Inverse Modeling of the upper Patapsco Aquifer, Maryland

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NDSU Geochemistry 628

Purpose

- To determine the age of groundwater along the northern and southern flow paths.
- Dated by ^{14}C, ^{36}Cl, and ^{4}He
- The aquifer is being increasingly used as a drinking water source, they wanted to know how long it takes to recharge the aquifer.

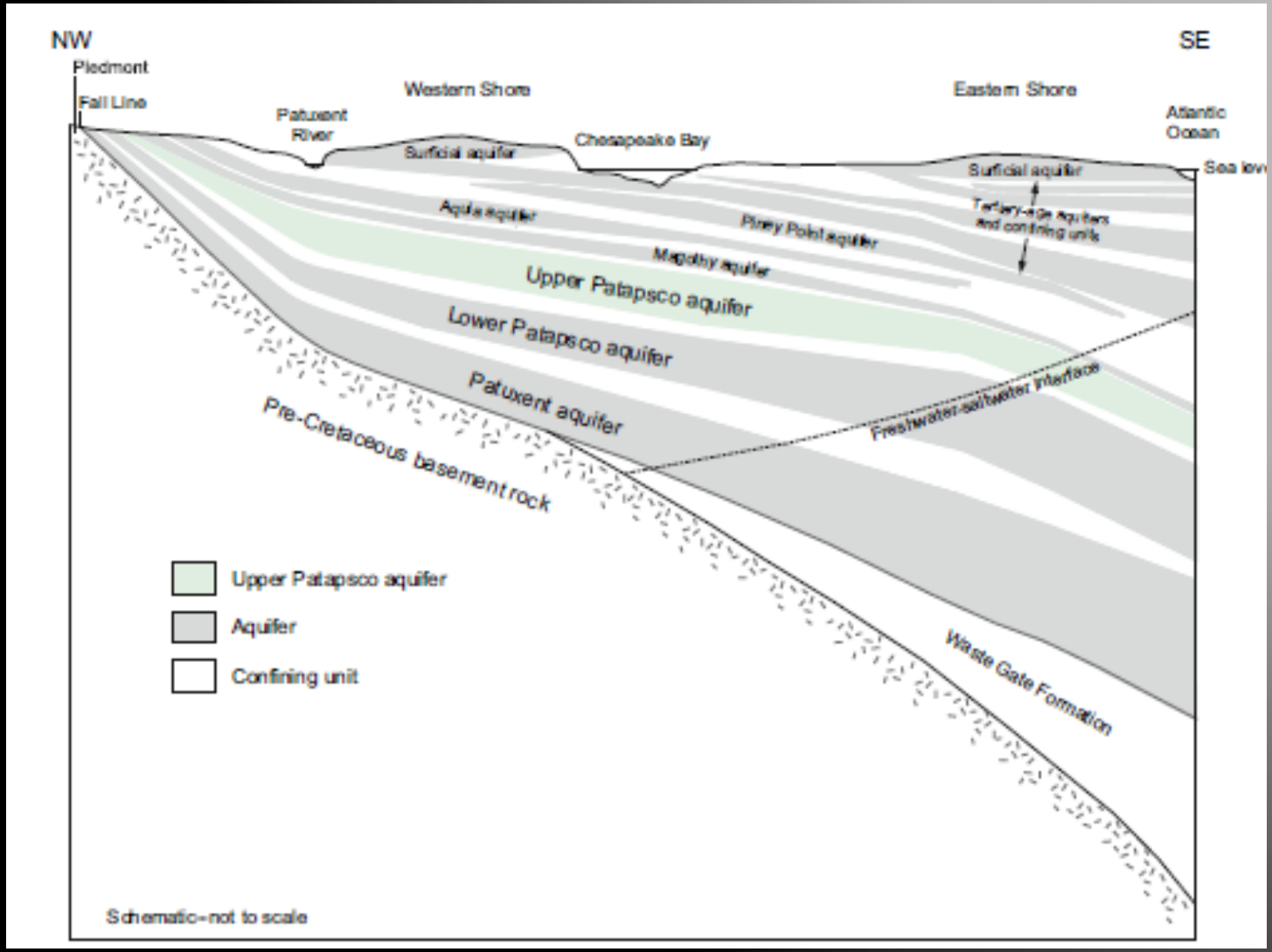
- To model geochemical changes in composition of groundwater along the flow paths.
- Pyrite precipitates and dissolves, want to find where it occurs using inverse modeling in PHREEQC

Original Paper

My Project

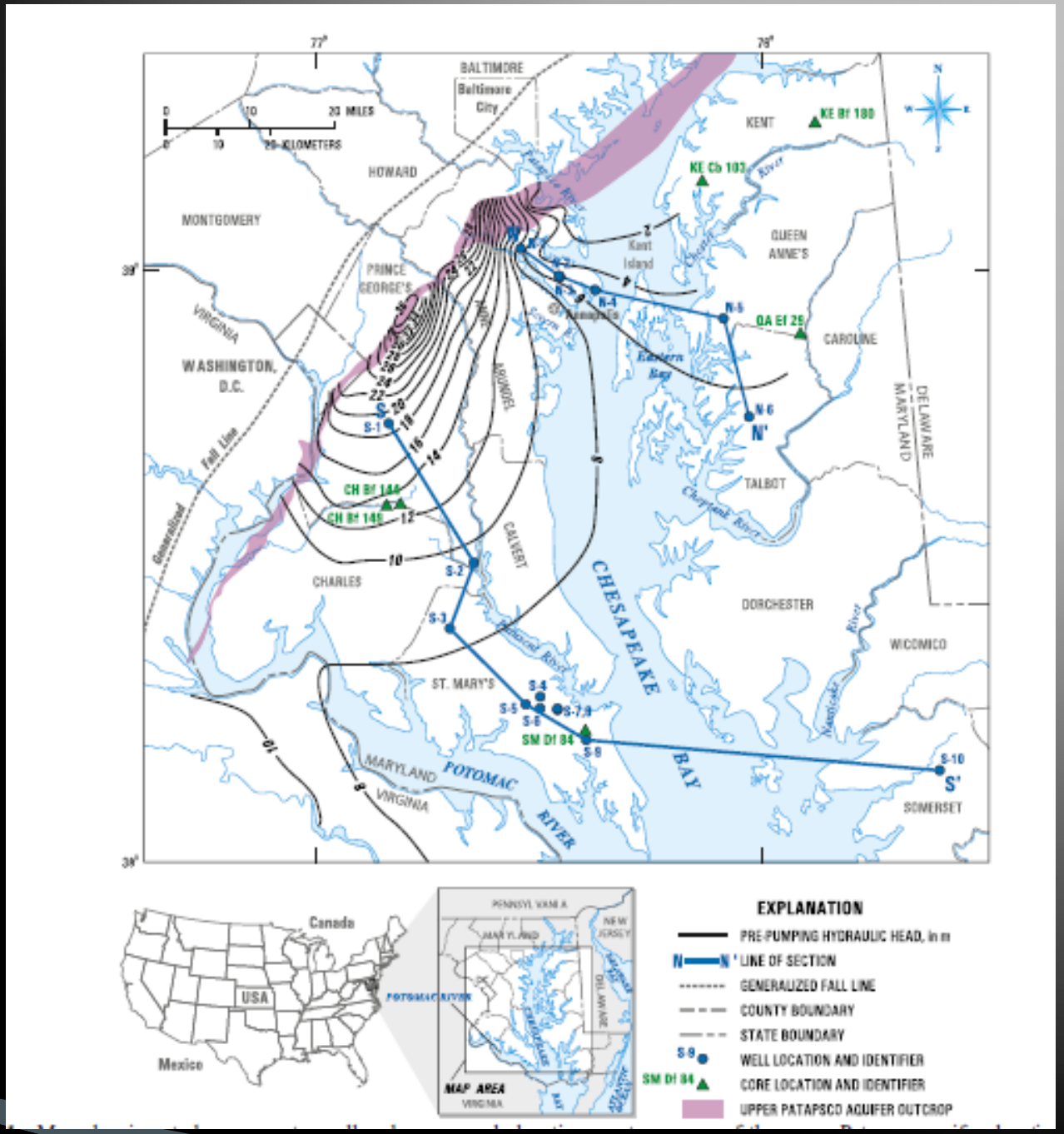
Hydrogeologic Setting of the upper Patapsco Aquifer

- Located in Maryland, in a series of aquifers called the Atlantic Coastal Plain
- The Coastal Plain sediments consist of layers unconsolidated sand, gravel, silt, and clay of varying thickness
  - Upper Patapsco is composed fine to medium grained quartoze sands and silt and clay.
- The aquifer has two parallel flow paths, the northern and southern from the outcrop belt to where it discharges in the Atlantic Ocean or Chesapeake Bay



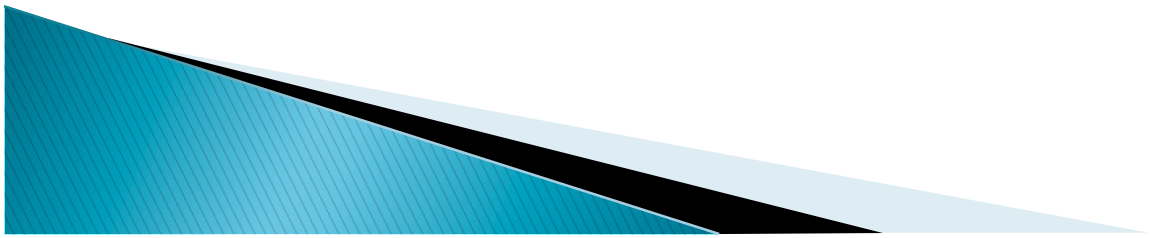
- Generalized cross section showing the major aquifers and confining units in the Atlantic Coastal Plain

- A map of the Maryland region.
- Northern and southern flow paths are labeled, well locations are also marked



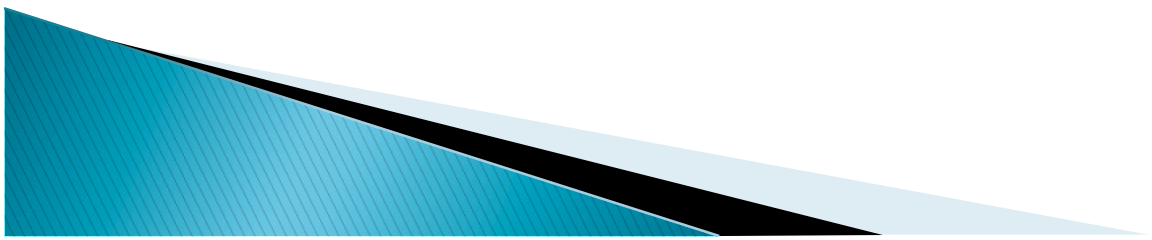
Methods

- Collected water samples from 16 wells along the flow paths (6 on the north path, 10 on the south)
  - 7 of the wells were sampled twice for quality assurance
- Authors dated the water samples using radiocarbon, Chlorine-36, and helium-4
- They used NetPath, similar to PHREEQC, to model the water chemistry of the aquifer



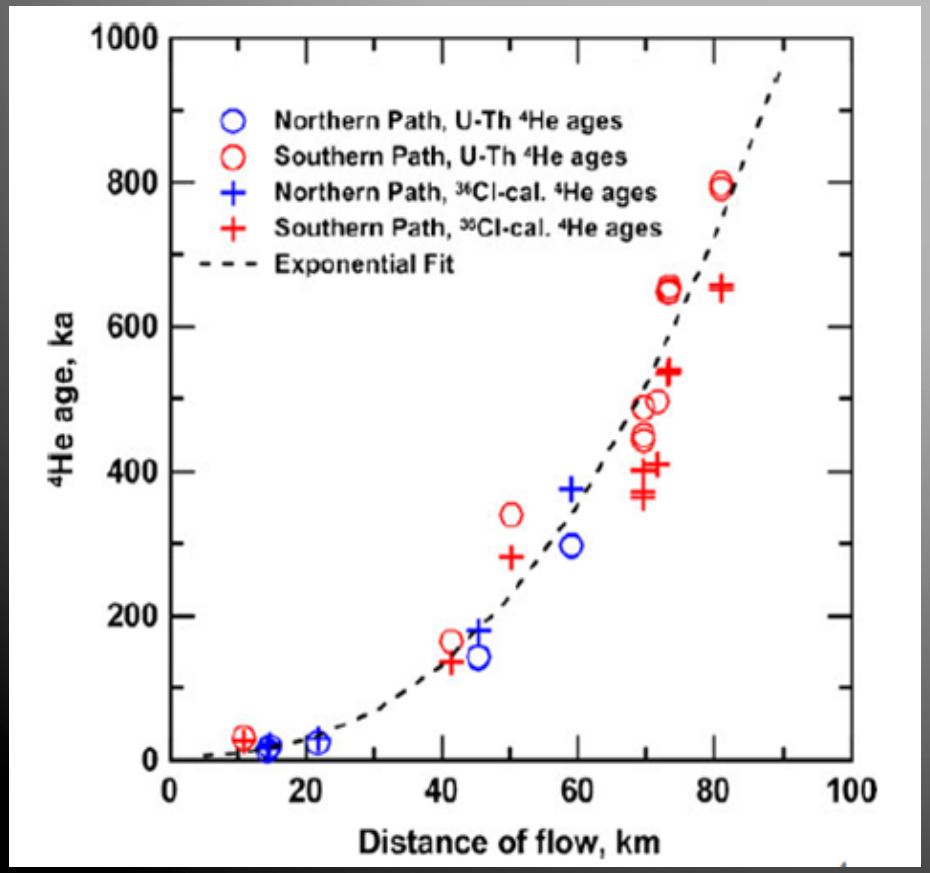
My Methods

- Used inversed modeling available in PHREEQC to look for changes in the chemistry.
- The original paper mentions that pyrite and calcite both dissolve and precipitate in various places along the flow path, but didn't mention where it occurs.
- Inverse modeling has the ability to find where it occurs.



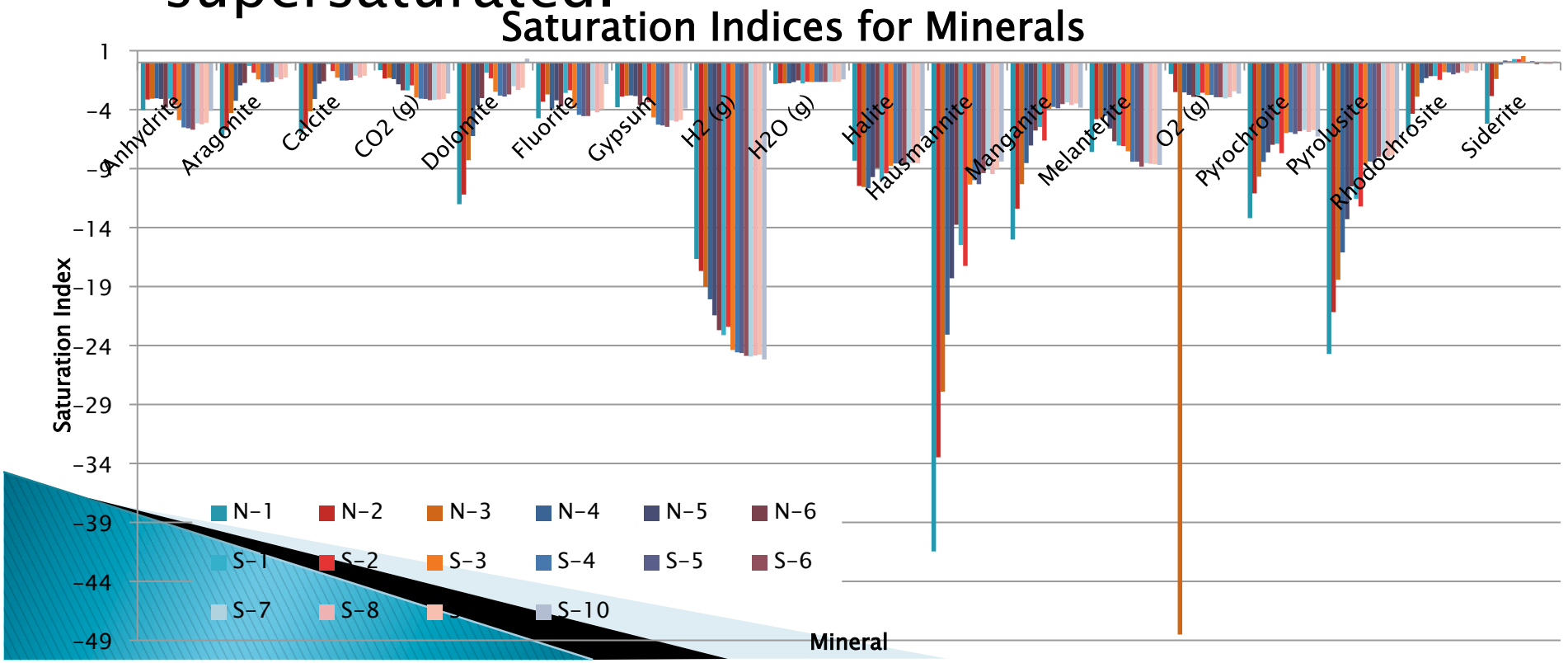
Original Paper's Results

- The water in the upper Patapsco aquifer is very old, spanning multiple glaciations
- Based on paleorecharge temperatures, most of the water samples were recharged during past glacial periods, water from the Last Glacial Maximum was sampled at well N-4
- Water is anywhere from modern aged at the beginning of the flow path to a million years old (S-10)



My Results

- PHREEQC returned very low, undersaturated SI values on almost all the minerals. Only Siderite (FeCO3) was consistently supersaturated.



Northern Flow Path Results

Phase Mole Transfers		
	calcite	Pyrite
N-1 to N-2	1.01E-02	5.15E-03
N-2 to N-3	1.03E-04	1.34E-06
N-3 to N-4	4.13E-04	2.28E-04
N-4 to N-5	-5.51E-05	-1.26E-04
N-5 to N-6	3.04E-04	-3.69E-06

Redox Mole Transfers			
	Fe (3)	O (0)	S (-2)
N-1 to N-2	-4.96E-03	3.29E-04	1.03E-02
N-2 to N-3	--	9.38E-06	2.68E-06
N-3 to N-4	--	-8.75E-06	4.56E-04
N-4 to N-5	--	3.75E-06	-2.45E-04
N-5 to N-6	-5.54E-05	1.88E-06	-7.37E-06

- Tables showing phase mole transfers and redox reactions occurring between each well location
- Mole transfers that are positive indicate dissolution; mole transfers that are negative indicate precipitation
- When no transfer occurs, the samples have the same composition within the uncertainty used (no reaction occurred between them)

Southern Flow Path Results

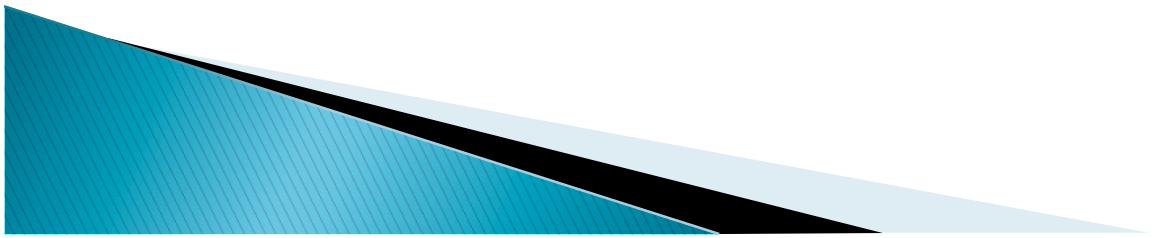
Phase Mole Transfers		
	Calcite	Pyrite
S-1 to S-2	-1.77E-04	-1.36E-05
S-2 to S-3	4.21E-04	2.03E-04
S-3 to S-4	-4.74E-06	-2.20E-05
S-4 to S-5	--	2.68E-07
S-5 to S-6	--	-1.86E-07
S-6 to S-7	1.05E-05	1.29E-05
S-7 to S-8	--	--
S-8 to S-9	3.74E-06	-9.17E-07
S-9 to S-10	-1.38E-02	-3.39E-03

Redox Mole Transfers			
	Fe (3)	O (0)	S (-2)
S-1 to S-2	2.15E-05	-1.88E-06	-2.72E-05
S-2 to S-3	-2.19E-04	2.50E-06	4.07E-04
S-3 to S-4	1.90E-05	--	-4.40E-05
S-4 to S-5	--	1.88E-06	5.36E-07
S-5 to S-6	-3.87E-07	-1.11E-06	-3.72E-07
S-6 to S-7	-1.28E-05	6.25E-07	2.58E-05
S-7 to S-8	--	--	--
S-8 to S-9	9.17E-07	-6.88E-06	-1.83E-06
S-9 to S-10	3.39E-03	4.37E-06	-6.78E-03

- No results for S-7 to S-8, even with changing the uncertainty and phases and trying to get a result, the samples are too similar for a reaction to occur

Discussion

- The water is very dilute, all SI values are very low, very undersaturated.
- Mole transfers of pyrite and calcite occur in several places, no reaction at all occurs between other wells.
- Redox reactions also occur
- Both calcite and pyrite dissolve in to the water between wells N-1 to N-4, more variability on the southern flow path



Well S-10

- Well S-10 located furthest along the southern flow path
- Had positive SI results for Calcite, Dolomite, and Siderite (supersaturated)

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

Phase	SI	log IAP	log KT	
Anhydrite	-4.11	-8.48	-4.37	CaSO4
Aragonite	-0.10	-8.45	-8.35	CaCO3
Calcite	0.04	-8.45	-8.50	CaCO3
CH2O	-54.49	-54.49	0.00	CH2O
CO2(g)	-2.63	-4.13	-1.50	CO2
Dolomite	0.34	-16.82	-17.15	CaMg(CO3)2
Fluorite	-1.84	-12.40	-10.57	CaF2
Gypsum	-3.90	-8.48	-4.58	CaSO4:2H2O
H2(g)	-25.18	-28.34	-3.16	H2
H2O(g)	-1.44	-0.00	1.44	H2O
Halite	-6.26	-4.67	1.59	NaCl
Hausmannite	-8.40	51.94	60.34	Mn3O4
Manganite	-3.83	21.51	25.34	MnOOH
Melanterite	-8.69	-10.87	-2.18	FeSO4:7H2O
O2(g)	-2.64	-5.55	-2.91	O2
Pyrochroite	-6.28	8.92	15.20	Mn(OH)2
Pyrolusite	-6.84	34.10	40.94	MnO2
Rhodochrosite	-0.71	-11.85	-11.14	MnCO3
Siderite	0.07	-10.84	-10.91	FeCO3

Solution fractions:

		Minimum	Maximum	
Solution 9	9.996e-001	0.000e+000	0.000e+000	
Solution 10	1.000e+000	0.000e+000	0.000e+000	

Phase mole transfers:

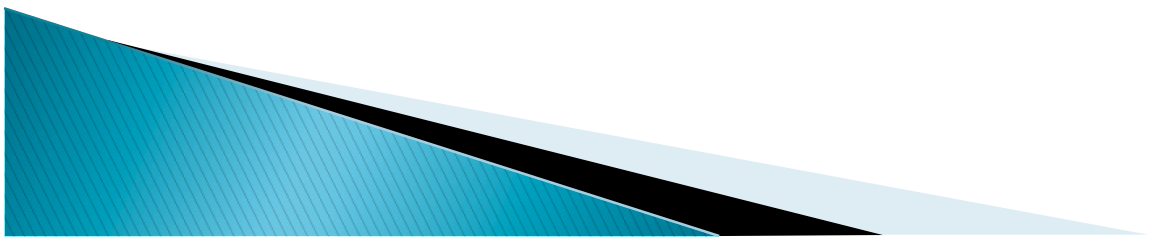
		Minimum	Maximum	
Calcite	-4.682e-004	0.000e+000	0.000e+000	CaCO3
CaX2	-6.678e-003	0.000e+000	0.000e+000	CaX2
CH2O	1.271e-002	0.000e+000	0.000e+000	CH2O
Dolomite	2.432e-005	0.000e+000	0.000e+000	CaMg(CO3)2
Goethite	3.389e-003	0.000e+000	0.000e+000	FeOOH
Gypsum	7.144e-003	0.000e+000	0.000e+000	CaSO4:2H2O
Halite	1.800e-003	0.000e+000	0.000e+000	NaCl
NaX	1.336e-002	0.000e+000	0.000e+000	NaX
Pyrite	-3.389e-003	0.000e+000	0.000e+000	FeS2

Redox mole transfers:

Fe(3)	3.389e-003
O(0)	4.366e-006
S(-2)	-6.779e-003

Future Studies/Things to do Differently

- Look at Well S-10 further, is there evidence of a salt water intrusion?
- A different method than Inverse Modeling might be more effective in looking for changes
- Study the changes in isotopes, attempt to see where the other glacial maximums occurred
- The uncertainties were really high (0.2+) to make the model run, probably changed the results from what is actually occurring



References

- *Frequently Asked Questions for PHREEQC and PhreeqcI*. (1999, February 3). Retrieved from PHREEQC (Version 2)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/faq.html
- Plummer, L. N., et al (2012). Old Groundwater in parts of the upper Patapsco Aquifer, Atlantic Coastal Plain, Maryland, USA: evidence of radiocarbon, chlorine-36 and helium-4. *Hydrogeology Journal*, 1269-1294.

Questions?