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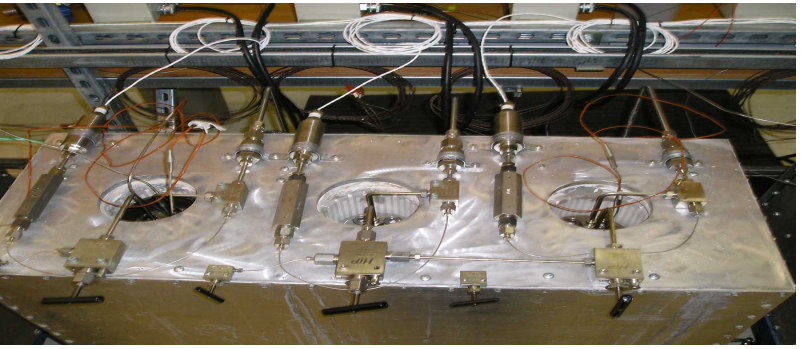
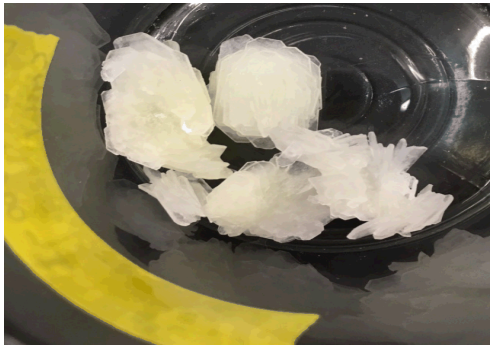


Synthesis and Characterization of Chukanovite, Fe2CO3(OH)2(s): An Elusive Ferrous Iron Carbonate Hydroxide Mineral

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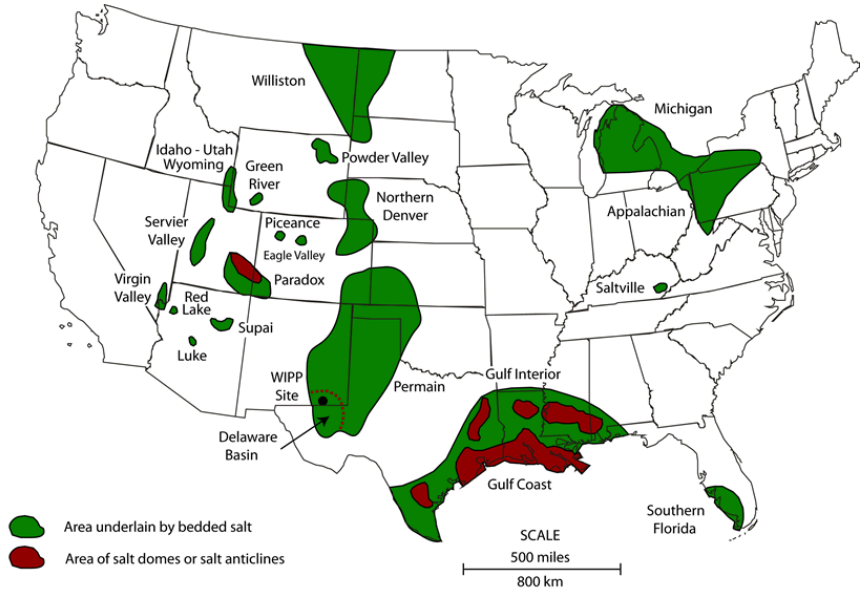
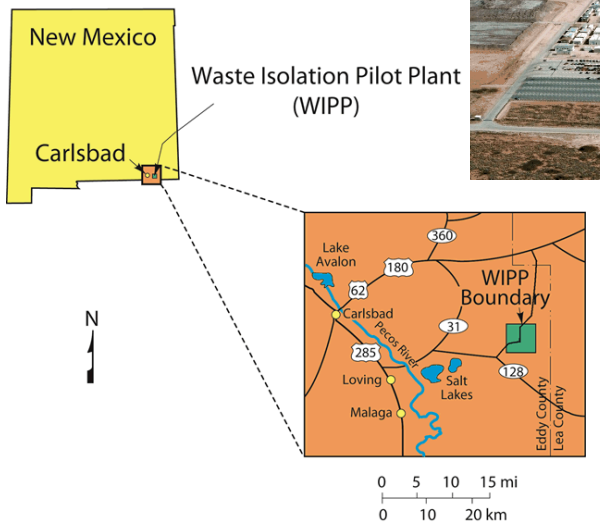
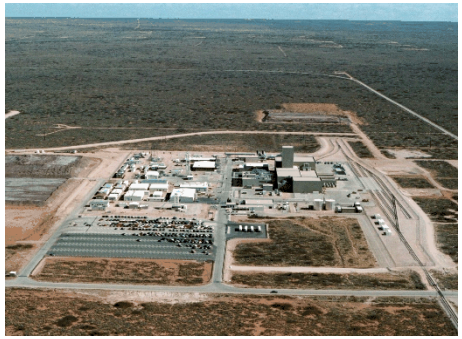
Waste Isolation Pilot Plant (WIPP)

- The Waste Isolation Pilot Plant (WIPP), located in southeastern New Mexico, has been developed by the U.S. Department of Energy (DOE) for the deep geologic disposal of transuranic (TRU) waste.



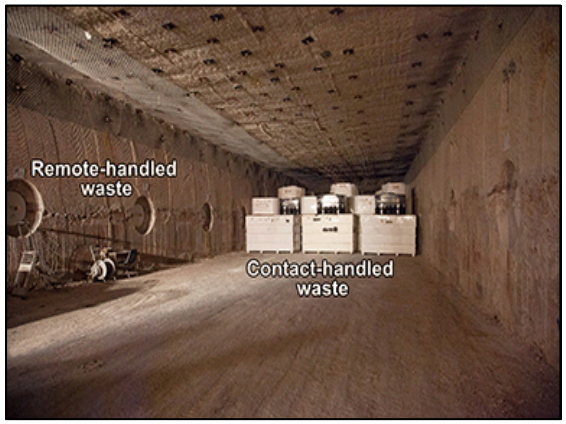
ROCK SALT DEPOSITS in the UNITED STATES





WIPP

- WIPP Performance Assessment calculations estimate the probability and consequence of potential mobile (dissolved and colloids) radionuclide releases from the repository to the accessible environment for a regulatory period of 10,000 years after facility closure.
- Steel (Fe) in waste containers and Lead (Pb) in shielded containers
- Anions – sulfide (S^{2-}), carbonate (CO_3^{2-}), etc.
- Organic ligands – citrate ($C_6H_8O_7$), EDTA
- ($C_{10}H_{16}N_2O_8$), oxalate ($C_2O_4^{2-}$), etc



- Updating WIPP thermodynamic database – Pitzer model

Chukanovite, $Fe_2CO_3(OH)_2(s)$

- Fe(s) in excess of the waste at WIPP
- Anoxic corrosion produces Fe^{+2}
- Ferrous “Carbonate” “Hydroxide”
  - pH and alkalinity
- A candidate for solubility limiting solid for dissolved Fe^{+2}
  - Electrochemical potential
  - Masking of Fe^{+2} against the solubilizing (in)organic ligands, such as, $EDTA^{-4}$, $Oxalate^{-2}$, $Acetate^{-}$, $citrate^{-3}$, SO_4^{-2}, CO_3^{-2}, etc.
- Not much known, especially the synthesis condition and the stability vs. other ferrous iron minerals

Thermodynamics known so far …

Reactions	logK	Source
Aqueous reactions		
$H^+ + OH^- = H_2O$	13.99	Harvie et al. (1984)
$CO_3^{-2} + H^+ = HCO_3^-$	10.33	Harvie et al. (1984)
$CO_2(aq) + H_2O = H^+ + HCO_3^-$	-6.33	Harvie et al. (1984)
$FeOH^+ + H^+ = Fe^{+2} + H_2O$	9.31	Shock et al. (1997)
$Fe(OH)_2(aq) + 2H^+ = Fe^{+2} + 2H_2O$	20.82	Stumm and Morgan (1996)
$Fe(OH)_3^- + 3H^+ = Fe^{+2} + 3H_2O$	31.00	Baes and Mesmer (1976)
$Fe(OH)_4^{-2} + 4H^+ = Fe^{+2} + 4H_2O$	46.00	Baes and Mesmer (1976)
$FeCO_3(aq) + H^+ = Fe^{+2} + HCO_3^-$	4.83	Bruno et al. (1992)
$Fe(CO_3)_2^{-2} + 2H^+ = Fe^{+2} + 2HCO_3^-$	13.89	Kim et al. (2017)
Dissolution		
$NaCl(s) = Na^+ + Cl^-$	1.57	Harvie et al. (1984)
$CO_2(g) + H_2O = H^+ + HCO_3^-$	-7.81	Wagman et al. (1982)
$Fe(OH)_2(s) + 2H^+ = Fe^{+2} + 2H_2O$ (Ferrous Iron Hydroxide, FIH)	12.89	Kim et al. (2017)
$Fe_2Cl(OH)_3(s) + 3H^+ = 2Fe^{+2} + Cl^- + 3H_2O$ (Hibbingite)	17.08	Kim et al. (2017)
$FeCO_3(s) + H^+ = Fe^{+2} + HCO_3^-$ (Siderite)	-0.12	Kim et al. (2017)
$Fe_2CO_3(OH)_2(s) + 3H^+ = 2Fe^{+2} + HCO_3^- + 2H_2O$ (Chukanovite)	12.32	Kim et al. (2017)

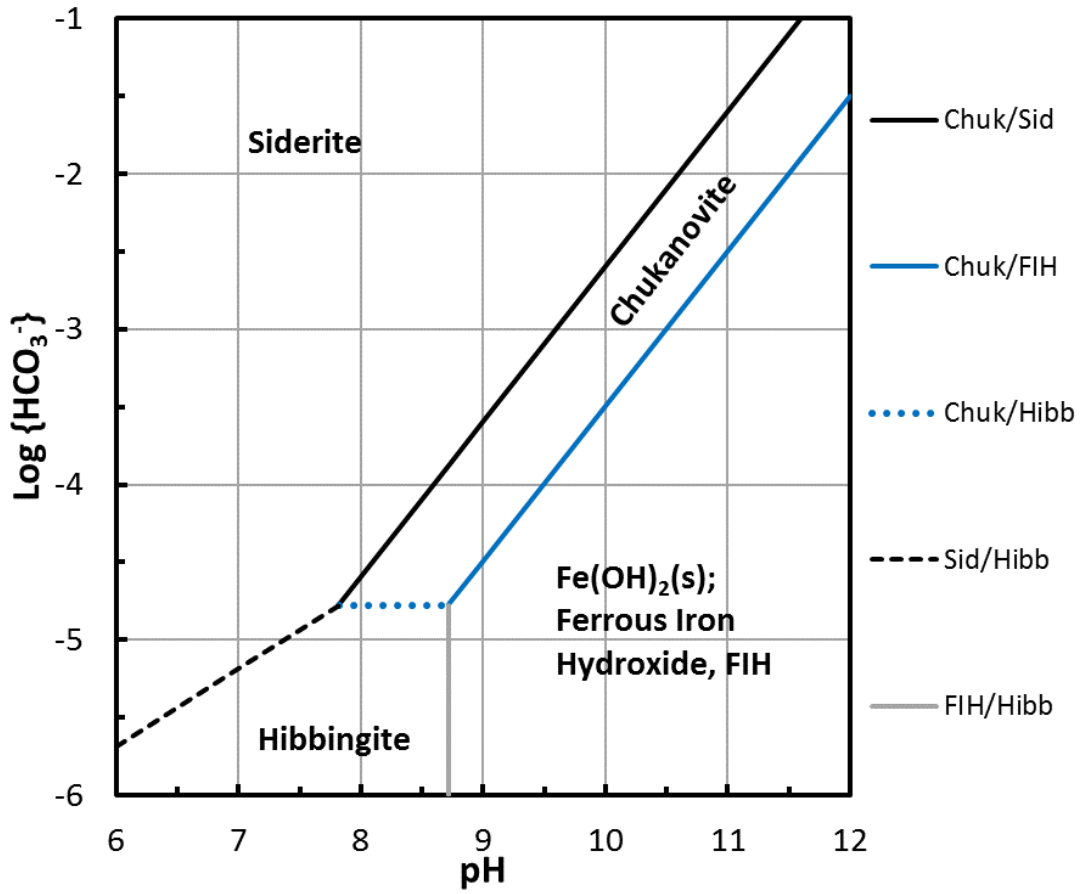
I	j	α_1/α_2[A]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^Φ	Source
Na^+	Cl^-	2.0/12.0	0.0765	0.2664	0.0	0.00127	Harvie et al. (1984)
Na^+	OH^-	2.0/12.0	0.0864	0.253	0.0	0.0044	Harvie et al. (1984)
Na^+	HCO_3^-	2.0/12.0	0.0277	0.0411	0.0	0.0	Harvie et al. (1984)
Na^+	CO_3^{-2}	2.0/12.0	0.0399	1.389	0.0	0.0044	Harvie et al. (1984)
H^+	Cl^-	2.0/12.0	0.1775	0.2945	0.0	0.0008	Harvie et al. (1984)
Fe^{+2}	Cl^-	2.0/12.0	0.37324	1.13499	0.0	-0.02152	Moog et al. (2004)
Na^+	$Fe(CO_3)_2^{-2}$	2.0/12.0	-0.230	6.26	0.0	0.0	Kim et al. (2017)

I	j	θ_{ij}	Source	k	ψ_{ijk}	Source
Na^+	H^+	0.036	Harvie et al. (1984)	Cl^-	-0.004	Harvie et al. (1984)
Cl-	OH^-	-0.05	Harvie et al. (1984)	Na^+	-0.006	Harvie et al. (1984)
Cl^-	HCO_3^-	0.03	Harvie et al. (1984)	Na^+	-0.015	Harvie et al. (1984)
Cl^-	CO_3^{-2}	-0.02	Harvie et al. (1984)	Na^+	0.0085	Harvie et al. (1984)
OH^-	CO_3^{-2}	0.1	Harvie et al. (1984)	Na^+	-0.017	Harvie et al. (1984)
HCO_3^-	CO_3^{-2}	-0.04	Harvie et al. (1984)	Na^+	0.002	Harvie et al. (1984)
Na^+	Fe^{+2}	0.10945	Moog et al. (2004)	Cl^-	-0.01605	Moog et al. (2004)

I	j	λ_{ij}	Source
CO_2 (aq)	H+	0.0	Harvie et al. (1984)
CO_2 (aq)	Na^+	0.1	Harvie et al. (1984)
CO_2 (aq)	Cl^-	-0.005	Harvie et al. (1984)

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only cation-anion binary pair. α_2 is not applied when $\beta^{(2)}$ is zero or not used. Unit for α_1 and α_2 is $kg^{1/2} \cdot mol^{-1/2}$.

Mineral boundary	Equation[A]
$Fe_2CO_3(OH)_2(s)$ vs. $Fe(OH)_2(s)$	$\log\{HCO_3^-\} = -\log\{H+\} + 2\log\{H_2O\} - 13.46$
$Fe(OH)_2(s)$ vs. $Fe_2Cl(OH)_3(s)$	$\log\{Cl^-\} = -\log\{H^+\} + \log\{H_2O\} - 8.70$
$Fe_2Cl(OH)_3(s)$ vs. $Fe_2CO_3(OH)_2(s)$	$\log\{HCO_3^-\} = \log\{Cl^-\} + \log\{H_2O\} - 4.76$
$Fe_2Cl(OH)_3(s)$ vs. $FeCO_3(s)$	$\log\{HCO_3^-\} = 0.5\log\{Cl^-\} + 0.5(-\log\{H^+\} + 3\log\{H_2O\} - 17.32)$
$Fe_2CO_3(OH)_2(s)$ vs. $FeCO_3(s)$	$\log\{HCO_3^-\} = 2\log\{H_2O\} - \log\{H^+\} - 12.56$



Chukanovite looks elusive …

Synthesis

- 2 solubility experiments; Kim et al. (2017)
  - initiated with the addition of siderite in 0.5 and 2.0 m Na_2CO_3 solutions spiked with NaCl = 1.5 m.
  - equilibrated for more than 4 years
- 8 synthesis experiments
  - Fe^{+2}:HCO_3^- fixed (~0.6:~0.5 mole:mole) with incremental NaOH (0 to ~0.9 mole)
  - equilibrated for more than 10 months

Aqueous Data: Draft, Do not cite

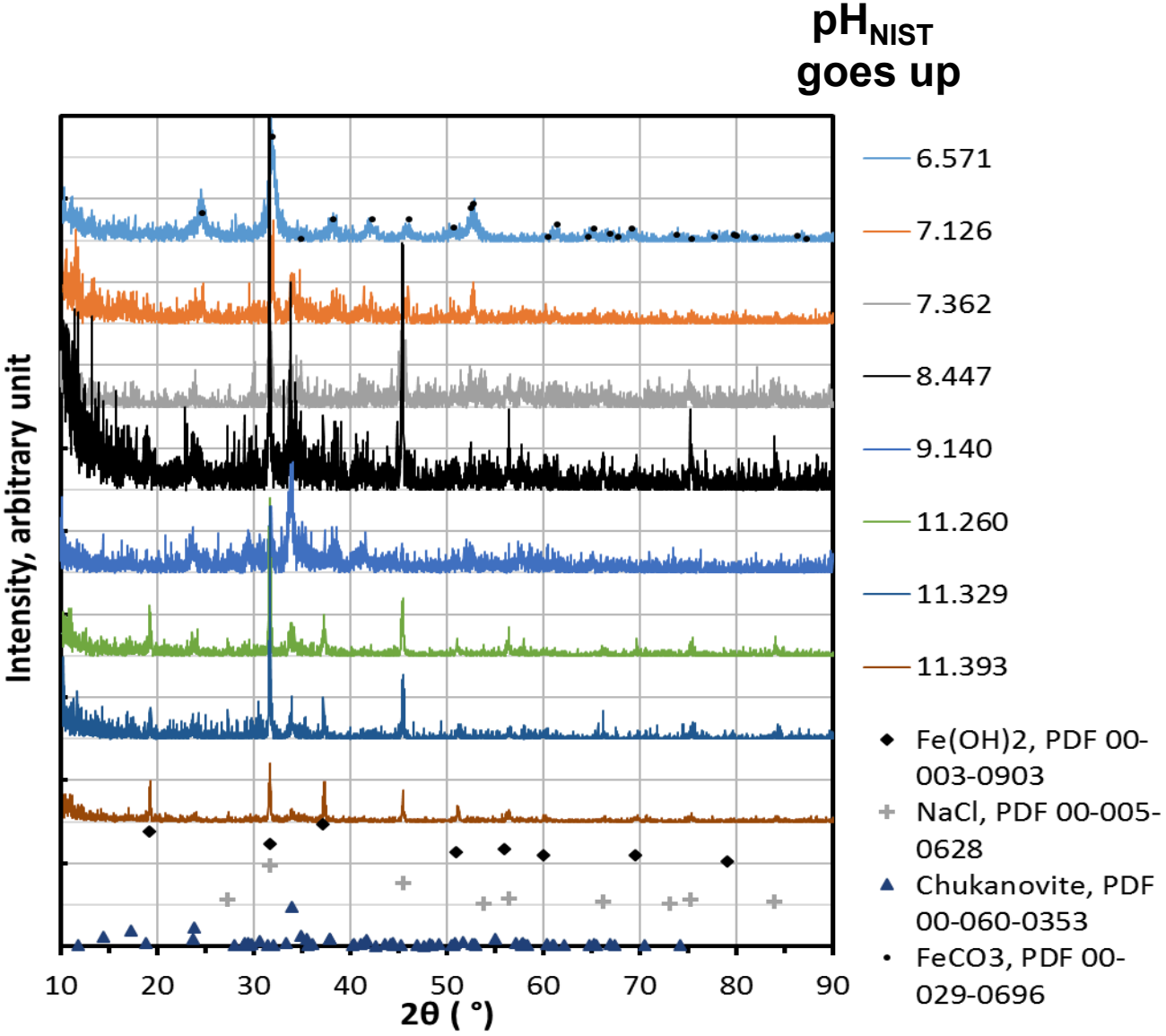
pmH	Density, g/mL	Na^+, m, ICPAES		Cl^-, m, IC		HCO_3^-, m, Coulometer		Fe^{+2}, m, ICPAES	
		Average	%2SD	Average	%2SD	Average	%2SD	Average	%2SD
6.55	1.044	0.48	5%	1.28	1%	0.0008	106%	0.435	3%
7.15	1.046	0.75	2%	1.25	6%	0.0012	83%	0.235	2%
8.55	1.035	1.17	6%	1.17	3%	0.0028	80%	NA	NA
11.38	1.030	1.25	2%	1.17	7%	0.0553	8%	NA	NA
7.43	1.032	0.98	8%	1.16	0%	0.0027	98%	0.093	1%
9.24	1.017	1.17	7%	1.18	1%	0.0071	17%	NA	NA
11.45	1.038	1.26	3%	1.12	4%	0.0864	9%	NA	NA
11.52	1.038	1.29	4%	1.08	4%	0.1039	3%	NA	NA

pmH: negative 10-based logarithm of molality of H^+
m: molality (mole solute in kg H_2O)
%2SD: Two Standard Deviation of three measurements divided by the average in percent
NA: Not Available

Fe^{+2}, m, Chg. Bal.	Fe^{+2}, m, ICP-AES	
	Average	%2SD
0.404	0.435	3%
0.237	0.235	2%
0.001	NA	NA
-0.009	NA	NA
0.090	0.093	1%
-0.014	NA	NA
-0.017	NA	NA
-0.025	NA	NA

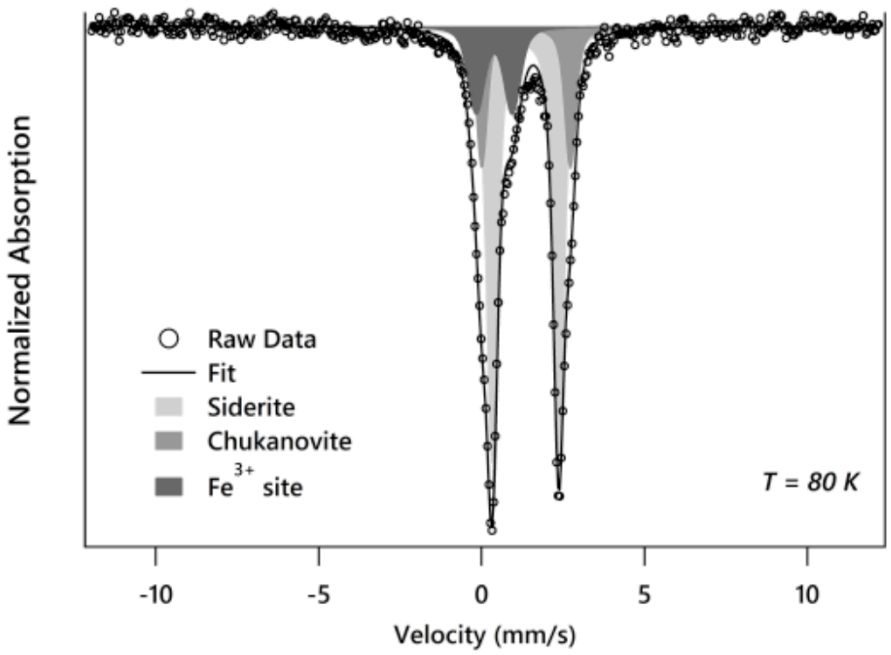
XRD

- pH
- Coexistence of at least two minerals



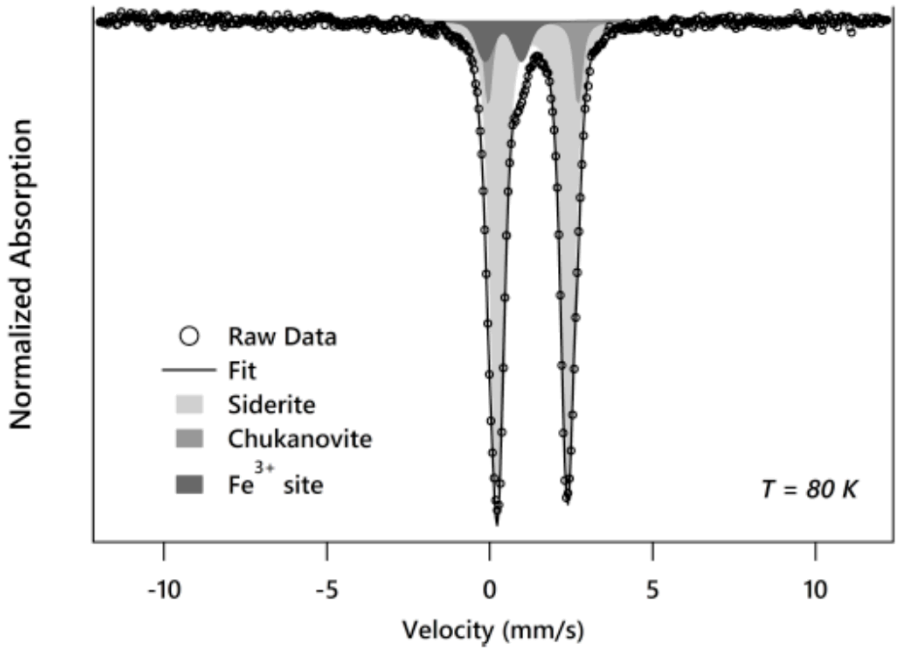
Mössbauer spectroscopy

- FeCO3 - 0.5CO3 - 3
  - 80K spectrum
  - Siderite, 63%
  - Chukanovite, 20%
  - Fe^{+3}, 17%

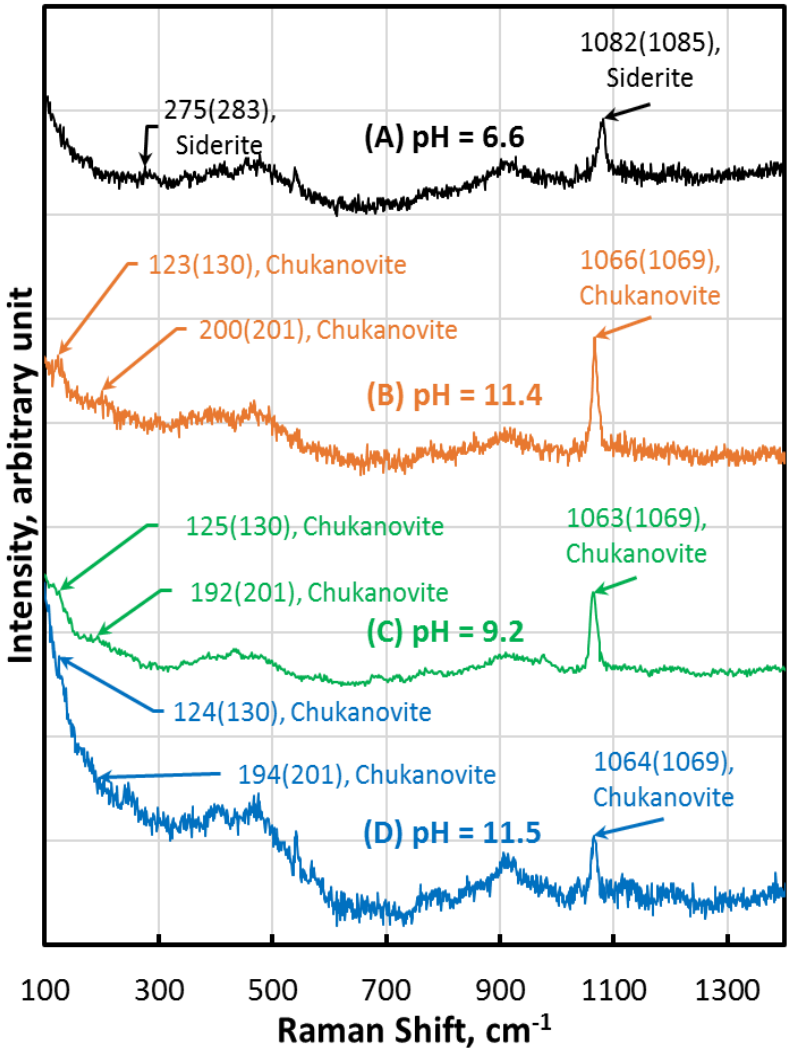


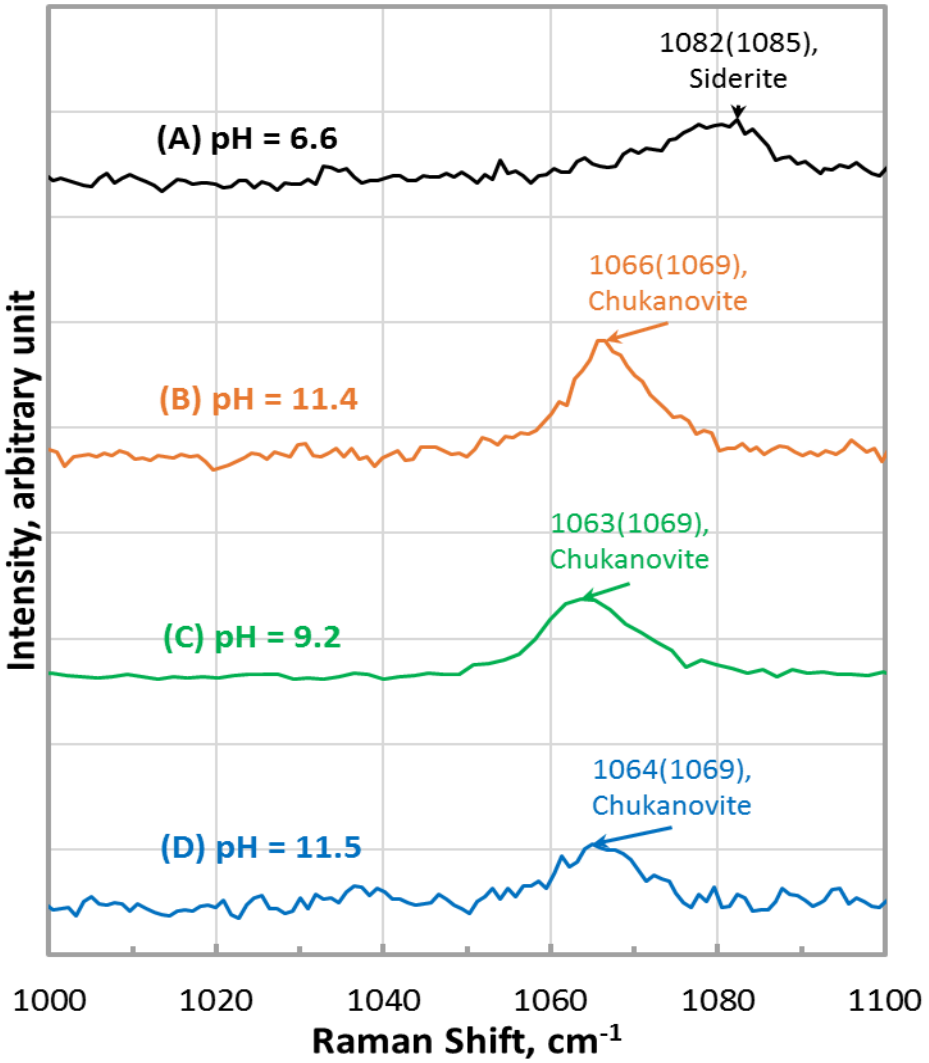
Mössbauer spectroscopy

- FeCO3 - 2.0CO3 - 3
  - 80K spectrum
  - Siderite, 82%
  - Chukanovite, 10%
  - Fe^{+3}, 8%

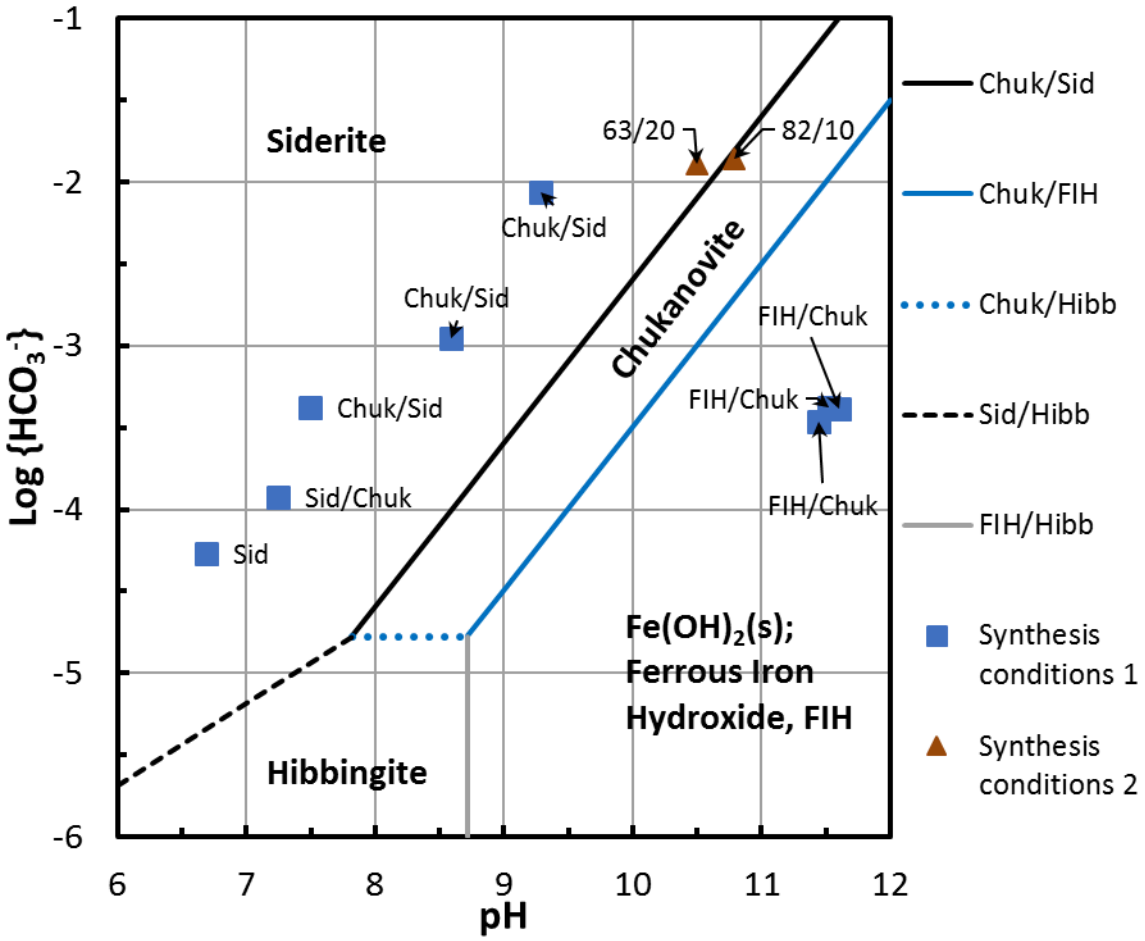


Raman


1082(1085), Siderite
275(283), Siderite
(A) pH = 6.6
123(130), Chukanovite
1066(1069), Chukanovite
200(201), Chukanovite
(B) pH = 11.4
125(130), Chukanovite
1063(1069), Chukanovite
192(201), Chukanovite
(C) pH = 9.2
124(130), Chukanovite
194(201), Chukanovite
1064(1069), Chukanovite
(D) pH = 11.5
Intensity, arbitrary unit
100
300
500
700
900
1100
1300
Raman Shift, cm-1


1082(1085), Siderite
(A) pH = 6.6
1066(1069), Chukanovite
(B) pH = 11.4
1063(1069), Chukanovite
(C) pH = 9.2
1064(1069), Chukanovite
(D) pH = 11.5
Intensity, arbitrary unit
1000
1020
1040
1060
1080
1100
Raman Shift, cm-1

Observations projected onto the Theory



Importance for WIPP Geochemistry

- Mössbauer and Raman spectroscopy indicated that siderite and chukanovite are distinguishable from each other
- Fe(s) vs. Siderite: Log fugacity $O_2(g)$ = ?
  - $Fe(s) + HCO_3^- + 0.5O_2(g) + H^+ = FeCO_3(s) + H_2O$
- Fe(s) vs. Chukanovite: Log fugacity $O_2(g)$ = ?
  - $2Fe(s) + HCO_3^- + O_2(g) + H^+ = Fe_2CO_3(OH)_2(s)$
- In near future, stability of ferric iron (Fe^{+3}) phase(s) will be investigated to evaluate the log fugacity $O_2(g)$
- Uncertainties checked: Dilution and titration

Special thanks to …

- Justin Dean, Taya Olivas: Sample preparation & maintenance
- Jonathan Icenhower, Shelly Nielsen: Internal reviews
- Christopher Gorski, Prachi Joshi: Mossbauer Analysis
  - Environmental Engineering, Pennsylvania State University
- Questions?