ENVIRONMENTAL AQUEOUS GEOCHEMISTRY OF URANIUM IN AQUIFER SYSTEMS, PAJARITO PLATEAU, NEW MEXICO

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Abstract

Los Alamos National Laboratory (LANL) has conducted multidisciplinary research on uranium since the mid-1940s. Treated and non-treated industrial aqueous discharges, mainly containing isotopically natural uranium with a $^{238}U/^{235}U$ atom ratio = 137.8813, have been discharged to Acid, Pueblo, Los Alamos, and Mortandad Canyons. These discharges provide recharge to shallow alluvial and perched-intermediate depth groundwater and the regional aquifer at typical depths of <24 meters (m), 183 m, and 296 m, respectively. Background water chemistry in the regional aquifer varies from an oxidizing (median Eh = 332 mV), calcium-sodium-bicarbonate to a sodium-calcium-bicarbonate composition. Small amounts of enriched uranium, containing a $^{238}U/^{235}U$ atom ratio <137.8813, have been locally measured in alluvial groundwater within Mortandad Canyon. The Environmental Protection Agency drinking water standard for total uranium and the New Mexico Water Quality Control Commission standard for dissolved uranium is 0.126 µM (0.030 mg/L). Upper tolerance limits have been calculated by the New Mexico Environment Department and LANL for numerous solutes naturally present in the regional aquifer. These include total dissolved uranium (5.336 nM, 0.00127 mg/L), dissolved oxygen (0.253 mM, 8.10 mg/L), nitrate(N) (0.056 mM, 0.78 mg/L), chloride (0.084 mM, 2.98 mg/L), perchlorate (4.324 nM, 0.00043 mg/L), and sulfate (0.061 mM, 5.84 mg/L). Background concentrations of dissolved uranium in the regional aquifer increase with average groundwater age, especially east of the Rio Grande. Concentrations of dissolved uranium(VI) elevated above background, with a maximum value of 0.0504 µM (0.012 mg/L), have been detected in several regional aquifer monitoring wells installed in Pueblo, Los Alamos, and Mortandad Canyons. Concentrations of nitrate, perchlorate, and/or tritium coreleased with aqueous uranium(VI) species are elevated above background in the regional aquifer at several monitoring wells. Thermochemical calculations suggest that uranyl carbonate-carbonato complexes, including $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $Ca(UO_2)_2(CO_3)_3^0$, and $UO_2(CO_3)_3^{4-}$, dominate in the regional aquifer. These uranyl complexes are mobile under oxidizing and circumneutral pH conditions characteristic of the regional aquifer at Los Alamos. Concentrations of natural reductants, including dissolved hydrogen sulfide, dissolved ferrous iron, dissolved organic carbon, and solid organic matter are not sufficient to enhance reduction of uranium(VI) to uranium(IV) aqueous complexes (UOH^{3+} and $U(OH)_4^0$). The regional aquifer is undersaturated with respect to amorphous UO_2, uraninite, and coffinite. Background concentrations of dissolved uranium(VI) in upper sections of the regional aquifer are initially controlled by partial dissolution of soluble volcanic glass followed by specific adsorption of uranium(VI) complexes onto hydrous ferric oxide and cation exchange of uranyl cation with calcium on smectite surfaces. Upper sections of the regional aquifer beneath the Pajarito Plateau are enriched in silica and groundwater shows variable saturation with respect to uranophane ($Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$) and are oversaturated with respect to haiweeite ($Ca(UO_2)_2Si_6O_{15} \cdot 5H2O$) depending on pH and calcium and silica activities.

Purpose and Scope

Evaluate natural and anthropogenic sources of uranium in the regional aquifer at Los Alamos National Laboratory.

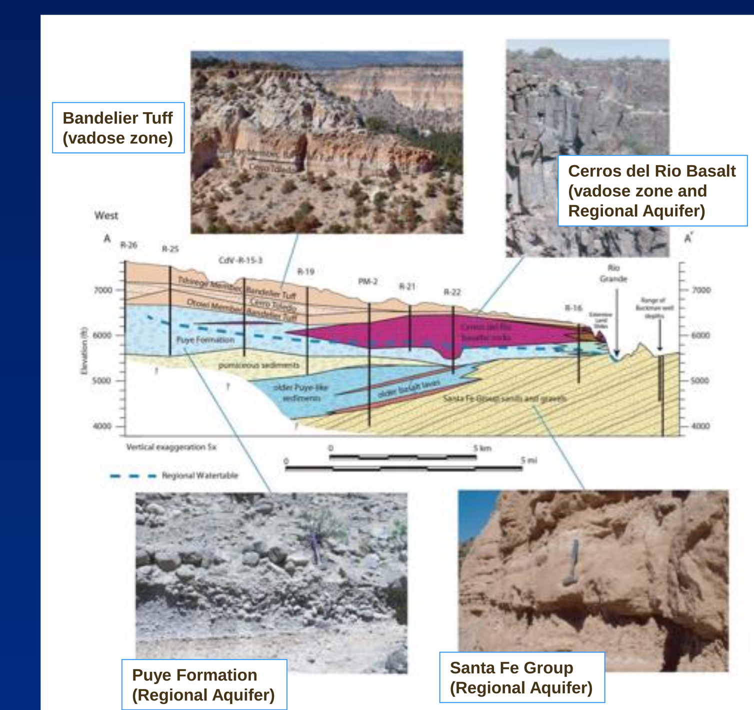
Topics of interest for uranium include:

- **Aqueous speciation**
- **Groundwater age**
- **Adsorption**
- **Mineral equilibrium**

Analytical Methods for Uranium

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (EPA Methods 6020 and 200.8)
Lowest method detection limit is 2.52E-10 M (0.06 µg/L), depending on sample dilution.
Quantitation limit is 2.1E-09 M (0.5 µg/L).
Thermal ionization Mass spectrometry

Hydrostratigraphy of the Pajarito Plateau



Median Background Composition of the Regional Aquifer, Los Alamos, New Mexico

Analyte	Millimoles/Liter	Milligrams/Liter
Ca	0.29	11.8
Mg	0.13	3.22
Na	0.47	10.9
K	0.04	1.64
Cl	0.06	2.09
SO_4	0.03	2.69
HCO_3	1.20	73.32
F	0.01	0.27
SiO_2	1.22	72.90
ClO_4	3.23e-06	0.00032
NO_3-NO_2(N)	0.03	0.44 (KM Mean)
U	1.51e-06	0.00036

Sources of Natural and Anthropogenic Uranium

Natural **- Whole rock concentrations of uranium range from <1 mg/kg to >15 mg/kg.**

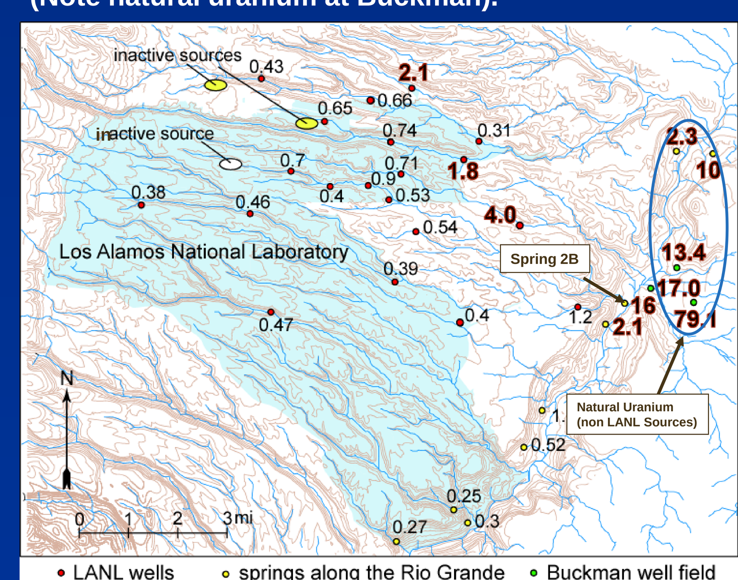
Uranium-bearing solids, at pH 7, have varying solubilities in which silica glass ($10^{-2.71}$ M) is the most soluble and $ZrSiO_4$ ($10^{-15.54}$ M) is the least soluble.

Natural total dissolved uranium concentrations in the regional aquifer range from $10^{-9.30}$ to $10^{-8.24}$ M (0.12 to 1.37 mg/L) beneath the Pajarito Plateau.

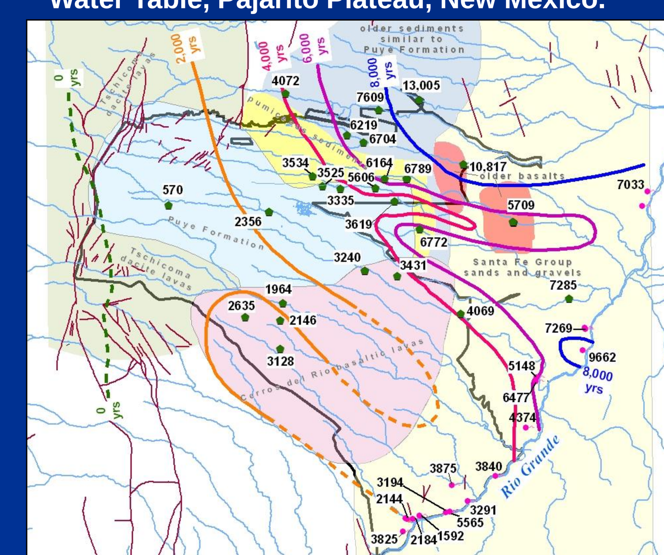
Aqueous solubilities of soddyite, uranophane, and haiweeite are $10^{0.39}$ M, $10^{17.29}$ M, and $10^{-7.04}$ M, respectively.

Anthropogenic **– Natural, enriched, and depleted uranium is used for research purposes at LANL.**

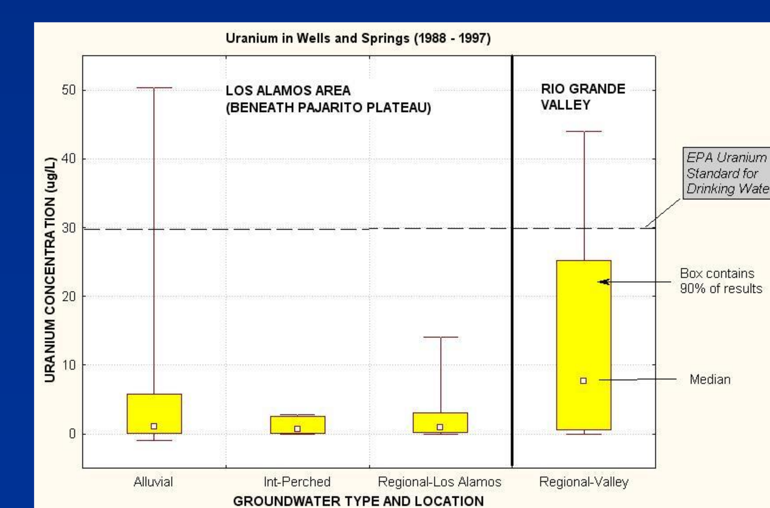
Mean Concentrations of Dissolved Uranium (µg/L) in the Regional Aquifer, Pajarito Plateau, (1 to 5 samples per location, mean background uranium = 0.43 µg/L). (Note natural uranium at Buckman).



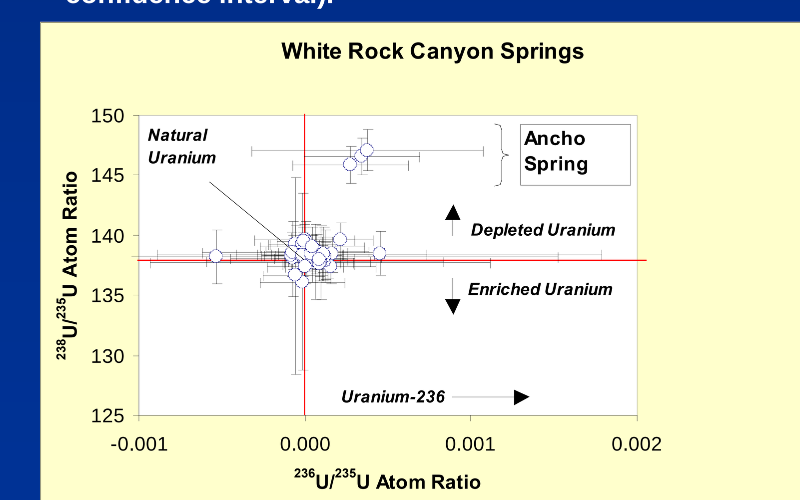
Unadjusted Radiocarbon Ages of DIC and Hydrogeology near the Regional Aquifer Water Table, Pajarito Plateau, New Mexico.



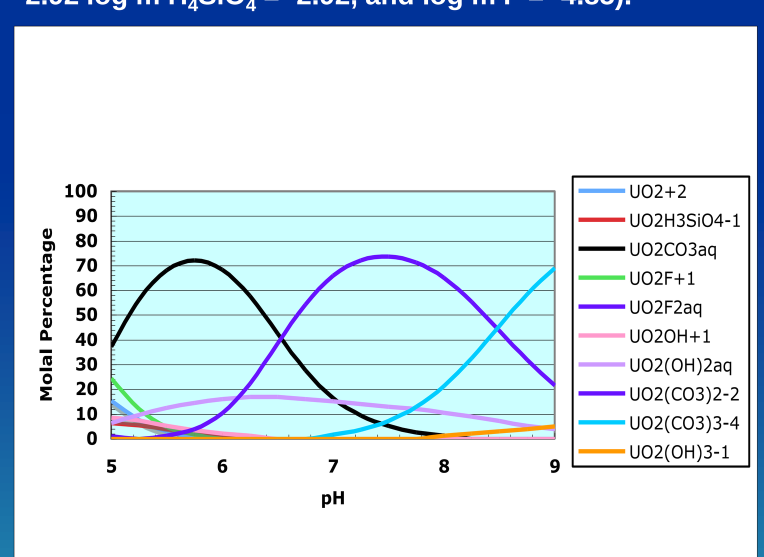
Concentrations of Uranium in Groundwater, Pajarito Plateau and Española Basin, NM (Gallaher et al. 1994).



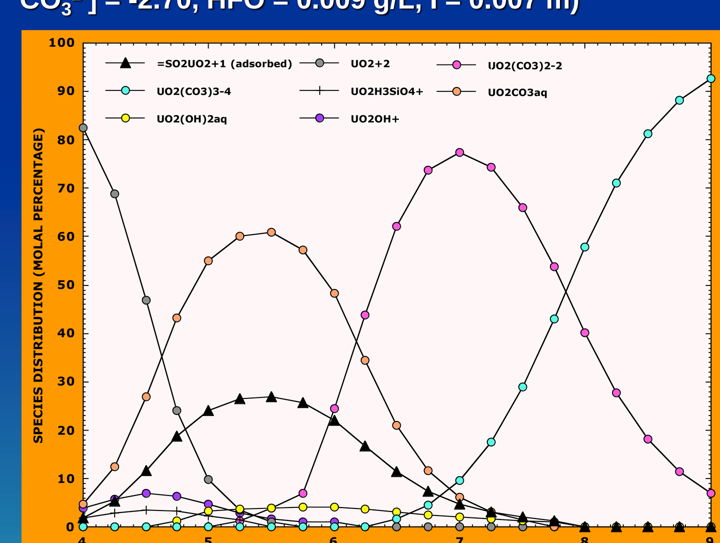
Uranium Isotopic Composition of White Rock Canyon Springs (Gallaher et al., 1994).(Gallaher et al. 1994). Error bars show three-sigma uncertainty (99th percent confidence interval).



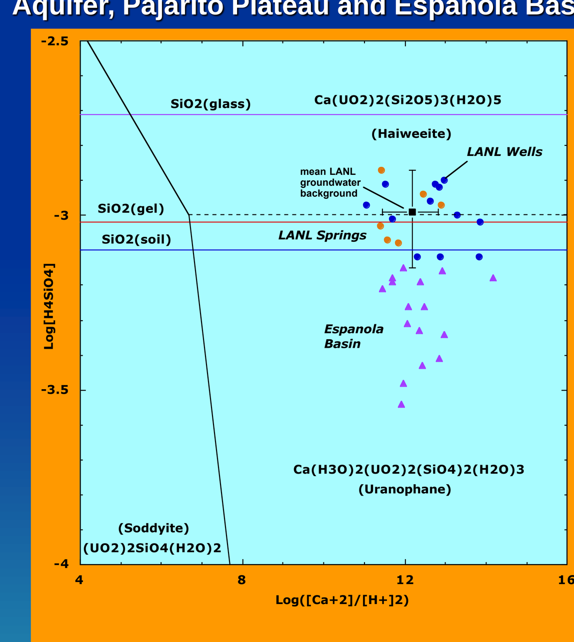
Calculated Distribution of Dissolved Uranium(VI) Species (MINTEQA2), Regional Aquifer (Median Composition), Los Alamos, New Mexico (log m U(VI) = -8.82, log m total CO_3 = -2.92 log m H_4SiO_4 = -2.92, and log m F = -4.85).



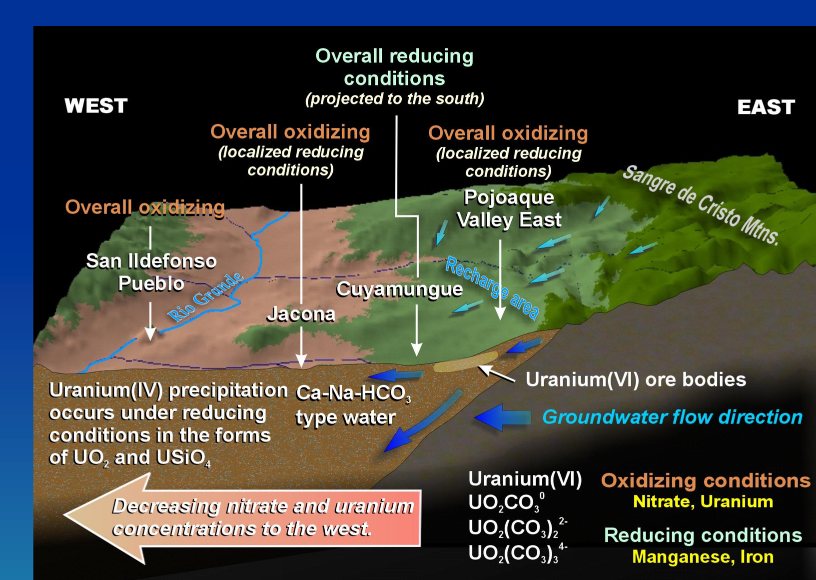
Surface Complexation Modeling (MINTEQA2) of U(VI) Onto Hydrous Ferric Oxide (HFO), Spring 2B, White Rock Canyon (log $[UO_2^{2+}]$ = -7.0, log $[H_4SiO_4]$ = -2.90, log [total CO_3^{2-}] = -2.70, HFO = 0.009 g/L, I = 0.007 m)



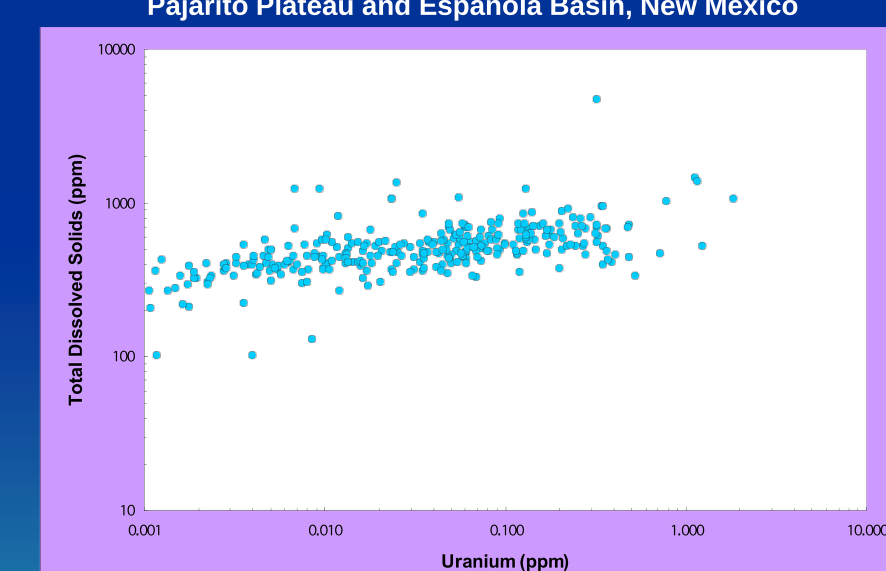
Log $[H_4SiO_4]$ Versus Log ($[Ca^{2+}]/[H^+]^2$) Diagram at 25ºC and 1 Bar Pressure for the Regional Aquifer, Pajarito Plateau and Española Basin



Hydrogeochemical Conceptual Model For Part of the Española Basin (east of the Rio Grande), New Mexico



Total Dissolved Solids Versus Dissolved Uranium, Pajarito Plateau and Española Basin, New Mexico



Summary and Conclusions

Determining natural and anthropogenic sources of uranium within the Pajarito Plateau requires knowledge of groundwater age and geochemical processes controlling fate and transport of this actinide in groundwater.

Background concentrations of natural uranium increase with average groundwater age in the Española Basin (near and east of the Rio Grande).

Presence of perchlorate, tritium, and/or nitrate is useful in determining the source of uranium in groundwater at LANL.

Background concentrations of dissolved uranium vary from 5.04e-10 to 5.76e-09 molar (0.12 to 1.37 µg/L) in regional aquifer groundwater beneath the Pajarito Plateau, NM

Uranium(VI) transport to the regional water table at Los Alamos, New Mexico has occurred at several locations. Dissolved concentrations of anthropogenic uranium are less than 6.30e-08 molar (15 µg/L).

Much higher concentrations of natural uranium are observed east of the Rio Grande in portions of the Española Basin that are hydrologically isolated from the Pajarito Plateau.

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