



Uranium isotope composition of waters from South Texas uranium ore deposits



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ABSTRACT

Redox conditions and associated changes in mobility of uranium (U) are tightly linked to a multitude of challenges connected with U mining in sandstone-hosted deposits and new methods that directly measure reduction or oxidation of U can inform on these questions. A novel proxy for understanding U redox chemistry has recently emerged, the volume dependent isotopic fractionation of uranium-238 (²³⁸U) from uranium-235 (²³⁵U). Novel measurements of ²³⁸U/²³⁵U isotopic ratio are combined with measurements of the more commonly utilized uranium-234/uranium-238 activity [(²³⁴U/²³⁸U)] ratio, as both isotopic ratios can be measured simultaneously. However, application of both U isotopic ratios in the contexts of exploration and environmental remediation of U ores requires characterization of these isotopic ratios across a variety of redox settings. Here, ²³⁸U/²³⁵U and (²³⁴U/²³⁸U) ratios are examined from eight transects in two U ore bodies (the Rosita and Kingsville Dome deposits) in South Texas; these sites are classic roll front deposits and exhibit a wide variety of both natural and altered redox conditions. Across all transects it is observed that (²³⁴U/²³⁸U) ratios decrease systematically towards the ore body from both the oxidizing and reducing sides, irrespective of whether the site has been mined or not. This pattern reflects geologically recent and significant U leaching and mobility and is characteristic of active roll fronts. Overall $\delta^{238}\text{U}$ values in these transects decrease systematically towards the reducing zone. A simple Rayleigh fractionation model, where U ore is deposited from an increasingly isotopically depleted reservoir of dissolved U best explains the overall trend; very negative $\delta^{238}\text{U}$ values likely reflect multiple cycles of U deposition and dissolution. The South Texas data set indicates that both (²³⁴U/²³⁸U) ratios and $\delta^{238}\text{U}$ values can be variable at an individual mine site. However, overall low (²³⁴U/²³⁸U) ratios and negative $\delta^{238}\text{U}$ values are characteristic of active roll front deposits. The comprehensive U isotopic composition of both ores and well waters represents a powerful new tool in prospecting of sandstone-hosted U ore and in environmental remediation following extraction of U ore.

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1. Introduction

Globally, the extraction and utilization of U ores are projected to grow over the coming decades (NEA and IAEA, 2012). Associated with the increased demand for U are both challenges of resource exploration and concerns about U contamination in surface and ground waters as a result of resource extraction. Ore deposits hosted in sandstones are likely to play an increasingly important role in future U resources (Boytssov, 2012). Indeed, U mineralization in sandstone is the most abundant type of U deposit and constitutes about one-quarter of the world's identified U resources (Boytssov, 2012). Beyond this, U ores in sandstones constitute a major share of world production because the cut-off grade for

such deposits is often significantly lower than magmatic or metamorphic counterparts. However, the very same geologic and hydrologic conditions that generate this type of U deposit also often create a situation where U is naturally mobile in and around such ore bodies, particularly after geochemical conditions are perturbed as a result of mining. Thus, both the exploration and environmentally sustainable extraction of sandstone-hosted U deposits rely on detailed understanding of U mobility in water.

Mobilization of U is fundamentally linked to solubility changes that result from reduction and oxidation (redox) processes. Uranium occurs predominantly in the tetravalent (U_{IV}) and hexavalent (U_{VI}) oxidation states. The tetravalent form is common in both crustal silicate minerals and ore minerals, such as uraninite, pitchblende, and coffinite (Ivanovich and Harmon, 1992). In contrast, the oxidized form of uranium (U_{VI}) occurs principally as the uranyl ion (U_{VI}O₂⁺), which is highly

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soluble (e.g. Langmuir, 1978). The uranyl ion is also found in U-bearing phosphates and carbonates (Ivanovich and Harmon, 1992). Broadly speaking, however, solid U occurs in the reduced form and oxidized U is aqueous or highly soluble in oxidizing fluids. Within sandstone-hosted U deposits, these redox induced changes in U solubility result in ore formation. For example, the classic U roll front forms when U-rich waters move across a transition from oxidizing to reducing conditions, causing deposition of U at the redox boundary (Spirakis, 1996).

The relationship between redox transformations and U mobility is utilized in the in situ recovery (ISR) processes of U extraction. This U recovery process involves the underground leaching and removal of U by oxidizing fluids (Campbell et al., 2007). This method results in minimal disturbance of the ground surface and does not produce tailings. However, it is critical to insure that ISR operations do not result in elevated U concentrations in ground water. Post extraction remediation generally involves reverse osmosis treatments and recirculation of groundwaters and a challenge that often arises at ISR sites is that natural U concentrations in the ground water outside the mineralized production zone are not only high, but also spatially and temporally variable. This complicates both determinations of “background” U levels and concentration monitoring as a method of assessing remediation.

New methods that directly measure reduction or oxidation of U can inform on many of these issues encountered in ISR mining of U. A novel proxy for understanding U redox chemistry has recently emerged, the volume dependent isotopic fractionation of ^{238}U from ^{235}U (e.g. Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Montoya-Pino et al., 2010; Brennecke et al., 2011; Kendall et al., 2013; Murphy et al., 2014; Basu et al., 2015). Measurements of $^{238}\text{U}/^{235}\text{U}$ isotopic ratios are a potentially powerful tool for understanding U mobility in the context of sandstone-hosted U ores. Novel measurements of $^{238}\text{U}/^{235}\text{U}$ isotopic ratios are likely to also be combined with measurements of the ($^{234}\text{U}/^{238}\text{U}$) ratio, as both isotopic ratios can be measured simultaneously. New conceptual models of ($^{234}\text{U}/^{238}\text{U}$) ratio variability within U ores have also recently been developed (Lowson and McIntyre, 2013a,b; Lowson, 2013), but require further validation. Application of both U isotopic ratios in either the exploration or environmental remediation of sandstone-hosted U bodies requires characterization of these isotopic ratios across a variety of redox settings. Here, $^{238}\text{U}/^{235}\text{U}$ and ($^{234}\text{U}/^{238}\text{U}$) ratios from two U ore bodies in South Texas are reported; these sites exhibit a wide variety of both natural and altered redox conditions. This data set will provide new understanding of these isotopic ratios in the context of U ore formation and ISR extraction.

2. Study location

Uranium ore is found in several significant deposits within the wedge of clastic Tertiary sediments that comprise the Gulf Coastal Plain of South Texas (Eargle et al., 1975; Hobday and Galloway, 1999; Ambrose, 2007). This study focuses on the Rosita and the Kingsville Dome sites, which are hosted in fluvial sandstones of the Goliad Formation (Fig. 1). Host formations are Miocene in age and, like most U ores within the Texas Coastal Plain, these deposits are considered classic roll-front deposits (Fig. 2).

Formation of U roll front deposits requires oxidative leaching of U from a source rock, the transport of this leached U in ground water, and precipitation/concentration of the U by reducing conditions (Fig. 2). The transition to a reducing environment can be caused by a variety of agents including: carbonaceous material, sulphides, hydrocarbons and ferro-magnesium minerals (Ambrose, 2007). The location and shape of these ores are the results of both spatial distribution of the redox boundary and local hydrology, with the classic “c” shape of such deposits resulting from differences in the transmissivity of ground water within the aquifer (Spirakis, 1996). In some cases, the ore deposition process is reversed, causing the formation of secondary ore minerals, migration of the roll front, or, if ongoing, introduction of U into ground waters. In South Texas, oxidative weathering of the Catahoula

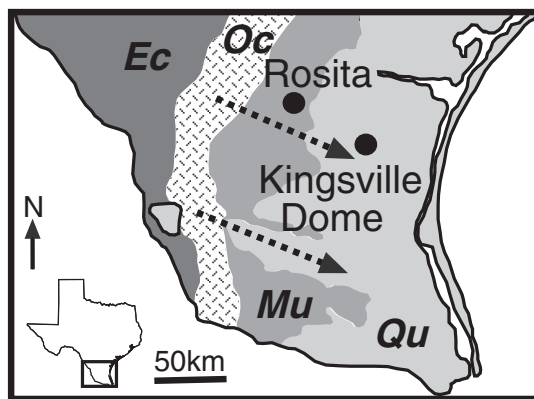


Fig. 1. Generalized geologic map of South Texas (after Bureau of Economic Geology, 1991). The Rosita and Kingsville Dome U sites are represented by circles. Regional ground water flow (dashed arrows) is towards the Gulf of Mexico. Light gray (Qu) indicates the distribution of undivided Quaternary sediments. Intermediate gray (Mu) designates the distribution of undivided Miocene sediments. The hashed pattern (Oc) indicates the distribution of Oligocene Catahoula Formation, a U-rich volcanic tuff. Dark gray (Ec) indicates the distribution of Eocene sediments belonging to the Clairborne Group.

Formation, which generally underlies the Goliad and Formation (Fig. 1), is considered the source of U ores.

The Goliad formation that host these U ores is up to 600 feet thick in the subsurface and are comprised of interbedded sands and shales, producing stacks of laterally-continuous aquifers separated by clay-rich aquitards (Hobday and Galloway, 1999). Sandstone units are lithic arenites containing minor carbonate and volcanics (Hobday and Galloway, 1999). These sandstones are characterized by high hydrologic conductivity. In contrast, floodplain shales deposited during channel migration have low hydraulic conductivity and form aquitards. Gulfward movement of ground water broadly follows the original depositional axes of the fluvial systems (Hobday and Galloway, 1999). At the Rosita site, ground water flow is to the southeast. At Kingsville Dome, original ground water flow rates were also to the southeast, but historic and ongoing pumping unrelated to ore extraction has locally reversed ground water flow directions. Ground water flow rate at the Rosita Site is on the order of a few meters per year, and original flow rates at Kingsville Dome were likely in the same range (Uranium Resources Incorporated, unpublished data).

At both South Texas sites, localized reducing conditions lead to the deposition of U ore within sandstone. The Gulf Coastal Plain is characterized by low organic concentrations, and hydrogen sulfide gas derived from petroleum reservoirs is implied as the primary reducing agent in the region (Eargle et al., 1975). This is particularly true at the Kingsville Dome site, which occurs in close proximity to normal faults that may facilitate gas migration (Eargle et al., 1975).

The Rosita and Kingsville dome sites have experienced ISR extraction by Uranium Resources Incorporated (URI). Natural waters at both the Rosita and Kingsville Dome sites exceeded federal drinking water standards for U prior to any U extraction efforts. The ISR procedure at these sites consists of pumping native ground water with an added oxidant (O_2) into the aquifer from a series of injection wells. Dissolved U is then removed via a recovery well and harvested using exchange resins. All stages of the leaching process are present at the Rosita site; these include an area that has not yet been leached, an area that has been leached but not restored, and areas that have been leached and remediated (Table 1). In contrast, all sites at the Kingsville Dome site have been leached and remediated (Table 1). In addition to extraction wells, baseline wells are present in the ore zone to monitor changes in water chemistry; within the ore zones, waters exhibit a variety of chemical changes, particularly changes in redox state and U concentration, as a result of the ISR process. Monitoring wells encircling the ore body are installed at both the Kingsville Dome and Rosita sites; these well are present in both the oxidizing and reducing zones. No significant change

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