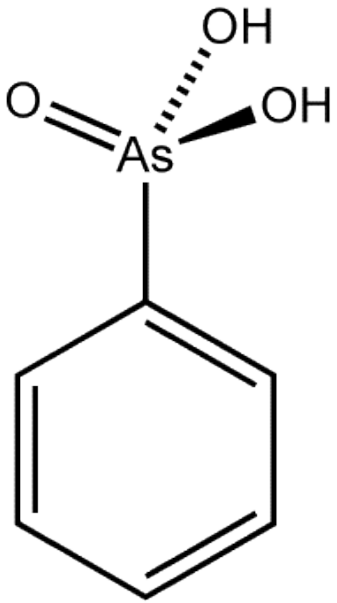
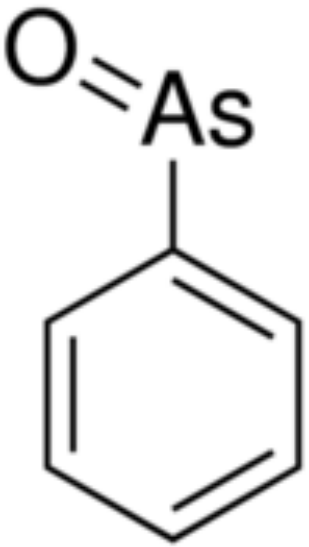
Modeling Arsenic Contamination in Groundwater near Dessau, Germany, due to Warfare Agents

Tyler Stadel
Geology 428/628
Dec 2, 2014

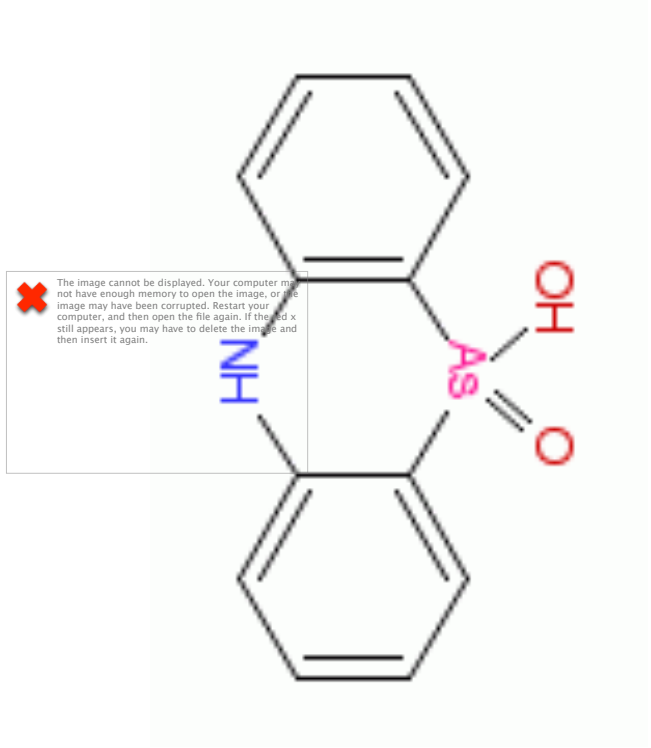
Arsenic as Warfare Agents



Phenylarsonic acid
(PAA)



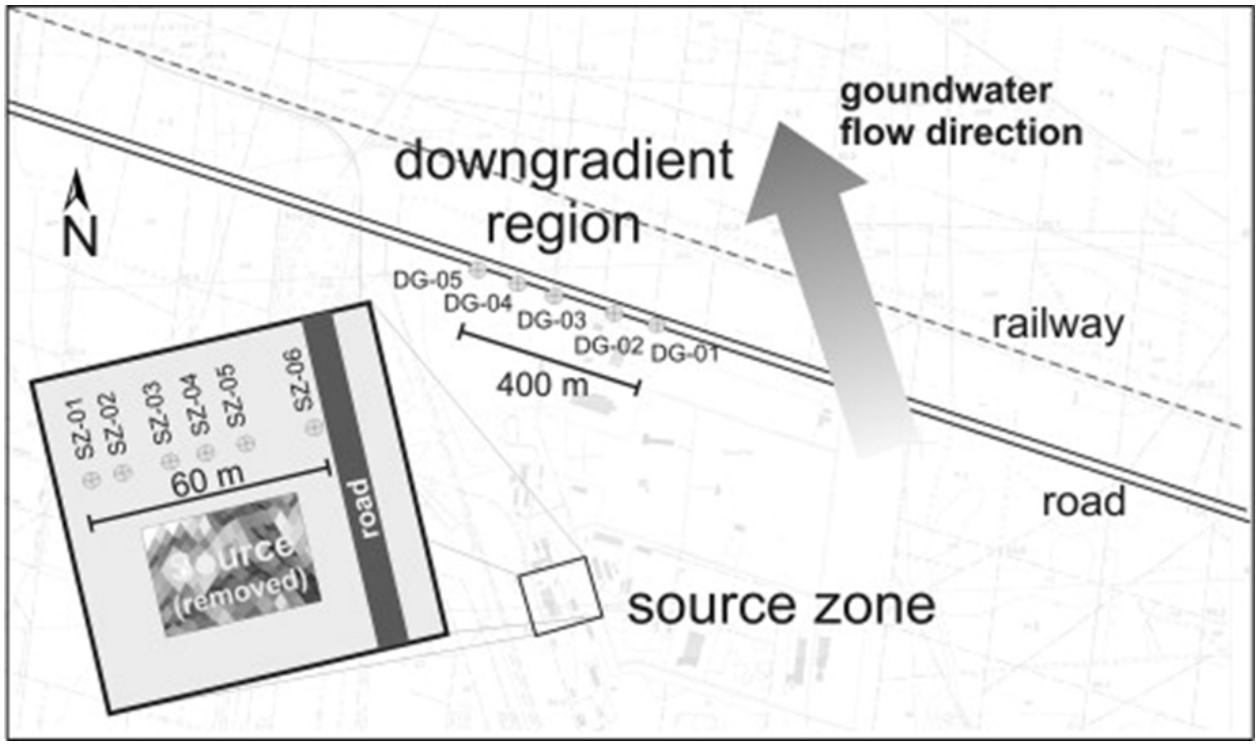
Phenylarsine oxide
(PAO)



Diphenylarsinic acid
(DPAA)

Location of Contamination

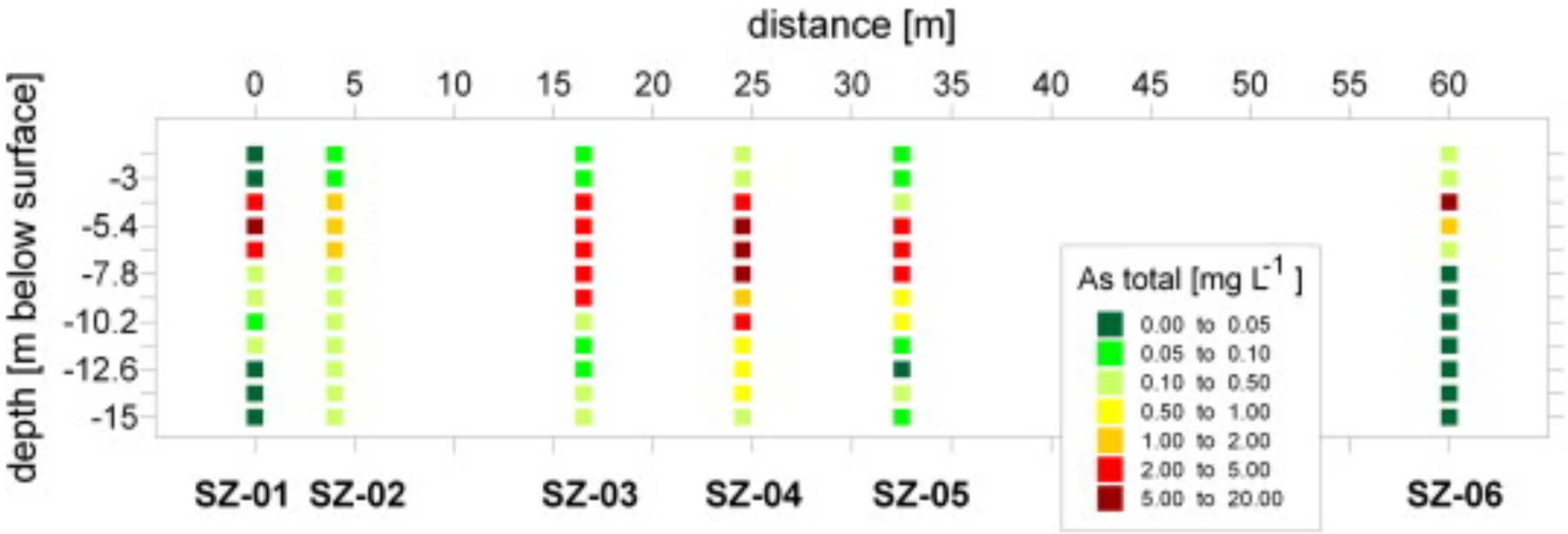
- Near Dessau, Saxony-Anhalt, Germany
- Contamination is due to old filling station of these arsenic warfare agents during WWI and WWII



- Source zone is the location of contamination
- Water was also sampled downgradient of the source zone. Around 1 km away.

Source Zone-02

Sampling depth	pH	Eh	O2	Conductivity	Cl-	NO3-	SO4 2-	NH4+	PO4 3-	Ca	Fe	As
2.0-3.0	7.1	34	1.34	331	10.2	2.53	59	0.06	<0.07	81.8	4.5	0.19
3.2-4.2	6.98	13	0.41	371	11.3	6.08	128	0.09	0.12	92.4	7.7	4.34
4.4-5.4	6.94	-248	0.28	429	13.6	8.35	193	0.11	0.82	98.3	5.1	10.7
5.6-6.6	8.76	-245	0.3	424	14.2	5.59	207	0.15	22.3	94	7.2	9.52
6.8-7.8	6.59	-243	0.23	407	13.1	3.21	189	0.59	<0.07	82.8	13.4	5.18
8.0-9.0	6.43	-237	< 0.2	437	19.5	1.95	219	0.68	<0.07	86.9	23.6	1.9
9.2-10.2	7.67	-217	< 0.2	442	22.3	<0.18	224	0.37	0.12	98.5	22.6	3.62
10.4-11.4	5.31	-184	< 0.2	463	25.1	<0.18	238	0.29	6.31	104.4	25.8	0.84
11.6-12.6	8.02	-194	< 0.2	418	19.5	<0.18	211	0.27	<0.07	87.2	35.5	0.61
12.8-13.8	6.52	-210	< 0.2	421	16.2	<0.18	231	0.29	<0.07	89.6	40.5	0.65
14.0-15.0	7.13	-181	<0.2	497	25.8	<0.18	258	0.27	0.36	91.4	39	0.34

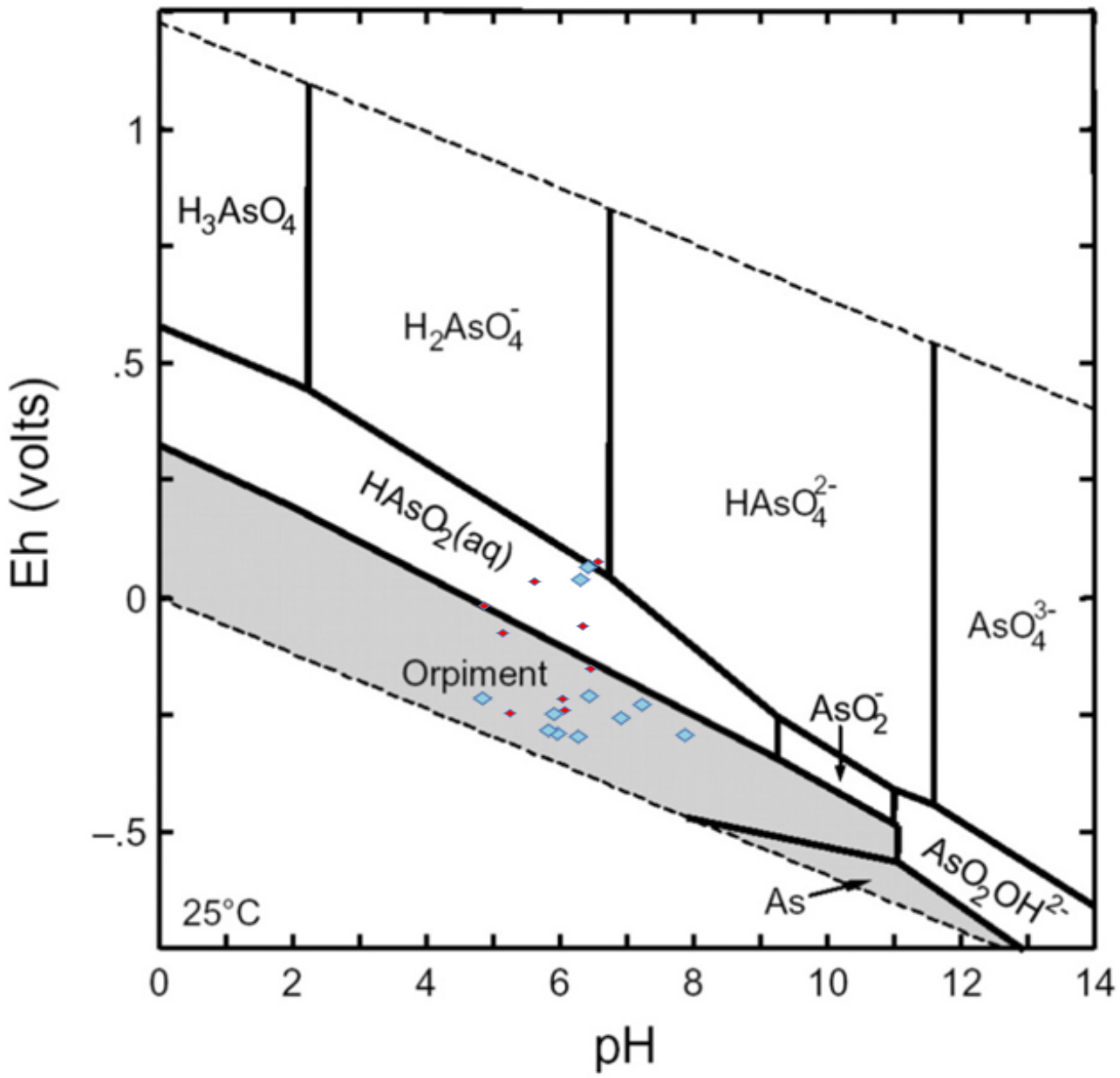

distance [m]
0
5
10
15
20
25
30
35
40
45
50
55
60
depth [m below surface]
-3
-5.4
-7.8
-10.2
-12.6
-15
SZ-01
SZ-02
SZ-03
SZ-04
SZ-05
SZ-06
As total [mg L-1]
0.00 to 0.05
0.05 to 0.10
0.10 to 0.50
0.50 to 1.00
1.00 to 2.00
2.00 to 5.00
5.00 to 20.00

Downgradient-04

Sampling	pH	Eh	Conductivity	O2	Cl-	NO3-	SO4 2-	NH4+	PO4 3-	Ca	Fe	As*
4.8-5.8	5.87	23	470	0.77	26.4	2.38	135	0.04	<0.07	66.8	3.2	26
6.0-7.0	5.07	9	509	<0.2	25.6	2.58	185	0.08	<0.07	69.3	4.1	89
7.2-8.2	5.37	-13	521	<0.2	24	0.74	196	0.08	<0.07	72.4	9.6	84
8.4-9.4	5.48	-69	508	<0.2	21.5	<0.18	194	0.34	0.1	68.5	18.4	50
10.8-11.8	6.35	-67	473	<0.2	12.8	<0.18	187	0.5	0.19	67.6	23.3	340
13.2-14.2	6.31	-59	449	<0.2	12.6	<0.18	172	0.49	0.12	63.3	28.6	300
16.8-17.8	6.63	-8	441	<0.2	12.7	<0.18	158	0.5	<0.07	71.1	24.9	88
20.4-21.4	6.75	-38	441	<0.2	11.7	<0.18	157	0.42	<0.07	71.3	18.3	98
25.0-24.0	6.87	37	444	<0.2	14.3	<0.18	150	0.52	<0.07	80.1	105	160

*Arsenic is in micrograms per Liter

- Significant drop in arsenic from the source zone to the downgradient.


Eh (volts)
1
.5
0
–.5
H_3AsO_4
$H_2AsO_4^-$
$HAsO_2(aq)$
$HAsO_4^{2-}$
AsO_4^{3-}
Orpiment
AsO_2^-
AsO_2OH^{2-}
As
25°C
0
2
4
6
8
10
12
14
pH

Orpiment

- An orange-yellow arsenic sulfide mineral
- As_2S_3
- It is naturally found in low temperature hydrothermal veins

- $HAsO_2$- Arsonite
- H_3AsO_4- Arsonic Acid
- AsO_2- Arsenic Dioxide
- AsO_4- Arsenate
- $HAsO_4$- Hydrogen Arsenate
- H_2AsO_4- Dihydrogen Arsenate

Hypothesis

- Hypothesized that Iron Oxides were precipitating out of solution
- Arsenic is adsorbed onto the precipitating Iron Oxide and is taken out of solution
- This would account for the significant drop in Arsenic from the source zone to the downgradient zone.

- Used inverse modeling to see what happened between the two areas.
- But in order to use this, I needed to know the composition of the aquifer, but this information was not given in the paper
- An average till composition was used:
  - Quartz
  - Calcite
  - Anorthite
  - Albite
  - Montmorillonite
  - Goethite

Source Zone-02

Sampling depth	pH	Eh	O2	Conductivity	Cl-	NO3-	SO4 2-	NH4+	PO4 3-	Ca	Fe	As
2.0-3.0	7.1	34	1.34	331	10.2	2.53	59	0.06	<0.07	81.8	4.5	0.19
3.2-4.2	6.98	13	0.41	371	11.3	6.08	128	0.09	0.12	92.4	7.7	4.34
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Downgradient-04

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16.8-17.8	6.63	-8	441	<0.2	12.7	<0.18	158	0.5	<0.07	71.1	24.9	88
20.4-21.4	6.75	-38	441	<0.2	11.7	<0.18	157	0.42	<0.07	71.3	18.3	98
25.0-24.0	6.87	37	444	<0.2	14.3	<0.18	150	0.52	<0.07	80.1	105	160

*Arsenic is in micrograms per Liter

```
EQUILIBRIUM_PHASES 1
   Quartz    0 10
   Anorthite 0 10
   Albite    0 10
   Calcite   0 10
   Montmorillonite-Ca 0 10
   Goethite  0 10
SOLUTION_SPREAD
   -units    mg/l
```

Number	pH	Ca	S(6)	Cl	As	N(5)	N(-3)	Fe	O(0)
1	7.445	91.625	146.75	13.325	6.1875	5.6375	0.1025	6.125	0.5825
2	5.436	69.5	172	25.33	0.0563	1.9	0.067	5.63	0.39

```
INVERSE_MODELING 1
   -solutions     1       2
   -uncertainty   1     1
   -phases
      Quartz
      Calcite
      Anorthite
      Albite
      Calcite
      Montmorillonite-Ca
      Goethite
   -range           1000
   -tolerance        1e-10
   -mineral_water     true
PHASES
END
```

----------Saturation indices----------

Phase	SI**	log IAP	log K(298 K, 1 atm)	
Anhydrite	-1.53	-5.89	-4.36	CaSO4
Arsenolite	-25.33	-26.71	-1.38	As2O3
As2O5(cr)	-27.85	-19.63	8.23	As2O5
As_native	-35.16	-47.69	-12.53	As
Ca3(AsO4)2:4w	-6.80	-25.70	-18.91	Ca3(AsO4)2:4H2O
Claudetite	-25.37	-26.71	-1.34	As2O3
Fe(OH)2.7Cl.3	8.16	5.12	-3.04	Fe(OH)2.7Cl0.3
Fe(OH)3(a)	3.50	8.39	4.89	Fe(OH)3
Fe3(OH)8	6.54	26.76	20.22	Fe3(OH)8
Goethite	9.39	8.39	-1.00	FeOOH
Gypsum	-1.31	-5.89	-4.58	CaSO4:2H2O
H2(g)	-22.89	-26.04	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Hematite	20.80	16.79	-4.01	Fe2O3
JarositeH	-5.30	-10.69	-5.39	(H3O)Fe3(SO4)2(OH)6
Maghemite	10.40	16.79	6.39	Fe2O3
Magnetite	23.02	26.76	3.74	Fe3O4
Melanterite	-5.76	-7.97	-2.21	FeSO4:7H2O
NH3(g)	-8.75	-6.98	1.77	NH3
O2(g)	-1.85	-4.74	-2.89	O2
Portlandite	-10.75	12.05	22.80	Ca(OH)2
Scorodite	-2.28	-22.53	-20.25	FeAsO4:2H2O

----------Saturation indices----------

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Fe(OH)3(a)	3.50	8.39	4.89	Fe(OH)3
Fe3(OH)8	6.54	26.76	20.22	Fe3(OH)8
Goethite	9.39	8.39	-1.00	FeOOH
Gypsum	-1.31	-5.89	-4.58	CaSO4:2H2O
H2(g)	-22.89	-26.04	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Hematite	20.80	16.79	-4.01	Fe2O3
JarositeH	-5.30	-10.69	-5.39	(H3O)Fe3(SO4)2(OH)6
Maghemite	10.40	16.79	6.39	Fe2O3
Magnetite	23.02	26.76	3.74	Fe3O4
Melanterite	-5.76	-7.97	-2.21	FeSO4:7H2O
NH3(g)	-8.75	-6.98	1.77	NH3
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   -units    mg/l
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INVERSE_MODELING 1
   -solutions     1       2
   -uncertainty   1     1
   -phases
      Quartz
      Calcite
      Anorthite
      Albite
      Calcite
      Montmorillonite-Ca
      Goethite
   -range           1000
   -tolerance       1e-10
   -mineral_water     true
PHASES
END
```

Equilibrium Phases

```
-----------------------------Description of solution-------

                                    pH  =  10.466
                                    pe  =   8.096
                        Activity of water  =   1.000
                           Ionic strength  =   7.236e-03
                         Mass of water (kg)  =   1.000e+00
                Total alkalinity (eq/kg)  =   1.858e-03
                      Total CO2 (mol/kg)  =   1.289e-04
                        Temperature (°C)  =  25.00
                 Electrical balance (eq)  =   6.604e-04
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   6.02
                                Iterations  =  58
                                   Total H  = 1.110118e+02
                                   Total O  = 5.551589e+01
```

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      Quartz
      Calcite
      Anorthite
      Albite
      Calcite
      Montmorillonite-Ca
      Goethite
   -range           1000
   -tolerance       1e-10
   -mineral_water     true
PHASES
END
```

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   -solutions     1       2
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   -phases
      Quartz
      Calcite
      Anorthite
      Albite
      Calcite
      Montmorillonite-Ca
      Goethite
   -range           1000
   -tolerance       1e-10
   -mineral_water     true
PHASES
END
```

Summary of Results

```
Summary of inverse modeling:

      Number of models found: 4
      Number of minimal models found: 1
      Number of infeasible sets of phases saved: 1
      Number of calls to cl1: 159
```

Solution 1:

	Input		Delta		Input+Delta
pH	7.445e+00	+	0.000e+00	=	7.445e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	1.316e-04	+	0.000e+00	=	1.316e-04
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	2.287e-03	+	-2.285e-03	=	1.476e-06
Fe(2)	1.891e-05	+	0.000e+00	=	1.891e-05
Fe(3)	9.079e-05	+	0.000e+00	=	9.079e-05
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
Na	0.000e+00	+	0.000e+00	=	0.000e+00
O(0)	3.642e-05	+	-2.580e-06	=	3.384e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00

Solution 2:

	Input		Delta		Input+Delta
pH	5.436e+00	+	0.000e+00	=	5.436e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-4.364e-06	+	4.364e-06	=	0.000e+00
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	1.735e-03	+	-1.735e-03	=	0.000e+00
Fe(2)	1.008e-04	+	-1.008e-04	=	0.000e+00
Fe(3)	1.098e-08	+	-1.098e-08	=	0.000e+00
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
Na	0.000e+00	+	0.000e+00	=	0.000e+00
O(0)	2.438e-05	+	0.000e+00	=	2.438e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00

Solution fractions:		Minimum	Maximum
Solution 1	1.000e+00	1.000e+00	1.000e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

	Input		Delta		Input+Delta
pH	5.436e+00	+	0.000e+00	=	5.436e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-4.364e-06	+	4.364e-06	=	0.000e+00
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	1.735e-03	+	-1.735e-03	=	0.000e+00
Fe(2)	1.008e-04	+	-1.008e-04	=	0.000e+00
Fe(3)	1.098e-08	+	-1.098e-08	=	0.000e+00
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
Na	0.000e+00	+	0.000e+00	=	0.000e+00
O(0)	2.438e-05	+	0.000e+00	=	2.438e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00

Solution fractions:		Minimum	Maximum
Solution 1	1.000e+00	1.000e+00	1.000e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

Phase mole transfers:		Minimum	Maximum	
Quartz	-1.978e-06	-1.763e-04	0.000e+00	SiO2
Anorthite	-1.720e-06	-1.533e-04	0.000e+00	CaAl2Si2O8
Montmorillonite	1.476e-06	0.000e+00	1.316e-04	Ca0.165Al2.33Si3.67O10(OH)2
Goethite	-1.097e-04	-2.194e-04	0.000e+00	FeOOH

Redox mole transfers:	
Fe(3)	-1.891e-05
O(0)	9.455e-06

Sum of residuals (epsilons in documentation):	5.070e+00
Sum of delta/uncertainty limit:	5.070e+00
Maximum fractional error in element concentration:	1.000e+00

	Input		Delta		Input+Delta
pH	5.436e+00	+	0.000e+00	=	5.436e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-4.364e-06	+	4.364e-06	=	0.000e+00
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	1.735e-03	+	-1.735e-03	=	0.000e+00
Fe(2)	1.008e-04	+	-1.008e-04	=	0.000e+00
Fe(3)	1.098e-08	+	-1.098e-08	=	0.000e+00
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
Na	0.000e+00	+	0.000e+00	=	0.000e+00
O(0)	2.438e-05	+	0.000e+00	=	2.438e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00

Solution fractions:		Minimum	Maximum
Solution 1	1.000e+00	1.000e+00	1.000e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

Phase mole transfers:		Minimum	Maximum	
Quartz	-1.978e-06	-1.763e-04	0.000e+00	SiO2
Anorthite	-1.720e-06	-1.533e-04	0.000e+00	CaAl2Si2O8
Montmorillonite	1.476e-06	0.000e+00	1.316e-04	Ca0.165Al2.33Si3.67O10(OH)2
Goethite	-1.097e-04	-2.194e-04	0.000e+00	FeOOH

Redox mole transfers:

Fe(3)	-1.891e-05
O(0)	9.455e-06

Sum of residuals (epsilons in documentation):	5.070e+00
Sum of delta/uncertainty limit:	5.070e+00
Maximum fractional error in element concentration:	1.000e+00

	Input		Delta		Input+Delta
pH	5.436e+00	+	0.000e+00	=	5.436e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-4.364e-06	+	4.364e-06	=	0.000e+00
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	1.735e-03	+	-1.735e-03	=	0.000e+00
Fe(2)	1.008e-04	+	-1.008e-04	=	0.000e+00
Fe(3)	1.098e-08	+	-1.098e-08	=	0.000e+00
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
Na	0.000e+00	+	0.000e+00	=	0.000e+00
O(0)	2.438e-05	+	0.000e+00	=	2.438e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00

Solution fractions:		Minimum	Maximum
Solution 1	1.000e+00	1.000e+00	1.000e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

Phase mole transfers:		Minimum	Maximum	
Quartz	-1.978e-06	-1.763e-04	0.000e+00	SiO2
Anorthite	-1.720e-06	-1.533e-04	0.000e+00	CaAl2Si2O8
Montmorillonite	1.476e-06	0.000e+00	1.316e-04	Ca0.165Al2.33Si3.67O10(OH)2
Goethite	-1.097e-04	-2.194e-04	0.000e+00	FeOOH

Redox mole transfers:	
Fe(3)	-1.891e-05
O(0)	9.455e-06

Sum of residuals (epsilons in documentation):	5.070e+00
Sum of delta/uncertainty limit:	5.070e+00
Maximum fractional error in element concentration:	1.000e+00

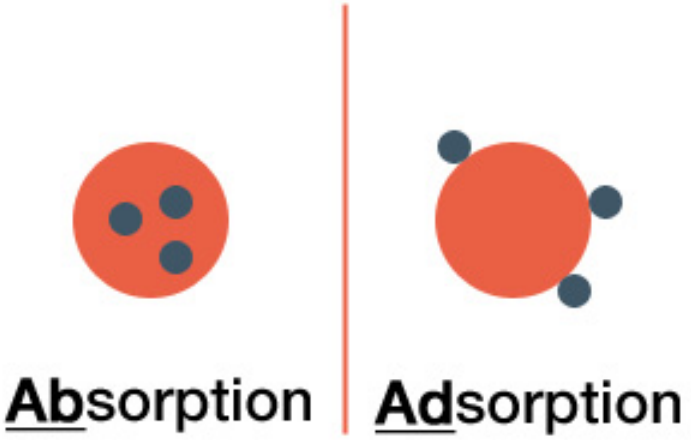
Goethite

- 2 of the 4 possible solutions had Goethite precipitating out of solution at

1.097×10^{-4} moles of Goethite per unit of solution

Adsorption

- the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface.



Reference

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