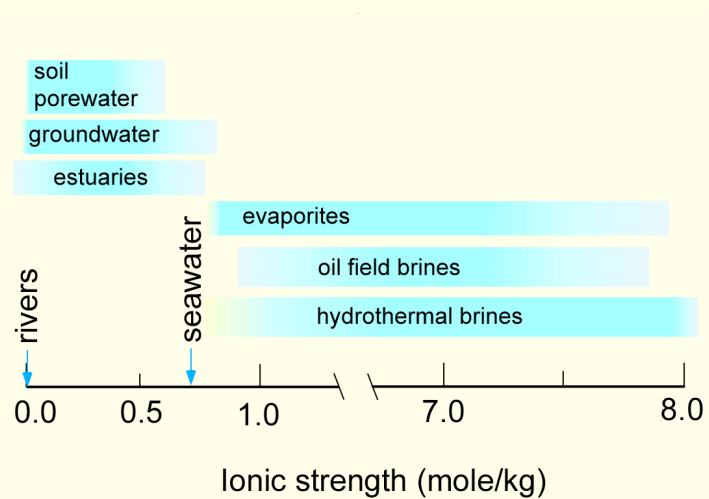


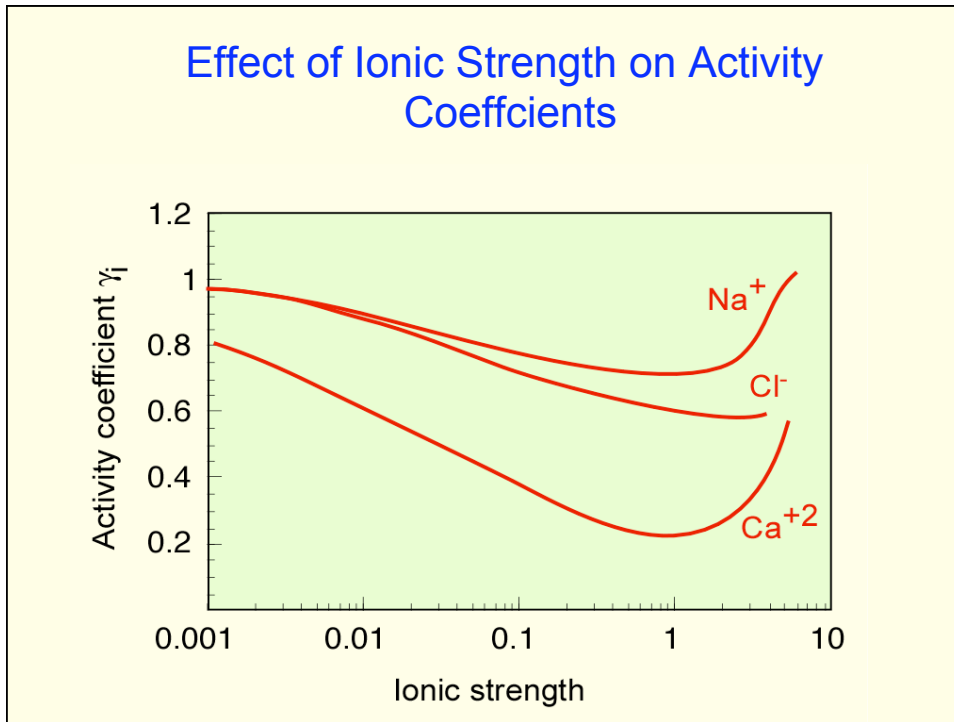
## Physical Chemistry of Aqueous Solutions II

### Concentrated Brines, Pitzer model

Advanced Aqueous Geochemistry  
DM Sherman, University of Bristol

### Ionic Strength of Natural Waters





### Pitzer Model

The Pitzer model is a formalism to deal with extremely concentrated brines:

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j D_{ij}(I) m_j + \sum_j \sum_k E_{ijk} m_j m_k$$

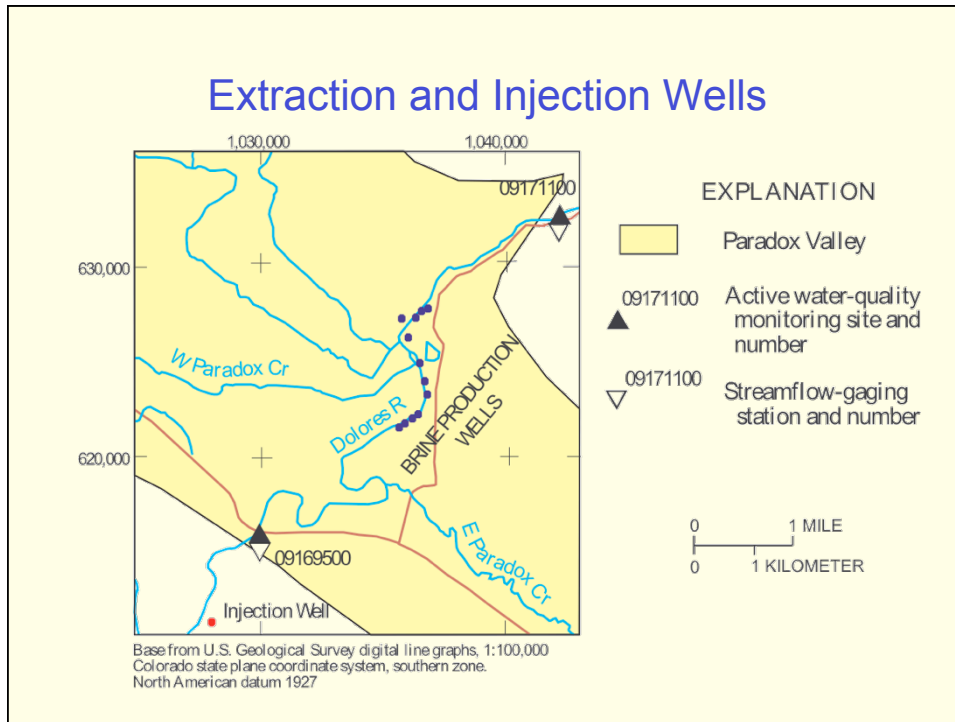
Here,  $D_{ij}$  are ion-ion interaction coefficients and  $E_{ijk}$  are ion-ion-ion interaction coefficients

## Case Study: Paradox Basin

### Deep Well Injection of a Brine

### Paradox Basin



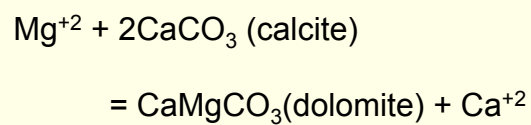
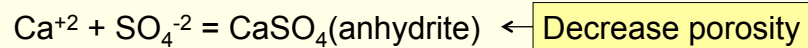


### Extraction and Injection Wells

SOLUTION 1 # Brine units mg/kgw temp 120.	SOLUTION 2 # Groundwater in # deep well Leadville # limestone units mg/kgw temp 120.
pH 6.32	pH 5.52
Li 0.42	Li 18.8
Na 91700	Na 52400
K 4200	K 1750
N(-3) 10.9 as NH4	N(-3) 40.1 as NH4
Mg 1480; Ca 1390	Mg 900; Ca 7,900
Sr 26.1; Ba 0.12	Sr 308; Ba 5.52
Mn 0.57; Fe 0.35	Mn 0.97; Fe 7.6
Cl 150000; Br 85.9	Cl 99600; Br 187
Alkalinity 313 as HCO3	Alkalinity 273 as HCO3
S(6) 5940 as SO4-2	S(6) 726 as SO4
S(-2) 91 as H2S	S(-2) 2.9 as H2S
Si 7.6 as SiO2	Si 69.7 as SiO2
B 8.8	B 16.8

## Precipitation of Anhydrite

Reactions that may result when waters are mixed:



Note: the high ionic strength of the brines means we must use the Pitzer database.

## Pitzer Model

The Pitzer model allows us to predict activity coefficients of ions in extremely concentrated brines:

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j D_{ij}(I) m_j + \sum_j \sum_k E_{ijk} m_j m_k$$

Here,  $D_{ij}$  are ion-ion interaction coefficients and  $E_{ijk}$  are ion-ion-ion interaction coefficients

## Modelling with Pitzer Activities

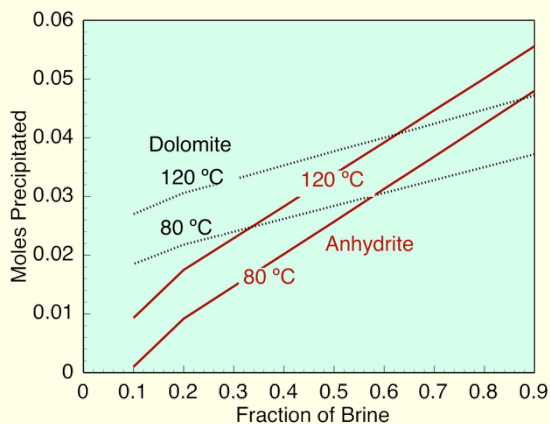
Predicted precipitation of Anhydrite during mixing using Pitzer model:

```

EQUILIBRIUM_PHASES
Anhydrite 0.0 0.0
Gypsum 0.0 0.0
Calcite 0.0 1000.0
Dolomite 0. 0.0

MIX
1 0.8
2 0.2

END
    
```



## Modelling with Davies Equation

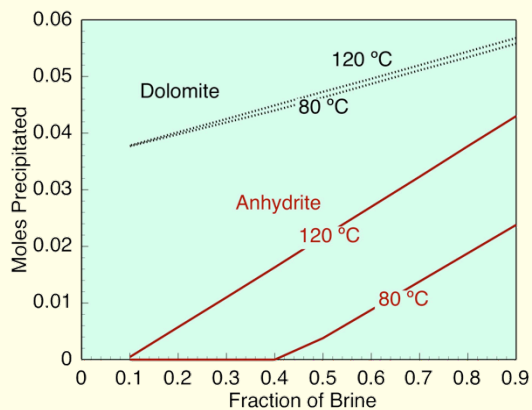
Predicted precipitation of Anhydrite during mixing using Davies equation (WRONG!):

```

EQUILIBRIUM_PHASES
Anhydrite 0.0 0.0
Gypsum 0.0 0.0
Calcite 0.0 1000.0
Dolomite 0. 0.0

MIX
1 0.8
2 0.2

END
    
```



## Summary

Geochemical modelling is used to predict consequences of deep well injection of waste fluids.

A major concern is mineral precipitation that will decrease porosity/permeability of the aquifer.

It is essential to use the Pitzer model for ion activity coefficients when treating high ionic strength fluids.