Direct Measurements of pH and Dissolved CO_2 Concentrations in H_2O-CO_2-NaCl Mixtures to Supercritical Conditions

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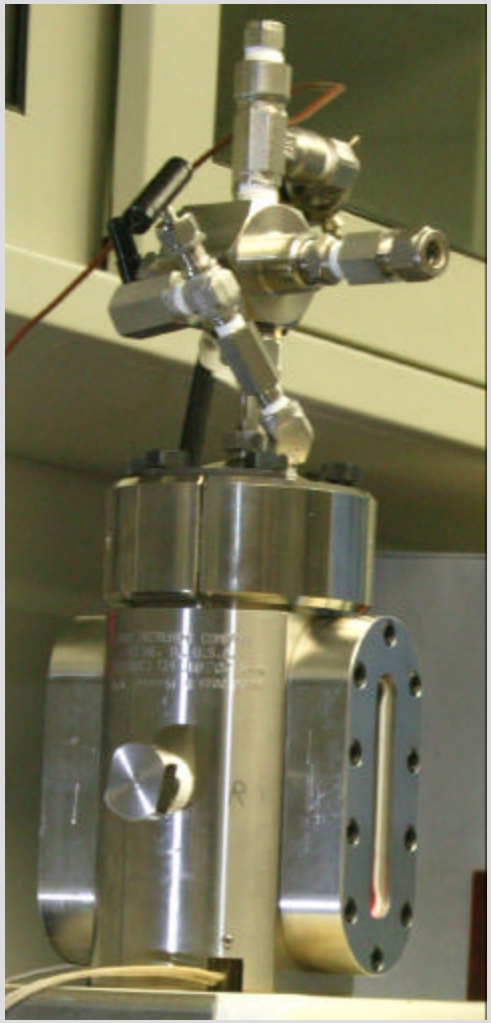
Objectives

- In-situ pH measurements of H_2O-NaCl-CO_2 mixtures as a function of pressure above scCO_2 conditions.
  - Fundamental data in the literature is limited and shows discrepancies.
  - How well do geological simulator models predict the pH?
  - Stability of certain clay and carbonate minerals are strongly affected by the pH changes in this region.
  - Important aspect for geologic sequestration.
- Characterize dissolved CO_2 subcritical to supercritical conditions with Raman spectroscopy.

Experimental Setup

- High-pressure view cell equipped with two quartz windows
  - Max working pressure 2000 psi @ 150°C
  - 100ml volume capacity
- Pressure-capable glass combination pH probe.
  - KCl reference gel, rated to 150°C
  - Blowout pressure above 10,000 psi
- UV-VIS transmission dip probe
  - In-situ absorbance measurement of solutions
  - Ocean Optics Spectrometer SL2000
- Raman Spectroscopy analysis
  - 532 nm diode-pumped solid state laser
  - Fiber optic probe head mounted on a digital transition table
  - Back illuminated CCD detector



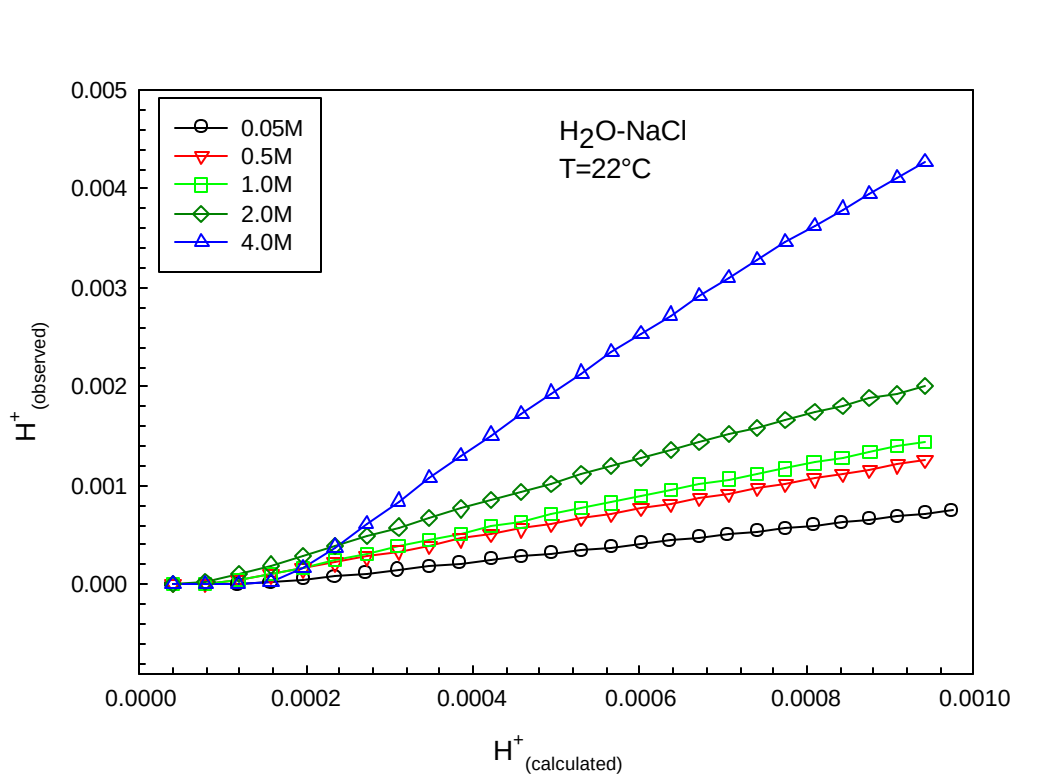
Correction Factor for pH Measurements in Aqueous Brine Mixtures

- NaCl solutions were titrated against standard HCl solutions to establish a correction factor.
- Logarithm of the slope of each curve is the correction factor A in the following equation:

$$pH_c = pH_{obs} + A$$

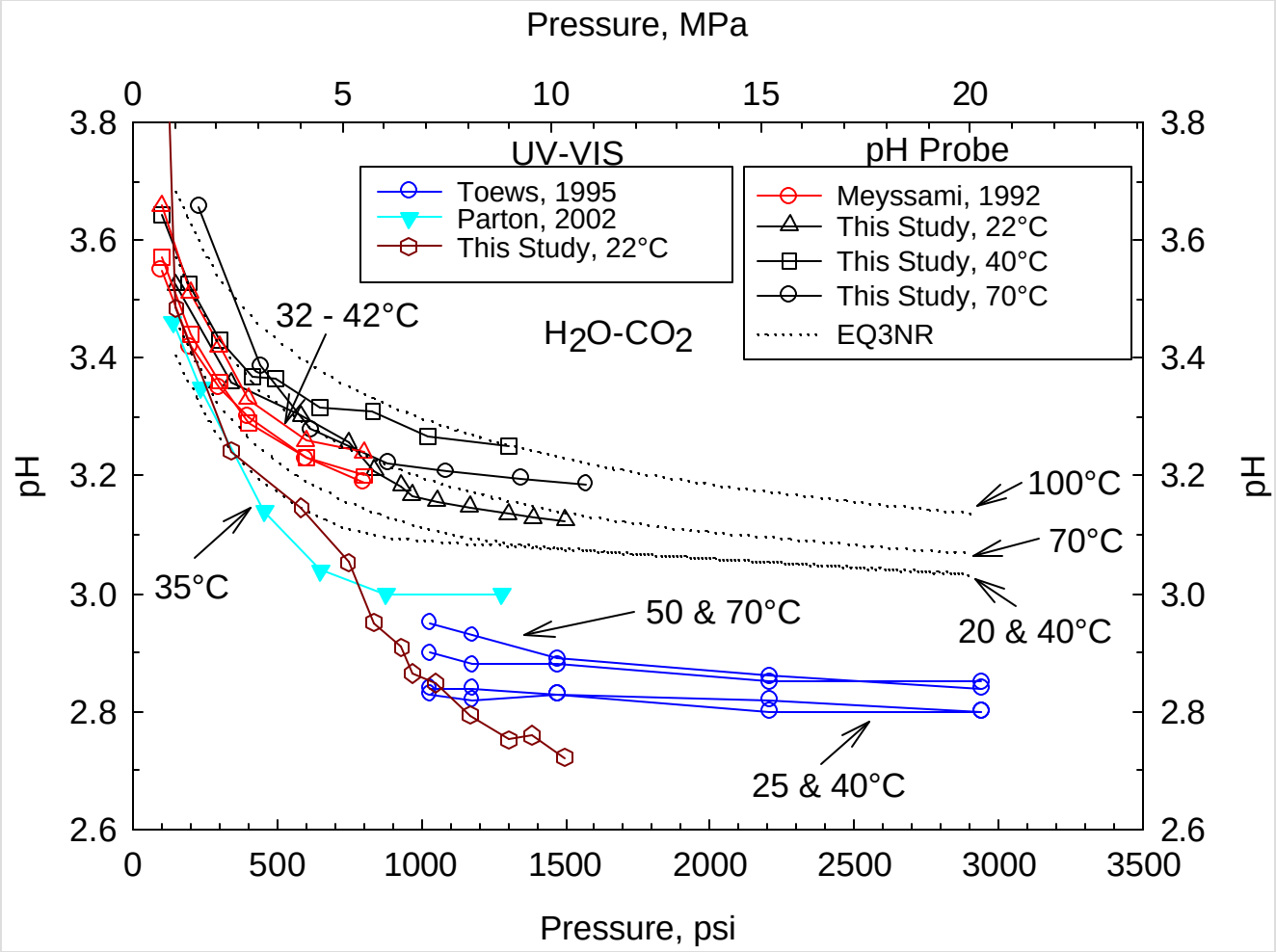
Correction Factor

NaCl (M)	A
0.05	-0.05
0.50	0.16
1.00	0.23
2.00	0.36
4.00	0.74

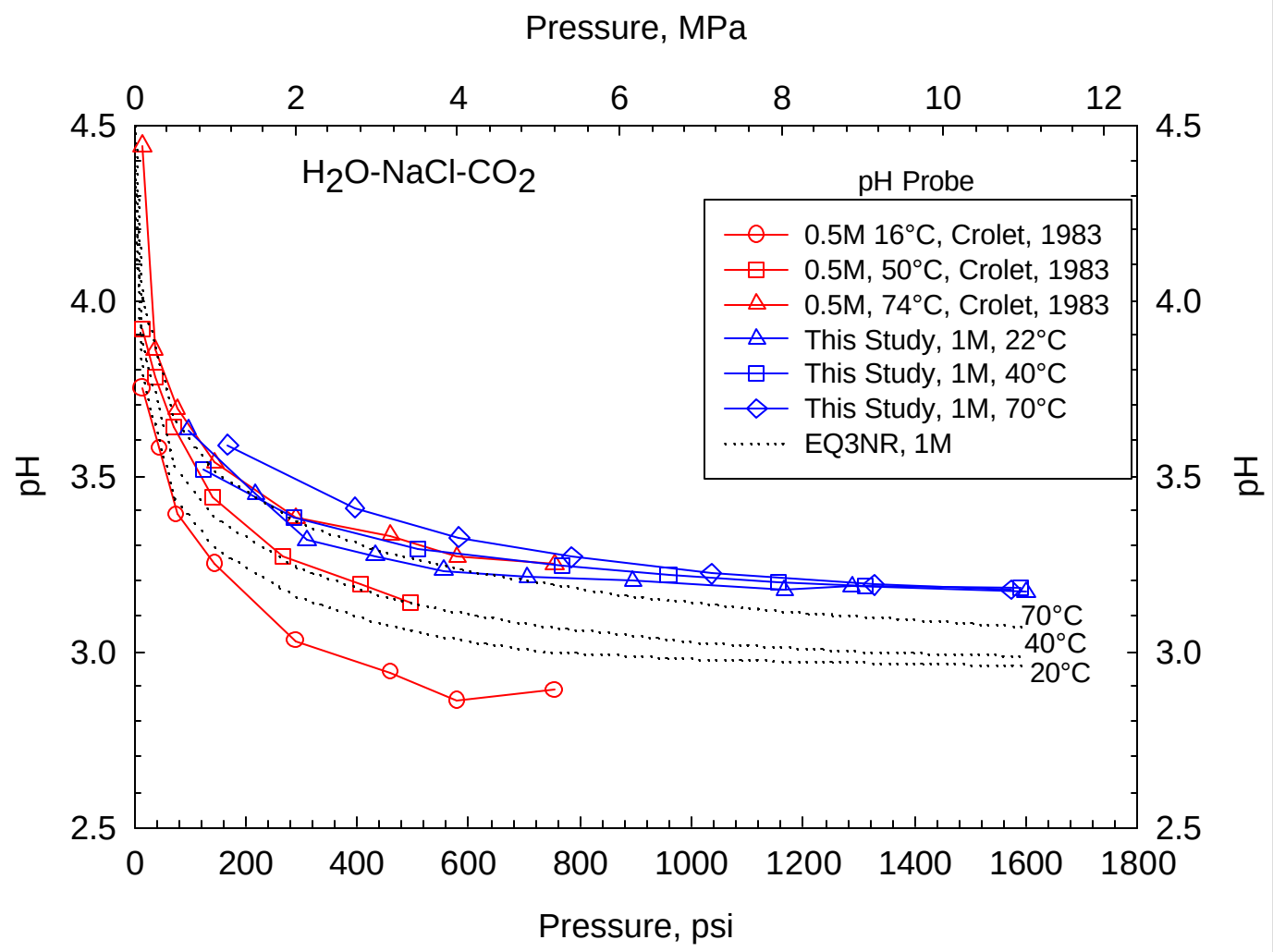


pH as a Function of CO_2 Pressure in H_2O-CO_2 System

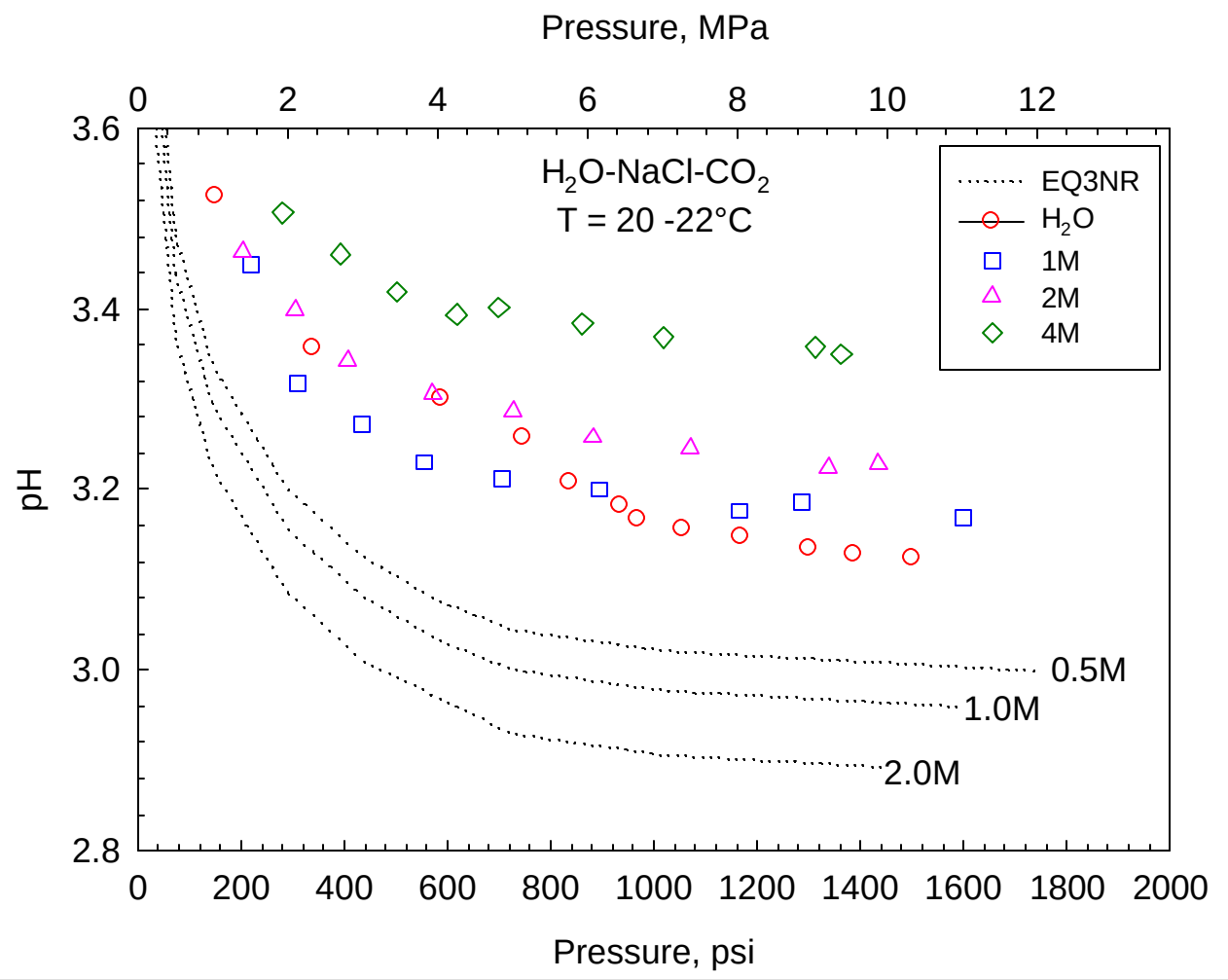
- Simplest system
- Lack of literature
- Two methods
- UV-VIS errors
- Important implications



pH as a Function of CO_2 Pressure in 1M NaCl-H_2O-CO_2 System

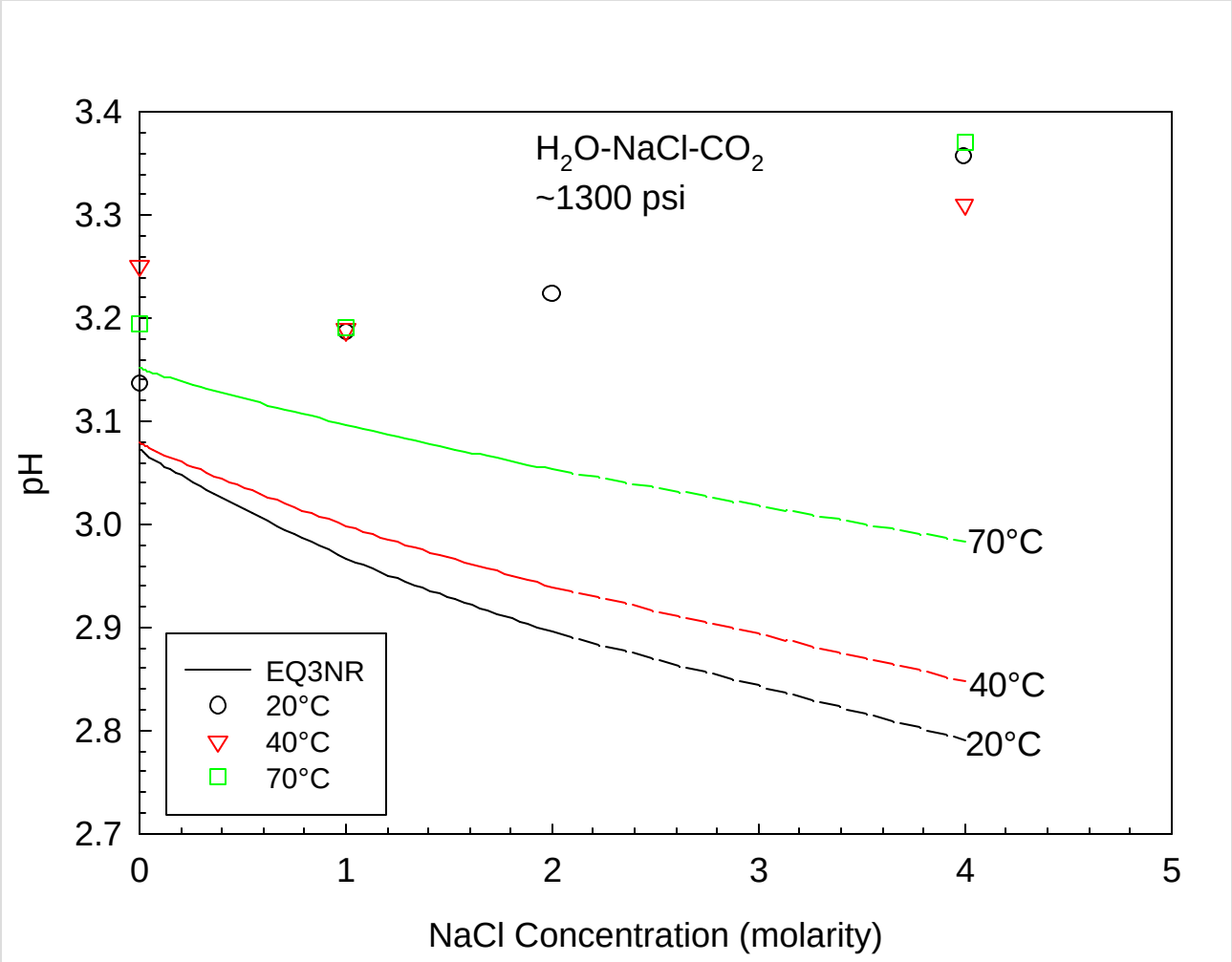


pH as a Function of Pressure for Different Concentrations of NaCl at 22°C

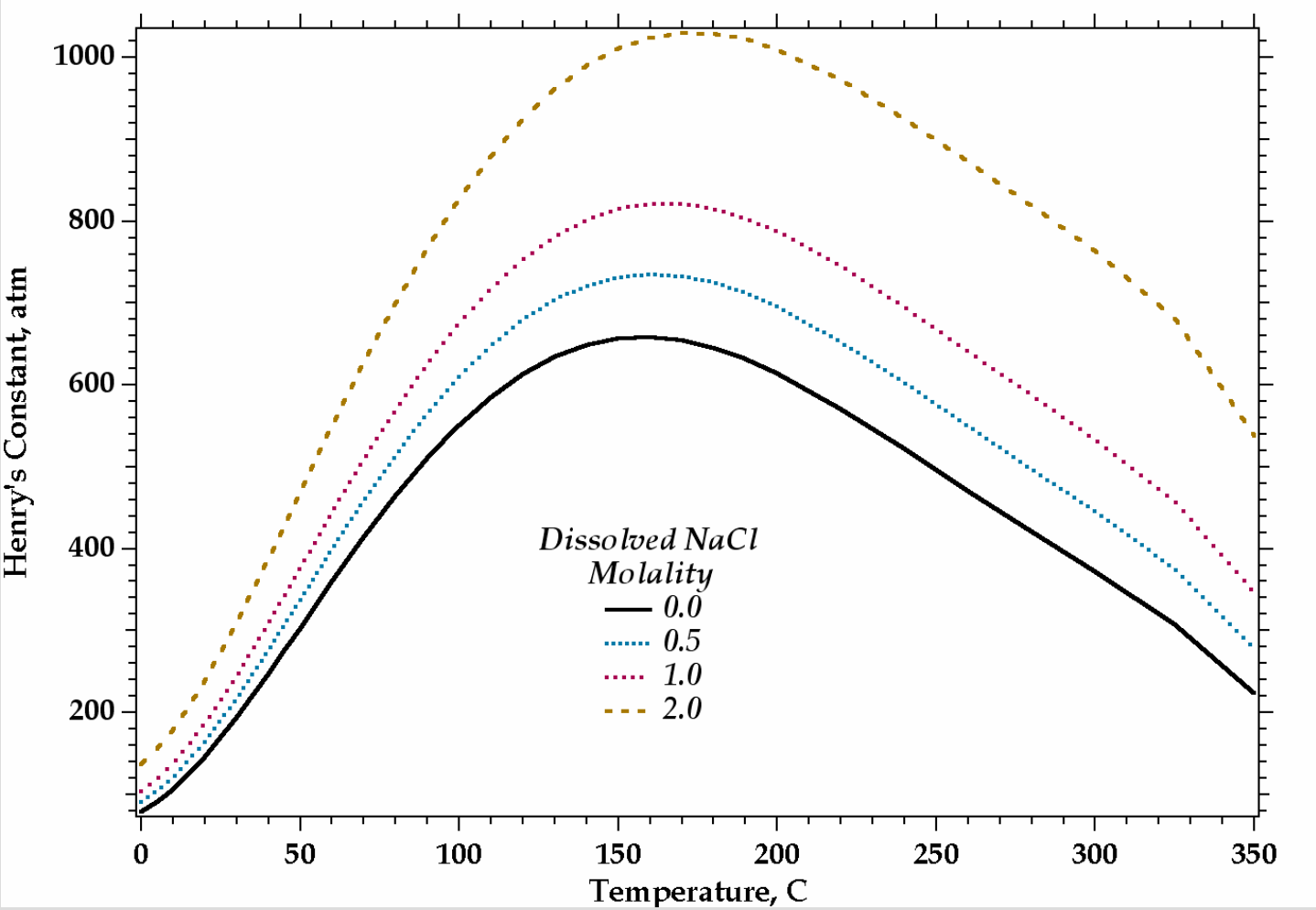


EQ3NR pH Calculations in H_2O-NaCl-CO_2 Mixtures

- EQ3NR predictions show decreasing pH with increasing salt concentration.
- No K_h correction.
- Na carbonate complexes form.

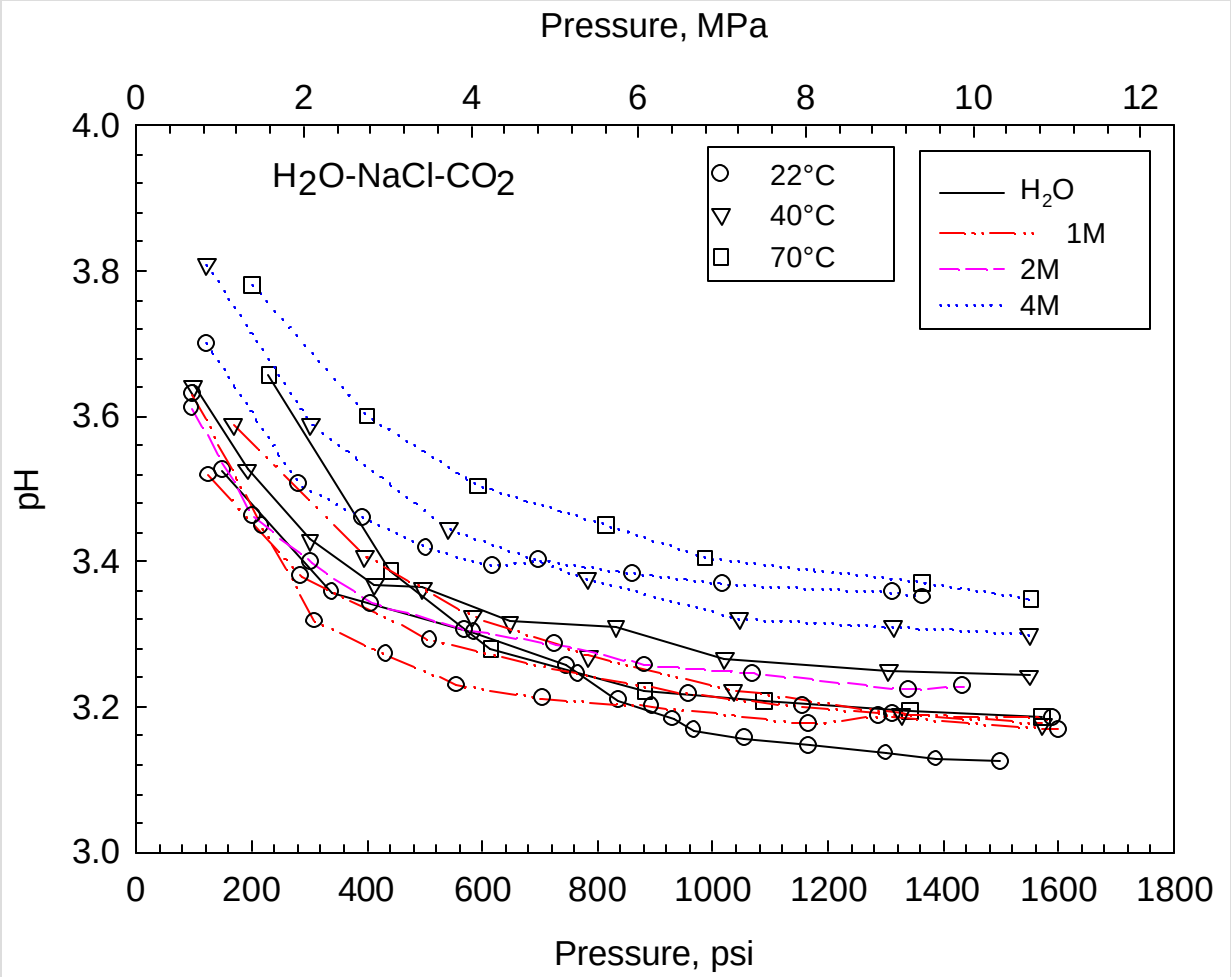


CO_2 Henry's Coefficient



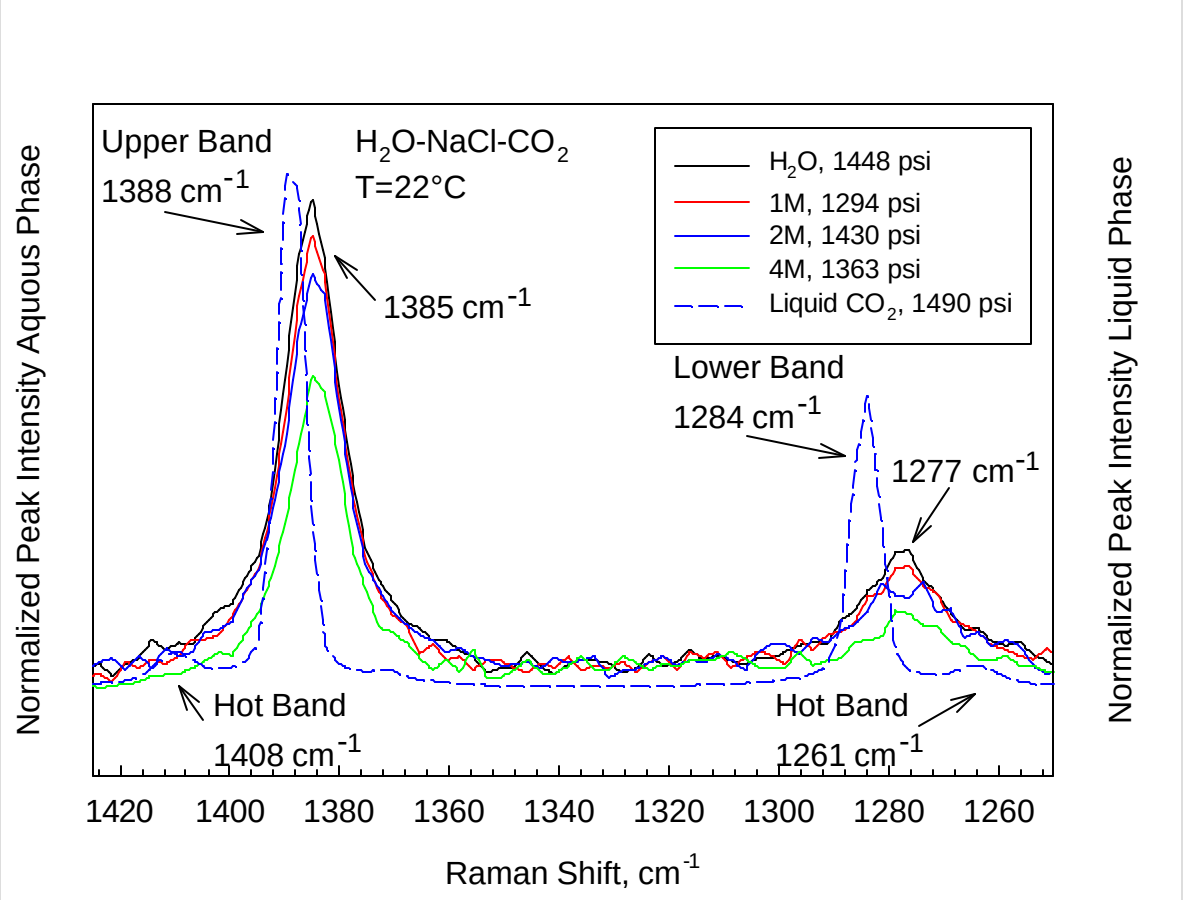
Variations of pH at Different Temperatures as a Function of CO_2 Pressure

- pH of aqueous phase increases as salt concentration increases.
- Small pH temperature dependence.
- pH range as a function of ionic strength is <0.4 pH units above $scCO_2$ pressures.

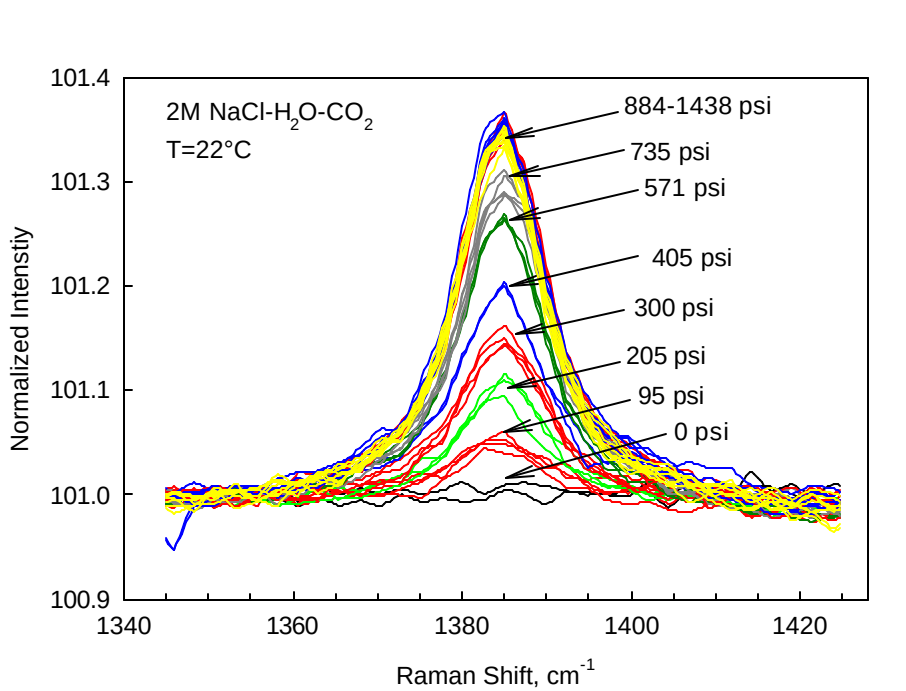


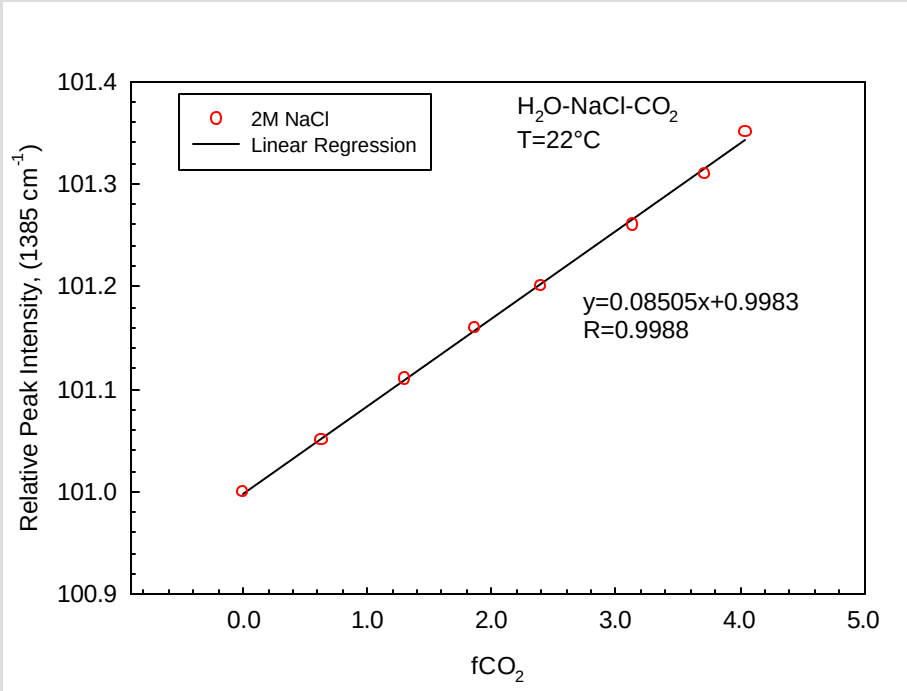
Raman Spectra of Dissolved CO_2 and Liquid CO_2

- Stretching bands shift to lower frequency and broaden in the aqueous phase.
- Stretching bands decrease in intensity with decreasing CO_2 concentrations.



Raman Spectra of 2M NaCl-H_2O-CO_2 System at 22°C





Conclusion

- Careful experiments and analysis reveal the pH of H_2O-NaCl-CO_2 mixtures above scCO_2 conditions vary <0.4 pH units.
  - More experimental work is needed to examine the effect of other salts that would be present in a real geological environment.
- Commonly available equilibrium geochemical simulators such as EQ3NR can accurately predict the pH of dilute salt solutions in scCO_2. However as salt concentrations increase the models are unable to predict the solution speciation.
  - Henry's constant correction needed.
  - Data from experimental work will allow these models to be modified.
- Raman spectroscopy shows promise for ex-situ measurements of dissolved CO_2 concentrations under scCO_2 conditions.