Award Number G10AP00053

Final Technical Report: Using $^{238}U/^{235}U$ analysis to understand U ore deposit formation at Redox Fronts

Craig C. Lundstrom
Dept of Geology
University of Illinois
208 Natural History Bldg
Urbana, IL 61801
(217) 244-6293
Fax: (217) 244-4996

Thomas M Johnson
Dept of Geology
University of Illinois
208 Natural History Bldg
Urbana, IL 61801
(217) 244-xxxx
Fax: (217) 244-4996

Final Technical Report: Using $^{238}U/^{235}U$ analysis to understand U ore deposit formation at Redox Fronts

Craig C. Lundstrom, Thomas Johnson

Abstract:

Introduction:

Uranium is an element of dramatic importance to modern society for two reasons. First, U represents a major energy resource that avoids a large carbon footprint. Second, the growth of the nuclear energy and weapons industries has produced numerous locations of U contamination in the subsurface that require remediation. Advancing knowledge in both of these areas hinges on understanding the process of biogeochemical reduction of U in the subsurface: For instance, the major form of economic ore deposit in the U.S. reflects chemical reduction of U during groundwater flow (tabular sands and roll front deposits) while biogeochemical reduction is the primary means of immobilization and hence remediation of anthropogenic U contamination.

Understanding chemical reduction of U in the natural environment of an aquifer presents considerable challenges. Simply monitoring concentration changes of any redox active element through time or space presents the challenge of separating the effects of processes such as sorption and dilution from that of reduction. All of these processes can significantly change U concentrations; however, only reduction leads to longer term immobilization as U(IV) is highly insoluble. Unfortunately, the redox processes involved with U are notoriously complex, involving interplay of groundwater flow, reductants in subsurface solids, and microbial dynamics. Over the past few years we have developed the tool of high-precision $^{238}U/^{235}U$ isotope ratio analysis to reveal and quantify U reduction reactions in the subsurface. This follows similar stable isotope ratio methods already used as indicators of nitrate, sulfate, chromate, and selenate reduction. Combining $^{238}U/^{235}U$ analysis with more established $^{234}U/^{238}U$ measurements, we have sought to understand the process of U reduction in several environments including this project involving a natural aquifer setting where chemical reduction of U was previously inferred to be occurring along the flowpath (Ivanovich et al., 1992; Cowart and Osmond, 1977; Osmond et al., 2000).

This project funded sample collection and analysis of uranium isotopes from waters from the Carrizo Aquifer in southern Texas. The purpose was to examine whether isotopic signatures of chemical reduction of U occurred as U concentration systematically decreased along the flowpath. Previous work on the Carrizo showed a systematic change in both the U concentration and the $^{234}U/^{238}U$ ratio down flow path; this generally corresponded to greater depths and more reducing water conditions (Cowart and Osmond, 1977).

Sampling Methods:

Graduate students Valerie Finlayson and Matt Kyrias drove with Lundstrom to Texas in June of 2010. There they met with Larry Akers of the Pleasanton Water District who had arranged sampling appointments at 12 different wells pulling water from the Carrizo (generally all in NW Atascosa County). Sampling locations are shown in Fig. 1. The previous U concentration map of Cowart and Osmond (1977) was used as a general guide for expected concentrations in order to make estimates of the amount of water needed to collect at a given site. This was important as the amount of water needed from some wells was on order 40 L based on previously reported concentrations.

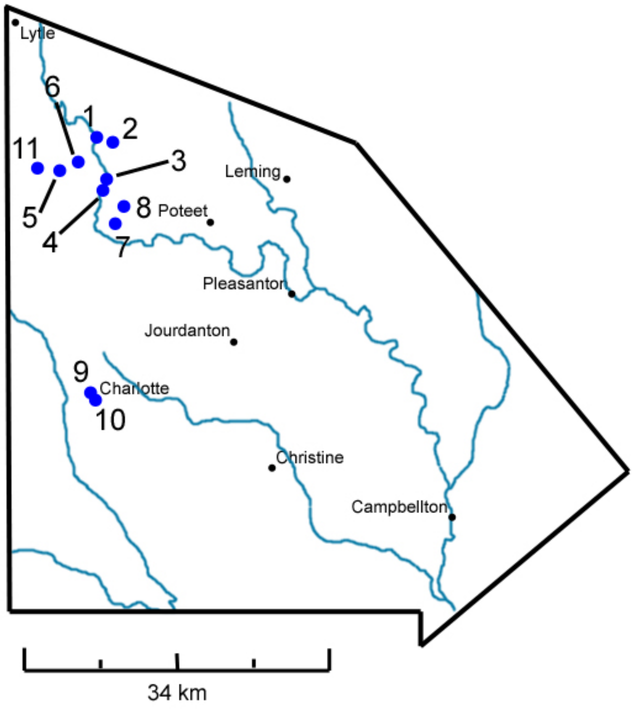

Fig. 1 Map of study area (irregular border defines Atascosa county) with dots indicating wells sampled.

Although the major task of the proposal tasks involved measurement of high precision $^{238}U/^{235}U$ and $^{234}U/^{238}U$ isotope ratios only, we decided that the study would benefit from addition of collection of two other pieces of data for each sample. Because a great deal of previous work including that of Osmond and Cowart, 1976, examined the (^{234}U)/(^{238}U) (parentheses denote activity ratio) of waters in the context of U-series disequilibria, we also made effort to measure ^{230}Th/^{238}U. In addition, our work on U reduction has focused on assessing the ability of different microbes to reduce U in the subsurface. Therefore, we also went to extra efforts to obtain microbial samples from the aquifer using methods developed at Illinois by Craig Bethke and Rob Sanford. Indeed, Kyrias had just finished his Masters degree developing such sampling techniques and therefore was an ideal team member for sample collecting.

In order to collect microbiological samples along with waters, we had to follow strict protocols to avoid contaminating the biological sample. The sampling apparatus involved placing a sterile 0.4 um filter within a stainless steel holder. Prior to a single water sample collection, the apparatus was sterilized with alcohol to prevent any cross contamination of microbiological material. After the water was pumped through the filter paper, the paper was immediately bagged and placed into a cooler. The water samples were acidified with ultra purity HNO_3 and placed in cold storage for return to Illinois.

Water was purged through the system until temperature and pH stabilized, then passed through the filter and into cleaned sample containers containing enough ultra pure nitric acid to result in 1% acidity when sampling finished. Temperature, specific conductivity and pH along with sampling location are given in Table 1. While most wells contained the necessary spicket/tap needed to connect the outlet hose to the filtering assembly, sample 7 from Ronnie Wheeler's farm was taken without filtering. Because of the difficulties with particulate effects (sorption), this sample is not discussed further.

Table 1: Pleasanton, Texas
Groundwater Sampling Event

Well Sample #	Location	Date Sampled	Time Sampled	pH	T (°C)	Spec. Cond. (µS)
1	Ross Forbe's Farm	6/8/10	11:10	6.11	24.7	541
2	The Farm	6/8/10	12:14	7.08	24	713
3	Water Plant 1 (Benton City, TX)	6/8/10	13:39	5.9	24.8	310
4	Water Plant 2 (Benton City, TX)	6/8/10	14:27	5.1	24.4	251
5	Turf Farm 1	6/8/10	15:44	5.58	24.1	432
6	Turf Farm 2	6/8/10	16:46	5.73	24.2	383
7	Ronnie Wheeler's Farm	6/9/10	-	6.49	25.8	980
8	near Ronnie Wheeler's Farm	6/9/10	9:44	5.86	24.7	346
9	Charlotte, TX Supply Well 1	6/9/10	11:38	6.9	36	609
10	Charlotte, TX Supply Well 2	6/9/10	13:55	6.93	35.5	608
11	Farm with lots of snakes	6/9/10	16:20	5.67	25.6	244

Methods of isotopic analysis:

Upon returning to Illinois, a preliminary determination of the U concentration of each sample was performed by removing a small aliquot of each sample and spiking it with ^{236}U to determine the concentration by isotope dilution methods. This was needed in order to allow us to add the proper amount of U double spike (a ^{233}U-^{236}U solution of known isotopic composition) as well as ^{229}Th spike for determination of ^{230}Th contents. These spikes were added either to the whole sample or to an aliquot of the sample big enough to give enough U for a high quality ^{238}U/^{235}U (hereafter, δ^{238}U) analysis (when U concentrations or water amounts allowed this). Once spikes were added, the water samples were warmed slightly through use of heat lamps and given weeks of time to ensure spike sample equilibration. It was determined during the initial concentration measurement time that the concentrations in waters from samples 3 and 4 were extremely low and isotopic analyses of 40L of either of these samples by themselves would not be possible. For this reason these two samples were combined in hopes of gaining a usable δ^{238}U analysis; in the end, this was not possible.

After spike equilibration had taken place, a high purity solution of $FeCl_3$ was added to each sample in order to facilitate co-precipitation. U and Th were then coprecipitated with $Fe(OH)_3$ by raising the pH following standard preconcentration methods.

Originally, the chemical purification of U involved standard anion chromatography methods involving AG1-X8 resin in nitric and HCl media. However, assessment of yields in this and other projects led us to examine a recently published method (Weyer et al., 2008) using the U-TEVA resin (made by Eichrom). This method significantly improved yields and effectiveness of the chemical separation of matrix from the purified U. Blanks remained low and all data reported below reflect processing through this latter method.

The processed samples were run on Nu Plasma HR multi-collector inductively coupled plasma mass spectrometer. The purified U samples were introduced as 2% nitric acid solutions into a DSN-100 desolvating nebulizer and the resulting aerosols transported in the mass spectrometer with Ar gas. After collecting baselines at half masses above and below the masses of interest, isotope ratio data were collected over 60 cycles of 10s integration. Signals were collected on masses 238, 236, 235, 234 and 233. Instrumental methods generally followed those given in Bopp et al. (2009).

A variety of U standards were run for QA over the course of the study. ^{238}U/^{235}U ratios calculated from reduction of the double spike isotope ratio change are reported relative to NIST SRM 112a using standard delta notation. The absolute value of this standard can drift over the course of an analytical session so three secondary standards (IRMM REIMP18A (U-A), NIST SRM 129a, and an in house standard Jackpile (made from a known isotopically heavy U roll front deposit)) are run within the samples to ensure that the offset between SRM112a and these other standards remains constant; the analytical precision reflects the standard deviation on the offset between SRM112a and these other standards during the course of the run and is generally 0.1 per mil (2s).

Results

Table 2 presents a summary of results for the U concentration and isotope analyses of the collected samples returned to Illinois. Sample 7 was not analyzed as explained above and samples 3+4 were not successfully analyzed for δ^{238}U although we were able to get U concentration and (^{234}U)/(^{238}U) data.

Table2

sample#	**U conc. (ppb)**	**δ238U**	**(234U)/(238U)**
5	56	0.10	0.745
6	8	0.10	0.770
8	0.21	0.00	0.780
9	0.26	0.07	0.864
10	0.15	0.00	0.950
11	2.6	0.30	0.760
1	0.39	-0.41	1.130
2	0.21	-0.10	1.120
3,4	0.0025	n.a.	2.496

Concentrations of U vary from 56 ppb to ~2.5 ppt (2.5 ng /L). Since we generally need on order 200ng for δ^{238}U analysis, it is immediately clear why no analysis of the combined 3 and 4 well sample was obtained. δ^{238}U for the rest of the samples varies between -0.41 and +0.10, within the range previously found for natural waters with the variations out side of analytical precision. (^{234}U)/(^{238}U) ranges from 0.745 in the highest U content waters up to 2.496 in the very depleted 3 + 4 well sample.

Comparing U concentration results in a spatial sense with those reported previously by Cowart and Osmond (1977) shows that for whatever reason, significant changes in water concentration have occurred in the 35 years since their study (Fig. 2). This is not all that strange given the amount of pumping that has occurred in this aquifer during this time but the discrepancy could also reflect analytical issues with the previous alpha spectrometry analyses. Generally the spatial pattern conforms to the previous distribution—our three highest concentration samples all come from the NW region of the study area; there is a general decrease in concentration away from this region. The lowest concentration samples we found came from the Benton water supply wells, which are located near the tongue of lower concentration that protrudes northward as observed by Cowart and Osmond (1977).

The primary goal was to assess if significant isotopic changes in δ^{238}U occurred in tandem with U concentration changes that were interpreted to reflect chemical reduction in the subsurface. The correlation between U concentration and δ^{238}U is weak (Fig. 3). The isotopically lightest sample is intermediate in U concentration although no data exist for the sample much lower in concentration (3+4). The most U rich samples are isotopically heavy relative to the intermediate concentration samples. Thus, there is a general change to isotopically lighter waters as concentration decreases, consistent with expectation.

There is a clear relationship between U concentration and (^{234}U)/(^{238}U) as observed previously by Cowart and Osmond (1977) and many other groundwater studies. As U content decreases, this activity ratio dramatically increases (Fig. 4).

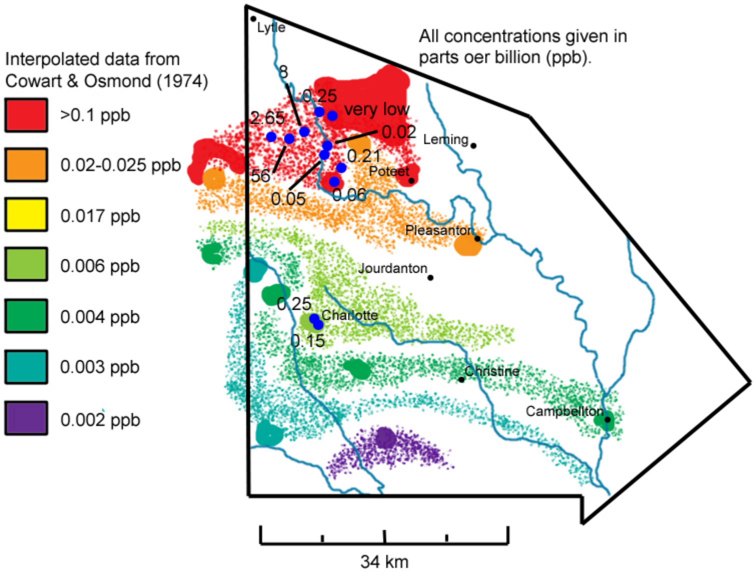

Fig. 2 Map of study area (irregular border defines Atascosa county) with dots indicating wells sampled with concentrations measured here given. Also shown is a colored contour of the previous U concentration distribution measured by Cowart and Osmond, 1977.

Discussion

The results of our δ^{238}U analyses are ambiguous concerning an indication of isotopic fractionation of U during chemical reduction. There is a general trend to lower $\delta^{238}U$ with decreasing concentration (Fig. 3) which is the direction of change consistent with both laboratory experiments and observations during stimulated bioreduction in the field (Bopp et al., 2010).

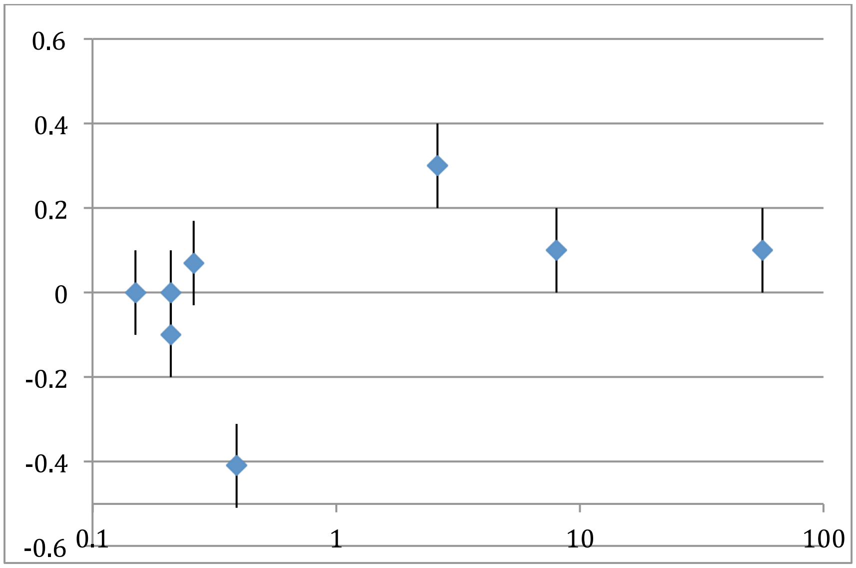

Fig. 3. $\delta^{238}U$ vs U concentration. A general decrease of $\delta^{238}U$ occurs with U decreasing, consistent with observed changes with chemical reduction; however a great deal of scatter exists.

The results for $(^{234}U)/(^{238}U)$ show very good consistency with previous results for ground waters in general and for the Carrizo specifically (Fig. 4). It has long been known that $(^{234}U)/(^{238}U)$ are elevated in low U concentration waters. This is generally attributed to the role of alpha recoil in accelerating the addition of ^{234}U into waters due to damage to crystal lattices (Ivanovich et al., 1992). In the Cowart and Osmond (1977) study, a pronounced increase in $(^{234}U)/(^{238}U)$ occurs as U concentrations decrease with $(^{234}U)/(^{238}U)$ reaching values as high as 9.0. In high U content waters, $(^{234}U)/(^{238}U)$ is often significantly lower than 1.0 (secular equilibrium with Carrizo waters reaching values as low as 0.71 (Cowart and Osmond, 1977). This is similar to the $(^{234}U)/(^{238}U)$ value of our most U rich water (well 5) which has a $(^{234}U)/(^{238}U)$ of 0.745.

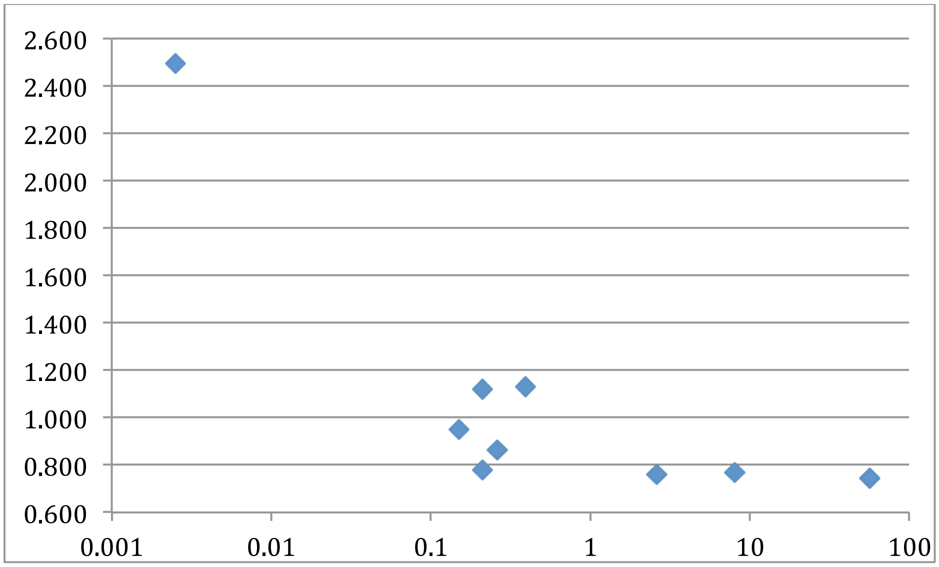

Fig. 4. (^{234}U)/(^{238}U) vs U concentration. A pronounced increase of (^{234}U)/(^{238}U) occurs with U decreasing. This is consistent with many previous observations and is generally attributed to the effect of alpha recoil on enriching 234U in low concentration U waters.

Given the extreme concentration change found in the combined 3 + 4 well, it is unfortunate that no analysis of the δ^{238}U was achieved. This amount of reduction (if it is reduction) is orders of magnitude greater than observed in other waters in the field undergoing chemical reduction; for instance, the concentration change in the Rifle waters is of order a factor of 3 (Bopp et al., 2010); that U concentrations change by 4 orders of magnitude in the Carrizo would imply very large δ^{238}U change. However, one parallel finding in our work at Rifle has been that pods of what appears to be natural reduction of U at Rifle show no isotopic fractionation; well 3 + 4 appears to represent an area of low U concentration due to its being a zone of great reduction potential. Thus, it may be that very large δ^{238}U might not be found.

Future work will attempt to relate microbial communities in Carrizo to those observed in other aquifer systems including those at Rifle. The microbiological samples from Carrizo have been sent to a lab in Maryland for characterization of the ecological community. We are currently performing laboratory experiments with a variety of microbes to assess the U isotope fractionation with different microbes. Thus we hope to be able to integrate our knowledge of the community in the Carrizo with known fractionation behavior to better understand the process of chemical reduction occurring in this aquifer.

References

Bopp, C. J., C.C. Lundstrom, T.M. Johnson, and J.J. Glessner, Variations in $^{238}U/^{235}U$ in Uranium Ore Deposits: Isotopic Signatures of the U Reduction Process? Geology, 37, 611-614 2009.

Bopp C.J. IV, C. C. Lundstrom, T.M. Johnson, R. Sanford, P. Long and K. Williams Uranium $^{238}U/^{235}U$ Isotope Ratios as Indicators of Reduction: Results from an *in situ* Biostimulation Experiment at Rifle, CO, USA, *Envir. Sci. Tech.* 44, 5927–5933, 2010.

Cowart, J. B. and J. K. Osmond, Uranium isotopes in groundwater: Their use in prospecting for sandstone-type uranium deposits, Journal of Geochemical Exploration, 8: 365-379, 1977.

Ivanovich, M., A. G. Latham and T. L. Ku. Uranium-series disequilibrium applications in geochronology.; 2. Uranium-series disequilibrium; applications to Earth, marine, and environmental sciences. M. Ivanovich and R. S. Harmon. Oxford, United Kingdom, Clarendon Press: 62-94, 1992.

Osmond, J. K. and J. B. Cowart. U-series nuclides as tracers in groundwater hydrology. Environmental Tracers in Subsurface Hydrology. P. Cook and A. L. Herczeg. Boston, Kluwer Academic Publishers: 145-174, 2000.