Uranium Mobility in Groundwater Near the Orphan Mine: Geochemical Modeling of Temperature and Redox Effects

Miranda Vanderhyde

Outline

1. Background

- Paper Sampling
- Lore
- Location
- Importance
- Objectives

2. Methods & Results

- Major Ion Chemistry/Piper Plots
- Uranium Speciation/Behavior
- Inverse Modeling

3. Conclusion

Background

GEEA

Research article

Geochemistry: Exploration, Environment, Analysis

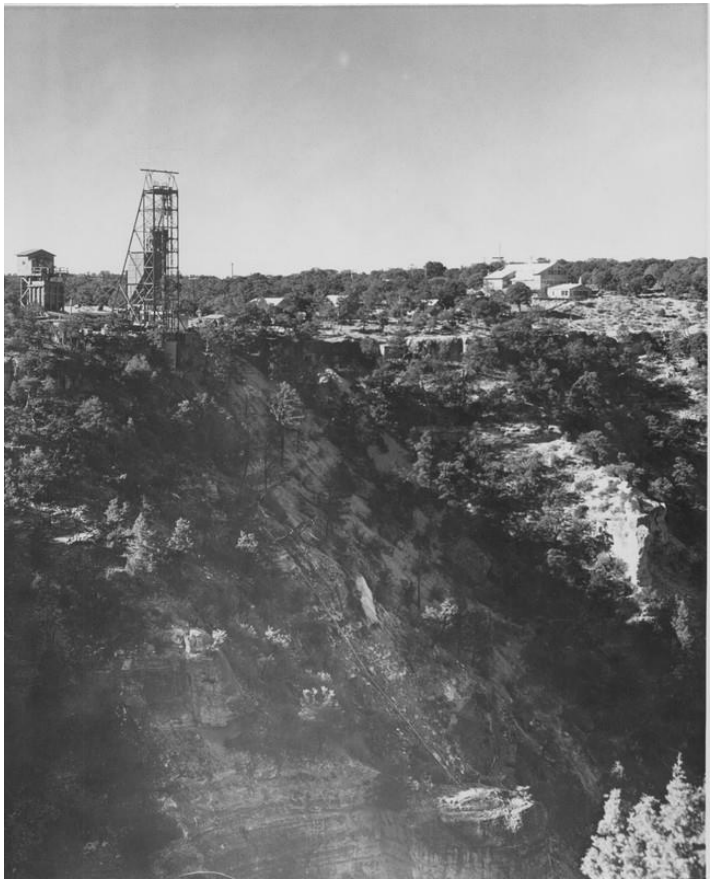
https://doi.org/10.1144/geochem2023-007 | Vol. 23 | 2023 | geochem2023-007

Anthropogenic influence on groundwater geochemistry in Horn Creek Watershed near the Orphan Mine in Grand Canyon National Park, Arizona, USA

Kimberly R. Beisner[1]*, Collin Davidson[2] and Fred Tillman[3]

[1] U.S. Geological Survey, 6700 Edith Blvd. NE, Albuquerque, NM 87111, USA
[2] University of Nevada Las Vegas, NV, USA
[3] U.S. Geological Survey, Tucson, AZ 85719, USA
KRB, 0000-0002-2077-6899; CD, 0000-0001-8814-9982; FT, 0000-0002-2922-402X
* Correspondence: kbeisner@usgs.gov

Collected Data - Beisner



https://www.flickr.com/photos/grand_canyon_nps/7944935142/in/photolist-d74Sqo

Sampling period: April 2018 – April 2022

Location: Springs in the Horn Creek watershed

Followed standard USGS field procedures

Samples

- pH
- Temperature
- Dissolved Oxygen
- Barometric Pressure
- Major ions
- Trace elements
- Nutrients
- Uranium isotopes
- Strontium isotopes
- Sulfate isotopes
- Stable water isotopes
- PFAS

Geochemical modeling with PHREEQC and WATEQ4F database

Orphan Mine Lore

- **Discovered:** Early 1900s (as a copper mine)
- **Uranium mined:** Primarily in the 1950s–1969
- **Production**: About 495,000 tons of uranium ore with 4.2 million pounds of uranium oxide
- **Environmental concern:** The mine site is now abandoned and a known source of uranium contamination, especially affecting Horn Creek and nearby groundwater.

Naming Controversy: Some sources say the original owner (early 1900s) was an orphan; others say it was due to the isolated location.

The uranium mine tunnel on the left, Dan Hogan's copper mine on the right.

https://www.hmdb.org/m.asp?m=108885

Location

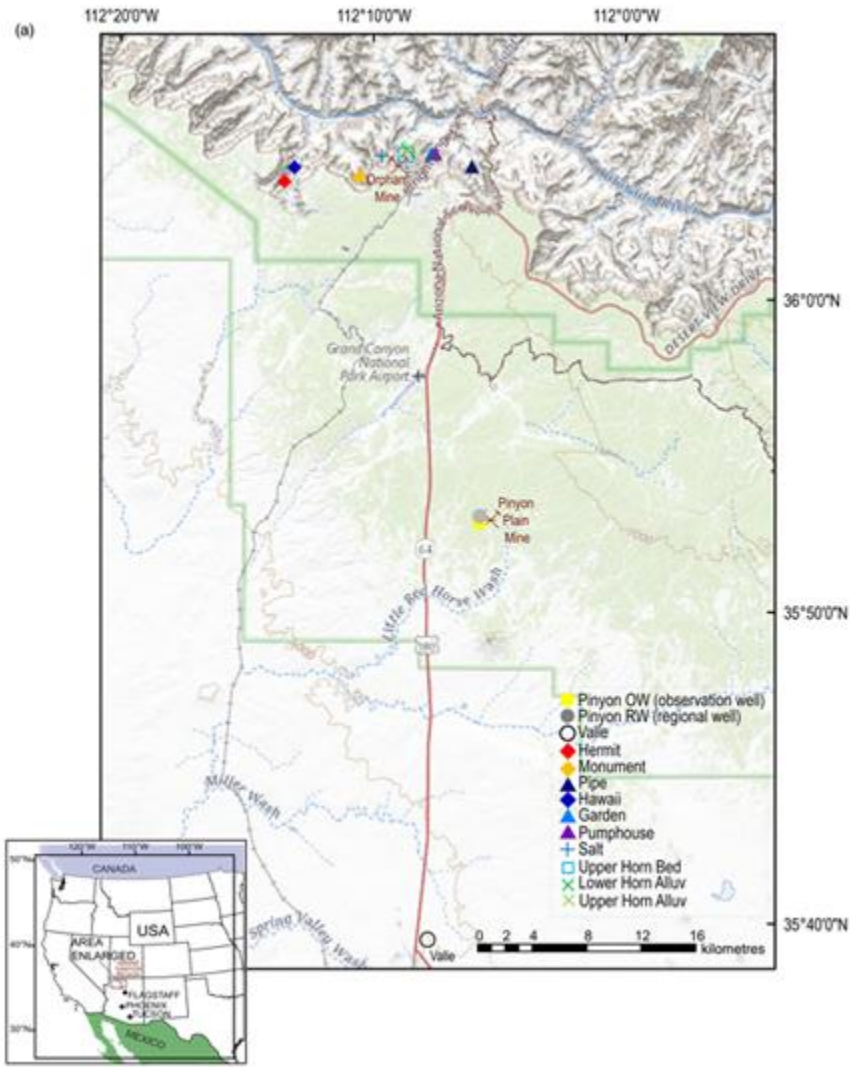


Fig. 1. (a) Map of groundwater sample locations and breccia pipe uranium mines south of Grand Canyon with (b) a map showing detail of the Horn Creek watershed sampling locations where solid blue lines represent the approximate location of perennial flow in Horn Creek below spring sites in this study, dashed blue lines represent ephemeral flow and the black line represents the fault expression, with geology from Billingsley (2000) and base map from USGS The National Map.

Location

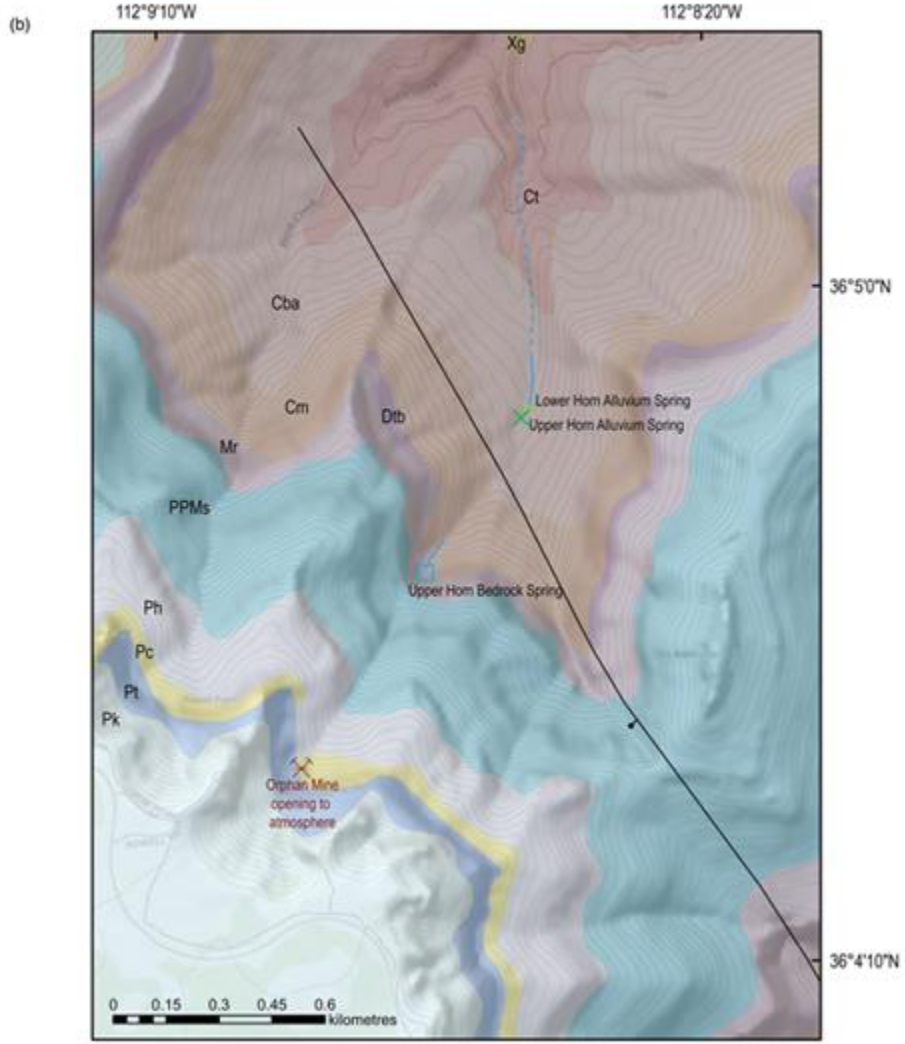


Fig. 1. (a) Map of groundwater sample locations and breccia pipe uranium mines south of Grand Canyon with (b) a map showing detail of the Horn Creek watershed sampling locations where solid blue lines represent the approximate location of perennial flow in Horn Creek below spring sites in this study, dashed blue lines represent ephemeral flow and the black line represents the fault expression, with geology from Billingsley (2000) and base map from USGS The National Map.

Location

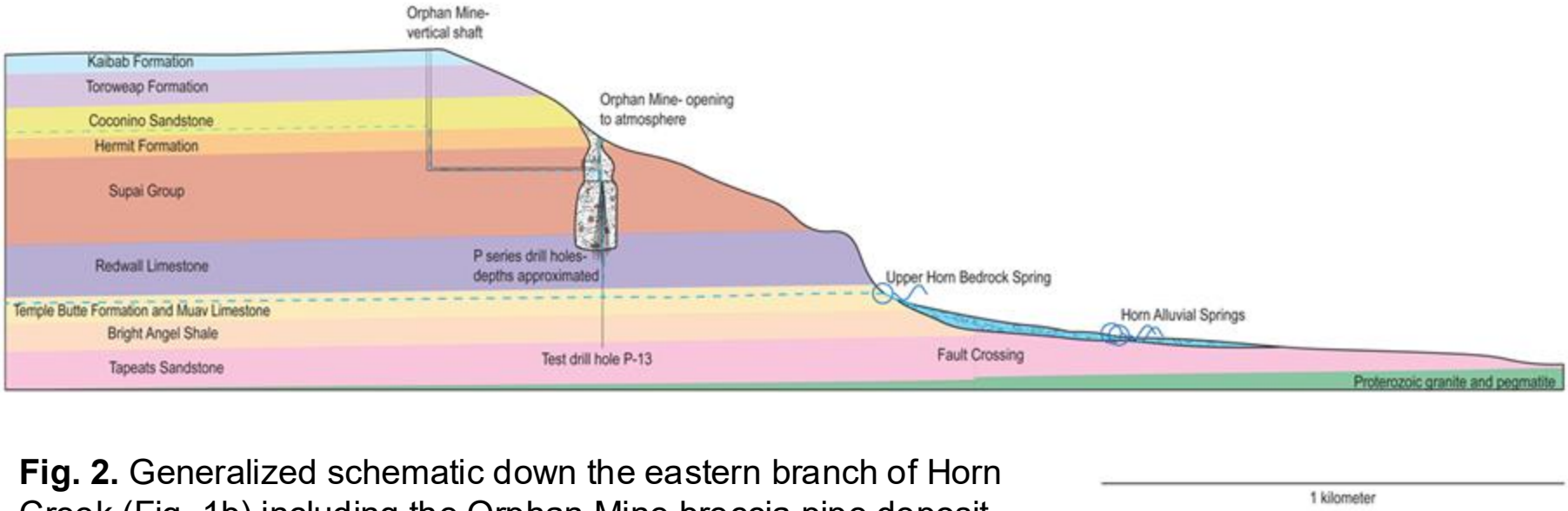


Fig. 2. Generalized schematic down the eastern branch of Horn Creek (Fig. 1b) including the Orphan Mine breccia pipe deposit and mine workings. Dashed blue lines show conceptual understanding of groundwater resources in the region and how they may interact with the Orphan Mine workings.

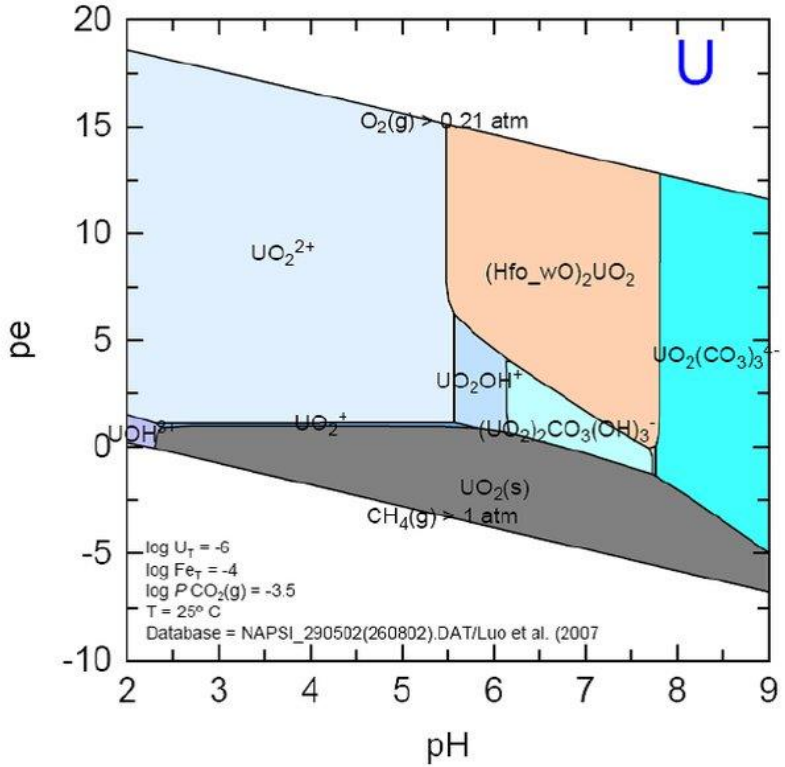
Importance

• Uranium mining can impact environmental and human health, especially in sensitive areas like the Grand Canyon

• Uranium mobility depends on its chemical form:
  - •U(VI): Oxidized, water-soluble, highly mobile (as uranyl ion)
  - •U(IV): Reduced, forms insoluble minerals (e.g., uraninite)

• Redox conditions, pH, and compounds like carbonates or phosphates control uranium transformations

• Some groundwater samples contain up to 400 µg/L uranium, exceeding safe drinking water standards



Kuells, 2013

Objectives

This study aims to investigate the geochemical controls on uranium mobility in groundwater near the Orphan Mine in Grand Canyon National Park. Specifically, the objectives were to:

1) Characterize and compare the major ion chemistry of groundwater from three hydrologically distinct sites using Piper diagrams.
2) Observe uranium speciation and activity using equilibrium modeling.
3) Evaluate the geochemical processes influencing uranium mobility using inverse modeling, with a focus on major mineral reactions and groundwater mixing.

While assessing the effects of elevated temperature and redox potential on these factors.

Piper Plots

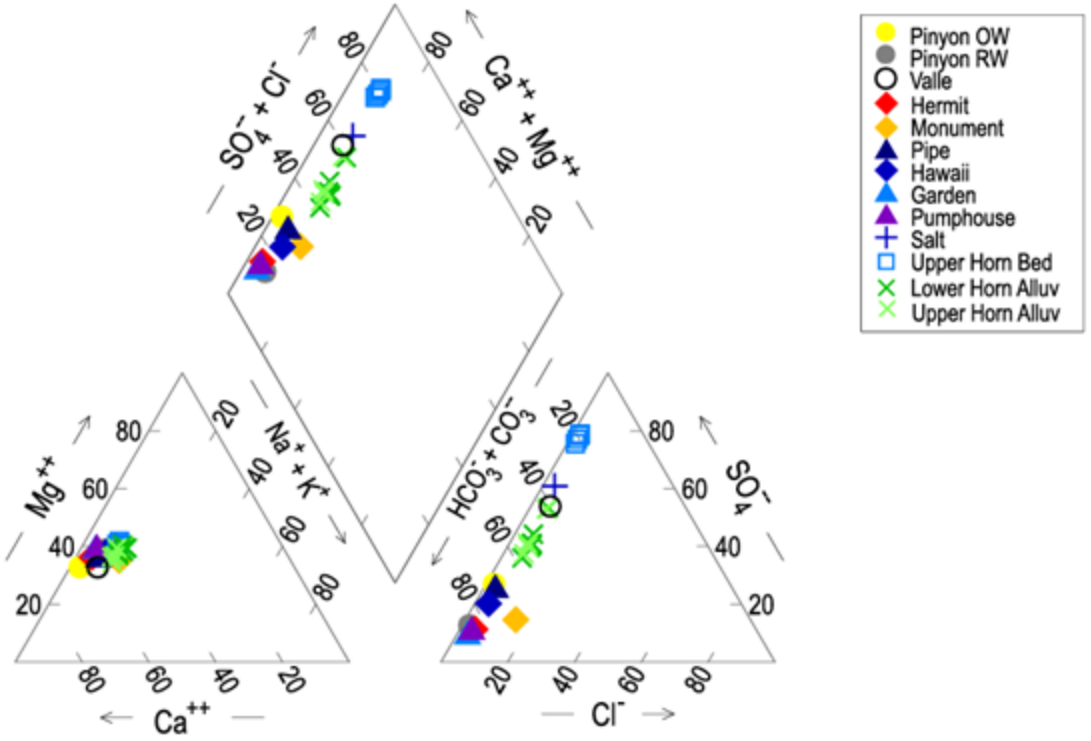


Fig. 3. Piper plot of major ion proportion for groundwater samples; values presented in per cent. (Beisner, et al. 2023)

Piper Plots

GW_Chart: A Program for Creating Specialized Graphs Used in Groundwater Studies

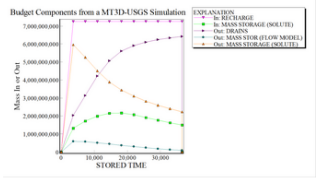
June 26, 2020

View Software Release

Overview of GW_Chart

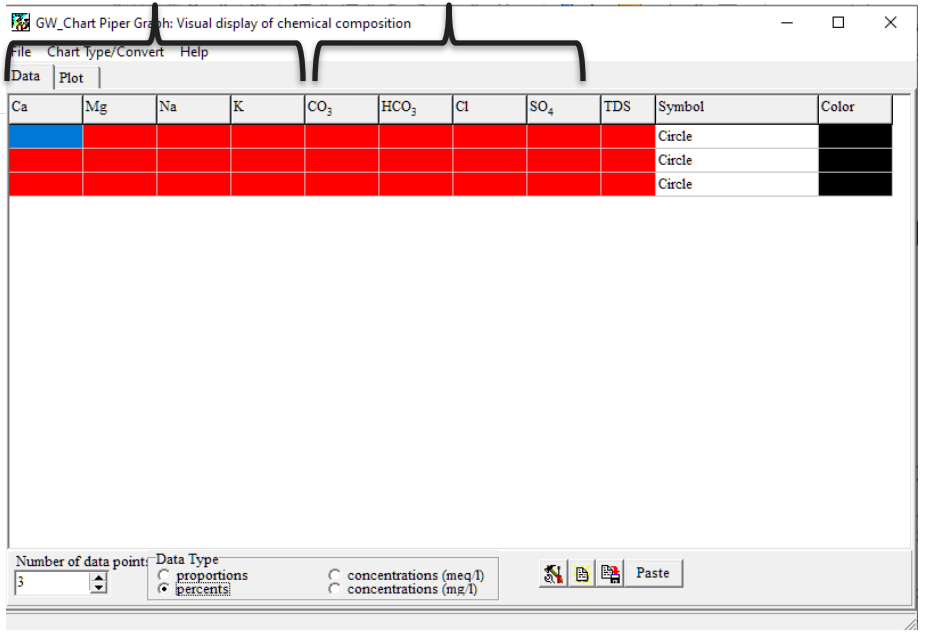
GW_Chart is a program for creating specialized graphs used in groundwater studies. It incorporates the functionality of two previous programs, Budgeteer and Hydrograph Extractor and adds additional new features. There are seven major types of graphs created with GW_Chart:

- Calibration Plots
- Water Budget Plots
- Hydrographs
- Lake Plots
- Piper Diagrams
- Cell Water Budgets
- Farm Budgets



Graph of budget components from a MT3D-USGS simulation versus time generated by GW_Chart based on results from a hypothetical model.

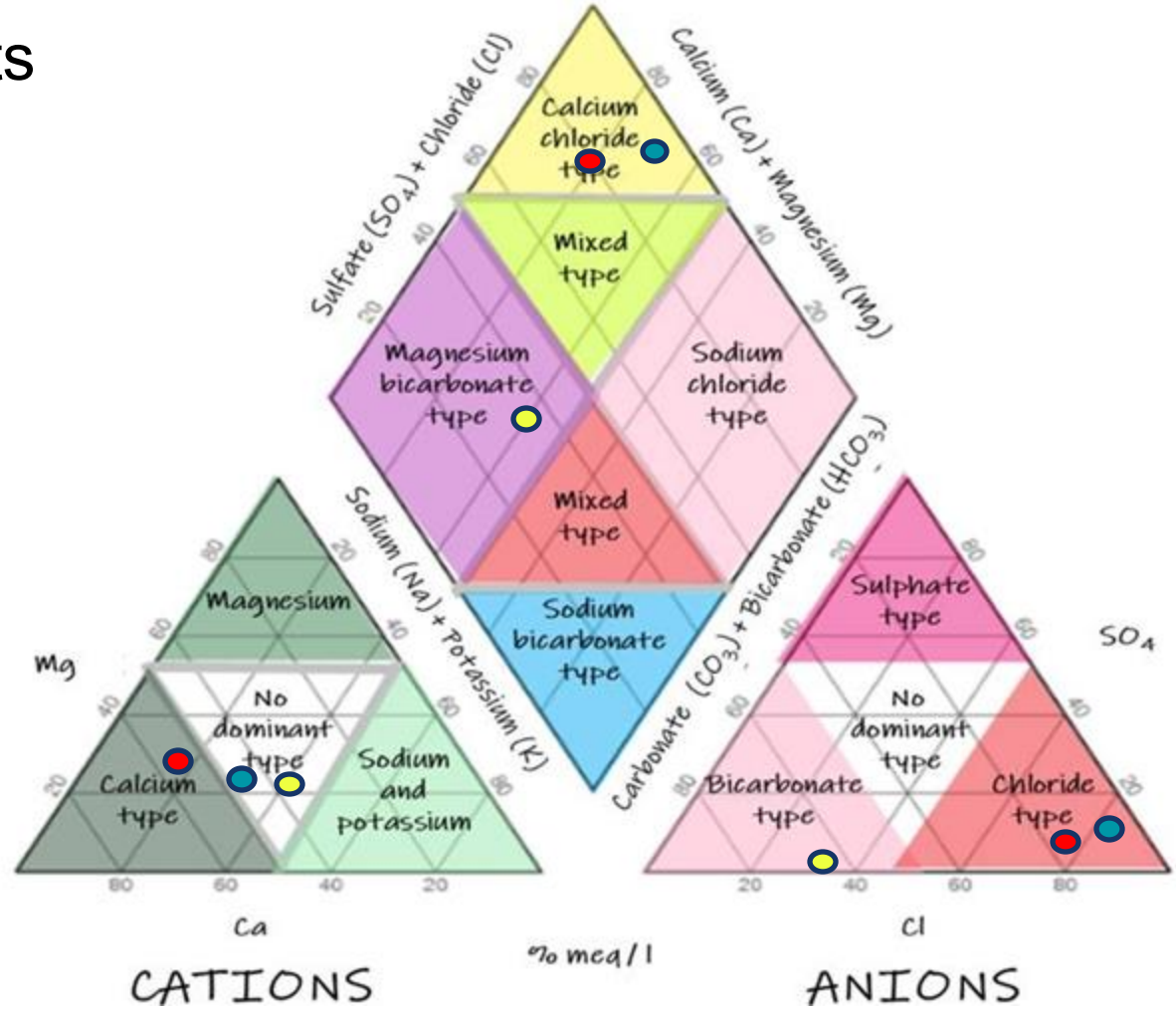
cations anions



https://www.usgs.gov/software/gwchart-a-program-creating-specialized-graphs-used-groundwater-studies

Piper Plots

- Mississippi River
- Colorado River
- Nile River

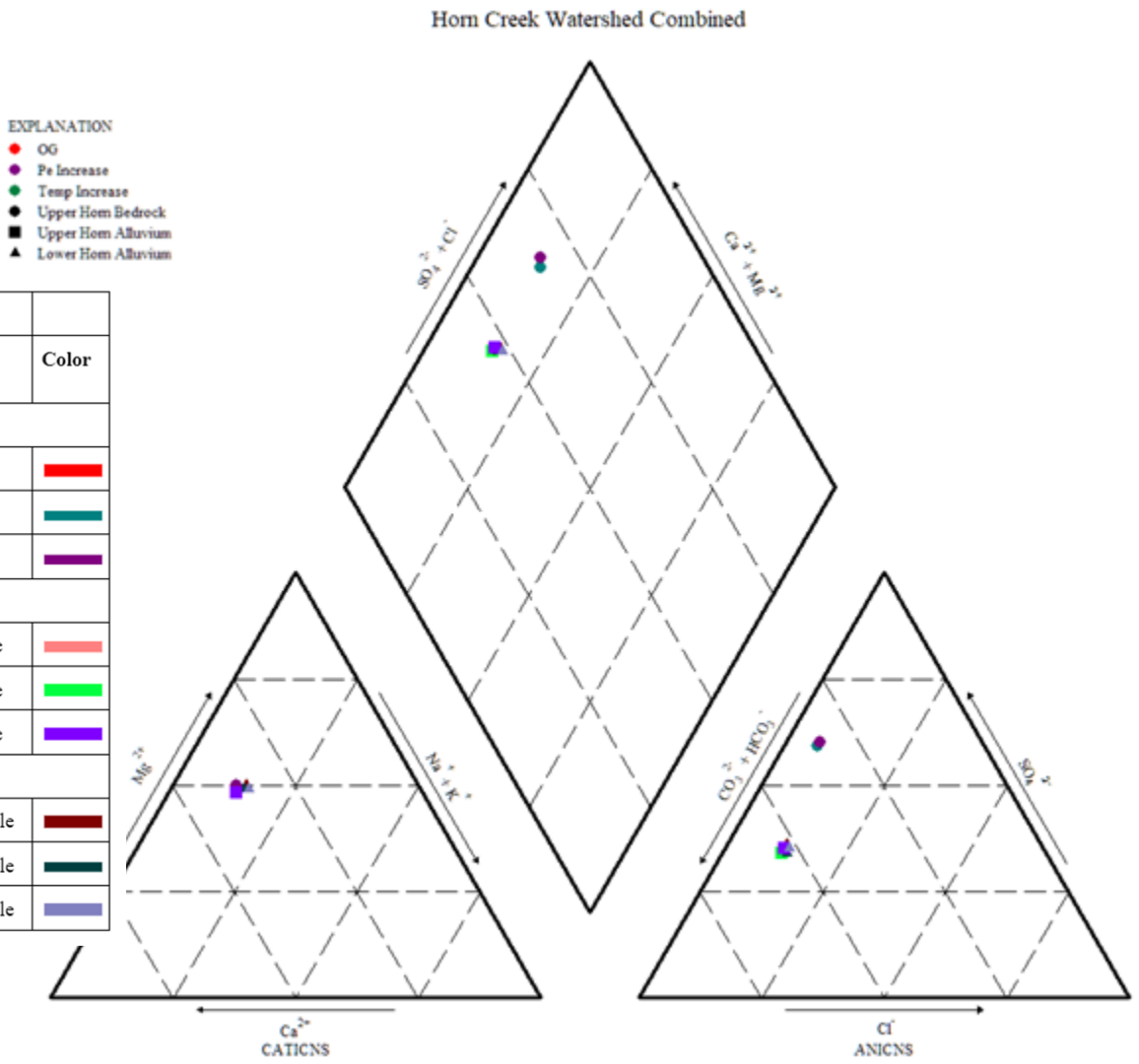


https://support.goldensoftware.com/hc/en-us/articles/115003101648-Create-a-Piper-Trilinear-diagram-in-Grapher

Major Ion Chemistry

Cations – no dominant type/magnesium type
Anions – bedrock = sulfate type, alluvium = bicarbonate type
Diamond – bedrock = mixed type, alluvium = mg bicarbonate type

	Cations (%)				Anions (%)				
Site & Condition	**Ca++**	**Mg ++**	**Na+**	**K+**	**HCO3-**	**Cl-**	**SO4- -**	**Shape**	**Color**
Upper Horn Bedrock									
Original	37	50	10	3	33	7	60	Circle	
+10 °C	37	49	11	3	34	7	59	Circle	
pe 4 → 7	37	50	10	3	33	7	60	Circle	
Upper Horn Alluvium									
Original	38	48	12	2	53	12	35	Square	
+10 °C	38	48	12	2	54	12	34	Square	
pe 4 → 7	38	48	12	2	53	12	35	Square	
Lower Horn Alluvium									
Original	35	50	13	2	52	12	36	Triangle	
+10 °C	36	49	13	2	53	13	34	Triangle	
pe 4 → 7	35	49	14	2	52	13	35	Triangle	



Uranium Speciation

Table 2. Uranium speciation of the top 4 U(6) species (in % of total U) for three Horn Creek watershed sites near the Orphan Mine under original, +10 °C temperature, and increased pe (4 → 7) conditions.

Site & Condition	Temp (°C)	Total U (mol/kg)	$UO_2(CO_3)_3^{4-}$ (%)	$UO_2(CO_3)_2^{2-}$ (%)	UO_2CO_3 (%)	$UO_2(OH)_3^-$ (%)
Upper Horn Bedrock						
Original	11.7	8.197E-07	57.91%	41%	0.49%	0.19%
+10 °C	21.7		44%	55.31%	0.42%	0.12%
pe 4 → 7	11.7		58%	41%	0%	0%
Upper Horn Alluvium						
Original	13.5	1.429E-07	50.00%	49.31%	0.66%	0.04%
+10 °C	23.5		36.54%	62.90%	0.55%	0.02%
pe 4 → 7	13.5		50%	49%	1%	0%
Lower Horn Alluvium						
Original	14.7	5.885E-08	40.75%	58.22%	0.99%	0.04%
+10 °C	24.7		28.39%	70.77%	0.79%	0.02%
pe 4 → 7	14.7		41%	58%	1%	0%

Uranium Behavior

Site & Condition	UO_2	U_3O_8	UO_3 (gamma)	U_4O_9
Upper Horn Bedrock				
Original	-10.33	-8.80	-5.63	-17.82
+10 °C	-11.43	-9.08	-5.33	-19.57
pe 4 → 7	-16.33	-14.80	-5.63	-35.82
Upper Horn Alluvium				
Original	-11.08	-11.68	-6.72	-20.91
+10 °C	-12.18	-11.99	-6.43	-22.69
pe 4 → 7	-17.08	-17.68	-6.72	-38.91
Lower Horn Alluvium				
Original	-11.29	-12.33	-6.95	-21.61
+10 °C	-12.39	-12.68	-6.69	-23.45
pe 4 → 7	-17.29	-18.33	-6.95	-39.61

Table 3. Saturation indices (SI) of selected uranium minerals under different environmental scenarios at three Horn Creek sites near the Orphan Mine.

Conclusion

- Temperature increase (+10 °C) shifted speciation slightly toward $UO_2(CO_3)_2^{2-}$,but uranium remained in highly soluble forms.
    - Redox increase (pe 4 → 7) had minimal effect, confirming uranium was already in the oxidized U(VI) state.
- Saturation indices for uranium minerals (e.g., uraninite, UO_3) were all negative, indicating uranium is not precipitating, it stays dissolved.
- Inverse modeling revealed consistent mineral reactions: Gypsum dissolution (adds sulfate), Calcite/dolomite precipitation (maintains carbonate buffering)
    - Even without uranium minerals in the model, these reactions reflect a stable, oxidizing, carbonate-rich system that favors U(VI) mobility.
    - Both pe and temperature change impacted the models.
- Together, the results suggest that uranium contamination from the Orphan Mine is persistent and not easily removed by natural geochemical processes.

Sources

Beisner KR, Davidson C, Tillman F. Anthropogenic influence on groundwater geochemistry in Horn Creek Watershed near the Orphan Mine in Grand Canyon National Park, Arizona, USA https://doi.org/10.5066/F7P55KJN.

Amundson MA. 2001. MINING THE GRAND CANYON TO SAVE IT: THE ORPHAN LODE URANIUM MINE AND NATIONAL SECURITY.

Cumberland, S. A., Douglas, G., Grice, K., & Moreau, J. W. (2016). Uranium mobility in organic matter-rich sediments: A review of geological and geochemical processes. In *Earth-Science Reviews* (Vol. 159, pp. 160–185). Elsevier B.V. https://doi.org/10.1016/j.earscirev.2016.05.010

Riedel T, Kübeck C. 2018. Uranium in groundwater – A synopsis based on a large hydrogeochemical data set. Water Res 129:29–38.

Samolczyk MA, Spooner IS, Stanley CR. 2012. A model for uranium mobility in groundwater in the Grand Pré region, Nova Scotia, Canada. Atlantic Geology 48:1–13.

Davidson, C. 2021. INVESTIGATING CONTROLS ON TEMPORAL AND SPATIAL VARIATION OF DISSOLVED URANIUM AT SPRINGS IN HORN CREEK DRAINAGE, GRAND CANYON NATIONAL PARK, ARIZONA, USA.

America E, Kerth R, Schneider J, Ridlington E, Aurilio A. 2011. Grand Canyon at Risk Uranium Mining Doesn’t Belong Near Our National Treasures.

Inverse Modeling – Supplementary

Inverse modeling asks:

> *"What chemical reactions (e.g., mineral dissolution, precipitation, redox, or mixing) could explain the difference in water chemistry between two or more water samples?"*

Instead of guessing what reactions might happen, you give PHREEQC two (or more) real-world water chemistries, and it calculates possible scenarios that could explain how one became the other.

Model Number	Percentage Initial Waters	Minerals Precipitating (mole transfers)	Minerals Dissolving (mole transfers)
2022 UHB reacting with mineral phases–UHA final water			
1	100% UHB	gypsum(-1.894×10^{-03}), dolomite (-7.348×10^{-04}), illite (-1.707×10^{-04}), hematite (-5.902×10^{-06}), uraninite (-8.829×10^{-07})	calcite (2.503×10^{-03}), kaolinite (1.963×10^{-04}), quartz (2.048×10^{-04}), halite (2.523×10^{-04}), pyrite (1.180×10^{-05}) CO_2(g) (1.594×10^{-03})
2	100% UHB	gypsum(-1.870×10^{-03}), dolomite (-7.348×10^{-04}), illite (-1.707×10^{-04}), uraninite (-8.829×10^{-07})	calcite (2.480×10^{-03}), kaolinite (1.963×10^{-04}), quartz (2.048×10^{-04}), halite (2.523×10^{-04}), CO_2(g) (1.618×10^{-03})
2022 UHB reacting with mineral phases–UHA final water (removed uranium balance, and uraninite, hematite and pyrite phases)			
1	100% UHB	gypsum (-1.870×10^{-03}), dolomite (-7.356×10^{-04}), illite (-1.707×10^{-04})	calcite (2.481×10^{-03}), kaolinite (1.963×10^{-04}), quartz (2.048×10^{-04}), halite (2.523×10^{-04}), CO_2(g) (1.619×10^{-03})

Inverse Modeling – Supplementary

Model Number	Percentage Initial Water	Minerals Precipitating (mole transfers)	Minerals Dissolving (mole transfers)	Sum of delta/uncertainty limit
2019 UHB mixing with VGW - UHA Final Water - Original				
1	45% UHB 55% VGW	Gypsum (−2.7854e−04)	CO2(g) (9.759e−04)	1.526e+01
2	38% UHB 62% VGW	Gypsum (−2.7854e−04) Kaolinite (−7.234e−05) Quartz (−7.549e−05)	Illite (6.291e−05)	1.334e+01
3	45% UHB 55% VGW	Gypsum (−4.335e−04)	Dolomite (2.164e−04)	1.176e+01
4	45% UHB 55% VGW	Gypsum (−5.589e−04)	Calcite (3.822e−04)	1.230e+01
2019 UHB mixing with VGW - UHA Final Water - 10C Temp Increase				
1	45% UHB 55% VGW	Gypsum (-2.785e-04)	CO2(g) (9.081e-04)	1.526e+01
2	38% UHB 62% VGW	Gypsum (-3.105e-04) Kaolinite (-7.234e-05) Quartz (-7.549e-05)	Illite (6.291e-05)	1.302e+01
3	45% UHB 55% VGW	Gypsum (-4.335e-04)	Dolomite (2.164e-04)	1.161e+01
4	45% UHB 55% VGW	Gypsum (-5.589e-04)	Calcite (3.822e-04)	1.215e+01
2019 UHB mixing with VGW - UHA Final Water - Pe increase (4 → 7)				
1	0% UHB 100% VGW	Kaolinite (-1.864e-04) Quartz (-1.945e-04)	Illite (1.621e-04)	6.017e+00
2	45% UHB 55% VGW	Gypsum (-2.785e-04)	CO2(g) (9.521e-04)	1.332e+01
3	45% UHB 55% VGW	Gypsum (-4.336e-04)	Dolomite (2.162e-04)	9.824e+00
4	45% UHB 55% VGW	Gypsum (-5.588e-04)	Calcite (3.820e-04)	1.037e+01

Table 4. Inverse PHREEQC models evaluating the geochemical evolution of 2019 Upper Horn Bedrock (UHB) and Village Groundwater (VGW) mixing to produce the final water chemistry observed in the Upper Horn Alluvium (UHA).