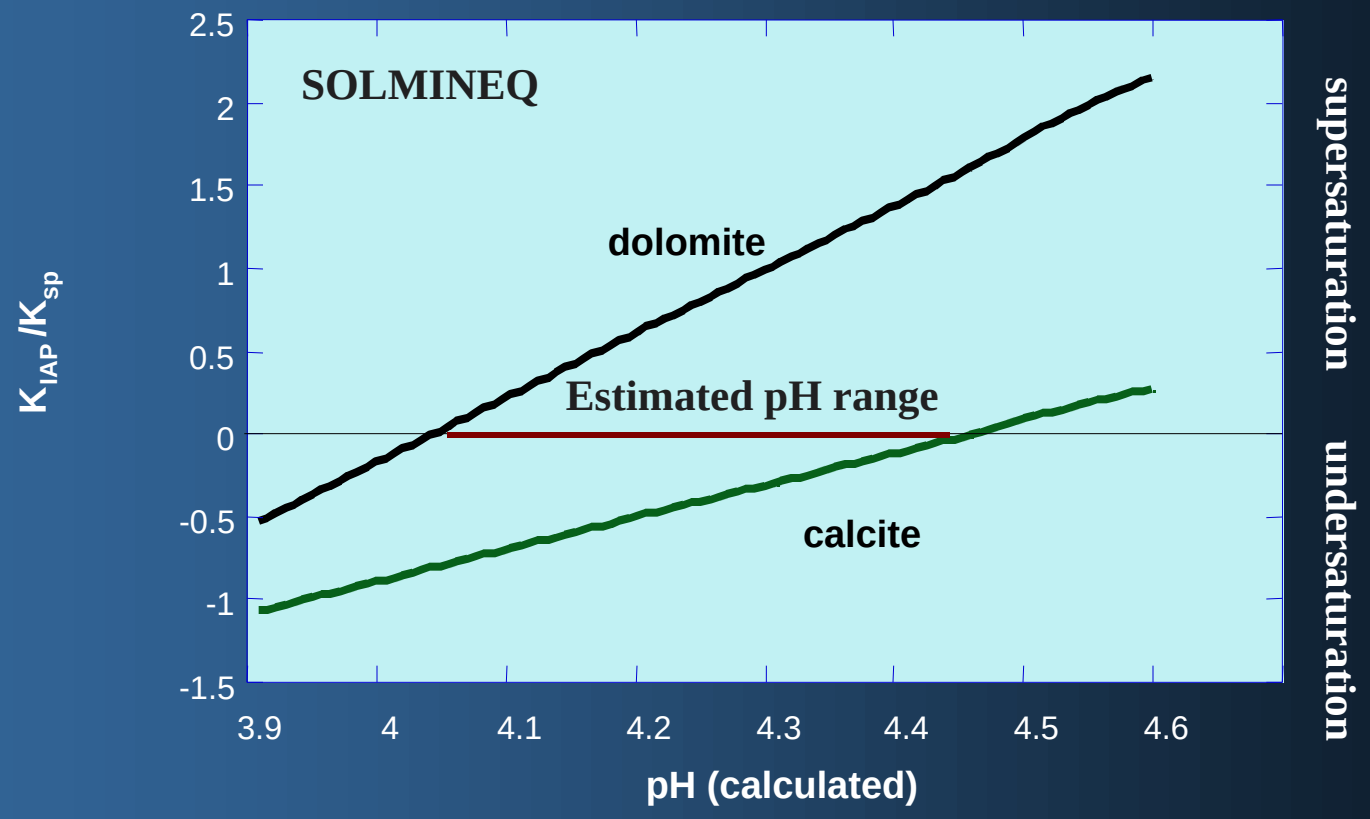
Early compositional changes in PVB during reaction with rocks from the Leadville Limestone in the presence of supercritical CO_2



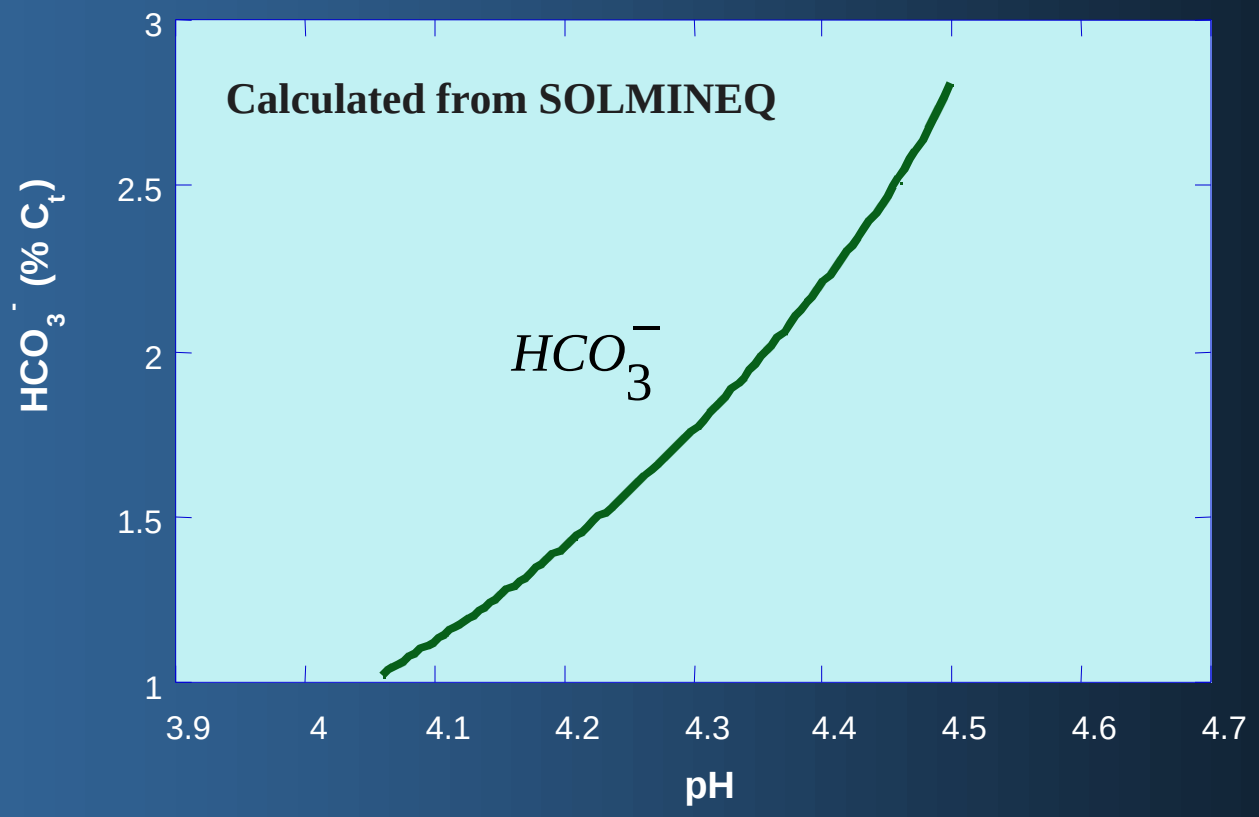
Modeled mineral saturation indices for PVB brine at 25° & 120°C and 300 bars

phase	Log (Q_{IAP}/ K_{SP})		
	25°	25° with CO_2	120° with CO_2
Anhydrite	-0.025	-0.027	.601
Calcite	-0.123	-2.73	-2.07
Dolomite	1.209	-3.83	-2.25
Dolomite disordered	-0.331	-5.37	-3.15

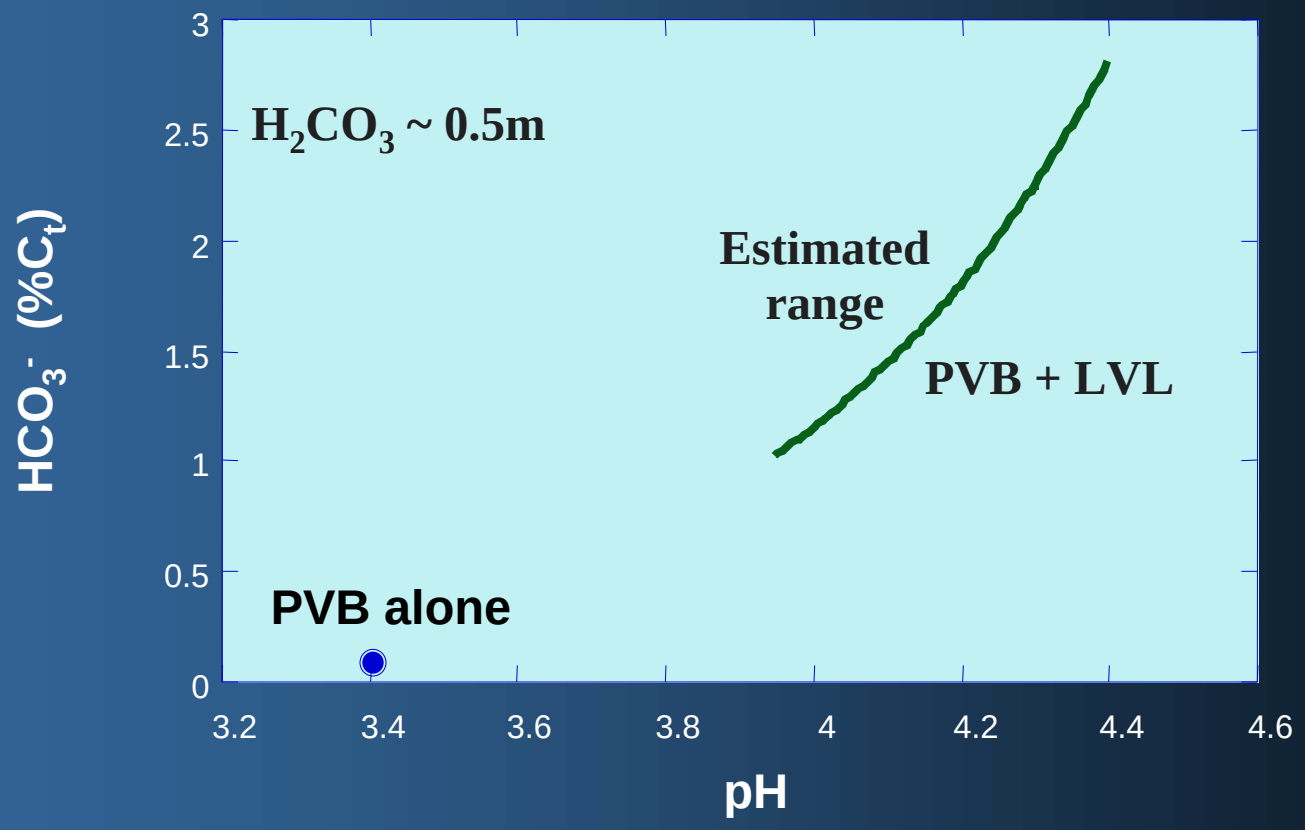
Estimated in situ pH range from the dolomitization of the Leadville Limestone by CO_2 saturated PVB



Estimated in situ bicarbonate from the dolomitization of the Leadville Limestone by CO_2 saturated PVB



Comparison of the relative amount of bicarbonate in CO_2 saturated PVB in the presence and absence of rocks from the Leadville Limestone (LVL).



Net porosity change?

Anhydrite precipitation

$$Ca^{+2} + SO_4^{-2} = CaSO_{4\,(anhydrite)}$$

dolomitization

$$2CaCO_{3(calcite)} + Mg^{+2} \leftrightarrow CaMg(CO_3)_{2(dolomite)} + Ca^{+2}$$

Net reaction:

$$2CaCO_{3(calcite)} + Mg^{+2} + SO_4^{-2} \leftrightarrow CaMg(CO_3)_{2(dolomite)} + CaSO_{4(anhydrite)}$$

2calcite + Mg^{+2} = dolomite + Ca^{+2}

Temp (°C) P = 200 bar	Log K	ΔG (cal)	ΔV (cc)
25	1.216	-1658	-6.2
50	1.323	-1956	-5.6
75	1.407	-2242	-5.1
100	1.473	-2515	-4.7
125	1.523	-2775	-4.2
150	1.561	-3023	-3.7
175	1.591	-3262	-3.0
200	1.613	-3492	-2.3

Mass balance

	Ca (moles)	SO_4 (moles)	Mg (moles)
START (solution)	.00533	.00841	.01030
Removed in sampling	.00236	.00146	.00390
Remaining in solution	.00144	.00049	.00130
Samples + remaining	.00380	.00195	.00520
Removed from solution	.00153	.00646	.00510

Ca budget

- Assume the amount of SO_4 removed is equivalent to the amount of anhydrite precipitated.
- Assume the amount of Mg removed is equivalent to the amount of dolomite formed
- Mass balance equation for Ca in moles:
  - starting soln. + reacted rock = samples + remaining soln. +anhydrite + dolomite
  - Ca from the rock = 0.010 moles = .40g

- Amount of Ca from the rock (38% calcite) that reacted: 27%
  - $0.40g_{reacted}/1.46g_{calcite} = 0.27$
- 27% of the original calcite dissolved or was dolomitized

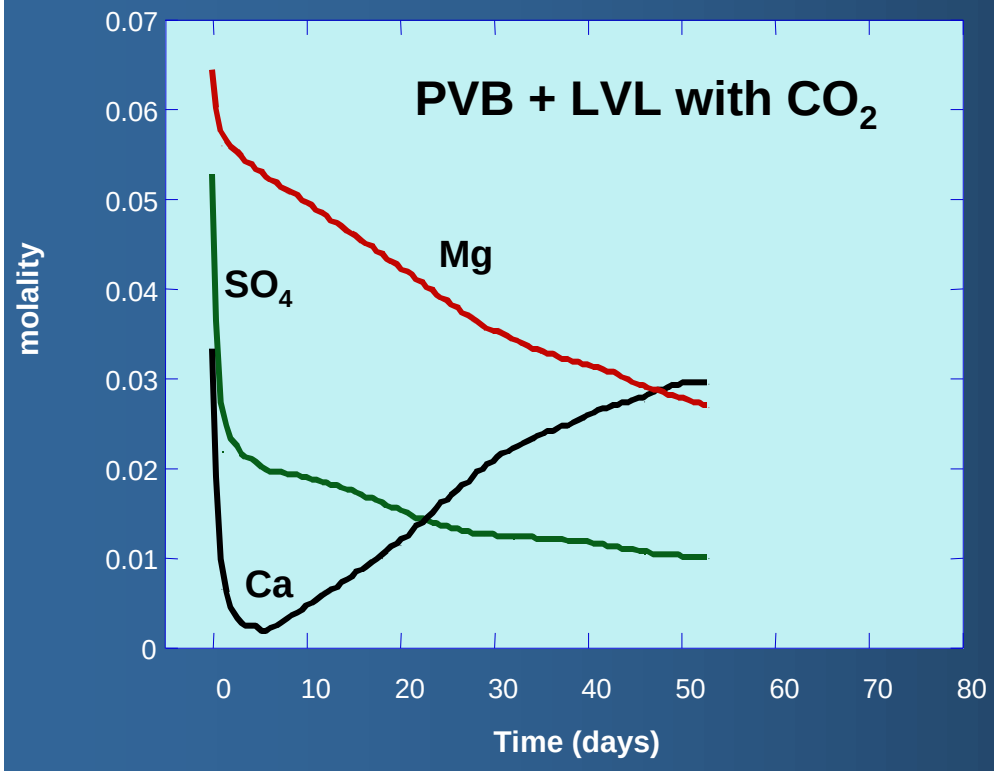
Porosity change due to calcite dissolution and anhydrite/dolomite formation

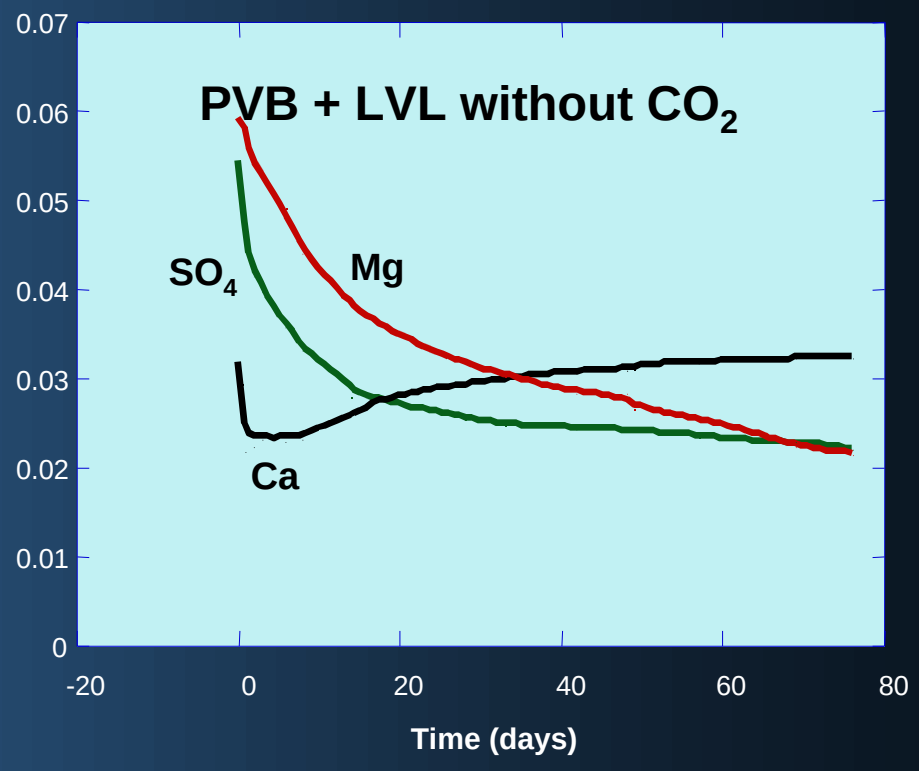
- Un-reacted composition Leadville Limestone: 38% calcite, 62% dolomite
- Un-reacted volume (16g) = 3.79 cm^3 (dolomite) + 1.35 cm^2 (calcite)
  - = 5.14 cm^3
- Δvolume of the solids in the reacted limestone:

calcite	dolomite	anhydrite	Net change
-0.369 cm^3	0.328 cm^2	0.297 cm^2	0.256 cm^2

Reacted volume of rocks= 5.4 cm^3 = net decrease in formation porosity = 5%

Compositional changes in PVB during reaction with rocks from the Leadville Limestone in the presence and absence of supercritical CO_2





Net porosity change during the reaction of PVB with the Leadville Limestone in the presence and absence of supercritical CO_2

- Δvolume of the solids in the reacted limestone with and without added CO_2:

	calcite	dolomite	anhydrite	volume change
w/ CO_2	-0.369 cm^3	0.328 cm^3	0.297 cm^3	0.256 cm^3
w/o CO_2	-0.406 cm^3	0.367 cm^3	0.240 cm^3	0.201 cm^3

Chemical composition of PVB brines: surface vs. aquifer brine

Species mg/kg	Surface (PVB)	Aquifer (PVA)
Na	77,000	70,000
K	3,630	2,100
Ca	1,187	10,900
Mg	1,278	1,220
Cl	127,100	132,000
SO_4	5,100	454
pH	6.18	5.42
TDS	215,000	218,000

Modeled mineral saturation indices for Paradox Valley brines at 25° & 125°C and 300 bars

phase	Log (Q_{IAP}/ K_{SP})		
	PVB 25°	PVB 125°	PVA 125°
Anhydrite	-0.025	0.644	0.152
Calcite	-0.123	0.066	-.048
Dolomite	1.209	2.044	.763
Dolomite disordered	-0.331	1.129	-.112

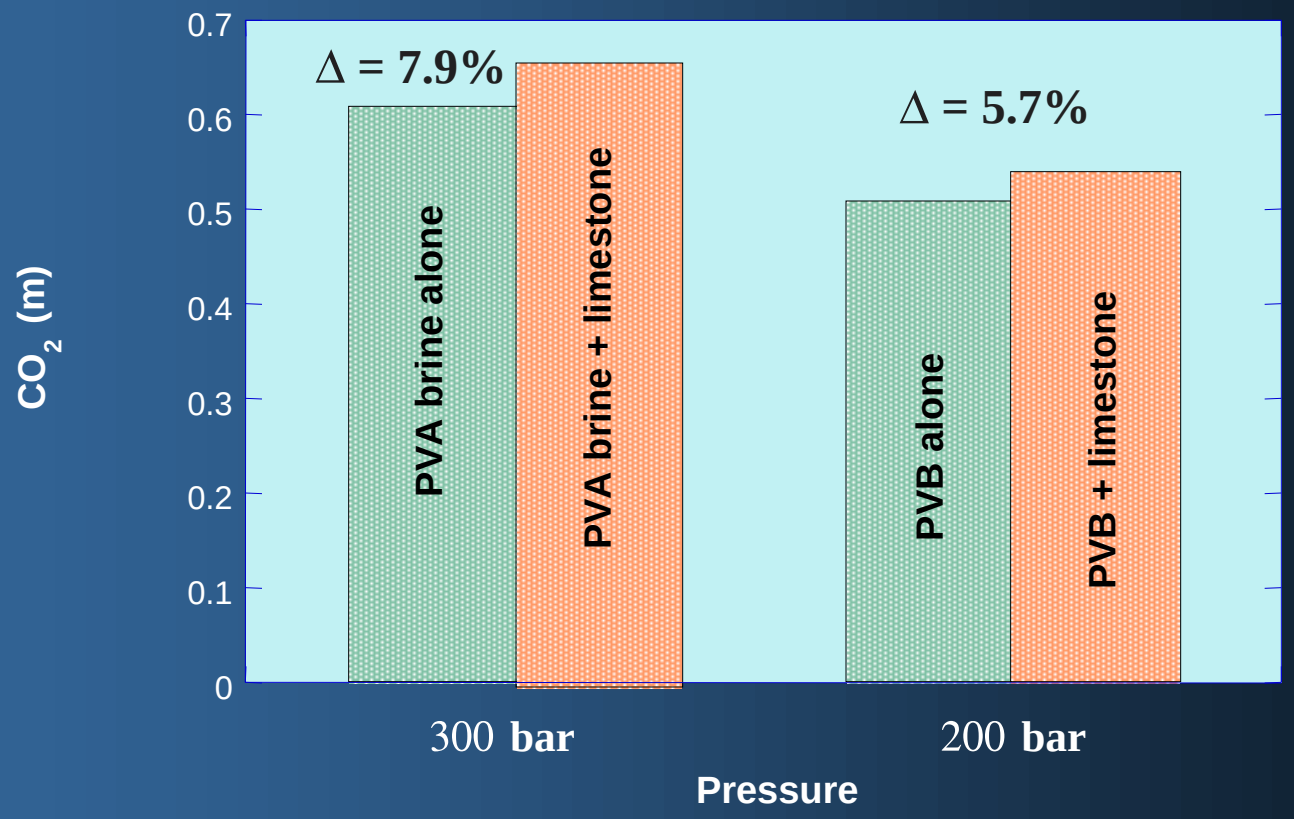
Modeled mineral saturation indices for PVA brine at 125°C and 300 bars

phase	Log (Q_{IAP}/ K_{SP})		
	PVA alone	PVA Saturated with CO_2	PVA Saturated with CO_2 & calcite
Anhydrite	0.15	0.15	.04
Calcite	-0.05	-1.68	0.01
Dolomite	0.76	-2.46	0.82
Dolomite disordered	-0.11	-3.37	-.06

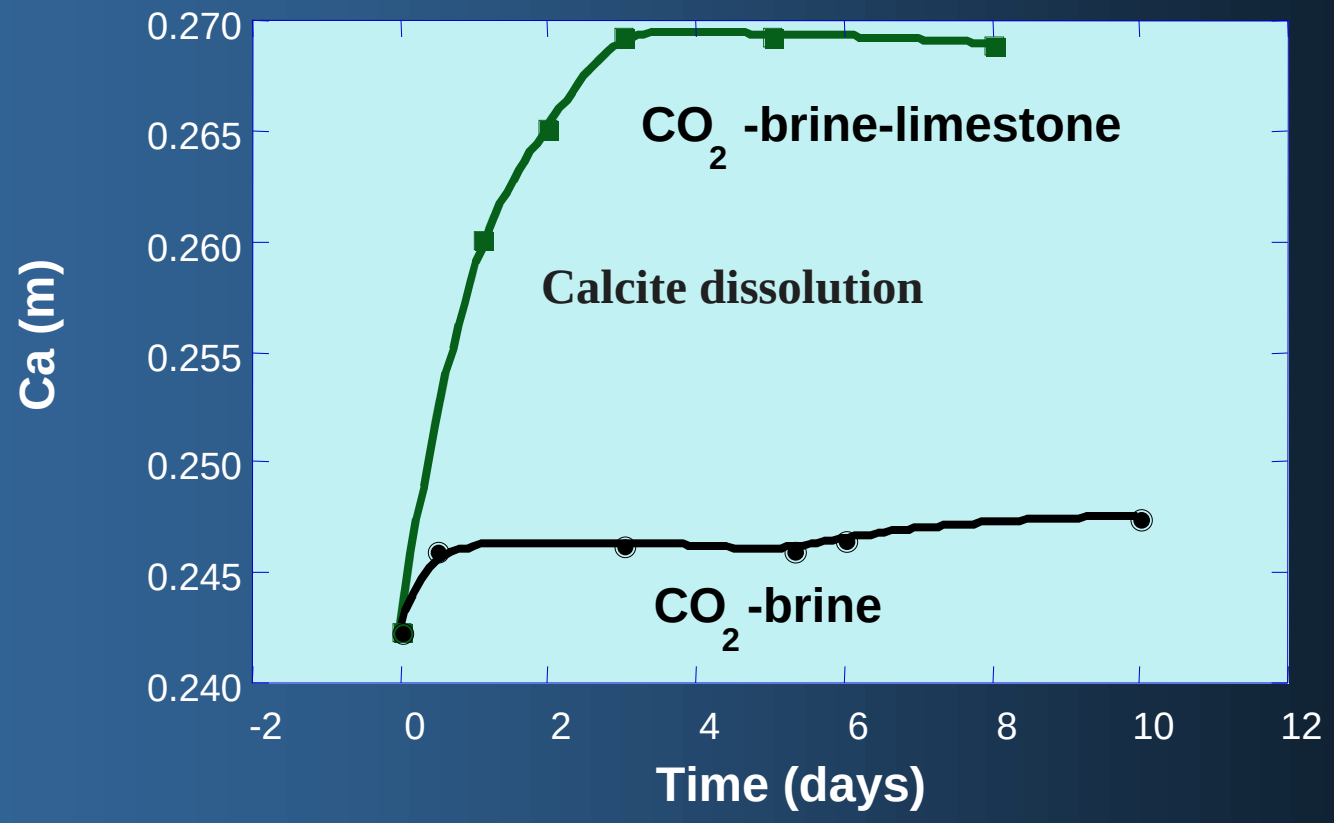
Modeled changes in PVA brine saturated with CO_2 and calcite at 125°C and 300 bars

phase			
	PVA alone	PVA Saturated with CO_2	PVASaturated with CO_2 & calcite
pH	5.3	3.4	4.2
H_2CO_3 (m)	0.003	0.61	0.60
HCO_3^- (m)	0.0005	0.013	0.10
HCO_3^-/ H_2CO_3	17%	2.1%	17%

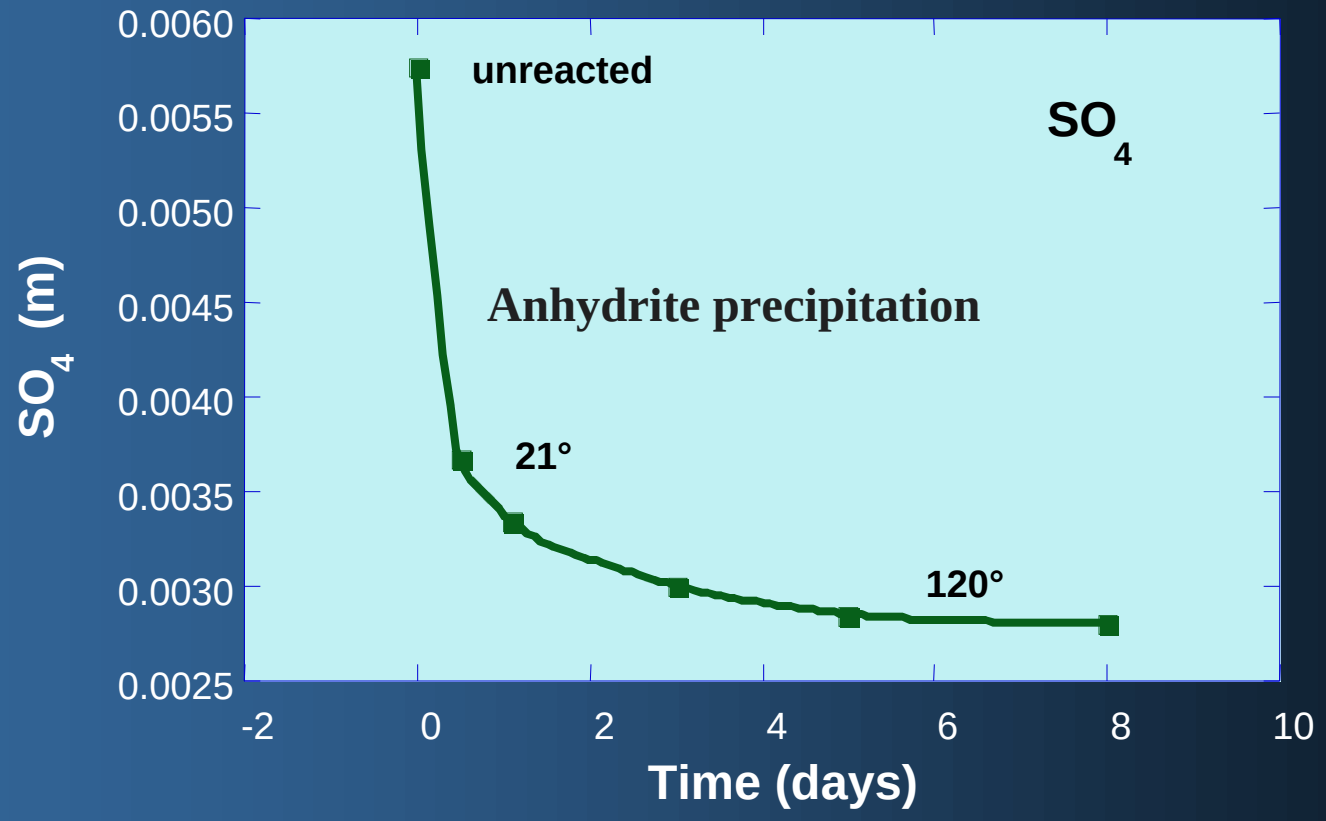
The relative solubility of CO_2 in Paradox Valley brines alone and in the presence of rocks from the Leadville Limestone at 120°C.



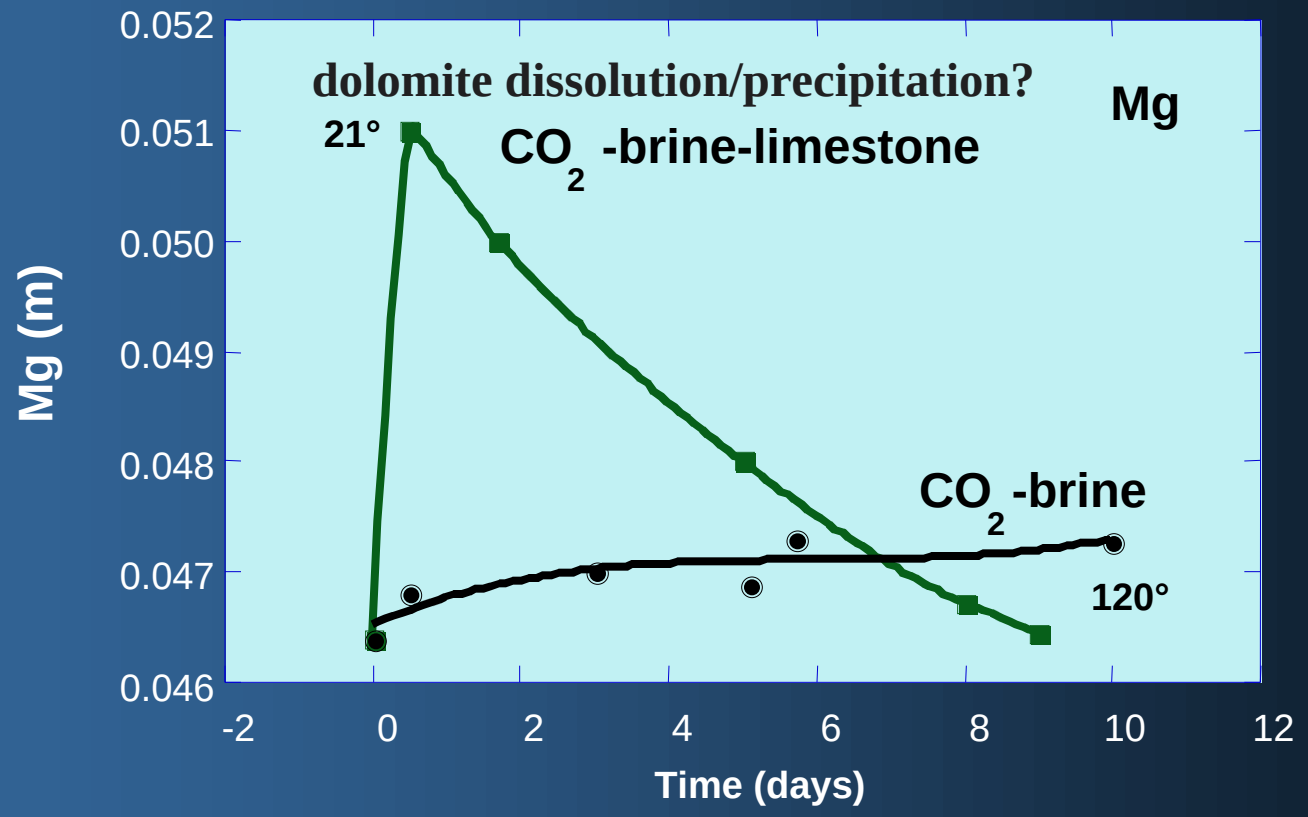
Dissolved Ca during reaction of CO_2 saturated PVA brine alone and with rocks from the Leadville Limestone



Dissolved SO_4 during reaction of CO_2 saturated PVA brine alone and with rocks from the Leadville Limestone



Dissolved Mg during reaction of CO_2 saturated PVA brine alone and with rocks from the Leadville Limestone



Porosity increase due to calcite dissolution

- .0036 moles or 10% of the calcite in the rock dissolved
  - Δvolume of the solids in the reacted limestone:

Initial rock volume	Calcite dissolved	Net volume change
5.14 cm^3	-0.13 cm^2	-2.6%

Summary

- Experimental results follow theoretical thermodynamic equilibrium calculations when a CO_2 -saturated brine is reacted with limestone rocks.
- The solubility of CO_2 is enhanced ~9% at 21°C and 6% at 125°C and 200 bars in PVB in the presence of rocks from the Leadville Limestone relative to PVB alone.
- The solubility of CO_2 is enhanced ~8% at 125°C and 300 bars in PVA brine in the presence of rocks from the Leadville Limestone relative to PVA brine alone.
- Formation porosity is increased by 2.6% due to the dissolution of calcite during reaction of CO_2 saturated PVA brine in the presence of rocks from the Leadville Limestone

Summary

- Reactions of PVB with rocks from the Leadville limestone are similar with or without liquid CO_2: anhydrite precipitation, calcite dissolution and dolomitization.

- Porosity changes due to anhydrite precipitation and dolomitization of calcite are similar with or without liquid CO_2.

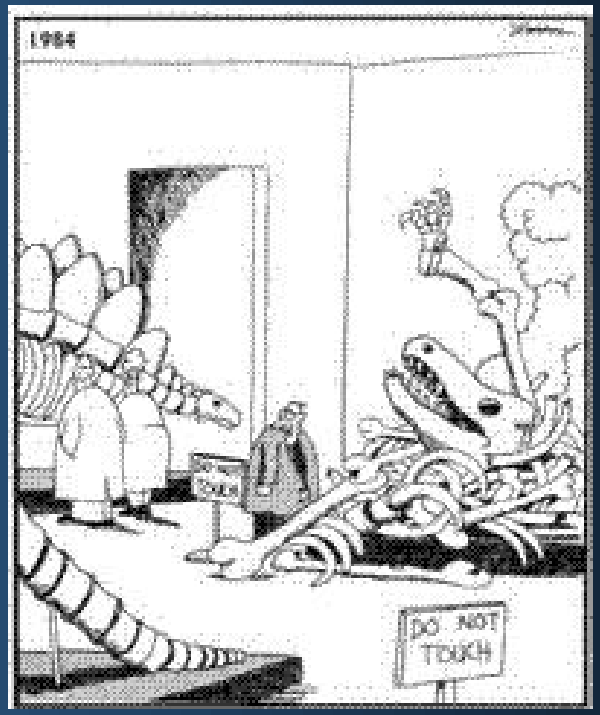
Future directions

CO_2-water-rock interactions

- Kinetic data
- Density data
- Investigate mineral trapping reactions in an arkosic sandstone

Technical questions

- Temporal and spatial development of acid gas bubble
- Geochemical reactions
  - Mineralization/demineralization
  - Long and short term (rates)
- Cap rock, wellbore integrity
- Impact of thermal/compositional gradients within the reservoir

Typical phase diagram

Equilibrium