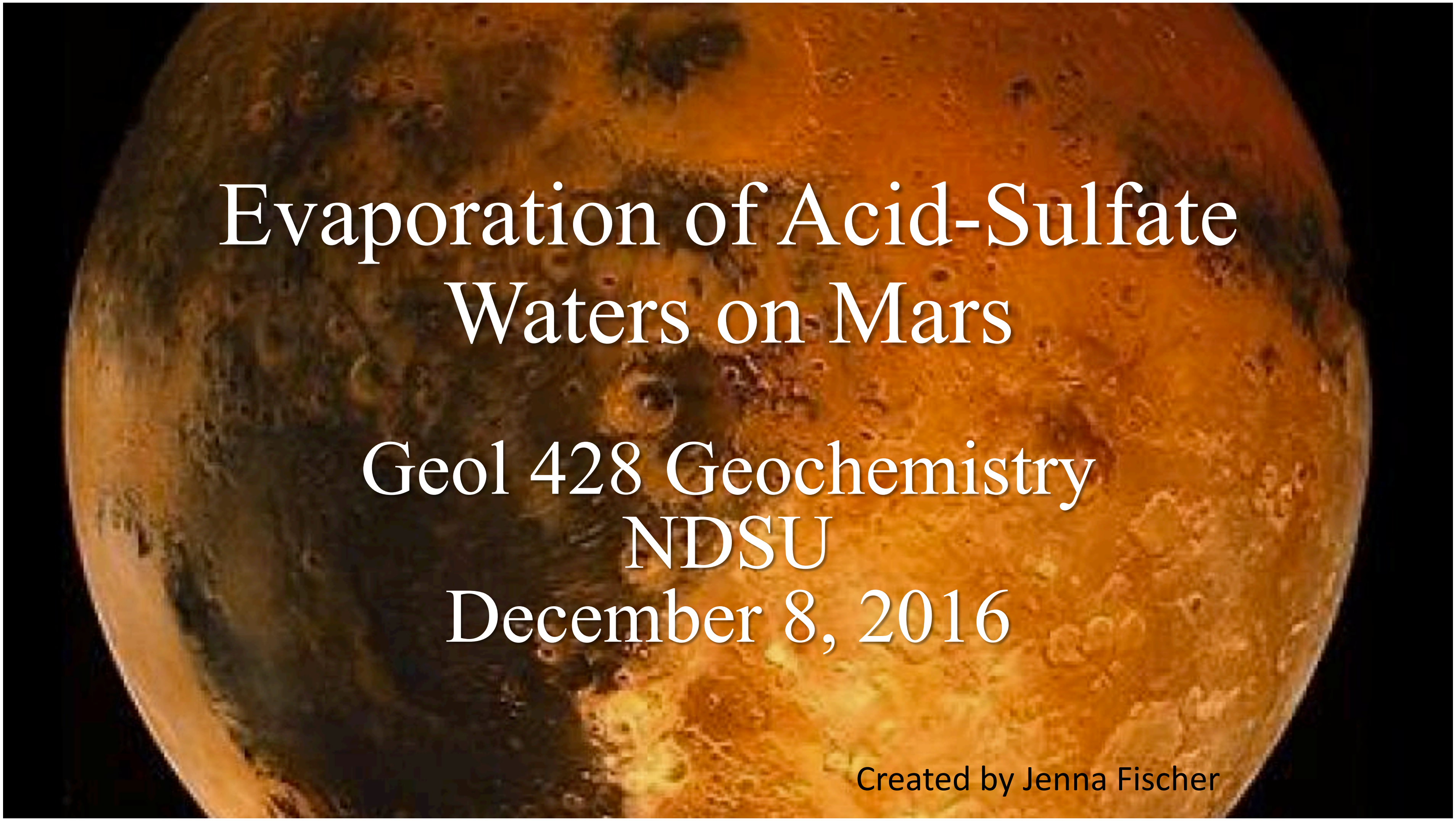

Evaporation of Acid-Sulfate Waters on Mars
Geol 428 Geochemistry
NDSU
December 8, 2016
Created by Jenna Fischer

The Experiment

- "Experimental constraints on the evaporation of partially oxidized acid- sulfate waters at the martian surface"

  by: Nicholas J. Tosca, Scott M. McLennan
  Geochimica et Cosmochimica Acta 73 (2009) 1205–1222
- Analyzing minerals on Mars suggest that a significant portion of its geologic history was characterized by the presence of brines
- Within these saline deposits are enriched with Fe-sulfates
- Trying to quantify sulfate mineral formation during evaporation processes occurring at the martian surface

Goals

- Identify Precipitates
- Identify kinematic factors that within the experiment on the production of precipitates
- Compare the experimental results to observations of sulfate- bearing deposits identified on Mars
- Compare experimental results to geochemical modeling simulations of evaporation processes at the surface of Mars. With the calculation of evaporate minerals, new constraints may be placed on the habitability of evaporate - bearing localities

Controls

- Focus on dilute substances that have not been affected by clay precipitation
- Hematite and Goethite were suppressed in all models

Problems for Geol 428

- The authors used Fe redox not at equilibrium
- This class only deals with modeling that's in equilibrium

Focus

- There focus was to investigate the effect of Fe redox disequilibrium on the resulting mineral assemblage produced upon evaporative concentration
- Mineral – water equilibrium
- Using one dilute solution

Basis for Fluid Composition

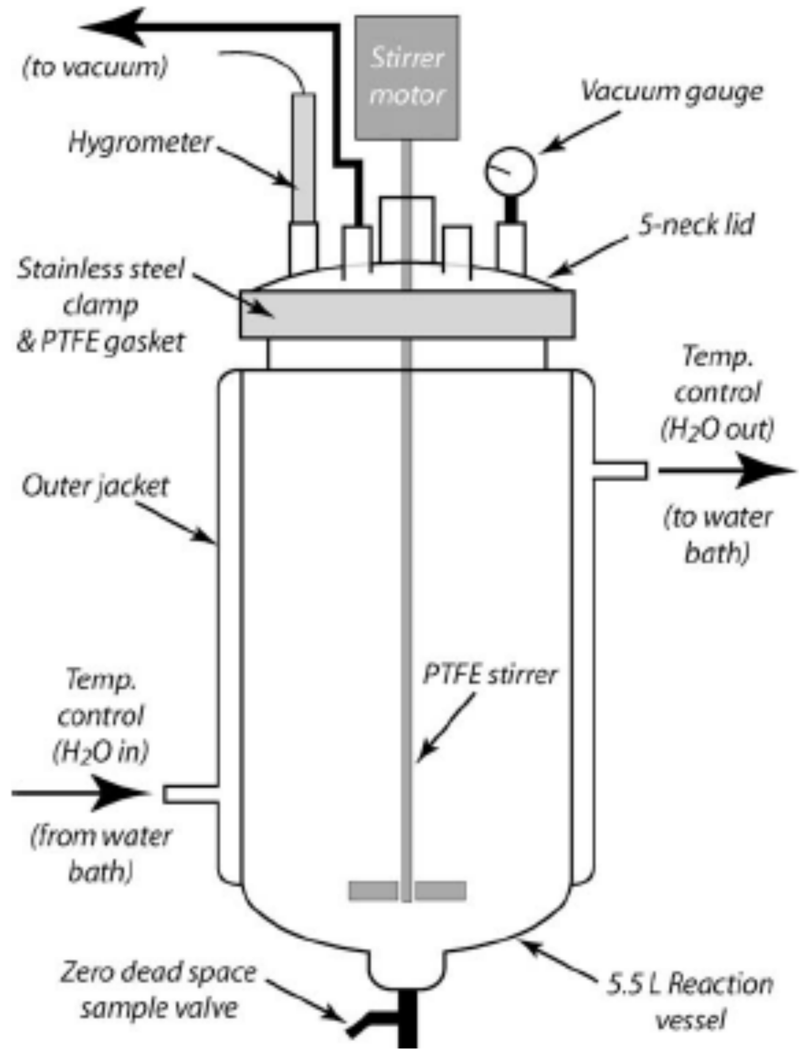
- Fluid is derived from the acidic chemical weathering of synthetic martian basalt
- From Mars Pathfinder
- Basalt is olivine- bearing and contains clinopyroxene, Fe- Ti oxides and a minor component of interstitial glass

Table 1
Initial and final fluid compositions (all concentrations in mol kg^{-1}).

	Component added[a]	Initial dilute fluid[b]	"Preconc." Initial fluid (target)[c]	"Preconc." Initial fluid (actual)[d]	Final brine[e] 1	Final brine 2	Final brine 3	Final brine 4	Final brine 5
H_2O remaining (g/kg)	–	1000	1000	1000	23.0	19.6	16.5	15.5	14.8
pH	–	2.00	1.55	1.43	−0.58	−1.06	−1.21	−1.30	−1.19
Ionic strength[*]	–	0.065	0.22	0.25	9.09	10.47	10.19	9.51	10.04
a_{H2O}[*]	–	0.999	0.997	0.997	0.780	0.661	0.639	0.655	0.649
Mg	$MgSO_4$ $7H_2O$	4.97E−03	1.76E−02	1.74E−02	0.761	0.805	0.857	0.892	0.990
Fe(II)	$FeSO_4$ $7H_2O$	1.98E−03	7.01E−03	6.18E−03	0.252	0.274	0.184	0.126	0.138
Fe(III)	$Fe_2(SO_4)_3$ xH_2O	1.98E−03	7.01E−03	7.96E−03	0.381	0.418	0.335	0.226	0.286
Ca	$CaSO_4$ $2H_2O$	1.65E−03	5.84E−03	6.33E−03	2.25E−03	8.42E−04	7.64E−04	7.18E−04	7.75E−04
Na	Na_2SO_4 $10H_2O$	2.48E−04	8.78E−04	8.60E−04	0.037	0.049	0.067	0.075	0.072
K	K_2SO_4	9.46E−05	3.35E−04	3.23E−04	1.49E−02	3.99E−03	1.99E−04	3.07E−05	2.56E−09
Al	$Al_2(SO_4)_3$ $18H_2O$	3.85E−05	1.36E−04	1.46E−04	4.73E−03	2.41E−03	1.55E−03	5.41E−04	6.26E−04
SO_4(total)	H_2SO_4 + salts	2.01E−02	8.55E−02	9.38E−02	3.95	5.24	5.48	5.57	5.47
Cl	HCl	2.82E−03	9.99E−03	5.17E−03	0.39	0.46	0.48	0.49	0.40

How did Tosca and McLennan do this?

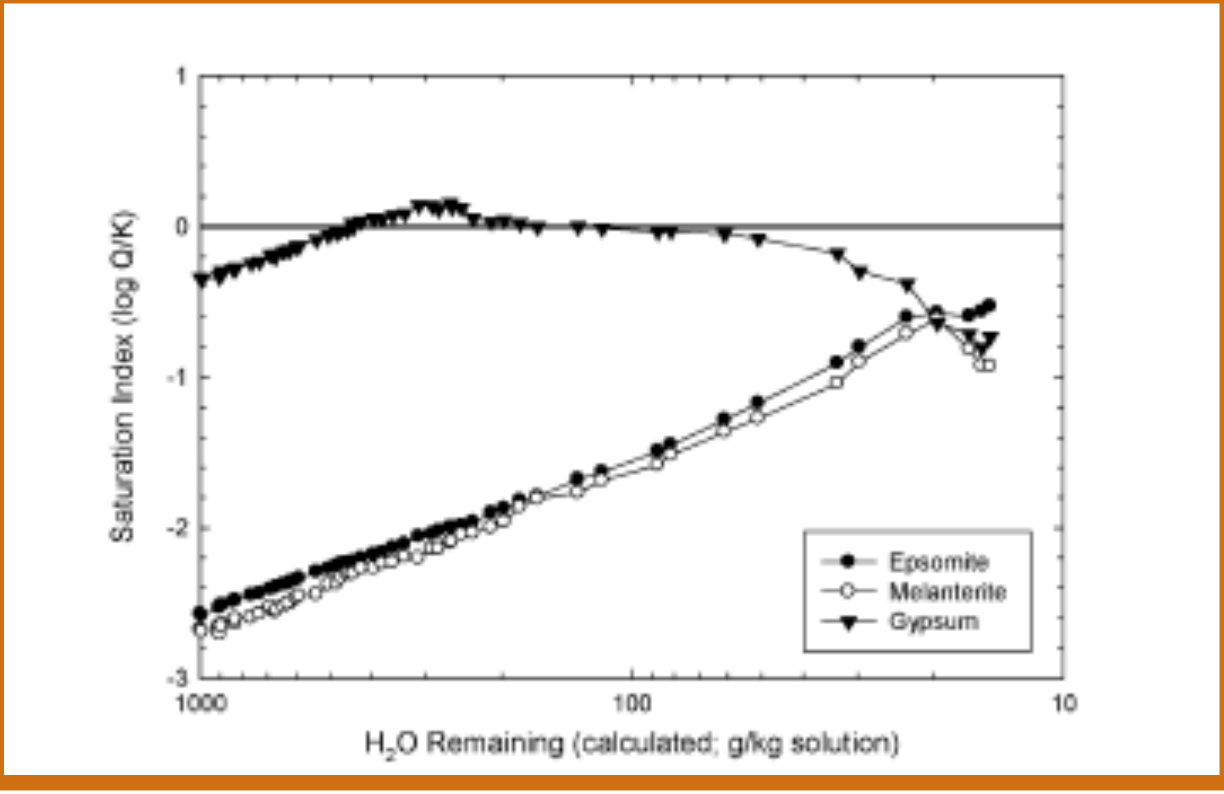
- 25 degrees C
- Water chemistry was calculated throughout evaporation process
- Vacuum over the headspace
- Precipitate chemistry calculated with SEM



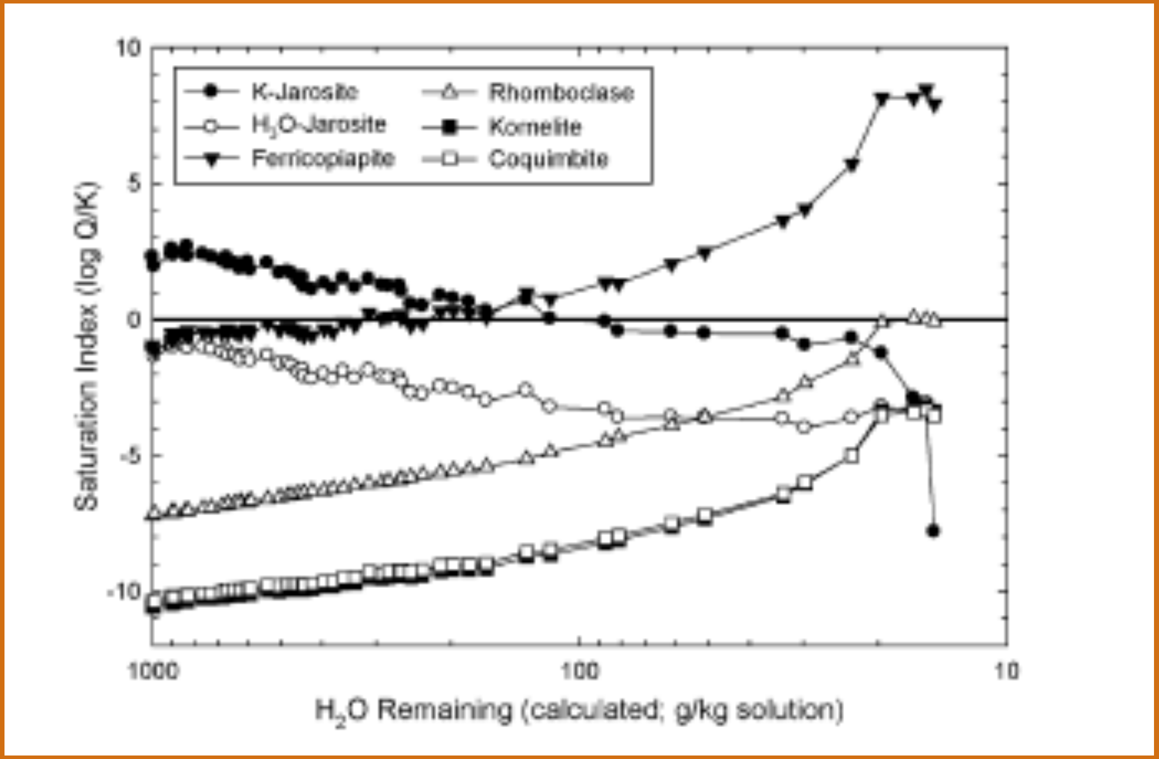
Phase	SI**	log IAP	log K(298 K, 1 atm)	
Al(OH)3(a)	-10.60	0.20	10.80	Al(OH)3
AlumK	-9.41	-14.58	-5.17	KAl(SO4)2:12H2O
Alunite	-12.78	-14.18	-1.40	KAl3(SO4)2(OH)6
Anhydrite	-1.23	-5.59	-4.36	CaSO4
Basaluminite	-28.23	-5.53	22.70	Al4(OH)10SO4
Boehmite	-8.38	0.20	8.58	AlOOH
Brucite	-15.63	1.21	16.84	Mg(OH)2
Diaspore	-6.68	0.20	6.88	AlOOH
Epsomite	-2.98	-5.12	-2.14	MgSO4:7H2O
Fe(OH)2.7Cl.3	3.07	0.03	-3.04	Fe(OH)2.7Cl0.3
Fe(OH)3(a)	-3.48	1.42	4.89	Fe(OH)3
Fe3(OH)8	-16.55	3.67	20.22	Fe3(OH)8
Gibbsite	-7.91	0.20	8.11	Al(OH)3
Goethite	2.42	1.42	-1.00	FeOOH
Gypsum	-1.01	-5.59	-4.58	CaSO4:2H2O
H2(g)	-27.20	-30.35	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.91	-6.33	1.58	NaCl
Hematite	6.84	2.83	-4.01	Fe2O3
Jarosite(ss)	-0.27	-10.10	-9.83	(K0.77Na0.03H0.2)Fe3(SO4)2(OH)6
Jarosite-K	-1.32	-10.53	-9.21	KFe3(SO4)2(OH)6
Jarosite-Na	-4.83	-10.11	-5.28	NaFe3(SO4)2(OH)6
JarositeH	-3.02	-8.41	-5.39	(H3O)Fe3(SO4)2(OH)6
Jurbanite	-2.90	-6.13	-3.23	AlOHSO4
Maghemite	-3.55	2.83	6.39	Fe2O3
Magnetite	-0.07	3.67	3.74	Fe3O4
Melanterite	-3.28	-5.49	-2.21	FeSO4:7H2O
Mirabilite	-8.61	-9.72	-1.11	Na2SO4:10H2O
O2(g)	-28.79	-31.69	-2.89	O2
Portlandite	-22.06	0.74	22.80	Ca(OH)2
Thenardite	-9.54	-9.72	-0.18	Na2SO4

Al(OH)3(a)	-12.86	-2.06	10.80	Al(OH)3
AlumK	-6.69	-11.86	-5.17	KAl(SO4)2:12H2O
Alunite	-14.52	-15.92	-1.40	KAl3(SO4)2(OH)6
Anhydrite	0.11	-4.25	-4.36	CaSO4
Basaluminite	-34.86	-12.16	22.70	Al4(OH)10SO4
Boehmite	-10.64	-2.06	8.58	AlOOH
Brucite	-16.57	0.27	16.84	Mg(OH)2
Diaspore	-8.94	-2.06	6.88	AlOOH
Epsomite	-1.54	-3.68	-2.14	MgSO4:7H2O
Fe(OH)2.7Cl.3	1.35	-1.69	-3.04	Fe(OH)2.7Cl0.3
Fe(OH)3(a)	-5.84	-0.95	4.89	Fe(OH)3
Fe3(OH)8	-22.37	-2.15	20.22	Fe3(OH)8
FeS(ppt)	-65.23	-69.15	-3.92	FeS
Gibbsite	-10.17	-2.06	8.11	Al(OH)3
Goethite	0.06	-0.94	-1.00	FeOOH
Greigite	-232.67	-277.70	-45.03	Fe3S4
Gypsum	0.32	-4.26	-4.58	CaSO4:2H2O
H2(g)	-24.68	-27.83	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
H2S(g)	-60.96	-61.96	-1.00	H2S
Halite	-5.52	-3.94	1.58	NaCl
Hematite	2.13	-1.88	-4.01	Fe2O3
Jarosite(ss)	-2.35	-12.18	-9.83	(K0.77Na0.03H0.2)Fe3(SO4)2(OH)6
Jarosite-K	-3.37	-12.58	-9.21	KFe3(SO4)2(OH)6
Jarosite-Na	-6.82	-12.10	-5.28	NaFe3(SO4)2(OH)6
JarositeH	-5.28	-10.67	-5.39	(H3O)Fe3(SO4)2(OH)6
Jurbanite	-2.74	-5.97	-3.23	AlOHSO4
Mackinawite	-64.50	-69.15	-4.65	FeS
Maghemite	-8.26	-1.88	6.39	Fe2O3
Magnetite	-5.87	-2.13	3.74	Fe3O4
Melanterite	-1.99	-4.20	-2.21	FeSO4:7H2O
Mirabilite	-5.74	-6.85	-1.11	Na2SO4:10H2O
O2(g)	-33.85	-36.74	-2.89	O2
Portlandite	-23.14	-0.34	22.80	Ca(OH)2
Pyrite	-94.89	-113.37	-18.48	FeS2
Sulfur	-42.12	-57.14	-15.03	S
Thenardite	-6.62	-6.80	-0.18	Na2SO4

Tosca and McLennan's SI's



Continuation



Issues with Results

In attempting to reproduce their results my

- pH was not as low
- Gypsum was not dehydrated completely

Modeling Mars Atmosphere

- According to Mahaffy et al., The atmosphere of Mars is roughly 600 pascals and 96% of those pascals are CO_2
- Converting pascals to atm for partial pressures

Mahaffy et al., 2013

Theory: Adding CO_2

- .0056 atm CO_2 added to the solution

Theory: Adding a Species to PHREEQ Database

- To observe precipitates

Here on Earth

- Closest brine the solution resembles is acid mine drainage because Fe- bearing minerals are more complex