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In-situ production of natural ^{236}U in groundwaters and ores in high-grade uranium deposits

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ABSTRACT

In nature, primordial ^{236}U has long since decayed to concentrations below detection. However, measurement of ^{236}U produced *in-situ* by neutron capture on ^{235}U in high-grade uranium deposits is made possible by recent advances in accelerator mass spectrometry (AMS). The detection of appreciable quantities of ^{236}U in groundwaters may reflect local uranium mineralisation, and thus prove useful in uranium exploration and potential age and ore grade estimations.

Nine mineralised sediments from the South Australian Beverley North sandstone-hosted uranium deposits have $^{236}U/^{238}U$ ratios ranging from $(1.57 \pm 0.43) \times 10^{-12}$ to $(9.09 \pm 0.55) \times 10^{-12}$, and U concentrations that vary by almost three orders of magnitude, ranging from 78.9 to 24,200 μg/g. Overall, the samples with the highest [U] have higher $^{236}U/^{238}U$ ratios, consistent with the generation of higher neutron fluxes with one notable exception with anomalously high [U] and a relatively low $^{236}U/^{238}U$ ratio. The observed variability in the $^{236}U/^{238}U$ ratio both within the deposits themselves, and between deposits may reflect heterogeneous mineralogy, elemental composition and water contents, which can affect the neutron flux generated within the samples.

A single groundwater sampled within mineralisation from the Pepegoona West deposit yielded a $^{236}U/^{238}U$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$. This is the first published data detecting natural, non-anthropogenic ^{236}U in groundwater in contact with a uranium deposit. The $^{236}U/^{238}U$ isotopic composition of the single groundwater sample is indistinguishable from that of the mineralised sediments from the same deposit. This is interpreted to reflect isotopic equilibration between the mineralisation and groundwater, rather than the *in-situ* production of ^{236}U by neutron capture on dissolved ^{235}U in the waters due to the low [U] typical of these highly reducing groundwaters. ^{236}U appears to have limited mobility in the Pepegoona West groundwater system, as evidenced by the lack of signature in groundwaters sampled from nearby wells in low-grade and un-mineralised portions of the deposit. This suggests that the detection of ^{236}U in the highly reducing groundwaters prevalent in this area may not be applicable as a proxy for uranium mineralisation. However, use of this technique as a potential exploration tool may have greater success in other areas with different hydrogeological conditions, specifically where the groundwaters are oxidising and uranium has a greater solubility as U(VI) complexes.

1. Introduction

In nature, uranium primarily exists as three long lived, α-emitting isotopes: primordial ^{238}U ($t_{1/2}$ = 4.47 billion years) and ^{235}U ($t_{1/2}$ = 700 million years); and radiogenic ^{234}U ($t_{1/2}$ = 246,000 years). Primordial ^{236}U has long since decayed to concentrations below detection using modern analytical techniques due to the short half-life of 23.4 million years. Although the main source of ^{236}U present in the environment is the by-product of anthropogenic activity, natural ^{236}U can be produced in high-grade uranium ores by neutron capture on ^{235}U. At depths below the influence of cosmic rays (~30 m), the sources of neutrons are: (1) (α, n) reactions, where α-particles produced by radioactive decay of ^{238}U, ^{235}U and ^{232}Th interact with light elements such as Li, Be, Na, Mg, Si and Al within the matrix, forming unstable atoms that return to the ground state by neutron emissions and (2) by the spontaneous and neutron-induced fission of ^{238}U and ^{235}U respectively (Hotchkis et al., 2000). Notionally, ^{236}U can also be produced by α-decay of ^{240}Pu ($t_{1/2}$ = 6563 years). However, in high-grade ores, appreciable abundances of ^{240}Pu are unlikely, as ^{240}Pu is produced by neutron capture on ^{239}Pu, which in turn is produced by neutron capture on ^{238}U (Curtis et al., 1999).

In the average crustal rock containing ~4–10 μg/g uranium, neutron fluxes are expected to be quite low, with an estimated natural $^{236}U/^{238}U$

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isotopic ratio of 1×10^{-14} to 5×10^{-14} (Steier et al., 2008). However, in high-grade uranium ores and ore concentrates (UOCs), the neutron flux is much greater, with $^{236}U/^{238}U$ ratios of the order of ~10^{-12} to ~10^{-10} being reported (Rokop et al., 1972; Zhao et al., 1994a, 1994b; Zhao et al., 1997; Ovaskainen et al., 1997; Richter et al., 1999; Berkovits et al., 2000; Wilcken et al., 2007, 2008; Srncik et al., 2011). Based on $^{236}U/^{238}U$ isotopic ratios measured in uranium ores, the possibility of detecting natural $^{236}U/^{238}U$ ratios elevated above background ratios in groundwaters in close proximity to high-grade uranium mineralisation was recognised as a potential exploration tool for deposits buried at depth (Wilcken et al., 2007, 2008; Fifield, 2008).

Here we investigate whether natural ^{236}U produced *in-situ* in uranium mineralisation by neutron capture on ^{235}U can be detected in groundwaters in the vicinity of mineralisation. To do this, $^{236}U/^{238}U$ isotopic ratios have been determined by accelerator mass spectrometry (AMS) in mineralised sediments from several South Australian sandstone-hosted deposits. Additionally, groundwaters within and adjacent to high-grade (>1 wt.% U) mineralisation have been analysed with the aim to evaluate the effectiveness of natural ^{236}U in groundwater as a tracer of uranium mineralisation.

2. Geological context

2.1. Hydrogeological setting

The semi-arid Frome Embayment, South Australia, is host to several sandstone-hosted uranium deposits and is considered a highly prospective region for future exploration (Fig. 1, inset). For this study, mineralised sediment samples and groundwaters have been collected from the Four Mile East and Four Mile West and the Pepegoona, Pepegoona West and Pannikan 'roll-front' deposits (with the latter three collectively called the Beverley North deposits). These deposits are located adjacent to the northeastern flanks of the Flinders Ranges, approximately 550 km north of Adelaide, South Australia (Fig. 1).

Sandstone-hosted uranium deposits form by the reduction of U(VI) to U(IV) at a redox interface within a permeable sandstone aquifer that is confined above and below by impermeable aquitards. 'Roll-front' deposits are so named because of the C-shaped mineralisation front that forms due to the continued redissolution/reprecipitation of uranium minerals as a consequence of ongoing groundwater movement (Hostetler and Garrels, 1962). The highest-grade portion of the roll is typically in the 'nose' which forms at a redox interface, whilst the 'limbs' of the C-shape mineralisation are typically of lower grade. Low temperature sandstone-hosted uranium deposits are typically lower-grade (up to several weight percent U) than other higher temperature magmatic style or unconformity related deposits.

The Four Mile East, Pepegoona, Pepegoona West and Pannikan deposits are located within the fluviatile sands of the Eocene Eyre Formation (SKM, 2008, 2010; Märten et al., 2011, 2012; Birch et al., 2013). The Four Mile West deposit is hosted within diamictite sands within the Cretaceous Cadna-Owie Formation (Stoian, 2010). The Four Mile West deposit was discovered in 2009, and additional uranium deposits have been found in the area in recent years. Each deposit spans 1–5 km across (Fig. 1); however the true extent of mineralisation is poorly delineated as exploration in the region is ongoing. The deposits are located at greater than 220 m depth below the surface, well below the zone of influence from cosmic rays. The Pepegoona deposit occurs as four stacked, irregularly shaped arcuate 'roll-fronts' (Murphy, 2013; Murphy et al., 2014). The Pepegoona West deposit comprises five complex stacked roll-fronts, and the ore geometry is strongly controlled by the presence of local faults. The Pannikan deposit is a single, well-defined 'roll-front'. The Four Mile East deposit is comprised of several arcuate, irregularly shaped roll-fronts, whilst the Four Mile West deposit is a single, well-defined 'roll-front' (Märten et al., 2011, 2012; Birch et al., 2013). At all deposits, the primary ore mineral is uraninite with minor coffinite present interstitially or precipitated on grain boundaries. Typical uranium concentrations within high-grade mineralisation range from 1 to 2 wt.% U. However, U concentrations are highly variable both within and between deposits. The ages of these deposits are at present poorly constrained. The deposits are hosted within Eocene (Four Mile East, Beverley North) and Cretaceous aged sediments (Four Mile West), which provides maximum ages of uranium mineralisation of 56 to 34 Ma and 144 to 65 Ma, respectively (Märten et al., 2011, 2012; Birch et al., 2013).

The Beverley North deposits are currently being mined by Heathgate Resources Pty Ltd. using *in-situ* recovery (ISR) mining techniques. This

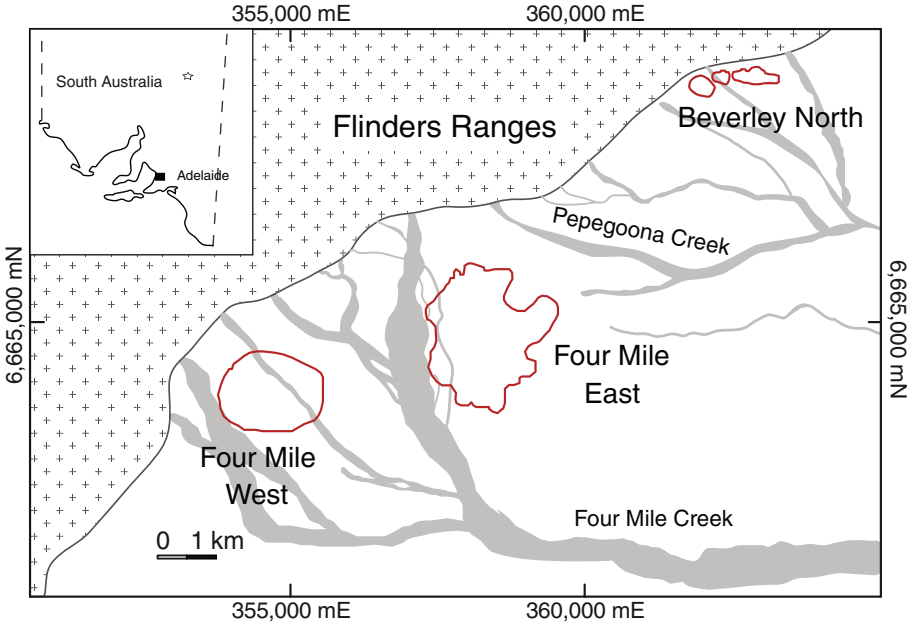

Fig. 1. Map showing the location of the Four Mile West, Four Mile East and Beverley North sandstone-hosted deposits. The Beverley North deposits consist of (from left to right) the Pannikan, Pepegoona West and Pepegoona deposits. For this study, mineralised sediments were sampled from the Beverley North deposits. Inset: South Australia map showing location of the deposits (star). Grid references are Geocentric Datum Australia GDA94 coordinates.