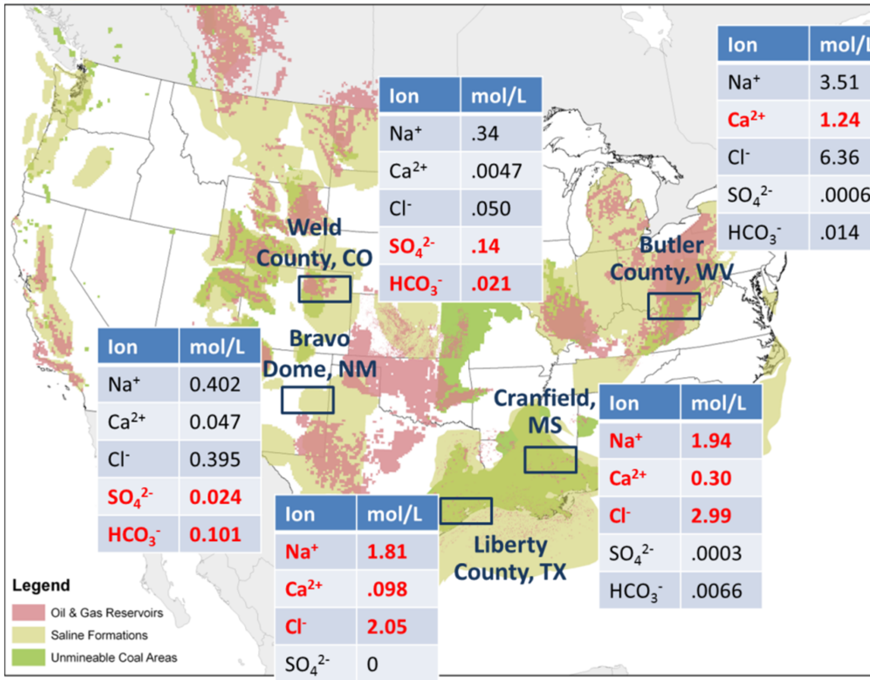
DISSOLVED CO_2 IN REAL BRINES



Weld County, CO

Ion	mol/L
Na^+	.34
Ca^{2+}	.0047
Cl^-	.050
SO_4^{2-}	**.14**
HCO_3^-	**.021**

Butler County, WV

Ion	mol/L
Na^+	3.51
Ca^{2+}	**1.24**
Cl^-	6.36
SO_4^{2-}	.0006
HCO_3^-	.014

Bravo Dome, NM

Ion	mol/L
Na^+	0.402
Ca^{2+}	0.047
Cl^-	0.395
SO_4^{2-}	**0.024**
HCO_3^-	**0.101**

Cranfield, MS

Ion	mol/L
Na^+	**1.94**
Ca^{2+}	**0.30**
Cl^-	**2.99**
SO_4^{2-}	.0003
HCO_3^-	.0066

Liberty County, TX

Ion	mol/L
Na^+	**1.81**
Ca^{2+}	**.098**
Cl^-	**2.05**
SO_4^{2-}	0
HCO_3^-	.0089

http://www.epa.gov/climatechange/ccs/index.html

Deep subsurface brines for carbon sequestration are not simple NaCl brines, but they are often modeled that way.

Scientific Achievement

Provide data and insights into the molecular interactions of CO_2, water and ions.

Significance and Impact

This research generates experimental data that provides insight into the molecular interactions in brine when CO_2 is dissolved; which modelers can use to more accurately predict dissolved CO_2 in subsurface brines.

Research Details

- Measured dissolved CO_2 in brines containing Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^- with increasing P_{CO2}.
- Found a strong correlation between dissolved CO_2 and electrolyte hydration number and the ΔG, ΔS and ΔH of electrolyte solvation.
- Used the regression equation to accurately predict CO_2 solubility in the Bravo Dome brine.

Work was performed at the Jackson School of Geosciences at the University of Texas at Austin (Kim Gilbert).

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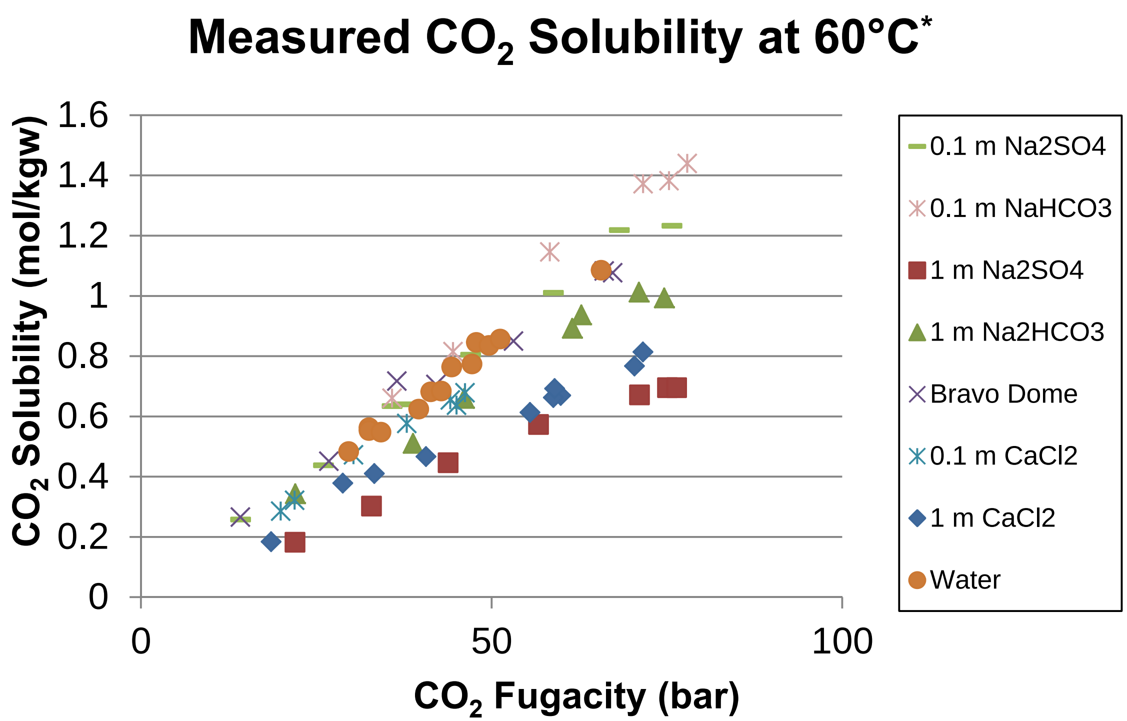
Measured CO_2 Solubility

CO_2 solubility ↑ with:

- ↑ CO_2 Fugacity (Effective CO_2 partial pressure)
- ↓ Ionic strength

Deviations from expected:

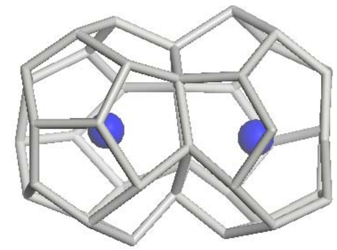
- **Ionic strength not a reliable predictor of CO_2 solubility:**
  - 15% less CO_2 in 1 molal Na_2SO_4 than $CaCl_2$.
- **CO_2 solubility in mixed Bravo Dome not well predicted**
  - CO_2 solubility is up to 17% more than predicted.



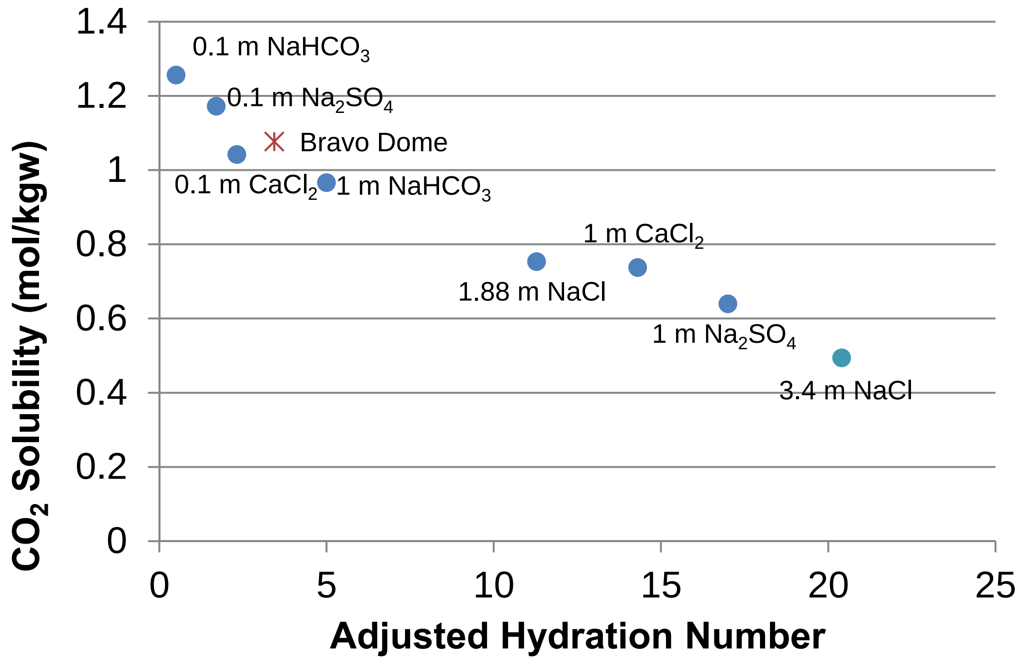
* CO_2 solubility also measured at 30°C, but not presented here because of space.

How Much Free Water?

- **Hydration Number: # of water molecules interact electrically with ions.**
  - How many free water molecules are there to cage around the CO_2?
- **ΔH, ΔS, ΔG of Hydration for the electrolyte allow for the prediction of CO_2 solubility.**
  - How much energy is required to extract a water molecule from ion ?
  - Is the system structured in a way to facilitate CO_2 hydration?



CH_4 caged
Randall Cygan,
Sandia National Labs



$R^2 > 0.92$ for hydration number, ΔH, ΔS, and ΔG

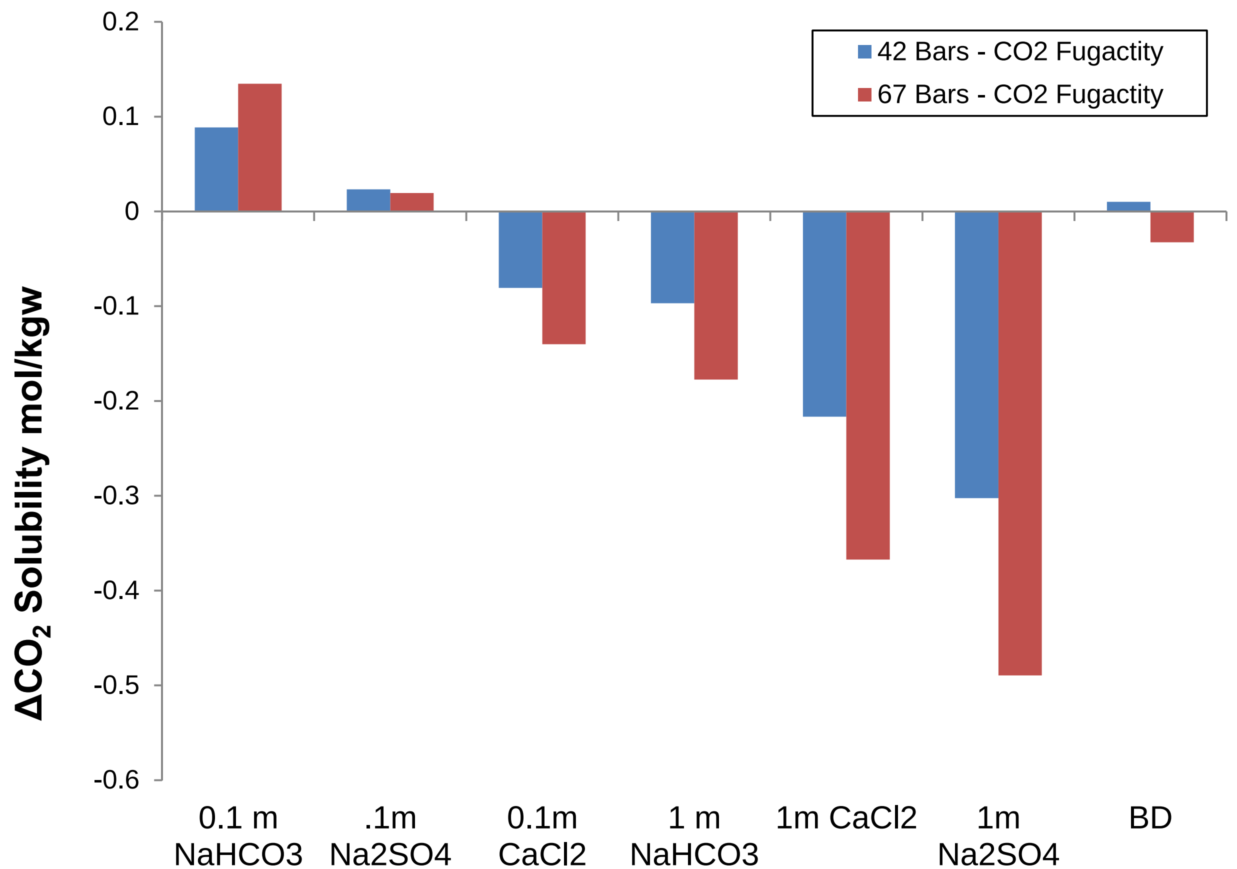
$R^2 = 0.9997$ for hydration number and ΔH combined.

Predicted CO_2 solubility in the Bravo Dome mixed brine to <1%.

CO_2 Solubility Sensitivity to Salts at 60°C

Difference in CO_2 solubility between salt solutions and water.

$\Delta solubility = m_{water} - m_{salt}$



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Conclusions

1. **CO_2 solubility decreases with increasing ionic strength for a give salt, but not necessarily for different salts.**
2. **CO_2 solubility has the highest sensitivity to 1 m Na_2SO_4, while 0.1 m $NaHCO_3$ resulted in an increase in CO_2 solubility over water.**
3. **CO_2 solubility can be best predicted based on**
   1. **Hydration number adjusted for the moles of each ion present.**
      1. Number of free water molecules
      2. Based on ion partial molar compressibility so represents only inner-ring water molecules
   2. **Enthalpy (ΔH) and free energy (ΔG) of hydration**
      1. Required energy to "free" water molecules that are electrostricted by ions
   3. **Entropy of hydration**
      1. Structure imposed or disrupted by ion (NOT CO_2) solvation