Fe isotope fractionation between aqueous Fe(II) and Fe(III)

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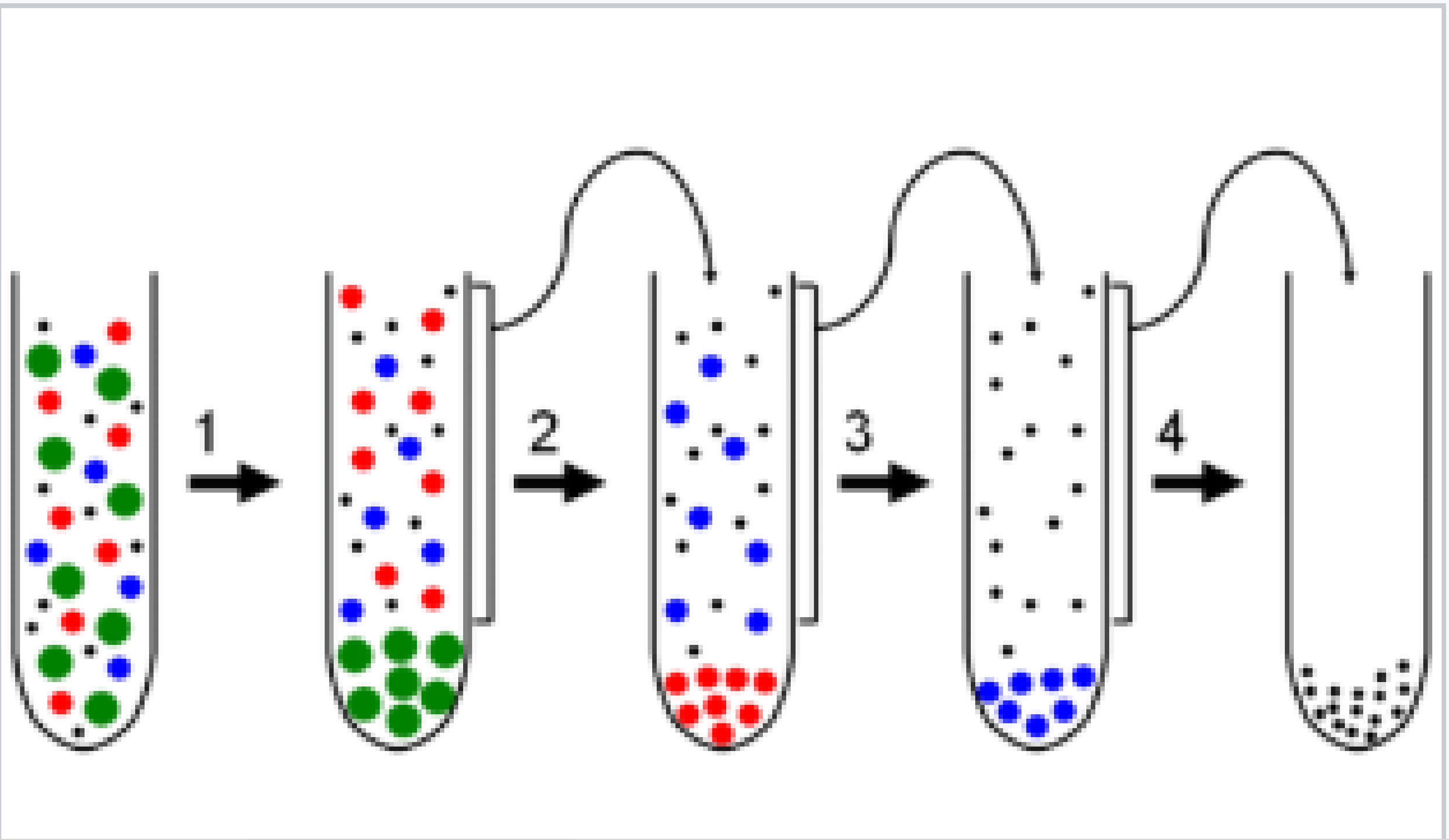
GEOL 428

What is Fractionation

Process in which Iron (Fe) is separated or partitioned into different forms or reservoirs based on its physical, chemical, or isotopic properties.
Three main categories of Fractionation

- **Chemical: Break into two oxidation states Fe(II) (ferrous) and Fe(III) (ferric)**
- Isotopic: Break into four stable isotopes ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe
- Phase Fractionation: Break into metal and silicate, or between liquid and solid phases

Examples:
Differential centrifugation, Blood fractionation into plasma, buffy coat and blood cells



Fractionation of the stable isotopes of Fe occurs through a combination of differences in **bonding environments** and **separation** of mobile Fe components.

Iron cycling (transition between **Fe (II)** and **Fe (III)**) at redox boundaries (change in their oxidation number occurs)

- Majority of Fe isotope variations are produced

Why is Fe Fractionation Important

Iron Isotope geochemistry is used to track the geochemical cycling of Fe.

Bacteria can cause Fe reduction, suggests that Fe isotope geochemistry may be involved in problems such as the origin and evolution of life on Earth or other planetary bodies (potential signature). Strong correlation in producing isotope variations.

- Fe^{3+}-reducing bacteria
- Fe sulfides formed by bacterial sulfate reduction
- Microbial fingerprints appear in ancient rocks up to 2.9 Ga, and may be as far back as 3.8 Ga.

Fe (II) and (III) as a Redox Pair

Redox Pair: Two forms of the same element that differ by one or more electrons:

- Oxidation = loss of electrons
- Reduction = gain of electrons

For Iron:

- $Fe^{3+} \rightarrow Fe^{2+}$ is a reduction (gains an electron)
- $Fe^{2+} \rightarrow Fe^{3+}$ is an oxidation (loses an electron)

The redox reaction:

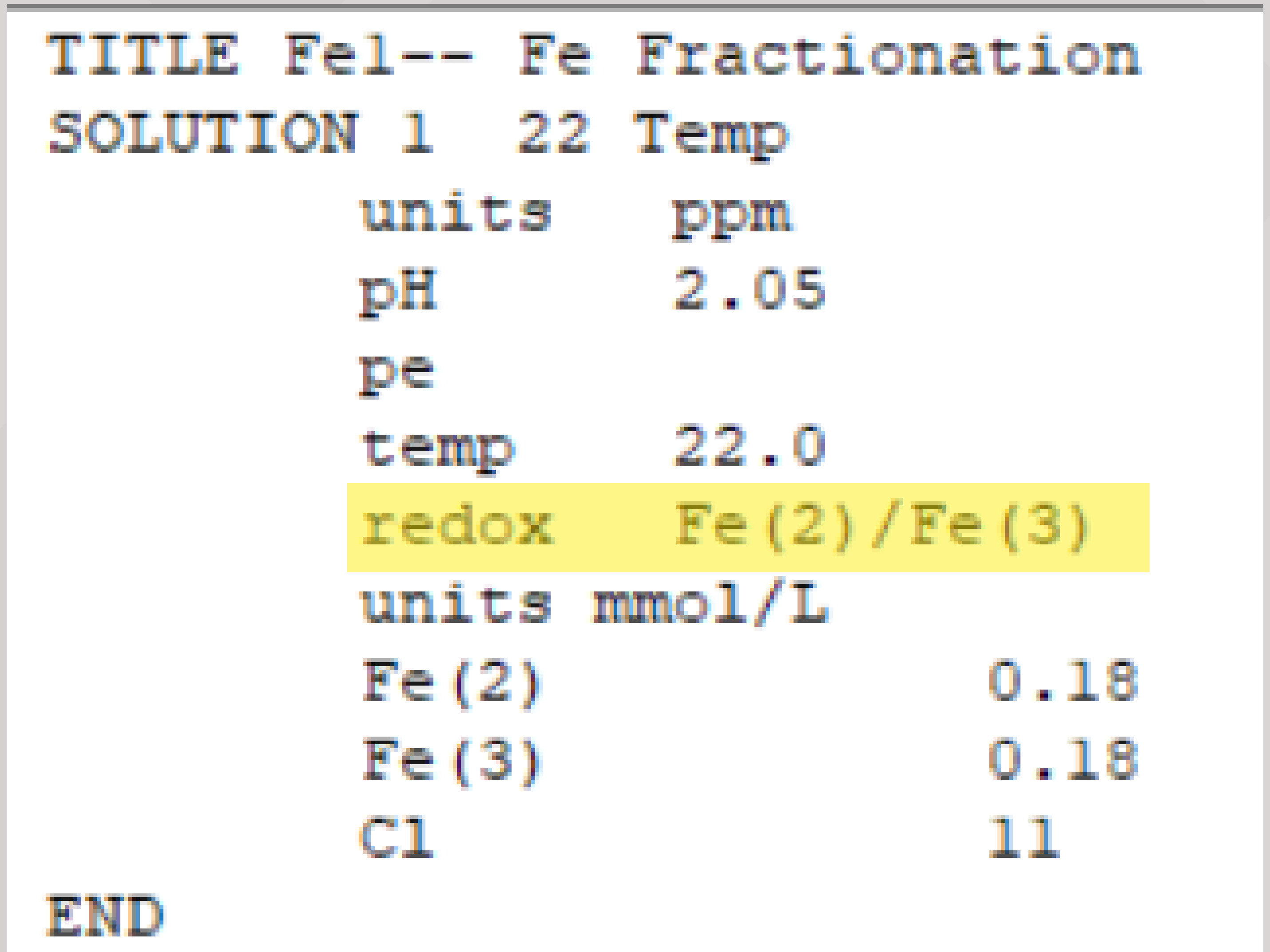
$$\mathrm{Fe\ 3+} + e- \rightleftharpoons \mathrm{Fe\ 2+}$$

Modeling in PHREEQ

Define as Redox Couple to explain the rate of

oxidation/reduction, standardized results

Only one redox pair at a time



```
TITLE Fe1-- Fe Fractionation
SOLUTION 1  22 Temp
        units   ppm
        pH      2.05
        pe
        temp    22.0
        redox   Fe(2)/Fe(3)
        units mmol/L
        Fe(2)           0.18
        Fe(3)           0.18
        Cl              11
END
```

PHREEQ Input - Resimulation of Welch et al. 2002

Input Data

- Temperatures at 0 and 22 degrees Celsius
- Ranges of 0-111 Cl (mmol/L)
  - Substitution into different isotopes FeCl +, FeCl +2, and FeCl2 +
- Ranges of 0.072-0.18 Fe (II) and Fe (III) (mmol/L)
  - Changes in oxidation/reduction
- pH of samples was set to 2.05 pH
  - Welch et al. chose this specification based on a previous paper Johnson et al. (2001)
    - Where largest isotopic fractionations appear in inorganic or biologic systems

PHREEQ Output – Resimulation of Welch et al. 2002

PHREEQ Molality converted to Fe(II) and Fe(III) %

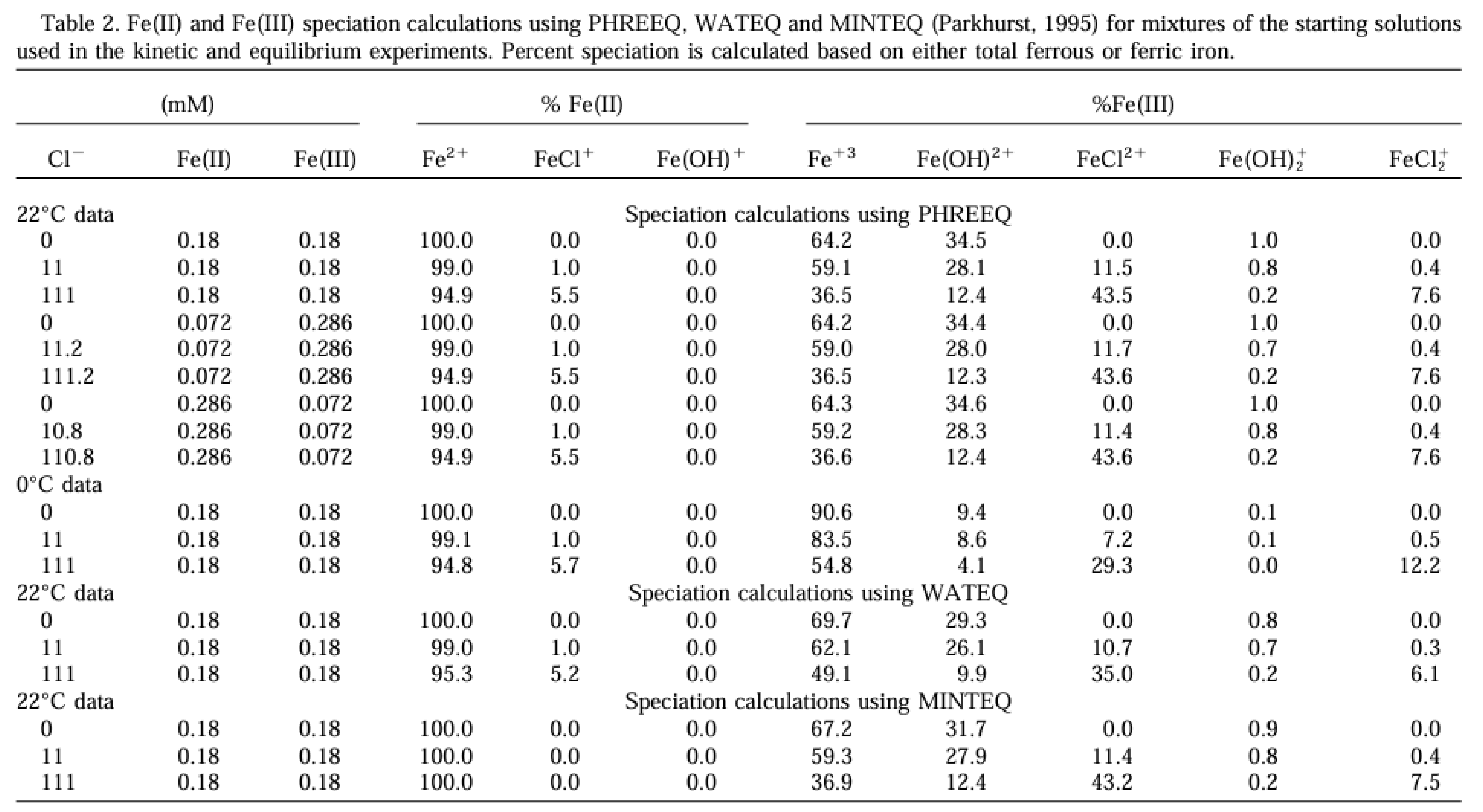


Table 2. Fe(II) and Fe(III) speciation calculations using PHREEQ, WATEQ and MINTEQ (Parkhurst, 1995) for mixtures of the starting solutions used in the kinetic and equilibrium experiments. Percent speciation is calculated based on either total ferrous or ferric iron.

(mM)			% Fe(II)			%Fe(III)				
Cl^-	Fe(II)	Fe(III)	Fe^{2+}	$FeCl^+$	$Fe(OH)^+$	Fe^{+3}	$Fe(OH)^{2+}$	$FeCl^{2+}$	$Fe(OH)_2^+$	$FeCl_2^+$
22°C data					Speciation calculations using PHREEQ					
0	0.18	0.18	100.0	0.0	0.0	64.2	34.5	0.0	1.0	0.0
11	0.18	0.18	99.0	1.0	0.0	59.1	28.1	11.5	0.8	0.4
111	0.18	0.18	94.9	5.5	0.0	36.5	12.4	43.5	0.2	7.6
0	0.072	0.286	100.0	0.0	0.0	64.2	34.4	0.0	1.0	0.0
11.2	0.072	0.286	99.0	1.0	0.0	59.0	28.0	11.7	0.7	0.4
111.2	0.072	0.286	94.9	5.5	0.0	36.5	12.3	43.6	0.2	7.6
0	0.286	0.072	100.0	0.0	0.0	64.3	34.6	0.0	1.0	0.0
10.8	0.286	0.072	99.0	1.0	0.0	59.2	28.3	11.4	0.8	0.4
110.8	0.286	0.072	94.9	5.5	0.0	36.6	12.4	43.6	0.2	7.6
0°C data										
0	0.18	0.18	100.0	0.0	0.0	90.6	9.4	0.0	0.1	0.0
11	0.18	0.18	99.1	1.0	0.0	83.5	8.6	7.2	0.1	0.5
111	0.18	0.18	94.8	5.7	0.0	54.8	4.1	29.3	0.0	12.2
22°C data					Speciation calculations using WATEQ					
0	0.18	0.18	100.0	0.0	0.0	69.7	29.3	0.0	0.8	0.0
11	0.18	0.18	99.0	1.0	0.0	62.1	26.1	10.7	0.7	0.3
111	0.18	0.18	95.3	5.2	0.0	49.1	9.9	35.0	0.2	6.1
22°C data					Speciation calculations using MINTEQ					
0	0.18	0.18	100.0	0.0	0.0	67.2	31.7	0.0	0.9	0.0
11	0.18	0.18	100.0	0.0	0.0	59.3	27.9	11.4	0.8	0.4
111	0.18	0.18	100.0	0.0	0.0	36.9	12.4	43.2	0.2	7.5

Welch et al. 2002

PHREEQ Output – My Calculations

In PHREEQ Modeling,

I found relatively similar

results for molarity and

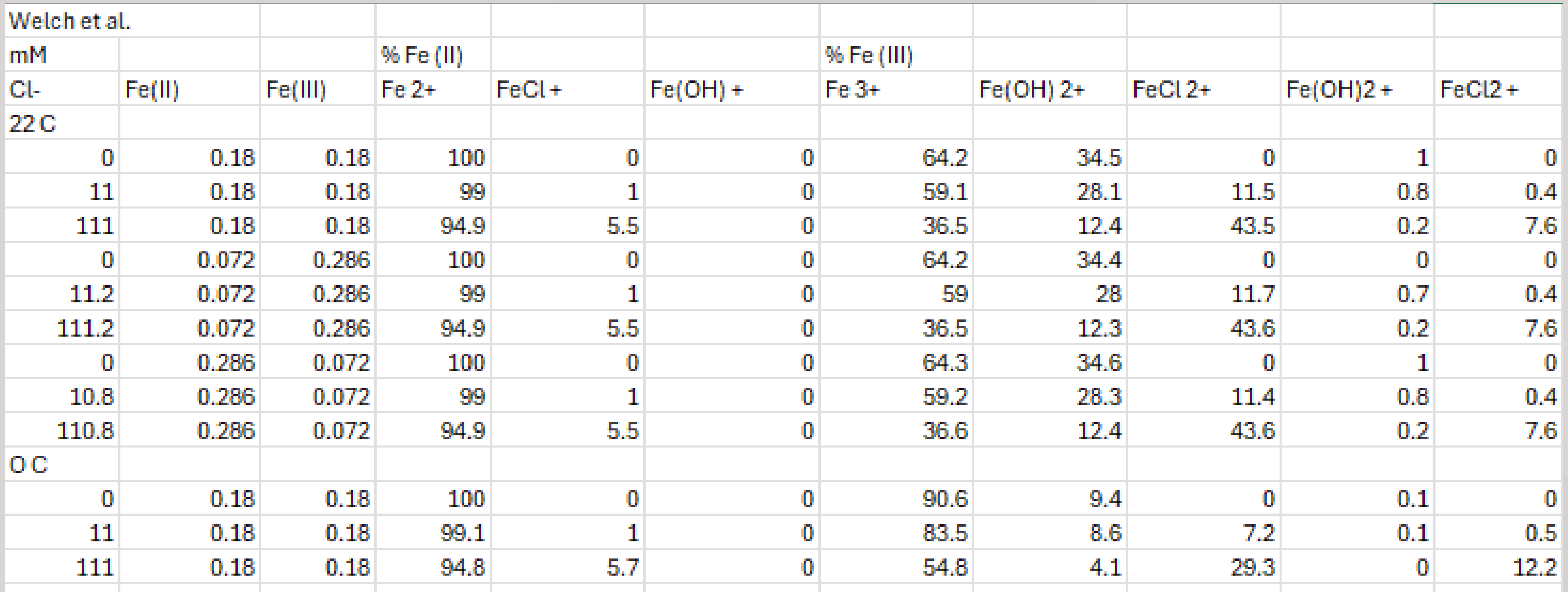
subsequent mineral

percentages.

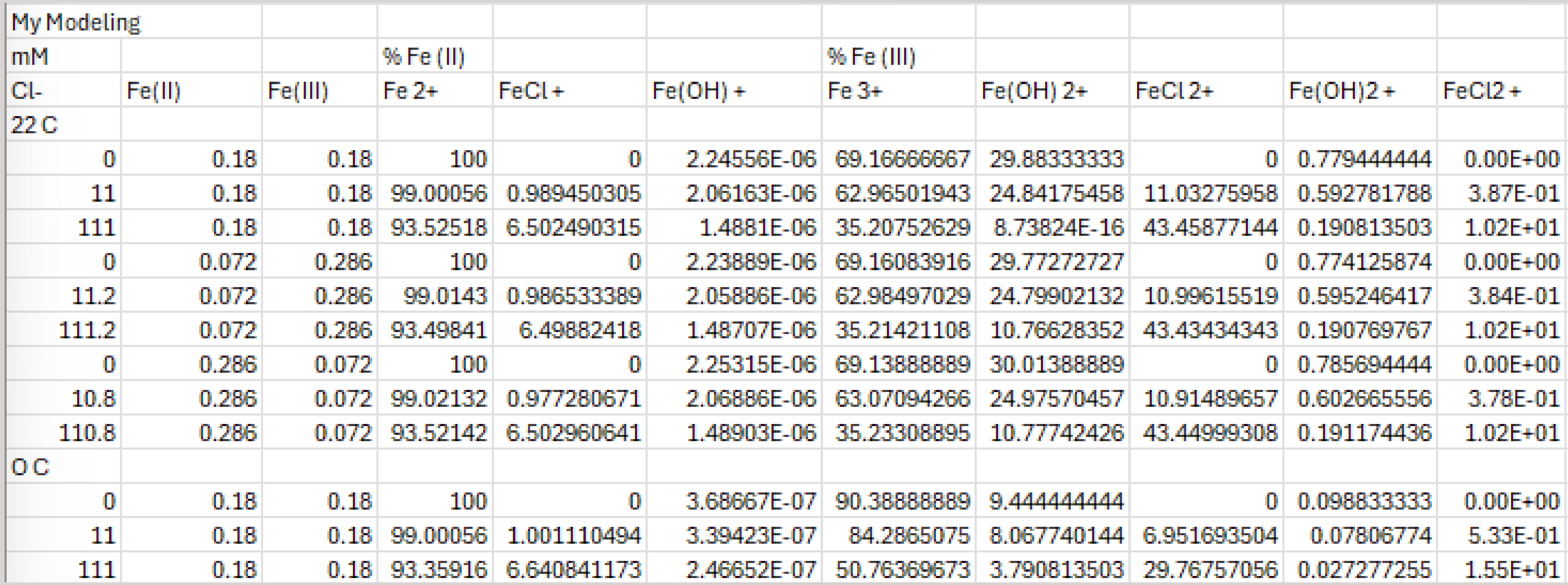
Hematite and Goethite

Precipitate out of system

- Slight decrease as Cl abundance increases



Welch et al.										
mM			% Fe (II)			% Fe (III)				
Cl-	Fe(II)	Fe(III)	Fe 2+	FeCl +	Fe(OH) +	Fe 3+	Fe(OH) 2+	FeCl 2+	Fe(OH)2 +	FeCl2 +
22 C										
0	0.18	0.18	100	0	0	64.2	34.5	0	1	0
11	0.18	0.18	99	1	0	59.1	28.1	11.5	0.8	0.4
111	0.18	0.18	94.9	5.5	0	36.5	12.4	43.5	0.2	7.6
0	0.072	0.286	100	0	0	64.2	34.4	0	0	0
11.2	0.072	0.286	99	1	0	59	28	11.7	0.7	0.4
111.2	0.072	0.286	94.9	5.5	0	36.5	12.3	43.6	0.2	7.6
0	0.286	0.072	100	0	0	64.3	34.6	0	1	0
10.8	0.286	0.072	99	1	0	59.2	28.3	11.4	0.8	0.4
110.8	0.286	0.072	94.9	5.5	0	36.6	12.4	43.6	0.2	7.6
0 C										
0	0.18	0.18	100	0	0	90.6	9.4	0	0.1	0
11	0.18	0.18	99.1	1	0	83.5	8.6	7.2	0.1	0.5
111	0.18	0.18	94.8	5.7	0	54.8	4.1	29.3	0	12.2



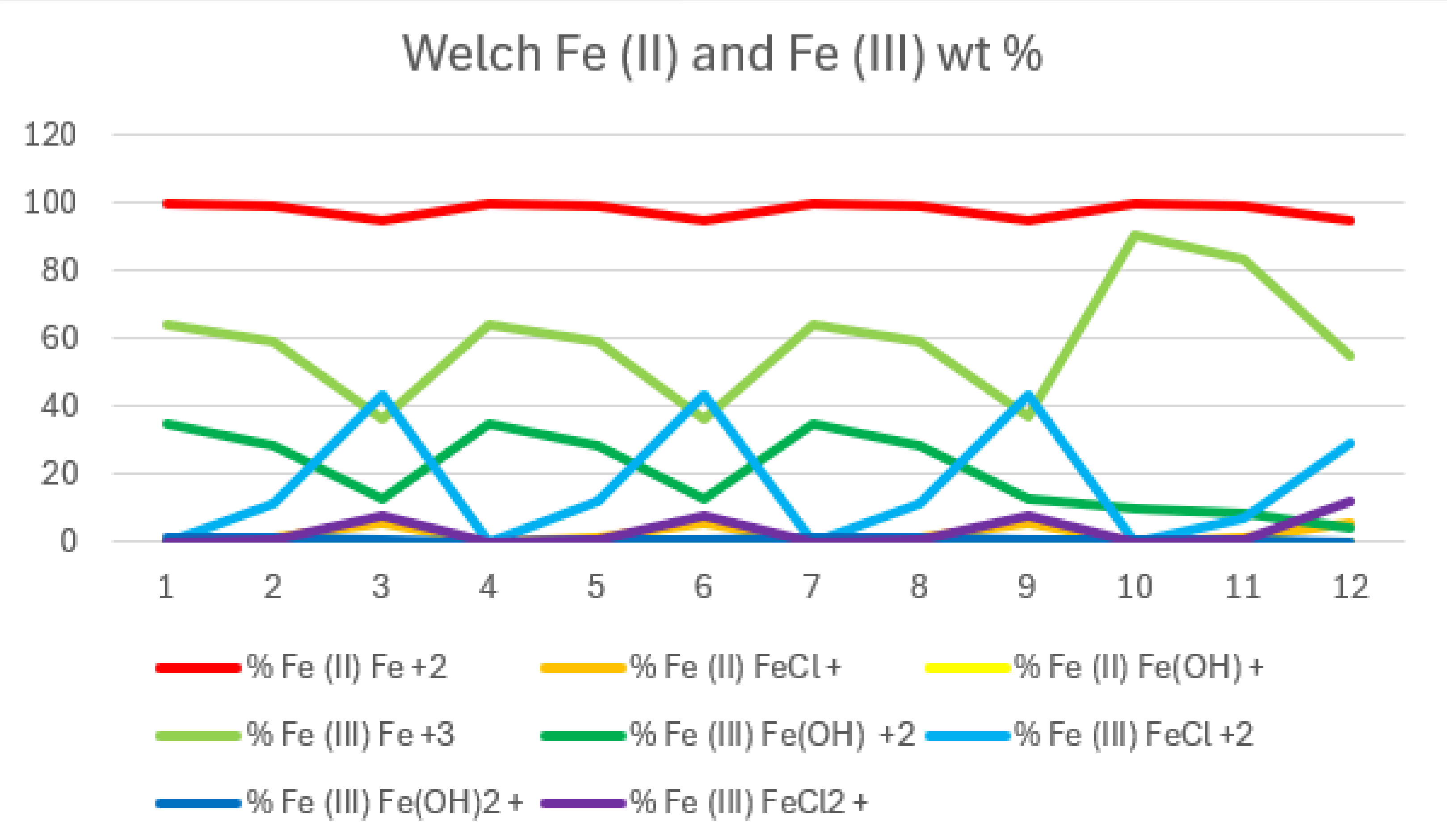
My Modeling										
mM			% Fe (II)			% Fe (III)				
Cl-	Fe(II)	Fe(III)	Fe 2+	FeCl +	Fe(OH) +	Fe 3+	Fe(OH) 2+	FeCl 2+	Fe(OH)2 +	FeCl2 +
22 C										
0	0.18	0.18	100	0	2.24556E-06	69.16666667	29.88333333	0	0.779444444	0.00E+00
11	0.18	0.18	99.00056	0.989450305	2.06163E-06	62.96501943	24.84175458	11.03275958	0.592781788	3.87E-01
111	0.18	0.18	93.52518	6.502490315	1.4881E-06	35.20752629	8.73824E-16	43.45877144	0.190813503	1.02E+01
0	0.072	0.286	100	0	2.23889E-06	69.16083916	29.77272727	0	0.774125874	0.00E+00
11.2	0.072	0.286	99.0143	0.986533389	2.05886E-06	62.98497029	24.79902132	10.99615519	0.595246417	3.84E-01
111.2	0.072	0.286	93.49841	6.49882418	1.48707E-06	35.21421108	10.76628352	43.43434343	0.190769767	1.02E+01
0	0.286	0.072	100	0	2.25315E-06	69.13888889	30.01388889	0	0.785694444	0.00E+00
10.8	0.286	0.072	99.02132	0.977280671	2.06886E-06	63.07094266	24.97570457	10.91489657	0.602665556	3.78E-01
110.8	0.286	0.072	93.52142	6.502960641	1.48903E-06	35.23308895	10.77742426	43.44999308	0.191174436	1.02E+01
0 C										
0	0.18	0.18	100	0	3.68667E-07	90.38888889	9.444444444	0	0.098833333	0.00E+00
11	0.18	0.18	99.00056	1.001110494	3.39423E-07	84.2865075	8.067740144	6.951693504	0.07806774	5.33E-01
111	0.18	0.18	93.35916	6.640841173	2.46652E-07	50.76369673	3.790813503	29.76757056	0.027277255	1.55E+01

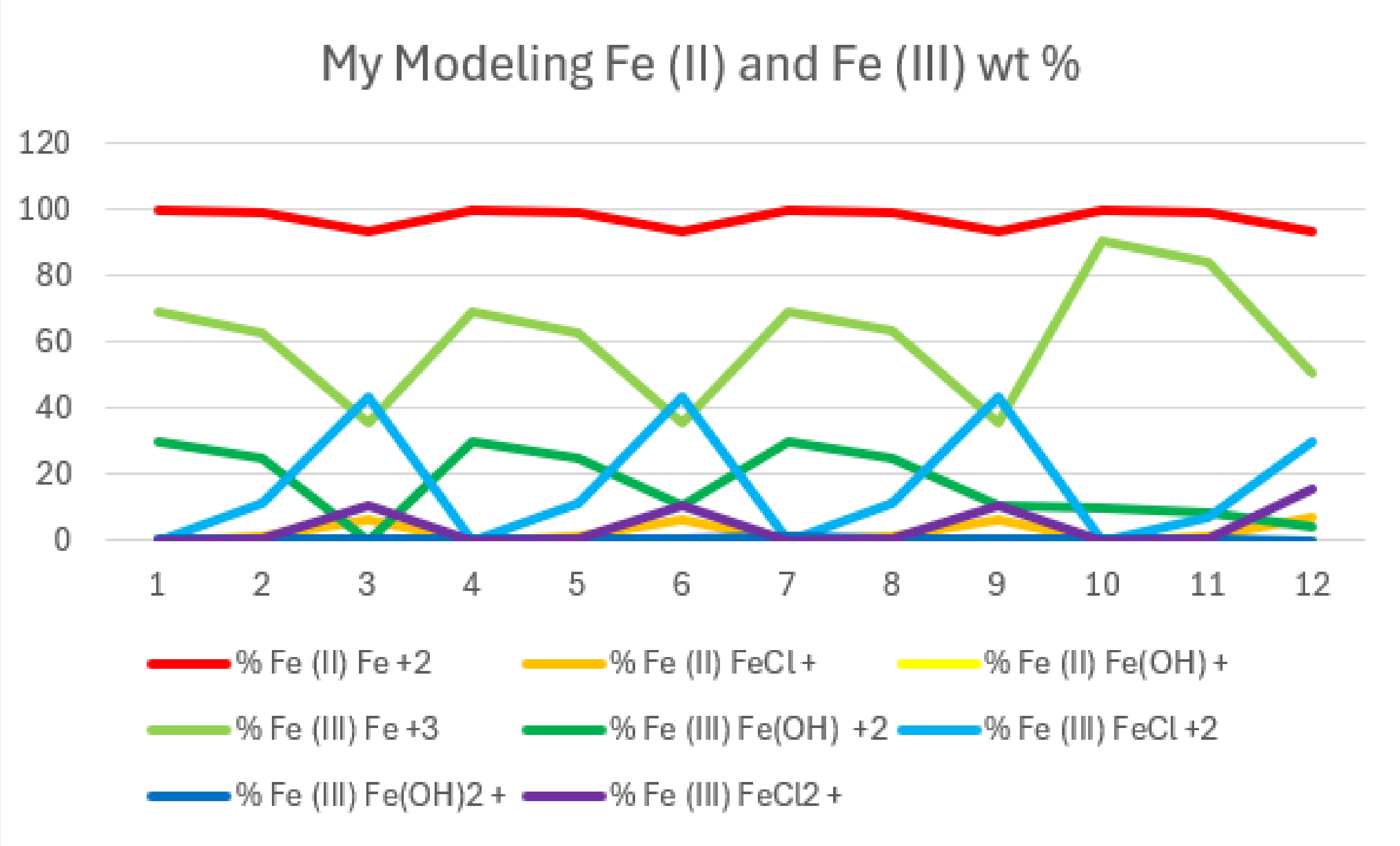
PHREEQ Output – My Calculations

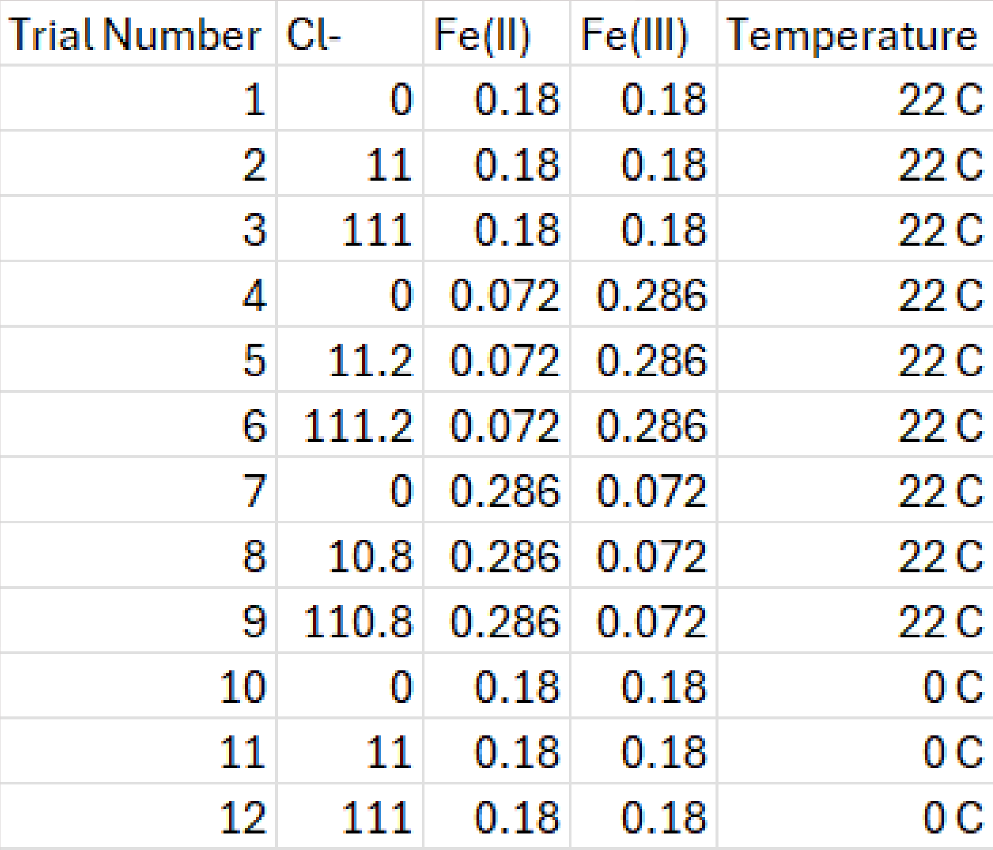
As we can see, I was able to essentially replicate the modeling of Welch to allow for further understanding of changes in Cl vs Temperature

Temperature does not effect wt%s as much

- The last 3 trials are all set to 0 C compared to 22 C of the previous 9 trials
- We see Cl abundance far greater effects Fe wt%s







Trial Number	Cl-	Fe(II)	Fe(III)	Temperature
1	0	0.18	0.18	22 C
2	11	0.18	0.18	22 C
3	111	0.18	0.18	22 C
4	0	0.072	0.286	22 C
5	11.2	0.072	0.286	22 C
6	111.2	0.072	0.286	22 C
7	0	0.286	0.072	22 C
8	10.8	0.286	0.072	22 C
9	110.8	0.286	0.072	22 C
10	0	0.18	0.18	0 C
11	11	0.18	0.18	0 C
12	111	0.18	0.18	0 C

My Questions

Welch specified redox of Fe (II) and Fe (III).

How would results change if it wasn't specified?

- Is redox important to note?
- What changes occur?

How would a different element effect Fe (II) and Fe (III) wt %?

I chose Sulfur S +6 as it is a common element to group with Fe (II) and Fe (III).

PHREEQ Input – Non redox couple

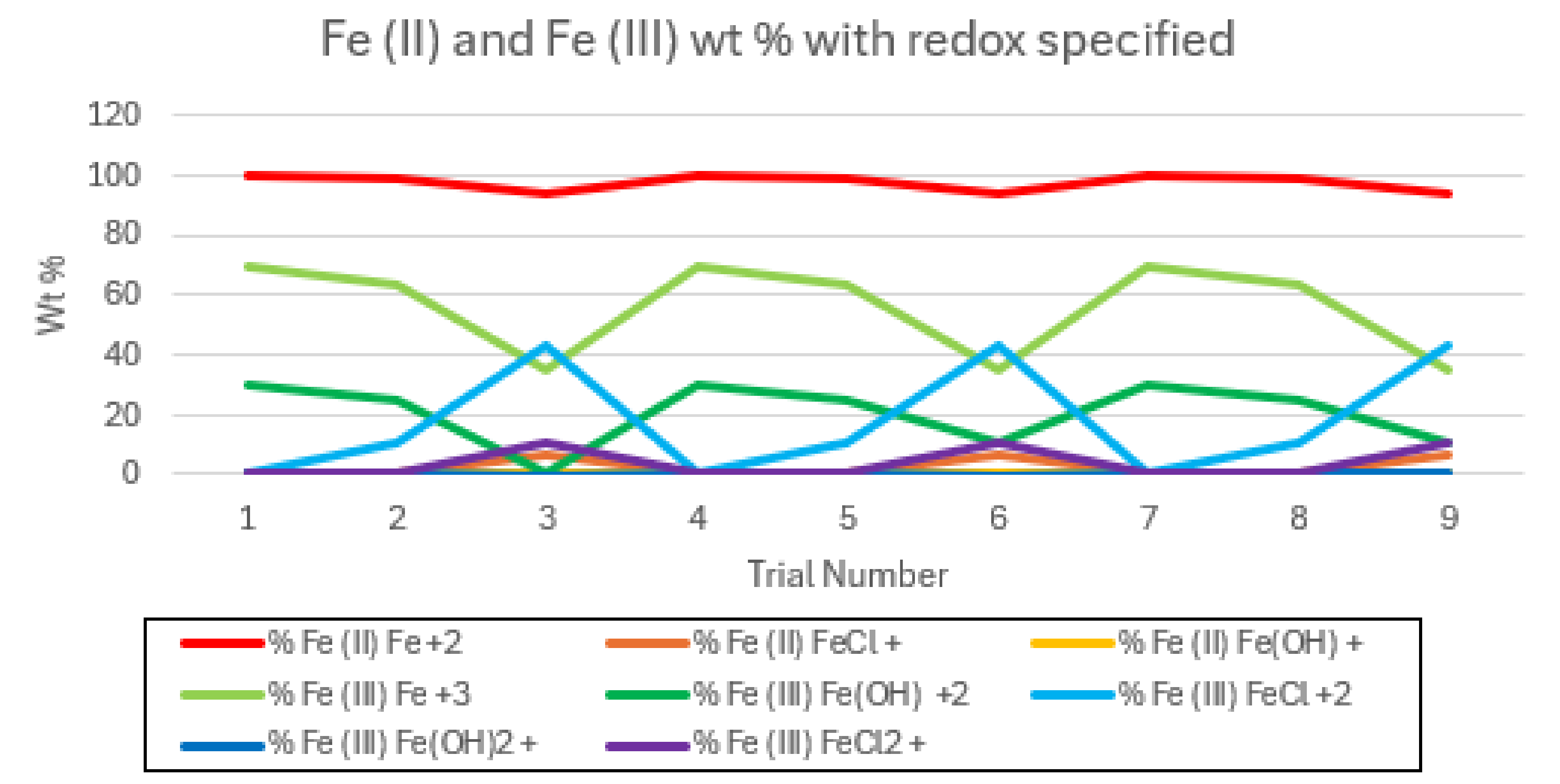
Input Data

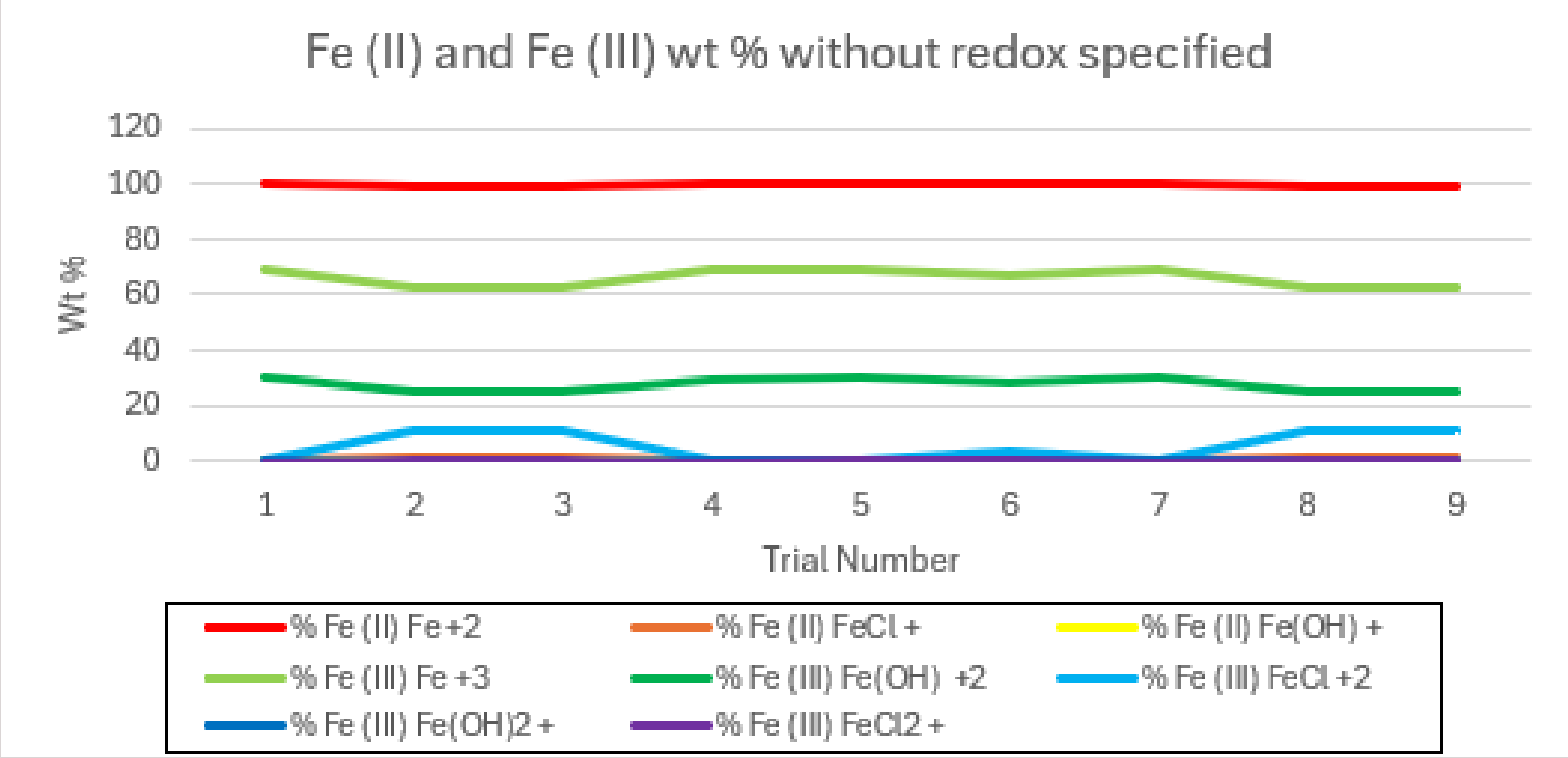
- Temperatures at 22 degrees Celsius
    - Since temperature was previously determined to not have a large impact
- Ranges of 0-111 Cl (mmol/L)
    - Substitution into different isotopes FeCl +, FeCl +2, and FeCl2 +
- Ranges of 0.072-0.18 Fe (II) and Fe (III) (mmol/L)
    - Changes in oxidation/reduction
    - **Not defining Fe (II) and Fe (III) as redox couple**
- pH of Samples was set to 2.05 pH

PHREEQ Onput – Non redox couple

With Redox specified, we see more drastic changes as Cl addition increases

Without redox specified, we do not see the wt% be as effected





Without redox specified, PHREEQ has inaccurate molality and SI outputs, leading to incorrect wt%s and mineral precipitations.

PHREEQ Input – Adding S to system

Input Data

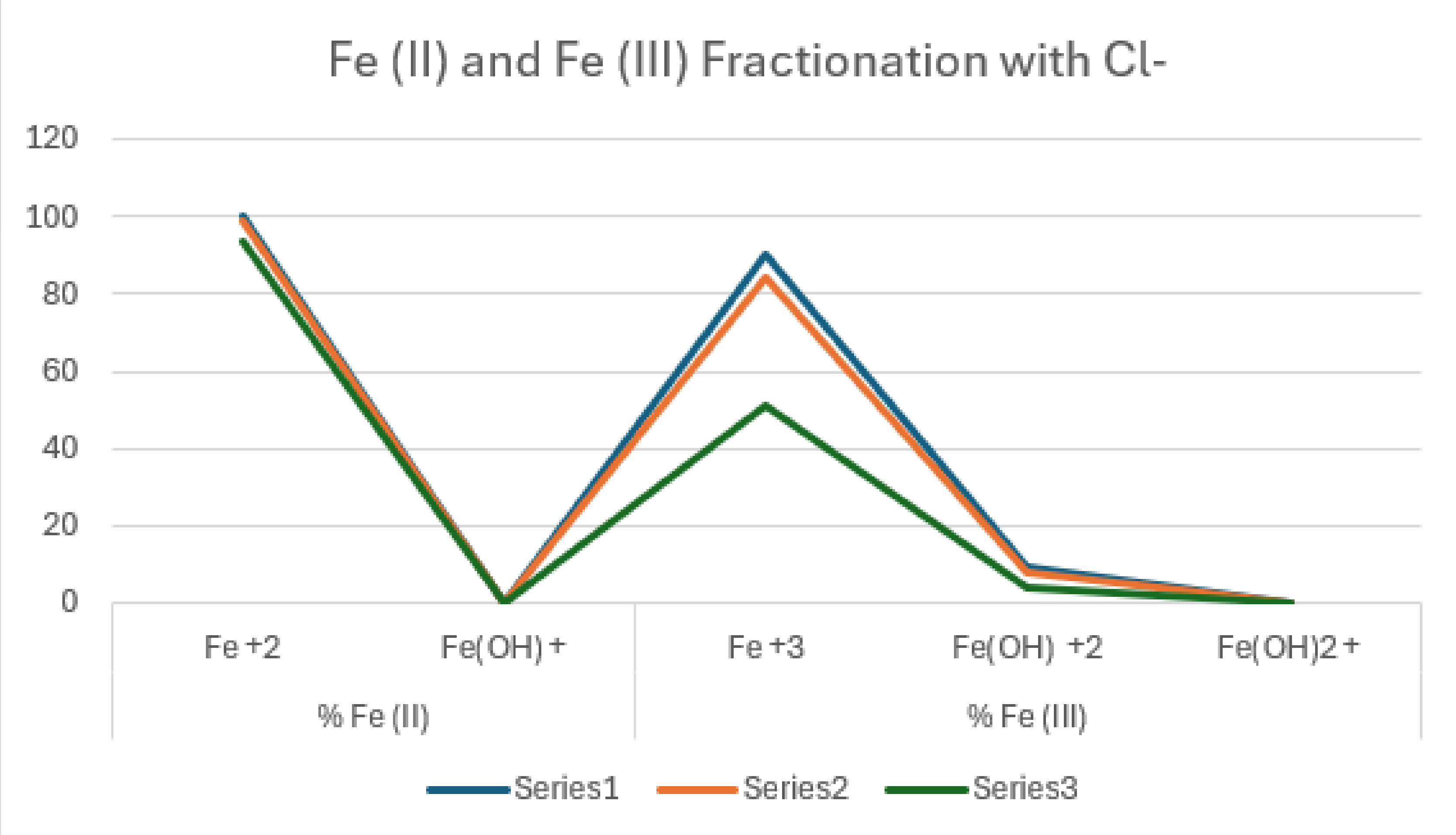
- Temperatures at 0 degrees Celsius
  - Since temperature was previously determined to not have a large impact
- Ranges of 0-111 S (mmol/L)
  - Substitution into different isotopes **FeCl +, FeCl +2, and FeCl2 +**
- Ranges of 0.18 Fe (II) and Fe (III) (mmol/L)
  - Same change in oxidation/reduction
  - Fe (II) and Fe (III) as redox couple
- pH of Samples was set to 2.05 pH

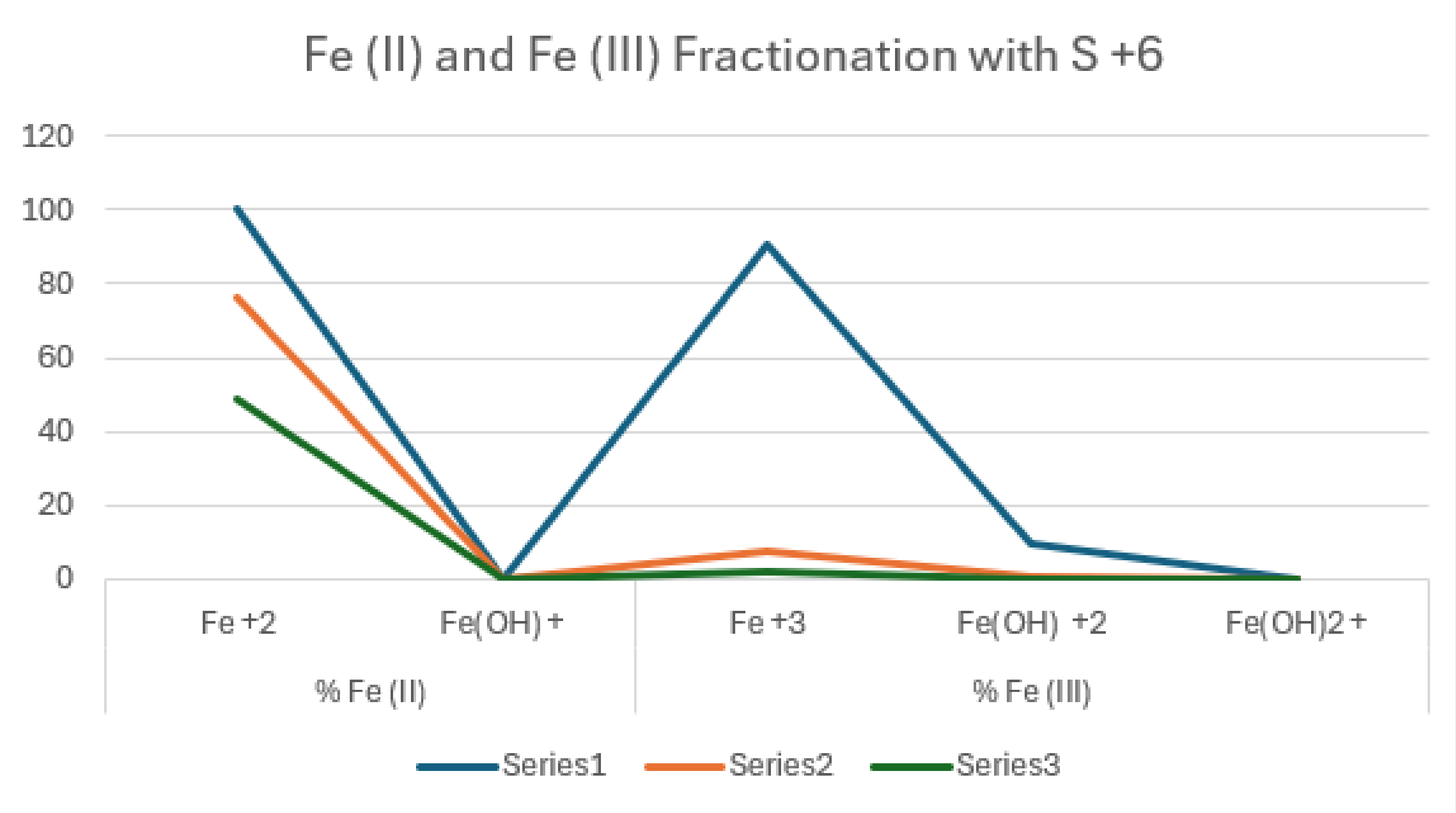
PHREEQ Onput – Adding S to system

What if we used S instead of Cl-?

More varied in Fe +2 and Fe +3, less change

in oxides.





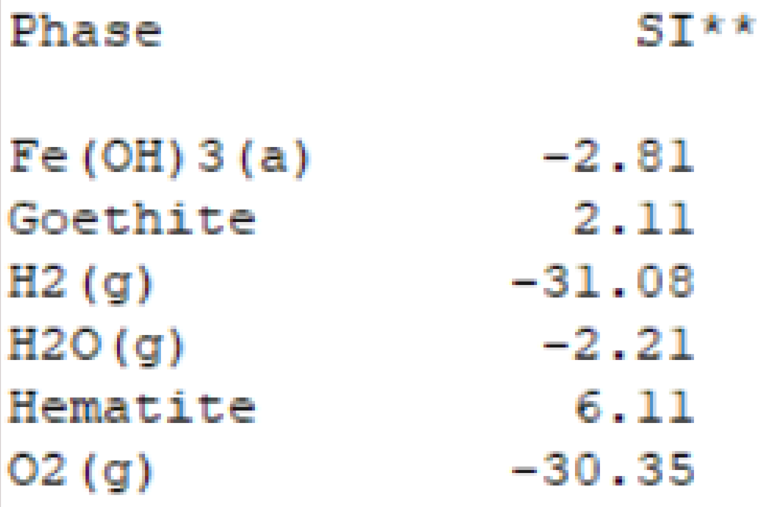
Series 1: Cl- or S +6 at 0
Series 2: Cl- or S +6 at 11
Series 3: Cl- or S +6 at 111

PHREEQ Onput - Adding S to system

Precipitation Changes, Cl- vs S

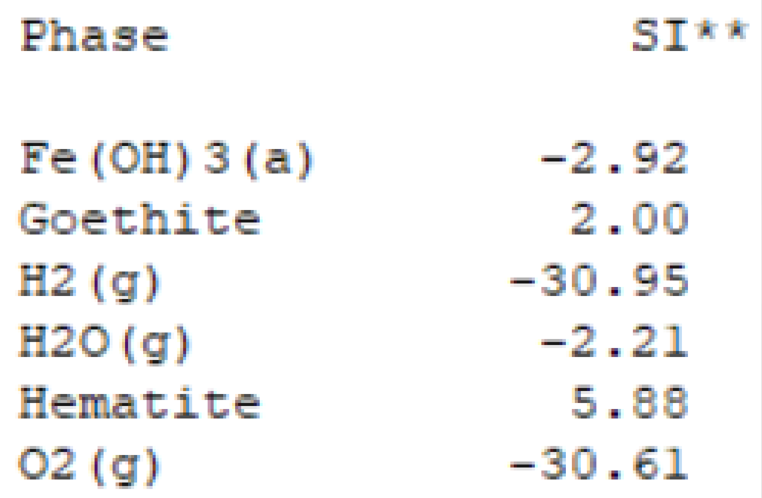
Precipitates in Cl-:

- Goethite & Hematite
- As Cl increases Goethite & Hematite only decrease slightly



```
Phase                SI**

Fe(OH)3(a)          -2.81
Goethite             2.11
H2(g)              -31.08
H2O(g)              -2.21
Hematite             6.11
O2(g)              -30.35
```



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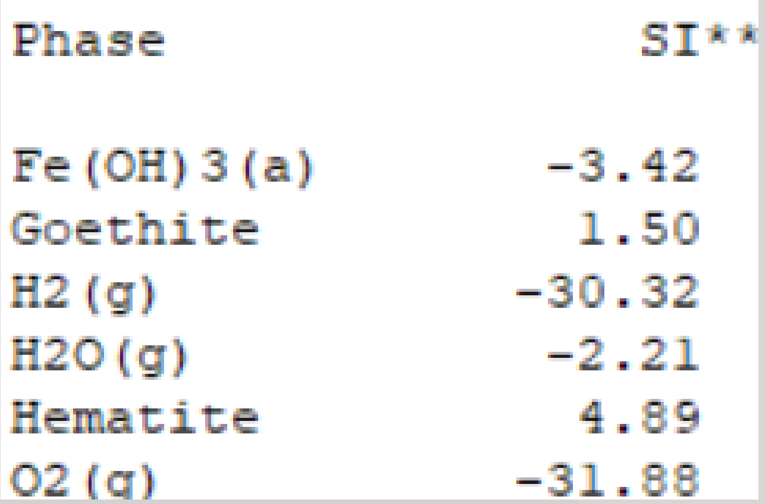
Phase                SI**

Fe(OH)3(a)          -2.92
Goethite             2.00
H2(g)              -30.95
H2O(g)              -2.21
Hematite             5.88
O2(g)              -30.61
```



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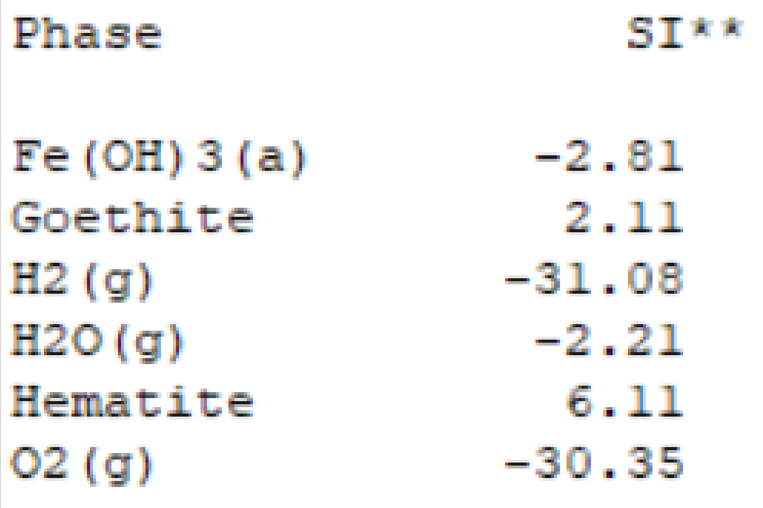
Phase                SI**

Fe(OH)3(a)          -3.42
Goethite             1.50
H2(g)              -30.32
H2O(g)              -2.21
Hematite             4.89
O2(g)              -31.88
```

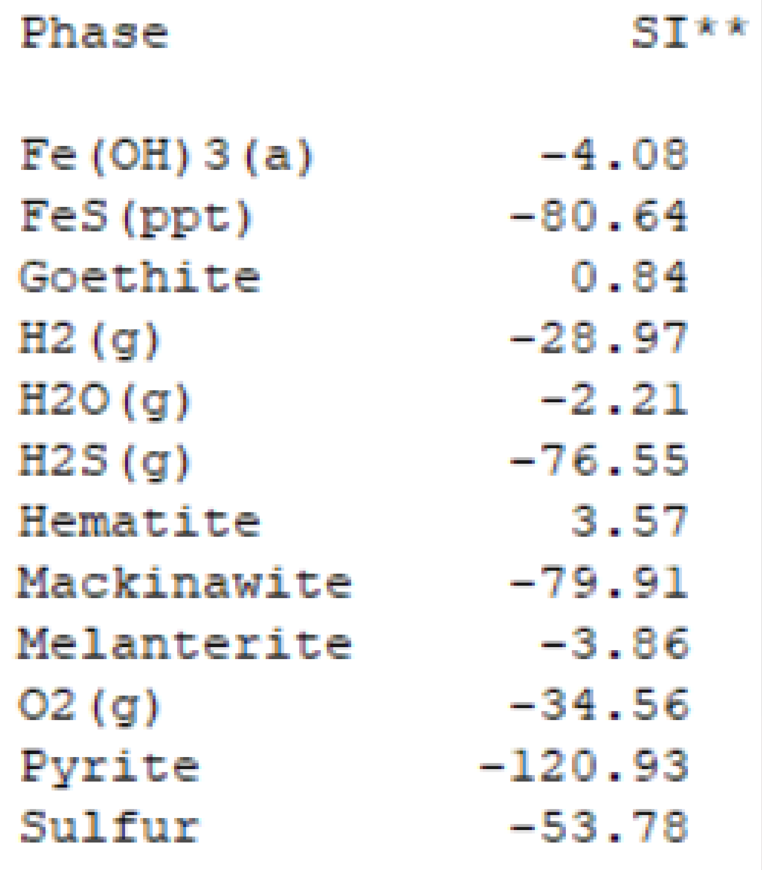
Precipitates in S:

- Goethite & Hematite
- As S increases, less Hematite precipitates and Geothite is dissolved



```
Phase                SI**

Fe(OH)3(a)          -2.81
Goethite             2.11
H2(g)              -31.08
H2O(g)              -2.21
Hematite             6.11
O2(g)              -30.35
```



```
Phase                SI**

Fe(OH)3(a)          -4.08
FeS(ppt)           -80.64
Goethite             0.84
H2(g)              -28.97
H2O(g)              -2.21
H2S(g)             -76.55
Hematite             3.57
Mackinawite        -79.91
Melanterite         -3.86
O2(g)              -34.56
Pyrite            -120.93
Sulfur             -53.78
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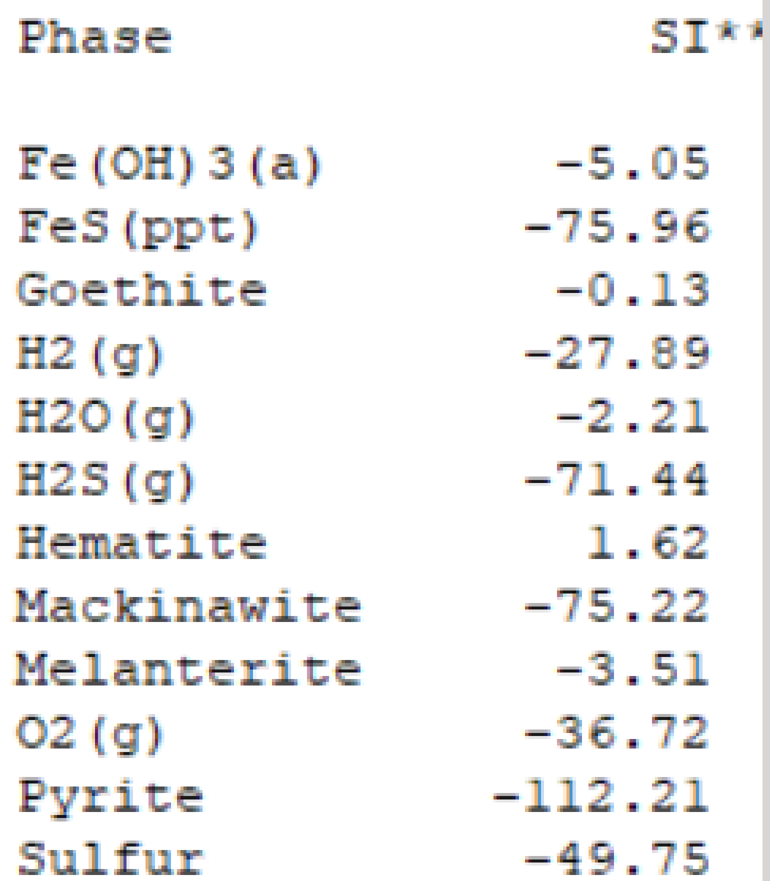

```
Phase                SI**

Fe(OH)3(a)          -5.05
FeS(ppt)           -75.96
Goethite            -0.13
H2(g)              -27.89
H2O(g)              -2.21
H2S(g)             -71.44
Hematite             1.62
Mackinawite        -75.22
Melanterite         -3.51
O2(g)              -36.72
Pyrite            -112.21
Sulfur             -49.75
```

Conclusions

- Redox is an important factor to consider when modeling a system
- Temperature has little effect on Fe fractionation
- Different elements have far greater effect on Fe fractionation, Cl and S explored in this presentation
- Hematite and Goethite are the only minerals that precipitate out of the system across all modeling, decreasing as Cl or S abundance increases

References

Johnson, C. M., & Beard, B. L. (2006). Fe isotopes: An emerging technique for understanding modern and ancient biogeochemical cycles. GSA Today, 16(11), 4. https://doi.org/10.1130/gsat01611a.1

Johnson, C. M., Skulan, J. L., Beard, B. L., Sun, H., Nealson, K. H., & Braterman, P. S. (2002). Isotopic fractionation between fe(iii) and fe(ii) in Aqueous Solutions. Earth and Planetary Science Letters, 195(1–2), 141–153. https://doi.org/10.1016/s0012-821x(01)00581-7

Welch, S. A., Beard, B. L., Johnson, C. M., & Braterman, P. S. (2003). Kinetic and Equilibrium Fe isotope fractionation between aqueous fe(ii) and fe(iii). Geochimica et Cosmochimica Acta, 67(22), 4231–4250. https://doi.org/10.1016/s0016-7037(03)00266-7