

*Applications of U-series disequilibria and ^{236}U isotopes:
Understanding low temperature redox uranium
mineralisation*

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THESIS ABSTRACT

Variations in uranium isotopic compositions are well documented in groundwaters and uranium ores. This is due to the different geochemical and radiogenic behaviours of uranium nuclides during water-rock interactions, and neutron capture processes. These variations are particularly evident within sandstone-hosted uranium deposits which are formed by the low temperature reduction of U(VI) to U(IV). This thesis investigates the behaviour of uranium-series and ^{236}U nuclides during ore formation processes using U and Th concentrations, U-series isotopic ratios, $^{238}\text{U}/^{235}\text{U}$ ratios and $^{236}\text{U}/^{238}\text{U}$ ratios determined within a suite of groundwaters and mineralised sediments in the vicinity of several South Australian deposits.

Groundwater ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the vicinity of the Four Mile East and Pepegooona deposits show significant disequilibrium, however do not display a systematic trend with the presence of mineralisation. The complex geology limits the applicability of using ($^{234}\text{U}/^{238}\text{U}$) activity ratios in groundwater as an exploration tool in this area.

$^{238}\text{U}/^{235}\text{U}$ ratios in mineralised sediments from the Pepegooona deposit span a *ca.* 5 ‰ range, the largest U isotopic variation found thus far in natural samples. Groundwaters are characterised by $^{238}\text{U}/^{235}\text{U}$ ratios enriched in the light isotope, whilst mineralised sediments are preferentially enriched in the heavier isotope.

$^{236}\text{U}/^{238}\text{U}$ ratios of the order of $\sim 10^{-12}$ were determined within mineralised sediments from the Beverley North deposits. A single groundwater sampled within high-grade mineralisation provides a $^{236}\text{U}/^{238}\text{U}$ ratio similar to that of the mineralised sediments. This is the first published data detecting natural ^{236}U in groundwater. The limited mobility of ^{236}U suggests that detection of ^{236}U in groundwaters may not be a suitable exploration tool in this area.

Lastly, U-series isotopes were determined within mineralised sediments from the Beverley Deep South deposit. The results indicate uranium mobilisation has occurred over the past Myr, which may be coincident with climate change or neotectonism during the Quaternary.

STATEMENT OF ORIGINALITY

I declare that this is an original piece of research and that the work presented in this thesis entitled “Applications of U-series disequilibria and ^{236}U isotopes: Understanding low temperature redox uranium mineralisation” has not previously been submitted for a degree or submitted as part of the requirements for part of a degree to any other university or institution. All data, interpretations and conclusions are my own, except where appropriately acknowledged.

I certify that any help and assistance that I have received whilst conducting this research and during the writing of this thesis is appropriately acknowledged. Similarly, all information sources and literature used throughout this thesis have been appropriately referenced.

Melissa Jean Murphy

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SUMMARY

Variations in uranium isotopic compositions are well documented in groundwaters and uranium ores. This is due to the different geochemical and radiogenic behaviours of uranium nuclides during water-rock interactions, and a result of neutron capture processes. These variations are particularly evident within sandstone-hosted uranium deposits which are formed by the low temperature reduction of U(VI) to U(IV). This thesis investigates the behaviour of uranium nuclides during ore formation processes using U and Th concentrations, U-series isotopic ratios (including $^{234}\text{U}/^{238}\text{U}$), $(^{230}\text{Th}/^{232}\text{Th})$, $(^{238}\text{U}/^{232}\text{Th})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios), $^{238}\text{U}/^{235}\text{U}$ ratios and $^{236}\text{U}/^{238}\text{U}$ ratios from a suite of groundwaters and mineralised sediments in the vicinity of several South Australian sandstone-hosted uranium deposits.

U concentrations and $(^{234}\text{U}/^{238}\text{U})$ activity ratios were analysed in a suite of groundwaters in the vicinity of the South Australian Four Mile East and Pepegooona sandstone-hosted uranium deposits to assess the use of $(^{234}\text{U}/^{238}\text{U})$ activity ratios in groundwaters as a tool for uranium exploration. The groundwaters show significant disequilibrium, with $(^{234}\text{U}/^{238}\text{U})$ activity ratios ranging from 0.889 ± 0.005 to 2.815 ± 0.005 . This variation is inferred to be the result of preferential leaching and/or alpha recoil processes during water-rock interactions. $(^{234}\text{U}/^{238}\text{U})$ isotopic ratios in the groundwaters in direct contact with high-grade mineralisation may reflect isotopic equilibration with the mineralisation itself. This might suggest that the Pepegooona and Four Mile East deposits have either formed or experienced recent remobilisation (within the past million years), as evidenced by disequilibrium $(^{234}\text{U}/^{238}\text{U})$ ratios in the groundwater sampled in mineralisation. The complex geology of these deposits however, limits the applicability of using $(^{234}\text{U}/^{238}\text{U})$ activity ratios in groundwater as an exploration tool in this area, however might prove to be more successful elsewhere.

$^{238}\text{U}/^{235}\text{U}$ ratios were measured in mineralised sediment samples and groundwaters from the Pepegooona deposit. Groundwaters are characterised by $^{238}\text{U}/^{235}\text{U}$ ratios enriched in the light isotope, with $^{238}\text{U}/^{235}\text{U}$ ratios between 137.508 ± 0.007 and 137.820 ± 0.007 . Mineralised sediments showed a preferential enrichment in the heavier isotope, exhibiting the largest U isotopic variation found thus far in natural samples, with $^{238}\text{U}/^{235}\text{U}$ ratios ranging from 137.267 ± 0.007 to 137.913 ± 0.016 . The preferential incorporation of ^{238}U during precipitation of uranium minerals leaves the groundwaters enriched in ^{235}U , corresponding to a Rayleigh fractionation factor (α) of 0.9997 to 0.9999. This may be attributed to the nuclear field shift effect during reduction of U(VI) to U(IV) during ore formation processes. This supports the use of $^{238}\text{U}/^{235}\text{U}$ as a potential tracer for redox processes, and may be insightful in studies of palaeoredox conditions.

Neutron capture processes within high-grade uranium ores can result in the production of natural ^{236}U . The detection of appreciable quantities of natural ^{236}U in groundwaters may reflect the presence of nearby mineralisation, and thus prove useful in uranium exploration. $^{236}\text{U}/^{238}\text{U}$ ratios from nine mineralised sediments from the Beverley North deposits were determined, with ratios ranging from $(1.16 \pm 0.06) \times 10^{-12}$ to $(9.48 \pm 0.83) \times 10^{-12}$. A single groundwater sampled within high-grade mineralisation from the Pepegooona West deposit provides a $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$. This is the first published data detecting natural ^{236}U in groundwater. The $^{236}\text{U}/^{238}\text{U}$ isotopic composition of the single groundwater is very similar to 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. ^{236}U however, has limited mobility in the Pepegooona 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 groundwaters may not be a suitable exploration tool in this area. This technique however, may have greater success in other areas with different hydrogeological conditions.

Lastly, in order to constrain the timescales of mineralisation within the Beverley Deep South deposit, U-series isotopes from mineralised sediments have been determined, and the validity of U-series dating techniques is evaluated. ^{230}Th -U ages from a limited number of samples have yielded two preliminary ages of ~30 ka and ~220 ka. Additionally, simple two-point isochrons suggest an isochron age of ~450 ka for mineralised sands, and an almost zero age for the mineralised clay-rich samples. Evidence for open-system behaviour however, contributes to a degree of uncertainty on these ages. Despite this, the inferred ages correspond remarkably well to periods of increased rainfall in the Lake Frome region and speleothem growth in semi-arid South Eastern Australia. The U-series isotopic compositions of the sediments are indicative of uranium mobilisation over the past Myr, which may be coincident with changes in climate or neotectonism during the Quaternary.

CHAPTER I

THESIS INTRODUCTION

1.1 INTRODUCTION AND SCOPE

Uranium is the heaviest naturally occurring radioactive element on Earth, and has been of considerable interest not only due to its potential applications in nuclear weaponry and as an alternate energy source, but also due to the unique geochemical, physical, radiogenic and neutron capture properties of the isotopes of uranium and uranium-series (U-series) decay chains.

The nuclides within the U-series isotopes decay chains (comprising the uranium-series, actinium-series and thorium-series decay chains) encompass a wide range of half-lives, and exhibit very different geochemical behaviours during geological processes (reviewed in Bourdon et al., 2003, Figure 1.1). Uranium is a redox sensitive metal, existing in nature as two primary oxidation states - hexavalent U(VI) and tetravalent U(IV). In contrast, thorium is only found in nature in the tetravalent Th(IV) state (Gascoyne, 1992). During water-rock interactions, U-series isotopes are fractionated not only by their geochemical behaviours during oxidation/reduction, but also as a result of radioactive processes such as alpha recoil mobilisation of radiogenic nuclides (e.g. Kigoshi, 1971; Fleisher, 1980) and preferential leaching of ^{234}U (e.g. Rosholt et al., 1963). Such fractionation processes results in a state of ‘disequilibrium’ between the parent/daughter nuclides of the decay chain.

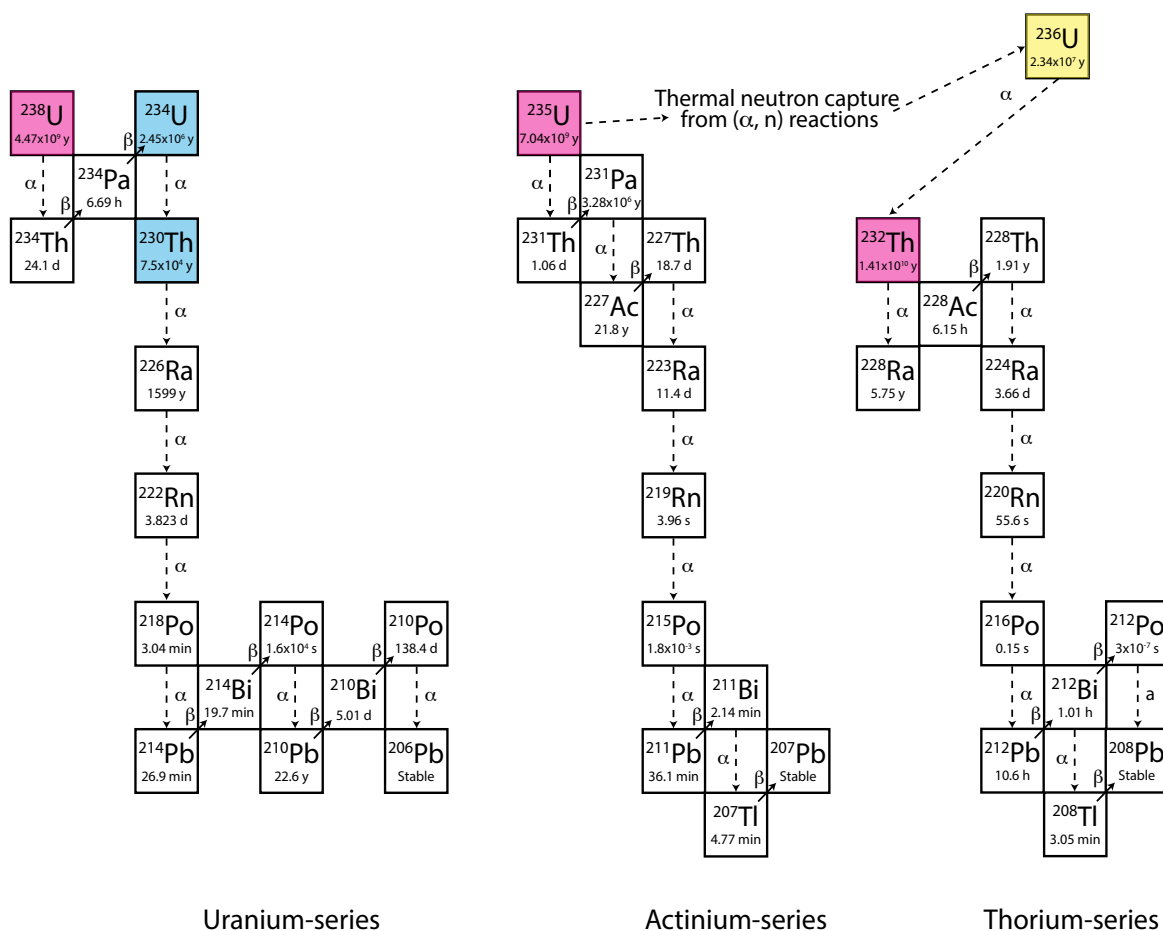


Figure 1.1: Isotopes of the uranium-, actinium- and thorium- decay series shown with their half-lives and principle modes of decay. Also shown is the nuclear process through which natural ^{236}U can form by thermal neutron capture on ^{235}U . Isotopes of interest in this study are highlighted, in particular: Primordial ^{238}U (shown in pink), the parent nuclide of the $(4n+2)$ uranium decay series, which decays to stable ^{206}Pb via a series of radiogenic intermediaries, including ^{234}U and ^{230}Th (shown in blue); Primordial ^{235}U (shown in pink), the parent nuclide of the $(4n+3)$ actinium-series, which decays to stable ^{207}Pb ; Primordial ^{232}Th (shown in pink), the parent nuclide of the $(4n)$ Th-series which decays to stable ^{208}Pb ; and natural ^{236}U (shown in yellow) formed by neutron capture processes. For this study, anthropogenic ^{236}U is not considered.

Additionally, fractionation between the long considered invariant parent nuclides of the U-series decay chains, ^{238}U and ^{235}U have recently been reported in a wide range of environments (e.g. Hiess et al., 2012; Stirling, 2012). The largest fractionations have been identified in samples formed in low temperature redox environments such as sandstone-hosted uranium deposits and speleothems (Stirling et al., 2007; Weyer et al., 2008; Bopp et

al., 2009; Brennecke et al., 2010a). Fractionation between ^{238}U and ^{235}U isotopes can either be attributed to mass-dependent equilibrium or mass-independent kinetic processes, however have largely been attributed to the mass-independent ‘nuclear field shift effect’ (Bigeleisen, 1996; Schauble, 2007). Furthermore, in high-grade uranium ores, appreciable quantities of ‘natural’ ^{236}U can be produced by thermal neutron capture on ^{235}U (e.g. Fifield, 2008). These fractionation and neutron capture properties inherent to uranium and U-series isotopes, in conjunction with their range of half-lives, have allowed for their widespread application in the earth and planetary sciences. The importance of these isotopes to low temperature (<50 °C) redox-controlled uranium ore formation processes will be discussed further below.

Sandstone-hosted uranium deposits are an important source of uranium, both in Australia and worldwide (IAEA, 2009). Sandstone-hosted uranium deposits form at a redox interface within a permeable sandstone aquifer confined above and below by impermeable aquitards by the reduction of U(VI) to U(IV) during low temperature water-rock interactions (Hostetler and Garrels, 1962; Hobday and Galloway, 1999). Due to the mechanisms through which sandstone-hosted uranium deposits are formed, fractionation of U-series isotopes is not only expected in the deposits themselves, but also in the groundwaters from which the mineralisation has precipitated. The fundamental role of hydrologic processes in the formation of sandstone-hosted uranium deposits suggests that investigation of U-series isotopic compositions and ‘natural’ ^{236}U isotopic abundances may prove useful in the exploration for such deposits.

With increasing global demand for uranium, an improved understanding of the behaviour of uranium and U-series isotopes and its decay products during low temperature ore formation processes is important to advance uranium exploration technologies, particularly for sandstone-hosted type deposits which often lack a surface expression. Additionally, the study of the mobility of U-series isotopes during water-rock interactions within ‘sandstone-hosted’ type uranium deposits can inform models for nuclear waste disposal and groundwater contamination studies. This thesis uses mass-spectrometric techniques to investigate the natural isotopic abundances and of behaviour of ^{236}U and U-series isotopes during uranium mineralisation processes formed by water-rock interactions, with a particular focus

on sandstone-hosted uranium deposits. The ultimate aim of this thesis is to evaluate the usefulness of ^{236}U and U-series isotope systematics as an exploration tool, and to provide constraints on the nature and timing of mineralisation processes. The isotopes of interest in this study are shown in Figure 1.1, including: ^{238}U , ^{235}U , ^{234}U , ^{232}Th and ^{230}Th from the U-series decay chains. Additionally, ‘natural’ ^{236}U formed by neutron capture processes will be investigated.

This study will consider the ^{236}U and U-series isotopic signatures both within the mineralised sediments, and within groundwaters sampled in the vicinity of several high-grade sandstone-hosted uranium deposits located within the semi-arid Frome Embayment, South Australia. This region is host to numerous sandstone-hosted uranium deposits (e.g. the Beverley, Beverley North, Four Mile, Gould’s Dam, Honeymoon and Oban deposits, Figure 1.2) and is considered highly prospective for future exploration. The primary focus of the PhD thesis will be the southern-most extension of the Beverley deposit (Beverley ‘Deep-South’), and the recently discovered Beverley North and Four Mile deposits (which comprise of the Pepegooona, Pepegooona West and Pannikan deposits; and Four Mile East and Four Mile West deposits respectively).

These deposits are located at several hundred meters depth below the surface, with no surficial expression. As the geology and hydrogeology are well constrained as a result of uranium exploration and drilling in the region by operating mining company Heathgate Resources Pty Ltd, these deposits are ideally suited for this study. The relevant geological and hydrogeological background for each of the deposits is detailed in the appropriate chapters, and to save repetition, will not be duplicated.

The Beverley and Beverley North deposits are currently being mined by *in-situ* recovery (ISR), whereby an acidic, oxidising solution is injected into the host aquifer in contact with the mineralisation, thereby dissolving the uranium minerals. The mining solution is then pumped to the surface for processing. As an environmental requirement of mining by ISR, the ore deposits are girt by groundwater wells screened at different aquifer depths to monitor potential groundwater contamination. This provides a rare opportunity to study the ^{236}U and U-series isotopic signatures within a well-defined, redox-controlled,

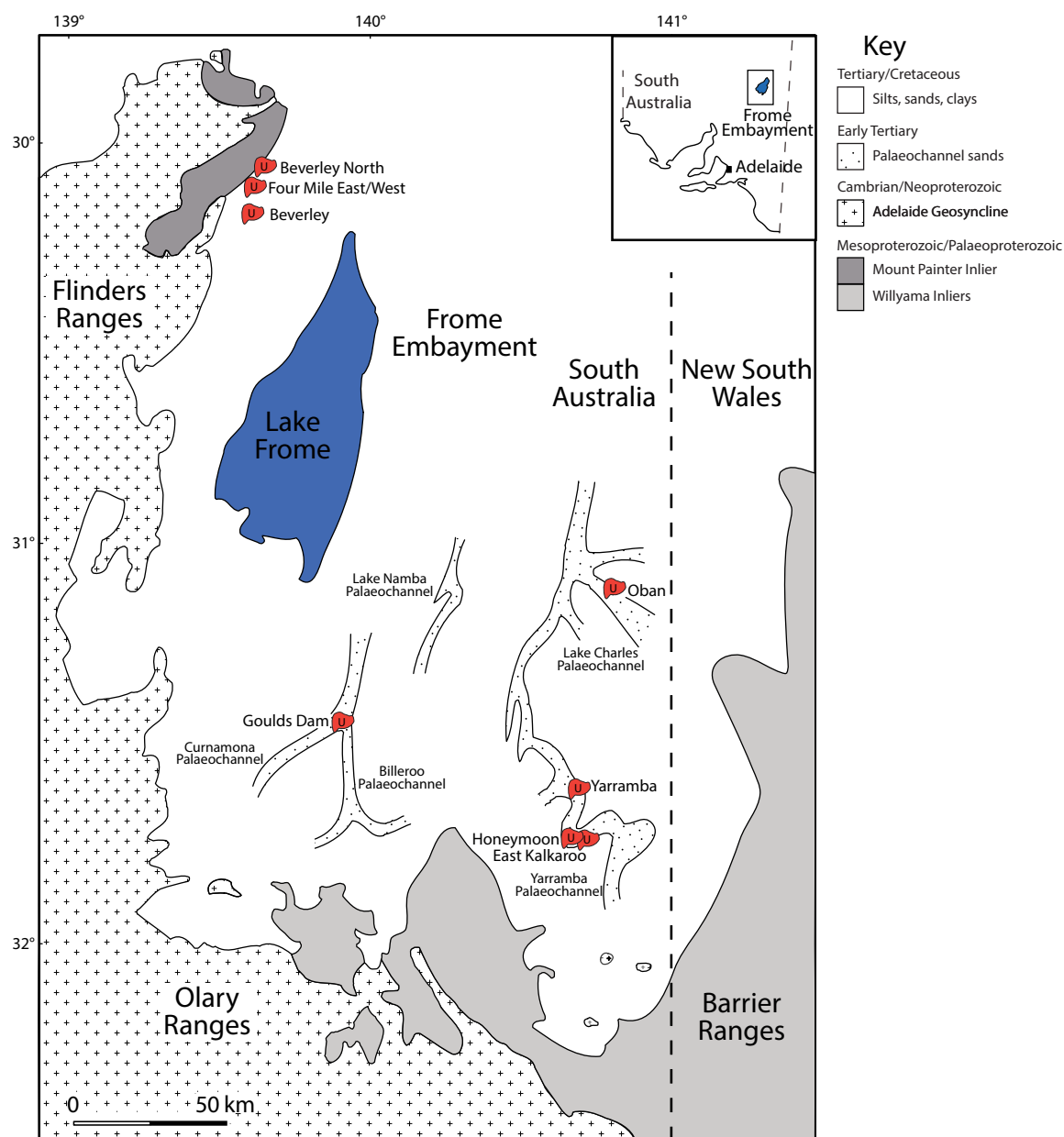


Figure 1.2: Major palaeodrainage channels and geological domains within the Frome Embayment, South Australia, with known sandstone-hosted type uranium deposits marked in red (modified after Curtis et al., 1990). Grid references are geographical coordinates. Weathering of the Mount Painter and Willyama Inliers, or sediments derived therefrom; are considered the most likely sources of uranium for the northern and southern Frome Embayment sandstone-hosted uranium deposits. Inset: location of the Frome Embayment within South Australia.

uranium mineralised environment.

Specifically in this PhD thesis U and Th concentrations; U-series isotopic activity ratios (including $(^{234}\text{U}/^{238}\text{U})$, $(^{230}\text{Th}/^{232}\text{Th})$, $(^{238}\text{U}/^{232}\text{Th})$, $(^{230}\text{Th}/^{238}\text{U})$, where ratios in parentheses are used to distinguish activity ratios from isotopic abundance ratios); $^{238}\text{U}/^{235}\text{U}$ ratios and $^{236}\text{U}/^{238}\text{U}$ ratios have been determined in a suite of groundwaters and mineralised sediments.

1.2 BACKGROUND

1.2.1 Sandstone-hosted uranium deposits

Sandstone-hosted uranium deposits typically occur in medium to coarse-grained sandstones, deposited within a continental fluvial or marginal marine sedimentary environment (Dahlkamp, 2009; IAEA, 2009). Sandstone-hosted uranium deposits can be divided into four major sub-types: tabular, basal-channel, roll-front or tectonic-lithologic (Figure 1.3). These classifications are based on the configuration and spatial relationship of the mineralised redox front (although these major sub-types can be somewhat gradational into each other). Sandstone-hosted deposits are different to surficial-type uranium deposits (such as calcrete- or silcrete-type deposits), which are broadly defined as Tertiary to Recent aged, near-surface uranium concentrations hosted within sediments or soils, e.g. Yeelirrie, Australia (IAEA, 2009).

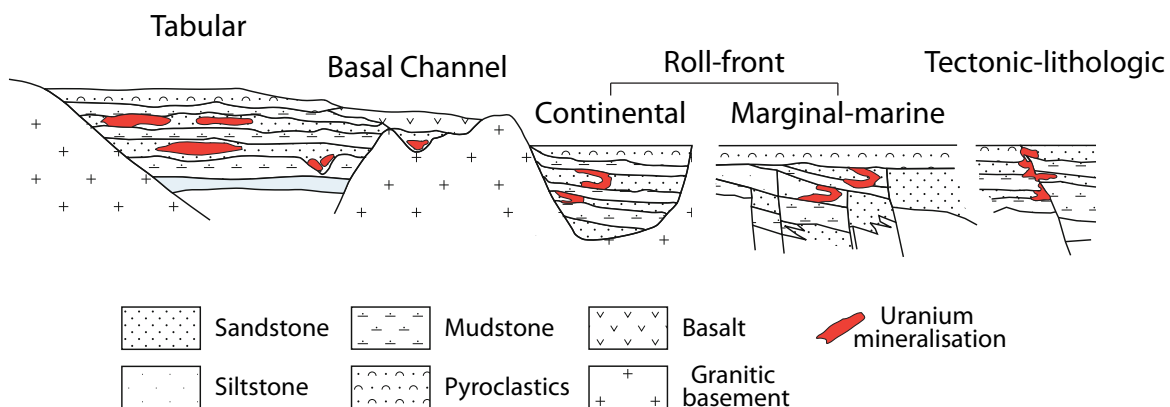


Figure 1.3: Schematic diagram showing the major sub-types of sandstone-hosted uranium deposits (modified after Dahlkamp, 2009). The major sub-type classifications are based on the configuration and spatial relationship of the mineralised redox front, and include: tabular, basal-channel (e.g. the Beverley deposit), roll-front (e.g. the Four Mile and Beverley North deposits) and tectonic-lithologic deposits.

Tabular deposits are typically hosted within blanket sands deposited within a braided fluvial system. The host sands are either unconformably overlies, or are incised into the underlying sedimentary or crystalline rocks. Mineralisation is largely oriented parallel to the depositional trend, but on a small scale occur as irregularly shaped tabular or lenticular zones that are peneconcordant to bedding (Dahlkamp, 2009; IAEA, 2009).

Basal-channel deposits are characteristically hosted within thick sequences of permeable alluvial or fluvial sediments within distinct palaeochannel or palaeodrainage systems that have been incised into underlying sedimentary or crystalline rocks. The ore bodies are typically elongate ribbon-like or lens structures in plan-view, or form lenticular or rare roll-shaped morphologies in cross-section (Dahlkamp, 2009; IAEA, 2009). The Beverley mineralised system is an example of a basal-channel type deposit (e.g. Wülser et al., 2011).

Roll-front deposits consist of arcuate zones of mineralisation that cross-cut bedding, appearing in cross-section as C-shaped mineralised fronts perpendicular to the direction of groundwater flow (Figure 1.4). In plan-view, the morphology of the roll-front typically appear as elongate and sinuous lenses trending approximately parallel to the strike of the host stratigraphy. This style of deposit can form within an intracratonic basin filled with continental alluvial or fluvial sediments, or within mixed fluvial/marine sediments deposited within a coastal plain (Dahlkamp, 2009; IAEA, 2009). As shown in Figure 1.4, the continued groundwater flow results in the redissolution of uranium minerals up-gradient of the main redox interface by oxidising groundwater; and reprecipitation of uranium minerals further down-gradient, resulting in migration of the C-shaped mineralisation 'roll-front' (Hostetler and Garrels, 1962). The Four Mile East, Four Mile West, Pepegoona, Pepegoona West and Pannikan deposits are examples of this type of deposit (Skirrow, 2009; Märten et al., 2012).

Tectonic-lithologic type deposits occur as mineralised zones discordant to the host stratigraphy, hosted within permeable sandstones adjacent to fault zones related to tectonic extension. Uranium is interpreted to have either precipitated (i) within the fault zone where it has permeated into adjacent horizons; or (ii) form via the redistribution of a pre-existing sandstone-hosted deposit (Dahlkamp, 2009; IAEA, 2009).

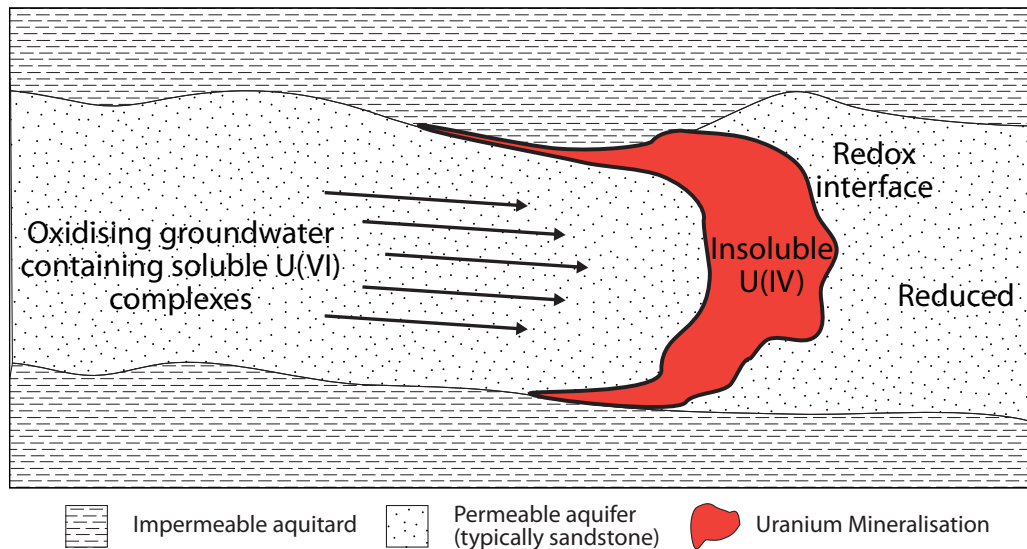


Figure 1.4: Schematic cross-section of a ‘roll-front’ sandstone-hosted uranium deposit. These deposits accumulate at a redox interface within a permeable sandstone aquifer, confined above and below by impermeable aquitards. Mineralisation occurs where oxidising uraniferous groundwaters transporting soluble U(VI) complexes are reduced by interaction with a source of reductant within the host aquifer; resulting in the precipitation of insoluble U(IV) minerals such as uraninite or coffinite, or adsorption of U(IV) complexes at the redox interface. The continued groundwater movement results in migration of the C-shaped mineralisation ‘roll-front’ from the redissolution and reprecipitation of uranium minerals.

1.2.2 Geochemistry of U and Th during redox-controlled ore formation processes

In groundwater systems, uranium predominantly occurs in two oxidation states, soluble U(VI) and insoluble U(IV). Under oxidising conditions, uranium can be leached from U-rich lithologies such as granites or volcanogenic sediments. The uranium is then transported by surface or groundwater as highly soluble uranyl U(VI) CO_3^{2-} , Cl^- , F^- , OH^- , SO_4^{2-} and PO_4^{2-} complexes (Hostetler and Garrels, 1962; Langmuir, 1978). The formation of sandstone-hosted uranium deposits involves the interaction of oxidising groundwaters carrying aqueous U(VI) complexes with a reductant source (e.g. H_2S , hydrocarbons, sulfide minerals or organic material) within a permeable sandstone aquifer, confined above and below by impermeable aquitards (Hobday and Galloway, 1999). At the oxidation-reduction interface, uranium (IV) minerals such as uraninite (UO_2) or coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) are precipitated; or adsorbed onto the aquifer host lithology or particulate matter as insoluble tetravalent uranium complexes (Hostetler and Garrels, 1962; Langmuir, 1978). The continual movement of groundwater

during the formation of sandstone-hosted uranium deposits results in the redissolution and reprecipitation of uranium minerals, and the subsequent migration of the mineralisation front (Hostetler and Garrels, 1962).

In contrast, under environmental conditions, thorium is present in one oxidation state - Th(IV), and is not sensitive to changes in redox. The poor solubility of thorianite (ThO_2) and thorite (ThSiO_4) at low temperatures results in groundwater concentrations rarely exceeding 1 $\mu\text{g/L}$ (Langmuir and Herman, 1980). Within an aquifer system, the mobility of thorium is strongly controlled by the precipitation of insoluble Th(IV) minerals such as thorianite; or by adsorption onto the surface of Fe-oxyhydroxide minerals such as goethite and haematite, clay minerals or organic materials (Langmuir and Herman, 1980). As a result of the strong sorption and complexation properties of Th(IV) and U(IV), inorganic and organic colloids can have a critical role in the mobility of U and Th, and hence the radioactive disequilibria (Porcelli and Swarzenski, 2003).

The difference in chemical behaviour during oxidation/reduction reactions is one mechanism through which uranium is fractionated from thorium during the formation of low temperature, redox-controlled sandstone-hosted uranium deposits. The immobility of thorium in groundwaters (e.g. Langmuir and Herman, 1980) is a fundamental assumption of many U-series dating techniques, which will be discussed further below.

1.2.3 General principles of ^{236}U and U-series isotope systematics

Natural uranium primarily exists as three α -emitting isotopes: long-lived primordial ^{238}U ($t_{1/2} \approx 4.47$ billion years; Jaffey et al., 1971) and ^{235}U ($t_{1/2} \approx 700$ million years; Jaffey et al., 1971) as the progenitors of the uranium-series and actinium-series decay chains respectively, and the shorter-lived radiogenic ^{234}U (progeny of ^{238}U ; $t_{1/2} \approx 245,250$ years; Cheng et al., 2000). In addition to the three main isotopes of uranium, in high-grade uranium ores, appreciable quantities of ‘natural’ ^{236}U can be produced by thermal neutron capture on ^{235}U (e.g. Fifield, 2008). Thorium has 6 naturally occurring isotopes, however of particular interest in this study are the α -emitting primordial ^{232}Th ($t_{1/2} \approx 14.05$ billion years; Holden et al., 1990) as the progenitor of the thorium-series decay chain, and radiogenic ^{230}Th (progeny of ^{238}U ;

$t_{1/2} \approx 75,690$ years; Cheng et al., 2000).

The natural relative isotopic abundances of the three major isotopes of uranium are markedly different, and are approximately 0.00542, 0.7204, and 99.274 atom percent for ^{234}U , ^{235}U and ^{238}U respectively (Richter et al., 1999). The most stable of the thorium isotopes, ^{232}Th has an isotopic abundance of $\sim 100\%$ (Gascoyne, 1992). Deviations from these values, however, have been reported, and are dependent upon the geological and geographical origins of the samples, fractionation processes, nuclear reactions, and by anthropogenic contamination (Richter et al., 1999).

In a geological system that has remained undisturbed for timescales greater than five to six half-lives of the daughter nuclide, a state of *secular equilibrium* is established whereby the rate of radioactive decay of the parent nuclide equals the rate of production of the daughter nuclide. This state of equilibrium is represented by a parent/daughter activity ratio equal to one. Secular equilibrium is typical in unweathered rocks, and is the state nuclides evolve towards after fractionation during natural geological process such as water-rock interactions.

During water-rock interactions, U-series disequilibrium is induced not only by the geochemical behaviours of uranium and thorium during oxidation/reduction, but also as a result of radioactive processes. Illustrated schematically in Figure 1.5, these fractionations have largely been attributed to: (i) the preferential leaching of ^{234}U from radiation damaged sites within the mineral lattice, or weakly bonded or interstitial sites (Rosholt et al., 1963); and (ii) alpha recoil displacement of daughter nuclides, whereby a parent nuclide situated on the edge of a grain boundary undergoes radioactive decay by the emission of an alpha particle with sufficient recoil energy to eject the daughter nuclide from the surface of the grain (Kigoshi, 1971; Fleisher, 1980). The alpha recoil induced mobility of the daughter nuclide can result in the daughter nuclide being ejected into solution such as pore or groundwaters, resulting in pore and groundwaters commonly displaying an enrichment of ^{234}U , and leaving the grain with a deficit of ^{234}U (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli and Baskaran, 2011). The daughter nuclide can also be recoiled within the grain causing recoil damage tracks within the grain; or ejected into adjacent grains (Rosholt, 1983; Ohnuki et al., 1990).

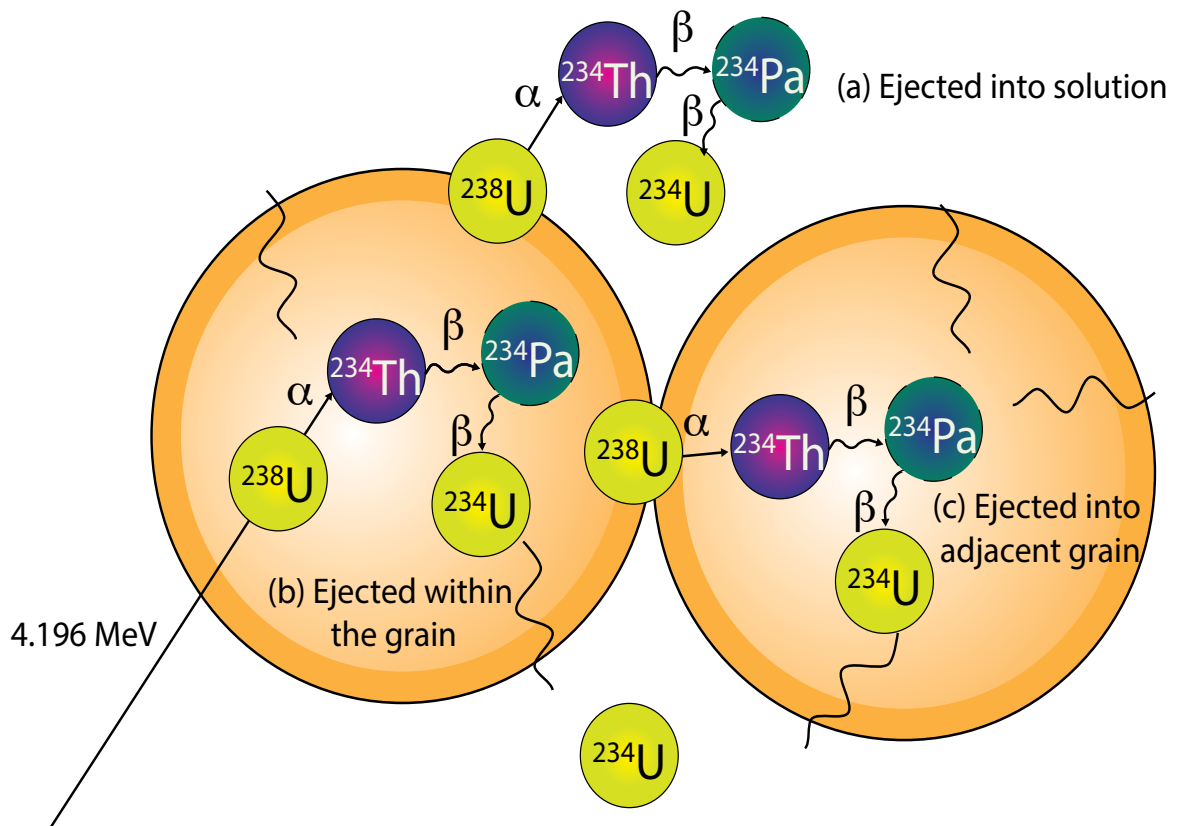


Figure 1.5: Schematic diagram showing alpha recoil displacement processes as a result of the radioactive decay of ^{238}U (modified after DePaolo et al., 2006). During radioactive decay of parent nuclide ^{238}U to ^{234}Th by the energetic emission of an α -particle, the daughter nuclide can be displaced due the recoil energy of 4.196 MeV (Kigoshi, 1971; Fleisher, 1980). The alpha recoil induced mobility can result in the daughter nuclide being ejected: (a) into solution such as pore or groundwaters, resulting in pore and groundwaters commonly displaying an enrichment of ^{234}U , and leaving the grain with a deficit of ^{234}U (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli, 2008); (b) recoiled within the grain causing recoil damage tracks within the grain; or (c) ejected into adjacent grains (Rosholt, 1983; Ohnuki et al., 1990). As a result of the emission of α - and β -particles during radioactive decay, extensive radiation damage can be caused to the mineral lattice which can facilitate (d) the preferential leaching of ^{234}U from radiation damaged, weakly bonded or interstitial sites (Rosholt et al., 1963), which can also contribute to an enrichment of ^{234}U in solution.

In high-grade uranium deposits with weight percent-level uranium concentrations, the contribution from alpha recoil induced mobility may be significant. A combination of both alpha recoil processes and preferential leaching may contribute to the fractionation of U-series isotopes during the formation of sandstone-hosted uranium deposits.

The existence of disequilibria within the U-series decay chain is time dependent, as the system returns to a state of secular equilibrium as a function of the half-life of the daughter product either by decay of the parent nuclide or by ingrowth of the daughter nuclide. These inherent properties form the basis of many isotopic fractionation studies to evaluate geochemical processes and providing timing constraints in a wide range of geological and environmental settings (e.g. Ivanovich and Harmon, 1992; Bourdon et al., 2003, Porcelli and Baskaran, 2011).

1.2.3.1 U-series disequilibria in groundwaters

Cherdyntsev and Russian co-workers first reported the fractionation between ^{234}U and ^{238}U isotopes during water-rock interactions in 1955 (translated in Cherdyntsev, 1971). Since then, large, percent-level variations in ($^{234}\text{U}/^{238}\text{U}$) isotopic activity ratios (where activity ratios denote the ratio of the activities of the two nuclides calculated by $N\lambda$ i.e. the atomic abundance times the decay constant, which is a function of the rate of decay per unit time) are the rule rather than the exception. This variability is observed in all surficial and groundwater hydrogeological environments including: (i) riverine and estuarine waters (e.g. Swarzenski et al., 2003), groundwaters (e.g. Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli, 2008) and ocean waters (e.g. Henderson and Anderson, 2003). This variation is largely attributed to the different behaviours of uranium nuclides during water-rock interactions, such as the well-known effects of alpha recoil displacement of daughter nuclides during radioactive decay (Kigoshi, 1971; Fleisher, 1980) and preferential leaching of ^{234}U (Rosholt et al., 1963), which are detailed in Figure 1.5.

The application of U-series isotopes to surficial and groundwater hydrogeological studies investigating water-rock interactions is well documented (e.g. Osmond and Cowart, 1977; 1992; Porcelli and Swarzenski, 2003; Porcelli, 2008). Applications include tracing groundwater flow and mixing (e.g. Osmond and Cowart, 2000); reactive transport modeling (e.g. Luo et al., 2000; Tricca et al., 2001; Reynolds et al., 2003; Ku et al., 2009) and determining chemical weathering rates in aquifers using a combination of U-series and strontium isotopes (e.g. Maher et al., 2006).

Given the fundamental role of hydrologic processes in the formation of sandstone-hosted uranium deposits, it is surprising how few studies have applied U-series isotopic signatures in groundwater to explore for concealed uranium deposits (e.g. Cowart and Osmond 1977; Osmond et al., 1983; Toulhoat and Beaucaire, 1991). This is partly due to the detailed chemical purification and sophisticated analytical instrumentation required to perform such analyses. The advent of the multi-collector inductively coupled plasma – mass spectrometer (ICP-MS) has improved the sensitivity and precision associated with the measurement of U-series isotopes. However, this application of U-series isotopes in groundwaters has remained relatively untested.

1.2.3.2 'Stable' uranium isotope fractionation between ^{238}U and ^{235}U

Historically, equilibrium mass-dependent fractionation was not expected between ^{238}U and ^{235}U due to their heavy mass and relatively small mass difference. Consequently, the $^{238}\text{U}/^{235}\text{U}$ ratio has been considered invariant, and a consensus value of 137.88 has been long assumed (Steiger and Jäger, 1977; Chen and Wasserburg, 1981). However recent advances in multi-collector ICP-MS allowing for the precise measurement of the $^{238}\text{U}/^{235}\text{U}$ ratio at the sub-0.1 permil level (Stirling et al., 2006; 2007; Weyer et al., 2008) have shown that this is not the case. The fractionation between ^{238}U and ^{235}U is similar to that observed in other heavy stable isotope systematics such as Tl and Hg, thus may be considered 'stable' uranium fractionation due to the relatively long half-lives compared to the timescales of geological processes (Stirling, 2012).

An increasing number of studies show significant (per mil) variation in $^{238}\text{U}/^{235}\text{U}$ isotopic compositions from the previously assumed value, in a wide range of meteoritic, (Stirling et al., 2005; Stirling et al., 2006; Amelin et al., 2010; Brennecka et al., 2010b) and terrestrial samples (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010a, Hiess et al., 2012). The largest $^{238}\text{U}/^{235}\text{U}$ isotopic fractionations typically accompany low temperature redox processes, and are found in sandstone-hosted uranium ores and speleothems (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010a). This 'stable' uranium fractionation can be explained by the effects of either mass-

dependent equilibrium or mass-independent kinetic processes (Bigeleisen, 1996; Schauble, 2007). Isotopic fractionation of ^{238}U and ^{235}U has largely been attributed to the nuclear field shift effect (also called the nuclear volume effect) during the reduction of U(VI) to U(IV) whereby the heavier isotope (^{238}U) is preferentially enriched in the reduced U(IV) species (Nomura et al., 1996; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; 2010; Brennecka et al., 2010a), arising from differences in the electric charge distribution, nuclear size and shape of the isotopic nuclei (Bigeleisen, 1996; Schauble, 2007). However, the exact role of reduction processes in the fractionation of ^{238}U and ^{235}U remains poorly understood. To date, no paired measurements of $^{238}\text{U}/^{235}\text{U}$ isotopic composition and concentration exist for both the U(IV)-bearing mineralised sediments and U(VI)-bearing groundwaters from within the same redox system allowing for the rigorous assessment of $^{238}\text{U} - ^{235}\text{U}$ isotope systematics during reduction. Likewise, the potential application of the ‘stable’ isotopes of uranium as a tracer of redox processes (e.g. Bopp et al., 2009) and to constrain the nature and timing of palaeoredox conditions (Montoya-Pino et al., 2010; Brennecka et al., 2011) is still an emerging field, and a greater understanding of the behaviour of these isotopes is required.

1.2.3.3 Natural ^{236}U produced by neutron capture on ^{235}U

Primordial ^{236}U ($t_{1/2} \approx 23.4$ million years; Ghiorso et al., 1951) has long since decayed to $^{236}\text{U}/^{238}\text{U}$ isotopic ratios of the order of $\sim 10^{-14}$ in average crustal rocks (Steier et al., 2008), which is beyond the detection limit of most modern analytical techniques. However, using accelerator mass spectrometry (AMS), natural $^{236}\text{U}/^{238}\text{U}$ ratios of the order of $\sim 10^{-12}$ to $\sim 10^{-10}$ have been reported in high-grade uranium ores and ore concentrates resulting from the *in-situ* production of ^{236}U by thermal neutron capture on ^{235}U (Rokop et al., 1972; Zhao et al., 1994a; 1994b; Richter et al., 1999; Berkovits et al., 2000; Wilcken et al., 2007; 2008; Srnecik et al., 2011). In contrast, the main source of ^{236}U present in nature is the by-product of anthropogenic activities associated with nuclear reprocessing and weapons testing. $^{236}\text{U}/^{238}\text{U}$ isotopic ratios as high as $\sim 10^{-2}$ have been reported (e.g. Steier et al., 2008 and references therein).

As shown in Figure 1.6, potential sources of neutrons within a high-grade uranium ore deposit are: (i) (α , n) reactions, where α -particles produced by radioactive decay of ^{238}U , ^{235}U and ^{232}Th interact with light elements within the matrix, forming unstable atoms that return to the ground state by the emission of neutrons, and (ii) by the spontaneous and neutron-induced fission of ^{238}U and ^{235}U respectively (Hotchkis et al., 2000; Wilcken et al., 2008). The production of ^{236}U within the ores is directly related to the neutron flux, which is a function of the concentration of uranium and thorium minerals within the ore, the age of the deposit relative to the half-life of ^{236}U , and the neutron capture probability of other constituents within the matrix (Wilcken et al., 2008).

Based on $^{236}\text{U}/^{238}\text{U}$ isotopic ratios measured in uranium ores, the possibility of detecting natural $^{236}\text{U}/^{238}\text{U}$ ratios elevated above background ratios in groundwaters in close proximity to high-grade uranium mineralisation has been recognised by Fifield (2008) as a potential exploration tool for deposits buried at depth.

1.2.3.4 U-series disequilibria and ^{230}Th -U dating of sandstone-hosted uranium deposits

During water-rock interactions, U-series disequilibrium can result from both instantaneous and/or continuous processes. The existence of disequilibria within the U-series decay chain is time dependent, as the system returns to a state of secular equilibrium as a function of the half-life of the daughter product either by decay of the parent nuclide or by ingrowth of the daughter nuclide. It is the time dependant return to the state of secular equilibrium that forms the basis of ^{230}Th -U dating techniques. As a consequence of the assumed insolubility of thorium in groundwaters, if uranium has precipitated from solution within five to six half-lives of ^{230}Th , and remained closed to further fractionation, the age of the samples may be calculated based on the ingrowth of ^{230}Th produced from the radioactive decay of parent nuclide ^{234}U . The ^{230}Th -U dating technique has been successfully applied to environmental samples which are precipitated from waters at low temperatures, such as marine and lacustrine carbonates, speleothems, corals and chimney deposits (e.g. Edwards et al., 2003; Richards and Dorale, 2003).

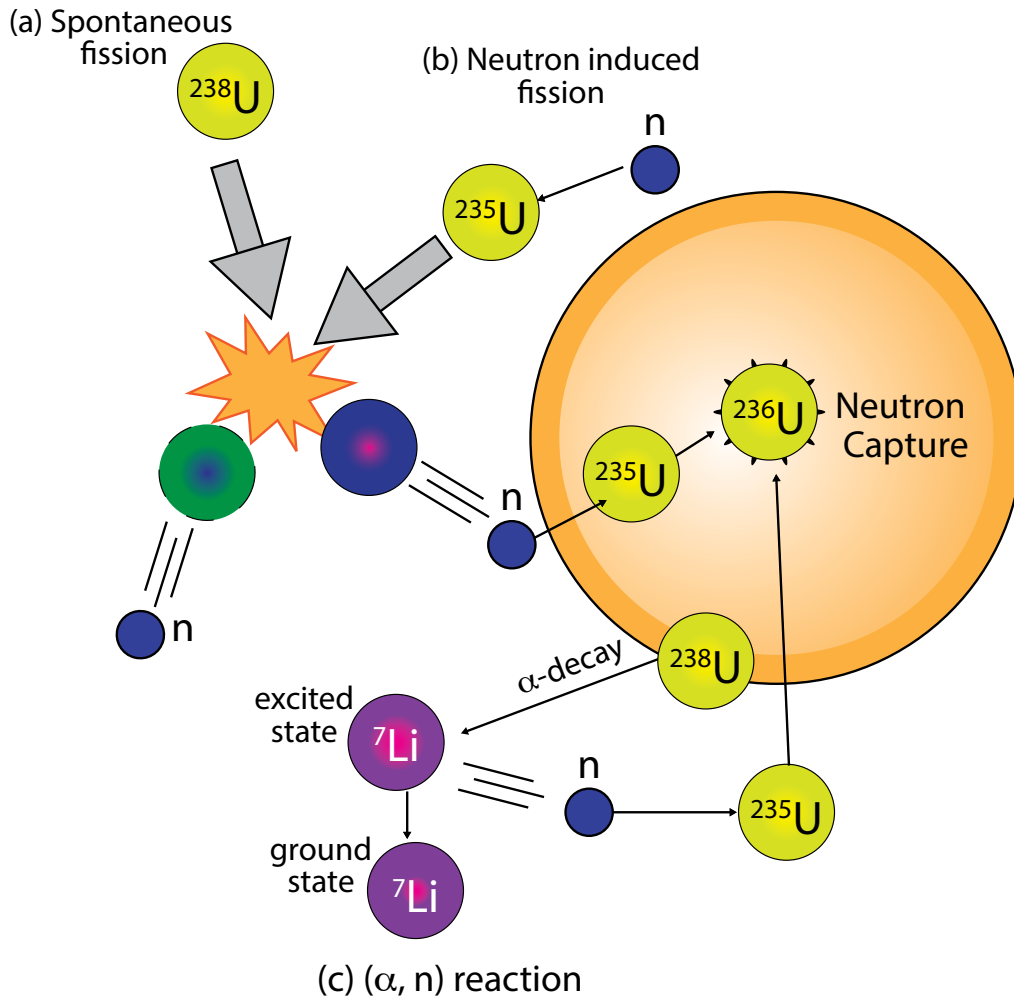


Figure 1.6: Schematic representation of the potential source of neutrons in high-grade uranium deposits that contribute to the production of *in-situ* ^{236}U via thermal neutron capture processes on ^{235}U . Potential sources of neutrons within a high-grade uranium ore deposit are: (a) spontaneous and (b) neutron-induced fission of ^{238}U and ^{235}U respectively; and (c) (α, n) reactions, where α -particles produced by the radioactive decay of ^{238}U , ^{235}U and ^{232}Th interact with light elements such as Li within the matrix, forming unstable atoms that return to the ground state by the emission of neutrons (Hotchkis et al., 2000; Wilcken et al., 2008).

Fractionation of U-series isotopes is well documented within uranium deposits formed by water-rock interactions, such as sandstone-hosted uranium deposits, e.g. the 'roll-front' type sandstone-hosted deposits in Wyoming, U.S.A. (Rosholt et al., 1964; Dooley et al., 1964; Rosholt et al., 1965a; 1965b) and Shihongtan, China (Min et al., 2005); the 'basal channel' Ambrosia Lake District, New Mexico (Dooley et al., 1966) and Coutras,

France deposits (Meunier et al., 1992). Fractionation has also been documented in surficial-type deposits such as ‘calcrete’ surficial-type Yeelirrie deposit, Australia (Lively et al., 1979; Airey and Roman, 1981; Airey, 1986) and three surficial deposits in British Colombia, Canada (Levinson et al., 1984).

Despite the common occurrence of U-series disequilibrium in uranium deposits resulting from water-rock interactions, few studies have attempted to constrain precise ages of the precipitated uranium minerals using U-series isotopes due to the difficulties associated with the open-system redissolution and reprecipitation of uranium minerals inherent in such deposits (Lively et al., 1979; Airey and Roman, 1981; Levinson et al., 1984; Zielinski et al., 1986). Knowledge of the age of mineralisation is of great interest because it can potentially constrain the timing and duration of uranium mobilisation, and inform future exploration.

1.3 BACKGROUND TO THIS PROJECT

The majority of the research presented in this thesis originates from an Australian Research Council Linkage grant (LP0990500) conducted in collaboration between Macquarie University and Heathgate Resources Pty Ltd under a project entitled “A novel approach for economic uranium deposit exploration and environmental studies” awarded to Professor Simon P. Turner; Dr. Bruce F. Schaefer (Macquarie University, Sydney, Australia); Dr. Anthony Dosseto (formerly Macquarie University, now at the GeoQuEST Research Centre, School of Earth and Environmental Sciences, University of Wollongong, Australia); and Geoffrey McConachy (former managing director of Quasar Resources, affiliate of Heathgate Resources Pty Ltd, Adelaide, Australia).

The overall objective of the project was to assess the use of U-series isotopes (specifically ^{234}U , ^{238}U , ^{230}Th , ^{232}Th) in groundwaters as a potential exploration tool for sandstone-hosted uranium deposits, using the Beverley and Four Mile deposits as a reference site. An additional aim of the linkage project was to further the knowledge of the behaviour of U and its decay products during water-rock interactions.

The initial premise was to investigate the hypothesis that groundwater passing through an area enriched in U with respect to Th (such as high-grade mineralisation) should exhibit ($^{234}\text{U}/^{238}\text{U}$) ratios at or very close to secular equilibrium due to the congruent dissolution of U rich minerals. Regional groundwaters sourced from non-mineralised areas should have disequilibrium values typical of water-rock interactions, thus the signatures acquired in the ore deposit should allow for the identification of the presence of mineralisation. The basis for this hypothesis is the observation reported by Cherdyntsev (1971) that leachates of rocks enriched in uranium (but not ore bearing) contain excess ^{234}U , whilst leachates of uranium minerals exhibited ($^{234}\text{U}/^{238}\text{U}$) ratios close to one. Additionally, Toulhoat and Beaucaire (1991) observed high uranium concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios close to one in oxidised groundwaters draining the clay bounded unconformity Cigar Lake ore deposit. This hypothesis is also supported by the observation of ($^{234}\text{U}/^{238}\text{U}$) ratios approaching one in groundwater in the oxidised zone draining the sandstone-hosted Coutras deposit, France, and ($^{234}\text{U}/^{238}\text{U}$) > 1 in the reduced zone where the ore is stable (Meunier et al., 1992); and oxidising groundwaters with ($^{234}\text{U}/^{238}\text{U}$) ratios of 1 to 1.2 closest to high-grade mineralisation within the sandstone-hosted Crow Butte deposit, Nebraska, U.S.A. (Spalding et al., 1984).

As part of the project, groundwaters in the vicinity of the Beverley and Four Mile deposits, both within and adjacent to mineralisation were to be collected to assess any potential correlations in isotopic ratios with the presence of high- versus low-grade mineralisation. By sampling groundwaters within and adjacent to a known deposit, the validity of the application of U-series isotopes as a tool for prospecting could be tested. Additionally, the behaviour of U and its decay products during water-rock interactions could be investigated.

The scope of the project originally was aimed towards testing the applicability of ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) in groundwaters as an exploration tool using the Beverley and Four Mile deposits as reference sites. The Beverley deposits (discovered in 1969, see Cooper, 2008 for further details), are located on mining leases wholly-owned by Heathgate Resources Pty Ltd, operators of the Beverley mine. The Central Beverley Ore Zone has been actively mined by ISR since 2000, under close environmental scrutiny (e.g. Märten et al., 2012). The southern-most extension of the Beverley deposit – the Beverley Deep South Ore

Zone - had not commenced mining by ISR at the time of the commencement of the research for this PhD thesis in early-2009. However, the narrow (~100 m wide) mineralisation trends, in conjunction with the possible influence from mining in the other portions of the Beverley system meant that this portion of the deposit was not ideal to test the original aim of the project.

The Four Mile deposits, comprising the Four Mile East and Four Mile West deposit were discovered in 2005 (Cooper, 2008). The deposits are located on mining leases under a joint venture lease with Quasar Resources, an affiliate of Heathgate Resources Pty Ltd (75 %) and Alliance Resources Pty Ltd (25 %). A move towards readying the deposits for mining by ISR began, with the drilling of environmental groundwater monitoring wells and delineation of the extent of the ore deposits – ideal for the scope of the project. In 2009, the discovery of the Beverley North deposits (comprising the Pepegooona, Pepegooona West and Pannikan deposits, located on a wholly-owned Heathgate Resources Pty Ltd mining lease) saw a shift in focus towards getting these deposits ready for mining by ISR (Märten et al., 2012). Consequently, the focus on gaining a greater understanding of the geology and delineating the extent of the Beverley North deposits resulted in the construction of infrastructure such as peripheral groundwater monitor wells surrounding the deposits, particularly the Pepegooona deposit. For this reason, in chapter II, there are some data from the Four Mile East deposit. However, the bulk of this research has focused on the Pepegooona deposit.

As the study progressed, it became apparent that the complicated geology of the Four Mile and Pepegooona deposits, in conjunction with the overall reducing groundwater conditions meant that the use of ^{234}U - ^{238}U isotopes as an exploration tool might not be possible in this area (Chapter II). In conjunction with the linkage project, an AINSE grant (10/068) was awarded to Anthony Dosseto to investigate the radiocarbon ages of groundwaters surrounding the Pepegooona deposit. The guidance from Dr. Dioni Cendón, (ANSTO, Lucas Heights, Australia) in groundwater sampling techniques and interpretations was instrumental in this work. This is also presented in Chapter II.

A secondary aim of the linkage project was to gain an improved understanding of the timing and conditions of formation and the evolution of the Beverley deposit using U-series disequilibria, with a particular focus on the Beverley Deep South portion of the deposit. For this purpose, several mineralised sediment samples were collected from a pristine diamond drill core that intersected mineralisation within the Beverley Deep South ‘Dragon’ deposit. This aspect of the linkage project is presented in Chapter V.

In addition to the research goals of the collaborative project, the research expanded to include several other objectives relevant to key questions about the fractionation of U-series isotopes during low-temperature redox-controlled mineralisation processes, in particular relating to the recently discovered fractionation of $^{238}\text{U}/^{235}\text{U}$ isotopes in low-temperature redox environments, and the *in-situ* production of ‘natural’ ^{236}U in high grade ores.

Upon reviewing the literature, it became apparent that the Pepegoona deposit provided an ideal setting in which to investigate the fractionation of $^{238}\text{U}/^{235}\text{U}$ isotopes in a well-constrained redox-controlled environment. Thus, a collaboration was established by the author with Dr. Claudine Stirling (Centre for Trace Element Analysis and Department of Chemistry, University of Otago, Dunedin, New Zealand) to investigate the fractionation of $^{238}\text{U}/^{235}\text{U}$ in both the groundwaters and associated mineralised sediments from the Pepegoona deposit. This is presented in Chapter III.

The final aspect of this research was to investigate the *in-situ* production of ‘natural’ ^{236}U in high-grade ores and groundwaters adjacent to the Beverley North deposits. This work has been conducted in collaboration with Professor L. Keith Fifield and Dr. Michaela Srncik (Department of Nuclear Physics, Research School of Physical Sciences and Engineering, The Australian National University, Australia). This area of research is presented in Chapter IV.

1.4 THESIS AIMS AND OBJECTIVES

From the review of the literature, it can be seen that many questions still remain to advance our understanding of the behaviour of uranium isotopes and its decay products during low-temperature redox-controlled uranium mineralisation processes. The main objective of this research is to investigate the behaviour of ^{236}U and U-series isotopes in groundwaters and mineralised sediments from several South Australian sandstone-hosted uranium deposits. This study focuses on sandstone-hosted uranium deposits as they provide an ideal location in which to investigate the role of reduction and water/rock interactions during ore formation and isotope fractionation processes. In addition, a greater understanding of the processes occurring in such deposits can assist with the exploration for concealed ore deposits, and can also inform models for nuclear waste disposal and groundwater contamination studies. The primary research questions to be investigated in this PhD thesis are:

1. *From the literature, ($^{234}\text{U}/^{238}\text{U}$) activity ratios approaching secular equilibrium have been observed in groundwaters draining high-grade uranium deposits, which may reflect congruent dissolution of ore minerals. Can ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) isotopic signatures in groundwaters in the vicinity of the Four Mile East and Pepegooona deposits be used to explore for sandstone-hosted uranium deposits, with a greater applicability for other potential deposits in the Frome Embayment?*
2. *Recently, fractionation of 'stable' uranium isotopes, ^{238}U and ^{235}U has been observed, with the greatest fractionation observed in low-temperature redox environments. What mechanisms control fractionation of these isotopes? What is the role of reduction of U(VI) to U(IV) during ore formation processes in fractionation of $^{238}\text{U}/^{235}\text{U}$, in both the groundwaters and concomitant mineralised sediments from the Pepegooona deposit?*
3. *The hypothesis of detecting 'natural' ^{236}U in groundwaters in contact with high-grade uranium ores has been proposed as a potential exploration tool for uranium. Is it possible to detect natural ^{236}U in groundwaters using AMS?*
4. *In the literature, few attempts have been made to constrain an absolute age of uranium mineralisation using U-series disequilibria dating. Is it possible to use this isotope systematic to date the Beverley Deep South deposit?*

Broadly, can the study of ^{236}U and U-series isotopes within sandstone-hosted uranium deposits formed by low-temperature redox-controlled processes allow for a greater understanding of the behaviour of these isotopes during water/rock interactions and reduction processes?

1.5 NOTES ON THESIS FORMAT

This thesis has been arranged with the intent that each chapter except for the introductory and synthesis chapters are complete, stand-alone manuscripts formatted in the style of a journal article. Each chapter represents an independent yet complementary area of research that explores a common theme investigating the behaviour of uranium isotopes within low temperature, redox-controlled uranium ore formation processes within a sandstone-hosted mineralised system. Chapters II through V will introduce the research and relevant background information; provide a description of the methods, results and discussion, and lastly some final concluding remarks. The references are provided at the end of each chapter. Structuring of this thesis in this manner has resulted in an inevitable degree of repetition of some descriptive text, such as the introduction and methodology sections. Each chapter is formatted to the publication style of the journal of planned submission, and as such formatting and reference style vary throughout this thesis. Figures, tables and references for each individual manuscript are included within the relevant chapter. Pagination begins with the title page and continues sequentially throughout the thesis.

This thesis will be arranged as follows:

Chapter II: U-series disequilibria in groundwaters in a low temperature redox uranium mineralised system

This research explores the behaviour of ^{234}U and ^{238}U isotopes in groundwater in the vicinity of the Four Mile East and Pepegoona sandstone-hosted uranium deposits, and discusses the potential applicability as a proxy for uranium exploration. An earlier version of the manuscript was submitted to *Geochimica et Cosmochimica Acta* and received comments from S. Krishnaswami and an anonymous reviewer. The present manuscript will be resubmitted to *Geochimica et Cosmochimica Acta* (Melissa J. Murphy, Anthony Dosseto, Simon P. Turner, Bruce F. Schaefer and Norman J. Pearson).

Contributions of authors and colleagues

The original idea for this research is part of the collaborative ARC project. Fieldwork and sample collection was performed by the author with the assistance of Heathgate Resources Pty Ltd personnel. All sample preparation and analysis was performed by the author under the guidance of Norman Pearson and Anthony Dosseto. The author prepared this manuscript, with the assistance from the co-authors in the development of interpretations and ideas, and editorial comments of the final manuscript.

Chapter III: Fractionation of $^{238}\text{U}/^{235}\text{U}$ by reduction during low temperature uranium mineralisation processes

This research investigates $^{238}\text{U}/^{235}\text{U}$ variability within groundwaters and uranium mineralised sediments sampled within a low temperature redox, mineralised system. This manuscript will be submitted to *Earth and Planetary Science Letters* (Melissa J. Murphy, Claudine H. Stirling, Angela Kaltenbach, Simon P. Turner and Bruce F. Schaefer).

Contributions of authors

The original idea for this study was initiated by the author. Fieldwork and sample collection was performed by the author with the assistance of Heathgate Resources Pty Ltd personnel. All sample preparation was performed by the author under the guidance of Dr. Claudine Stirling and Angela Kaltenbach. Analysis of the groundwater samples by multi collector ICP-MS was performed by the author, whilst mineralised sediments samples were analysed by Claudine Stirling. The manuscript was prepared by the author, with the assistance from the co-authors in the development of interpretations and ideas, and editorial comments of the final manuscript.

Chapter IV: Detection of natural ^{236}U in groundwaters and ores in the vicinity of several high-grade sandstone-hosted uranium deposits

This chapter presents a preliminary study investigating the presence of ^{236}U in groundwaters produced *in-situ* from neutron capture on ^{235}U as a result of the high neutron flux within

high-grade uranium ore deposits.

Contributions of authors and colleagues

This work forms part of a collaborative idea initiated by Professor L. Keith Fifield. This work benefited from early discussions with David Child and Dr. Michael Hotchkis (ANSTO, Lucas Heights, Australia) and Dr. Steve Tims (ANU, Canberra, Australia). Fieldwork and sample collection was performed by the author with assistance during the May 2012 field campaign by Dr. Michaela Srncik, with the support of Heathgate Resources personnel. Chemical preparation of the first batch of samples was undertaken by the author; final stages of preparation of those samples for analysis by accelerator mass spectrometry (AMS) was performed by Rajeev Lal. Chemical purification of the second batch of groundwater and mineralised sediments, in addition to preparation for analysis by AMS, was conducted by Michaela Srncik. The measurements were carried out at the ANU by the AMS group lead by Keith Fifield. The data reduction was performed by Keith Fifield. The chapter was prepared by the author with the assistance from Keith Fifield, Michaela Srncik, Simon Turner and Bruce Schaefer in the development of interpretations and ideas, and editorial comments of the final manuscript.

Chapter V: Timescales of uranium mineralisation: U-series disequilibria in the Beverley sandstone-hosted uranium deposit

Using U-series disequilibria, this chapter attempts to constrain the timescales of uranium mobility within the Beverley Deep South sandstone-hosted uranium deposit.

Contributions of authors and colleagues

The original idea for this research is part of the collaborative ARC project. All fieldwork, sample collection, preparation and analysis were performed by the author. The assistance from Dr. Bernd Michaelson (formerly at Heathgate Resource Pty Ltd, now at the Geological Survey of South Australia, DMITRE, Adelaide, Australia) whilst sampling drill core is greatly appreciated. The chapter was prepared by the author with the assistance from Simon

Turner and Bruce Schaefer in the development of interpretations and ideas, and editorial comments of the final manuscript.

Chapter VI: Synthesis

This final chapter provides a brief summary of the research findings and indicates some of the implications of this study for future research.

Appendices

Attached at the end of this thesis are several appendices. Appendix A contains supplementary material relating to the chemical preparation and analysis of thorium isotopes in groundwater, relevant to Chapter II. Appendix B presents additional chemical and analytical techniques for the separation of ^{236}U from groundwaters (Chapter IV). Appendix C collates a series of conference abstracts presented during the duration of the PhD candidature.

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CHAPTER II

U-SERIES DISEQUILIBRIA IN GROUNDWATERS IN A LOW TEMPERATURE REDOX URANIUM MINERALISED SYSTEM

Keywords: uranium-series isotopes, mineralisation, water-rock interactions, ore deposit

ABSTRACT

Groundwaters often exhibit ($^{234}\text{U}/^{238}\text{U}$) activity ratios greater than one as a result of fractionation between ^{234}U and ^{238}U nuclides during water-rock interactions. However, in the literature, ($^{234}\text{U}/^{238}\text{U}$) activity ratios approaching secular equilibrium have been observed in groundwaters draining high-grade uranium deposits, which may reflect congruent dissolution of ore minerals. This may allow for the use of uranium-series (U-series) isotopic as an exploration tool for concealed uranium deposits buried at depth.

U-series isotopes were measured in groundwaters in the vicinity of two known occurrences of sandstone-hosted uranium mineralisation – the Four Mile East and Pepegooa deposits located in the semi-arid Eromanga Basin, South Australia. Using this data we evaluate the potential use of disequilibria in groundwater for uranium exploration. The current hydrological regime is characterised by highly reducing groundwaters with low U concentrations with uranium present as U(IV) complexes. This suggests the deposits are relatively stable, and no longer accumulating or being remobilised by continued groundwater movement. A wide range of ($^{234}\text{U}/^{238}\text{U}$) activity ratios (ranging from 0.889 ± 0.005 to 2.815 ± 0.005) are observed over a relatively narrow range of highly reducing redox potentials, suggesting that disequilibrium is not governed by changes in redox or interaction with mineralisation, rather that the isotopic signatures reflect dynamic hydrogeologic processes such as preferential leaching and alpha recoil of ^{234}U , and the geological complexity of the deposits.

Radiocarbon ages range from 15,070 to 38,020 yrs BP. No correlation between radiocarbon ages and ($^{234}\text{U}/^{238}\text{U}$) activity ratios is observed. This indicates that over the short

timescales relative to the half-life of ^{234}U , alpha recoil processes do not contribute significantly to the range of ($^{234}\text{U}/^{238}\text{U}$) disequilibria observed in the Eyre Formation groundwaters.

Groundwater ($^{234}\text{U}/^{238}\text{U}$) activity ratio maps and depth profiles of the Pepegooona deposit are constructed to examine the spatial and three-dimensional variability. Laterally, ($^{234}\text{U}/^{238}\text{U}$) activity ratios broadly increase along the groundwater flow path, however an overall decreasing trend with increasing depth from the uppermost to lower Eyre Formation aquifers is observed. This is interpreted to reflect local heterogeneity in the aquifer host lithology and groundwater flow rate.

Groundwaters sampled within the uranium mineralisation have ($^{234}\text{U}/^{238}\text{U}$) activity ratios of ~ 1.2 to 1.4 , which conflicts with the initial hypothesis. If however, the ($^{234}\text{U}/^{238}\text{U}$) isotopic signature in the groundwaters in direct contact with high-grade mineralisation reflects isotopic equilibration with the mineralisation itself, this would imply that these deposits have either formed or experienced recent remobilisation (within the past million years), evidenced by disequilibrium ($^{234}\text{U}/^{238}\text{U}$) ratios in these waters.

The ($^{234}\text{U}/^{238}\text{U}$) activity ratios in groundwaters sampled within the uranium mineralisation are rapidly overprinted by water-rock interactions in non-mineralised areas of the aquifer. The limited mobility of uranium in these highly reducing groundwaters suggests that the use of U-series disequilibrium may not be applicable as a proxy for uranium mineralisation in this area. 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.

2.1 INTRODUCTION

Sandstone-hosted uranium deposits are an important source of uranium, both in Australia and worldwide (IAEA, 2009). Sandstone-hosted uranium deposits form at a redox interface within a permeable sandstone aquifer confined above and below by impermeable aquitards by the reduction of U(VI) to U(IV) during low temperature water-rock interactions (Hostetler and Garrels, 1962; Hobday and Galloway, 1999). During water-rock interactions, U-series isotopes are fractionated as a result of their different half-lives, and radioactive and chemical behaviour (Porcelli and Swarzenski, 2003). Due to the mechanisms through which sandstone-hosted deposits form, fractionation of U-series isotopes is not only expected in the deposits themselves, but also in the groundwaters from which the mineralisation has precipitated.

With increasing global demand for uranium, an improved understanding of the behaviour of uranium and U-series isotopes and its decay products during low temperature ore formation processes is important to advance uranium exploration technologies, particularly for sandstone-hosted type deposits which often lack a surface expression. Additionally, the study of the mobility of U-series isotopes during water-rock interactions within ‘sandstone-hosted’ type uranium deposits can inform models for nuclear waste disposal and groundwater contamination studies.

Given the fundamental role of hydrologic processes in the formation of sandstone-hosted uranium deposits, it is surprising how few studies have applied U-series isotopic signatures in groundwater to explore for concealed uranium deposits (e.g. Cowart and Osmond 1977; Osmond et al., 1983; Toulhoat and Beaucaire, 1991). This is partly due to the detailed chemical purification and sophisticated analytical instrumentation required to perform such analyses. The advent of the multi-collector inductively coupled plasma – mass spectrometer (ICP-MS) has improved the sensitivity and precision associated with the measurement of U-series isotopes. However, this application of U-series isotopes in groundwaters has remained relatively untested.

Regional groundwaters sourced from non-mineralised areas should have disequilibrium ($^{234}\text{U}/^{238}\text{U}$) values typical of water-rock interactions. However, it might be expected that groundwaters passing through an area enriched in U with respect to Th (such as high-grade mineralisation) should exhibit ($^{234}\text{U}/^{238}\text{U}$) ratios at or very close to secular equilibrium due to the congruent dissolution of U rich minerals. If this is the case, the isotopic signatures in groundwaters acquired in the ore deposit might allow for the identification of the presence of mineralisation. The basis for this hypothesis is the observation by Cherdyntsev (1971) that leachates of rocks enriched in uranium (but not ore bearing) contain excess ^{234}U , whilst leachates of uranium minerals exhibited ($^{234}\text{U}/^{238}\text{U}$) ratios close to one. Additionally, Toulhoat and Beaucaire (1991) observed high uranium concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios close to one in oxidised groundwaters draining the clay bounded unconformity Cigar Lake ore deposit. This hypothesis is also supported by the observation of ($^{234}\text{U}/^{238}\text{U}$) ratios approaching one in groundwater in the oxidised zone draining the sandstone-hosted Coutras

deposit, France, and $(^{234}\text{U}/^{238}\text{U}) > 1$ in the reduced zone where the ore is stable (Meunier et al., 1992); and oxidising groundwaters with $(^{234}\text{U}/^{238}\text{U})$ ratios of 1 to 1.2 closest to high-grade mineralisation within the sandstone-hosted Crow Butte deposit, Nebraska, U.S.A. (Spalding et al., 1984).

The primary objective of this study was to test this hypothesis by characterising the U-series isotopic signature in groundwaters passing through a mineralised redox interface. By sampling groundwaters within and adjacent to a known deposit, the validity of the application of U-series isotopes as a tool for prospecting could be tested. Additionally, the behaviour of U and its decay products during ore formation processes within sandstone-hosted uranium deposits could be investigated. To achieve this, the distribution of $(^{234}\text{U}/^{238}\text{U})$ activity ratios have been determined by MC-ICP-MS in groundwater samples taken along the groundwater flow path, within and surrounding the Four Mile East and Pepegooona sandstone-hosted uranium mineralised deposits in South Australia. Preliminary attempts to characterise the thorium isotopic compositions of the groundwaters were also made. Additionally, field parameters such as pH, redox potential (Eh), conductivity and temperature, and radiocarbon groundwater ages are presented.

2.2 BACKGROUND AND PREVIOUS RESEARCH

2.2.1 Geochemistry of U and Th during redox-controlled ore formation processes

In groundwater, uranium exists predominantly in either the U(VI) or U(IV) valance states, and are thus sensitive to changes in oxidation/reduction. Uranium concentrations may reach up to 1 mg/L in oxidising groundwater, contrasting with extremely low concentrations ($\sim 0.06 \mu\text{g/L}$) under reducing conditions (Gascoyne, 1992). In oxygenated environments, such as near surface conditions, uranium can be dissolved from uranium-rich lithologies and transported by surface or groundwater as highly soluble hexavalent uranyl CO_3^{2-} , Cl^- , F^- , OH^- , SO_4^{2-} and PO_4^{2-} complexes (Langmuir, 1978). Upon interaction of oxidising groundwaters carrying aqueous uranyl U(VI) complexes with a reductant source within the aquifer (e.g. H_2S , hydrocarbons, sulfide minerals or organic material), uranium forms insoluble tetravalent complexes, and subsequently adsorbs onto iron, manganese or titanium oxyhydroxide minerals, iron oxides such as goethite, clays or organic materials, or is precipitated as uranium ore minerals such as

coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$), or uraninite (UO_2) (Hostetler and Garrels, 1962; Langmuir, 1978). The interaction between oxidising uranium-rich groundwaters and reducing conditions is fundamental in the formation of the sandstone-hosted ‘roll-front’ uranium deposits. These deposits form at a redox interface within a permeable sandstone aquifer confined above and below by impermeable aquitards (Hobday and Galloway, 1999). Continued groundwater movement results in the redissolution of uranium minerals up-gradient of the main redox interface by oxidising groundwater; and reprecipitation of uranium minerals further down-gradient, resulting in migration of the C-shaped mineralisation ‘roll-front’ (Hostetler and Garrels, 1962).

In contrast, thorium is not sensitive to changes in redox and is present in one oxidation state - Th(IV). The poor solubility of thorianite (ThO_2) and thorite (ThSiO_4) at low temperatures results in groundwater concentrations rarely exceeding 1 $\mu\text{g/L}$ (Langmuir and Herman, 1980). Within an aquifer system, the mobility of thorium is strongly controlled by the precipitation of insoluble Th(IV) minerals such as thorianite; or by adsorption onto the surface of Fe-oxyhydroxide minerals such as goethite and haematite, clay minerals or organic materials (Langmuir and Herman, 1980). As a result of the strong sorption and complexation properties of Th(IV) and U(IV), inorganic and organic colloids can have a critical role in the mobility of U and Th, and hence the radioactive disequilibria (Porcelli and Swarzenski, 2003).

The difference in chemical behaviour during oxidation/reduction reactions is one mechanism through which uranium is fractionated from thorium during the formation of low temperature, redox-controlled sandstone-hosted uranium deposits.

2.2.2 *Uranium-series systematics*

In a geological system that has remained undisturbed for a timescale greater than five half-lives of the daughter nuclide, secular equilibrium is established (i.e. ($^{234}\text{U}/^{238}\text{U}$) activity ratios equal to one, where activity ratios are denoted by parentheses), whereby the rate of radioactive decay of the parent nuclide is equal to that of the daughter nuclides. For the parent ^{238}U and daughter ^{234}U nuclides, secular equilibrium is achieved after ~ 1 Myr.

During water-rock interactions, U-series disequilibrium is induced not only by the geochemical behaviours of uranium and thorium during oxidation/reduction, but also as a result of radioactive processes. These fractionations have largely been attributed to: (i) the preferential leaching of ^{234}U from radiation damaged sites within the mineral lattice, or weakly bonded or interstitial sites (Rosholt et al., 1963); and (ii) alpha recoil displacement of daughter nuclides, whereby a parent nuclide situated on the edge of a grain boundary undergoes radioactive decay by the emission of an alpha particle with sufficient recoil energy to eject the daughter nuclide from the surface of the grain (Kigoshi, 1971; Fleisher, 1980). The alpha recoil induced mobility of the daughter nuclide can result in the daughter nuclide being ejected into solution such as pore or groundwaters, resulting in pore and groundwaters commonly displaying an enrichment of ^{234}U , and leaving the grain with a deficit of ^{234}U (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli and Baskaran, 2011). The daughter nuclide can also be recoiled within the grain causing recoil damage tracks within the grain; or ejected into adjacent grains (Rosholt, 1983; Ohnuki et al., 1990). Both alpha recoil and preferential leaching processes produce excess ^{234}U in solution, resulting in groundwaters commonly exhibiting ($^{234}\text{U}/^{238}\text{U}$) ratios > 1 , with values reported up to 20 (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli, 2008).

2.3 HYDROGEOLOGIC SETTING

The Four Mile East and Pepegooona sandstone-hosted uranium deposits are located adjacent to the north-eastern flanks of the Flinders Ranges within the Eromanga Basin in the Frome Embayment, South Australia, approximately 550 km north of Adelaide (Figures 2.1 and 2.2). The semi-arid Frome Embayment is host to several other sandstone-hosted uranium deposits (e.g. the Beverley, Pannikan, Pepegooona West, Four Mile West, Gould's Dam, Honeymoon and Oban deposits) and the region is considered highly prospective for future exploration.

The Eromanga Basin is underlain by Palaeo-Mesoproterozoic metasediments, metavolcanics and granitic intrusives, including the Mount Painter and Mount Babbage Inliers (Coats and Blisset, 1971). Along the Paralana Fault Zone, basement rocks are thrust faulted over Mesozoic sediments, outcropping as the Flinders Ranges. These basement rocks

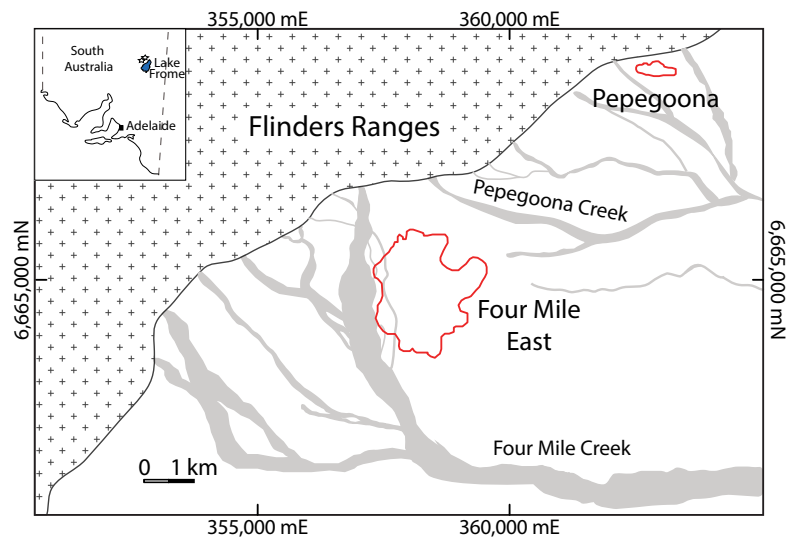


Figure 2.1: Simplified map showing the location of the Four Mile East and Pepegoona deposits. Inset shows South Australia and location of the deposits (stars).

have anomalously high uranium concentrations up to 120 $\mu\text{g/g}$ (Neumann et al., 2000), compared to typical granites with ~ 4 to 10 $\mu\text{g/g}$ U (Kemp and Hawkesworth, 2004); and are considered the likely source of uranium. An intense palaeoweathering profile formed over the basement rocks prior to the deposition of Cretaceous marine sediments. The basement is highly fractured and acts as an aquifer in the Frome Embayment. Recharge to the overlying aquifers is via slow vertical water infiltration through faults and fracture networks within the Fractured Basement Aquifer along the Paralana fault zone.

Unconformably overlying the Mesoproterozoic basement in the Four Mile East area is a thin ($\sim 10 - 20$ m) sequence of Cretaceous diamictite (Figure 2.3a), which predominantly consists of cobbles cemented with silts and fine-grained sands, locally interbedded with coarse-grained sand (SKM, 2010). At Pepegoona, the diamictite has not been identified, rather a thick (50 – 150 m) sequence of Cretaceous marine Bulldog Shale Formation overlies the basement (Figure 2.3b). The Bulldog Shale formation acts as an aquitards between the basement and the overlying Eyre Formation (SKM, 2010). Hydrocarbons identified at the Pepegoona deposit are likely to have derived from the underlying marine Bulldog Shale Formation.

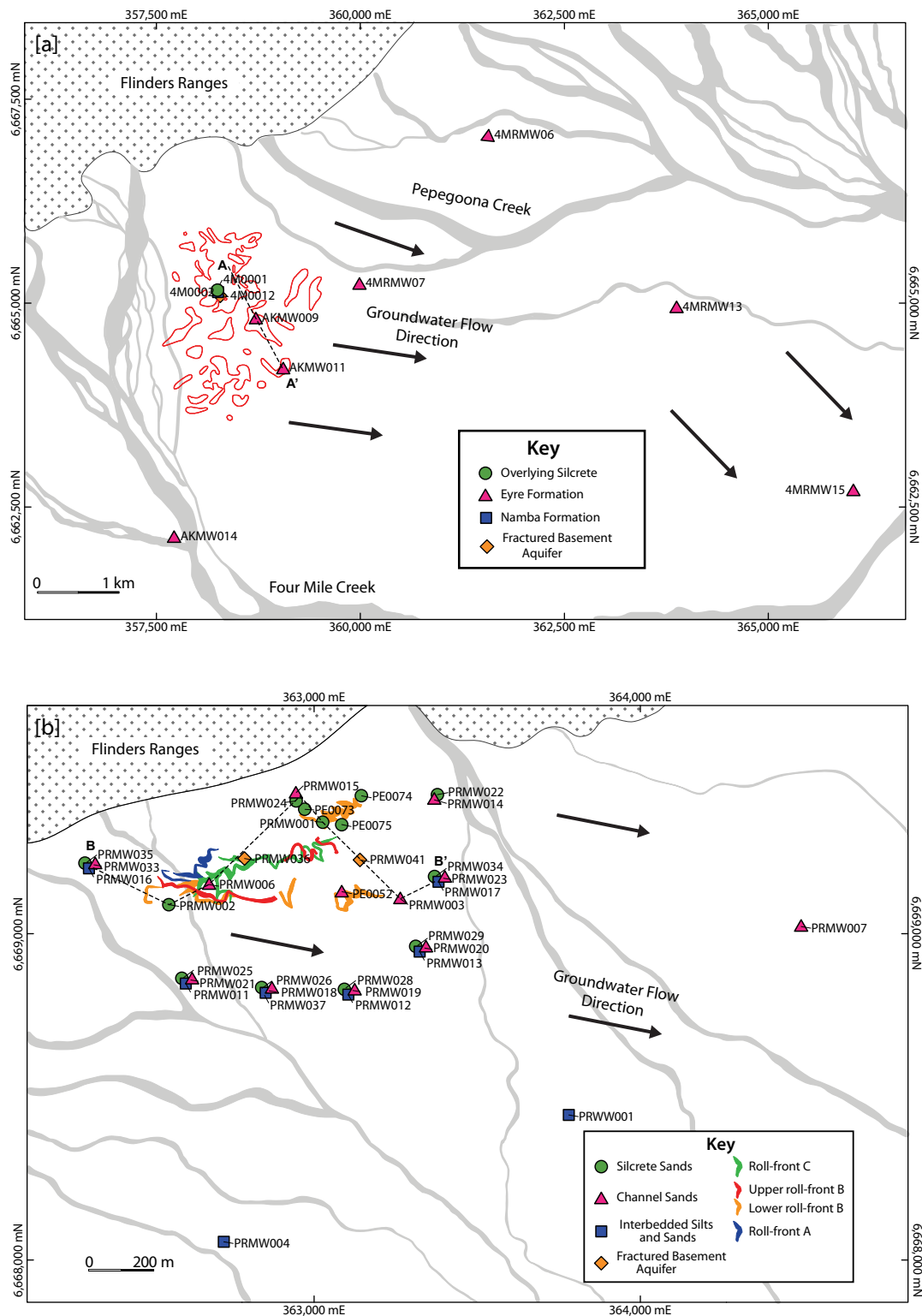


Figure 2.2: Map of the Four Mile East (a) and Pepegoona (b) deposits showing location of groundwater monitor wells from different stratigraphic horizons sampled for this study. Individual roll-fronts for each horizon are shown. Arrows denote Eyre Formation potentiometric groundwater flow paths. Figure (a) shows the transect A to A' for the Four Mile East geological cross section in Figure 2.3a. Figure (b) shows the transect B to B' for the Pepegoona geological cross section in Figure 2.3b.

Overlying the Cretaceous sediments lies the Eocene Eyre Formation, host for both the Four Mile East and Pepegoona deposits. The Eyre Formation consists of several cycles of carbonaceous sands and silts interbedded with clays, deposited in laterally discontinuous fluvial braided channels (SKM, 2008).

A disconformity marks the contact between the Eyre Formation and the overlying Miocene Namba Formation. Locally, the Namba Formation is predominantly comprised of impermeable mud and siltstone, forming a confining aquitard between the Eyre Formation and the Willawortina Formation. Regionally, the Namba Formation comprises three to four fining-upward fluvial/lacustrine cycles of unconsolidated sands, silts, clays and carbonaceous mudstones, and is host to the nearby Beverley palaeochannel deposit (Wülser et al. 2011). Unconformably overlying the area are the Quaternary sands of the Willawortina Formation. This aquifer is largely unsaturated in the Frome Embayment area (SKM, 2010).

Regional groundwater flow direction in the Eyre, Namba and Willawortina Formations is in an overall west to east direction from the recharge areas along the Paralana Fault Zone, discharging toward Lake Frome. In the vicinity of the Four Mile East deposit, local groundwater flow within the Eyre Formation becomes channelled slightly northward by uplifted basement of the Poontana Inlier (Figure 2.2a) (SKM, 2008).

The Pepegoona and Four Mile East deposits are both geometrically complex mineralised systems, consisting of multiple stacked roll-fronts within three sub-aquifer horizons of the Eyre Formation (Figures 2.2 and 2.3). Presently, the understanding of the local geology and delineation of roll-fronts in the vicinity of the Pepegoona deposit by the operating mining company, Heathgate Resources Pty Ltd. has been completed in greater detail than at Four Mile East.

Locally within the Eyre Formation at Pepegoona (Figures 2.2b and 2.3b), the uppermost unit predominantly consists of fine-grained sands capped by a layer of silicified fine-grained sand, informally named the silcrete sand horizon (roll front C). The middle unit, informally named the stacked channel sands horizon, comprises stacked channel sand deposits. The horizon has two mineralised fronts, subdivided into upper and lower B roll fronts. The lower Eyre Formation horizon, the interbedded silts and sands aquifer (roll front

A), consists of predominantly fluvatile silts and sands. Locally, an impervious mudstone overlies the stacked channel sands, separating the two aquifers (A. Marsland-Smith, pers. comm., 2011).

At Four Mile East, the Eyre Formation is comprised of coarse-grained unconsolidated sands with thin clay, silt and cemented pyritic layers, deposited in a number of sedimentary cycles. As with the Pepegooona deposit, a layer of silicified fine-grained sands up to 10 m thick overlies the main body of sand, which is then overlain by package of unconsolidated sands (Heathgate Resources, 2008). Mineralisation is present within all horizons, although individual roll-fronts have not yet been delineated at Four Mile East, thus a stacked ore outline is illustrated in Figure 2.2a.

Mineralisation is typically peneconcordant in both the Four Mile East and Pepegooona deposits, occurring as irregularly shaped lenticular or tabular pods forming arcuate roll fronts. In the silcrete sand horizons of both the Four Mile East and Pepegooona deposits, significant mineralisation is both entrained within the silcrete and concentrated at the silcrete/sand interface, suggesting that mineralisation and silicification may be contemporaneous. In both deposits, minor mineralisation occasionally transgresses into the lowermost layers of the above lying Namba Formation. The ore mineral is primarily uraninite with minor coffinite. Uraninite is present precipitated on grain boundaries and is closely associated with carbonaceous material. Pyrite is widely distributed throughout the ore zone in both deposits, but is more abundant at Pepegooona (A. Marsland-Smith, pers. comm., 2011).

The age of mineralisation at Four Mile East and Pepegooona remains poorly constrained. Both deposits are hosted within the Eocene aged silts and sands, providing a maximum age of mineralisation of 56 to 34 Ma. Carnotite and coffinite U-Pb ages of 3.4 to 6.7 Ma were determined by Wülser et al. (2011) for the nearby Beverley deposit. The Beverley deposit is hosted within Miocene sediments, which provides a maximum age of mineralisation of *ca.* 23 Ma. Despite the proximity of the deposits (within approximately 20 km), mineralogical differences (Schofield et al., 2009) and fluid flow models (Bastrakov and Jaireth, 2009) suggest that the Four Mile and Beverley systems are the result of separate mineralising events.

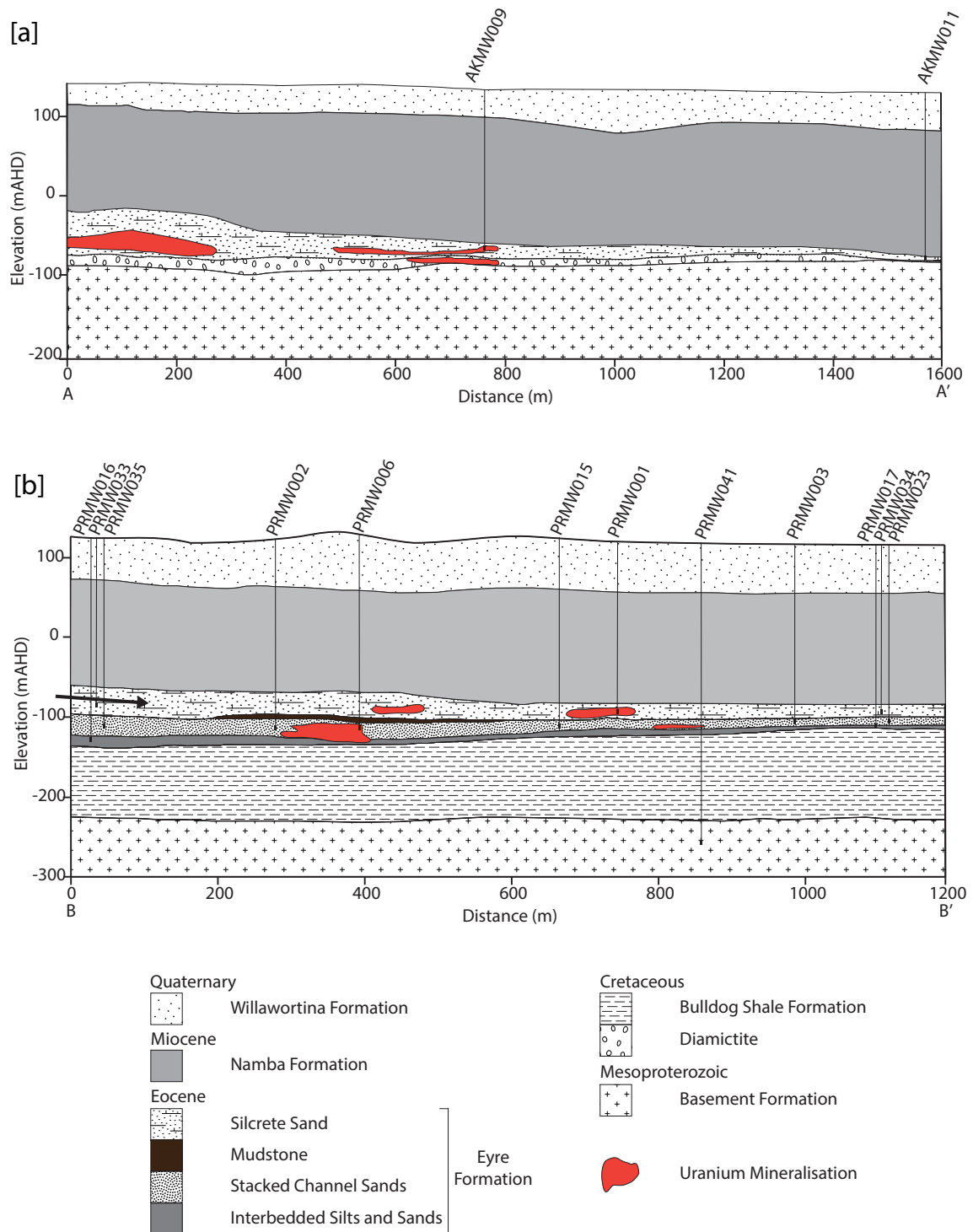


Figure 2.3: Geological cross-section of the (a) Four Mile East deposit from transect A to A' and (b) Pepegooona deposit from transect B to B' showing the complexity of the geology and location of groundwater wells sampled in this study. In figure (a), the direction of groundwater flow within the Eyre Formation is into the page. In Figure (b), arrows indicate Eyre Formation groundwater flow direction.

The Four Mile East and Pepegooona deposits are ideally suited for this study, as the geology and hydrogeology are well constrained as a result of uranium exploration and drilling in the region. The Pepegooona deposit is currently being mined by *in-situ* recovery (ISR), whereby an acidic, oxidising solution is injected into the host aquifer in contact with the mineralisation, thereby dissolving the uranium minerals. The mining solution is then pumped to the surface for processing. As an environmental requirement of mining by *in-situ* recovery (ISR), both ore deposits are girt by groundwater wells screened at different aquifer depths to monitor potential groundwater contamination (SKM, 2010). As the Pepegooona deposit is currently being mined by ISR, more groundwater wells screened at different horizons are available for sampling within the Pepegooona mineralised system, and have resulted in a greater dataset from this locality. This provides a rare opportunity to study the U-series isotopic signature within a uranium mineralised system in three dimensions.

2.4 SAMPLING AND ANALYTICAL PROCEDURES

2.4.1 Groundwater Sampling

Groundwater samples were collected over three field campaigns (June 2009, April 2010 and December 2010). Groundwater wells are cased and screened at a single lithological interval corresponding to the permeable stratigraphic horizon within the aquifer to prevent cross-aquifer contamination. Sampling sites were chosen to include wells within and adjacent to mineralisation, down-gradient and where possible up-gradient along the groundwater flow direction (Figure 2.2). At both deposits, groundwater samples were collected from wells screened at different sub-aquifer horizons within the Eyre Formation. At the Pepegooona deposit, clusters of three nested wells are screened in each of the three sub-aquifers surround the deposit (Figure 2.2b). In addition to the primary Eyre Formation aquifers hosting mineralisation, samples were also collected from the fractured basement aquifer underlying each deposit, and one sample was collected from the overlying Namba Formation aquifer at Four Mile East (Table 2.1). The location of wells from the Four Mile East and Pepegooona deposits are shown in Figure 2.2. Samples were collected from the Four Mile East deposit prior to commencement of ISR. Some wells adjacent to the Pepegooona deposit were sampled several months after ISR had commenced in certain areas of the deposit (see Table 2.1).

Ongoing groundwater monitoring post-ISR indicated that the groundwater chemistry in the perimeter wells had not been affected by mining solution at the time of sampling and are interpreted to be representative of the natural mineralised system.

Two sampling artefacts have been observed in a small number of samples. First, groundwater samples from wells PE0052, PE0073, PE0074, PE0075, PRMW006, PRMW024 and PRMW035 (as noted in Table 2.1) were sampled above the screened interval, resulting in sampling of overlying water. These waters, although taken from the aquifer of interest, may be biased toward higher Eh and lower pH values. Consequently, results from these wells must be treated with caution and are omitted from Figure 2.4. The oxidising conditions may result in the release of any reduced U(IV) adsorbed onto colloidal materials into solution. This may result in slightly higher U concentrations, and might be expected to lower the ($^{234}\text{U}/^{238}\text{U}$) ratio as a result of the congruent dissolution of the mineralised uranium minerals.

A second potential sampling artefact was due to the presence of fluid hydrocarbons whilst sampling PRMW029. A definite hydrocarbon slick was observable on the surface of the water however the well was purged until no visible layer was noticeable prior to sampling. The presence of hydrocarbons offers the potential for uranium fractionation due to the formation of organo-uranium complexes (ie metalloporphyrins, cf. Filby and Van Berkel, 1987). Hydrocarbons are an abundant reductant source throughout the Pepegooona deposit, and micro droplets are expected to be present in many of the water samples. For this study, this was not believed to be a significant source of fractionation, and as such sample PRMW029 has not been excluded from the dataset.

With the exception of PRWW001, groundwater samples were drawn up using dedicated Micropurge[®] low flow bladder pumps permanently installed in each well, at flow rates of 100 – 300 mL/min. Low flow sampling minimises aeration of the groundwater and agitation of aquifer materials, hence representing the optimum groundwater chemistry. Pepegooona sample PRWW001 was air-lifted, which may have lowered the groundwater pH slightly due to carbonic acid formation. Prior to sample collection, all wells were purged until stabilisation of pH, dissolved oxygen (dO), redox potential (Eh), conductivity and temperature (TPS 90 FLMV multimeter). All samples were filtered using Waterra[®] inline

0.45 μm disposable filters. Samples for U-series analysis were collected in acid-washed HDPE bottles and acidified in the field to $\text{pH} < 2$ using Teflon-distilled nitric acid. Within 24 hours of sample collection, un-acidified subsamples were analysed for alkalinity by titration using 0.1 M HCl in accordance with standard method 2320 (APHA, 1998).

Samples for dissolved inorganic carbon $\delta^{13}\text{C}_{\text{DIC}}$ analysis were collected in 12 mL Exetainer[®] screw capped vials with no headspace. Samples for ^{14}C analysis were collected in 1 L HDPE bottles with no headspace and sealed with electrical tape to prevent oxygen exchange with the environment.

2.4.2 Radiocarbon analysis by accelerator mass spectrometry

Radiocarbon isotope analyses were determined by accelerator mass spectrometry using the ANSTO 2 MV Tandatron accelerator (Fink et al., 2004). The ^{14}C activities are reported as percent Modern Carbon (pMC). Radiocarbon age calculations were performed following the methods outlined in Stuiver and Polach (1977) and are presented as conventional radiocarbon ages (years Before Present), not calendar ages.

$\delta^{13}\text{C}_{\text{DIC}}$ were determined by gas chromatography mass spectrometry (GC-MS) at ANSTO following protocols outlines in Meredith et al. (2012). Briefly, CO_2 was liberated from each sample and injected into a helium stream, which was then separated from other gases using a Finnigan[™] Conflo III gas chromatograph attached to a Finnigan[™] 252 mass spectrometer.

2.4.3 Chemical Preparation

Given the difference in solubility of uranium and thorium, samples were processed separately for U and Th isotopic analysis. All acids and standard solutions were prepared with 18 m Ω MilliQ[®] water and Teflon-distilled acids. For uranium isotopic analysis ($n = 50$), aliquots of sufficient sample volume ($\sim 0.5 - 250$ mL) to yield 200 ng of uranium were prepared to optimise sample-spike ratios, based on concentrations determined by quadrupole ICP-MS (Agilent 7500cs; Geochemical Analysis Unit, Macquarie University). To maximise thorium concentrations for isotopic analysis ($n = 20$), the remainder of the 1 L sample was prepared (typically 750 mL to 1 L, although ~ 250 mL was prepared for the duplicate sample

PRMW004). The aliquots were spiked with ~ 0.04 g of ^{236}U - ^{229}Th tracer (Turner et al., 1997), and prior to evaporation were allowed to stand overnight at room temperature to ensure sample-spike equilibration. Uranium and thorium were purified from the groundwater matrix without further pre-concentration by ion exchange chromatography (Biorad® AG1-X8, 100-200 mesh in a 4 mL volume Savillex® column). The chemical preparation procedure for thorium is given in Appendix A. Dried uranium aliquots were redissolved in 4 mL 7 M HNO_3 prior to loading onto the column. The samples were then loaded onto the column that had been previously cleaned with 7 M HNO_3 , 6 M HCl and 0.2 M HNO_3 , and preconditioned with 12 mL 7 M HNO_3 . Matrix constituents were eluted with 18 mL 7 M HNO_3 . Following the elution of the matrix, 8 mL 6 M HCl was passed through the columns, for which uranium samples were discarded to waste, and samples for thorium were collected. Uranium was subsequently eluted from the column with 7 mL 0.2 M HNO_3 . Prior to analysis by multi-collector ICP-MS, the uranium were evaporated to dryness and redissolved in 2 % HNO_3 .

As a check on the method, a single aliquot of certified seawater reference material NASS-5 (National Research Council of Canada, NRCC) was prepared from which uranium and thorium were collected from a single pass through the column purification stages, and the thorium fraction was then further purified a second time as per the samples in this study. The NASS-5 standard was chosen rather than a digested rock standard, which undergoes a different chemical preparation to the waters. Additionally, seawater has a higher salinity than the groundwaters and as such, any artefacts from the chemical purification procedure can be verified. In addition to the seawater standard, three groundwater samples for uranium and one for thorium were prepared in duplicate to assess the external reproducibility of the total procedure.

2.4.4 *U-series isotopic determination by Multi Collector ICP-MS*

U-series isotopes were determined using a Nu Plasma HR MC-ICP-MS at the Geochemical Analysis Unit, Macquarie University. Samples were introduced using a Nu Instruments DSN-100 desolvating nebuliser fitted with a Glass Expansion Micromist 100 μL concentric nebuliser. The U-series analytical procedure for thorium isotopes are presented in Appendix

A. Analyses for uranium were performed in dynamic mode, with ^{235}U and ^{238}U measured on Faraday cups, and ^{234}U and ^{236}U collected on an ion counter. Mass fractionation was corrected using synthetic standard CRM145 (New Brunswick Laboratory (NBL), U.S.A.) using an exponential law and assuming a natural $^{235}\text{U}/^{238}\text{U}$ ratio of 7.253×10^{-3} (Cheng et al., 2000). Ion counter gain was calculated by analysis of CRM145 assuming a $^{234}\text{U}/^{238}\text{U}$ ratio of 5.286×10^{-5} (Cheng et al., 2000). Synthetic standard U010 (NBL, USA) was employed as the bracketing standard for the measurement of uranium isotopes. The U010 certified $^{234}\text{U}/^{238}\text{U}$ ratio of 5.47×10^{-5} (NBL certificate) was used for linear drift correction and normalisation of samples. Synthetic standard U005-A (NBL, U.S.A.) was routinely analysed as an unknown to check the robustness of instrumental corrections. The average U005-A corrected $^{234}\text{U}/^{238}\text{U}$ ratio was $3.43 \pm 0.01 \times 10^{-5}$ (2SD, $n = 30$), which is within error of the published value (3.42×10^{-5} ; NBL certificate). Activity ratios were determined using half-lives calculated using decay constants of Jaffey et al. (1971) for ^{238}U and ^{235}U , Cheng et al. (2000) for ^{234}U and ^{230}Th , and Holden (1990) for ^{232}Th .

Results for U concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios for sample duplicate measurements are presented in Table 2.2. Results for Th concentrations and isotopic compositions are presented in Appendix A. The total procedural blanks for U as determined by isotope dilution are less than 3 pg, thus no blank correction was applied to the samples. Total procedural blanks for Th were ~ 8 pg.

The NASS-5 measured U concentration is $2.65 \pm 0.002 \mu\text{g/L}$ ($2\sigma_{\text{M}}$), which is within $\sim 2\%$ of the compiled information value of $2.6 \mu\text{g/L}$ (NRCC certificate). There are no reported ($^{234}\text{U}/^{238}\text{U}$) ratios for NASS-5, however, given that a uniform open-ocean water composition of 1.1468 has been reported by Andersen et al. (2010), the NASS-5 measured ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.152 ± 0.002 ($2\sigma_{\text{M}}$) is within 5 ‰ of this reported value. For this study, reproducibility of uranium sample duplicates indicated ($^{234}\text{U}/^{238}\text{U}$) variability $< 2\%$, however, a conservative uncertainty of 5 ‰ (2σ) is assigned to the ($^{234}\text{U}/^{238}\text{U}$) activity ratio measurements by taking into consideration the deviation of NASS-5 from the uniform high-precision open-ocean water values of Andersen et al. (2010). External uncertainties on the U concentrations are estimated to be $\sim 15\%$ based sample duplicate measurements (Table 2.2).

2.5 RESULTS

Uranium concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios, as well as field data for groundwater samples from the Four Mile East and Pepegoona deposits are given in Table 2.1. Thorium concentrations and isotopic data are presented in Appendix A.

($^{234}\text{U}/^{238}\text{U}$) activity ratios in groundwaters from both deposits showed considerable disequilibrium, ranging from 0.889 ± 0.005 to 2.815 ± 0.005 . Uranium concentrations vary over several orders of magnitude, ranging from 0.25 to 196 $\mu\text{g/L}$. Both deposits have ambient groundwater temperatures ranging from 22.1 to 31.4 $^{\circ}\text{C}$. Radiocarbon analyses are given in Table 2.3. $\delta^{13}\text{C}_{\text{DIC}}$ results are reported as per mil (‰ VPDB) deviation from the international carbonate standard, NBS19 with a precision of $\pm 0.1\%$. Groundwaters from the Eyre Formation show a narrow range in $\delta^{13}\text{C}_{\text{DIC}}$ of -6.9 to -11 ‰. Radiocarbon activities ranged from 15.32 pMC closest to the recharge zone, to 0.88 pMC in the distal wells. Groundwater ages range from 15,070 to 38,020 years Before Present.

2.5.1 Four Mile East Deposit

2.5.1.1 Eyre Formation Aquifer

In the Four Mile East region, Eyre Formation aquifer samples are typically characterised by highly reducing groundwaters, with Eh values ranging from -148 to -257 mV and conductivity ranged from 3.57 to 4.75 mS. Sample 4M0001, sampled above a confining layer of silcrete from the upper Eyre Formation, is moderately reducing, with an Eh of -26 mV, and has a low ($^{234}\text{U}/^{238}\text{U}$) ratio of 0.970, but the highest U concentration of 196 $\mu\text{g/L}$. The groundwater sampled within mineralisation (AKMW009) has an unusually low U concentration of 4.3 $\mu\text{g/L}$, and a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.135. Sample AKMW009, in low-grade mineralisation showed a U concentration of 73 $\mu\text{g/L}$ and a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.062. Regional monitor well 4MRMW015, located approximately 8 km down-gradient of mineralisation has a U concentration of 4.6 $\mu\text{g/L}$, but the highest ($^{234}\text{U}/^{238}\text{U}$) ratio of 2.116. Regional monitor well 4MRMW014 is located due south of the deposit and is not directly within the groundwater flow path down-gradient of mineralisation. Sample 4MRMW014 has a U concentration of 1.1 $\mu\text{g/L}$, and a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.617.

Table 2.1: Field data, uranium concentrations and ($^{234}\text{U}/^{238}\text{U}$) activity ratios for Four Mile East and Pepegooona groundwaters.

Water Sample	Eastings ^a	Northings ^a	Date Collected	SWL (m) ^b	Screen height (m) ^c	pH	dO (mg/L)	EC (mS)	Redox (mV)	T (°C)	Alkalinity (mg/L CaCO ₃)	U (µg/L)	($^{234}\text{U}/^{238}\text{U}$)	2σ _M ^d
Four Mile East														
Eyre Formation														
AKMW009	358718	6664816	6/7/2009	79.0	213	7.13	-0.04	4.18	-227	24.5	353	4.7	1.135	0.002
AKMW011	359048	6664200	6/7/2009	72.4	182	11.64	0.39	3.85	-172	25.8	305	73	1.062	0.002
4MRMW15	366028	6662672	6/5/2009	55.6	187	7.56	0.34	4.19	-229	25.9	273	4.6	2.116	0.004
4MRMW13	363903	6664942	6/5/2009	66.0	204	7.45	1.07	3.65	-169	25.2	335	1.6	1.094	0.002
4MRMW13	363903	6664942	4/17/2010	66.0	204	7.34	1.04	3.57	-163	26.7	360	0.35	1.291	0.005
AKMW014	357717	6662138	6/6/2009	54.3	159	6.9	0.17	4.75	-148	26	309	1.1	1.617	0.003
4MRMW06	361567	6667059	6/7/2009	62.2	258	7.09	0.21	3.85	-197	26.6	379	0.56	1.131	0.003
4MRMW06**	361567	6667059	4/17/2010	63.4	258	7.13	0.15	3.8	-205	26	305	0.53	1.108	0.004
4MRMW07	359988	6665248	6/7/2009	74.2	256	7.23	0.27	4.42	-257	26.7	390	0.82	1.328	0.003
4M0001	358250	6665158	6/7/2009	81.9	156	7	0.68	2.87	-26	24.9	305	196	0.970	0.002
Namba Formation														
4M0002	358254	6665134	6/7/2009	61.3	117	7.08	0.11	3.24	-164	25.9	398	73	1.200	0.003
Fractured Basement Aquifer														
4M0012	358297	6665122	6/7/2009	72.2	265	6.77	0.52	2.4	93	26.1	235	184	1.141	0.002
Pepegooona														
Eyre Formation - Silerete Sands horizon														
PE0073^	362972	6669380	12/20/2010	93.00	218	7.32	4.67	4.43	758	22.1	198	13	1.259	0.002
PE0074^	363146	6669422	12/19/2010	94.30	217	7.02	0.84	4.21	107	29.9	234	21	1.421	0.003
PE0075^	363084	6669334	12/20/2010	92.22	221	6.98	2.69	4.18	810	27.8	212	6.1	1.274	0.003
PRMW001	363026	6669341	4/18/2010	91.15	216	7.24	0.52	4.17	-252	31.4	280	62	1.396	0.003
PRMW001	363026	6669341	12/20/2010	91.84	216	6.98	0.52	3.94	-191	27.7	250	23	1.372	0.003
PRMW002	362555	6669088	4/18/2010	83.55	216	7.56	0.78	4.09	-249	30.1	215	8.9	1.025	0.002

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Table 2.1 continued

Water Sample	Easting ^a	Northings ^a	Date Collected	SWL (m) ^b	Screen height (m) ^c	pH	dO (mg/L)	EC (mS)	Redox (mV)	T (°C)	Alkalinity (mg/L CaCO ₃)	U (µg/L) (²³⁴ U/ ²³⁸ U)	2σ _M ^d
Pepegoona Eyre Formation - Silcrete Sands horizon (continued)													
PRMW002	362555	6669088	12/18/2010	83.81	216	7.51	0.47	4.08	-196	28.2	240	2.8	0.003
PRMW022	363377	6669422	12/16/2010	95.04	208	9.18	0.67	3.90	-274	28.8	171	0.46	0.003
PRMW024 [^]	362944	6669406	12/16/2010	93.83	208	7.32	0.11	3.95	18	29.2	230	6.4	0.003
PRMW025	362601	6668862	12/18/2010	nd	206	7.01	0.28	5.00	-198	29.5	293	0.25	0.002
PRMW026**	362858	6668834	12/19/2010	81.11	219	7.54	0.62	4.31	-248	28.4	nd	1.3	0.003
PRMW028	363110	6668828	12/19/2010	82.99	217	7.25	0.59	4.71	-265	27.5	303	1.0	0.002
PRMW029†	363326	6668961	12/17/2010	85.59	204	7.04	0.28	3.15	-57	26.8	346	1.9	0.004
PRMW034	363386	6669164	12/17/2010	89.18	204	7.40	0.38	5.26	-210	27.8	302	0.72	0.003
PRMW035 [^]	362310	6669204	12/18/2010	88.35	204	6.91	0.48	4.05	-30	27.9	249	20	0.003
Eyre Formation - Stacked Channel Sands horizon													
PE0052 [^]	363089	6669131	12/20/2010	89.22	226	7.14	2.44	4.18	761	28.6	210	5.2	0.002
PRMW003	363264	6669107	4/18/2010	89.18	226	7.3	0.16	4.17	-272	27.9	245	10	0.003
PRMW006	362677	6669149	4/18/2010	84.2	227	7.02	0.43	4.05	-244	29.4	270	3.1	0.003
PRMW006 [^]	362677	6669149	12/21/2010	84.70	227	6.93	0.72	4.00	152	28.3	217	28	0.003
PRMW007	364493	6669022	4/18/2010	81.1	228	7.29	0.38	4.32	-234	29.4	270	4.4	0.002
PRMW014	363371	6669415	12/16/2010	94.86	223	8.04	0.46	3.93	-274	29.0	124	3.9	0.002
PRMW015	362945	6669430	12/16/2010	96.79	228	7.20	0.41	3.91	-237	29.2	242	2.8	0.003
PRMW018	362848	6668826	12/19/2010	82.90	241	7.01	0.65	4.38	-200	27.9	246	1.2	0.002
PRMW019	363103	6668819	12/18/2010	84.99	242	7.04	0.66	4.22	-137	27.2	241	3.7	0.002
PRMW020	363331	6668952	12/17/2010	86.53	227	7.03	0.42	4.17	-154	26.4	311	1.2	0.003
PRMW021	362626	6668853	12/18/2010	83.60	242	7.33	0.23	4.24	-240	29.6	296	0.47	0.002
PRMW023	363394	6669167	12/17/2010	90.02	222	7.00	0.50	3.40	-101	27.8	231	20	0.003
PRMW033	362320	6669213	12/18/2010	88.00	229	7.01	0.51	4.03	-198	29.0	242	2.9	0.002

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Table 2.1 continued

Water Sample	Eastings ^a	Northings ^a	Date Collected	SWL (m) ^b	Screen height (m) ^c	pH	dO (mg/L)	EC (mS)	Redox (mV)	T (°C)	Alkalinity (mg/L CaCO ₃)	U (µg/L) (²³⁴ U/ ²³⁸ U)	2σ _M ^d
Pepegoona													
Eyre Formation - Interbedded Silts and Sands horizon													
PRMW004**	362723	6668055	4/19/2010	81.6	256	7.38	0.52	4.03	-258	25.3	nd	5.4	0.965
PRMW011	362611	6668854	12/18/2010	82.11	262	7.22	1.53	4.30	-221	29.5	285	1.3	0.994
PRMW012	363112	6668819	12/18/2010	84.75	259	7.02	0.46	4.188	-138	27.9	252	3.9	1.084
PRMW013	363322	6668951	12/17/2010	89.14	259	6.96	0.55	4.16	-120	27.1	251	5.5	0.930
PRMW016	362304	6669212	12/18/2010	88.02	243	8.44	0.37	3.82	-231	28.7	140	0.66	0.889
PRMW017	363383	6669174	12/17/2010	90.53	237	7.13	0.54	4.23	-131	27.8	248	2.9	1.156
PRMW037	362858	6668822	12/19/2010	82.97	260	6.9	0.48	4.11	-201	28.6	241	2.9	1.430
PRMW001	363780	6668444	4/19/2010	n/a	238	6.85	1.03	2.75	-148	30.6	245	2.5	1.017
Fractured Basement Aquifer													
PRMW036	362787	6669230	12/20/2010	2.07	378	7.16	0.10	5.46	-271	26.0	331	1.1	1.754
PRMW041	363140	6669225	12/20/2010	5.34	384	7.45	0.17	4.46	-271	25.3	221	1.1	1.709

^a Eastings and Northings (Geocentric Datum Australia GDA94 coordinates).^b Standing water level measured from the top of well casing.^c Depth to middle of the screen, below ground surface.^d 2σ_M is the internal measurement uncertainty of the sample, however a conservative external uncertainty of 5 ‰ is assumed, see text for detail.

† Sample with hydrocarbons, see text for more detail.

^ Sampled above screened interval, see text for more detail.

nd not determined.

** Average of total procedural duplicates, see Table 2.2 for individual measurements.

Samples collected in December, 2010 were collected after ISR had commenced within sections of the deposit, however are interpreted to reflect natural groundwater conditions.

Table 2.2: U concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios for total procedural duplicates

Sample	U ($\mu\text{g/L}$) ^a	($^{234}\text{U}/^{238}\text{U}$)	$2\sigma_{\text{M}}$ ^b
4MRMW06			
(1)	0.52	1.108	0.004
(2)	0.53	1.108	0.003
Average	0.53	1.108	
2SD	0.02	0.000	
PRMW026			
(1)	1.4	1.133	0.002
(2)	1.2	1.131	0.003
Average	1.27	1.132	
2SD	0.30	0.003	
PRMW004			
(1)	5.6	0.966	0.002
(2)	5.2	0.964	0.002
Average	5.41	0.965	
2SD	0.61	0.002	

^a Uncertainty on U concentrations is less than 15 % based on sample duplicate measurements

^b $2\sigma_{\text{M}}$ is the internal measurement uncertainty of the sample, however a conservative external uncertainty of 5 ‰ is assumed, see text for detail

Table 2.3: Radiocarbon data for Eyre Formation groundwaters.

Sample	Radiocarbon Age (yrs BP) ^a	σ	pMC	2σ	$\delta^{13}\text{C}$ (‰)	2σ
PRMW001	17,940	80	10.72	0.40	-6.9	0.8
PRMW002	15,760	70	14.06	0.44	-10.1	1.2
PRMW003	18,070	80	10.54	0.40	-10.6	0.8
PRMW004	18,940	90	9.46	0.40	-11	1.6
PRMW006	15,070	60	15.32	0.44	-10.8	1.6
PRMW007	18,440	90	10.7	0.44	-9.5	0.4
4MRMW06	38,020	360	0.88	0.16	-7.8	0.8
4MRMW13	33,140	350	1.62	0.28	-8.4	0.8

^a Radiocarbon age calculations were performed following the methods outlined in Stuiver and Polach (1977).

2.5.1.2 Fractured Basement Aquifer

One groundwater sample (4M0012) was collected from the Fractured Basement Aquifer underlying the Four Mile East deposit. It has a neutral pH of 6.77 and is moderately oxidising, with an Eh of +93 mV. Conductivity is quite low (2.4 mS), when compared with groundwaters in the above lying aquifers. Alkalinity is 235 mg/L CaCO₃. The U concentration of 184 µg/L, is at the higher end of the range of values observed in Four Mile East groundwaters, and is characterised by a (²³⁴U/²³⁸U) ratio of 1.141.

2.5.1.3 Namba Formation Aquifer

One sample (4M0002) was collected from the Namba Formation Aquifer, overlying the Four Mile East deposit. The groundwater has a neutral pH of 7.08, alkalinity of 398 mg/L CaCO₃ and conductivity of 3.24 mS. The aquifer is reducing, with an Eh of -164 mV. The U concentration is 73 µg/L, and the (²³⁴U/²³⁸U) ratio is 1.200.

2.5.2 Pepegoona Deposit

2.5.2.1 Eyre Formation Aquifer - Silcrete Sand Horizon

The silcrete sand horizon of the Eyre Formation Aquifer at Pepegoona is characterised by predominantly neutral groundwater pH values ranging from 6.91 to 7.56, with one slightly alkaline sample collected from PRMW022, with a pH of 9.18. Groundwater samples collected close to the range front, up-gradient of mineralisation vary from slightly reducing in the west to highly oxidising in the east, with Eh ranging from -30 to +810 mV, which is due to sampling above the screened interval, as discussed above. Groundwater samples collected down-gradient of mineralisation are strongly reducing (Eh ranging from -191 to -274 mV), with the exception of sample PRMW029, which is slightly reducing (Eh -57 mV). This sample is unusual, as fluid mobile hydrocarbons were pumped whilst sampling the well and the implications of this were discussed above. Conductivity in groundwaters from the silcrete sand horizon ranged from 3.90 to 5.26 mS, with the exception of PRMW029 (3.15 mS). Groundwaters exhibit alkalinities ranging from 171 to 346 mg/L CaCO₃. Groundwaters sampled up-gradient of mineralisation have U concentrations ranging from 6.1 to 20.6 µg/L whereas those collected down-gradient of mineralisation have U concentrations ranging

from 0.3 to 8.9 µg/L. Maximum U concentrations are found in samples from mineralised groundwater well PRMW001, which was sampled both prior to mining (62 µg/L) and after ISR had commenced in nearby wells for comparison (23 µg/L). This sample showed some variability in groundwater chemistry and field parameters post-ISR. The pre-ISR values were pH 7.24, conductivity 4.17 mS, Eh -252 mV, alkalinity 280 mg/L CaCO₃ and a (²³⁴U/²³⁸U) ratio of 1.396. Post-ISR values were pH 6.98, conductivity 3.94 mS, Eh -191 mV, alkalinity 250 mg/L CaCO₃ and a (²³⁴U/²³⁸U) ratio of 1.372. These differences may arise as a result of seasonal variability rather than as a result of contact with mining solution. If the waters had experienced contact with the acidic, oxidising mining solution, this would be reflected by lower pH values and higher redox potentials. Additional sampling is required to determine any annual variations. (²³⁴U/²³⁸U) ratios in the silcrete sand horizon are all greater than 1, typically ranging from 1.025 to 1.955, with the exception of sample PRMW029, which has a much higher (²³⁴U/²³⁸U) ratio of 2.815. This may be due to the presence of fluid mobile hydrocarbons present whilst sampling.

2.5.2.2 Eyre Formation Aquifer – Stacked Channel Sands Horizon

The stacked channel sand horizon is also characterised by predominantly neutral pH groundwater values ranging from 6.93 to 7.33, with the exception of sample PRMW014 with a pH 8.04. Groundwater samples collected from this horizon are strongly reducing (Eh ranging from -101 to -274 mV), with the exception of two samples. Sample PE0052 is located up-gradient of mineralisation within the stacked channel sand horizon, and is very oxidising with an Eh of +761 mV, however this sample was collected above the screen (as discussed above). Conductivity values ranged from 3.40 to 4.38 mS and alkalinities range from 124 to 311 mg/L CaCO₃. Groundwaters sampled up-gradient of mineralisation have U concentrations ranging from 2.8 to 5.2 µg/L, whereas down-gradient samples have variable U concentrations, ranging from 0.5 to 20 µg/L. Mineralised groundwater well PRMW006 was sampled both prior to mining (3.1 µg/L) and after ISR had commenced in nearby wells for comparison (28.4 µg/L). This well has also shown some variability in groundwater chemistry and field parameters post-ISR. The pre-ISR groundwater showed a

pH of 7.02, conductivity of 4.05 mS, reducing Eh of -244 mV, alkalinity of 270 mg/L CaCO₃ and a (²³⁴U/²³⁸U) ratio of 1.414. Post-ISR, the sample pH became slightly more acidic (pH of 6.93), whereas conductivity remained the same (4.00 mS). The redox potential post-ISR is oxidising (Eh of +152 mV), and the alkalinity slightly lower at 217 mg/L CaCO₃. Post-ISR, sample PRMW006 has a (²³⁴U/²³⁸U) ratio of 1.490. The low flow pump was removed and reinstalled between field campaigns, and it is interpreted that these results reflect sampling groundwater above the screened interval rather than effects from ISR mining. (²³⁴U/²³⁸U) ratios in the stacked channel sand horizon are quite variable, ranging from 0.972 to 1.644.

2.5.2.3 Eyre Formation Aquifer - Interbedded Silts and Sand Horizon

The interbedded silts and sand horizon has a similar range of predominantly neutral groundwater pH values of 6.85 to 7.38 to the other Eyre Formation aquifers, with the exception of one slightly alkaline sample PRMW016 with a pH 8.44. Groundwater samples collected from this horizon are strongly reducing (Eh ranging from -120 to -258 mV). Conductivity values ranged from 3.82 to 4.30 mS, with the exception of sample PRWW001 with a conductivity of 2.75 mS, which was an airlifted sample. Groundwater alkalinities range from 140 to 285 mg/L CaCO₃. Uranium concentrations are typically quite low, ranging from 0.7 to 5.6 µg/L. The interbedded silts and sand horizon is typically characterised by lower (²³⁴U/²³⁸U) ratios than the two upper horizons, ranging from 0.889 to 1.430.

2.5.2.4 Fractured Basement Aquifer

Two samples were collected from the underlying Fractured Basement Aquifer. The two samples have neutral pH values of 7.16 and 7.45. The Fractured Basement Aquifer at Pepegooona is strongly reducing, with an Eh of -271 mV. Conductivity was slightly variable, ranging from 4.46 to 5.46 mS. Alkalinity also varied slightly, ranging from 221 to 331 mg/L CaCO₃. Uranium concentrations are low, (1.1 µg/L), but (²³⁴U/²³⁸U) ratios are quite high, ranging from 1.709 to 1.754.

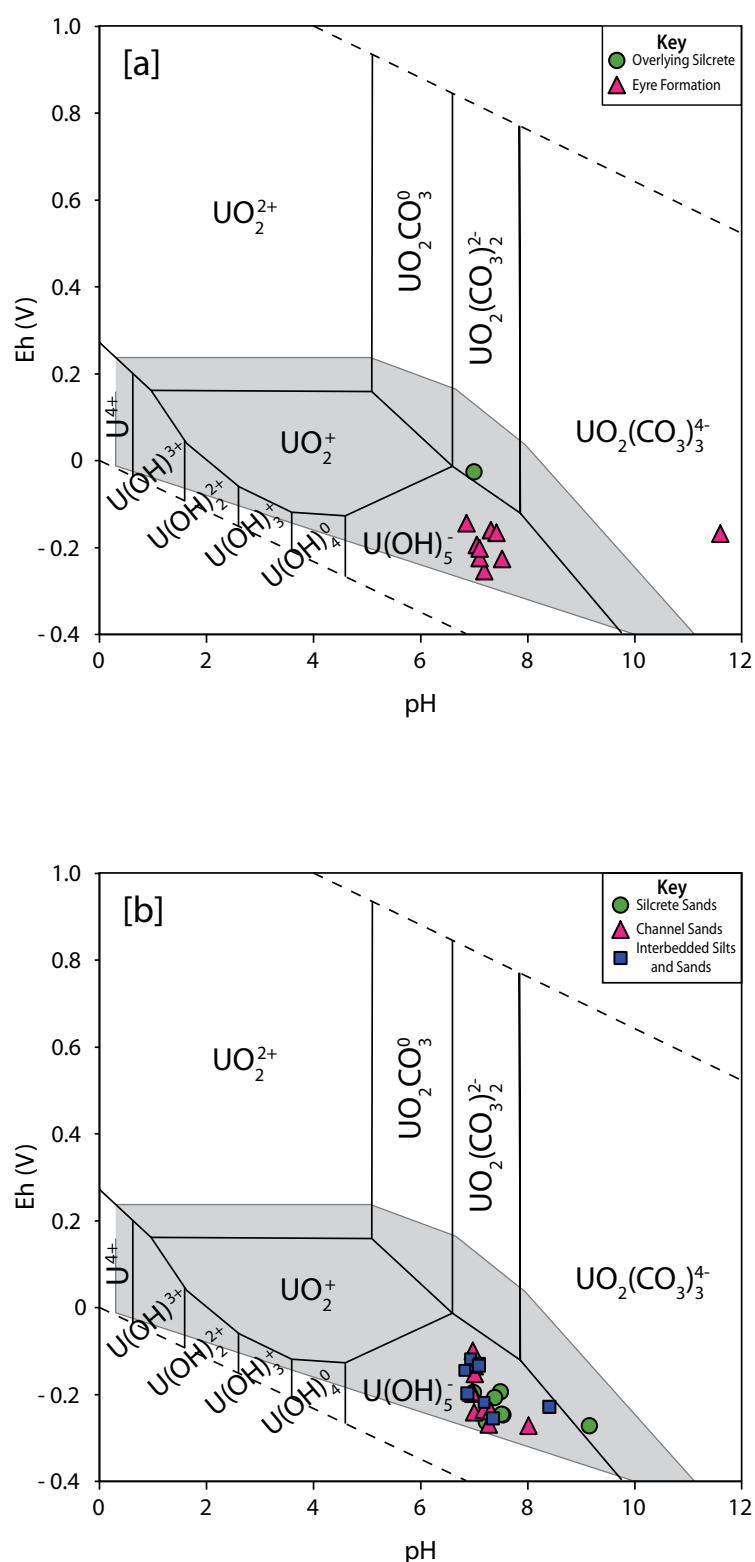


Figure 2.4: Redox potential (Eh) vs. pH diagram for Eyre Formation groundwaters from Four Mile East (a) and Pepegooona (b). Fields show aqueous uranium species at 25°C, with typical groundwater CO_2 pressure of 10^{-2} atm and $\Sigma\text{U} = 10^{-6}$ M. Uranium is present predominantly as aqueous U(IV) hydroxyl and U(VI) carbonate complexes, and plots within the uraninite solubility field, shown in grey (fields modified after Langmuir, 1978 and Langmuir and Chatham, 1980).

2.6 DISCUSSION

The primary objective of this study is to characterise the U-series isotopes in groundwater with respect to high-grade uranium mineralisation. In the following discussion we explore the potential usefulness of U-series isotopes as an exploration tool. In addition, uranium speciation and radiocarbon ages will be presented. Discussion of the thorium isotopic signatures is presented in Appendix A.

2.6.1 *Uranium speciation*

Groundwaters from within the Eyre Formation aquifers at Four Mile East and Pepegoona are highly reducing in nature, consistent with the high abundance of potential reductant sources within the host aquifers. The range of U concentrations (0.25 to 196 µg/L) observed are typical of reducing groundwaters (Gascoyne, 1992). Under reducing groundwater conditions, uranium is present in the U(IV) valence state and is relatively immobile (Langmuir, 1978). The limited mobility of uranium in the tetravalent state under reducing conditions and low uranium concentrations suggests that the Four Mile East and Pepegoona deposits are relatively stable, and are no longer accumulating or being remobilised by continued groundwater movement.

In an aqueous uranium speciation diagram plot of groundwater pH against Eh (Figure 2.4), the data from Four Mile East and Pepegoona suggest that uranium is present predominantly as aqueous U(IV) hydroxyl and U(VI) carbonate complexes, which are typical of sandstone-hosted uranium deposits (Langmuir, 1978). Over the range of pH and Eh values observed in groundwater samples from Four Mile East and Pepegoona, most samples are located within the solubility field of uraninite ± coffinite as defined by Langmuir and Herman (1980), which is in agreement with the observed mineralogy at both deposits.

2.6.2 *Uranium fractionation mechanisms*

2.6.2.1 ($^{234}\text{U}/^{238}\text{U}$) ratios > 1

The ($^{234}\text{U}/^{238}\text{U}$) ratios > 1 observed in the groundwaters from Four Mile East and Pepegoona are typical of most groundwaters (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli, 2008) and can be attributed to the preferential leaching and alpha recoil of

^{234}U into solution. At Four Mile East and Pepegoona, observed ($^{234}\text{U}/^{238}\text{U}$) ratios > 1 and up to ~ 3 are consistent with ratios observed in natural waters sampled from arid environments (e.g. Reynolds et al., 2003). The increase in ($^{234}\text{U}/^{238}\text{U}$) ratio along the groundwater flow path is consistent with preferential leaching of ^{234}U from radiation damaged sites. Another explanation for the increasing ratios along the flow path might be from incongruent dissolution or weathering of the aquifer host material (Porcelli and Swarzenski, 2003). If the groundwaters showed ($^{234}\text{U}/^{238}\text{U}$) ratios approaching secular equilibrium along the groundwater flow path, this might be interpreted to reflect the congruent dissolution of the aquifer host rock with a ($^{234}\text{U}/^{238}\text{U}$) ratio equal to one, however this is not observed at this locality.

2.6.2.2 ($^{234}\text{U}/^{238}\text{U}$) ratios < 1

The ($^{234}\text{U}/^{238}\text{U}$) ratios < 1 observed at Four Mile East and Pepegoona are less common in natural groundwaters. High uranium concentrations and ($^{234}\text{U}/^{238}\text{U}$) ratios < 1 were observed in groundwaters down-gradient of a roll-front within the Floridian karstic aquifer system by Cowart and Osmond (1980), who propose that roll-front has undergone remobilisation by oxidising groundwaters.

One possible explanation for ratios < 1 is the congruent dissolution of uranium minerals that have, over time, become depleted in the easily leachable or recoilable ^{234}U on the outer edges of grain boundaries. Based on the half-life of ^{234}U , this mobilisation occurred over the timescale within the previous million years. Dissolution of uranium minerals with ($^{234}\text{U}/^{238}\text{U}$) ratio < 1 would subsequently impart that signature into the next volume of groundwater to pass through the sediments.

Granite leaching experiments conducted by Andersen et al. (2009) showed initial ($^{234}\text{U}/^{238}\text{U}$) ratios above unity, evolving to ratios < 1 over time with progressive leaching. High ($^{234}\text{U}/^{238}\text{U}$) ratios can be explained either by two weathering regimes: (1) a slow weathering regime with high rates of alpha recoil, and (2) by a fast weathering regime dominated by high chemical weathering and preferential leaching.

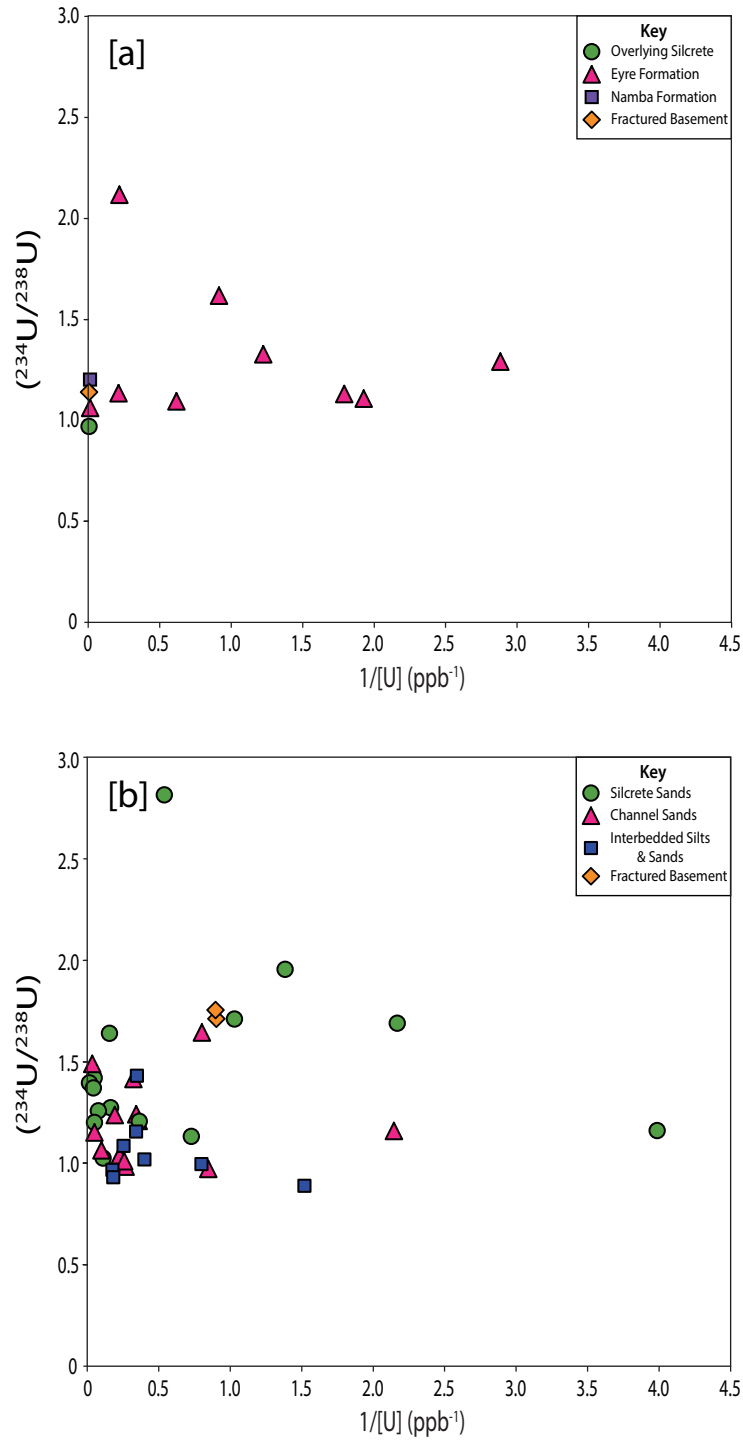


Figure 2.5: Uranium isotope mixing diagrams for Four Mile East (a) and Pepegoona (b), where $(^{234}\text{U}/^{238}\text{U})$ is plotted as a function of reciprocal uranium concentration, in which conservative mixing relationships form a straight line trend. Two-sigma error is smaller than the symbols. The observed isotopic compositions cannot be explained by groundwater mixing.

An alternative explanation proposed by Yanase et al. (1995) suggests that alpha recoil emplacement of daughter nuclides into resistant mineral phases will reduce their availability for leaching. It has also been that the continual process of irreversible adsorption of daughter nuclides onto clay or iron oxyhydroxide minerals may contribute towards low ($^{234}\text{U}/^{238}\text{U}$) ratios (Rosholt 1983; Ohnuki et al., 1990).

2.6.3 *Groundwater mixing*

On a uranium isotopic mixing diagram where ($^{234}\text{U}/^{238}\text{U}$) is plotted against reciprocal uranium concentration (Figure 2.5), straight line trends are indicative of conservative mixing of two end-members. Data for both the Four Mile East and Pepegoona groundwaters do not show a linear correlation, suggesting the non-conservative behaviour of dissolved uranium in exchange with uranium adsorbed onto the host aquifer materials; or the mixing of multiple end-member groundwater sources within the aquifer. The lack of mixing trends within the Eyre Formation is consistent with complex groundwater flow within permeable sediments of variable thickness, interrupted by impermeable clay lenses and local fault displacements. Further, the lack of correlation between ($^{234}\text{U}/^{238}\text{U}$) ratios with U concentration indicates that the activity ratios are independent of U concentration.

2.6.4 *Spatial variability of ($^{234}\text{U}/^{238}\text{U}$) ratios*

A contoured map of ($^{234}\text{U}/^{238}\text{U}$) ratios for each of the three Eyre Formation horizons at Pepegoona is shown in Figure 2.6. Contours lines were generated with a continuous curvature surface gridding algorithm with variable grid spacing (Smith and Wessel, 1990). Given the small number of samples in each horizon, the contoured maps at most provide an indication of the general horizontal isotopic trends. The distribution of ($^{234}\text{U}/^{238}\text{U}$) ratios in all three horizons indicates a general trend of increasing ratio along the groundwater flowpath with groundwaters closest to recharge along the Paralana Fault Zone having the lowest ($^{234}\text{U}/^{238}\text{U}$) ratios. The degree of ($^{234}\text{U}/^{238}\text{U}$) disequilibrium at Pepegoona is highly variable, even between samples that are closely spaced. The complex ($^{234}\text{U}/^{238}\text{U}$) contours shown in Figure 2.6 are interpreted to reflect the heterogeneity in the host lithology and variability in flow rates.

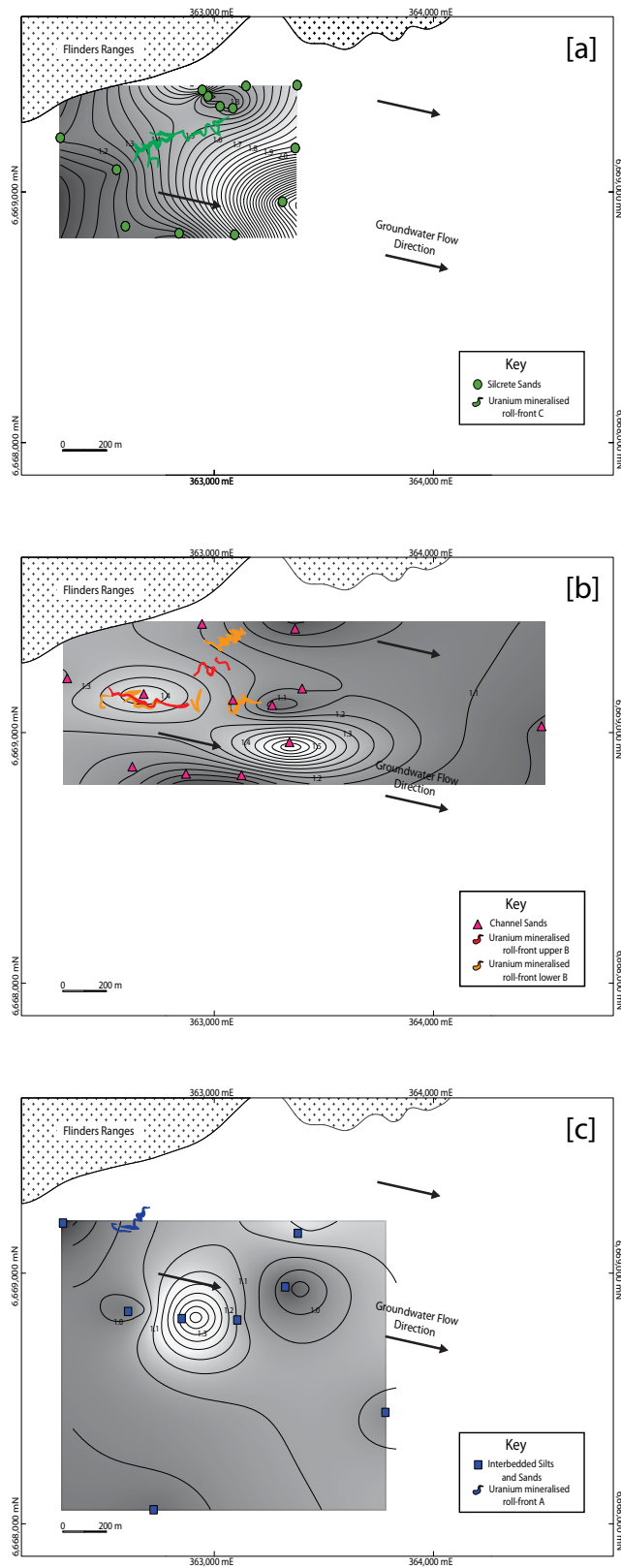


Figure 2.6: Distributions of $(^{234}\text{U}/^{238}\text{U})$ activity ratios surrounding the Pepegooona deposit for the Eyre Formation (a) silcrete sand horizon, (b) stacked channel sand horizon, (c) interbedded silts and sand horizon. Individual roll-fronts for each horizon are shown. All three horizons show increasing $(^{234}\text{U}/^{238}\text{U})$ activity ratios along the groundwater flow path. With increasing aquifer depth, an overall decreasing $(^{234}\text{U}/^{238}\text{U})$ activity ratio trend can be seen. This may reflect changes in aquifer host lithology, which in turn influences the particle size, alpha recoil mobility, and groundwater flow rate.

At the map scale, identification of the presence of mineralisation from ($^{234}\text{U}/^{238}\text{U}$) ratios is not possible. Groundwaters sampled within the uranium mineralisation have ($^{234}\text{U}/^{238}\text{U}$) ratios of ~ 1.2 to 1.4 , which are significantly lower than ratios typically measured in arid areas. The isotopic signature in the groundwater acquired in the mineralisation is only seen proximal to mineralisation and within several hundred meters along the groundwater flow path, ($^{234}\text{U}/^{238}\text{U}$) ratios return to values of ~ 2 to 3 , which are typical of waters sampled in arid environments (Reynolds et al., 2003).

In the Pepegoona deposit, ($^{234}\text{U}/^{238}\text{U}$) ratios show an overall decreasing trend with increasing depth from the uppermost to lower Eyre Formation aquifers, particularly where groundwaters have been collected from close proximity from the three nested wells. One exception is noted, with sample PRMW037 from the interbedded silts and sands horizon possessing a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.430 , which is greater than the overlying horizons (samples PRMW021 and PRMW025 with ($^{234}\text{U}/^{238}\text{U}$) ratios of 1.159 and 1.161 respectively). This might reflect local heterogeneity in the aquifer host lithology and groundwater flow rate. The upper Eyre Formation horizons are comprised of silicified sand and stacked channel sand deposits, which are coarser grained and more permeable than the underlying interbedded silt and sand horizon. The greater porosity of the upper horizons should result in faster flow rates than the finer grained interbedded silt and sand horizon. Faster flow rates would be expected to have lower ($^{234}\text{U}/^{238}\text{U}$) ratios as the water has less time for ^{234}U to accumulate in solution from preferential leaching or alpha recoil. At Pepegoona, the opposite trend is observed, with the interbedded silts and sands horizon showing the lowest activity ratios. This makes it clear that significant three-dimensional complexity exists, confounding simple models for ($^{234}\text{U}/^{238}\text{U}$) distribution.

2.6.5 Radiocarbon analyses

Groundwaters in the vicinity of the Pepegoona deposit have ^{14}C ages ranging from $15,070$ to $18,940$ yrs BP, increasing uniformly along the direction of groundwater flow with distance from the recharge region within the Flinders Ranges. Regional Four Mile well 4MRMW06 has the oldest radiocarbon age of $38,020 \pm 360$ yrs BP, and is interpreted to have recharged

further west along the Flinders Ranges. 4MRMW13 has a radiocarbon age of $33,140 \pm 350$ yrs BP, and is more than likely the result of mixing of older Eyre Formation waters recharged along the Flinders Ranges to the west near the Four Mile East deposit, and younger waters draining the Pepegooona area.

A simple approximation of flow rate within the Eyre Formation has been calculated by dividing the radiocarbon age (in years BP) by the distance (in meters) between wells along inferred west to east groundwater flow lines. This yields an estimated flow rate of 0.2 to 3.4 m y^{-1} .

Progressively higher ($^{234}\text{U}/^{238}\text{U}$) ratios should be expected in response to greater water-rock interaction due to alpha recoil processes as a function of the half-life of ^{234}U ($^{234}\text{U } t_{1/2} = 246 \text{ ky}$). No correlation between radiocarbon age and ($^{234}\text{U}/^{238}\text{U}$) disequilibrium is observed, suggesting that over the short timescales relative to the half-life of ^{234}U , alpha recoil processes do not contribute significantly to the range of ($^{234}\text{U}/^{238}\text{U}$) disequilibria observed in the Eyre Formation groundwaters.

2.6.6 Implications for the use of ($^{234}\text{U}/^{238}\text{U}$) as an exploration tool

2.6.6.1 Comparison with previous studies

Whilst some literature has shown ($^{234}\text{U}/^{238}\text{U}$) activity ratios approaching secular equilibrium in groundwaters draining high-grade uranium deposits, other studies have shown quite different trends, particularly in reducing groundwater conditions such as those at Four Mile East and Pepegooona. The wide range in ($^{234}\text{U}/^{238}\text{U}$) activity ratios and uranium concentrations observed in the reducing groundwaters from these deposits suggest that ^{234}U - ^{238}U systematics are not simply governed by changes in redox conditions. No systematic trends are observed in the groundwaters from either up-gradient of the deposit within presumably oxidised sediments, or down-gradient in reduced sediments. The range of ($^{234}\text{U}/^{238}\text{U}$) ratios observed are consistent with the range of variability in other uranium deposits described elsewhere.

In the study of the clay-bounded unconformity Cigar Lake ore deposit in Saskatchewan, Canada, Toulhoat and Beaucaire (1991) reported high uranium concentrations and equilibrium ($^{234}\text{U}/^{238}\text{U}$) ratios in oxidised groundwaters draining a high-grade uranium deposit. However, the study also found that reducing groundwaters, or groundwaters that

are close to uraninite saturation will produce either (i) high ($^{234}\text{U}/^{238}\text{U}$) ratios if the exchange surface between uranium-bearing phases and groundwater is large enough to promote preferential ^{234}U enrichment in the fluid phase (selective leaching or alpha recoil); or (ii) low ($^{234}\text{U}/^{238}\text{U}$) ratios if the exchange surface is smaller. High ($^{234}\text{U}/^{238}\text{U}$) ratios are observed above dispersed uranium accumulations, frequently situated in the vicinity of massive uranium deposits. Likewise, Meunier et al. (1992) reported ($^{234}\text{U}/^{238}\text{U}$) ratios in groundwater draining approaching one in the oxidised zone where the ore is redistributed, and ($^{234}\text{U}/^{238}\text{U}$) > 1 in the reduced zone where the ore is stable in the sandstone-hosted Coutras deposit, France. Spalding et al. (1984) reported ($^{234}\text{U}/^{238}\text{U}$) ratios of 1 to 1.2 and uranium concentrations greater than 48 μL in oxidising groundwaters closest to high-grade mineralisation within the sandstone-hosted Crow Butte deposit, Nebraska, U.S.A. In groundwaters draining the fracture bound unconformity style Ranger One deposit, Australia, ($^{234}\text{U}/^{238}\text{U}$) ratios of 0.8 to 1.2 were reported, with ratios increasing with distance from the deposit (Airey, 1986).

In the Carrizo sandstone aquifer system in Texas, U.S.A., Cowart and Osmond (1977) found the occurrence of uranium mineralisation at a redox interface was associated with groundwaters with low dissolved U concentrations, but high ($^{234}\text{U}/^{238}\text{U}$) ratios. These features were interpreted to result from significant alpha recoil input from the precipitated uranium at the redox interface.

Yanase et al. (1995) observed ($^{234}\text{U}/^{238}\text{U}$) ratios < 1 in groundwaters from shallow weathered zone overlying the fracture bound unconformity style Koongarra deposit, Australia, and found higher ($^{234}\text{U}/^{238}\text{U}$) ratios in deeper wells. It was proposed that the ratios less than one could be a result the weathering of materials previously leached and depleted in ^{234}U , or a result of the implantation of ^{234}U into resistant phases.

2.6.6.2 Isotopic equilibration with high-grade mineralisation - possible age constraints

The ($^{234}\text{U}/^{238}\text{U}$) ratio of groundwaters collected within high-grade mineralisation are suggested to reflect the isotopic composition of the uranium minerals. If the hypothesis of congruent dissolution of uranium minerals was valid, groundwaters sampled within and down-gradient of mineralisation should exhibit ratios close to equilibrium values, which is not observed in

groundwaters from the Four Mile East and Pepegooona deposits. An inherent assumption of this model is that the uranium ore minerals congruently dissolving are in secular equilibrium (i.e. the deposit is older than 1 Ma). However, if the uranium minerals have been deposited or remobilised within the past million years and have not attained secular equilibrium ratios, the disequilibrium ratios of the minerals being dissolved would be transferred to the groundwaters down-gradient of the deposit.

Fractionation of U-series isotopes is well documented within sandstone-hosted uranium deposits formed by water-rock interactions, e.g. the 'roll-front' type sandstone-hosted deposits in Wyoming, U.S.A. (Rosholt et al., 1964; Dooley et al., 1964; Rosholt et al., 1965a; 1965b) and Shihongtan, China (Min et al., 2005); the 'basal channel' Ambrosia Lake District, New Mexico (Dooley et al., 1966) and Coutras, France deposits (Meunier et al., 1992).

We suggest that the groundwater ($^{234}\text{U}/^{238}\text{U}$) isotopic signature sampled directly within high-grade mineralisation is dependent on the age of the deposit. A stable deposit that has not undergone deposition or remobilisation within the past million years should impart a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1, whereas an actively dispersing or accumulating deposit will impart disequilibrium signatures into the groundwater. Therefore, the disequilibrium ratios observed from groundwaters with the Pepegooona mineralising system might be indicative of a recently active system that is now attempting to return to equilibrium. In order to test this alternate hypothesis, U-series compositions (and ^{230}Th -U ages) of the mineralisation will need to be determined.

2.6.6.3 Implications for exploration

The uranium isotopic signature acquired in the Pepegooona groundwaters from water-ore interactions resulted in ($^{234}\text{U}/^{238}\text{U}$) ratios of ~1.2 to 1.4. Wells proximal to mineralisation typically show higher ($^{234}\text{U}/^{238}\text{U}$) ratios. This may imply that the groundwater isotopic signature fingerprinting the presence of high-grade uranium mineralisation is rapidly overprinted by water-rock interactions in non-mineralised areas of the aquifer. This is likely the result of the highly reducing groundwater conditions, which favour uranium in the

tetravalent state, resulting in strong sorption to the aquifer host materials. Considerably more monitor wells are necessary before the complexities of the U-series disequilibria associated with mineralisation at Pepegooona can be evaluated.

Additionally, in order to gain a better understanding of the behaviour of ^{234}U and ^{238}U within such an aquifer system, a comparative study relating the groundwater isotopic compositions with that of the host aquifer rocks would allow for greater constraints on the chemical weathering rates (e.g. Maher et al., 2006) and for reactive transport modelling (e.g. Luo et al., 2000; Tricca et al., 2001; Reynolds et al., 2003; Bourdon et al., 2009; Ku et al., 2009). Such studies would allow for the respective role of congruent versus incongruent dissolution, or isotopic equilibration between mineralisation and groundwaters to be established.

2.7 CONCLUSIONS

The present study has established that the Eyre Formation aquifer is very complex in terms of lithology, three-dimensional geology, mineralisation and in terms of the evolution of the isotopic signature in groundwater. The use of U-series disequilibrium in groundwater as a tool for uranium exploration is not supported by our observations from the Eyre Formation sandstone-hosted deposits, rather, we infer that ($^{234}\text{U}/^{238}\text{U}$) ratios reflect dynamic hydrogeologic processes instead of ore formation or remobilisation processes. The limited mobility of uranium in these highly reducing groundwaters suggests that the use of U-series disequilibrium may not be applicable as a proxy for uranium mineralisation in this area, however, might prove useful in other more simplified hydrologic regimes.

We propose that the uranium isotopic signature of groundwater sampled directly within mineralisation reflects the stability of the deposit. The U-series isotopic composition of groundwaters draining high-grade uranium mineralisation may differ depending on the age of the mineralisation: where the deposit has been stable for > 1 Ma, ($^{234}\text{U}/^{238}\text{U}$) ratios near unity could be expected, whilst disequilibrium ($^{234}\text{U}/^{238}\text{U}$) ratios might be expected where mineralisation has been deposited or remobilised within 1 Ma. Future work will determine the age of mineralisation at Pepegooona using U-series to constrain this alternate model.

Additionally, future work will consider uranium isotopic variations between ^{238}U and ^{235}U within groundwaters from the Pepegooona deposit. The deviation of natural $^{238}\text{U}/^{235}\text{U}$ ratios from the long considered invariant value was observed in uranium ores formed by the reduction of U(VI) to U(IV) at low temperatures by Cowan and Adler (1976), and more recently investigated by Stirling et al. (2007); Bopp et al. (2009); and Brennecke et al. (2010). The observed variability in $^{238}\text{U}/^{235}\text{U}$ ratios may act a tracer of oxidation/reduction processes. This highlights the potential application in exploration for sandstone-hosted 'roll-front' uranium deposits, which form by the low temperature reduction of aqueous U(VI) in groundwaters to U(IV) at a redox interface.

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CHAPTER III

FRACTIONATION OF $^{238}\text{U}/^{235}\text{U}$ BY REDUCTION DURING LOW TEMPERATURE URANIUM MINERALISATION PROCESSES

Keywords: uranium isotopes, water-rock interactions, ore deposit, nuclear field shift effect, groundwater

Research Highlights:

- $^{238}\text{U}/^{235}\text{U}$ ratios decrease systematically with U(VI) reduction in groundwater and can be modeled by Rayleigh fractionation (α) of ~ 0.9995 to 0.9997 .
- Isotopic fractionation is inferred to be a result of the nuclear field shift effect during reduction of U(VI) to U(IV) during ore formation processes.
- $^{238}\text{U}/^{235}\text{U}$ isotopes can be used as a tracer for oxidation/reduction processes, and may be insightful in studies of palaeoredox conditions.

ABSTRACT

Investigations of ‘stable’ uranium isotope fractionation during low temperature, redox transformations may provide new insights into the usefulness of the $^{238}\text{U}/^{235}\text{U}$ isotope system as a tracer of palaeoredox processes. Sandstone-hosted uranium deposits accumulate at an oxidation/reduction interface within an aquifer from the low temperature reduction of soluble U(VI) complexes in groundwaters, forming insoluble U(IV) minerals. This setting provides an ideal environment in which to investigate the effects of redox transformations on $^{238}\text{U}/^{235}\text{U}$ fractionation. Here we present coupled measurements of $^{238}\text{U}/^{235}\text{U}$ isotopic compositions and U concentrations for groundwaters and mineralised sediment samples collected in the vicinity of the high-grade Pepegooona sandstone-hosted uranium deposit, Australia.

The mineralised sediment samples display extremely variable $^{238}\text{U}/^{235}\text{U}$ ratios, ranging between 137.267 ± 0.007 and 137.913 ± 0.016 , spanning a 5 ‰ range, which is the largest U isotopic variation found thus far in natural samples. The groundwaters show a greater than 2 ‰ variation in their $^{238}\text{U}/^{235}\text{U}$ ratios, ranging between 137.508 ± 0.007 to 137.820 ± 0.007 . The majority of the groundwater data exhibit a clear systematic relationship between $^{238}\text{U}/^{235}\text{U}$ isotopic composition and U concentration; samples with the lowest U concentrations have

the lowest $^{238}\text{U}/^{235}\text{U}$ ratios. The preferential incorporation of ^{238}U during the precipitation of uranium minerals leaves the groundwaters enriched in ^{235}U , resulting in a progressive shift in $^{238}\text{U}/^{235}\text{U}$ towards lighter values in the aqueous phase as U is removed. These data can be modeled by a closed system Rayleigh fractionation model, with a fractionation factor (α , representing the $^{238}\text{U}/^{235}\text{U}$ composition of the groundwater relative to the solid uranium minerals) of ~ 0.9995 to 0.9997 . Previous studies on the same groundwaters have shown significant disequilibrium between ^{234}U and ^{238}U , with ($^{234}\text{U}/^{238}\text{U}$) activity ratios ranging from ~ 0.9 to 3 . $^{238}\text{U}/^{235}\text{U}$ ratios show a poor correlation with ($^{234}\text{U}/^{238}\text{U}$) activity ratios, which suggests that mineral leaching during weathering is unlikely to control the observed uranium $^{238}\text{U}/^{235}\text{U}$ isotopic variability within this low temperature, redox-controlled mineralised system. Rather, the results imply that $^{238}\text{U}/^{235}\text{U}$ fractionation may be controlled by the nuclear field shift effect during the reduction of U(VI) to U(IV) during mineralisation processes. The findings of this study support the use of the $^{238}\text{U}/^{235}\text{U}$ isotopic system as a palaeoredox tracer to constrain the nature and timing of palaeoredox conditions.

3.1 INTRODUCTION

Recently, $^{238}\text{U}/^{235}\text{U}$ variations have emerged as a potential tool for investigating oxidation-reduction processes in the environment (Bopp et al., 2009) and may provide new insights to better constrain the nature and timing of palaeoredox conditions (Montoya-Pino et al., 2010; Brennecke et al., 2011a). Historically, equilibrium mass-dependent fractionation was not expected between the two long-lived isotopes of uranium, ^{238}U and ^{235}U due to their heavy mass and relatively small mass difference. Consequently, the $^{238}\text{U}/^{235}\text{U}$ ratio has long been considered invariant, and a consensus value of 137.88 has been assumed (Steiger and Jäger, 1977; Chen and Wasserburg, 1981).

In recent years, advances in analytical techniques have allowed for the measurement of $^{238}\text{U}/^{235}\text{U}$ at the sub- 0.1 ‰ level in natural materials (Stirling et al., 2006; 2007; Weyer et al., 2008). The $^{238}\text{U}/^{235}\text{U}$ composition of the Bulk Silicate Earth (BSE), representative of the continental crust and depleted mantle, appears uniform at the 0.1 ‰ level, but is offset from the previously assumed value of 137.88 by *ca.* 0.5 ‰. To this end, the adoption of an updated $^{238}\text{U}/^{235}\text{U}$ ratio of 137.818 ± 0.045 for BSE was recently recommended by Hiess et al. (2012), based on a compilation of published $^{238}\text{U}/^{235}\text{U}$ observations and the analysis of zircons from a diverse range of lithologies. This value for BSE will be used throughout this

contribution. The majority of ‘bulk’ samples of meteorites also display consistent $^{238}\text{U}/^{235}\text{U}$ compositions that overlap with the value of BSE (Stirling et al., 2005; 2006; Amelin et al., 2010). However, an increasing number of studies show significant variation in uranium isotopic compositions in a wide range of other terrestrial and extra-terrestrial environments (Stirling, 2012). Specifically, large 1 to 10 ‰ level variations have recently been observed in some early formed inclusions extracted from meteorites (Amelin et al., 2010; Brennecka et al., 2010b), partly attributed to the decay of extinct ^{247}Cm to ^{235}U in the early solar system (Stirling et al., 2005;2006; Brennecka et al., 2010b). Significant $^{238}\text{U}/^{235}\text{U}$ variations have also been observed in a wide range of terrestrial samples, especially those formed in low-temperature environments (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010a, Hiess et al., 2012).

The fractionation of uranium $^{238}\text{U}/^{235}\text{U}$ isotopes have variously been attributed to: (i) oxidation-reduction reactions, particularly during the reduction of U(VI) to U(IV), sometimes mediated by biological activity (Rademacher et al., 2006; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010a); (ii) differences in uranium coordination geometry between dissolved and adsorbed species (Brennecka et al., 2011); (iii) leaching during continental weathering (Stirling et al., 2007; Bopp et al., 2009; Hiess et al., 2012); and (iv) magmatic processes (Hiess et al., 2012). Such isotopic fractionation can be explained by the effects of either mass-dependent equilibrium or mass-independent kinetic processes (Bigeleisen, 1996; Schauble, 2007). The observed $^{238}\text{U}/^{235}\text{U}$ fractionation is similar to that observed in other heavy stable isotope systematics, thus may be considered ‘stable’ uranium fractionation due to the relatively long half-lives compared to the timescales of geological processes (Stirling, 2012).

In low temperature settings, the largest variations in uranium isotopes have been identified in samples formed in redox environments (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010a). In particular, oxidation-reduction processes play a significant role in the formation of sandstone-hosted uranium deposits. The interaction of oxidising groundwaters carrying aqueous uranyl U(VI) complexes with a reductant source within a permeable sandstone aquifer results in the precipitation of uranium (IV) minerals

such as uraninite (UO_2) or coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$), or the adsorption of insoluble tetravalent uranium complexes onto the aquifer host lithology or organic materials (Langmuir, 1978). Continual groundwater movement results in the redissolution and reprecipitation of uranium minerals, resulting in migration of the mineralised 'roll-front' (Hostetler and Garrels, 1962).

Early studies of uranium ore samples by Cowan and Adler, (1976) suggested that sandstone-hosted uranium ore samples formed at low temperatures were enriched in ^{238}U by 0.3 ‰ with respect to ^{235}U , relative to high temperature magmatic ores. More recent measurements of low temperature mineralised samples have focused on uranium ores and uranium ore concentrates (UOCs) from sandstone-hosted uranium deposits, where $^{238}\text{U}/^{235}\text{U}$ ratios vary from 137.821 ± 0.018 to 137.961 ± 0.018 in UOCs (Brennecka et al., 2010a) and 137.902 ± 0.014 to 137.907 ± 0.022 in tabular sandstone uranium ores (Bopp et al., 2009), representing isotopic shifts of up to 1 ‰. The variability observed in these low temperature uranium deposits contrasts with deposits formed at high temperatures, which show a restricted 0.4 ‰ variation in $^{238}\text{U}/^{235}\text{U}$ ratio (Cowan and Adler, 1976; Bopp et al., 2009; Brennecka et al., 2010a).

The exact processes responsible for fractionating U isotopes in low temperature sandstone-hosted uranium mineralised systems, however, remains poorly understood. Isotopic fractionation of ^{238}U and ^{235}U has largely been attributed to the nuclear field shift effect (also called the nuclear volume effect) during the reduction of U(VI) to U(IV) (Nomura et al., 1996; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; 2010; Brennecka et al., 2010a) whereby the heavier isotope (^{238}U) is preferentially enriched in the reduced U(IV) species. This arises from differences in the electric charge distribution, nuclear size and shape of the isotopic nuclei (Bigeleisen, 1996; Schauble, 2007). In all cases, ^{238}U is preferentially enriched over ^{235}U relative to the composition of BSE in the precipitating uranium mineral phases. It might therefore be expected that the groundwaters from which the uranium has precipitated would be enriched in ^{235}U with respect to BSE. Certainly, biostimulated groundwaters at Rifle Range, U.S.A (Bopp et al., 2010), show a systematic shift in $^{238}\text{U}/^{235}\text{U}$ ratios towards lighter values as the reduction and removal of U progressed. However, to date, no paired measurements of uranium isotopic composition and concentration exist for both

the U(IV)-bearing mineralised sediments and U(VI)-bearing groundwaters from within the same redox system allowing for the rigorous assessment of ^{238}U - ^{235}U isotope systematics during U reduction.

In order to better assess the behaviour of uranium isotopes during mineralisation processes, and to investigate the role of reduction on uranium fractionation, we have measured $^{238}\text{U}/^{235}\text{U}$ ratios and uranium concentrations from groundwaters and mineralised sediment samples collected from the vicinity of the South Australian Pepegooona sandstone-hosted uranium deposit. This deposit provides an ideal natural laboratory for studying isotopic fractionation between ^{235}U and ^{238}U in a natural low temperature redox aqueous system.

3.2 GEOLOGICAL SETTING

The Pepegooona uranium mineralised system is situated within the Eromanga basin of the semi-arid Frome Embayment, South Australia, approximately 550 km north of Adelaide (Figure 3.1, inset). The Frome Embayment is host to several sandstone-hosted uranium deposits and is a highly prospective target for future exploration. This deposit is well suited for such a study, as the geology and hydrogeology have been well constrained as a result of uranium exploration and drilling in the region by the operating mining company, Heathgate Resources Pty Ltd.

Detailed descriptions of the study area are given in Chapter II and only a brief summary is provided here. The Pepegooona deposit is a complex mineralised system, hosted within carbonaceous fluvial sediments of the Eocene Eyre Formation. The Pepegooona deposit consists of four arcuate stacked mineralised roll-fronts hosted within three Eyre Formation sub-aquifer horizons (Figure 3.2). The uppermost unit predominantly consists of fine-grained sands capped by a layer of silicified fine-grained sand, informally named the silcrete sand horizon (roll front C). The middle unit, informally named the stacked channel sands horizon, comprises stacked channel sand deposits. This horizon has two mineralised fronts, subdivided into upper and lower B roll fronts. The lower Eyre Formation horizon, the interbedded silts and sands aquifer (roll front A), consists of predominantly fluvial silts and sands. Locally, an impervious mudstone overlies the stacked channel sands, separating the

two aquifers. Uranium mineralisation is present as uraninite \pm coffinite, precipitated on grain boundaries. The source of the uranium has been largely attributed to leaching from the anomalously high U granites of the Mount Painter District that comprise the basement and outcrop to the west as the Flinders Ranges (see Figures 3.1 and 3.2), or sediments derived from these rocks (Wülser et al., 2011). At Pepegooona, there is an abundance of potential reductants in the system, including H₂S gas, hydrocarbons, sulfide minerals, carbonaceous material, organic complexes or reduction by microbial activity (Chapter II and references therein).

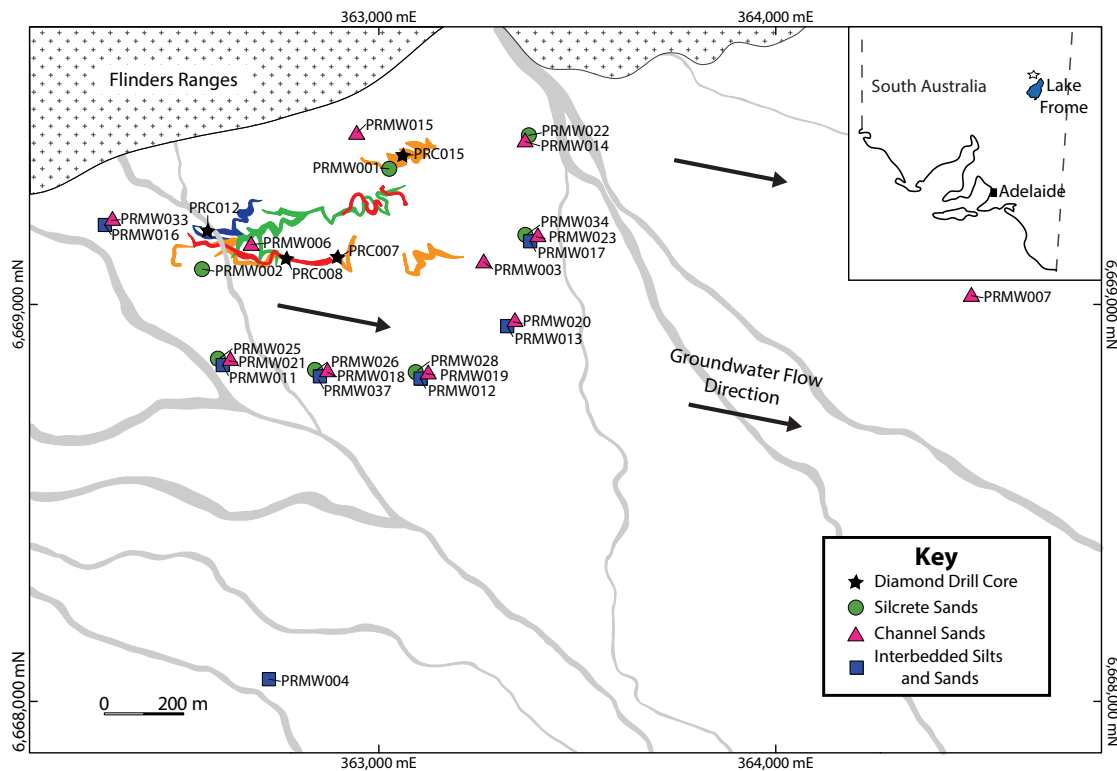


Figure 3.1: Map of the Pepegooona ore deposit (adapted from Chapter II) showing location of groundwater monitor wells from different stratigraphic horizons sampled for this study. Individual mineralised roll-fronts for each horizon are shown. Blue is in the interbedded silts and sand horizon, roll-front A. Red and orange are upper and lower B roll-fronts within the stacked channel sands horizon. Green is in the silcrete sand horizon, roll-front C. The grid coordinates for sample PR1321, not shown on map, are presented in Table 3.2. Arrows denote Eyre Formation potentiometric groundwater flow paths. Inset: Location map showing the location of the Pepegooona deposit (star) in South Australia.

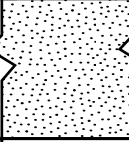
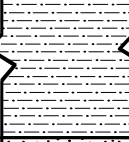
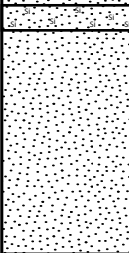
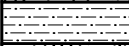
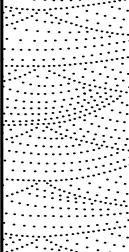
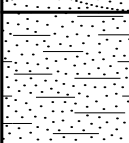
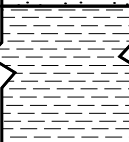
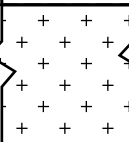
Age	Unit	Unit Thickness	Column	Major Lithology
Quaternary	Willawortina Formation	~60 m		Unconsolidated Sands
Miocene	Namba Formation	~130 m		Mudstone
Eocene	Eyre Formation	~50 m		Silcrete Sands
				Mudstone
				Stacked Channel Sands
				Interbedded Silts & Sands
Cretaceous	Bulldog Shale	~100 m		Mudstone & Shale
Precambrian	Granite Basement			Granite

Figure 3.2: Representative stratigraphic log of the geological units comprising the Pepegooona sandstone-hosted uranium deposit. Note the broken scale for some lithologies. Mineralisation is present within the silcrete sands, stacked channel sands and interbedded silts and sands horizons of the Eyre Formation.

The Pepegoona deposit is currently being mined by *in-situ* recovery (ISR), whereby an acidic, oxidising solution is injected into the host aquifer in contact with the mineralisation. The uranium minerals are subsequently dissolved, and the mining solution is then pumped to the surface for processing.

3.3 SAMPLING AND ANALYTICAL PROCEDURES

3.3.1 Groundwater sampling

A total of 28 groundwater samples were collected over two field campaigns in April and December, 2010. Detailed descriptions of the study site as well as groundwater sampling methods are given in Chapter II. Sampling locations were chosen to include wells within and adjacent to mineralisation, as well as down-gradient and where possible up-gradient along the groundwater flow direction (Figure 3.1). All samples were filtered using inline Waterra® 0.45 µm disposable filters and acidified in the field to pH <2 using Teflon-distilled nitric acid. Some wells adjacent to the Pepegoona deposit were sampled several months after mining by ISR had commenced in certain areas of the deposit (see Table 3.1). Ongoing groundwater monitoring post-ISR indicated that the groundwater chemistry in the perimeter wells had not been affected by mining solution at the time of sampling, and are interpreted to be representative of the natural mineralised system. Additionally, groundwater well PRMW002 was sampled in both field campaigns to assess the effect of seasonal variability and the potential effects of mining on the isotopic variability. Field parameters for the same Pepegoona groundwater samples, such as pH, redox potential (Eh), alkalinity and temperature, along with ($^{234}\text{U}/^{238}\text{U}$) activity ratios, are reported in Chapter II.

3.3.2 Mineralised sediment sampling

Mineralised sediments were collected from four diamond drill cores intersecting the Pepegoona deposit (Figure 3.1). The basement granite sample, PR1321 was collected from rotary mud drill chips (not shown on map). The granite chips were ultrasonicated in ultrapure MilliQ® water and oven dried prior to crushing using an agate mortar. To minimise contamination of the crushing equipment with potentially high U samples, the core samples were broken into fine grains and homogenised using a ceramic spatula prior to digestion.

Mineralogical descriptions for Pepegooa drill core samples are based on the visual inspection of polished blocks prepared for Heathgate Resources Pty Ltd by an external laboratory (ALS Ammtec Ltd, Perth, Australia) using reflected light microscopy and semi-quantitative analysis by Scanning Electron Microscopy (SEM; Zeiss EVO MA15; Geochemical Analysis Unit, Macquarie University).

3.3.3 *Chemical preparation*

All acids and standard solutions were prepared with 18 M Ω MilliQ[®] water and high-purity quartz- and Teflon-distilled acids. For uranium isotopic analysis, a mixed ^{233}U – ^{236}U double spike was used to reliably correct for instrumental mass fractionation during isotopic analysis, as well as any potential isotopic fractionation that may occur during the chemical purification of the sample (Stirling et al., 2005; 2006; 2007; Amelin et al., 2010). For the groundwater samples, aliquots of sufficient sample volume to yield 200 ng of natural U were prepared. Sample-spike ratios were optimised based on initial U concentrations determined by quadrupole ICP-MS (Agilent 7500cs; Geochemical Analysis Unit, Macquarie University). The aliquots, ranging in volume from ~0.5 – 200 mL were spiked with a weighed volume of the ^{233}U – ^{236}U double spike, and prior to evaporation, were allowed to stand overnight at room temperature to promote sample-spike equilibration.

Mineralised sediment samples (~500 mg) were digested by the addition of *ca.* 1 mL HF: 2 mL 14 N HNO₃ in sealed 15 mL Savillex[®] beakers held on a hotplate at 120 °C. To prevent the formation of insoluble fluoride precipitates due to addition of HF, trace amounts of HClO₄ (with a higher boiling point than HF) was added to the samples. The samples were evaporated to dryness in 10 °C increments from 120 °C to 170 °C. After digestion, the samples were redissolved in 2 % HNO₃, from which a small aliquot was taken to determine U concentration by quadrupole ICP-MS (Agilent 7500cs; Geochemical Analysis Unit, Macquarie University). An additional aliquot of sufficient sample volume to yield 200 ng of U was then taken for U isotopic analysis. As with the groundwater samples, the aliquots were spiked with an appropriate volume of ^{233}U – ^{236}U double spike, then allowed to stand overnight at room temperature to promote sample-spike equilibration.

Both groundwater and mineralised sediment samples were refluxed in a mixture of HNO_3 + H_2O_2 (Optima[®] grade) to further ensure sample-spike equilibration and oxidation of any organic material. All samples were then evaporated to dryness, and then taken up in 1.5 N HNO_3 prior to ion exchange chromatography.

Uranium was chemically extracted and purified from the sample matrix using ion exchange chromatography in two stages following protocols reported elsewhere (Stirling et al. 2006; 2007; Andersen et al., 2008). In brief, the sample was first loaded onto custom made Teflon columns containing 550 μL TRU-spec resin (EiChrom[®]), previously cleaned with 0.2 N HCl and 0.1 N HCl + 0.3 N HF , and preconditioned with 1.5 N HNO_3 . Matrix components were eluted with 12 mL 1.5 N HNO_3 , followed by 3 mL 3 N HCl and 6 mL 0.2 N HCl . Uranium was eluted in 9 mL 0.1 N HCl + 0.3 N HF . The samples were evaporated to dryness before refluxing in a HNO_3 + H_2O_2 mixture to ensure complete oxidation of organics from the resin, then taken up in 3 N HNO_3 for the second purification stage. The samples were then loaded onto the same columns containing U-TEVA resin (EiChrom[®]), previously cleaned with 0.2 N HCl and 0.1 N HCl + 0.3 N HF , and preconditioned with 3 N HNO_3 . Matrix components were eluted with 3 mL 3 N HNO_3 , followed by 5 mL 3 N HNO_3 + trace amounts of HF , a further 2 mL 3 N HNO_3 , and 2 mL 3 N HCl . Uranium was eluted in 7 mL 0.2 N HCl and 7 mL 0.1 N HCl + 0.3 N HF . After purification by ion exchange chemistry, the uranium solutions were refluxed in a HNO_3 + H_2O_2 mixture. The uranium fractions were evaporated to dryness and redissolved in 0.25 N HCl + 0.05 N HF prior to analysis by multiple-collector ICP-MS.

3.3.4 *Uranium concentration and isotope ratio determination by Multi-Collector ICP-MS*

Uranium isotope measurements were determined using a Nu Plasma HR MC-ICP-MS at the Centre for Trace Element Analysis, University of Otago using methods outlined in Stirling et al., (2007). Briefly, samples were introduced using a Nu Instruments DSN-100 desolvating nebuliser fitted with a Glass Expansion 50 μL PFA nebuliser, operating at flow rates of approximately 60 $\mu\text{L}/\text{min}$. Typically, signal intensities of ^{238}U ($1.2\text{-}1.6 \times 10^{-10}$ A), ^{236}U ($1.5\text{-}2.0 \times 10^{-12}$ A), ^{235}U ($0.8\text{-}1.1 \times 10^{-12}$ A) and ^{233}U ($1.5\text{-}2.0 \times 10^{-12}$ A) were measured simultaneously

on Faraday cups operating with $10^{11} \Omega$ resistors. $^{238}\text{U}/^{235}\text{U}$ analyses were performed as a single static measurement, with a data acquisition sequence consisting of 50 on-peak integrations of 2 s each, in blocks of 6. The instrumental background was characterised at the start of each block. All data were processed offline at the cycle level to correct for the contributions of ^{238}U and ^{235}U from the ^{233}U - ^{236}U spike, and instrumental mass fractionation using the measured $^{236}\text{U}/^{233}\text{U}$ ratio normalised to the true value and the exponential mass fractionation law (Hart and Zindler, 1989; Habfast, 1998). Washout between sample/standard measurements was achieved using sequential solutions of 0.3 N HCl + 0.1 N HF and 0.25 N HCl + 0.05 N HF. The uranium metal standard CRM 145 (New Brunswick Laboratory, USA) was employed to monitor the performance of the U isotopic protocols and for the calibration of the ^{236}U - ^{233}U mixed spike, adopting a $^{238}\text{U}/^{235}\text{U}$ ratio of 137.837 ± 0.015 (Richter et al., 2010). Repeat measurements of the CRM 145 standard gave a long-term average $^{238}\text{U}/^{235}\text{U}$ ratio of 137.838 ± 0.002 (2 S.E; n = 58). The total procedural U blank was less than 5 pg. Given the small contribution of the blank relative to the total amount of U analysed, no blank correction was applied to the samples. For ease of comparison between samples, all $^{238}\text{U}/^{235}\text{U}$ measurements have also been reformulated into δ -notation, with respect to the isotopic composition of the CRM 145 uranium metal standard, as defined in Equation 3.1 below. Using this nomenclature, isotopically “heavy” samples are characterised by more positive $\delta^{238}\text{U}$ values and conversely, isotopically “light” samples display more negative $\delta^{238}\text{U}$ values. All reported uncertainties are quoted as 2 S.E, unless stated otherwise.

$$\delta^{238}\text{U} = \left(\left[\frac{(^{238}\text{U}/^{235}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{235}\text{U})_{\text{standard}}} \right] - 1 \right) \times 10^3 \text{ ‰} \quad (3.1)$$

3.4 RESULTS

3.4.1 *Pepegoona groundwaters*

The uranium concentrations and $^{238}\text{U}/^{235}\text{U}$ isotopic data for the Pepegoona groundwaters are presented in Table 3.1. The groundwaters at Pepegoona are highly reducing, with highly negative redox potential (Eh) values. They have ambient groundwater temperatures ranging

Table 3.1: Uranium isotope compositions for Pepegoona groundwaters

Sample	Eastings ^a	Northings ^a	²³⁸ U/ ²³⁵ U	2 S.E	δ ²³⁸ U (‰) ^b	2 S.E	[U] ng/g	(²³⁴ U/ ²³⁸ U) ^c
Eyre Formation - Stacked Channel Sands horizon								
PRMW003	363264	6669107	137.725	0.007	-0.81	0.05	0.63	1.065
PRMW006	362677	6669149	137.652	0.009	-1.35	0.07	0.20	1.414
PRMW007	364493	6669022	137.672	0.008	-1.20	0.06	0.31	1.037
PRMW014*	363371	6669415	137.625	0.006	-1.54	0.04	0.19	1.010
PRMW015*	362945	6669430	137.601	0.007	-1.71	0.05	0.16	1.209
PRMW018*	362848	6668826	137.558	0.008	-2.03	0.05	0.069	0.972
PRMW019*	363103	6668819	137.638	0.007	-1.44	0.05	0.22	0.983
PRMW019*^	363103	6668819	137.652	0.009	-1.34	0.06	0.22	0.983
PRMW020*	363331	6668952	137.676	0.008	-1.17	0.06	0.072	1.644
PRMW020*^	363331	6668952	137.680	0.007	-1.14	0.05	0.072	1.644
PRMW021*	362626	6668853	137.548	0.008	-2.09	0.06	0.027	1.159
PRMW023*	363394	6669167	137.732	0.007	-0.76	0.05	1.16	1.152
PRMW023*†	363394	6669167	137.728	0.007	-0.79	0.05	1.16	1.152
PRMW023*^	363394	6669167	137.739	0.007	-0.71	0.05	1.16	1.152
PRMW033*	362320	6669213	137.820	0.012	-0.12	0.09	0.22	1.241
Eyre Formation - Silcrete Sands horizon								
PRMW001	363026	6669341	137.679	0.008	-1.14	0.06	4.60	1.396
PRMW002a	362555	6669088	137.709	0.007	-0.93	0.05	0.45	1.025
PRMW002a †	362555	6669088	137.696	0.007	-1.02	0.05	0.45	1.025
PRMW002b*	362555	6669088	137.670	0.008	-1.21	0.06	0.18	1.206
PRMW022*	363377	6669422	137.537	0.013	-2.18	0.09	0.016	1.690
PRMW025*	362601	6668862	137.640	0.017	-1.43	0.12	0.027	1.161
PRMW025*^	362601	6668862	137.647	0.010	-1.38	0.07	0.027	1.161
PRMW026*	362858	6668834	137.566	0.006	-1.97	0.04	0.069	1.133
PRMW028*	363110	6668828	137.618	0.008	-1.59	0.06	0.058	1.711
PRMW034*	363386	6669164	137.629	0.008	-1.51	0.06	0.044	1.955
Eyre Formation - Interbedded Silts and Sands horizon								
PRMW004	362723	6668055	137.645	0.008	-1.39	0.06	0.37	0.966
PRMW011*	362611	6668854	137.606	0.007	-1.68	0.05	0.084	0.994
PRMW012*	363112	6668819	137.689	0.031	-1.08	0.22	0.25	1.084
PRMW013*	363322	6668951	137.713	0.007	-0.90	0.05	0.32	0.930
PRMW016*	362304	6669212	137.508	0.010	-2.39	0.07	0.039	0.889
PRMW017*	363383	6669174	137.604	0.007	-1.69	0.05	0.17	1.156
PRMW037*	362858	6668822	137.628	0.007	-1.52	0.05	0.17	1.430

^a Eastings and Northings (Geocentric Datum Australia GDA94 coordinates).

^b ²³⁸U/²³⁵U ratios have been reformulated in δ-notation with respect to the isotopic composition of the CRM 145, using Equation 3.1.

^c Parentheses denote (²³⁴U/²³⁸U) activity ratios, from Chapter II, calculated by Nλ, using decay constants of Jaffey et al. (1971) for ²³⁸U and Cheng et al. (2000) for ²³⁴U. The associated 2σ uncertainty is 5 %.

† Duplicate analysis on independently processed sample.

^ Replicate analysis on the same solution aliquot.

* Samples were collected after ISR had commenced within sections of the deposit, however are interpreted to reflect natural groundwater conditions.

from 25.3 to 31.4 °C and have neutral to slightly alkaline pH of 6.9 to 9.2. Uranium is predominantly present as aqueous hydroxyl and carbonate complexes (Chapter II)

Uranium concentrations are typically quite low but span two orders of magnitude, ranging from 0.02 to 4.60 µg/L, with the highest concentrations found in groundwaters sampled within mineralisation. These concentrations are typical of reducing groundwaters (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003). Overall, the groundwaters show a preferential enrichment of ^{235}U over ^{238}U with respect to the composition of BSE, with $^{238}\text{U}/^{235}\text{U}$ ratios ranging from 137.508 ± 0.007 to 137.820 ± 0.007 spanning a >2 ‰ range. These ratios correspond to $\delta^{238}\text{U}$ shifts of -0.12 ± 0.09 to -2.39 ± 0.07 ‰. Samples PRMW002a and PRMW023 were analysed in duplicate. Additionally, samples PRMW002a and PRMW002b collected prior to and after ISR had commenced respectively, was processed to assess the effects of seasonal variability and determine any effects of mining. All replicate analyses are identical within analytical error. The lack of variability in groundwater well PRMW002 pre- and post-ISR indicates that seasonal variability has little effect on groundwater $^{238}\text{U}/^{235}\text{U}$ isotopic ratios, supporting the inference that samples collected after mining by ISR had commenced are representative of the natural groundwater system.

No systematic trends were observed between $^{238}\text{U}/^{235}\text{U}$ ratios and field parameters, including the ($^{234}\text{U}/^{238}\text{U}$) activity ratio, as well as pH, alkalinity, temperature and redox potential (Chapter II). In addition, there is no observable trend in $^{238}\text{U}/^{235}\text{U}$ for samples collected from the different aquifer horizons within the Eyre Formation, and as such, the groundwater dataset is treated as a single dataset.

3.4.2 *Pepegoona mineralised sediments*

Mineralogical descriptions, uranium concentrations and $^{238}\text{U}/^{235}\text{U}$ isotope data for the Pepegoona mineralised sediments are presented in Table 3.2. The Pepegoona mineralised sediment samples show significant variations in $^{238}\text{U}/^{235}\text{U}$ within the deposit, spanning a range of approximately 5 ‰ (Figure 3.3). The majority of samples have $^{238}\text{U}/^{235}\text{U}$ ratios between 137.657 ± 0.007 and 137.913 ± 0.016 ($\delta^{238}\text{U}$ -0.12 ± 0.06 to 0.55 ± 0.12 ‰). However, one of the investigated mineralised sediment samples (PRC012-22) was significantly lighter than

Table 3.2: $^{238}\text{U}/^{235}\text{U}$ compositions and mineralogical descriptions for mineralised sediments from the Pepegooa deposit.

Sample	Easting ^a	Northings ^a	$^{238}\text{U}/^{235}\text{U}$	2 S.E	$\delta^{238}\text{U}$ (‰) ^b	2 S.E	[U] ng/g	From depth (m) ^c	To depth (m) ^c	Sample description and mineralogy
PR1321	362025	6669105	137.751	0.009	-0.62	0.07	534	~60	~80	Granitic basement, fault offset of several hundred meters
PR1321†	362025	6669105	137.748	0.007	-0.65	0.05	506	~60	~80	
PRC007-20	362896	6669120	137.793	0.007	-0.32	0.05	1464	201.22	201.40	Weakly mineralised silcrete, ~98 % quartz, minor kaolinite, rutile, ilmenite & zircon
PRC008-21	362768	6669112	137.657	0.007	-1.30	0.05	2208	210.35	210.41	Weakly mineralised silcrete, ~95 % quartz, minor kaolinite, pyrite, rutile, ilmenite & zircon
PRC012-22	362592	6669193	137.267	0.007	-4.13	0.05	38	211.45	211.53	Weakly mineralised sands, ~90 % quartz, 5 % barite, minor pyrite rutile, ilmenite & zircon
PRC015-23	363058	6669379	137.913	0.016	0.55	0.12	20887	219.60	219.67	Weakly mineralised sands, sampled above thin ferricrete layer, ~45 % quartz, 45 % pyrite, ~2 % U minerals, trace rutile & ilmenite
PRC015-24	363058	6669379	137.782	0.008	-0.40	0.06	7363	219.80	219.86	Mineralised sands, sampled below thin ferricrete layer, ~65 % quartz, 25 % pyrite, ~8 % U minerals, trace rutile & ilmenite
PRC015-24†	363058	6669379	137.792	0.007	-0.33	0.05	7369	219.80	219.86	
PRC015-25	363058	6669379	137.820	0.009	-0.12	0.06	1455	219.86	219.92	Weakly mineralised sands, ~90 % quartz, 5 % pyrite, minor kaolinite, U minerals, rutile & ilmenite

^a Eastings and Northings (Geocentric Datum Australia GDA94 coordinates).^b $^{238}\text{U}/^{235}\text{U}$ ratios have been reformulated in δ -notation with respect to the isotopic composition of the CRM 145, using Equation 3.1.^c To and from depths refer to depth below surface. Sample PR1321 was taken from rotary mud drill chips, depth is approximate.

† Duplicate analysis on independently processed aliquot of digested sample.

the others, with a $^{238}\text{U}/^{235}\text{U}$ value of 137.267 ± 0.007 ($\delta^{238}\text{U} -4.13 \pm 0.05 \text{ ‰}$). The samples display U concentrations that vary by almost three orders of magnitude, ranging from 0.038 to 20 $\mu\text{g/g}$. Sample PRC015-24 (collected within high-grade mineralisation) was analysed in duplicate, and both measurements were identical within analytical error. Interestingly, $^{238}\text{U}/^{235}\text{U}$ ratios and U concentrations systematically increase along the groundwater flow path, from drill core sample PRC012 in the west, to sample PRC015 in the east.

3.4.3 *Pepegoona granitic basement*

Sample PR1321 from the granitic basement was analysed in duplicate, yielding results that are identical within error (Table 3.2). This sample has a U concentration of $\sim 520 \text{ ng/g}$, and an averaged $^{238}\text{U}/^{235}\text{U}$ ratio of 137.749 ± 0.008 ($\delta^{238}\text{U} -0.64 \pm 0.06 \text{ ‰}$), only marginally lighter than the composition of BSE.

3.5 DISCUSSION

The observed variability in the $^{238}\text{U}/^{235}\text{U}$ ratios in both the groundwaters and the mineralised sediments is approximately 5 ‰, exceeding the analytical uncertainty by about a factor of 100, and far larger than observed previously in low temperature uranium systems (Figure 3.3).

Uranium isotopic composition is plotted against U concentration for the Pepegoona samples in Figure 3.3. In both the groundwater samples and mineralised sediments, the results show a broadly positive array between $^{238}\text{U}/^{235}\text{U}$ and U concentration on a log-normal diagram. The log-linear relationship between these two parameters, combined with the observation that both the groundwaters and the mineralised sediments plot along the same general array, is strongly indicative, at least to a first order, that a single dominant mechanism controls fractionation between ^{238}U and ^{235}U in this system. In the groundwater samples, there is a progressive removal of U and a shift in $^{238}\text{U}/^{235}\text{U}$ towards lighter isotopic compositions as U is precipitated from solution as U(IV) minerals. In parallel, there is a concomitant fractionation towards heavier $^{238}\text{U}/^{235}\text{U}$ compositions in the mineralised sediments as U is incorporated into U(IV) minerals. To this end, groundwaters with the lowest U concentrations and $^{238}\text{U}/^{235}\text{U}$ signatures, having experienced the greatest extent of U removal, likely

correlate with uranium mineralised sediments displaying the highest U concentrations and $^{238}\text{U}/^{235}\text{U}$ compositions. Certainly, the highest groundwater U concentrations are found in samples collected directly within the mineralised portion of the Eyre Formation aquifer. However, the high complexity of the ore geometry within the Pepegooona deposit, in addition to the limited access to mineralised samples throughout the deposit means that the exact relationship between the interactions of the groundwaters with the host aquifer rock in each location cannot be constrained in the present study.

3.5.1 Mechanisms controlling uranium isotope fractionation

The fractionation of $^{238}\text{U}/^{235}\text{U}$ isotopes is likely controlled by one of the following fractionation mechanisms during the formation of sandstone-hosted uranium deposits: (1) the source region isotopic composition/s, and (2) kinetic and/or equilibrium processes during mineralisation due to leaching during weathering; adsorption onto minerals or organic matter; or U(VI) reduction and the formation of U(IV) minerals. These mechanisms are discussed in turn below.

3.5.1.1 $^{238}\text{U}/^{235}\text{U}$ isotopic signature inherited from the source region

The wide range of $^{238}\text{U}/^{235}\text{U}$ compositions of both the groundwaters and mineralised sediments may reflect the complex geology and geochemical conditions at the Pepegooona deposit. For example, a recent study of U-bearing minerals such as zircon, monazite, titanite, and uraninite from a variety of lithologies by Hiess et al. (2012) reported a range of $^{238}\text{U}/^{235}\text{U}$ compositions. In these accessory phases, the U isotopic signatures typically vary from 137.743 to 138.862 ($\delta^{238}\text{U} = -0.68$ to 7.44 ‰), although several isolated samples show more extreme fractionations (as large as 5 ‰) away from the composition of BSE. These variable isotopic signatures will be reflected in the bulk composition of the host rock, albeit with reduced magnitude due to the dilution effects of whole rock sampling. It is therefore feasible that the $^{238}\text{U}/^{235}\text{U}$ isotopic systematics of the Pepegooona locality predominantly reflects the leaching of U from multiple U-rich lithologies with variable U isotopic compositions, which is then transported and precipitated at a redox boundary within the aquifer during ore formation processes without further fractionation of ^{238}U and ^{235}U isotopes.

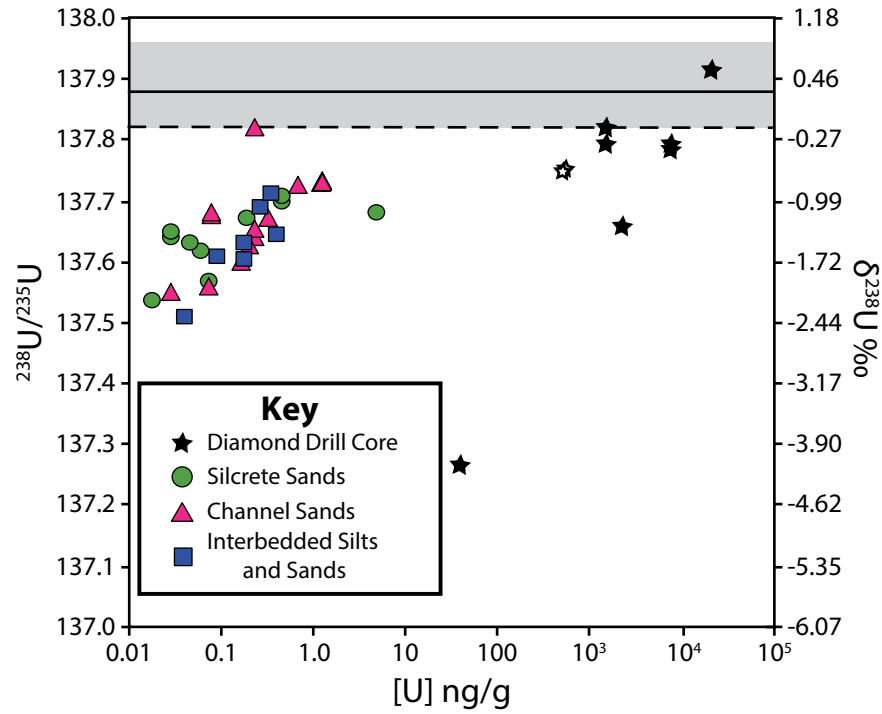


Figure 3.3: $^{238}\text{U}/^{235}\text{U}$ ratios versus U concentration for groundwaters, basement granite and mineralised sediments from this study. The symbols are as per Figure 3.1. Open star symbols denote granitic basement sample PR1321. Note the logarithmic scale on the x-axis. For comparison, $^{238}\text{U}/^{235}\text{U}$ ratios have been reformulated in δ -notation with respect to the isotopic composition of the CRM 145, using Equation 3.1. The grey shaded box represents the range of isotopic values determined for low temperature redox ore samples by Bopp et al. (2009) and Brennecke et al. (2010a). The solid black line denotes the previously considered invariant $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88 (Steiger and Jäger, 1977). The dashed line represents the revised BSE isotopic composition of 137.818 (Hiess et al., 2012). $^{238}\text{U}/^{235}\text{U}$ ratios in mineralised sediments span a *ca.* 5 ‰ range, the largest U isotopic variation found thus far in natural samples. Groundwaters are characterised by $^{238}\text{U}/^{235}\text{U}$ ratios enriched in the light isotope, whilst mineralised sediments are preferentially enriched in the heavier isotope.

This scenario is considered unlikely to give rise to the coupled $^{238}\text{U}/^{235}\text{U}$ isotopic composition and U concentration behavior observed at the Pepegoona locality unless there is groundwater mixing between two distinct, and highly fractionated groundwater end-member components within the aquifer. To provide a first order approximation to the observed data, the $^{238}\text{U}/^{235}\text{U}$ isotopic signatures of the groundwater end-members sourced from different lithologies must exhibit $^{238}\text{U}/^{235}\text{U}$ ratios higher and lower than the range of groundwater values observed at Pepegoona (137.820 and 137.508, respectively).

This is at odds with current knowledge of the groundwater system at this locality for two primary reasons. First, in an earlier study of the same groundwaters by Murphy et al. (Chapter II), a mixing diagram based on the combined ($^{234}\text{U}/^{238}\text{U}$) activity ratio versus U concentration systematics shows that no significant groundwater mixing is occurring at the study locality. Second, if the source of dissolved U to the Pepegooona deposit is derived from the granitic basement and/or uplifted granites of the Mount Painter District comprising the Flinders Ranges, then the source region would be required to have a variable $^{238}\text{U}/^{235}\text{U}$ composition that is both isotopically heavier and lighter than the groundwaters. In this study, the basement granite sample PR1321 has an averaged $^{238}\text{U}/^{235}\text{U}$ ratio of 137.749 ± 0.008 . This is in very good agreement with a compilation of all available U isotopic observations for granitoid rocks by Heiss et al. (2012), together with our own unpublished results for granites, which give an average $^{238}\text{U}/^{235}\text{U}$ composition of 137.782 ± 0.030 , which is only marginally lighter than BSE. The fact that granitic rocks show only minor variability in $^{238}\text{U}/^{235}\text{U}$ ratios at the 0.2 ‰-level implies that sample PR1321 is also representative of other potential source granites that may provide the dissolved uranium to the Pepegooona system. Hence the observed $^{238}\text{U}/^{235}\text{U}$ fractionation is unlikely to be inherited from the granitic source region.

3.5.1.2 Kinetic versus equilibrium isotopic fractionation during mineralisation

The preceding discussion suggests that the $^{238}\text{U}/^{235}\text{U}$ isotope systematics characterising the Pepegooona locality reflect process-driven kinetic and/or equilibrium isotope fractionation during ore formation processes rather than the mixing of two end-member groundwaters with distinct compositions reflecting different sources of the uranium. In this scenario, uranium is leached from U-rich lithologies, most likely basement granite, with $^{238}\text{U}/^{235}\text{U}$ signatures representative of BSE. The isotopic signature of the groundwater is then altered (a) by water-rock interaction with the aquifer host lithology along the flow path during leaching, or (b) during uranium mineralisation processes. In turn, there are two main mechanisms through which uranium isotopes may fractionate during the formation of U-rich minerals: (1) authigenic U mineral formation involving adsorption, and (2) the reduction of U(VI)

to U(IV) involving the formation of U(IV)-bearing minerals. Each of these processes offer the potential to result in variable $^{238}\text{U}/^{235}\text{U}$ isotopic compositions in the groundwater and ultimately the precipitated uranium minerals.

With the exclusion of a few outliers, $^{238}\text{U}/^{235}\text{U}$ isotopic composition and U concentration are well correlated, particularly for a natural system. Logarithmic lines of best fit for each of the Eyre Formation aquifers are shown in Figure 3.4, inset. The aquifers show an increasing correlation with depth, with an r^2 of 0.57 for the silcrete sand horizon, 0.68 for the stacked channel sand horizon and 0.79 for the interbedded silts and sands horizon. The increasing correlation with depth may reflect the changes in permeability of the aquifers, which in turn affects the groundwater flow rate and hence mobility of U. In the higher permeability sand horizons, faster groundwater flow, and less reactive surfaces (such as clay particles) would allow for the greater mobility of U compared to the less permeable interbedded silts and sands horizon.

To initially quantify the relationship between $^{238}\text{U}/^{235}\text{U}$ and U concentration in the groundwaters, and investigate the extent to which kinetic U uptake may control $^{238}\text{U}/^{235}\text{U}$ isotopic fractionation in the Pepegooona mineralisation system, we considered the results (Figure 3.4) in relation to a closed-system kinetic Rayleigh fractionation model. This model requires that U is present as a finite pool that is not replenished. It also assumes that dissolved U present in the groundwater is incorporated into solid U rich minerals as a forward reaction, in the absence of a significant back-reaction, and without any further interactions between the groundwater and the zones of mineralisation. Compositional changes in the U concentration and $^{238}\text{U}/^{235}\text{U}$ isotopic composition in the groundwaters (and accumulating solid precipitate) as the reaction progresses can then be modeled by the following equation (Mariotti et al., 1981):

$$^{238}\text{U}/^{235}\text{U}_{\text{groundwater}} = ^{238}\text{U}/^{235}\text{U}_{\text{initial}} * F^{(1/\alpha-1)} \quad (3.2)$$

where $^{238}\text{U}/^{235}\text{U}_{\text{groundwater}}$ and $^{238}\text{U}/^{235}\text{U}_{\text{initial}}$ denote the uranium isotopic ratio of the remaining and initial groundwater respectively. The fraction of remaining dissolved U is given by

$F = c/c_o$, where c and c_o represent the residual and initial groundwater U concentrations respectively.

The composition of $^{238}\text{U}/^{235}\text{U}_{\text{initial}}$ is assumed to be that of BSE ($^{238}\text{U}/^{235}\text{U} = 137.818 \pm 0.045$; Hiess et al., 2012), and the U concentration of the basement granite sample PR1321 of $\sim 500 \mu\text{g/L}$ has been assumed for c_o . The predicted closed-system Rayleigh fractionation trends for a range of fractionation factors are displayed together with the observational data in Figure 3.4. With the exception of a few outlying datapoints which reflect second-order complexity in the system, the majority of groundwater data for the Pepegooona deposit can be fitted to a closed system Rayleigh fractionation model, with a fractionation factor (α , describing the $^{238}\text{U}/^{235}\text{U}$ ratio of the groundwater relative to the $^{238}\text{U}/^{235}\text{U}$ composition of the precipitating U-rich minerals) of ~ 0.9997 to 0.9999 .

Other initial U concentrations and starting compositions are equally valid, however only result in minor changes in α . For example, using the $^{238}\text{U}/^{235}\text{U}$ ratio of the basement granite for $^{238}\text{U}/^{235}\text{U}_{\text{initial}}$ results in a values predominantly between ~ 0.9997 and 1.000 . Likewise, using a c_o of $5 \mu\text{g/L}$ (approximately the concentration of the highest U groundwater found in the Pepegooona area), α values dominantly fall between ~ 0.9996 to 0.9999 . These findings suggest that heavy ^{238}U is preferentially removed over lighter ^{235}U by kinetic isotope effects during the precipitation of uranium minerals. The data do not define a single fractionation line, which may be explained by the fractionation of uranium isotopes by the continued dissolution and reprecipitation of U minerals during ore formation processes. However, the small range of α indicate that U uptake during ore formation processes predominantly occurs in a semi-closed system, without appreciable replenishment of dissolved U to the groundwater system.

3.5.1.3 Fractionation inherited from the leaching of U-rich minerals

There is a growing body of evidence suggesting that the leaching of uranium during low temperature weathering preferentially releases the light ^{235}U isotope and leaves the heavier ^{238}U in the residue. For example, zircon-leaching experiments by Hiess et al. (2012) showed that uranium released into solution is isotopically lighter than the bulk zircon starting

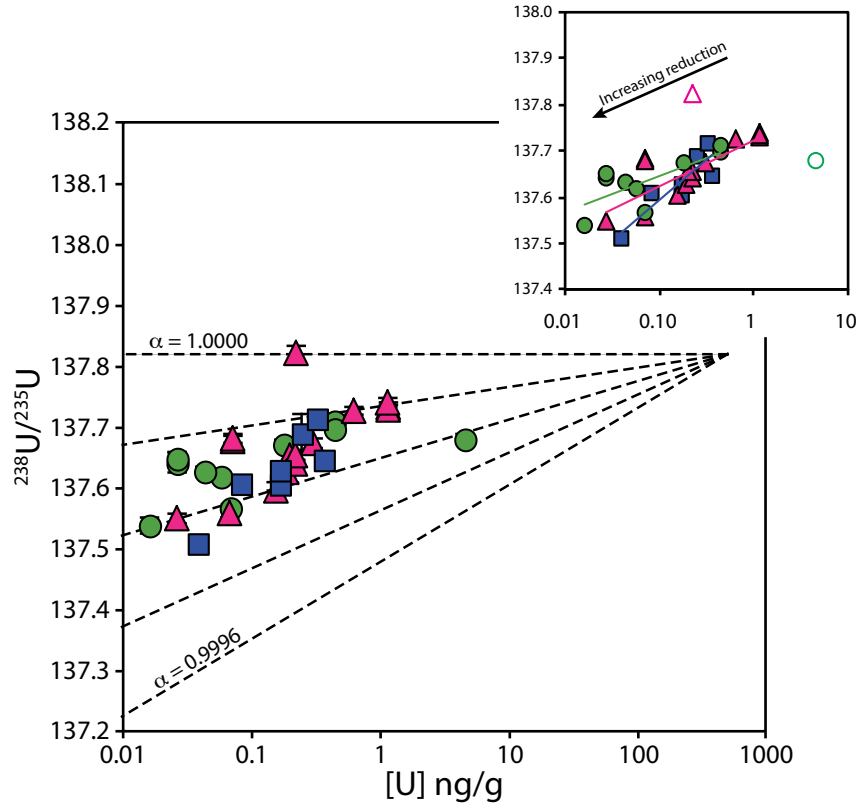


Figure 3.4: $^{238}\text{U}/^{235}\text{U}$ isotopic composition versus U concentration for Eyre Formation groundwaters in the Pepegoona region. Note the logarithmic scale on the x-axis. The various aquifers are denoted by distinct symbols as per Figure 3.1. Uncertainty on the y-axis is 2SE; x-axis error bars are contained within the size of the symbol. The dashed lines indicate the calculated isotopic evolution of dissolved U in groundwater, assuming precipitation of U as uranium minerals occurs by closed-system Rayleigh fractionation, assuming a bulk Earth starting $^{238}\text{U}/^{235}\text{U}$ composition of 137.818 (Hiess et al., 2012) and uranium starting concentration of 500 ng/g. $^{238}\text{U}/^{235}\text{U}$ ratios decrease systematically with U(VI) reduction in groundwater, and can be modeled by Rayleigh fractionation factor (α) of ~ 0.9997 to 1.0000. Inset: Logarithmic lines of best fit for each aquifer. Outliers are shown as open symbols and have been excluded. The silcrete sand horizon (shown as green line) has an r^2 of 0.57. The stacked channel sand horizon (shown as pink line) has an r^2 of 0.68. The interbedded silts and sands horizon (shown as blue line) has an r^2 of 0.79. For further details, see text.

material. Leaching experiments of euxenite showed evidence of ^{235}U enrichment in the leachate (Stirling et al., 2007). Additionally, Bopp et al. (2009) observed variability whilst leaching the Mt. Painter haematite breccia sample, suggesting the uranium might be held in multiple phases.

If leaching through low temperature weathering were the dominant mechanism controlling U isotope fractionation at the study site, then a broadly negative correlation would be anticipated between $^{238}\text{U}/^{235}\text{U}$ and U concentration. Specifically, a shift towards

lighter $^{238}\text{U}/^{235}\text{U}$ values would be expected with increasing U concentration, as groundwaters containing the largest U concentrations, having received higher levels of U released from minerals, would also be enriched in ^{235}U and would display lower $^{238}\text{U}/^{235}\text{U}$ ratios than groundwaters with lower U contents. This is contrary to the $^{238}\text{U}/^{235}\text{U}$ isotope – U concentration systematics observed within the Pepegooona deposit, which show a positive rather than negative correlation between $^{238}\text{U}/^{235}\text{U}$ and U concentration.

These findings are reinforced by independent observations of the $(^{234}\text{U}/^{238}\text{U})$ activity ratios determined on the same Pepegooona groundwater samples, reported in Murphy et al. (Chapter II). Disequilibria between ^{234}U and ^{238}U can be attributed to α -recoil processes and the preferential leaching of ^{234}U from radiation damaged sites in the crystal lattice over lattice-bound ^{238}U during low temperature weathering. Therefore, if preferential leaching was the primary mechanism for uranium isotope variability, a negative correlation between $^{238}\text{U}/^{235}\text{U}$ and the $(^{234}\text{U}/^{238}\text{U})$ activity ratio might be expected, bearing in mind that $(^{234}\text{U}/^{238}\text{U})$ is a complex function of a range of parameters, including groundwater age and the time since the leaching event, which may obscure its exact relationship with $^{238}\text{U}/^{235}\text{U}$.

Earlier studies have documented a broad anti-correlation between $^{234}\text{U}/^{238}\text{U}$ and $^{238}\text{U}/^{235}\text{U}$ in some low temperature environments (Stirling et al., 2007; Hiess et al., 2012), with speleothems showing the most extreme fractionations (Stirling et al., 2007). This indicates that weathering through leaching is likely to influence the $^{238}\text{U}/^{235}\text{U}$ isotope systematics at some localities. However, the $(^{234}\text{U}/^{238}\text{U})$ activity ratios for the Pepegooona groundwater samples showed no correlation with $^{238}\text{U}/^{235}\text{U}$ (Figure 3.5). This is consistent with the lack of correlation also observed in UOCs by Brennecke et al. (2010a).

Taken together, the absence of a correlation between $^{238}\text{U}/^{235}\text{U}$ and $(^{234}\text{U}/^{238}\text{U})$, combined with the positive rather than negative correlation between $^{238}\text{U}/^{235}\text{U}$ and U concentration strongly suggests that leaching of uranium minerals during low temperature weathering is not the dominant mechanism controlling $^{238}\text{U}/^{235}\text{U}$ isotopic fractionation at the Pepegooona locality.

3.5.1.4 Fractionation inherited from adsorption

The adsorption of uranium onto the surface of precipitating minerals is also a possible explanation for the correlated $^{238}\text{U}/^{235}\text{U}$ and U concentration compositions in the Pepegooona mineralisation system. In this regard, Brennecke et al. (2011b) conducted a series of laboratory-controlled experiments to investigate the effects of adsorption on uranium isotope fractionation. Their study found that the adsorption of uranium onto clay minerals (birnessite) produces only minor isotopic fractionation of 0.2 ‰, where the lighter isotope (^{235}U) was preferentially adsorbed, leaving the residual fluid enriched in ^{238}U . In these experiments, no change in redox state was observed, and the $^{238}\text{U}/^{235}\text{U}$ fractionation was attributed to differences in uranium coordination geometry between dissolved and adsorbed species. This sense of fractionation, consistent with closed-system equilibrium effects (Schauble et al., 2009), is opposite to the fractionation trends observed in the Pepegooona samples. Therefore, adsorption is not regarded as the primary mechanism controlling the $^{238}\text{U}/^{235}\text{U}$ isotope systematics at the study site.

3.5.1.5 Fractionation inherited from kinetically-driven U reduction

The most likely mechanism controlling $^{238}\text{U}/^{235}\text{U}$ isotopic fractionation in the Pepegooona mineralisation system is the reduction of U(VI) to U(IV), leading to the removal of U(VI) from the aqueous phase and the formation of U(IV)-bearing minerals. U reduction is prevalent at the Pepegooona locality, as evidenced by the highly reducing groundwaters of the system, with uranium present as hydroxyl and carbonate complexes (Chapter II), coupled with reduced U(IV)-bearing uraninite and coffinite mineralisation. The magnitude and direction of the observed isotopic fractionation between ^{238}U and ^{235}U is in agreement with the predictions of the nuclear field shift effect during U(VI)-U(IV) reduction, yielding depleted $^{238}\text{U}/^{235}\text{U}$ values in the unreacted dissolved U(IV) species of the groundwaters and enriched $^{238}\text{U}/^{235}\text{U}$ compositions in the solid U(IV)-bearing minerals. It is also possible that the observed fractionation can be attributed to the nuclear spin effect which fractionates the lighter isotope due to non-zero nuclear spin (Epov et al., 2011). The sense of fractionation for both the nuclear field shift and nuclear spin effects are the same, and are indistinguishable

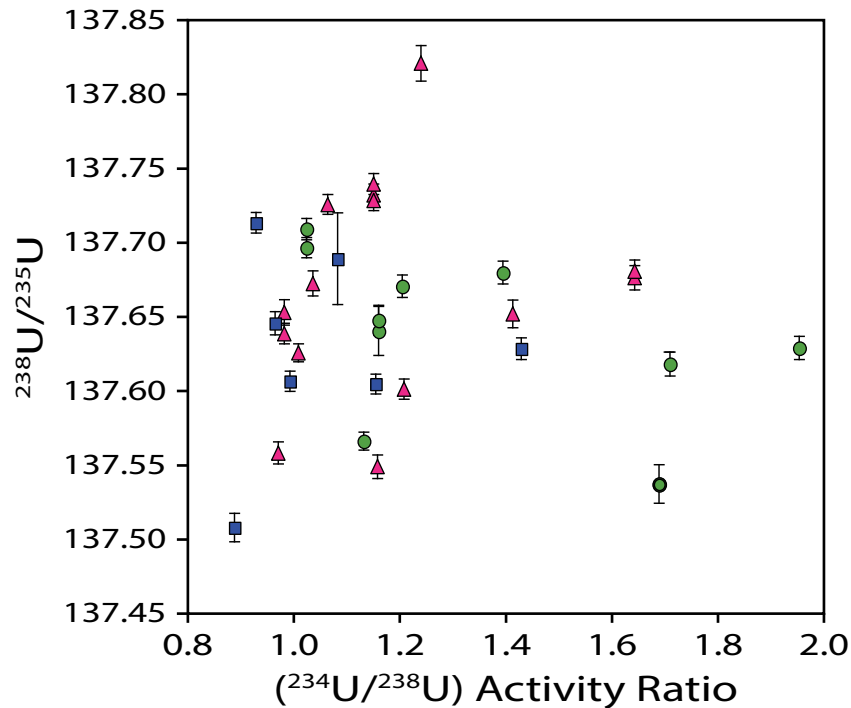


Figure 3.5: $^{238}\text{U}/^{235}\text{U}$ ratios for groundwater from this study versus ($^{234}\text{U}/^{238}\text{U}$) activity ratios from the same waters from Chapter II. The various Eyre Formation aquifers are denoted by distinct symbols as per Figure 1. If preferential leaching is the primary mechanism controlling fractionation of both $^{238}\text{U}/^{235}\text{U}$ and ($^{234}\text{U}/^{238}\text{U}$), then a broadly negative correlation should be observed. The lack of correlation suggests that uranium $^{238}\text{U}/^{235}\text{U}$ isotopic fractionation within the Pepegooona mineralised system is not dominantly controlled by mineral leaching during weathering (see text for further details).

from each other.

The U isotope systematics of the Pepegooona locality are consistent with other field-based $^{238}\text{U}/^{235}\text{U}$ observations describing the U(VI)-U(IV) redox transformation in low temperature redox environments. These include sandstone roll-front deposits and artificially biostimulated groundwaters from the Rifle Range aquifer, which also support a nuclear field shift control on U reduction, the latter during the enzymatic reduction of U(VI) to U(IV) (Bopp et al., 2010). These new data are also in agreement with recent biologically-mediated, laboratory reduction experiments of Stirling et al. (in submission) who observed an isotopic shift towards lower $^{238}\text{U}/^{235}\text{U}$ ratios in the residual medium during U(VI) reduction mediated by *Desulfovibrio brasiliensis* U-reducing bacteria. However, these results contrast with the findings of Rademacher et al. (2006) who also conducted bacterial reduction experiments,

but reported a progressive enrichment in ^{238}U in the U(VI) of the unreacted growth medium with decreasing U concentration in the presence of U-reducing bacteria (*Geobacter sulfurreducens* and *Anaeromyxobacter dehalogenans*), consistent with mass-dependent equilibrium fractionation. This is the opposite of what has been observed thus far in other studies. However, uranium isotopic fractionation may vary among bacterial species, with other physicochemical parameters such as pH, redox conditions or temperature, or with reaction rate. It is also possible that the Rademacher et al. (2006) experiments were controlled by the adsorption of U, which creates U isotopic shifts of opposite sign to those generated by U reduction (Brennecke et al., 2011), as discussed earlier in section 5.1.4. Further studies are required to resolve this apparent discrepancy.

Within the Pepegooona deposit, there are several potential sources of reductants within the aquifer system, including for example, H_2S gas, pyrite, organic matter, and microbial activity. Therefore, it is not currently possible to ascertain whether U reduction in this system is abiotically controlled or biologically mediated. In abiotic laboratory experiments of U(VI) reduction with Fe^0 (Rademacher et al., 2006) and Zn^0 (Stirling et al., 2007), no isotopic fractionation was detected, which may suggest that microbial activity is required to create U isotopic shifts during U reduction. Within an aquifer, long water-rock interaction promotes chemical and isotopic equilibration with phases in the aquifer host rock. Thus, the fast reaction rates of the laboratory experiments are not representative of the long water-rock interaction times within the aquifer. Slow abiotic reduction by sulfide minerals within the aquifer may fractionate uranium isotopes, however further experiments are needed to test this hypothesis.

Previous attempts to model $^{238}\text{U}/^{235}\text{U}$ fractionation during U reduction in aqueous systems are limited to the biostimulated Rifle Range aquifer (Bopp et al., 2010) and biologically mediated U reduction experiments (Stirling et al., in submission). In both studies, U reduction was artificially mediated by the controlled introduction of microbes to the system. Both studies reported a decrease in $^{238}\text{U}/^{235}\text{U}$ with decreasing U concentration, corresponding to respective fractionation factors of 0.9993 (following conversion of the data to the notation used in this study) for the Rifle Range aquifer and 0.9992 to 0.99985 for the

laboratory reduction experiments when a kinetic Rayleigh fractionation model is applied. These findings are both in excellent agreement with the results presented here. Although the fractionation factors derived from each study are comparable, the magnitude of $^{238}\text{U}/^{235}\text{U}$ isotopic fractionation characterising the Pepegooona mineralisation system of *ca.* 5 ‰ is far larger than that observed in any other low-temperature study. Given the open nature of sandstone-hosted uranium deposits, it is likely that the uranium has been remobilised several times via the continued and/or episodic redissolution and reprecipitation of uranium minerals. These repeated cycles might generate large degrees of fractionation as isotopically heavy ^{238}U is retained in the U(IV)-bearing precipitated solid, and ^{235}U is preferentially mobilised in the groundwater. Additionally, the formation of insoluble secondary uranium and Fe oxyhydroxide minerals during remobilisation may irreversibly trap the heavier isotope, further enriching the groundwater in ^{235}U .

3.6 CONCLUSIONS

In this study, $^{238}\text{U}/^{235}\text{U}$ isotopic compositions were determined for both groundwaters and mineralised sediments within the vicinity of a high-grade sandstone-hosted uranium deposit. The data provide the first comprehensive evidence for uranium ‘stable’ isotope fractionation between lattice-bound ^{238}U and ^{235}U in a natural aqueous environment and $^{238}\text{U}/^{235}\text{U}$ variations spanning a *ca.* 5 ‰ range with isotopic shifts both higher and lower than the composition of Bulk Silicate Earth. Large isotopic variations in the groundwater approaching 2 ‰ reflect unidirectional kinetic fractionation that follows a closed-system Rayleigh fractionation trend, involving a shift in $^{238}\text{U}/^{235}\text{U}$ towards lighter isotopic compositions as U is removed from the groundwater and precipitated as uranium minerals. To this end, ^{238}U is preferentially incorporated into the solid, leaving an enrichment of the lighter isotope in the aqueous phase. The system is described by isotopic fractionation factors (α), describing the $^{238}\text{U}/^{235}\text{U}$ of the groundwater relative to the composition of the uranium mineralization, falling between 0.9997 to 0.9999.

Our results suggest that uranium isotope fractionation in the Pepegooona uranium mineralised system is governed by the nuclear field shift effect during the reduction of U(VI)

to U(IV) during mineralisation processes. However, second-order processes, most likely related to water-rock interactions during weathering, as well as uranium adsorption and/or precipitation, also influence the $^{238}\text{U}/^{235}\text{U}$ compositions of the uranium ores and groundwaters of the study location. Further work, involving both natural systems and laboratory-controlled experiments, are necessary for interpretation of $^{238}\text{U}/^{235}\text{U}$ isotope variations in such low temperature redox environments and their potential as a tracer of reduction processes.

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CHAPTER IV

DETECTION OF NATURAL ^{236}U IN GROUNDWATERS AND ORES IN THE VICINITY OF SEVERAL HIGH-GRADE SANDSTONE-HOSTED URANIUM DEPOSITS

CHAPTER SUMMARY

In nature, primordial ^{236}U has long since decayed to concentrations below detection. However, the detection of *in-situ* ^{236}U produced by thermal neutron capture on ^{235}U in high-grade uranium deposits is made possible by recent advancements 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. To investigate this further, mineralised sediments and groundwaters sampled from several South Australian sandstone-hosted uranium deposits have been analysed by AMS to quantify any $^{236}\text{U}/^{238}\text{U}$ isotopic variability in the sediments, and determine whether natural ^{236}U can be detected in groundwaters.

Nine mineralised sediments from the Beverley North sandstone-hosted uranium deposits have $^{236}\text{U}/^{238}\text{U}$ ratios ranging from $(1.16 \pm 0.06) \times 10^{-12}$ to $(9.48 \pm 0.83) \times 10^{-12}$, and U concentrations that vary by almost three orders of magnitude, ranging from 78.9 to 24200 $\mu\text{g/g}$. Overall, the mineralised sediments display a weakly positive correlation between $^{236}\text{U}/^{238}\text{U}$ and U concentration, with the exception of one sample. This is consistent with the generation of higher neutron fluxes due to high concentrations of U. The observed variability in $^{236}\text{U}/^{238}\text{U}$ ratio both within the deposits themselves, and between deposits may reflect (i) changes in mineralogy; (ii) the presence of neutron modifiers which have large neutron capture cross-sectional areas or (iii) high water content (which can also absorb neutrons), which can affect the neutron flux generated within the samples.

A single groundwater sampled within mineralisation from the Pepegoona West deposit yielded a $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$. This is the first published data detecting natural ^{236}U in groundwater in contact with a high-grade uranium deposit. The $^{236}\text{U}/^{238}\text{U}$ isotopic composition of the single groundwater sampled in high-grade mineralisation is very similar to that of the mineralised sediments from the same deposit. This reflects 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.

^{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.

4.1 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 nature is the by-product of anthropogenic activities, natural ^{236}U can be produced in high-grade uranium ores by thermal neutron capture on ^{235}U . At depths below the influence of cosmogenic particles (~ 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 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 (Wilcken et al., 1998; Hotchkis et al., 2000). Notionally, ^{236}U can also be produced by the 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 several $\mu\text{g/g}$ uranium, neutron fluxes are expected to be quite low, with an estimated natural $^{236}\text{U}/^{238}\text{U}$ 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 $^{236}\text{U}/^{238}\text{U}$ ratios of the order of $\sim 10^{-12}$ to $\sim 10^{-10}$ being reported (Rokop et al., 1972; Zhao et al., 1994a; Zhao et al., 1994b; Richter et al., 1999; Berkovits et al., 2000; Wilcken et al., 2007; 2008; Srncik et al., 2011). Based on $^{236}\text{U}/^{238}\text{U}$ isotopic ratios measured in uranium ores, the possibility of detecting natural $^{236}\text{U}/^{238}\text{U}$ ratios elevated above background ratios in groundwaters in close proximity to high-grade uranium mineralisation was recognised by Fifield (2008) as a potential exploration tool for deposits buried at depth.

This research aims to investigate whether natural ^{236}U produced *in-situ* in high-grade uranium mineralisation by neutron capture on ^{235}U can be detected in groundwaters in the vicinity of mineralisation. To do this, $^{236}\text{U}/^{238}\text{U}$ 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 mineralisation have been analysed with the aim to evaluate the effectiveness of natural ^{236}U in groundwater as a tracer of uranium mineralisation.

4.2 GEOLOGICAL CONTEXT

4.2.1 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 (Figure 4.1, inset). Sandstone-hosted uranium deposits form as a result of changes in the oxidation state of U during water-rock interactions (see Chapter I for further detail). For this study, mineralised sediment samples and groundwaters have been sampled from the Four Mile East and Four Mile West; and the Pepegooona, Pepegooona West and Pannikan ‘roll-front’ deposits (with the latter three collectively called the Beverley North deposits). These deposits are located adjacent to the north-eastern flanks of the Flinders Ranges, approximately 550 km north of Adelaide, South Australia (Figure 4.1).

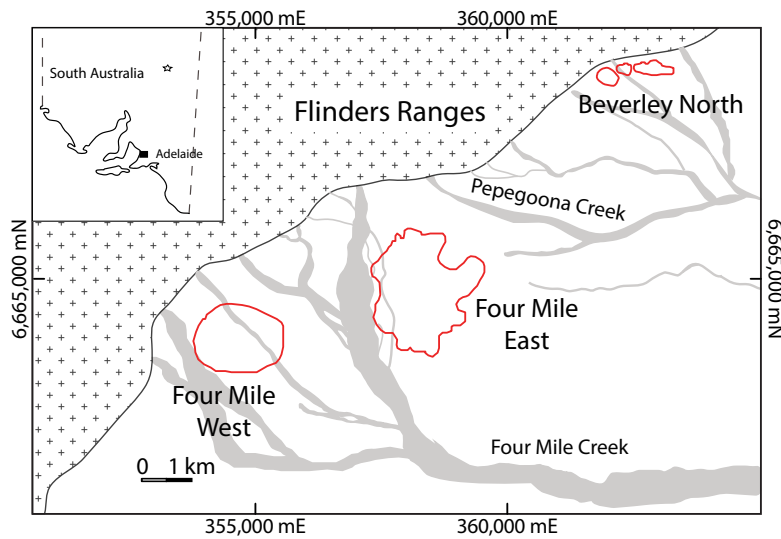


Figure 4.1: Map showing the location of the Four Mile West, Four Mile East and Beverley North sandstone-hosted deposits. The Beverley North deposits consist of (from left to right) the Pannikan, Pepegooona West and Pepegooona deposits. For this study, mineralised sediments were sampled from the Beverley North deposits. Low volume groundwaters were sampled from the Four Mile West, Four Mile East and Pepegooona deposits. Large volume groundwaters were sampled from the Pepegooona West deposit. Inset: South Australia map showing location of the deposits (star). Grid references are Geocentric Datum Australia GDA94 coordinates.

‘Roll-front’ deposits are so named because of the C-shaped mineralisation front that forms as a result of the continued redissolution/reprecipitation of uranium minerals due to 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, while the ‘limbs’ of the C-shape mineralisation are typically of lower grade.

The Four Mile East, Pepegooona, Pepegooona West and Pannikan deposits are located within the fluvial sands of the Eocene Eyre Formation (SKM, 2008; 2010). The Four Mile West deposit is hosted within diamictite sands within the Cretaceous Cadna-Owie Formation (Woods and Jeuken, 2010). The deposits are located at greater than 220 m depth below the surface, well below the zone of influence from cosmogenic rays. The Pepegooona deposit occurs as four stacked, irregularly shaped arcuate ‘roll-fronts’ (see Chapters II and III for more detail). The Pepegooona 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’ (A. Marsland-Smith, pers. comm., 2012). The Four Mile East deposit is comprised of several arcuate, irregularly shaped roll-fronts (see

Chapter II) whilst the Four Mile West deposit is a single, well-defined ‘roll-front’ (SKM, 2008). At all deposits, the primary ore mineral is uraninite with minor coffinite; which is present interstitially or precipitated on grain boundaries. Typical uranium concentrations within high-grade mineralisation range from 1-2 wt % U. However, U concentrations are highly variable both within and between deposits (A. Marsland-Smith, pers. comm., 2012). The age 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 a maximum age of uranium mineralisation of 56 to 34 Ma and 144 to 65 Ma, respectively.

The Beverley North deposits are currently being mined by Heathgate Resource Pty Ltd using *in-situ* recovery (ISR) mining techniques. This consists of injection of an acidic, oxidising solution into the host aquifer in contact with the mineralisation. The uranium minerals are subsequently dissolved, and the mining solution is then pumped to the surface for processing. As an environmental requirement of mining by ISR, the ore deposits are girt by groundwater wells screened at different aquifer depths to monitor potential groundwater contamination (SKM, 2008; 2010). This well geometry provides a rare opportunity to study the production of ^{236}U within a uranium mineralised system, in both the mineralised sediments and in the natural groundwaters flowing through the deposits prior to commencement of ISR.

Groundwaters sampled within or adjacent to the Four Mile East, Pepegooona, Pepegooona West and Pannikan deposits were sampled within the Eyre Formation aquifer. Samples from within the Four Mile West deposit were sampled within the Cadna-Owie Formation aquifer. Locally, the groundwater flow direction in the Eyre Formation and Cadna-Owie Formation aquifers is in an overall west to east direction from the recharge areas along the Flinders Ranges toward Lake Frome. Radiocarbon ages for groundwaters sampled within the Eyre Formation in the vicinity of the Pepegooona and Four Mile East deposits are 15,070 to 38,020 yrs BP (Chapter II). As such, they have not experienced recent recharge, and are therefore unlikely to have been contaminated by anthropogenic ^{236}U . Groundwaters from Four Mile West, Pannikan and Pepegooona West have not been dated, however are similarly

unlikely to have been contaminated by anthropogenic ^{236}U .

Groundwater wells sampled within the Pepegooona and Pepegooona West deposit were sampled several months after mining by ISR had commenced in certain areas of the deposit. Ongoing groundwater monitoring post-ISR indicated that the groundwater chemistry in the perimeter wells had not been affected by mining solution at the time of sampling, and are interpreted to be representative of the natural mineralised system.

4.3 SAMPLING AND ANALYTICAL PROCEDURES

4.3.1 Groundwater sampling and chemical preparation

Twelve groundwater samples of approximately 1 L volume were collected from the Four Mile East, Four Mile West and the Pepegooona deposits during field sampling campaigns in 2009 and 2010, following procedures outlined in Chapter II. The groundwater wells were selected to include samples both within and adjacent to high-grade mineralisation, over a range of U concentrations (from 0.3 to 819 $\mu\text{g/L}$). All samples were prepared under clean room conditions to minimise contamination with anthropogenic ^{236}U . The groundwater samples were pre-concentrated by two methods: evaporation and iron co-precipitation, and subjected to chemical purification using anion exchange chromatography. The former pre-concentration method was conducted at the Geochemical Analysis Unit, Macquarie University; the latter at the Department of Nuclear Physics, Research School of Physical Sciences and Engineering at the Australian National University. Further details of the groundwater sample preparation and chemical separation for these low volume samples are presented in Appendix B.

A dedicated field trip to collect larger volume groundwater samples and drill core samples was conducted in May, 2012. Sample volumes ranging from 10 to 20 L were collected in 5 L acid washed HDPE bottles using sampling procedures outlined in Chapter II. The groundwater wells were selected to include samples both within and adjacent to the Pepegooona West ore deposit. For the sample collected in high-grade mineralisation, (Table 4.1). 10 L was collected, 15 L in low-grade mineralisation, and 20 L from wells in un-mineralised portions of the aquifer. The following chemical preparation procedure for separation of uranium was conducted in the clean laboratory facilities in the Department of Nuclear Physics, Research School of Physical Sciences and Engineering at the Australian

National University.

Prior to chemical preparation, the water was transferred quantitatively to a 5 L beaker and the mass of groundwater within each 5 L bottle for each sample was determined. The sampling bottles were then carefully rinsed with 100 ml 2% HNO_3 and the rinsate was combined with its respective sample. For each 5 L aliquot of groundwater for each sample, an accurately known mass of ^{233}U tracer (CRM 111-A, New Brunswick Laboratory (NBL), USA) was added dependant upon the total volume of the sample. In addition, 5 mL of an iron solution equivalent to 10 mg Fe/g was also added to each beaker.

The groundwaters in the 5 L beakers were then left on a hotplate for 2 h to allow for equilibration with the tracer and Fe solution. The hotplate was turned off, and uranium was co-precipitated with ferric hydroxide by the dropwise addition of 25 % ammonia solution until a pH of 9 was achieved. The hotplate was then turned on for a further 1 h before the hotplate was switched off and the samples were allowed to sit for 2 h or overnight to allow quantitative co-precipitation of $\text{Fe}(\text{OH})_3$. The samples were then centrifuged and the supernatant discarded. The precipitate was dissolved in 1 mL of 69 % HNO_3 and the centrifuge tube was rinsed twice with 69 % HNO_3 prior to being combined with the aliquots of the same sample. The combined samples were then allowed to evaporate to dryness, before fuming once with a $\text{HNO}_3 + \text{H}_2\text{O}_2$ mixture to ensure oxidation of any organic material. The samples were then taken up in 30 mL 3 M $\text{HNO}_3 - 1\text{M Al}(\text{NO}_3)_3$ for further purification.

Chemical purification of U was achieved using a column containing 0.5 g U-TEVA resin (EiChrom®; 50-100 μm) pre-conditioned with 15 mL 3M HNO_3 . Matrix components were eluted with 15 mL 3 M HNO_3 , followed by the elution of Th by addition of 15 mL 6 M HCl. Uranium was eluted in 30 mL 1 M HCl. The samples were evaporated to dryness before fuming in 69 % HNO_3 to ensure complete oxidation of any organics that may have eluted from the resin.

Prior to analysis by AMS, 100 μL of Fe (equivalent to 14.6 mg Fe/g) was added to provide bulk to the samples prior to total evaporation. The samples were then allowed to dry for at least 48 hours. The samples were then calcined at 800°C in porcelain crucibles for 8 h to convert the $\text{Fe}(\text{OH})_3$ to Fe_2O_3 . The U_3O_8 sample was mixed with *ca.* 1 mg aluminium to

increase the conductivity, and then pressed into a cathode suitable for analysis by AMS.

Total procedural blanks for 20 L, 15 L and 10 L water samples were prepared using the same methodology.

4.3.2 Mineralised sediment sampling and chemical preparation

During the May 2012 field trip, subsamples from 9 powdered drill cores intersecting the Pepegooona, Pepegooona West and Pannikan deposits were collected. Samples were selected to represent high-grade and low-grade mineralised sections of the deposits based on descriptions provided by Heathgate Resource Pty Ltd, and availability. Given the highly heterogeneous nature of these deposits, the samples may not be representative of each individual deposit. However, it is anticipated that the samples will provide an indication of the degree of intra-deposit isotopic variability and variability between the Beverley North deposits. The drill core samples were processed using standard rock crushing techniques at an external laboratory (ALS Ammttec Ltd, Perth, Australia).

The following chemical preparation procedure for separation of uranium was conducted in the clean laboratory facilities in the Department of Nuclear Physics, Research School of Physical Sciences and Engineering at the Australian National University. Briefly, the powdered drill core samples were dried in oven overnight at 70 °C. Sufficient sample mass (~ 0.3 – 7.5 g) was weighed to yield ~ 0.5 to 3 mg of uranium, based on U concentrations provided by Heathgate Resources Pty Ltd as determined by the external laboratory (ALS AMMTEC, Perth, Australia). Prior to aqua regia leaching, the samples were spiked with ~600 µl of ²³³U tracer (CRM 111-A, NBL, USA) and ~200 µl of ²⁴²Pu tracer (SRM 4334H, National Institute of Standards and Technology (NIST), USA). Leaching was performed under refluxing conditions (3 h) using 36 mL of 37 % HCl/69 % HNO₃ (3:1) mixture. After allowing to cool to room temperature, the samples were centrifuged, the leachate removed, and the residue phases were subsequently aqua regia leached a second time. Following removal of the second leachate, the residue phases were rinsed twice using 70 % HNO₃. The resultant supernatant solutions from the aqua regia leaching and HNO₃ washes were combined. The samples were evaporated to near dryness before fuming three times with

a $\text{HNO}_3 + \text{H}_2\text{O}_2$ mixture to further ensure sample-spike equilibration and oxidation of any organic material. The samples were then taken up in 15 mL 8 N HNO_3 prior to further purification. To this solution, NaNO_2 was added to convert the Pu to the tetravalent state.

Chemical purification of U was achieved using the following procedure. A first column containing 4 g Biorad® AG1-X8 (100-200 mesh) was placed directly above a second column containing 0.5 g U-TEVA resin (EiChrom®, 50-100 μm). Both columns were preconditioned with 8 M HNO_3 . The sample then was loaded onto the first column, with the eluent flowing through to the second column. The columns were subsequently washed with 30 mL 8 M HNO_3 , followed by 50 mL 3 M HNO_3 . Following the initial loading of the samples onto the column and elution of matrix constituents, the columns were separated for the elution of Pu and U, respectively.

The first column containing the Biorad® AG1-X8 resin underwent further purification for separation of Pu. The elution of Pu and its further treatment is beyond the scope of this study. To the column containing the U-TEVA resin, Th was eluted with 15 mL 6 M HCl. Uranium was subsequently eluted from the column by the addition of 40 mL 1M HCl. The samples were evaporated to near dryness before being transferred into Teflon beakers, rinsed thrice with 2 mL 69 % HNO_3 , and then evaporated to near dryness.

Prior to analysis by AMS, 100 μL of Fe (equivalent to 14.6 mg Fe/g) was added to provide bulk to the samples prior to total evaporation. The samples were then allowed to dry for at least 48 hours. The samples were then calcined at 800°C in porcelain crucibles for 8 h to convert the $\text{Fe}(\text{OH})_3$ to Fe_2O_3 . The U_3O_8 sample was mixed with *ca.* 1 mg aluminium to increase the conductivity, and then pressed into a cathode suitable for analysis by AMS.

Two total procedural blanks were prepared in parallel to the samples using the same methodology. Additionally, duplicate analyses on three independently processed mineralised sediment samples were prepared.

4.3.3 ^{236}U determination by AMS

AMS measurements of the $^{236}\text{U}/^{238}\text{U}$ ratios were performed using the 14 UD Pelletron accelerator at the Australian National University. Detailed methods have been described in

Fifield (2008) and Fifield et al. (2010; in press). Briefly, uranium oxide negative ions (UO^-) are extracted from the caesium sputter source, mass-analysed by a magnet, and injected into the accelerator operating at 4 MV. After acceleration to the high-voltage terminal of the accelerator, the UO^- ions are dissociated and additional electrons stripped off the uranium ions in a gas stripper. Following a second stage of acceleration, U^{5+} ions are selected by the high-energy mass analyser. In order to determine $^{236}\text{U}/^{238}\text{U}$, a “slow cycling” procedure was employed whereby the mass-analysis magnet was switched periodically between $^{236}\text{U}^{16}\text{O}$ and $^{238}\text{U}^{16}\text{O}$ ions, while at the same time the terminal voltage of the accelerator was adjusted to ensure that the $^{236}\text{U}^{5+}$ and $^{238}\text{U}^{5+}$ ions were transmitted around the post-acceleration analysing magnet. The rare $^{236}\text{U}^{5+}$ ions were counted individually using a time-of-flight (TOF) detector with a flight path of 6 m (acquisition time of 10 mins per cycle), and the abundant $^{238}\text{U}^{5+}$ ions were detected as a current in a Faraday cup (acquisition time of 10 s). The ^{238}U - ^{236}U cycle was repeated twice, with an additional ^{238}U measurement at the end.

A small contribution of ^{236}U was observed in the blanks. Some, but not all, of this may be attributed to the small amount of ^{236}U (0.017 %) in the ^{233}U spike that was added to each sample. At present, the source of the remainder is a mystery, and is being investigated. It is unlikely to reflect a contribution from the reagents or resins used in the chemical preparation, as ^{236}U is not detected in all of the prepared blanks. Hence, it was necessary to subtract this background from the measured ^{236}U for each of the samples. In addition, a small ^{235}U background contribution was present in samples with a higher rate of ^{235}U ions entering the detection system due to imperfect separation of ^{235}U and ^{236}U ions by the TOF system. The samples were also corrected for this. As a consequence, the uncertainties associated with the measured $^{236}\text{U}/^{238}\text{U}$ ratios are quite large. The rates in the detection system of ^{235}U ions was somewhat higher than normal in this run due to a recent opening of the acceleration tube, and hence a somewhat poorer than normal vacuum in the tube. In order to arrive at the detector, a ^{235}U ion must undergo a collision with residual gas in the acceleration tube that changes it from a $^{235}\text{U}^{4+}$ to $^{235}\text{U}^{5+}$ ion, and this process is more likely when the vacuum is poorer. Any potential background contribution from other ions was effectively eliminated by the TOF detection system. All uncertainties on individual $^{236}\text{U}/^{238}\text{U}$ ratios are quoted as 1σ based on

counting statistics and include propagated uncertainties associated with subtraction of the contributions from ^{236}U in the blank and the ^{235}U background counts. One sample, PRC021-12, was analysed with and without a 3 mm diameter aperture immediately upstream of the ‘start’ detector of the TOF detection system. This aperture reduced considerably the rate of ^{238}U ions entering the detector, and allowed an assessment of whether ^{238}U ions might also be contributing a background under the ^{236}U peak in the TOF spectrum. In fact, the ^{238}U ions were found to be well separated from ^{236}U by the TOF detector (Figure 4.2). This sample was also analysed a third time later in the run sequence to check reproducibility. The quoted $^{236}\text{U}/^{238}\text{U}$ ratio is a weighted average of the three measurements, with the appropriate 1σ error of the weighted mean, which includes the propagated uncertainties of the individual ratios. Similarly, a weighted mean and associated 1σ error of the weighted mean is presented for all prepared samples duplicates, as the measurements are all within analytical uncertainty.

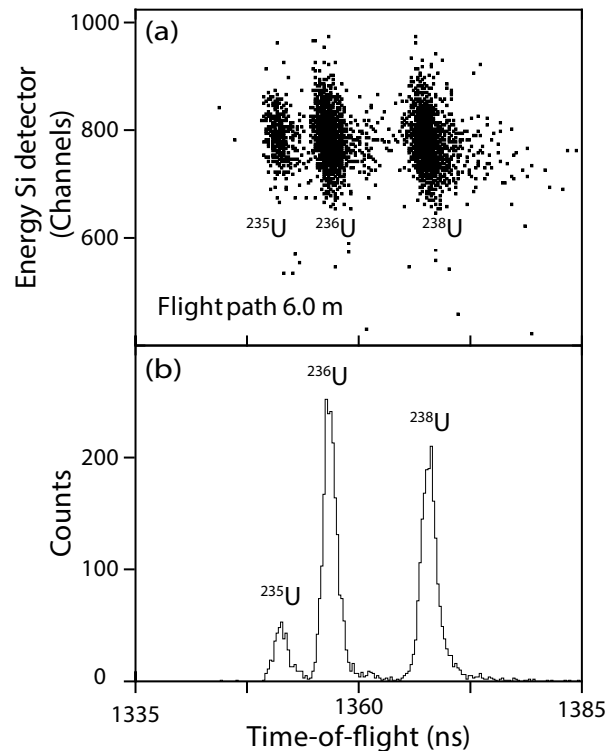


Figure 4.2: (a) Two-dimensional spectrum of energy deposited in the Si detector versus time-of-flight (TOF) for ~ 24 MeV uranium ions. The flight path is 6 m. The TOF detector effectively separates the ^{236}U ions from the background ^{235}U and ^{238}U ions. This spectrum is for a uranium sample Vienna-KkU, with a $^{236}\text{U}/^{238}\text{U}$ ratio of 6×10^{-11} . Figure (b) is one-dimensional projection of (a) on to the TOF axis (modified after Fifield et al., in press).

Where relevant throughout the text and in figures, a weighted mean $^{236}\text{U}/^{238}\text{U}$ is referred to rather than the individual measurements.

An in-house uranyl nitrate standard (Vienna-KkU from the Joachimsthal mine, in what is now the Czech Republic; Steier et al., 2008) was prepared in duplicate and periodically analysed ($n = 4$) to monitor the efficiency of the detection system and as a measure of the instrument stability. The efficiency of the detection system was determined to be 31.3 % based on the weighted average of the four measurements and the known $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.98 \pm 0.32) \times 10^{-11}$ for this material determined by Steier et al. (2008).

4.4 RESULTS

4.4.1 Groundwaters

For the low volume (1 L) groundwater samples, insufficient uranium was obtained to yield a detectable beam current, and consequently no ^{236}U was detected in these samples. The groundwaters at Pepegooona and Four Mile are highly reducing and as such have very low uranium concentrations (Chapter II). Two groundwater samples had uranium concentrations greater than 500 $\mu\text{g/L}$, which should have been sufficient to provide a detectable signal. Chemical yields for the column separation procedure for these low volume samples have not been determined; low chemical yields may have contributed to the lack of signal for these samples.

Of the large volume groundwater samples collected in May 2012, only one (PW0061), which was sampled directly within high-grade mineralisation within the Pepegooona West deposit, yielded enough uranium to produce a ^{238}U beam that was sufficient to be able to measure a $^{236}\text{U}/^{238}\text{U}$ ratio at the low levels that are characteristic of this deposit. The result, $(6.57 \pm 2.97) \times 10^{-12}$, is similar to the ratios measured in the ore itself (see below). The remaining groundwater samples from low-grade and un-mineralised areas in the vicinity of the Pepegooona West deposit had such low uranium concentrations ($\sim\mu\text{g/L}$) that even 15-20 litres of water contained insufficient uranium to produce a ^{238}U beam of comparable magnitude to the PW0061 sample or the mineralised sediment samples. Although uranium was certainly extracted from these samples, typical beam currents were a factor of 10 or more less than from the ore samples, which contained several mg of uranium. At these low

currents, and at the low ratios expected here, there simply aren't enough ^{236}U atoms in the sample to give a detectable signal. Conversely, the situation is very different for anthropogenic ^{236}U , where the $^{236}\text{U}/^{238}\text{U}$ ratios can be considerably higher, in the range of 10^{-7} to 10^{-8} . For example, Srncik et al. (2010) report measurements of anthropogenic ^{236}U in Austrian river waters where the amount of uranium available for measurement was only ~ 20 mg.

The field data including pH, dissolved oxygen (dO), redox potential (Eh), conductivity and temperature, in addition to the $^{236}\text{U}/^{238}\text{U}$ ratio for the one sample in which ^{236}U was detected, are presented in Table 4.1 for the groundwaters sampled from the Pepegoona West area. In the Pepegoona West region, Eyre Formation aquifer samples are typically characterised by highly reducing groundwaters, with Eh values ranging from -288 to -556 mV and conductivity values ranging from 3.72 to 4.12 mS. Sample PW0061 has a slightly oxidising redox potential of 103 mV, which is interpreted to be an artefact from the sampling technique. No dedicated low flow pump was installed in this well, and consequently a pump had to be lowered on the day of sampling. It is interpreted that the results for this well reflect sampling groundwater above the screened interval, resulting in sampling of overlying water, rather than groundwaters directly at the aquifer screen. These waters, although taken from the aquifer of interest, may be biased toward higher Eh and lower pH values. The oxidising conditions may result in the release of any reduced U(IV) adsorbed onto colloidal materials into solution. This may result in slightly higher U concentrations, although this process is not expected to fractionate U isotopes and thus groundwater $^{236}\text{U}/^{238}\text{U}$ values should be unaffected.

The Pepegoona West deposit is characterised by ambient groundwater temperatures ranging from 27.7 to 29.1 °C, and neutral pH ranging from 6.65 to 6.97. Groundwater U concentrations for these samples were not determined prior to separation for ^{236}U analysis. For comparison, the groundwaters in the adjacent Pepegoona and Four Mile East deposit (also hosted within the Eyre Formation) yield U concentrations ranging from 0.25 to 196 $\mu\text{g/L}$, with the higher concentrations observed in groundwaters sampled directly within mineralisation (see Chapter II).

4.4.2 Mineralised sediments

Table 4.1: $^{236}\text{U}/^{238}\text{U}$ ratios and field data for groundwaters sampled within the Pepegoona West sandstone-hosted uranium deposit.

Water Sample	Eastings ^a	Northings ^a	SWL (m) ^b	Screen height ^c (m)	pH	dO (mg/L)	EC (mS)	Redox (mV)	T (°C)	$^{236}\text{U}/^{238}\text{U}$ (x 10 ⁻¹²) ^d	Sample description
Pepegoona West Deposit											
PRMW055	362039	6668809	82.4	254	6.95	0.39	3.82	-323	27.8	nd	Sampled in unmineralised area, ~ 200 m up-gradient of mineralisation
PRMW047	362383	6668763	82.8	234	6.85	0.47	4.09	-288	27.7	nd	Sampled in unmineralised area, ~ 100 m down-gradient of high-grade mineralisation
PRMW072	362595	6668870	87.1	218	6.97	0.32	3.72	-566	29.1	nd	Sampled in unmineralised area, ~ 300 m down-gradient of low-grade mineralisation
PW0060	362291	6668868	83.8	213	6.65	0.62	4.12	-304	28.2	nd	Sampled directly within low-grade mineralisation (~0.5 % U cutoff)
PW0061 [^]	362261	6668782	86.2	215	6.72	0.95	3.80	103	28.2	(6.57 ± 2.97)	Sampled directly within high-grade mineralisation (>1 % U cutoff)

^a Eastings and Northings (Geocentric Datum Australia GDA94 coordinates).

^b Standing water level measured from the top of well casing.

^c Depth to middle of the screen, below ground surface.

^d Uncertainty on $^{236}\text{U}/^{238}\text{U}$ ratios is 1σ based on counting statistics and include propagated uncertainties associated with blank subtraction.

[^] Sampled above screened interval hence more oxidising redox potential, see text for more detail.
nd not detected.

Table 4.2: $^{236}\text{U}/^{238}\text{U}$ ratios, U concentrations and mineralogical descriptions for Beverley North mineralised sediments.

Sample	$^{236}\text{U}/^{238}\text{U}$ ($\times 10^{-12}$) ^a	U ($\mu\text{g/g}$) ^b	From depth (m) ^c	To depth (m) ^c	Sample description ^d and mineralogy ^e
Pepegoona Deposit					
PRC015-23	(2.63 \pm 1.1)	173	219.60	219.67	Weakly mineralised sands directly above thin ferricrete layer, ~45 % quartz, 45 % pyrite, ~2 % U minerals, trace rutile & ilmenite
PRC015-24	(1.16 \pm 0.60) (2.01 \pm 0.62)	24200	219.80	219.86	Mineralised sands directly below thin ferricrete layer, ~65 % quartz, 25 % pyrite, ~8 % U minerals, trace rutile & ilmenite
Wtd Avg.†	(1.57 \pm 4.3)				
PRC015-25	(2.43 \pm 0.60)	2253	219.86	219.92	Weakly mineralised sands, ~90 % quartz, 5 % pyrite, minor clays, U minerals, rutile & ilmenite
Pepegoona West Deposit					
PRC023-15	(3.64 \pm 0.59)	895	240.84	240.93	Mineralised pyritic sands (main mineralised zone)
PRC023-16†	(3.93 \pm 0.66) (3.79 \pm 0.59)	4797	244.38	244.46	Mineralised silt to fine-grained carbonaceous sands (main mineralised zone)
Wtd Avg.†	(3.85 \pm 0.44)				
PRC023-19	(3.24 \pm 0.54)	403	262.22	262.3	Mineralised fine-grained sands (lower mineralised zone)
Pannikan Deposit					
PRC019-03	(1.41 \pm 0.46)	610	247.93	248.00	Mineralised fine to medium-grained, reduced carbonaceous sands
PRC021-11†	(8.79 \pm 0.72) (9.48 \pm 0.83)	7876	260.36	260.42	Mineralised carbonaceous sands (lower limb on the main roll front)
Wtd Avg.†	(9.48 \pm 0.55)				
PRC021-12*	(7.86 \pm 2.5) (8.61 \pm 1.9) (3.30 \pm 1.37)	78.9	261.61	261.68	Weakly mineralised sands (lower limb on the main roll front)
Wtd Avg.†	(5.58 \pm 1.4)				

^a Uncertainty on $^{236}\text{U}/^{238}\text{U}$ ratios are 1 σ based on counting statistics and include propagated uncertainties associated with blank subtraction.

^b Uranium concentrations provided by Heathgate Resources Pty Ltd.

^c To and from depths refer to depth below surface.

^d Sample description provided by Heathgate Resources Pty Ltd.

^e Mineralogy for Pepegoona mineralised sediment samples PRC015 determined by polished thick section reflected light microscopy and semi-quantitative analysis by SEM at the GAU, Macquarie University (see chapter III). Mineralogy not determined for other samples.

† Where sample replicates have been prepared, a weighted average $^{236}\text{U}/^{238}\text{U}$ ratio is quoted with an associated 1 σ error of the weighted mean, which includes the propagated uncertainties of the individual ratios.

* Sample PRC012-12 was analysed in triplicate throughout the analytical session, see text for further details.

Uranium concentrations and $^{236}\text{U}/^{238}\text{U}$ ratios (including weighted average ratios) for the mineralised sediments from the Beverley North sandstone-hosted uranium deposits are shown in Table 4.2. The analysed samples from the Pannikan, Pepegooona West and Pepegooona deposits are from a range of different depths and positions (i.e. nose or limbs) within the mineralised roll-fronts for each of the respective deposits, based on sample descriptions for the sediments provided by Heathgate Resources Pty Ltd. These sample descriptions are given in Table 4.2. Mineralogical descriptions for Pepegooona drill core PRC015 samples are also included, based on polished thick section reflected light microscopy and semi-quantitative analysis by Scanning Electron Microscopy (SEM; Zeiss EVO MA15; Geochemical Analysis Unit, Macquarie University, see Chapter III).

^{236}U was detected in all of the mineralised sediment samples that yielded $^{236}\text{U}/^{238}\text{U}$ ratios of the order of $\sim 10^{-12}$, ranging from $(1.16 \pm 0.06) \times 10^{-12}$ to $(9.48 \pm 0.83) \times 10^{-12}$. The samples have U concentrations that vary by almost three orders of magnitude, ranging from 78.9 to 24200 $\mu\text{g/g}$. Replicate measurements for each of the three sample duplicates are all within analytical uncertainty.

4.5 DISCUSSION

The primary objective of this study was to characterise the $^{236}\text{U}/^{238}\text{U}$ isotopic ratios in uranium mineralised sediments and groundwaters in the vicinity of several sandstone-hosted uranium deposits. Specifically, this study aims to characterise the $^{236}\text{U}/^{238}\text{U}$ isotopic signatures in the waters with respect to the presence of high-grade uranium mineralisation. This can ultimately be used to assess the potential applicability of natural ^{236}U in groundwaters as an exploration tool for uranium in the Frome Embayment.

4.5.1 *Comparison with other uranium ores or uranium ore concentrate $^{236}\text{U}/^{238}\text{U}$ isotopic ratios*

The $^{236}\text{U}/^{238}\text{U}$ ratios of the mineralised sediments from this study, together with other published values for uranium ores and UOCs from the literature are detailed in Table 4.3 and Figure 4.3 (Rokop et al., 1972; Zhao et al., 1994a; Zhao et al., 1994b; Berkovits et al., 2000; Wilcken et al., 2008; Srncik et al., 2011). The $^{236}\text{U}/^{238}\text{U}$ ratios observed in the mineralised

sediments from the Beverley North deposits are two orders of magnitude higher than ratios of $\sim 10^{-14}$ expected in average crustal rocks (Steier et al., 2008). However they are at the low end of the range of values previously reported from uranium ores. This is not surprising as sandstone-hosted uranium deposits are typically lower grade ($\sim 1\text{--}2$ wt % U) and hence have lower neutron fluxes than unconformity or magmatic uranium deposits which typically have 5 – 15 wt % U. Some deposits however can reach up to 50 wt % U, such as at the Canadian unconformity Cigar Lake deposit (IAEA, 2009). Uranium ores from within the Cigar Lake deposit have a $^{236}\text{U}/^{238}\text{U}$ ratio at the higher end of published values ($^{236}\text{U}/^{238}\text{U} = (5.56 \pm 1.5) \times 10^{-10}$; Zhao et al., 1994a; 1994b), which is due to high concentrations of uranium minerals generating a high neutron flux, which in turn results in higher $^{236}\text{U}/^{238}\text{U}$ ratios. $^{236}\text{U}/^{238}\text{U}$ ratios of the order of $\sim 10^{-8}$ to 10^{-9} are unlikely to represent natural ^{236}U , rather are more likely to reflect anthropogenic contamination (Richter et al., 1999).

4.5.2 *Factors controlling the neutron flux and production of ^{236}U in high-grade ores*

In high-grade ores, the neutron flux depends upon: (i) the concentration and homogeneity of uranium and thorium mineralogy; (ii) the composition and homogeneity of the rock matrix (which is related to the ore geometry); (iii) the water content (which can also absorb neutrons); and (iv) the extent to which ^{236}U has attained steady state equilibrium (whereby the rate of production ^{236}U from neutron capture on ^{235}U is equal to that of the radioactive decay of ^{236}U as a function of its half-life; 23.4 Ma), which is dependent upon the age of the deposit (Wilcken et al., 2008).

In Figure 4.4, $^{236}\text{U}/^{238}\text{U}$ isotopic composition is plotted against U concentration for mineralised sediments from the Beverley North deposits. The mineralised sediments have $^{236}\text{U}/^{238}\text{U}$ ratios all of the order of $\sim 10^{-12}$, and U concentrations that vary by almost three orders of magnitude, ranging from 78.9 to 24200 $\mu\text{g/g}$. Also shown in Figure 4.4 is the $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$ for a single Pepegona West groundwater sample (PW0061) that was sampled directly within high-grade mineralisation. Overall, the mineralised sediments display a weakly positive correlation between $^{236}\text{U}/^{238}\text{U}$ and U concentration, with the exception of sample PRC015-24 from the Pepegona deposit, which does not fall on the

Table 4.3: Compilation of $^{236}\text{U}/^{238}\text{U}$ ratios obtained from a range of UOCs and uranium ores from this study and literature sources.

Locality	$^{236}\text{U}/^{238}\text{U}_{\text{a,b}}$	Reference
Haematite Breccia Complex		
Olympic Dam 4, Australia	$(1.51 \pm 0.44) \times 10^{-11}$	Srncik et al. (2011)
Intrusive		
Davidite, Radium Hill, Australia	$(10.2 \pm 1.6) \times 10^{-12}$	Wilcken et al. (2008)
Davidite + Carnotite, Radium Hill, Australia	$(1.35 \pm 0.55) \times 10^{-12}$	Wilcken et al. (2008)
U-Thorianite, Tranomaro, Madagascar	$(14.6 \pm 1.7) \times 10^{-12}$	Wilcken et al. (2008)
Roessing, Namibia	$2.0(1.8) \times 10^{-10}$	Richter et al. (1999)
Askola, Finland	$(2.16) \times 10^{-8}$	Richter et al. (1999)
Thucolite, Parry Sound, Ontario, Canada	$(0.8 \pm 1.5) \times 10^{-10}$	Rokop et al. (1972)
Metasomite		
Lagoa Real, Brazil	$(4.12 \pm 0.04) \times 10^{-9}$	Srncik et al. (2011)
BL-3, reference material, CANMET, Canada	$(88.5 \pm 4.3) \times 10^{-12}$	Wilcken et al. (2008)
BL-5, reference material, CANMET, Canada	$(220 \pm 8.4) \times 10^{-12}$	Wilcken et al. (2008)
Sandstone-hosted - roll-front		
Davidite, Billeroo Prospect, Australia	$(1.03 \pm 0.5) \times 10^{-12}$	Wilcken et al. (2008)
Pitchblende, Bocenago, Italy	$(8.7 \pm 1.4) \times 10^{-12}$	Wilcken et al. (2008)
Pepegoona, Australia	$(2.63 \pm 1.1) \times 10^{-12}$	This study
Pepegoona, Australia †	$(1.57 \pm 4.3) \times 10^{-12}$	This study
Pepegoona, Australia	$(2.43 \pm 0.60) \times 10^{-12}$	This study
Pepegoona West, Australia	$(3.64 \pm 0.59) \times 10^{-12}$	This study
Pepegoona West, Australia †	$(3.85 \pm 0.44) \times 10^{-12}$	This study
Pepegoona West, Australia	$(3.24 \pm 0.54) \times 10^{-12}$	This study
Pannikan, Australia	$(1.41 \pm 0.46) \times 10^{-12}$	This study
Pannikan, Australia †	$(9.48 \pm 0.55) \times 10^{-12}$	This study
Pannikan, Australia †	$(5.58 \pm 1.4) \times 10^{-12}$	This study
Sandstone-hosted - tabular		
Pitchblende, Novo-mesto, Czech Republic/Slovenia	$(65.5 \pm 3.9) \times 10^{-12}$	Wilcken et al. (2008)
DIAMO, Stráž pod Ralskem, Czech Republic	$2.540(92) \times 10^{-8}$	Richter et al. (1999)
Paukkajanvaara, Finland	$(1.45) \times 10^{-8}$	Richter et al. (1999)
Sandstone-hosted - tectonolithic		
GL-3513-MO48, Oklo Zone 9, Gabon	$(180 \pm 9.5) \times 10^{-12}$	Wilcken et al. (2008)
GL-3518-MO43, Oklo Zone 9, Gabon	$(153 \pm 8) \times 10^{-12}$	Wilcken et al. (2008)
Comuf Mounana, Gabon	$9.32(69) \times 10^{-9}$	Richter et al. (1999)
Cogema Lodeve, France	$1.9(1.7) \times 10^{-10}$	Richter et al. (1999)

Continued on following page

Table 4.3 continued

Locality	$^{236}\text{U}/^{238}\text{U}_{\text{a,b}}$	Reference
Unconformity - Proterozoic, fracture bound		
Ranger 4, Australia	$(1.92 \pm 0.28) \times 10^{-11}$	Šrnčík et al. (2011)
Ranger 3, Australia	$(1.73 \pm 0.30) \times 10^{-11}$	Šrnčík et al. (2011)
Ranger 2, Australia	$(1.76 \pm 0.30) \times 10^{-11}$	Šrnčík et al. (2011)
Rabbit Lake, Canada	$(1.12 \pm 0.06) \times 10^{-10}$	Šrnčík et al. (2011)
Cigar Lake, Canada	$(33.0 \pm 5.0) \times 10^{-11}$	Berkovits et al. (2000)
Nabarlek, Australia	$(229 \pm 7.4) \times 10^{-12}$	Wilcken et al. (2008)
Cigar Lake, Canada	$(5.6 \pm 1.5) \times 10^{-10}$	Zhao et al. (1994a; 1994b)
Rabbit Lake, Canada	$2.8(1.7) \times 10^{-10}$	Richter et al. (1999)
Vein		
Schwartzwalder, USA	$(1.2 \pm 1.0) \times 10^{-11}$	Berkovits et al. (2000)
Joachimsthal (Jáchymov), Bohemia, Czech Republic	$(7.3 \pm 1.9) \times 10^{-11}$	Berkovits et al. (2000)
Joachimsthal, Bohemia, Czech Republic	$(11.6 \pm 2.4) \times 10^{-11}$	Berkovits et al. (2000)
Joachimsthal, Bohemia, Czech Republic	$(17.0 \pm 3.0) \times 10^{-11}$	Berkovits et al. (2000)
Pitchblende, Peny, France	$(280 \pm 11.9) \times 10^{-12}$	Wilcken et al. (2008)
Pitchblende, Solwezi, Zambia	$(59.5 \pm 3.4) \times 10^{-12}$	Wilcken et al. (2008)
Pitchblende, Zambia	$(60.5 \pm 5.1) \times 10^{-12}$	Wilcken et al. (2008)
Uraninite, Shinkolobwe Katanga, Congo	$(2.3 \pm 0.8) \times 10^{-10}$	Rokop et al. (1972)
Volcanic		
Osamu Utsumi, Brazil	$(1.8 \pm 1.0) \times 10^{-11}$	Berkovits et al. (2000)
Pitchblende, Valvedello, Italy	$(8.2 \pm 1.5) \times 10^{-12}$	Wilcken et al. (2008)
Pitchblende, Bergamon, Novazza, Italy	$(81.4 \pm 4.2) \times 10^{-12}$	Wilcken et al. (2008)
UOC		
CETAMA Amethyste, France	$2.0(1.4) \times 10^{-10}$	Richter et al. (1999)
Olympic Dam, Australia	$(4.46 \pm 0.48) \times 10^{-11}$	Šrnčík et al. (2011)
Ranger, Australia	$(1.48 \pm 0.26) \times 10^{-11}$	Šrnčík et al. (2011)
Lagoa Real, Brazil	$(3.09 \pm 0.38) \times 10^{-11}$	Šrnčík et al. (2011)
Rabbit Lake, Canada	$(5.17 \pm 0.48) \times 10^{-11}$	Šrnčík et al. (2011)
Great Bear Lake, Ontario, Canada	$(6.2 \pm 2.2) \times 10^{-10}$	Rokop et al. (1972)
Unknown Origin		
Pitchblende, Cesmina Jackymanu, Czech Republic	$(31.8 \pm 4.3) \times 10^{-12}$	Wilcken et al. (2008)
Torbernite, ANU radioactive storage	$(55.2 \pm 2.7) \times 10^{-12}$	Wilcken et al. (2008)
Coffinite, Tasmania, Australia	$(236 \pm 11.9) \times 10^{-12}$	Wilcken et al. (2008)

^a $^{236}\text{U}/^{238}\text{U}$ ratios and associated uncertainties are presented in the same format as that of the reference, for further information the reader is directed towards the original paper.

^b Caution should be taken with $^{236}\text{U}/^{238}\text{U}$ ratios of the order of 10^{-8} to 10^{-9} , as the samples may reflect anthropogenic contamination (Richter et al., 1999).

† Where sample replicates were prepared for this study, weighted average $^{236}\text{U}/^{238}\text{U}$ ratios are presented.

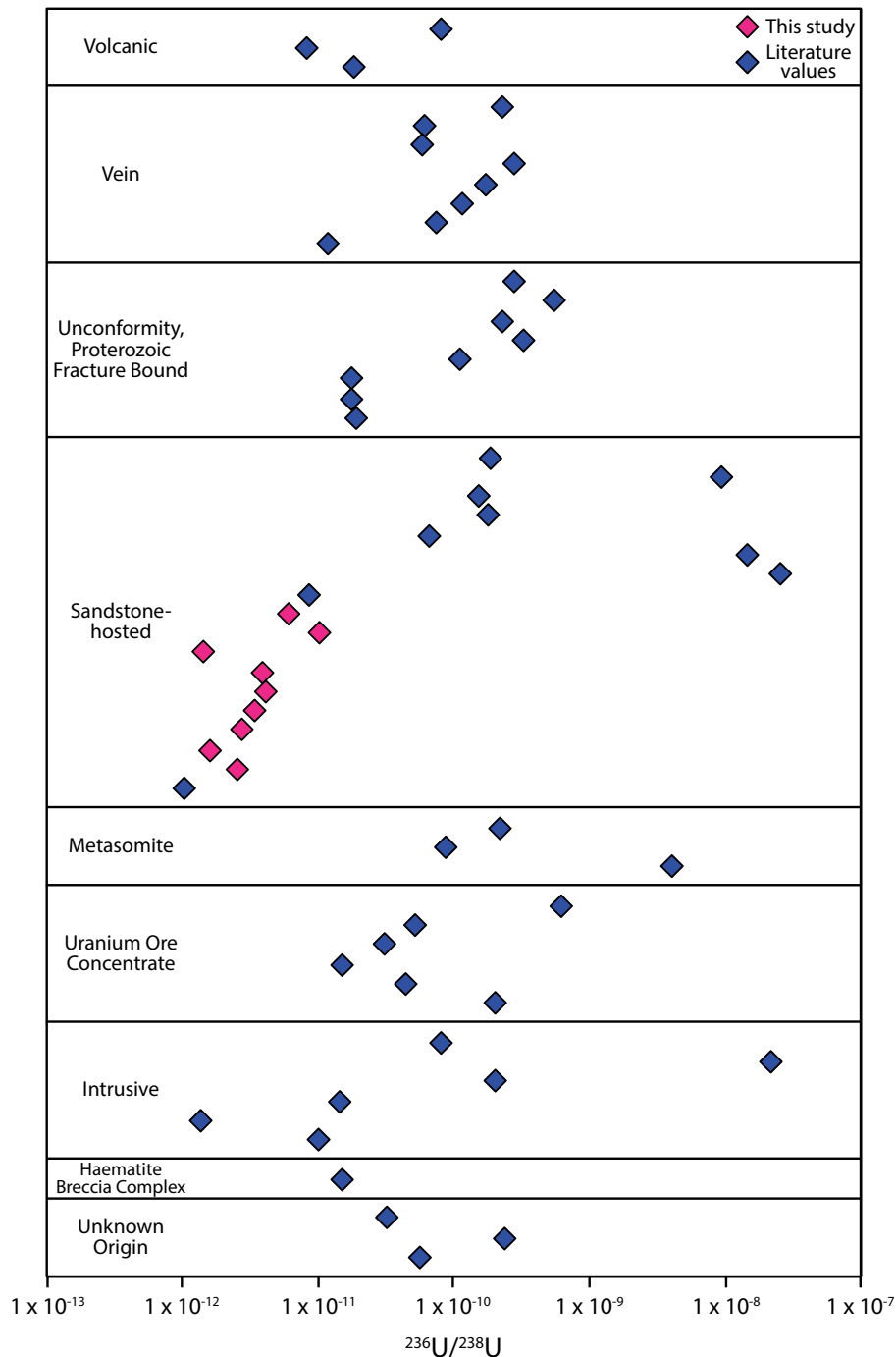


Figure 4.3: Compilation of $^{236}\text{U}/^{238}\text{U}$ ratios obtained from a range of UOCs and uranium ores from literature sources (Rokop et al., 1972; Zhao et al., 1994a; 1994b; Richter et al., 1999; Berkovits et al., 2000; Wilcken et al., 2008; Srmcik et al., 2011) and this study (Table 4.3). Data are grouped according to deposit type. Samples from this study are shown as pink diamonds, literature values are shown in blue diamonds. Note logarithmic scale on x -axis. Where sample duplicates were prepared for this study, a single weighted average $^{236}\text{U}/^{238}\text{U}$ ratio is presented (denoted in Table 4.2). Uranium ores with $^{236}\text{U}/^{238}\text{U}$ ratios of the order of 10^{-8} to 10^{-9} may reflect anthropogenic contamination, and are not interpreted to be representative of natural $^{236}\text{U}/^{238}\text{U}$ ratios (Richter et al., 1999). The mineralised sediments from the Beverley North deposits have $^{236}\text{U}/^{238}\text{U}$ ratios at the low end of the range of values measured previously in uranium ores. Sandstone-hosted uranium deposits are typically lower grade (~ 1 -2 wt % U) and hence expected to have lower neutron fluxes than hydrothermal or magmatic style uranium deposits.

same trend. Possible mechanisms to explain this anomalous ratio are discussed below.

The predominantly linear relationship between $^{236}\text{U}/^{238}\text{U}$ ratio and U concentration suggests that the U concentration, and hence the percentage of U minerals present within each sample, exerts a strong control over the $^{236}\text{U}/^{238}\text{U}$ ratio. This is not unexpected, and is consistent with the generation of higher neutron fluxes due to high concentrations of U minerals. The average distance a neutron will travel before interacting with a nucleus is known as the *mean free path* (λ). The mean free path of thermal neutrons is ~ 30 cm in rocks with low uranium concentrations. In high-grade ores, the mean free path can be as little as 10 cm due to the high resonance integral of uranium (Curtis et al., 1999). Therefore, the

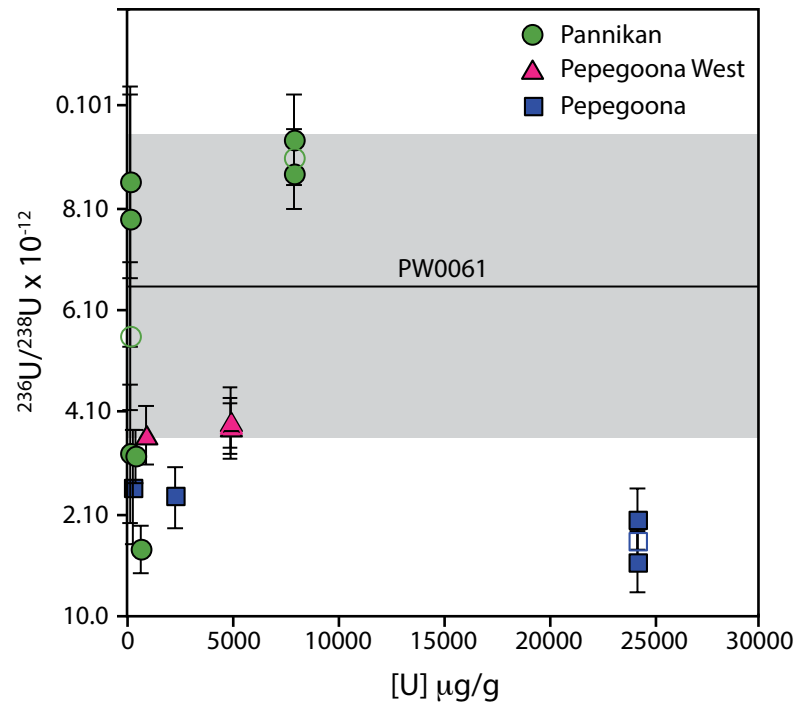


Figure 4.4: $^{236}\text{U}/^{238}\text{U}$ ratios versus U concentration for mineralised sediments from the Beverley North sandstone-hosted uranium deposits. Solid symbols indicate individual $^{236}\text{U}/^{238}\text{U}$ ratio measurements as reported in Table 4.2, with 1σ uncertainty error bars based on counting statistics, including the propagation of uncertainties associated with blank subtraction. Weighted average $^{236}\text{U}/^{238}\text{U}$ ratios are presented as open symbols with their associated uncertainties, as denoted in Table 4.2. The solid black line denotes the $^{236}\text{U}/^{238}\text{U}$ ratio for groundwater sample PW0061 sampled directly within high-grade mineralisation in the Pepegooona West deposit (Table 4.1). The grey shaded box is the associated 1σ uncertainty. The mineralised sediments have $^{236}\text{U}/^{238}\text{U}$ ratios ranging from $(1.16 \pm 0.06) \times 10^{-12}$ to $(9.48 \pm 0.83) \times 10^{-12}$, and U concentrations that vary by almost three orders of magnitude, ranging from 78.9 to 24200 $\mu\text{g/g}$. Overall, the mineralised sediments display a weak positive correlation between $^{236}\text{U}/^{238}\text{U}$ and U concentration, with the exception of sample PRC015-24 which does not fall on the same trend.

highest $^{236}\text{U}/^{238}\text{U}$ ratios are expected where the samples are surrounded by ~10 to 30 cm of high-grade ore, depending upon the mineralogy of the deposit. Given that sandstone-hosted type uranium deposits typically have low uranium contents (~1 to 2 wt % U) compared with other higher grade types of deposits, and the ore geometry is generally quite heterogeneous, the maximum neutron flux is expected to be generated where the minerals are surrounded by greater than 30 cm of high grade U.

In Figure 4.5, the distribution of $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations with depth below the surface for mineralised sediments from the (a) Pannikan; (b) Pepegooona West and (c) Pepegooona deposits are shown. For all of the deposits, there is no systematic trend with depth. For samples from the Pannikan and Pepegooona West deposits, the $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations are well correlated and follow similar trends, which appear to be related to position in the roll-front (and hence low/high grade mineralisation evidenced by U concentration) rather than depth (Figures 4.5a and 4.5b).

The Pannikan deposit contains the highest $^{236}\text{U}/^{238}\text{U}$ ratios of the Beverley North suite of samples, with a ratio of $(9.09 \pm 0.55) \times 10^{-12}$ for sample PRC021-11. It is not surprising that the highest $^{236}\text{U}/^{238}\text{U}$ ratios were obtained in samples within this deposit, as the Pannekin deposit consists of a single, well-defined roll-front. PRC021-11, sampled within high-grade mineralisation on the lower limb of the main roll-front has a uranium concentration of ~8000 $\mu\text{g/g}$. It is likely that this sample would have been surrounded by ore of similar concentration. The second highest ratio, $(5.58 \pm 1.44) \times 10^{-12}$ for sample PRC021-12 comes from the same drill core approximately 1.3 m below PRC021-11 in a weaker mineralised area within the lower limb of the roll-front. Although the uranium concentration of this sample is a factor of 100 lower, it is sufficiently close to the high-grade roll-front to be exposed to a higher neutron flux than that generated from the uranium in its immediate vicinity, resulting in the higher $^{236}\text{U}/^{238}\text{U}$ ratio. No sample directly within the highest-grade mineralisation within the nose of the Pannekin roll-front was measured, however it might be expected to have an even higher $^{236}\text{U}/^{238}\text{U}$ ratio than that found in the limbs.

The lowest value within the Pannikan deposit of $(1.41 \pm 0.46) \times 10^{-12}$ is from a separate

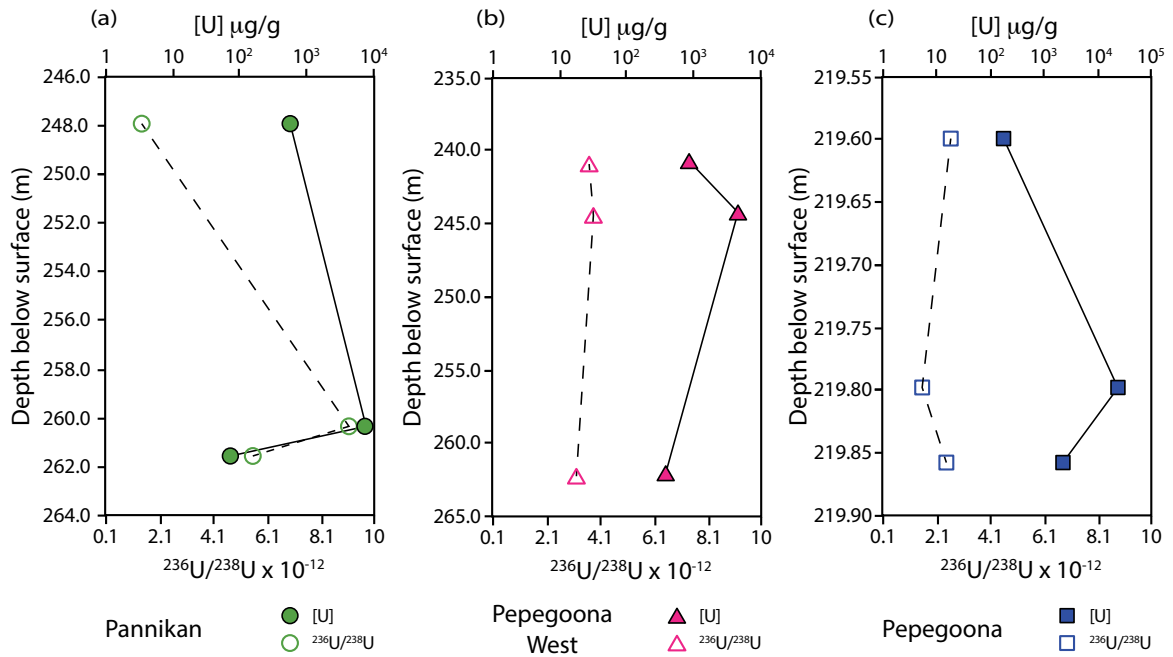


Figure 4.5: Distribution with depth below the surface for $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations for mineralised sediments from the (a) Pannikan; (b) Pepegooona West and (c) Pepegooona deposits. Note the logarithmic scale for U concentrations on the secondary x-axis. Where sample duplicates were prepared, a single weighted average $^{236}\text{U}/^{238}\text{U}$ ratio is presented (denoted in Table 4.2). The data shown in Figure (a) for Pannikan are from two separate drill cores, whereas Figures (b) and (c) from the Pepegooona West and Pepegooona deposits are from the same drill cores. For samples from the Pannikan and Pepegooona West deposits, the $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations are well correlated and follow similar trends with depth. $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations for mineralised sediments from the Pepegooona deposit, however, are not coupled. A large disparity is observed with sample PRC015-24, which has the highest U concentration by several orders of magnitude, but the lowest $^{236}\text{U}/^{238}\text{U}$ ratio which may reflect local heterogeneities or ‘nugget effect’.

drill core PRC019. The sample was taken from a depth ~ 13 m shallower than the other two samples from drill core PRC021. The location of this sample within the roll-front is not well constrained, however is likely outside the range of influence of the neutrons produced in the high-U environment of the nose of the roll-front. Hence, its $^{236}\text{U}/^{238}\text{U}$ ratio is likely to be determined by its local U concentration. As the U concentration of PRC019-03 is an order of magnitude lower than within the higher-grade mineralisation, a similar factor would be expected in the $^{236}\text{U}/^{238}\text{U}$ ratios, which is approximately what is observed.

The mineralised sediments from Pepegooona West (Figure 4.5b) have relatively constant $^{236}\text{U}/^{238}\text{U}$ ratios ranging from $(3.24 \pm 0.54) \times 10^{-12}$ to $(3.85 \pm 0.44) \times 10^{-12}$ over approximately 21 m of core from drill core PRC023. These samples were all sampled within

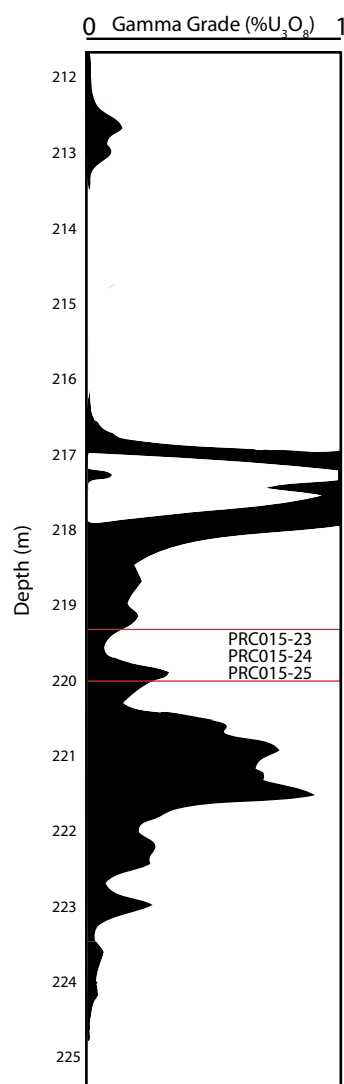


Figure 4.6: Down-hole gamma log showing location of samples analysed in this study from diamond drill core PRC015 intersecting mineralisation within the Pepegoona deposit (provided by Heathgate Resources Pty Ltd). The samples have been collected within a few centimetres of each other, thus should experience the same neutron flux.

mineralised horizons within the deposit. The exact location within each of the stacked roll-fronts present at Pepegoona West, however, is not well constrained. Despite the fact that the U concentrations vary over an order of magnitude, the constancy of the $^{236}\text{U}/^{238}\text{U}$ ratio suggests that the neutron flux is relatively homogenous within this section of the Pepegoona West deposit.

Interestingly, the $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations for mineralised sediments from the Pepegoona deposit are not coupled (Figure 4.5c). All three samples from the Pepegoona deposit were collected within ~25 centimeters of each other from a single drill core PRC015. Despite the very large spread in U concentrations observed within the three samples, it is expected that the samples would all have been exposed, to more or less the same neutron flux. Hence, they should have similar $^{236}\text{U}/^{238}\text{U}$ ratios. The vertical extent of mineralisation intersected by drill core PRC015 is ~ 10 cm, as determined by a down-hole gamma log

provided by Heathgate Resources Pty Ltd (Figure 4.6). The lateral extent of mineralisation surrounding this drill core remains speculative due to the irregular ore geometry of the Pepegoona Deposit. However, the lateral extent is likely greater than 30 cm as the ore zone typically spans ~ 1 m in the Pepegoona deposit (Chapter II). Indeed, the measured $^{236}\text{U}/^{238}\text{U}$ ratios support this, and are in agreement within uncertainties, ranging from $(1.57 \pm 4.3) \times$

10^{-12} to $(2.63 \pm 1.1) \times 10^{-12}$.

The absence of a correlation between $^{236}\text{U}/^{238}\text{U}$ ratios and U concentrations in drill core PRC015 is primarily a result of sample PRC015-24. This sample has the highest U concentration by several orders of magnitude, but the lowest $^{236}\text{U}/^{238}\text{U}$ ratio. As the three samples from this drill core should be experiencing the same neutron flux, the extremely high U concentration may reflect a small localised enrichment zone (a ‘nugget effect’), however the isotopic ratios are controlled by the overall neutron flux rather than the abundance of U and Th minerals.

4.5.3 Implications for the use of ^{236}U as an exploration tool

This study presents the first confirmation that natural ^{236}U can be detected in groundwater, with sample PW0061 sampled directly within high-grade mineralisation within the Pepegooona West deposit, having a $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$. The groundwaters sampled in low-grade and un-mineralised areas in the vicinity of the Pepegooona West deposit contained insufficient uranium to produce a detectable ^{238}U beam current, and likewise for ^{236}U . The detection of ^{236}U in groundwater may be a result of several factors.

The $^{236}\text{U}/^{238}\text{U}$ signature in the groundwater in contact with high-grade mineralisation is unlikely to reflect contamination from anthropogenic ^{236}U . If this were the case, it might be expected that a ^{236}U signature also would be detected in the low-grade and unmineralised portions of the aquifer, and that the ratios would be of higher magnitude. Recent applications using anthropogenic ^{236}U as a tracer in surficial waters have shown $^{236}\text{U}/^{238}\text{U}$ isotopic ratios of the order of $\sim 10^{-9}$ in seawaters from the Atlantic Ocean (Christl et al., 2012; Eigl et al., 2013), Pacific Ocean and Black Sea (Eigl et al., 2013), and Japan Sea (Sakaguchi et al., 2012). Anthropogenic $^{236}\text{U}/^{238}\text{U}$ isotopic ratios ranging from $\sim 10^{-9}$ to $\sim 10^{-7}$ have also been reported for river waters in the Northern hemisphere (Srncik et al., 2010; Eigl et al., 2013). The preceding assertion is further supported by the fact that the $^{236}\text{U}/^{238}\text{U}$ ratio of the single groundwater sampled in high-grade mineralisation is very similar to that of the mineralised sediments from the same deposit (Figure 4.4). This may reflect either the production of ^{236}U by neutron capture on dissolved ^{235}U within the groundwaters themselves, or isotopic

equilibration between ^{236}U formed *in-situ* within the mineralisation and the groundwaters directly in contact with it. The latter hypothesis is favoured, as the groundwaters are highly reducing in the Beverley North region, which promotes precipitation of U(IV) minerals or strong sorption of U(IV) complexes onto clay particles, resulting in low U concentrations (Langmuir, 1978).

^{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 provide an increased exploration target that can be used as a proxy for uranium mineralisation. This technique however, 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, and certainly warrants further attention.

4.5.4 Age constraints from $^{236}\text{U}/^{238}\text{U}$ ratios

In a high-grade ore deposit, steady state equilibrium is attained after approximately 5 to 6 half-lives. For ^{236}U , this state of equilibrium is achieved after ~ 120 Ma. It is unlikely that these deposits are in equilibrium with respect to ^{236}U as the maximum depositional age of mineralisation is constrained by the age of the sediments in which the deposits are hosted. For the Four Mile East and Beverley North deposits hosted within Eocene aged sediments (SKM 2008; 2010), this is ~ 56 to 34 Ma. The Four Mile West deposit is hosted within Cretaceous aged sediments, which correspond to ages of ~ 144 to 65 Ma (Woods and Jeuken, 2010). If the Four Mile West deposit formed during the early Cretaceous and experienced no further remobilisation after formation, it is conceivable that the deposit may be in equilibrium, however this assertion cannot be further investigated at this time.

In order to extract age information for the deposits based on the $^{236}\text{U}/^{238}\text{U}$ ratios of the mineralised sediments (or indeed from the isotopic signatures from the groundwaters directly in contact with high-grade mineralisation, on the assumption that the signature in the waters reflects that of the deposit); detailed modeling of neutron production and absorption

will be required, which is beyond the scope of this study.

A simple model has been developed by Wilcken et al. (2008) to allow for the semi-quantitative interpretation of the neutron production and capture processes occurring in ore deposits. In this model, the trace elemental composition of the ore is required; in particular, knowledge of neutron modifiers with large neutron capture cross-sectional areas (such as Na, Al, Mg, Si, B, Gd and Sm), which have an effect on neutron absorption. This model can then be compared with more complicated neutron production/absorption modeling using the Monte-Carlo neutron-transport code (Monte-Carlo N-Particle or MCNP code) after Hendricks et al. (2005); described in Wilcken et al. (2008).

The model developed by Wilcken et al. (2008) is based upon several assumptions: (i) that the thorium- and uranium- decay series isotopes are in secular equilibrium and (ii) that the rock matrix in which the ore is homogeneous on the scale of the neutron mean free path of ~ 10 to 30 cm (Curtis et al, 1999). The issue however remains, that sandstone-hosted uranium deposits (i) typically have very complex geology (as seen with the Pepegooona and Four Mile deposits in Chapter II) and may not be homogeneous on a relevant scale; (ii) are formed by water-rock interactions and have variable water contents depending on the pore space of the lithology of the host aquifer (Hostetler and Garrels, 1962); and (iii) are notoriously open-systems susceptible to fractionation of U-series isotopes due to water-rock interactions (see Chapters II, III and V), thus Th- and U-series isotopes may not be in secular equilibrium for these deposits, and remains to be tested. The use of models such as that of Wilckens et al. (2008), or by MCNP modeling (Hendricks et al., 2005) will provide an excellent first approximation of the processes occurring in such deposits, but further studies investigating the role of such factors on production of ^{236}U is required.

In order to apply the models described above, a detailed mineralogical study and determination of major and trace element compositions, including accurate U and Th concentrations and isotopic ratios is recommended for each of the mineralised sediment samples from the Beverley North deposits. This is beyond the scope of this study and is a direction for future research.

4.6 CONCLUSIONS

In this study, $^{236}\text{U}/^{238}\text{U}$ isotopic compositions were determined for both groundwaters and mineralised sediments within the vicinity of several South Australian high-grade sandstone-hosted uranium deposits. The $^{236}\text{U}/^{238}\text{U}$ ratios determined in the mineralised sediments from the Beverley North sandstone-hosted deposits range from $(1.16 \pm 0.06) \times 10^{-12}$ to $(9.48 \pm 0.83) \times 10^{-12}$, which lie at the low end of ratios measured previously in high-grade uranium ores and UOCs. The low $^{236}\text{U}/^{238}\text{U}$ ratios predominantly reflect the low ($\sim 1\text{-}2$ wt % U) uranium typical of such deposits, which results in lower neutron fluxes than those generated in higher concentration unconformity or magmatic style deposits.

A single groundwater sampled within the Pepegooona West deposit yielded a $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.57 \pm 2.97) \times 10^{-12}$, similar to that of the host mineralisation. This is interpreted to reflect isotopic equilibration of ^{236}U during water-rock interactions rather than the production of ^{236}U by neutron capture on dissolved ^{235}U . The results of this study show that natural ^{236}U can be detected in groundwaters, which is encouraging for future application as an exploration tool. However, in the reducing groundwater systems prevalent in the Beverley North deposits, the poor mobility and strong sorption of uranium may limit the use of ^{236}U as an exploration tool.

Recommendations for future work include sampling large volumes of water (greater than 20 L) from oxidising groundwaters in the vicinity of a high-grade deposit. In oxidising groundwaters, uranium is present as soluble U(VI) complexes, and the likelihood of ^{236}U remaining dissolved in solution is far greater than in reducing groundwater such as those observed at the Pepegooona West deposit. Additionally, modelling of the neutron production and neutron capture processes occurring in the Beverley North ore deposits is recommended, which may allow for an age of mineralisation to be estimated within these deposits.

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CHAPTER V

U-SERIES DISEQUILIBRIA IN THE BEVERLEY SANDSTONE-HOSTED URANIUM DEPOSIT (SOUTH AUSTRALIA): EVIDENCE FOR RECENT URANIUM MOBILISATION

CHAPTER SUMMARY

The Beverley sandstone-hosted uranium deposit is one of several high-grade deposits in the uranium-rich Frome Embayment area, South Australia. The age of mineralisation is of great interest because it can potentially constrain the timing and duration of uranium mobilisation, and inform future exploration in the area. Here we attempt to constrain the age of mineralisation using Uranium-series disequilibria. To do this, U-series isotopes have been measured in mineralised sediments from the Beverley Deep South ‘Dragon’ deposit.

Significant disequilibrium is observed in the U-series isotopic compositions of the mineralised sediments, suggestive of varying degrees and intensities of both leaching and deposition within the past million years. The highest ^{230}Th excesses are found in the sand samples, with $(^{230}\text{Th}/^{238}\text{U})$ activity ratios of 1.59 to 11.05. The large thorium excesses indicate that leaching of uranium has occurred, consistent with remobilisation of uranium further down the groundwater flow regime. Clay-rich samples are characterised by $(^{230}\text{Th}/^{238}\text{U})$ activity ratios < 1 , ranging from 0.21 to 0.95. These ratios are indicative of recent accumulation of uranium. All mineralised sediments are characterised by $(^{234}\text{U}/^{238}\text{U})$ activity ratios > 1 , which may reflect the isotopic signature of the initial groundwaters from which the uranium has precipitated. This is suggestive of uranium deposition within the past million years.

The attempts to calculate an absolute ^{230}Th -U age of mineralisation from a limited number of sediments have yielded two ages of ~ 30 ka and ~ 220 ka. Simple two-point isochrons suggest an isochron age of ~ 450 ka for mineralised sands, and an almost zero age for the mineralised clay-rich samples. The evidence for open-system behaviour, however, suggests that the validity of using U-series isotopic systematics may not be useful to constrain

an ‘absolute’ age for uranium mineralisation within sandstone-hosted deposits.

The age constraints provided by the observation of disequilibrium within the U-series decay chain, and preliminary ^{230}Th -U and two-point isochron ages allow for a first order approximation of the processes affecting mineralisation processes within the Beverley Deep South Ore Zone. The observed disequilibria may reflect changes to the hydrological regime due to neotectonics and the onset of aridification in southeastern Australia during the Quaternary.

5.1 INTRODUCTION

The study of U-series isotopes can provide valuable information on the age of mineralisation and timescales of uranium mobility in low temperature aqueous environments (Osmond and Cowart, 1992). Vastly different chemical and radioactive properties, coupled with the range of half-lives for uranium and thorium form the basis of ^{230}Th -U dating techniques, which can be used to date materials up to ~500 ka (Porcelli and Swarzenski, 2003; Richards and Dorale, 2003). The ^{230}Th -U dating technique has been successfully applied to environmental samples which are precipitated from waters at low temperatures, such as marine and lacustrine carbonates, speleothems, corals and chimney deposits (e.g. Edwards et al., 2003; Richards and Dorale, 2003). However, as a result of the open-system nature of sandstone-hosted uranium deposits, few studies have thoroughly investigated the use of U-series isotopes to date recent uranium deposition within sandstone-hosted uranium deposits (Lively et al., 1979; Airey and Roman, 1981; Levinson et al., 1984; Zielinski et al., 1986), which also form via the low temperature precipitation of uranium from groundwater (Hostetler and Garrels, 1962).

This study attempted to determine absolute ^{230}Th -U ages of uranium mineralisation and constrain the timescales and evolution of uranium mobility within a sandstone-hosted uranium deposit. This study also evaluates some of the potential pitfalls associated with the dating of such deposits. To achieve this, U and Th concentrations, in addition to ($^{234}\text{U}/^{238}\text{U}$), ($^{230}\text{Th}/^{238}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios (where activity ratios are denoted by parentheses) have been measured in mineralised sediments from the Beverley Deep South ‘basal channel’ sandstone-hosted uranium deposit in South Australia.

5.1.1 Geochemistry of U and Th during redox-controlled ore formation processes

The formation of sandstone-hosted uranium deposits involves the interaction of oxidising groundwaters carrying aqueous uranyl U(VI) complexes with a reductant source (e.g. H_2S , hydrocarbons, sulfide minerals or organic material) within a permeable sandstone aquifer, confined above and below by impermeable aquitards (Hobday and Galloway, 1999). At the oxidation-reduction interface, uranium (IV) minerals such as uraninite (UO_2) or coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) are precipitated; or adsorbed onto the aquifer host lithology or particulate matter as insoluble tetravalent uranium complexes (Hostetler and Garrels, 1962; Langmuir, 1978). The continual movement of groundwater during the formation of sandstone-hosted uranium deposits results in the redissolution and reprecipitation of uranium minerals, and the subsequent migration of the mineralisation front (Hostetler and Garrels, 1962).

In contrast, thorium is not sensitive to changes in redox and is present in the Th(IV) valence state. The poor solubility of thorianite (ThO_2) and thorite (ThSiO_4) at low temperatures results in groundwater concentrations rarely exceeding 1 $\mu\text{g/L}$ (Langmuir and Herman, 1980). Within an aquifer system, the mobility of thorium is strongly controlled by the precipitation of insoluble Th(IV) minerals such as thorianite; or by adsorption onto the surface of Fe-oxyhydroxide minerals such as goethite and haematite, clay minerals or organic materials (Langmuir and Herman, 1980). The difference in chemical behaviour during oxidation/reduction reactions is one mechanism through which uranium is fractionated from thorium during the formation of low temperature, redox-controlled sandstone-hosted uranium deposits. As a result of the strong sorption and complexation properties of Th(IV) and U(IV), inorganic and organic colloids can have a critical role in the mobility of U and Th, and hence the radioactive disequilibria (Porcelli and Swarzenski, 2003).

The immobility of thorium in groundwaters is a fundamental assumption of ^{230}Th -U dating techniques (Langmuir and Herman, 1980). Additional mechanisms through which U-series isotopes are fractionated during water-rock interactions and the implications for ^{230}Th -U dating are discussed below.

5.1.2 *General principles of U-series systematics and ^{230}Th -U dating*

In a geological system that has remained undisturbed for timescales greater than five to six half-lives of the daughter nuclide, secular equilibrium is established whereby the rate of radioactive decay of the parent nuclide equals the rate of production of the daughter nuclide. This state of equilibrium is represented by a parent/daughter activity ratio equal to one. Secular equilibrium is typical in unweathered rocks, and is the state nuclides evolve towards after fractionation during natural geological process such as water-rock interactions.

During water-rock interactions, U-series isotopes are fractionated not only by the geochemical behaviours of uranium and thorium during oxidation/reduction, but also as a result of processes during radioactive decay. These fractionations have been attributed to: (i) the preferential leaching of ^{234}U from radiation damaged sites within the mineral lattice, or weakly bonded or interstitial sites (Rosholt et al., 1963); and (ii) alpha recoil displacement of daughter nuclides, whereby a parent nuclide situated on the edge of a grain boundary undergoes radioactive decay by the emission of an alpha particle with sufficient recoil energy to eject the daughter nuclide from the surface of the grain (Kigoshi, 1971; Fleisher, 1980). The alpha recoil induced mobility of the daughter nuclide can result in the daughter nuclide being ejected into solution such as pore or groundwaters, resulting in pore and groundwaters commonly displaying an enrichment of ^{234}U , and leaving the grain with a deficit of ^{234}U (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003; Porcelli and Baskaran, 2011). The daughter nuclide can also be recoiled within the grain causing recoil damage tracks within the grain; or ejected into adjacent grains (Rosholt, 1983; Ohnuki et al., 1990). In high-grade uranium deposits with weight percent-level uranium concentrations, the contribution from alpha recoil induced mobility may be significant. A combination of both alpha recoil processes and preferential leaching may contribute to the fractionation of U-series isotopes during the formation of sandstone-hosted uranium deposits.

During water-rock interactions, U-series disequilibrium can result from both instantaneous and/or continuous processes. The existence of disequilibria within the U-series decay chain is time dependent, as the system returns to a state of secular equilibrium as a function of the half-life of the daughter product either by decay of the parent nuclide or

by ingrowth of the daughter nuclide. It is the time dependant return to the state of secular equilibrium that forms the basis of ^{230}Th -U dating techniques. If the uranium has precipitated from solution within five to six half-lives of ^{230}Th ($t_{1/2} = 75,690$ y) and remained closed to further fractionation, the age of the samples may be calculated based on the ingrowth of ^{230}Th produced from the radioactive decay of parent nuclide ^{234}U . In addition to the assumed insolubility of thorium in groundwaters, assuming closed-system behaviour and no initial ^{230}Th (i.e. not produced *in-situ* by radioactive decay), apparent ^{230}Th -U ages for the mineralised sediment samples can be determined according to Equation 1 (after Kaufman and Broecker, 1965):

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right) = 1 - e^{-\lambda_{230}t} - \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) - 1\right)\left(\frac{\lambda_{230}}{\lambda_{234} - \lambda_{230}}\right)\left[1 - e^{(\lambda_{234} - \lambda_{230})t}\right] \quad (5.1)$$

in which $(^{230}\text{Th}/^{238}\text{U})$ and $(^{234}\text{U}/^{238}\text{U})$ are measured activity ratios; t is the age in years; and λ_{230} , λ_{234} and λ_{238} are the decay constants for ^{230}Th , ^{234}U and ^{238}U , respectively.

5.1.3 Previous U-series disequilibrium studies in sandstone-hosted uranium deposits

Since the early observation of fractionation between ^{234}U and ^{238}U nuclides during water-rock interactions reported by Cherdynstev and Russian co-workers in 1955 (translated in Cherdynstev, 1971), fractionation of U-series isotopes has been well documented in uranium deposits, however few studies have investigated the migration of uranium within sandstone-type deposits. Early studies showed disequilibrium $(^{234}\text{U}/^{238}\text{U})$ ratios within the ‘roll-front’ type sandstone-hosted deposits in Wyoming, U.S.A. (Rosholt et al., 1964; Dooley et al., 1964; Rosholt et al., 1965a; 1965b). Only slight ^{234}U excesses relative to ^{238}U were observed in unaltered sands above and below mineralisation, whilst greater ^{234}U excesses were observed within mineralised sands, which were related to the C-shaped mineralisation features of the mineralised roll-fronts resulting from uranium remobilisation resulting from oxidising groundwater conditions (Rosholt et al., 1964). More analogous to the Beverley deposit, studies of $(^{234}\text{U}/^{238}\text{U})$ disequilibrium by Dooley et al. (1966) within the

‘basal channel’ Ambrosia Lake District, New Mexico sandstone-hosted uranium deposits showed a preferential enrichment of ^{234}U at the top boundary of ore layers, and a relative deficiency within the highest-grade ore. This was interpreted to represent redistribution of ^{234}U towards the boundaries of mineralisation. Permeability differences within the samples were interpreted to have affected the migration of ^{234}U , with less permeable mudstone conglomerate or calcite cemented samples being subject to less loss or gain of uranium than more permeable sandstone samples. Variable disequilibrium between ($^{231}\text{Pa}/^{235}\text{U}$) activity ratios, where Pa exhibits similar mobility during water rock interactions to Th, in addition to disequilibrium ($^{230}\text{Th}/^{238}\text{U}$) ratios, indicated that the history of migration and redistribution of uranium throughout the deposit was complex (Dooley et al., 1966).

Meunier et al. (1992) studied the mobility of U-series isotopes in two mineralised areas of the ‘basal-channel’ style sandstone-hosted Coutras deposit in France: the outcropping, oxidised Jean Vincent area, and the confined, reduced Le Feiu area. In the Jean Vincent area, disequilibrium ($^{230}\text{Th}/^{238}\text{U}$) values (ranging from 0.52 to 3.13) were reported in organic-rich clay horizons, indicative of both leaching and accumulation of uranium. Sand horizons, however, indicated recent leaching of uranium, evidenced by ($^{230}\text{Th}/^{238}\text{U}$) > 1. Near equilibrium ($^{234}\text{U}/^{238}\text{U}$) values however were observed in a few samples from within the clay rich horizons. This was interpreted to represent accumulation of uranium followed by the subsequent closure of the system, such that the clays attained a state of secular equilibrium. A succeeding period of uranium leaching then followed. The clays that retained secular equilibrium isotopic ratios were located in the center of clay-rich horizons, interpreted to reflect the protection from the subsequent periods of uranium leaching and accumulation by the surrounding clays. In contrast, the reduced Le Feiu area has not experienced recent leaching of uranium. This part of the Coutras deposit has experienced a complex history of uranium accumulation (Meunier et al., 1992), similar to what was interpreted by Dooley et al. (1966) for the Ambrosia Lake District deposits.

In the shallow oxidising Yeelirrie calcrete deposit, Australia, disequilibrium values were reported for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) activity ratios, attributed to the recent remobilisation of near-surface uranium mineralisation as a result of a fluctuating water table

(Lively et al., 1979; Airey and Roman, 1981; Airey, 1986). Within the Shihongtan ‘roll-front’ sandstone-hosted deposit in China, Min et al. (2005) found that most of the uranium ores had ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios close to secular equilibrium values, indicative that uranium has been little affected by remobilisation within the deposit over the last million years. However, some of the older uranium ore bodies exhibit disequilibrium values, indicative of having undergone localised leaching and deposition of uranium within the past Myr.

5.1.4 *Previous U-series disequilibrium studies in other uranium deposits*

U-series disequilibrium has also been observed in other types of uranium deposits of hydrothermal or igneous origin, however the disequilibrium has largely been attributed to recent water-rock interactions with meteoric waters. Disequilibrium was observed along fracture zones as a result of recent water-rock interactions within the alkaline volcanic/plutonic-type Poços de Caldas uranium, and Morro de Ferro thorium deposits of hydrothermal origin in Brazil (MacKenzie et al., 1992). Similarly, Min et al. (1998) reported minor remobilisation of U-series nuclides along fracture zones within the granite-hosted Sanerliu uranium deposit, China.

U-series disequilibrium was also observed within the Koongarra fracture controlled unconformity-style deposit, Australia. The uranium was predominantly associated with Fe-oxide phases, with higher ($^{234}\text{U}/^{238}\text{U}$) ratios in the more resistant phases, and ($^{234}\text{U}/^{238}\text{U}$) ratios less than unity in the more accessible uranium phases. These ratios were attributed to the recent remobilisation of mineralisation as a result of a fluctuating water table (Snelling and Dickson, 1979; Yanase et al., 1995; Payne and Airey, 2006).

A study by Condomines et al. (2007) of the mineralised episyenites (which formed via the extensive hydrothermal alteration of granite) within the Bernardan uranium deposit, French Massif Central showed near equilibrium ($^{230}\text{Th}/^{238}\text{U}$) and ($^{231}\text{Pa}/^{235}\text{U}$) values for the mineralised system as a whole. However, considerable redistribution of shorter-lived ^{226}Ra ($t_{1/2} = 1599$ y) was observed within the mineralised episyenitic pipes, thus it was suggested that minor remobilisation of uranium has occurred within the past 350 ka, however localised water-rock interactions occurred sometime between 8 ka and 0.1 ka.

5.1.5 *Previous attempts to date sandstone-hosted uranium deposits*

Despite the common occurrence of U-series disequilibrium in uranium deposits resulting from water-rock interactions, few studies have attempted to constrain precise ages of the precipitated uranium minerals due to the difficulties associated with the open-system redissolution and reprecipitation of uranium minerals inherent in such deposits. The attempts to date carnotite minerals within the calcrete-type Yeelirrie deposit using ^{230}Th -U dating by Lively et al. (1979) and Airey and Roman (1981) were hampered by the open-system behaviour and recent remobilisation of near-surface uranium mineralisation as a result of a fluctuating water table.

U-series isotopic compositions and ages were determined for three surficial uranium deposits in Southern British Columbia, Canada, by Levinson et al. (1984), assuming the closed-system behaviour of U-series nuclides for age calculations. ($^{234}\text{U}/^{230}\text{Th}$) ratios as high as 100 were reported, which were inferred to represent the recent deposition of uranium, such that little ^{230}Th ingrowth had occurred. ($^{234}\text{U}/^{238}\text{U}$) ratios of 0.87 to 1.28 were also reported (Levinson et al., 1984). The extreme variability in U-series isotopic compositions may be suggestive of open-system behaviour. Open-system behaviour would therefore invalidate the calculated ages, as was noted in the studies by Lively et al. (1979) and Airey and Roman (1981) for the Yeelirrie deposit.

Zielinski et al. (1986) determined ^{230}Th - ^{234}U apparent ages of uranium deposition within a surficial deposit hosted within late Pleistocene to Holocene valley-fill sediments in northeastern Washington, U.S.A. An overall increasing age trend with depth was reported, and was correlated to the estimated depositional ages of the host sediments, indicating the syndepositional or early-post depositional emplacement of uranium.

Attempts to date secondary uranium minerals formed by a single, instantaneous process (rather than the result of ongoing, continual ore formation processes) using U-series isotopes have had greater success, such as the dating of carnotite minerals formed during fault movement (Kaufman and Ku, 1989; Kaufman et al., 1995). ^{230}Th -U ages for secondary uranium mineralisation from the granite-type El Atshan and El Erydiya deposits from the south Eastern Desert of Egypt have been reported (Osmond et al., 1999; Osmond and

Dabous, 2004). Additional ^{230}Th -U age determinations for deposition of secondary uranium mineralisation within the granite-hosted Um Ara deposit, south Eastern Desert of Egypt have also proven successful (Dawood, 2001). In both of these studies, secondary uranium minerals such as uranophane and soddyite have precipitated from groundwaters in fractures and joints within the host-granite (Osmond et al., 1999; Dawood, 2001; Osmond and Dabous, 2004).

The variable success in using U-series isotopes to date uranium mineralisation is largely based on the premise of closed-system behaviour, and as discussed below, the Beverley sandstone-hosted uranium is presently stable and no longer accumulating uranium, thus provides an ideal area in which to attempt to constrain the age of mineralisation using U-series disequilibria.

5.2 HYDROGEOLOGICAL SETTING OF THE BEVERLEY DEEP SOUTH DEPOSIT

The Beverley sandstone-hosted uranium deposit is situated within the semi-arid Frome Embayment, South Australia, approximately 550 km north of Adelaide (Figure 5.1). The Beverley deposit is one of several sandstone-hosted deposits in the uranium-rich Frome Embayment area in South Australia. The Beverley deposit consists of a number of ore bodies (Figure 5.2), however the major focus of this study is the southern-most extension of the Beverley deposit, the Beverley Deep South ‘Dragon’ deposit (Figure 5.2 inset). The regional geology and mineralogy of the Beverley deposit has been extensively reviewed and reported elsewhere (e.g. Brugger et al., 2005; URS, 2007; Wölser et al., 2011; Armit et al., 2012), and only a brief description is detailed below.

The Beverley deposit is a ‘basal-channel’ type sandstone-hosted deposit (IAEA, 2009) hosted within palaeodrainage channel sands incised into underlying impermeable mudstones of the Miocene Namba Formation. The exact environment in which the palaeochannel sands were deposited remains contentious. It has been suggested that the sands were formed by alluvial sand dunes, fluvial stream or scour channels, were outwash deposits, or that the sands preserve a palaeoshoreline with curved beaches (Wölser et al., 2011 and references therein).

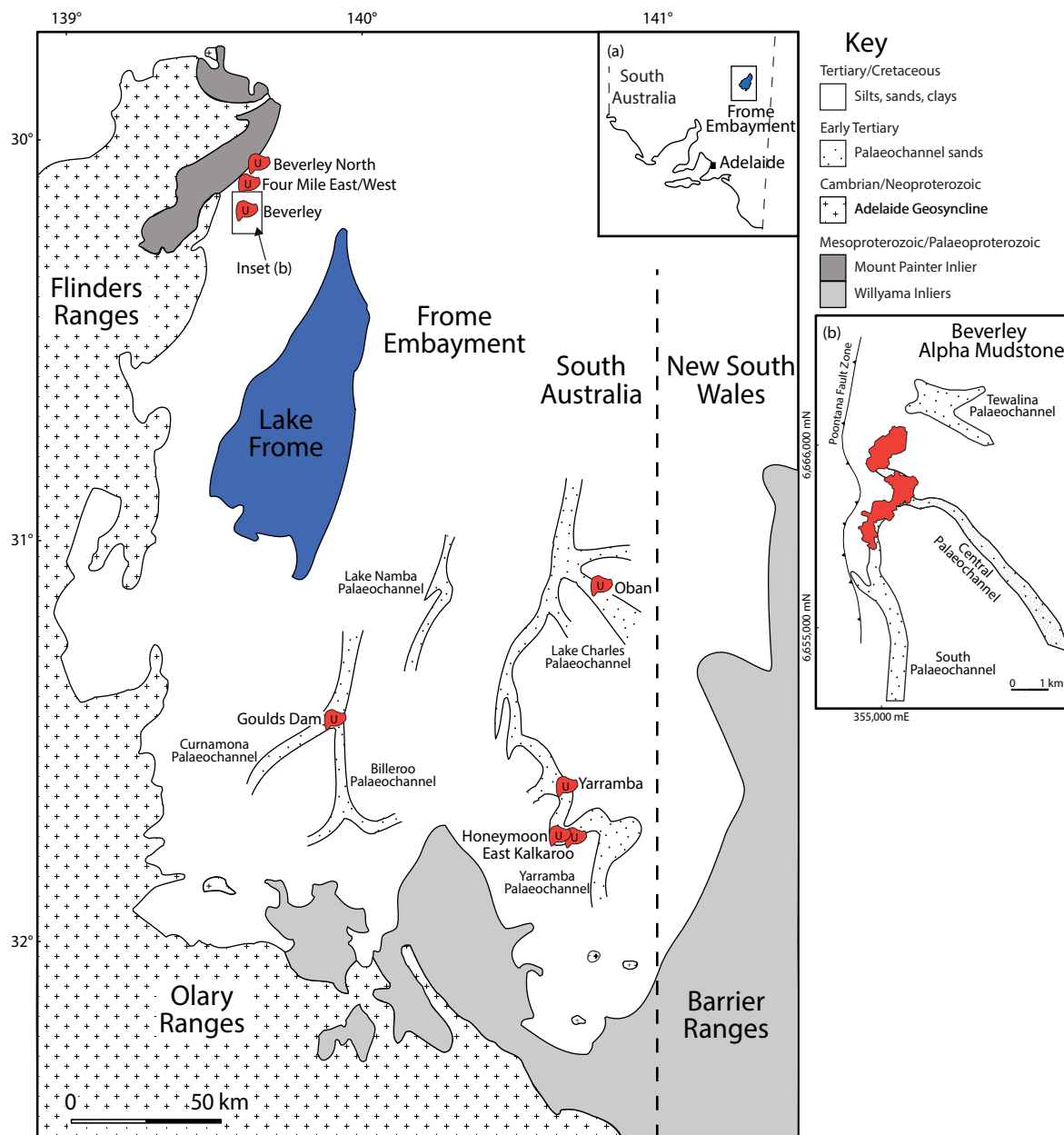


Figure 5.1: Major palaeodrainage channels and geological domains within the Frome Embayment, South Australia, with known sandstone-hosted type uranium deposits marked in red (modified after Curtis et al., 1990). Grid references are geographical coordinates. Weathering of the Mount Painter and Willyama Inliers, or sediments derived therefrom; are considered the most likely sources of uranium for the northern and southern Frome Embayment sandstone-hosted uranium deposits. Inset (a) shows the location of the Frome Embayment within South Australia. Inset (b) is an expansion of the region surrounding the Beverley deposit, detailing major palaeodrainage channels and approximate locations of uranium mineralisation within the Alpha Mudstone unit of the Namba Formation (modified after URS, 2007). Grid references are Geocentric Datum Australia GDA94 coordinates.

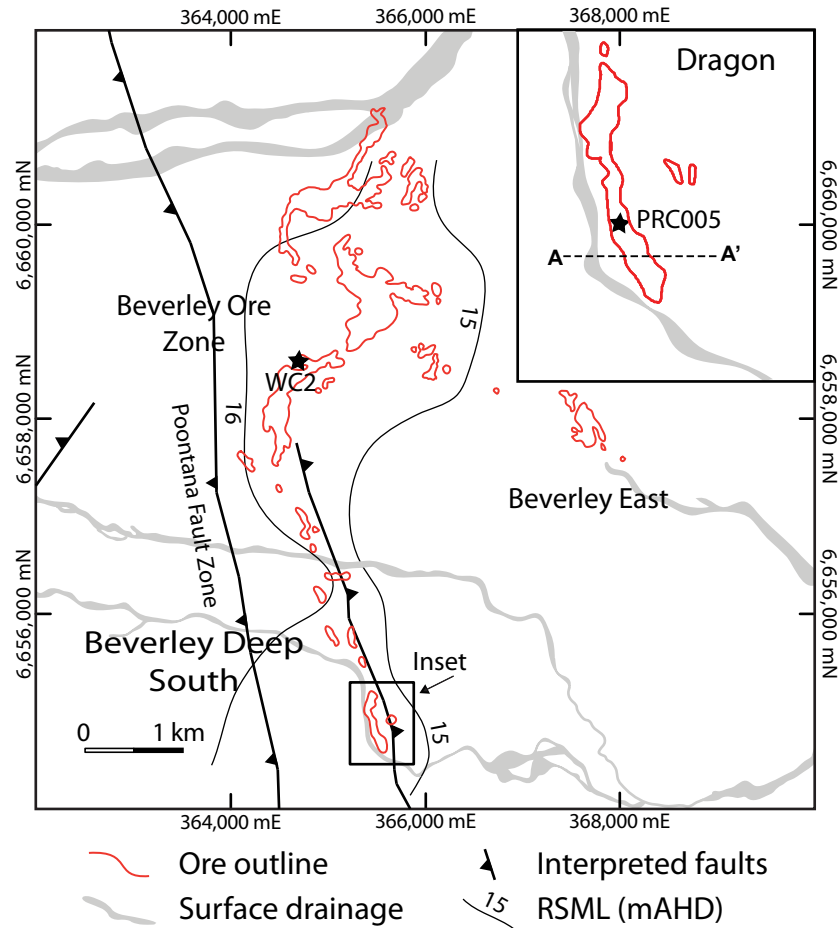


Figure 5.2: Map of the Beverley sandstone-hosted uranium deposit. Ore outline is shown in red. Regional Namba Formation potentiometric groundwater flow direction is in an approximately west to east direction, although locally is essentially stagnant. RSWL (reduced standing water level) is the elevation of the watertable above mean sea level. mAHd means meters Australian Height Datum, where AHD is set to mean sea level. Grid references are Geocentric Datum Australia GDA94 coordinates. RSWL and interpreted fault locations after SKM (2008). Inset: Beverley Deep South 'Dragon' deposit. A to A' denotes approximate location of geological cross section transect shown in Figure 5.3. Stars indicate location of drill cores PRC005 (this study) and WC2 (Wülser et al., 2011).

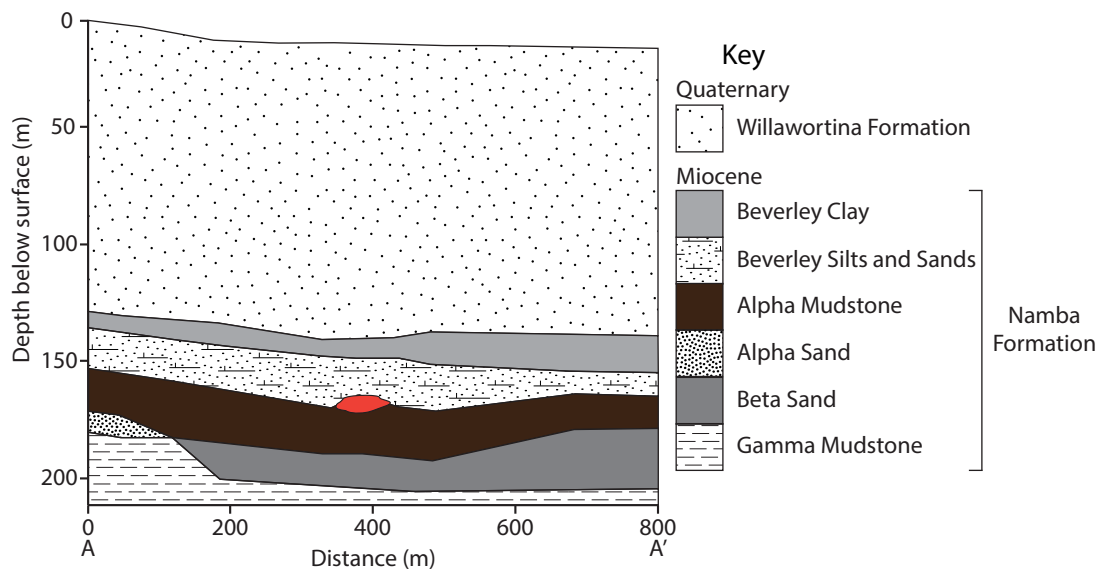


Figure 5.3: Geological cross-section of the Beverley Deep South 'Dragon' deposit from transect A to A' (from Figure 5.2); modified after URS (2007). Locally, groundwater flow within the Namba Formation is essentially stagnant. Uranium mineralisation within the Beverley Deep South 'Dragon' deposit (shown in red) predominantly occurs as tabular or lenticular pods within the Beverley Sand unit at the contact with the underlying organic rich Alpha Mudstone unit.

The uranium mineralisation within the Beverley deposit occurs as tabular and lenticular pods within the Beverley Clay, Beverley Sands and Alpha Mudstone units of the Namba Formation (McConachy et al., 2006). Mineralisation within the Beverley Deep South 'Dragon' ore body predominantly occurs within the Beverley Sand unit at the contact with the underlying organic rich Alpha Mudstone unit (Figure 5.3; URS, 2007). The primary uranium minerals within the Beverley deposit occur as interstitial coffinite \pm uraninite and carnotite; occurring in close association with pyrite, marcasite, sphalerite, carnotite, native copper, barite and chalcopyrite (Wülser et al., 2011).

The overall Beverley ore trend parallels the north-south orientation of the Poontana Fault Zone, which lies immediately to the west of the deposit (Figure 5.2). As shown in Figure 5.2 inset, the Beverley Deep South 'Dragon' ore trend is hosted within a very thin (~ 100 m wide) palaeochannel structure. The steeply westward dipping kinematics along the Poontana Fault Zone have uplifted a section of the basin into a graben known as the Poontana Inlier, which strongly controls the present hydraulic regime in the Beverley area (URS, 2006; Armit

et al., 2012). The regional Namba Formation potentiometric groundwater flow direction is in an approximately west to east direction, although locally within the Beverley region is essentially stagnant as a result of the uplifted Poontana Inlier. The mineralised sands are hydraulically confined above and below by the overlying low permeability Beverley Silts and impermeable Beverley Mudstone unit (Figure 5.3; Marsland-Smith, 2005; URS, 2007; Armstrong and Jeuken, 2009). Laterally, groundwater flow is confined within the channel sands due to changes in lithology to less permeable silty-clays. Pumping tests conducted by Heathgate Resources Pty Ltd. show some degree of hydraulic connectivity between sand packages in the Central and South Beverley Ore Zones (URS, 2007). In the Beverley Deep South 'Dragon' deposit, aquifer pressure within the Beverley Sand unit ranges from 14.9 to 15.4 mAHD (meters Australian Height Datum, where AHD is set to mean sea level) with no discernable hydraulic gradient (Heathgate Resources, 2009). Groundwaters within the Namba Formation are highly reducing, and have low uranium concentrations of only a few µg/L (URS, 2007).

The most likely source of the uranium is from the weathering of the highly uraniferous Palaeo-Mesoproterozoic metasediments, metavolcanics and granitic intrusives (collectively termed the Mount Painter District) that comprise the basement and outcrop to the west of the deposit as the Northern Flinders Ranges; or from sediments derived from the Mount Painter District, e.g. the Willawortina Formation (directly overlying the host-Namba Formation), which formed approximately 3.5 to 0.7 Ma, during uplift of the Flinders Ranges (Coats and Blisset, 1971; Neumann et al., 2000; Brugger et al., 2005; Wülser et al., 2011).

The Beverley deposit is hosted within Miocene sediments, which provides a maximum age of mineralisation of *ca.* 23 Ma. Late Miocene to early Pliocene U-Pb ages of 5.6 to 3.4 Ma were determined by Wülser et al. (2011) on framboidal carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$); where uranium is present in the oxidised U(VI) valence state. Attempts to date nodules of coffinite ($USiO_4 \cdot nH_2O$), where uranium is in the reduced U(IV) state provided a single concordant age of 6.7 Ma, with the majority of samples displaying discordance, suggestive of the open-system behaviour of Pb. The samples are from a single diamond drill core (WC2), which intersects mineralisation within the Central Beverley Ore Zone (Figure 5.2) and was

drilled prior to mining. These data are suggestive of mineralisation occurring prior uplift of the Flinders Ranges during the Pliocene (Wülser et al., 2011).

The Beverley deposit is currently being mined by in-situ recovery (ISR), whereby an acidic, oxidising solution is injected into the host aquifer in contact with the mineralisation. The uranium minerals are subsequently dissolved, and the mining solution is then pumped to the surface for processing. Mining commenced in the main Beverley Ore Zone in 2002, however ISR did not commence in the Beverley Deep South 'Dragon' deposit until mid-2009.

The present day reducing nature of the Namba Formation aquifer, low groundwater uranium concentrations and limited groundwater flow and recharge (URS, 2007) suggests that the Beverley Uranium deposit is presently stable and uranium accumulation is no longer occurring. As the deposit is no longer forming, the Beverley sandstone-hosted uranium deposit provides an ideal environment to attempt to constrain an age of recent uranium mineralisation U-series disequilibrium, where the term 'recent' refers to the mobility of uranium within the past *ca.* million years (the time required for the ^{238}U - ^{234}U parent - grand-daughter pair to reattain a state of secular equilibrium).

5.3 SAMPLING AND ANALYTICAL PROCEDURES

5.3.1 Samples

All samples analysed in this study are from diamond drill core PRC005 which intersects mineralisation within the Beverley Deep South 'Dragon' deposit, the location of which is shown in Figure 5.2, inset. The PRC005 core was drilled by Heathgate Resources Pty Ltd. prior to commencement of ISR in the southern part of the Beverley deposit. For this preliminary study, a total of four samples from the high-grade mineralised zone were selected; two medium grained sands and two clay-rich samples (Figure 5.4). Samples PRC005-21 and PRC005-23 are medium-grained, grey quartz rich sands. PRC005-22 is a clay-rich sample with minor silty sands, with abundant carbonaceous material. PRC005-20 is a highly heterogeneous sample containing some goethite \pm haematite (Fe oxyhydroxide minerals) and abundant clay minerals.

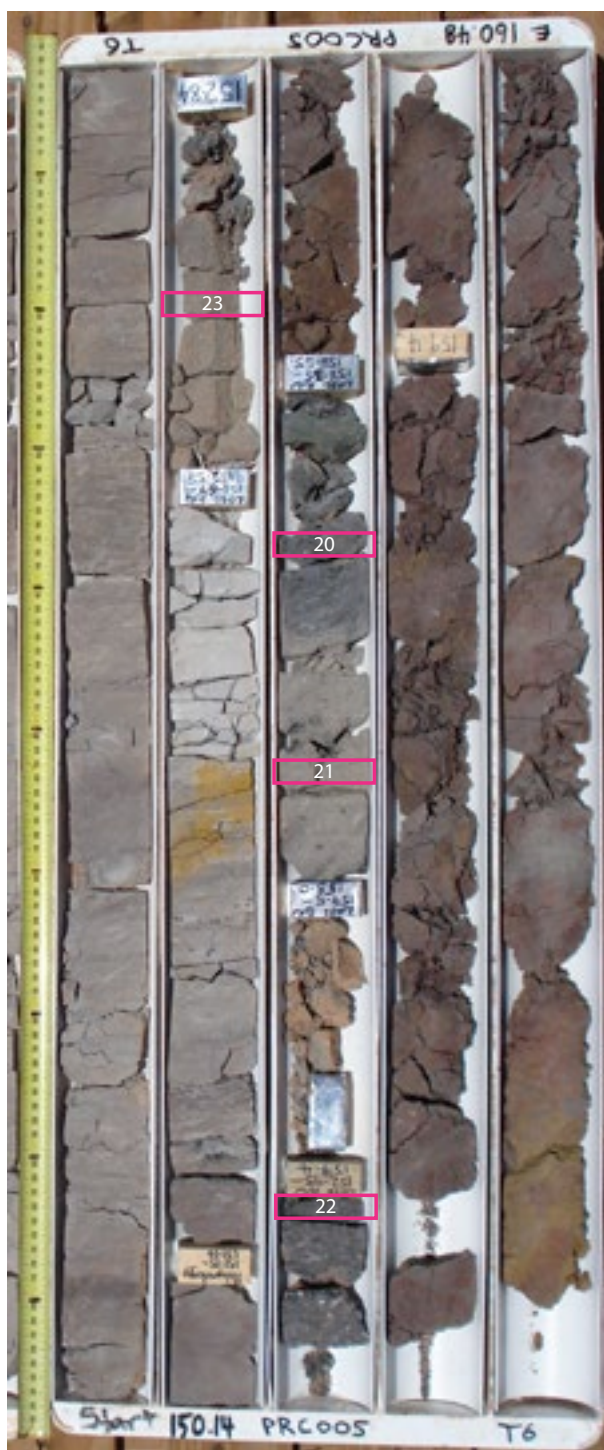


Figure 5.4: Photograph showing location of samples analysed in this study from diamond drill core PRC005 intersecting mineralisation within the Beverley Deep South ‘Dragon’ deposit. Scale is 1 m long. The core tray represents a depth of 150.14 m (lower left hand corner) to 160.48 m (upper right hand corner) due to some loss during recovery of the core. Samples PRC005-21 and PRC005-23 are medium-grained grey sands. PRC005-22 is a clay-rich sample with minor silty sands, with abundant carbonaceous material. PRC005-20 is a highly heterogeneous sample containing some goethite and abundant clay minerals. Sample depths are presented in Table 5.1.

The uranium mineralisation within the Beverley Deep South deposit is predominantly interstitial coffinite precipitated on quartz grains within the Beverley Sand unit or uranium adsorbed onto clays (McConachy et al., 2006). As a result of the large disparity between the solubility of U and Th in the groundwaters from which the uranium minerals have precipitated, the coffinite mineralisation should not have incorporated Th during precipitation (Langmuir and Herman, 1980). The host lithology for the two mineralised sand samples (PRC005-21 and PRC005-23) comprises predominantly quartz grains, and thus expected to contain little detrital Th. The clay samples however may contain a detrital Th component, however the exact mineralogy for the four samples have not been quantitatively determined for this preliminary study. Prior to digestion the drill core samples were broken into fine grains and homogenised using a ceramic spatula. These samples were not powdered to minimise the risk of contamination of laboratory equipment.

5.3.2 *Chemical preparation*

All acids and standard solutions were prepared with 18 mΩ MilliQ® water and Teflon distilled acids. Mineralised sediment samples (~200 mg) were digested by the addition of *ca.* 1 mL HF: 2 mL 14 N HNO₃ in sealed 15 mL Savillex® beakers held on a hotplate at 120 °C. To prevent the formation of insoluble fluoride precipitates due to addition of HF, trace amounts of HClO₄ (with a higher boiling point than HF) was added to the samples. The samples were evaporated to dryness in 10 °C increments from 120 °C to 170 °C. After digestion, a small aliquot from the digest was taken to determine U concentrations by quadrupole ICP-MS (Agilent 7500cs; Geochemical Analysis Unit, Macquarie University). An additional aliquot of sufficient sample volume to yield 200 ng of U was then taken for isotopic analysis. The aliquots were spiked with ~ 0.04 g of ²³⁶U-²²⁹Th tracer (Turner et al., 1997), and prior to evaporation were allowed to stand overnight at room temperature to ensure sample-spike equilibration.

Uranium and thorium were separated from the groundwater matrix by ion exchange chromatography (Biorad® AG1-X8, 100-200 mesh in a 4 mL volume glass Biorad® column). Sample aliquots were redissolved in 4 mL 7 M HNO₃ prior to loading onto the column that

had been previously cleaned with 7 M HNO₃, 6 M HCl and 0.2 M HNO₃, and preconditioned with 12 mL 7 M HNO₃. Matrix constituents were eluted with 18 mL 7 M HNO₃. Thorium was eluted from the column with 8 mL 6 M HCl, and uranium was subsequently eluted with 7 mL 0.2 M HNO₃. Prior to analysis by multi-collector ICP-MS, the fractions were evaporated to dryness and redissolved in 2 % HNO₃.

5.3.3 *U-series analysis by Multi Collector ICP-MS*

U-series isotopic measurements were determined using a Nu Plasma HR MC-ICP-MS at the Geochemical Analysis Unit, Macquarie University. Samples were introduced using a Nu Instruments DSN-100 desolvating nebuliser. Uranium analyses were performed in dynamic mode, with ²³⁵U and ²³⁸U measured on Faraday cups, and ²³⁴U and ²³⁶U collected on an ion counter. Mass fractionation was corrected using synthetic standard CRM145 (New Brunswick Laboratory (NBL), USA) using an exponential law and assuming a natural ²³⁵U/²³⁸U ratio of 7.253×10^{-3} (Cheng et al., 2000). Ion counter gain was calculated by analysis of CRM145 assuming a ²³⁴U/²³⁸U ratio of 5.286×10^{-5} (Cheng et al., 2000). Synthetic standard U010 (NBL, USA) was employed as the bracketing standard for the measurement of uranium isotopes. The U010 certified ²³⁴U/²³⁸U ratio of 5.47×10^{-5} (NBL certificate) was used for linear drift correction and normalisation of samples. Synthetic standard U005-A (NBL, USA) was routinely analysed as an unknown to check the robustness of instrumental corrections. The average U005-A corrected ²³⁴U/²³⁸U ratio was $3.43 \pm 0.003 \times 10^{-5}$ (2SD, n = 2), which is within 1 % of the published value (3.42×10^{-5} ; NBL certificate). Activity ratios were determined using half-lives calculated using decay constants of Jaffey et al. (1971) for ²³⁸U and ²³⁵U, Cheng et al. (2000) for ²³⁴U and ²³⁰Th, and Holden (1990) for ²³²Th.

Thorium isotopes were measured in dynamic mode with ²³²Th measured on Faraday cups, while ²²⁹Th and ²³⁰Th were collected on an ion counter. Samples were bracketed with synthetic standard Th'U (Open University) to determine mass bias and drift correction assuming a ²³⁰Th/²³²Th ratio of 6.176×10^{-6} (Turner et al., 2001). Tail correction was performed by collecting at half mass and using a linear extrapolation as outlined in Appendix A in Sims et al. (2008). Synthetic standard Th'A (UCSC) was analysed as an unknown to check the robustness of instrumental corrections. Measured ²³⁰Th/²³²Th ratios for Th'A ($5.86 \pm 0.3 \times$

10^{-6} ; 2SD, $n = 2$) were within 5 % of the published value (5.856×10^{-6} ; Rubin, 2001).

A single analysis of secular equilibrium rock standard TML was analysed to assess external analytical uncertainty. Measured U and Th concentrations of $10.55 \pm 0.02 \mu\text{g/g}$ (2SE) and $31.53 \pm 0.14 \mu\text{g/g}$ are within error of values published in Sims et al. (2008). The calculated ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.008 ± 0.004 ($2\sigma_{\text{M}}$) is slightly higher than the high-precision secular equilibrium values published by Cheng et al. (2000), thus a conservative estimate of uncertainty of 8 % has been adopted for ($^{234}\text{U}/^{238}\text{U}$) activity ratios rather than the $2\sigma_{\text{M}}$ internal measurement uncertainties. The ($^{230}\text{Th}/^{232}\text{Th}$) ratio of 1.082 ± 0.01 ($2\sigma_{\text{M}}$) is within error of published values (Sims et al., 2008). The ($^{230}\text{Th}/^{238}\text{U}$) ratio of 1.066 ± 0.008 ($2\sigma_{\text{M}}$) is ~6 % higher than previously published near equilibrium values by Sims et al. (2008), thus a conservative uncertainty of 6 % is assumed for this ratio. The apparent discrepancy may be a result of somewhat variable U/Th concentrations and isotopic abundances of TML noted by Sims et al. (2008), however may also be a result of instrument instability.

Total procedural U and Th blanks as determined by isotope dilution, were less than 20 pg. Given the small contribution of the blank relative to the total amount of U and Th analysed, no blank correction was applied to the samples.

5.4 RESULTS AND DISCUSSION

The sample depths in the drill core, ($^{234}\text{U}/^{238}\text{U}$), ($^{230}\text{Th}/^{232}\text{Th}$), ($^{238}\text{U}/^{232}\text{Th}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios, U and Th concentrations and ^{230}Th -U ages are presented for four mineralised sediments from the Beverley Deep South ‘Dragon’ deposit in Table 5.1.

The distributions of U and Th, ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios as a function of depth below surface within the high-grade mineralised zone of drill core PRC005 are shown in Figure 5.5. Uranium concentrations within the sediments vary over several orders of magnitude, ranging from 606 $\mu\text{g/g}$ to 0.86 wt %. Thorium concentrations are also quite heterogeneous throughout the profile, ranging from 182 to 1672 $\mu\text{g/g}$. The highest U and Th concentrations are observed in clay-rich PRC005-22. This sample contains the most abundant carbonaceous material of the samples in this study. The elevated U and Th concentrations are consistent with adsorption onto clay particles or Fe-oxyhydroxide minerals (Langmuir and

Table 5.1: U-series isotopic data for mineralised sediments from the Beverley Deep South 'Dragon' sandstone-hosted uranium deposit.

Sample	Lithology	From depth (m) ^a	To depth (m) ^a	U (μg/g) ^b	Th (μg/g) ^c	(²³⁰ Th/ ²³² Th) ±2σ _M ^d	(²³⁴ U/ ²³⁸ U) ±2σ _M ^d	(²³⁸ U/ ²³² Th) ±2σ _M ^d	(²³⁰ Th/ ²³⁸ U) ±2σ _M ^d				
PRC005-23	Sand	152.65	152.68	606	1419	14.32	0.166	1.011	0.004	1.30	0.01	11.05	0.053
PRC005-22	Clay	152.84	152.95	8609	1672	14.88	0.106	1.086	0.003	15.60	0.06	0.952	0.004
PRC005-21	Sand	158.06	158.09	4839	681	34.25	0.124	1.022	0.002	21.50	0.03	1.589	0.005
PRC005-20	Clay	158.15	158.17	3761	182	13.35	0.063	1.009	0.004	62.6	0.11	0.213	0.001

^a To and from depths refer to depth below surface.

^b Internal measurement uncertainty on [U] is typically less than 0.09 %

^c Internal measurement uncertainty on [Th] is typically less than 0.7 %

^d 2σ_M represents the internal measurement uncertainty of the sample, however a more conservative estimate of 8 ‰ is adopted for (²³⁴U/²³⁸U) activity ratios (see text for more detail).

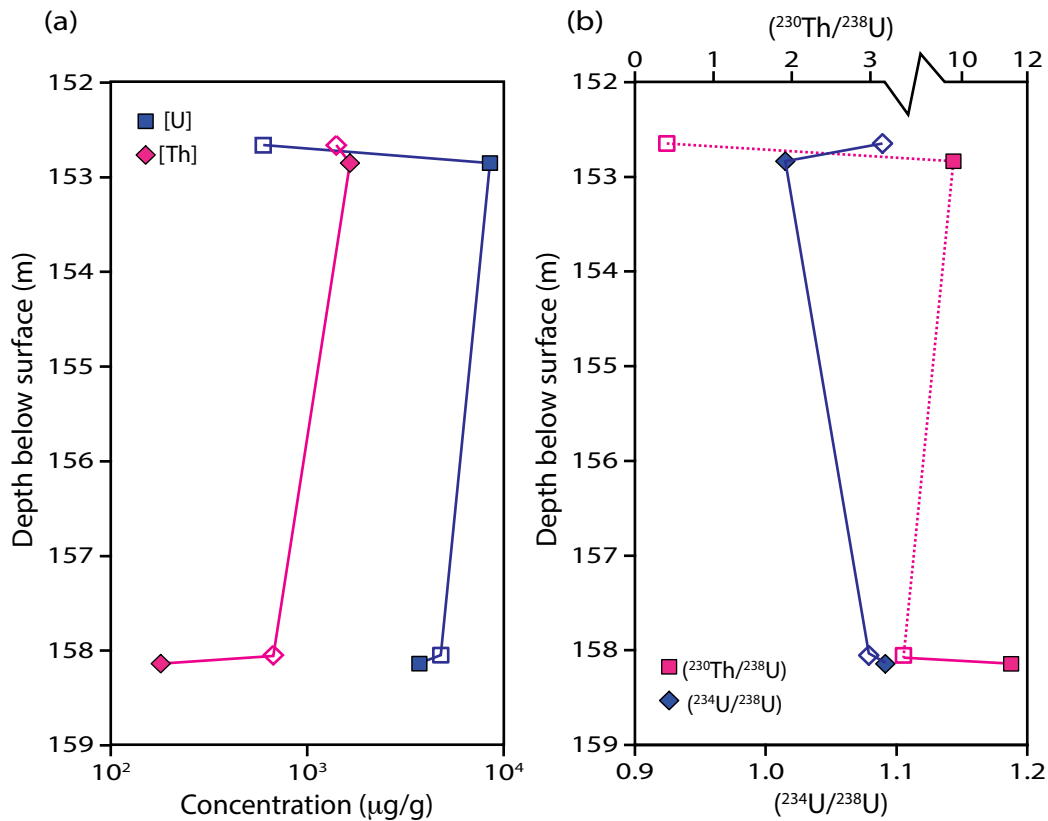


Figure 5.5: Distribution with depth below the surface for (a) uranium and thorium concentrations; and (b) $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios for samples from diamond drill core PRC005 intersecting mineralisation within the Beverley Deep South ‘Dragon’ deposit. Note the logarithmic scale for U and Th concentrations on the x-axis in Figure (a); and broken secondary x-axis for $(^{230}\text{Th}/^{238}\text{U})$ activity ratios (denoted by dashed line) in Figure (b). Sand samples are represented by open symbols; filled symbols represent clay-rich samples. Uncertainties on $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios are included within the symbols.

Herman, 1980) and the greater abundance of organic material (Ames et al., 1983; Spirakis, 1996), which can act as a source of reductant within the system. The strong spatial association of U with organic-rich clay lenses is characteristic of tabular type deposits (Meunier et al., 1989).

Only minor variation in $(^{234}\text{U}/^{238}\text{U})$ activity ratios is observed throughout the profile, with ratios ranging between 1.009 and 1.086 (Figure 5.5b). The percent-level variation observed in $(^{234}\text{U}/^{238}\text{U})$ ratios is greater than the external analytical uncertainty of 8 %, and thus is interpreted to represent true variability within the samples. This variability may reflect the precipitation of uranium minerals from multiple groundwater ‘pulses’ with different $(^{234}\text{U}/^{238}\text{U})$ isotopic compositions within the past million years. Conversely, the variability

may reflect the alpha recoil induced mobility of ^{234}U into adjacent grains such as quartz that have a high resistance to weathering (Rosholt, 1983; Ohnuki et al., 1990). Unlike the Ambrosia Lake District sandstone-hosted deposits where the highest-grade uranium samples had a relative deficiency in ^{234}U , (Dooley et al., 1966), clay-rich Sample PRC005-22, which has the highest U and Th concentrations, also has the highest ($^{234}\text{U}/^{238}\text{U}$) ratio. This may suggest that ^{234}U and ^{238}U isotopes have not been redistributed vertically towards the margins of mineralisation, as is inferred within the Ambrosia Lake deposits (Dooley et al., 1966), however this observation may be an artefact of the analysis of mineralised sediments within the Beverley Deep South core that have been sampled with large spacing between samples.

In contrast to the ($^{234}\text{U}/^{238}\text{U}$) ratios, significant disequilibrium is observed in ($^{230}\text{Th}/^{238}\text{U}$) activity ratios, and the trends appear to be strongly controlled by lithology. The two sand samples (PRC005-21 and especially PRC005-23) show large ^{230}Th excesses with respect to the grandparent ^{238}U , with ($^{230}\text{Th}/^{238}\text{U}$) ratios of 1.56 and 11.05 respectively. The two clay-rich samples (PRC005-20 and PRC005-22), however, show uranium excesses, with ($^{230}\text{Th}/^{238}\text{U}$) ratios of 0.213 and 0.952 respectively. The implications of the relative ^{230}Th or ^{238}U excesses in constraining the mobility of uranium within the deposit will be discussed below.

The range of U-series isotopic compositions may be controlled by permeability differences within the deposit as suggested by Dooley et al. (1966), which in turn is controlled by variations in mineralogy and grain size. Lower groundwater flow rates are expected in the low permeability clay-rich horizons, and greater adsorption of U and Th nuclides to proportions of Fe-oxyhydroxide minerals, clays or organic materials is expected. This is supported by the observation of less loss or gain of uranium within the low permeability clay-rich horizons. The greater permeability of the sand horizons (comprised predominantly of quartz) allows for the greater transport of uranium as soluble U(VI) complexes in groundwaters, leaving behind the insoluble thorium, resulting in the observed ^{230}Th excesses.

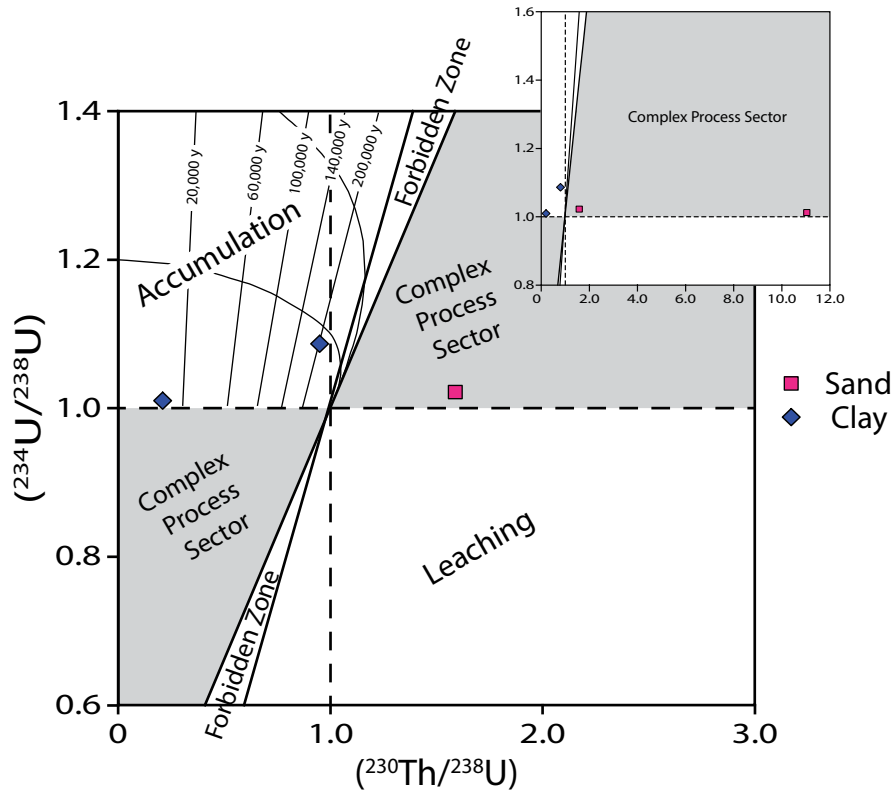


Figure 5.6: Thiel diagram where $(^{234}\text{U}/^{238}\text{U})$ versus $(^{230}\text{Th}/^{238}\text{U})$ are plotted for uranium mineralised sediments from the Beverley Deep South ‘Dragon’ deposit (modified after Thiel et al., 1983). Horizontal and vertical dashed lines indicate secular equilibrium for $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios respectively, and the solid black lines delineate the boundaries of the fields. For discussion of ^{230}Th -U ages for the two clay-rich samples, radioactive decay isochrons are plotted as thin black lines. Bent paths show the radioactive decay trajectory for samples with different $(^{234}\text{U}/^{238}\text{U})_{\text{initial}}$ compositions. Uncertainties are smaller than the symbols. The top left sector represents recent uranium accumulation; the bottom right sector is indicative of uranium leaching. The small triangular wedges in the upper and lower halves of the diagram represent the ‘forbidden zone’ for any single process. The dark grey shaded area represents the ‘forbidden zone’ for any single continuous process. These ‘forbidden’ sectors are indicative of complicated uranium transport. The sand samples plot within the complex process zone, suggesting the sand horizons have experienced a complicated history of uranium mobility within ~350 kyr, whereas the clay-rich samples show uranium has been accumulated recently (within ~1 Myr, see text for further details).

5.4.1 *Recent mobilisation of U-series nuclides by water-rock interactions*

In Figure 5.6, ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios are plotted on a Thiel diagram (Thiel et al., 1983), which can be used to interpret zones of uranium deposition (accumulation) or leaching (dispersion). If uranium has remained a closed-system over the past million years, the samples will have attained secular equilibrium for both the ^{238}U - ^{234}U and ^{238}U - ^{230}Th parent-daughter-granddaughter systematics, and thus will plot at the equipoint in the centre of the diagram. Based on the assumption of the insolubility of thorium in groundwater relative to uranium, it is possible to determine whether uranium has been deposited or leached by the relative excess or deficit of ^{230}Th . Samples that have experienced leaching of uranium will plot in the lower half of the diagram, whilst recent accumulation of uranium is characterised by compositions plotting in the upper portion of the diagram. The ‘forbidden zone’ represents isotopic compositions not expected in nature. The grey shaded area is representative of the complex depositional behaviour of uranium as a consequence of fractionation of the U-series isotopes due to multiple instantaneous and/or ongoing processes.

The U-series compositions of the samples suggest that the Beverley Deep South ‘Dragon’ deposit has undergone varying degrees and intensities of both uranium dispersion and accumulation. The clay-rich samples show uranium excesses, plotting with the accumulation field, which is indicative of recent addition of uranium. In contrast, the two sand samples are characterised by ^{230}Th excesses, plotting within the complex process zone. This suggests that closed-system conditions may not apply to the mineralised sand samples. The large ^{230}Th excess may result from a initial period of uranium deposition being overprinted by a more recent period of uranium leaching. If open-system behaviour has occurred within these samples, this would invalidate the assumptions required to date the samples U-series disequilibria.

Conversely, the ($^{230}\text{Th}/^{238}\text{U}$) isotopic signatures greater than one are possible within a closed-system if the ($^{234}\text{U}/^{238}\text{U}$)_{initial} composition of the groundwaters from which the uranium was deposited from was sufficiently high, and the samples have returned to secular equilibrium by radioactive decay. Observations of ($^{234}\text{U}/^{238}\text{U}$) ratios as high as ~ 9 have been reported by Reynolds et al. (2003) in groundwaters from an arid environment, and up to

~40 elsewhere (Cowart and Osmond, 1992), suggesting that the $(^{234}\text{U}/^{238}\text{U})_{\text{initial}}$ composition of the groundwaters could conceivably have been high enough to generate the observed $(^{230}\text{Th}/^{238}\text{U})$ ratios.

An additional suggestion for the extreme ^{230}Th excess observed in PRC005-23 may be the contribution from the alpha recoil induced mobility of ^{230}Th (or ^{234}U which subsequently decays into ^{230}Th) into resistant quartz grains (Ohnuki et al., 1990) which are then unavailable for further leaching by ongoing water-rock interactions. Additionally, the observation of large thorium excesses in the sandy horizons may indicate that U(VI) dissolved in groundwater has passed through the Beverley Deep South deposit, leaving an excess of Th(IV) with the migration of the mineralised redox front. The large ^{230}Th excess observed in PRC005-23 may also be indicative of significant mobilisation of uranium through this horizon within the deposit, which has implications for future uranium exploration in the Frome Embayment.

If the palaeo-groundwater flow direction was in a north-south direction, these trends are consistent with remobilisation of uranium from the Beverley deposit along connective palaeochannel sand packages in a southerly direction. This may suggest the possibility of additional high-grade uranium deposits further to the north or south. The presence of other sandstone-hosted uranium deposits within the Frome Embayment, located several hundred kilometres farther south of the Beverley deposit (such as the Gould's Dam, Oban and Honeymoon deposits, Figure 5.1) may support this hypothesis. If the palaeo-groundwater flow direction was north-south, uranium leached from the Mount Painter District may provide a potential source of uranium for these deposits. Conversely, the Beverley deposits might be a product of the northward migration of uranium, possibly by remobilisation of uranium from the southern Frome Embayment deposits, or uranium sourced from the Willyama Inlier.

If, however, the palaeo-groundwater flow direction was in a west-east direction prior to uplift of the Poontana Inlier, as is inferred from the present day potentiometric groundwater flow direction, further mineralisation may lie to the East of the Beverley deposit. This alternate flow direction is supported by the location of the Beverley 'East' extension of the ore zone, which may point towards additional mineralisation even further to the east. As suggested by Skirrow et al. (2009) the palaeo-groundwater flow direction

may have changed orientation several times since the Miocene, and further exploration and research into the source of the uranium, directions of palaeo-groundwater flow and location of potential reducing ‘traps’ will shed some light on exploratory efforts for uranium within South Australia.

5.4.2 *Constraining the age of mineralisation*

5.4.2.1 *Apparent ^{230}Th -U ages*

If we assume that the Beverley Deep South ‘Dragon’ mineralised system has behaved as closed-system behaviour and contained no initial ^{230}Th , apparent ^{230}Th -U ages can be calculated using Equation 1. ^{230}Th -U ages have been solved iteratively for the mineralised sediment samples using Isoplot version 2.49 (Ludwig, 2001), using decay constants of Jaffey et al. (1971) for ^{238}U and ^{235}U , Cheng et al. (2000) for ^{234}U and ^{230}Th , and Holden (1990) for ^{232}Th . ^{230}Th -U ages are presented in Table 5.2. The 2σ errors on the ^{230}Th -U age calculations reflect the propagated analytical uncertainties and include the decay constant errors.

The two sand samples (PRC005-21 and PRC005-23) could not be dated by ^{230}Th ingrowth due to thorium excesses, with $(^{230}\text{Th}/^{238}\text{U}) > 1$, which may be a result of the complex uranium migration (as shown in Figure 5.6). The two clay samples provide ^{230}Th -U ages of 25.9 ± 0.2 and 215 ± 3.5 ka, which are shown diagrammatically with age isochrons after Thiel et al. (1983) in Figure 5.6. The large range in ages observed within a few centimetres of each other is surprising, with the youngest age found at a greater depth within the drill core. These ^{230}Th -U ages may represent: (i) two discrete mineralisation events, an initial mineralisation event at ~ 220 ka and a more recent mobilisation event ~ 30 ka; (ii) a single continuous mineralisation from ~ 220 ka to ~ 30 ka; (iii) a mixture of young and old ages from multiple events; or (iv) admixtures of uranium ore with a contribution of ^{230}Th from non-decay related processes such as detrital or alpha recoil induced mobility of daughter nuclides. The inferred mobility of uranium in the sandy horizons (Figure 5.6) might suggest that these ages may not be valid due to open-system behaviour, and further research is required to investigate this further.

Table 5.2: ^{230}Th -U ages and simple two-point isochron ages for mineralised sediments from the Beverley Deep South ‘Dragon’ deposit.

Sample	Lithology	^{230}Th -U age ^a		Isochron Slope	Isochron age ^b (ka)
		(ka)	$\pm 2\sigma$		
PRC005-23*	Sand		
PRC005-21*	Sand	0.98	~ 446
PRC005-22^	Clay	215	3.5		
PRC005-20^	Clay	25.9	0.2	-0.03	~ 0

^a ^{230}Th -U age calculated iteratively using Equation 1 (Isoplot v2.49, Ludwig, 2001). 2σ uncertainty includes propagated analytical uncertainties and decay constants.

^b Isochron age calculated using Equation 2, using the slope of the line. No estimation of uncertainty has been calculated (see text for further details).

* ^{230}Th -U age cannot be calculated for the sands due to $(^{230}\text{Th}/^{238}\text{U}) > 1$.

^ The two-point isochron age for the clay-rich sediments yields a slightly negative isochron age, which corresponds to an approximately zero age isochron (see text for further details).

5.4.2.2 Simple isochron ages

If we assume (i) that closed system behaviour existed in the Beverley Deep South ‘Dragon’ deposit, (ii) that the sediments contained no initial ^{230}Th , and (iii) that uranium was deposited as two separate, cogenetic mineralisation events in the clay-rich samples and sand samples separately; a simple age isochron can be determined according to Equation 2 (after Ludwig, 2003):

$$t = -\frac{1}{\lambda_{230}} \ln \left(1 - \frac{^{230}\text{Th}}{^{238}\text{U}} \right) \quad (5.2)$$

in which $(^{230}\text{Th}/^{238}\text{U})$ is the measured activity ratio; t is the age in years; and λ_{230} is the decay constant for ^{230}Th . Graphically, this is represented on a $(^{230}\text{Th}/^{232}\text{Th})$ versus $(^{238}\text{U}/^{232}\text{Th})$ equiline diagram (Figure 5.7), where the slope of the line (m) constructed between the samples yields the $(^{230}\text{Th}/^{238}\text{U})$ ratio corrected for initial ^{230}Th . The age is then calculated using a two-point isochron approach using Equation 2, using the decay constant of Cheng et al. (2000) for ^{230}Th .

As shown in Figure 5.7, the two sand samples (PRC005-21 and PRC005-23) lie to the left of the ($^{230}\text{Th}/^{238}\text{U}$) equiline, which is suggestive of uranium loss. Clay-rich sample PRC005-22, however, lies close to the ($^{230}\text{Th}/^{238}\text{U}$) equiline, and clay sample PRC005-20 lies to the right of the equiline. This is consistent with the recent addition of uranium. The overall trends observed in the equiline diagram are in agreement with the Thiel diagram (Figure 5.6). Given the small dataset, and the strong influence of lithology on the U-series isotopic compositions, crude age isochrons have been constructed for the clay-rich samples and sand samples separately to provide a basic first order constraint on age. The two-point isochrons have been constructed for both the clay-rich and sand samples using a simple y -on- x line of best fit regression in Excel. Due to the limited number of samples, and the use of a simple approximation method for calculation of the slope to determine ($^{230}\text{Th}/^{238}\text{U}$)_{initial}, no estimation of the uncertainty on the isochron age has been conducted. The two-point isochron ages are presented in Table 5.2.

The calculated two-point isochron age for the sand samples provides an age of 446 ka. The slope of the line for the clay-rich samples yields a negative slope of -0.3, which given the large degree of uncertainty associated with the calculation of the crude isochrons suggests an isochron age of approximately zero. This may reflect uranium deposition occurring so recently (i.e. within 5 kyr) such that little ingrowth of ^{230}Th has occurred.

An interesting observation on the equiline diagram (Figure 5.7) is that the sand sample PRC005-23 and the two clay rich samples lie along a broadly horizontal array. Thus, a simple first order approximation of uranium mass balance can be estimated from the isotopic compositions of the mineralised sediments, if sand sample PRC005-21 is excluded (Figure 5.7, inset). If we consider that the initial ($^{230}\text{Th}/^{238}\text{U}$) isotopic composition of sand sample PRC005-23 started on the equiline with ($^{230}\text{Th}/^{238}\text{U}$) = 1, followed by a period whereby a considerable amount (~80-90 %) of U is leached or remobilised, leaving the sand with an ($^{230}\text{Th}/^{238}\text{U}$) activity ratio far greater than one, consistent with the observed ($^{230}\text{Th}/^{238}\text{U}$) activity ratios of 11.05. The amount of U lost is approximately equal to that gained by the clay-rich sample with the highest ($^{238}\text{U}/^{232}\text{Th}$) ratio, which displays U excess as evidenced by the ($^{230}\text{Th}/^{238}\text{U}$) activity ratio of 0.213. This may suggest that uranium lost from the high

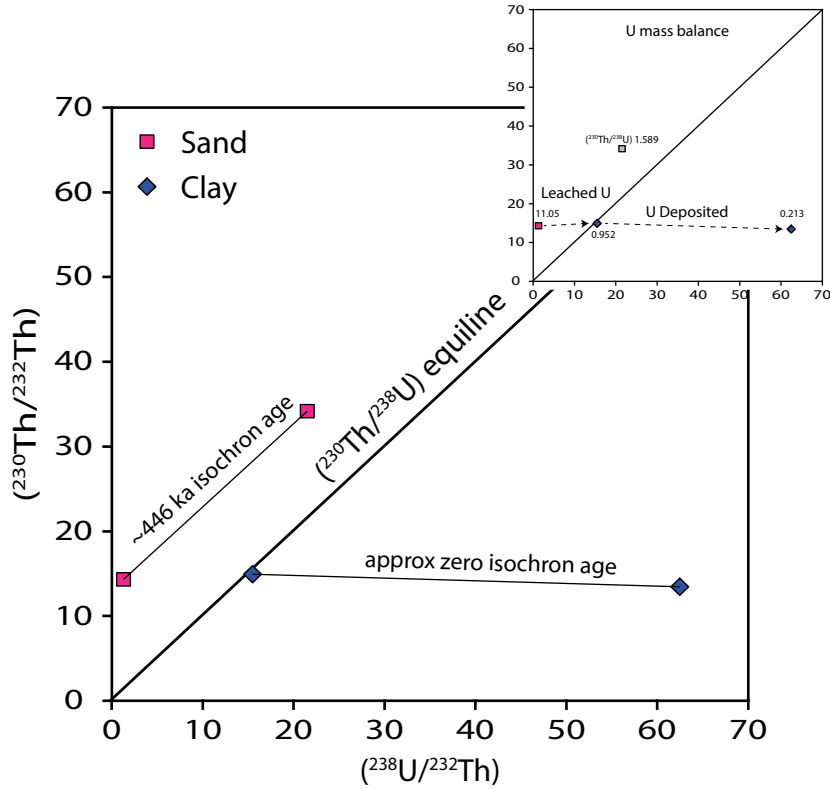


Figure 5.7: $(^{230}\text{Th}/^{232}\text{Th})$ versus $(^{238}\text{U}/^{232}\text{Th})$ equiline diagram for uranium mineralised sediments from the Beverley Deep South 'Dragon' deposit. Uncertainties are included within the size of the symbols. Given the small dataset, and the strong influence of lithology on the U-series isotopic compositions, crude two-point isochrons have been constructed for the clay-rich samples and sand samples separately to provide a basic first order approximation of an isochron age from the slope (m) of the line (see text for further detail). An isochron constructed between the sand samples has a slope of 0.98, corresponding to an isochron age of ~446 ka. The clay-rich samples provide a slightly negative slope of -0.3, which given the large degree of uncertainty associated with the calculation of the crude isochrons suggests an isochron age of approximately zero. This may reflect uranium deposition occurring so recently (i.e. within 5 kyr) such that little ingrowth of ^{230}Th has occurred. Inset: A uranium mass balance can be estimated from the isotopic compositions of the mineralised sediments, if sand sample PRC005-21 (shown in grey) is excluded. If the $(^{230}\text{Th}/^{238}\text{U})_{\text{initial}}$ isotopic composition of sand sample PRC005-23 started on the equiline with $(^{230}\text{Th}/^{238}\text{U}) = 1$, and then had a considerable amount of U leached (~80-90 %), this would leave the sand with an $(^{230}\text{Th}/^{238}\text{U})$ activity ratio far greater than one. The amount of U lost is approximately equal to that gained by the clay-rich samples, which display U excess. All of the mineralised sediments display $(^{234}\text{U}/^{238}\text{U})$ ratios greater than one, which may suggest a more recent episode of uranium deposition (see text for further details).

permeability sands during water-rock interactions may have been remobilised into the less permeable clay-rich horizons, where the uranium has a tendency to strongly sorb (Langmuir and Herman, 1980). Without more closely spaced samples, it is difficult to determine whether the uranium nuclides have been lost from one lithologic layer and redistributed into another layer. The observation, however, that all of the mineralised sediments display ($^{234}\text{U}/^{238}\text{U}$) ratios greater than one, (as described previously), may suggest a more recent episode of uranium deposition that has overprinted the isotopic signature preserved due to leaching and remobilisation.

5.4.2.3 *Potential pitfalls in calculating ^{230}Th -U ages*

The accuracy of using U-series isotopes to constrain an absolute age of mineralisation is based on several assumptions, hence the calculated apparent ^{230}Th -U ages or isochron ages may not be valid if (i) the Beverley Deep South ‘Dragon’ deposit has behaved as an open-system; or (ii) if the samples contained detrital ^{230}Th .

If the deposit has behaved as an open-system, the mineralised sediment ages may be affected by: (i) the addition of uranium, and thus the true age of mineralisation would be older than the calculated ages; or (ii) the leaching of uranium, which would mean that the true age would be younger than the calculated ages. The U-series isotopic compositions of the mineralised samples imply that both accumulation and leaching of uranium has occurred within the Beverley Deep South deposit (Figure 5.6); contradicting the assumption of closed-system behaviour. Models to account for the open-system behaviour and the contribution from the recoil mobility of daughter nuclides have been developed and applied to other low temperature samples formed via precipitation e.g. calcium carbonate tufa deposits formed in semi-arid environments (Stone et al., 2010) using models after Villemant and Feuillet (2003). As the underlying principles of formation are similar, the application of such models might prove useful in the ^{230}Th -U dating of uranium mineralisation formed within sandstone-hosted uranium deposits.

Samples in this study have not been corrected for detrital ^{230}Th in the age calculations on the assumption that both ^{230}Th and ^{232}Th behave similarly in groundwater, and observed

($^{230}\text{Th}/^{232}\text{Th}$) activity ratios greater than one imply low abundances of detrital ^{232}Th , and hence the same can also be assumed for ^{230}Th . This assumption is perhaps not entirely valid, as the mass spectrometric ^{230}Th -U dating of speleothems requires ($^{230}\text{Th}/^{232}\text{Th}$) > 300 to be considered reliable to not account for the contribution of detrital thorium (Richards and Dorale, 2003; Hellstrom, 2006). The implications for this in speleothems is that age estimates can be overestimated by several percent (Hellstrom, 2006), and would be expected to have a similar effect on ^{230}Th -U age estimates for sandstone-hosted uranium ores. Given the few samples that have been analysed in this preliminary study, reliance on the absolute or isochron ages should be treated with caution irrespective of detrital ^{230}Th correction until further expansion of the dataset. For future analyses, a more accurate estimation of contamination from detrital ^{230}Th should be estimated from the direct measurement of the isotopic composition of multiple sub-samples of the same samples using an isochron dating technique (e.g. Luo and Ku, 1991; Ludwig and Titterton, 1994; Ludwig, 2003).

Whilst a reliable ‘absolute’ age of mineralisation cannot be constrained through the use of U-series isotopes at this stage, the evidence of disequilibrium can provide an estimate of the timescales of uranium mobility occurring within the past *ca.* million years.

5.4.3 *Implications for ore formation processes within the Beverley deposit*

Although the size of the present dataset is limited, the age constraints provided by the observation of disequilibrium within U-series decay chain and preliminary ^{230}Th -U and two-point isochron ages can provide a first order approximation for the interpretation of processes affecting mineralisation within the Beverley Deep South Ore Zone. The age constraints presented here are interpreted to represent a minimum age of mineralisation or remobilisation within the system, and may reflect neotectonism or changes in climate which in the area over the past million years. Changes in climate and tectonic uplift are considered to be major controls on the rate and intensity of erosion (Dosseto et al., 2010 and references therein), and thus are likely to be significant drivers for ore formation processes in the Frome Embayment. The recent mobilisation of uranium within the Beverley Deep South deposit, evidenced by the disequilibrium within the U-series isotopes, may be a result of several

climatic and/or tectonic events, which will be discussed below.

5.4.3.1 Tectonic influences on uranium mobilisation events

The mobility of uranium resulting from a single tectonic event, or the most recent of several tectonic events that have occurred within the past million years, may release a large pulse of uraniferous oxidising waters into the aquifer system. The ‘pulse’ of groundwater could be directed along faults, or enter the aquifer system at recharge points along the range front. Additionally, the added topographical relief due to tectonic uplift can result in increased gravity-fed groundwater recharge. In the Frome Embayment, uplift of the Flinders Ranges due to reactivation along the Paralana Fault Zone; or uplift of the Poontana Inlier due to reactivation along the Poontana Fault Zone could provide sufficient change to the hydrological regime, and hence result in an instantaneous or continuous mineralisation event. The fault offsets along the Paralana and Poontana Fault Zones are evident within the Pliocene Willawortina Formation which overlies the mineralised host Namba Formation, suggesting these faults were active as recently as ~ 67 ka (Preiss, 1995; Quigley et al., 2007a, 2007b).

Cosmogenic ^{10}Be concentrations determined in bedrock and alluvium shed off the Flinders Ranges indicate that rapid and spatially variable rates of bedrock erosion has incurred during three large, surface-rupturing earthquakes as recently ~67 ka (Quigley et al., 2007a). These processes may be coincident with the formation of large pulses of oxidising uraniferous fluids, and hence drivers of uranium mineralisation processes. Changes to the hydrological regime due to neotectonism may also facilitate the continual redistribution of uranium due to ongoing groundwater flow.

The continual mobilisation of uranium is also supported by the spread in coffinite and carnotite U-Pb ages reported by Wülser et al. (2011), which may be representative of true variability in the deposit caused by the precipitation of uranium minerals over several million years. The observation of discordant U-Pb ages within the coffinite ages also suggests open-system behaviour of Pb within the Central Zone of the Beverley deposit.

5.4.3.2 *The effect of climatic changes on uranium mobilisation events*

Speleothem ^{230}Th - ^{234}U dates obtained by Ayliffe et al. (1998) from the Naracoorte Caves in South Australia, on the southeastern margin of semi-arid Australia, indicate four major periods of peak deposition, occurring 20 to 35 ka, and 115 to 220 ka, 270 to 300 ka and 340 to 420 ka. Interestingly, three of these periods of maximum speleothem growth correspond quite well with the two ^{230}Th -U ages of ~ 30 ka and ~ 220 ka determined in this study, and also with the crude two-point isochron age of the mineralised sands of ~ 450 ka. The deposition of the speleothems were interpreted by Ayliffe et al. (1998) to have formed during pluvial periods of high effective precipitation (i.e. rainfall that contributes to stream channel runoff) during stadials and cool interstadials, rather than forming during interglacial and warm interstadial periods, and relative aridity was observed during glacial maxima.

Additionally, based on optically stimulated luminescence (OSL) and thermoluminescence (TL) ages from stratified palaeo-shoreline deposits reported by Cohen et al. (2011), the disappearance of the Mega-Lake Frome (the coalescence of Lakes Frome, Blanche, Callabonna and Gregory) commenced ~ 47 to 50 ka. The disappearance of the Mega-Lake Frome is consistent with the onset of aridification at this time. However, evidence for a lake-filling episode occurring ~ 17.6 to 15.8 ka where the Mega-Lake Frome refilled to a depth of 6.8 m (15 to 20 times the modern lake volume) is suggestive of a period of high effective precipitation after the last glacial maximum (Cohen et al., 2011).

The correlation of these periods of high effective precipitation reported by Ayliffe et al. (1998) and Cohen et al. (2011) with the two preliminary ^{230}Th -U ages and the crude isochron age from this study might suggest that periods of greater rainfall have contributed to greater recharge to the Namba Formation, possibly either by remobilisation of the pre-existing mineralisation, or by the initiation of a mineralisation event. The observation of the onset of aridification of central Australia *ca.* 50 ka, evidenced by the decreasing of water levels within the Mega-Lake Frome by Cohen et al., (2011) may have contributed to the cessation of ore forming processes and the subsequent preservation of the Beverley deposit. In contrast, Quigley et al. (2007a) argue that erosion rates within the arid northern Flinders Ranges of ~ 14 m/Myr constrained from ^{10}Be concentrations suggest a minimal climatic

influence on the rates of mountain erosion. This evidence for decreased erosion rates, however does not necessarily influence the leaching and transportation of uranium with which changes in climate would be expected to vary considerably.

5.4.3.3 Redistribution of U-series nuclides via vertical migration of groundwaters

The mineralised Beverley Sands in the Beverley Deep South area are hydraulically confined above and below by the overlying low permeability Beverley Silts and impermeable Beverley Mudstone units (URS, 2007; Heathgate Resources, 2009). Whilst these units serve as aquitards, over timescales relevant to the half-lives of the U-series isotopes, a minor degree of vertical recharge might be expected from the slow equilibration from differential pressure gradients from the above and underlying aquifer systems.

In order for the mobilisation of uranium as U(VI) complexes, the groundwaters must be oxidising. Presently, groundwaters in the underlying Eyre Formation are reducing, thus are unlikely to mobilise uranium. Groundwaters within the overlying Willawortina Formation are variably unsaturated and/or oxidising (URS, 2007), which provides a likely candidate for the downward vertical migration of uranium, particularly using faults as conduits. The present-day hydrological regime, however, undoubtedly has changed and likewise the mobility of uranium.

Of the two ^{230}Th -U ages determined in this study, the ~30 ka aged sample was deeper in the drill core, which may support vertical migration from the underlying aquifer. This observation may reflect the vertical migration of oxidising uraniferous groundwaters sourced from the fractured crystalline basement aquifer or the mixing of two fluids such as oxidising uranium bearing groundwaters with reduced, possibly hypersaline groundwaters present within the palaeochannels. In order to further constrain these hypotheses, the systematic sampling and determination of U-series isotopic composition of the sediments underlying and overlying mineralisation is recommended as a direction for future research. Determination of the source of the mineralising fluids may have implications for the source of the uranium for the Beverley deposit, and possibly other sandstone-hosted uranium deposits in the Frome Embayment area.

5.4 CONCLUSIONS

The U-series isotopic compositions of mineralised sediments from the Beverley Deep South deposit have been determined in an attempt to constrain the mobility of uranium within the system over the past million years. The attempts to derive absolute ^{230}Th -U ages of mineralisation from a limited number of clay-rich sediments have yielded two ages of ~ 30 ka and ~ 220 ka. As a result of $(^{230}\text{Th}/^{238}\text{U}) > 1$ in the sands, ^{230}Th -U ages were able to be determined. For the same samples, a crude two-point isochron age has been calculated, yielding ages of ~ 450 ka for the mineralised sands and near zero isochron age (possibly within 5 kyr) within the clay-rich samples.

The U-series isotopic compositions of the sediments, however, are suggestive of varying degrees and intensities of both leaching ($(^{230}\text{Th}/^{238}\text{U}) > 1$) within the past *ca.* 350 ka, and deposition of uranium ($(^{230}\text{Th}/^{238}\text{U}) < 1$) within the past million years ($(^{234}\text{U}/^{238}\text{U}) > 1$). This implies that the mineralised system has behaved as an open-system, which contributes to the uncertainty on the reliability of the ^{230}Th -U and simple two-point isochron ages.

As few data exist attempting to date sandstone-hosted uranium deposits using U-series, it is difficult to ascertain the most appropriate methods to account for the poorly constrained, open-system nature of such deposits. The issues of correcting for detrital ^{230}Th and assessing the contributions of alpha recoil induced mobility of daughter nuclides remain. The application of techniques that have been successful in constraining a precipitation age for other low temperature systematics such as speleothems, corals, tufas, chimney deposits etc might prove useful in solving some of these issues, and are a starting point for further research into constraining absolute ages of uranium mineralisation precipitating within notoriously open-system sandstone-hosted uranium deposits.

Despite the small dataset, and the inherent difficulties with the determination of ^{230}Th -U ages in such systems, the two inferred ages correspond remarkably well to periods of increased rainfall in the Lake Frome region and speleothem growth in semi-arid South Eastern Australia, which are likely a result of changes in climate during the Quaternary. The U-series isotopic compositions of the mineralised sediments also provide some constraints on the mobility of uranium over the past million years.

The gradual change in climate to the present-day semi-arid conditions may have influenced the groundwater flow within the host aquifer and in turn altered the ore formation process. Conversely, the recent uranium mobility might also reflect changes in the hydrologic regime due to recent neotectonism and reactivation along the Paralana and Poontana Fault Zones resulting in the subsequent uplift of the Flinders Ranges and Poontana Inlier respectively. The stagnation of groundwater flow within the host aquifer as a result of the uplift of the Poontana Inlier may have caused a cessation in mobilisation of oxidising, uraniferous groundwaters and hence halted the mineralisation process.

Further expansion of the dataset may prove useful for future uranium exploration with the Lake Frome region. The additional determination of shorter-lived isotopes within the U-series decay chain such as Pa, Ra or Pb isotopes, each of which fractionates differently during water-rock interactions, would allow for greater interpretation of the recent climatic and tectonic influences on ore formation processes.

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CHAPTER VI

SYNTHESIS AND DIRECTIONS FOR FUTURE RESEARCH

6.1 DIRECTIONS FOR FUTURE RESEARCH

Throughout this thesis, a common theme investigating the behaviour of ^{236}U and U-series isotopes in groundwaters and mineralised sediments from several South Australian sandstone-hosted uranium deposits is explored. This study has focused on this type of mineralisation as these deposits provide an ideal location in which to investigate the role of reduction and water/rock interactions during ore formation and isotope fractionation processes. The access provided by Heathgate Resources Pty Ltd to groundwater wells screened at different aquifer depths both within and adjacent to mineralisation, in addition to drill core samples, provided a rare opportunity to study the isotopic signatures within a well-defined, redox-controlled, uranium mineralised environment.

The primary intention of this research was to investigate the use of ^{236}U and U-series isotopic signatures in groundwaters as a proxy for U mineralisation, although the implications of this research are not only limited to this potential application. This work demonstrates the usefulness of these isotope systematics in furthering our understanding of mineralisation processes occurring in such low temperature, redox-controlled environments. This is despite some of the inherent difficulties associated with the application of these techniques in a complex geological area. The conclusions for each of the four studies have been presented at the end of each of the relevant chapters, thus

for the sake of avoiding repetitiveness, they will not be reiterated. Instead, this section highlights several areas for future research, with broader implications for furthering the understanding of uranium mineralisation processes, and uranium isotopic studies.

The wide range in ($^{234}\text{U}/^{238}\text{U}$) activity ratios and uranium concentrations observed in groundwaters from the Four Mile East and Pepegooona deposits under a narrow range of reducing redox potentials suggest that ^{234}U - ^{238}U systematics are not simply governed by changes in redox conditions. No systematic trends are observed in the groundwaters from either up-gradient of the deposit within presumably oxidised sediments, or down-gradient in reduced sediments. The isotopic signatures have been interpreted to reflect dynamic hydrogeologic processes such as preferential leaching and alpha recoil of ^{234}U , and the geological complexity of the deposits (Chapter II). In order to gain a better understanding of the behaviour of ^{234}U and ^{238}U within such an aquifer system, a comparative study relating the groundwater isotopic compositions with that of the host aquifer rocks would allow for greater constraints on the chemical weathering rates (e.g. Maher et al., 2006) and for reactive transport modeling (e.g. Luo et al., 2000; Tricca et al., 2001; Reynolds et al., 2003; Bourdon et al., 2009; Ku et al., 2009). Such studies would allow for the respective role of congruent versus incongruent dissolution, or isotopic equilibration between mineralisation and groundwaters to be established.

Conventionally, the $^{238}\text{U}/^{235}\text{U}$ ratio has been considered invariant (Steiger and Jäger, 1977), although a growing body of research has shown fractionation occurs in a wide range of environments, resulting in the recent revision of the value proposed by Heiss et al. (2012). The emerging field investigating the fractionation of ‘stable’ uranium isotopes has now been applied to a range of different geological environments as a tracer of reduction processes (e.g. Bopp et al., 2009; 2010) and as a palaeoredox tracer (e.g. Montoya-Pino et al., 2010; Brennecka et al., 2011).

The ‘stable’ uranium isotope systematics within the Pepegooona groundwaters and concomitant mineralised sediments were found to be strongly dependent upon the reduction of U(VI) to U(IV); consistent with fractionation resulting from the mass-independent nuclear field shift (NFS) effect (Chapter III). Another plausible mass-independent fractionation mechanism that, to date, has received little attention is related to the nuclear magnetic spin effect associated with the odd isotopes (i.e. ^{235}U), as proposed by Epov et

al. (2011). The sense of fractionation for both the NFS and nuclear spin effects are the same, and are indistinguishable from each other. Further experiments to quantify these effects warrant further attention. As described in Chapter III, other plausible fractionation mechanisms are also possible, including mass-dependent, equilibrium isotope fractionation.

The role of weathering on fractionation of ‘stable’ uranium isotopes has only been briefly investigated (Stirling et al., 2007; Bopp et al., 2009; Hiess et al., 2012). The $^{238}\text{U}/^{235}\text{U}$ isotopic ratios observed in groundwaters from the Pepegooona deposit were not correlated with ($^{234}\text{U}/^{238}\text{U}$) activity ratios, suggesting that a separate mechanism is responsible for fractionation of the two isotopic systems. Undoubtedly, ^{234}U and ^{238}U isotopes are also fractionated by the NFS effect. However, the more significant alpha recoil and preferential leaching processes dominate the lesser fractionation resulting from the NFS effect. To investigate the role of weathering on fractionation between ^{238}U and ^{235}U further, it might be interesting to perform similar leaching experiments to the granite leaching experiments conducted by Andersen et al. (2010) assessing the fractionation of ^{234}U and ^{238}U during simulated weathering conditions.

Few studies have conducted abiotic laboratory experiments investigating U(VI) reduction with Fe^0 (Rademacher et al., 2006) and Zn^0 (Stirling et al., 2007). No isotopic fractionation was detected in these experiments, which may be a result of the fast and irreversible reaction rates. Within an aquifer, long water-rock interaction promotes chemical and isotopic equilibration with phases in the aquifer host rock. Slow abiotic reduction by sulfide minerals such as pyrite may fractionate uranium isotopes. However, further experiments are needed to test this hypothesis.

The large range of $^{238}\text{U}/^{235}\text{U}$ isotopic ratios observed in the mineralised sediments has implications for studies of low-temperature redox-controlled uranium ores, or indeed any matrix that has experienced water/rock interactions such as sandstone-hosted uranium ores, speleothems, etc. As highlighted recently by Hiess et al. (2012) and Stirling (2012), the variability in $^{238}\text{U}/^{235}\text{U}$ ratios has obvious implications for geochronological dating techniques such as U-Pb dating which assume the ratio is constant. U-Pb ages for accessory minerals such as monazite, titanite and zircon may be inaccurate by up to 10 million years depending upon the magnitude of $^{238}\text{U}/^{235}\text{U}$ isotopic variability. The $^{238}\text{U}/^{235}\text{U}$ ratios span a

ca. 5 % range within the Pepegooona deposit alone, highlighting that even within a single deposit, the variations can be substantial. Thus, quantification of the $^{238}\text{U}/^{235}\text{U}$ isotopic ratio should be independently characterised for each sample to obtain accurate U-Pb ages.

In addition to the variability in $^{238}\text{U}/^{235}\text{U}$ ratios observed in sandstone-hosted uranium deposits, Chapter V has shown that variability in U-series isotopic ratios is also prevalent in such deposits. This has implications for constraining an absolute age of mineralisation of these deposits due to the open-system behaviour of uranium and its decay products. As a recommendation for future research, mineralised sediments from the Pepegooona, Pepegooona West and Pannikan deposits, in addition to further samples from the Beverley Deep South deposit, should be characterised for U-series isotopes. The application of models to account for the open-system behaviour and contribution from the recoil mobility of daughter nuclides that have been successful in constraining a precipitation age for other low temperature matrices such as speleothems, corals, tufas, chimney deposits etc (e.g. Villemant and Feuillet, 2003) might prove useful in solving some of the issues inherent with open-system behaviour characteristic of these type of deposits. This will help to constrain the timescales of uranium mobilisation, which will allow for interpretation of the hydrogeological, tectonic and climate change factors that have influenced mineralisation processes within the Frome Embayment. Knowledge of the history of uranium mobilisation will have implications for future exploration in the area.

Characterisation of the U-series isotopic signature of the mineralisation at Pepegooona is particularly recommended. This will allow for the testing of the hypothesis proposed in Chapter II, whereby the ($^{234}\text{U}/^{238}\text{U}$) isotopic signature in the groundwaters in direct contact with high-grade mineralisation reflects isotopic equilibration with the mineralisation itself. If this is the case, this would imply that the Pepegooona deposit has either formed or experienced recent remobilisation (within the past million years), evidenced by disequilibrium ($^{234}\text{U}/^{238}\text{U}$) ratios in these waters.

This suggestion is supported by the detection of a $^{236}\text{U}/^{238}\text{U}$ signature in a single groundwater sampled in contact with high-grade mineralisation from the Pepegooona West deposit (Chapter IV). This was 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 low groundwater U concentrations.

The findings of Chapter II and Chapter IV suggested that the use of variations in ($^{234}\text{U}/^{238}\text{U}$) isotopic ratios and detection of ^{236}U in the highly reducing groundwaters prevalent in the Frome Embayment area may not be useful as a exploration tool for uranium mineralisation. However, these techniques may have greater success as a potential exploration tool in other areas with different hydrogeological conditions, specifically where the groundwaters are oxidising and uranium has a greater solubility as U(VI) complexes. These techniques might also be more applicable to groundwaters in the vicinity of higher-grade uranium deposits (of the order of ~10-15 wt % U), such as unconformity-, hydrothermal-, or magmatic-style deposits, e.g. the Ranger deposit in the Northern Territory, Australia.

Finally, as described in Chapter IV, application of the model developed by Wilcken et al. (2008) to allow for the semi-quantitative interpretation of the neutron production and capture processes occurring in ore deposits could allow age information to be extracted from the deposits. This model utilises the $^{236}\text{U}/^{238}\text{U}$ ratios of the mineralised sediments, in addition to the trace elemental composition of the host matrix. This model could potentially be used to extract age information based on the isotopic signatures from the groundwaters directly in contact with high-grade mineralisation, on the assumption that the signature in the waters reflects that of the deposit. These model ^{236}U ages could then be compared with ages determined by U-series dating techniques as comparison between both methods.

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APPENDICES

SUPPLEMENTARY MATERIAL

APPENDIX A – THORIUM ISOTOPES IN GROUNDWATER

In nature, thorium primarily exists in the tetravalent state. In groundwaters, Th concentrations rarely exceed 1 µg/L due to the low solubility of thorium minerals such as thorianite, and its tendency to strongly adsorb onto the surface of oxyhydroxide minerals, clays and organic materials (Langmuir and Herman, 1980). An attempt was made to isolate thorium isotopes from 20 groundwaters sampled within the vicinity of the Four Mile East and Pepegoona sandstone-hosted deposits in order to investigate the behaviour of thorium isotopes in groundwater, and ultimately assess their potential use as an exploration tool for uranium. Detailed descriptions of the study site as well as groundwater sampling methods are given in Chapter II. Briefly, with the exception of PRWW001, groundwater samples were drawn up using dedicated Micropurge® low flow bladder pumps permanently installed in each well, at flow rates of 100 – 300 mL/min. Low flow sampling minimises aeration of the groundwater and agitation of aquifer materials. Sample PRWW001 was air-lifted. Approximately 1 L samples were filtered using Waterra® inline 0.45 µm disposable filters and acidified in the field to pH <2 using Teflon-distilled nitric acid.

Chemical Preparation

Given the difference in solubility of uranium and thorium, samples were processed separately for U and Th isotopic analysis. All acids and standard solutions were prepared with 18 mΩ MilliQ® water and Teflon distilled acids. For thorium isotopic analysis, approximately 750 mL to 1 L of sample was prepared, although ~250 mL was prepared for the duplicate sample PRMW004. The aliquots were spiked with ~ 0.04 g of ²³⁶U-²²⁹Th tracer (Turner et al., 1997), and prior to evaporation were allowed to stand overnight at room temperature to ensure sample-spike equilibration.

Uranium and thorium were separated from the groundwater matrix by ion exchange chromatography (Biorad® AG1-X8, 100-200 mesh in a 4 mL volume Savillex® column) using the method outlined in Chapter II. Prior to loading onto the column, dried thorium aliquots required large volumes of HNO₃ (~20 to 50 mL) to redissolve the matrix components.

The samples were then loaded onto the column that had been previously cleaned with 7 M HNO_3 , 6 M HCl and 0.2 M HNO_3 , and preconditioned with 12 mL 7 M HNO_3 . Matrix constituents were eluted with 18 mL 7 M HNO_3 . Following the elution of the matrix, 8 mL 6 M HCl was passed through the columns, for which uranium samples were discarded to waste, and samples for thorium were collected. As a result of the evaporation of larger volumes of sample for thorium isotopic analysis, matrix components including salts were concentrated. As mentioned, large volumes of acids were required to process the samples through the column, which was a lengthy process. At times, a single column would take > 48 hours to elute. The first batch of samples for thorium isotopic analysis had a considerable amount of salt in the final elution stage, which contributes to plasma instability and isobaric interferences when analysed by MC-ICP-MS. The remainder of samples for thorium isotopic analysis were therefore processed through the entire column separation procedure a second time in order to eliminate matrix effects. Prior to analysis by multi-collector ICP-MS, the thorium fractions were evaporated to dryness and redissolved in 2 % HNO_3 .

As a check on the method for both uranium and thorium isotopes, a single aliquot of certified seawater reference material NASS-5 (National Research Council of Canada, NRCC) was prepared from which uranium and thorium were collected from a single pass through the column purification stages, and the thorium fraction was then further purified a second time as per the samples in this study. The NASS-5 standard was chosen rather than a digested rock standard, which undergoes a different chemical preparation to the waters. Additionally, seawater has a higher salinity than the groundwaters and as such, any artefacts from the chemical purification procedure can be verified. In addition to the seawater standard, one groundwater sample was prepared in duplicate to assess the external reproducibility of the total procedure for thorium.

U-series isotopic determination by Multi Collector ICP-MS

U-series isotopes were determined using a Nu Plasma HR MC-ICP-MS at the Geochemical Analysis Unit, Macquarie University. Samples were introduced using a Nu Instruments DSN-100 desolvating nebuliser fitted with a Glass Expansion Micromist 100 μL concentric

nebuliser. Thorium isotopes were determined in dynamic mode with ^{232}Th measured on Faraday cups, while ^{229}Th and ^{230}Th were collected on an ion counter. Samples were bracketed with synthetic standard Th'U (Open University) to determine the mass bias assuming a $^{230}\text{Th}/^{232}\text{Th}$ ratio of 6.176×10^{-6} (Turner et al., 2001). Tail correction was performed by collecting at half mass and using a linear extrapolation as outlined in appendix A in Sims et al. (2008). Synthetic standard Th'A (UCSC) was routinely analysed as an unknown to check the robustness of instrumental corrections. The average Th'A corrected $^{230}\text{Th}/^{232}\text{Th}$ ratio was $5.810 \pm 0.1 \times 10^{-6}$ (2SD, $n = 16$), which is within 5 % of the published value (5.856×10^{-6} ; Rubin, 2001). Activity ratios were determined using half-lives calculated using decay constants of Jaffey et al. (1971) for ^{238}U and ^{235}U , Cheng et al. (2000) for ^{234}U and ^{230}Th , and Holden (1990) for ^{232}Th .

Results and discussion

The total procedural blanks for U are ~ 3 pg, thus no blank correction was applied to the samples. The total procedural blanks for Th however, were ~ 8 pg. Because of the low Th concentrations in groundwaters, the contribution from the blanks can be significant. As this is only a preliminary assessment of the method for Th isotope purification without further pre-concentration, the samples have not been blank corrected in this study. This is however, an important consideration for high precision Th isotope analyses.

As a check on the method, a single aliquot of certified seawater reference material NASS-5 (National Research Council of Canada (NRCC)) was prepared from which uranium and thorium were collected from a single pass through the column purification stages, and the thorium fraction was then further purified a second time as per the samples in this study. The NASS-5 standard was chosen rather than a digested rock standard, which undergoes a different chemical preparation to the waters. NASS-5 is not certified for Th concentrations or isotopic ratios. The measured Th concentration is 2.36 ± 0.03 ng/L ($2\sigma_M$), which is higher than the published value of 0.17 ± 0.02 ng/L (Grinberg et al., 2005). The ($^{230}\text{Th}/^{234}\text{U}$) ratio was $0.0007 \pm 4.05 \times 10^{-5}$. The ($^{230}\text{Th}/^{238}\text{U}$) ratio was $0.0008 \pm 4.66 \times 10^{-5}$. The ($^{230}\text{Th}/^{232}\text{Th}$) ratio was 2.803 ± 0.57 .

Sample PRMW004 was processed through the procedure in duplicate as seen in Table A1. Although the reproducibility for uranium concentration and ($^{234}\text{U}/^{238}\text{U}$) activity ratio was in good agreement (Chapter II), the comparative data for both Th concentrations and isotopic ratios is poor (Table A1). Different volumes were weighed out for analysis (approximately 250 mL and 750 mL) for the sample duplicates. As a result of the different volumes, the samples passing through the column would have different matrix constituents, which may have affected the retention of Th onto the resin. Because of the difficulties associated with the chemical purification and hence analysis of Th isotopes, and limited volume of sample collected, further attempts to isolate Th isotopes were not pursued.

Table A1: Thorium isotopic data for Four Mile East and Pepegoona groundwaters

Sample	Date Collected	Th (pg/g)	($^{230}\text{Th}/^{232}\text{Th}$)	$2\sigma_{\text{M}}^{\text{a}}$	($^{230}\text{Th}/^{238}\text{U}$)	$2\sigma_{\text{M}}^{\text{a}}$	($^{230}\text{Th}/^{234}\text{U}$)	$2\sigma_{\text{M}}^{\text{a}}$
Four Mile East								
4MRMW07	6/7/2009	691	0.454	0.002	0.126	7.32E-04	0.095	5.51E-4
4MRMW06	6/7/2009	2.53	23.55	0.095	0.035	1.69E-04	0.031	1.50E-4
4MRMW06	4/17/2010	105	0.796	0.003	0.052	2.63E-04	0.047	2.38E-4
AKMW014	6/6/2009	16.53	13.68	0.378	0.068	1.92E-03	0.042	1.19E-3
4MRMW13	6/5/2009	18.73	269.2	0.179	1.023	1.39E-03	0.936	1.27E-3
4MRMW13	4/17/2010	6.68	1.299	0.023	0.008	1.58E-04	0.006	1.22E-4
4MRMW15	6/5/2009	19.75	448.8	0.288	0.636	9.04E-04	0.300	4.27E-4
4M0012	6/7/2009	5.03	9.039	0.136	0.000	1.29E-06	0.000	1.13E-6
AKMW009	6/7/2009	173	200.3	9.116	2.418	1.12E-01	2.131	9.86E-2
AKMW011	6/7/2009	24.96	341.1	2.232	0.038	2.81E-04	0.036	2.65E-4
4M002	6/7/2009	3.67	397.3	1.636	0.007	3.51E-05	0.005	2.92E-5
4M001	6/7/2009	0.84	260.6	21.37	0.000	3.04E-05	0.000	3.14E-5
Pepegoona								
PRMW001	4/18/2010	13.34	10.66	0.011	0.001	1.81E-06	0.001	1.30E-6
PRMW002	4/18/2010	3.35	6.753	0.037	0.001	5.22E-06	0.001	5.09E-6
PRMW003	4/18/2010	12.01	1.796	0.045	0.001	1.88E-05	0.001	1.76E-5
PRMW004	4/19/2010	542	0.532	0.004	0.017	1.33E-04	0.017	1.38E-4
PRMW004 (d)	4/19/2010	54.09	0.468	0.003	0.002	1.13E-05	0.002	1.17E-5
PRMW006	4/18/2010	8.47	6.231	0.031	0.006	3.49E-05	0.004	2.47E-5
PRMW007	4/18/2010	24.45	1.995	0.004	0.004	1.14E-05	0.003	1.10E-5
PRWW001	4/19/2010	11.11	243.4	0.249	0.357	8.22E-04	0.351	8.09E-4

^a $2\sigma_{\text{M}}$ is the measurement uncertainty.

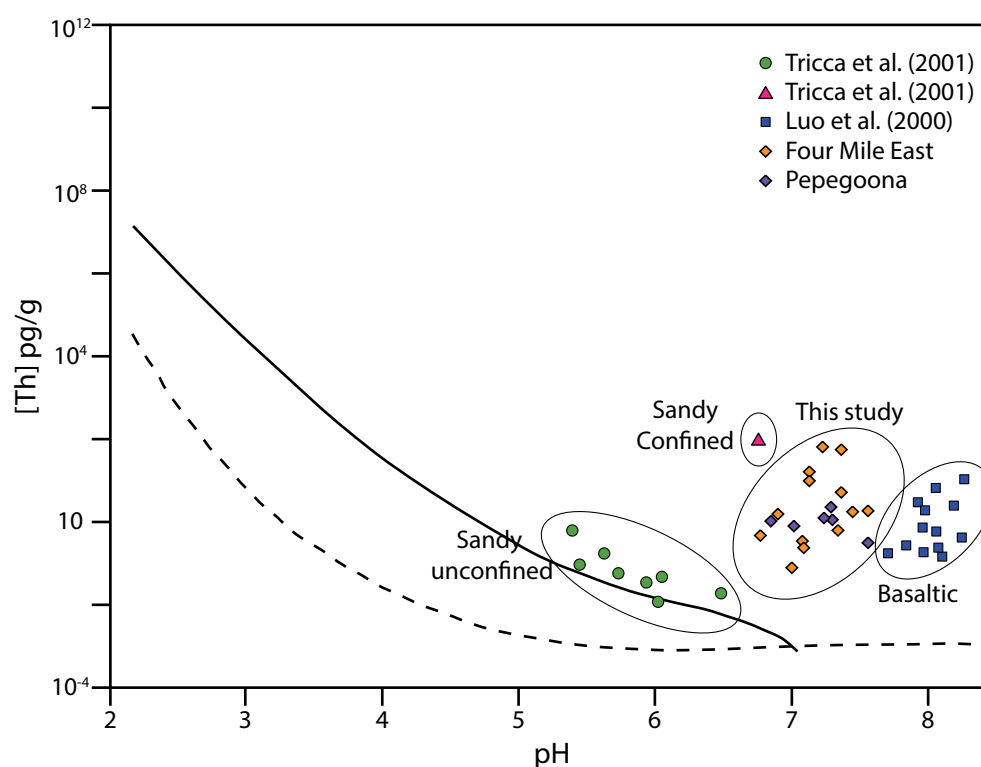


Figure A1: Th concentrations versus pH for groundwaters from this study and literature values (Modified after Porcelli and Swarzenki, 2003, data from Luo et al., 2000; Tricca et al., 2001). Note the logarithmic scale on the y-axis. The dashed line indicates the solubility of thorianite at 25°C in pure water. The solid line represents the solubility of thorianite at 25°C in the presence of typical inorganic ligands (Langmuir and Herman, 1980). Th concentrations above the thorianite solubilities shown can be attained in the presence of organic compounds or colloids. Sample AKMW011 not shown due to high pH.

The present chemical purification method for Th isotopes is time consuming and wasteful of reagents, and the Th blanks are similar to the concentrations expected in the groundwaters themselves. Despite the low confidence in the accuracy and reproducibility of this dataset, Th concentrations and isotopic data, along with pH data are presented in Table A1. Groundwater Th concentrations ranged from 0.57 pg/g to 691 pg/g. Thorium concentrations 1 to 3 orders of magnitude higher than the calculated solubility of 0.01 pg/g for thorianite (ThO_2) in pure water or in the presence of typical inorganic ligands for a given range of pH values (Langmuir and Herman, 1980) are observed in groundwaters from the Four Mile East and Pepegooona deposits (Figure A1). This is consistent with other published thorium data e.g. the basaltic Snake River aquifer (Luo et al., 2000) and a sandy unconfined aquifer and underlying confined aquifer (Tricca et al., 2001). The solubility of Th is increased

in the presence of organic compounds or colloids (Porcelli and Swarzenski, 2003). The groundwater samples were filtered at 0.45 μm , which may contain colloids in addition to dissolved Th. While some of this variability might be a result of sample heterogeneity, some of the discrepancy might be due to the presence of colloidal particles. Thorium strongly adsorbs onto the surface of oxyhydroxide minerals, clays and organic materials (Langmuir and Herman, 1978).

The groundwaters have a wide range in ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios from 0.45 to 448. The ($^{230}\text{Th}/^{234}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) compositions show a similar range of values, from 0.0001 to 2.13, and 0.0001 to 2.42 respectively. The range of isotopic compositions for the Pepegooona and Four Mile East deposits (both of which are hosted within the Eyre Formation) are similar, which is likely due to the similar aquifer host lithologies. No consistent relationship between Th concentrations and Th isotopic composition is observed.

Unlike uranium isotopes, which behave conservatively in seawater, ^{230}Th and ^{232}Th have variable isotopic compositions (Andersson and Schöberg, 2012). This might also be expected for groundwaters. The low Th concentrations in seawater require the pre-concentration of large sample volumes ($\sim 3\text{--}10\text{ L}$) in order to obtain sufficient Th for precise measurements. This is comparable to the saline groundwaters of this study.

In the future, it is recommended that larger volumes of groundwater are sampled. In order to prevent colloids, it is recommended that the samples undergo ultra-filtration at less than 20 nm. Additionally, it is also recommended that the samples are pre-concentrated via an iron co-precipitation step. The separation of thorium from matrix components might also be enhanced by the use of TRU-spec and U-TEVA column chemistry.

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APPENDIX B - ^{236}U IN GROUNDWATER

In high-grade uranium ores, ‘natural’ ^{236}U can be produced by thermal neutron capture on ^{235}U . Based on $^{236}\text{U}/^{238}\text{U}$ isotopic ratios measured in uranium ores, the possibility of detecting natural $^{236}\text{U}/^{238}\text{U}$ ratios elevated above background ratios in groundwaters in close proximity to high-grade uranium mineralisation was recognised by Fifield (2008) as a potential exploration tool for deposits buried at depth.

Twelve groundwater samples of approximately 1 L volume were collected from the Four Mile East, Four Mile West and the Pepegooona deposits during field sampling campaigns in 2009 and 2010, following sampling procedures outlined in Chapter II. The groundwater wells were selected to include samples both within and adjacent to high-grade mineralisation, over a range of U concentrations (from 0.3 to 819 $\mu\text{g/L}$). All samples were prepared under clean room conditions to minimise contamination with anthropogenic ^{236}U . The groundwater samples were pre-concentrated by two methods: evaporation and iron co-precipitation, and subjected to chemical purification using anion exchange chromatography. The former pre-concentration method was conducted at the Geochemical Analysis Unit, Macquarie University; the latter at the Department of Nuclear Physics, Research School of Physical Sciences and Engineering at the Australian National University.

For half of the samples, approximately 1 L of water was accurately weighed and evaporated to dryness before processing by anion exchange chromatography following procedures similar to the extraction of Th isotopes in Appendix A. As a result of the evaporation of relatively large volumes of sample, matrix components including salts were concentrated. Consequently, large volumes of acids were required to process the samples through the column, which may have altered the efficiency of the resin.

For the remainder of samples, approximately 1 L of sample was accurately weighed, spiked with ~ 0.4 g of ^{233}U tracer (CRM 111-A, New Brunswick Laboratory (NBL), USA) and allowed to equilibrate overnight. To the waters, 2 mL of 1 M $\text{Fe}(\text{NO}_3)_3$ solution (equivalent to 2 mg Fe/g) with vigorous stirring to ensure equilibration. The uranium was co-precipitated with ferric hydroxide by the dropwise addition of 30 % ammonia solution until the pH was adjusted to 8-9. The sample was allowed to rest for several hours at room temperature to allow

quantitative precipitation, before the samples were centrifuged and the supernatant discarded. The precipitate was washed with ultrapure Milli-Q® water prior to chemical purification using procedures outlined in Chapter II. Due to remaining impurities after column separation, the uranium fractions were further purified by processing through the column twice.

Prior to analysis by AMS, 60 µL Fe(NO₃)₃, equivalent to ~2 mg Fe was added to provide bulk. The samples were calcined at 800°C in porcelain crucibles. The U₃O₈ sample was mixed with silver (1:4) to increase the conductivity, which is then pressed into aluminium sample holders for analysis by AMS using methods outlined in Chapter IV. Insufficient uranium was obtained to yield a detectable beam current for these samples, and consequently no ²³⁶U was detected.

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APPENDIX C - CONFERENCE ABSTRACTS

Uranium isotopic variability during low T redox mineralisation

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Variations in uranium isotopic compositions are well documented in groundwaters and uranium ores as a result of the very different geochemical and radiogenic behaviours of uranium nuclides. Additionally, natural ²³⁶U is produced in-situ in high-grade uranium ores as a result of neutron capture processes.

In order to gain a better understanding of the behaviour of uranium nuclides during ore formation processes within sandstone-hosted uranium deposits, U concentrations and (²³⁴U/²³⁸U) activity ratios were analysed in a suite of groundwaters in the vicinity of the South Australian Pepegooona sandstone-hosted uranium deposit. The groundwaters show significant disequilibrium, resulting from preferential leaching, α-recoil processes and the congruent dissolution of ore minerals.

Additionally, ²³⁸U/²³⁵U ratios were characterised in mineralised sediment samples and groundwaters from the Pepegooona deposit. Groundwaters are characterised by ²³⁸U/²³⁵U ratios enriched in the light isotope (²³⁵U), whilst mineralised sediments showed a preferential enrichment in the heavier isotope (²³⁸U). This can be attributed to the nuclear field shift effect during reduction of U(VI) to U(IV). Poor correlation between (²³⁴U/²³⁸U) activity ratios with ²³⁸U/²³⁵U ratios in the groundwaters indicates that the fractionation processes are independent of each other.

Lastly, based on ²³⁶U/²³⁸U ratios measured in uranium ores, the detection of appreciable quantities of ²³⁶U in groundwaters may reflect local uranium mineralisation, and thus prove useful in uranium exploration. In order to test this, ²³⁶U/²³⁸U ratios were determined by accelerator mass spectrometry in groundwaters and uranium ores from the Pepegooona deposit. Preliminary results will be presented.

Application of U-series isotopes in understanding sandstone-hosted uranium mineralisation in the Frome Embayment, South Australia.

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Abstract presented as an oral presentation at the Sprigg Symposium, Adelaide, Australia 2011.

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Introduction

Sandstone-hosted 'roll-front' uranium deposits form at a redox interface within a permeable sandstone aquifer confined above and below by impermeable aquitards. Economically significant quantities of uranium can accumulate from the interaction of oxidising groundwaters carrying aqueous uranyl U(VI) complexes with a reductant source within the aquifer (such as H₂S (g), hydrocarbons, sulfide minerals or organic material) (Hobday, 1999). Upon encountering reducing conditions, uranium is precipitated from the groundwater as uranium (IV) minerals such as uraninite or coffinite, or is adsorbed onto the aquifer host lithology as insoluble tetravalent uranium complexes. Continued groundwater movement results in the redissolution of uranium minerals up-gradient of the main redox interface by oxidising groundwater; and reprecipitation of uranium minerals further down-gradient, resulting in migration of the roll-front (Hostetler and Garrels, 1962). Improved understanding of the ore formation processes and of the behaviour of uranium and its decay products in sandstone-hosted deposits are important as global demand for alternate energy sources has necessitated advances in exploration techniques for prospecting for uranium mineralisation buried at depth.

Uranium-series (U-series) isotopes are useful tracers of water-rock interactions due to the different chemical and radiological behaviours of the decay products of uranium. Additionally, information on geological process timescales can be inferred from the range of nuclide half-lives within the U-series decay chain.

During water-rock interactions, fractionation of ²³⁴U from parent isotope ²³⁸U is attributed to two main processes; (1) the preferential leaching of ²³⁴U from radiation damaged sites within the mineral lattice or from weakly bonded sites (Rosholt, 1963); and (2) by energetic recoil of ²³⁴Th into solution during alpha decay of a ²³⁸U nuclide situated on the edge of a grain boundary, which subsequently decays via ²³⁴Pa to ²³⁴U (Kigoshi, 1971). Both alpha recoil and preferential leaching processes result in excess ²³⁴U in solution, resulting in groundwaters commonly exhibiting (²³⁴U/²³⁸U) activity ratios > 1, and have been observed at (²³⁴U/²³⁸U) activity ratios of up to 10 (Osmond and Cowart, 1992).

Previous research by Cherdyntsev (1971), Cowart and Osmond (1977), Osmond and Cowart (1983), Lively et al. (1979) and Toulhoat and Beaucaire (1991) observed (²³⁴U/²³⁸U) activity ratios that approached secular equilibrium values (i.e. ratio of 1) in groundwaters draining high-grade uranium mineralisation. This observation might be explained by the congruent dissolution of high-grade uranium minerals imparting an (²³⁴U/²³⁸U) activity ratio at or very close to equilibrium in the water. For ²³⁴U - ²³⁸U, secular equilibrium is attained after ~ 1 Ma.

The primary objective of this research is to test this hypothesis, and gain a better understanding of ore formation processes within sandstone-hosted uranium deposits by characterising the evolution of U-series isotopes in groundwater with respect to high-grade

uranium mineralisation, and assess any potential implications for uranium exploration. To achieve this, the natural distribution of ($^{234}\text{U}/^{238}\text{U}$) activity ratios in groundwater have been determined by MC-ICP-MS along the groundwater flow path, within and surrounding the South Australian Pepegooona sandstone-hosted uranium mineralised system.

Geological setting and groundwater sampling

The Pepegooona uranium mineralised system is situated within the Eromanga basin of the semi-arid Frome Embayment, South Australia, approximately 550 km north of Adelaide (Figure 1, inset). The Frome Embayment is host to several sandstone-hosted uranium deposits and is a highly prospective target for future exploration. This deposit is well suited for such a study, as the geology and hydrogeology have been well constrained as a result of uranium exploration and drilling in the region by the operating mining company, Heathgate Resources.

The Pepegooona deposit is a geometrically complex mineralised system, consisting of four stacked roll-fronts within three sub-aquifer horizons of the Eocene Eyre Formation. These units have been informally named the Silcrete Sand horizon (roll front C), the Channel Sands horizon (further subdivided into upper and lower B roll fronts) and the Interbedded Silts and Sands horizon (roll front A) (A. Marsland-Smith, pers. comm., 2011). Groundwater samples have been collected adjacent to and within the Pepegooona deposit from the three Eyre Formation subaquifers, as shown in Figure 1.

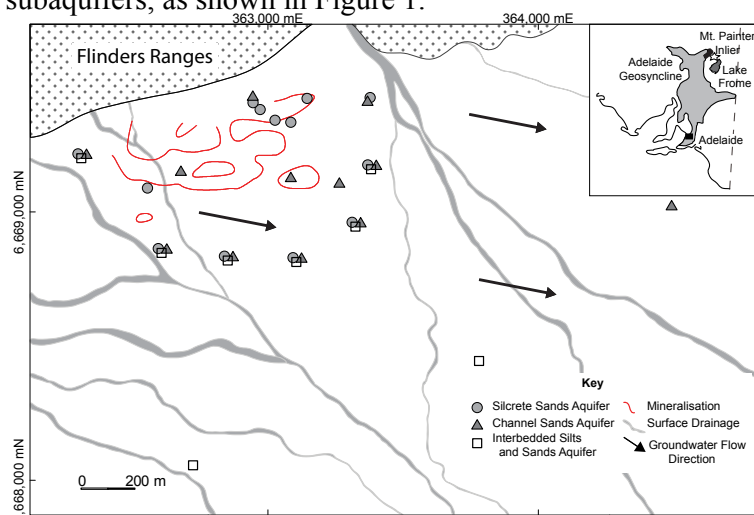


Figure 1: Map of the Pepegooona deposit showing location of groundwater wells from different stratigraphic horizons sampled for this study. Inset: Adelaide Geosyncline (grey area) in South Australia and location of the Pepegooona Deposit (star).

within mineralisation. ($^{234}\text{U}/^{238}\text{U}$) activity ratios are all greater than one, ranging from 1.03 to 1.96. The groundwater sample collected within mineralisation has an ($^{234}\text{U}/^{238}\text{U}$) activity ratio of 1.40.

In the Channel Sand aquifer, groundwaters are characterised by typically lower U concentrations ranging from 0.5 to 20 $\mu\text{g/L}$. ($^{234}\text{U}/^{238}\text{U}$) activity ratios are quite variable, ranging from 0.97 to 1.64. The groundwater sample collected within mineralisation has a low uranium concentration of 3.1 $\mu\text{g/L}$, and an ($^{234}\text{U}/^{238}\text{U}$) activity ratio of 1.41.

The Interbedded Silts and Sands aquifer has lower U concentrations than the two upper horizons, ranging from 0.7 to 5.6 $\mu\text{g/L}$. Similarly, this horizon is typically characterised by lower ($^{234}\text{U}/^{238}\text{U}$) activity ratios than the two upper horizons, ranging from 0.89 to 1.43. No mineralised sample was collected from this horizon.

Results

Groundwaters sampled from the three Eyre Formation subaquifers are consistently highly reducing, with Eh values ranging from -101 to -274 mV. The three aquifers show similar variability in pH, ranging from 6.85 to 9.18. However, the three horizons show considerable variability in uranium concentration and ($^{234}\text{U}/^{238}\text{U}$) activity ratios.

In the Silcrete Sand aquifer, groundwaters have U concentrations ranging from 0.3 to 63 $\mu\text{g/L}$, with the highest concentrations found in groundwaters sampled

Discussion

The present-day reducing nature of the three Eyre Formation aquifers at Pepegooona are consistent with the high abundance of pyrite in the host lithology. In an aqueous uranium speciation diagram (Figure 2), this data suggest that uranium is present predominantly as aqueous hydroxyl and carbonate complexes, which are typical of sandstone-hosted uranium deposits (Langmuir, 1978). Groundwater samples are located within the stability field of uraninite \pm coffinite as defined by Langmuir and Herman (1980), which is in agreement with the observed mineralogy at Pepegooona (A. Marsland-Smith, pers. comm., 2011).

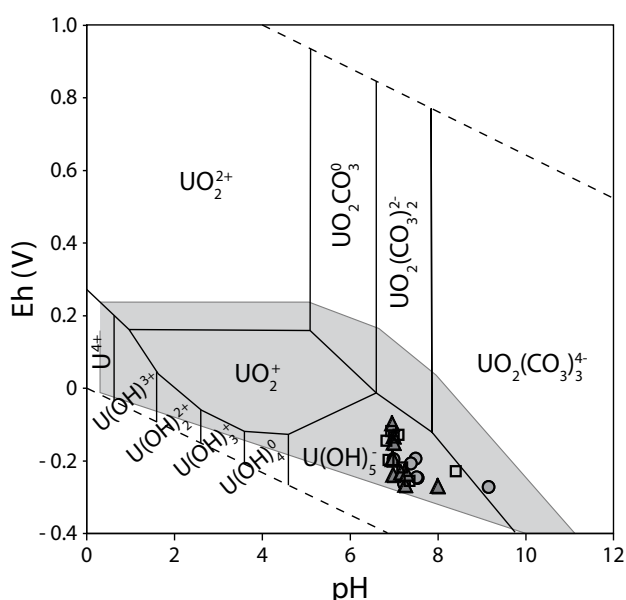


Figure 2: Eh vs. pH diagram showing aqueous uranium species at 25°C, with typical groundwater CO_2 pressure of 10^{-2} atm and $\Sigma\text{U} = 10^{-6}$ M. Uraninite stability field shown in grey. Fields modified after Langmuir (1978) and Langmuir and Herman (1980). Symbols as per Figure 1.

explanation for these ratios < 1 might be attributed to the congruent dissolution of uranium minerals that have over time become depleted in the easily leachable or recoilable ^{234}U on the outer edges of grain boundaries. Dissolution of uranium minerals with $(^{234}\text{U}/^{238}\text{U})$ activity ratio < 1 would subsequently impart that signature into the groundwater.

Groundwaters sampled within uranium mineralisation showed $(^{234}\text{U}/^{238}\text{U})$ activity ratios of ~ 1.4 , which are significantly lower than ratios typically measured in arid areas. The isotopic signature in the groundwater acquired in the mineralisation is only seen proximal to mineralisation and within several hundred meters along the groundwater flow path, $(^{234}\text{U}/^{238}\text{U})$ activity ratios return to values of ~ 2 , which are typical of waters sampled in arid environments (Kronfeld, 1991). This may imply that the groundwater isotopic signature fingerprinting the presence of high-grade uranium mineralisation is rapidly overprinted by water-rock interactions in non-mineralised areas of the aquifer.

However, if the hypothesis of congruent dissolution of uranium minerals was valid, groundwaters sampled within and down-gradient of mineralisation should exhibit ratios close to equilibrium values, which is not observed in groundwaters from the Pepegooona deposit. An inherent assumption of this model is that the uranium ore minerals congruently dissolving are in secular equilibrium (i.e. older than 1 Ma). However, if the uranium minerals have been deposited or remobilised within the past million years and have not attained secular equilibrium ratios, the

The $(^{234}\text{U}/^{238}\text{U})$ activity ratios show an overall decreasing trend with increasing depth from the uppermost to lower Eyre Formation aquifers. This might reflect the changes in aquifer host lithology and groundwater flow rate. Faster flow rates would be expected to have lower ratios as the water has less time for ^{234}U to accumulate in solution from preferential leaching or alpha recoil.

The $(^{234}\text{U}/^{238}\text{U})$ activity ratios > 1 observed in the groundwaters from Pepegooona are typical of most groundwaters (Osmond and Cowart, 1992) and can be attributed to the preferential leaching and alpha recoil of ^{234}U into solution. Moreover, these $(^{234}\text{U}/^{238}\text{U})$ activity ratios > 1 up to ~ 2 are consistent with ratios observed in natural waters sampled from arid environments (Kronfeld, 1991).

The $(^{234}\text{U}/^{238}\text{U})$ activity ratios < 1 observed at Pepegooona are less common in natural groundwaters. A possible

disequilibrium ratios of the minerals being dissolved would be preserved in the groundwater down-gradient of the deposit.

Thus, we suggest an alternate hypothesis that groundwater signature down-gradient from high-grade mineralisation is dependent on the relative stability of the deposit. A stable deposit that has not undergone deposition or remobilisation within the past million years should impart an ($^{234}\text{U}/^{238}\text{U}$) activity ratio of 1; whereas an actively dispersing or accumulating deposit will impart disequilibrium signatures into the groundwater. Therefore, the disequilibrium ratios observed from groundwaters with the Pepegooona mineralising system might be indicative of a recently active system that is now attempting to return to equilibrium.

Conclusions and future work

The U-series isotopic composition of groundwaters draining high-grade uranium mineralisation may differ depending on the age of the mineralisation: where the deposit has been stable for > 1 Ma, ($^{234}\text{U}/^{238}\text{U}$) activity ratios near unity could be expected, whilst disequilibrium ($^{234}\text{U}/^{238}\text{U}$) activity ratios might be expected where mineralisation has been deposited or remobilised within 1 Ma. Future work is aimed at determining the age of mineralisation at Pepegooona using U-series to investigate this alternate hypothesis.

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U-Series disequilibrium in groundwater as a vector for U mineralisation

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Groundwaters often exhibit ($^{234}\text{U}/^{238}\text{U}$) activity ratios greater than one as a result of fractionation between ^{234}U and ^{238}U nuclides during rock/water interactions. However, when groundwaters pass through high-grade uranium mineralisation, congruent dissolution of uranium minerals should impart a ($^{234}\text{U}/^{238}\text{U}$) activity ratio which is at or very close to secular equilibrium.

This research characterises the uranium-series (U-series) disequilibria in groundwater surrounding a high-grade uranium deposit, and investigates the use of disequilibria in groundwater as a proxy for uranium exploration. U-Series isotopes have been analysed by isotope dilution MC-ICP-MS in groundwater samples along the groundwater flow path, within and surrounding the South Australian Four Mile and Pepegooona sediment-hosted uranium mineralised systems.

Samples collected down-gradient of the Four Mile mineralisation have ($^{234}\text{U}/^{238}\text{U}$) activity ratios ranging from 1.12 proximal to mineralisation, up to 2.08 approximately 10 kms down-gradient from mineralisation. U concentrations range from 0.5 – 200 ppb, with highest concentrations found in samples collected in mineralisation. Groundwaters sampled within the high-grade mineralisation show ($^{234}\text{U}/^{238}\text{U}$) activity ratios close to unity (1.05) which is consistent with the congruent dissolution of uranium minerals. The observation of increasing disequilibrium with distance from mineralisation highlights the potential application of U-series isotopes as an indicator of high-grade uranium deposits.

However, the extent and distribution of disequilibrium at the Pepegooona deposit is not entirely consistent with proximity to the mineralisation. Groundwaters samples within mineralisation exhibit much higher ($^{234}\text{U}/^{238}\text{U}$) activity ratios than at Four Mile, averaging 1.41. Samples collected down-gradient have typically lower U concentrations and ($^{234}\text{U}/^{238}\text{U}$) activity ratios approaching unity. This signature reflects the highly variable local geology of the Pepegooona deposit.

U-Series Isotopic Characterisation of an Arid Region Sedimentary-hosted Uranium Mineralised System

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Sedimentary uranium deposits are an economically significant source of uranium worldwide, with Australia host to some of the largest known recoverable resources of uranium. Hydrologic processes are fundamental in the formation of such deposits, and the use of U-series isotopes in groundwater provides a powerful tool in understanding such systems.

The Beverley uranium mine, (South Australia) operated by Heathgate Resources, is the largest and most advanced in-situ recovery (ISR) mine in the world. The almost completely confined hydrology of the Beverley host aquifer allows for uranium to be mined using advanced acidic ISR technology (Armstrong and Jeuken, 2009). This mineralised system possesses extensive drilling and historical groundwater records, as well as data from ongoing regional monitoring wells that facilitate the monitoring of ISR mining. Hence, the well-characterised Beverley mineralised system offers a unique natural laboratory to investigate the behaviour of U-series isotopes in an arid region mineralised system. These records include detailed geologic and hydrologic data, in addition to time integrated well monitoring data.

Mineralisations occur in the permeable sands of the saline Beverley aquifer, hosted within Tertiary aged Namba sequences (Armstrong and Jeuken, 2009), which consists of interfingering sands, silts, clays and carbonaceous mudstones. The units overlie Precambrian crystalline granitic basement, which outcrops as the Mt. Painter and Mt. Babbage inliers. These basement rocks have unusually high U concentrations and are considered a potential source of the uranium (Callen et al., 1995).

Groundwater samples have been collected along the groundwater flow path upstream, within and surrounding mineralised ore deposits. Preliminary analyses for ($^{234}\text{U}/^{238}\text{U}$), ($^{230}\text{Th}/^{234}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are presented. Additionally, preliminary U-series data from diamond drill core samples collected through the oxidised zone, ore horizon and into the reduced zone will be presented.

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