

# Geochemical alteration associated with uranium roll front mineralisation in the Lake Frome Basin

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## **TITLE**

Geochemical alteration associated with uranium roll front mineralisation in the Lake Frome Basin

## **RUNNING TITLE**

Geochemical alteration signature at Beverley North

## **ABSTRACT**

Sedimentary uranium systems represent a significant source of economically recoverable material, with deposits frequently clustered where conditions are favourable for roll-front formation. Exploration for sedimentary uranium usually attempts to target redox fronts within paleochannels or clastic sedimentary sequences which could be potential sites for roll front style uranium mineralisation. Sediments altered by oxidation can be re-reduced at a later date by bacteria making it difficult to determine if an oxidised fluid has moved through the sequence.

The movement of oxidising fluids through sediment will inevitably alter both the chemistry of the sediment and the fluid supplying uranium. Elements which are sensitive to redox conditions dissolve and precipitate as conditions change creating a recognisable geochemical footprint. In particular the uranium, molybdenum and arsenic contents of the sediments are changed in a way which is not reversed by re-reduction. These changes are distinctive enough to be detected using a handheld X-Ray fluorescence device which enables rapid decision making in the field even if traditional methods allow for far greater precision and accuracy.

The findings of this study describe geochemical changes linked to oxidation in the Pepegoona East and Pannikan deposits, Lake Frome region, South Australia, for use as an exploration tool. It is hoped that by studying changes in the chemistry of these sediments that we may not only improve the efficiency of exploration but also gain a better understanding of how the fluids responsible for uranium mineralisation evolve over time. The addition of data from new deposits will enhance the accuracy of the data set and provide a better understanding of how sediment composition effects alteration.

## **KEYWORDS**

Geochemical alteration, Lake Frome, Uranium, Roll Front, Beverley North, uranium exploration

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## INTRODUCTION

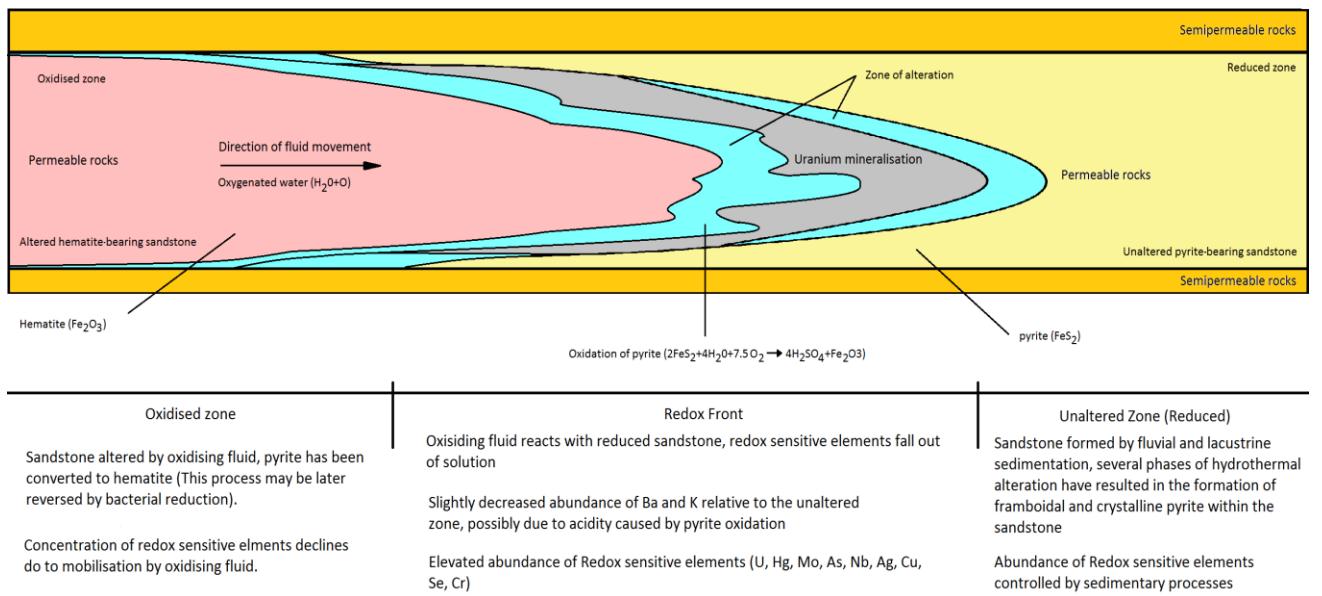
Geochemical ratios are an effective method for recognising alteration associated with roll-front uranium mineralization (Whitbread 2002). These ratios exploit the change in relative concentration of elements brought about by the passage of oxidised water to identify and map potentially mineralised zones. In order to establish useable ratios it is necessary to have an understanding of how and why geochemistry changes across the roll front. Through careful analysis of mineralogy and deportment of the elements of interest as well as changes in mineral speciation associated with changes in intensity of alteration across a known mineralised zone, changes directly associated with fluid flow can be identified.

Ratios have significantly greater utility if they can be measured in the field, enabling exploration programs to adapt to new data without sending samples to a lab. The use of a portable X-Ray Fluorescence device enables samples to be analysed on site but restricts the range of elements which can be used as well as the accuracy of measurement. The identification of geochemical ratios which are robust enough to identify regions of oxidised sediment in the field using portable XRF equipment would thus significantly improve the efficiency of exploration.

Uranium-rich groundwater from the Northern Flinders Ranges has been flowing into the Lake Frome Basin since the Tertiary leading to the development of multiple phases of mineral growth associated with uranium mineralisation (Ingham *et al.* 2014). Movement of oxidised meteoric water is essential for the formation of economic grades of uranium in the region, forming ‘roll-fronts’ located where the aquifer meet a reduced environment (Figure 1). The ability to trace the movement of oxidising fluids within the basin would be invaluable in

exploration for as-yet undiscovered deposits. Mapping these channels using traditional means has, however, proven difficult (Skirrow 2009), notably because of significant lithological variation both vertically and laterally across the basin and due to the narrow habit of roll front style deposits which are easily missed during exploration drilling.

This study uses drill chips from existing holes drilled during exploration and resource definition of the Pepegoona East and Pannikan deposits in order to create a geochemical cross-section of typical roll front mineralisation in the Lake Frome region. A portable XRF device was used to determine the geochemistry of these samples, scanning electron microscopy and electron probe microanalysis provided mineralogical data to establish why these changes are occurring. By linking these changes to paths of fluid flow, it is possible to distinguish between channels and sedimentary sequences of unaltered sediment and those which have been exposed to oxidising fluid. The results are considered to be a vector for uranium mineralisation.



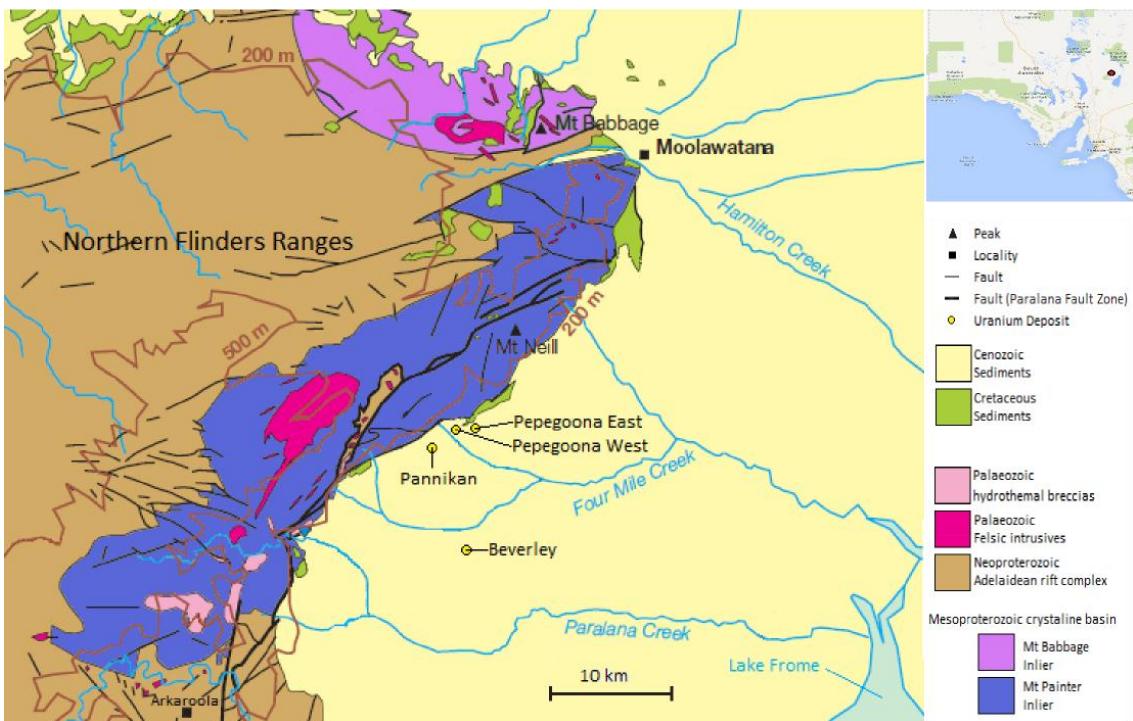
**Figure 1: Vertical cross section of a typical sandstone-hosted roll front including geochemical changes associated with redox conditions**

## GEOLOGICAL SETTING

### Background

Lake Frome is located to the South East of the Northern Flinders ranges, specifically the area known as the Mount Painter Domain. The Mount Painter Domain represent the eastern most part of a region of anomalously high heat flow known as the South Australian Heat Flow Anomaly which extends from the Mount Painter inlier to the Eastern Part of the Gawler Craton (Neumann *et al.* 2000). Heat production in this region is elevated due to unusually high levels of uranium, thorium and potassium found in felsic intrusives of Proterozoic age. These intrusives produce double the global mean heat production for Proterozoic rocks and four times the heat production of average granites (Brugger *et al.* 2005). It has been suggested that crustal weakening in the area due to excessive heat is responsible for the formation of the present day Flinders Ranges (Skirrow 2009). Rocks of the Mount Painter Domain consist of Paleozoic granites, gneisses and metasediments overlain by Neoproterozoic to Cambrian sediments. The Proterozoic units of the domain are thought to represent the source of uranium mineralisation in the region (Brugger *et al.* 2005), with ongoing uplift of the Mount Painter Inlier (100-200 m since the early Pliocene) providing a continuous source of material (Wulser *et al.* 2011).

The Mount Painter Domain is separated from the Lake Frome region which hosts the Pannikan and Pepegoona uranium deposits by the Paralana Fault Zone which consists of a series of roughly NE-SW-trending and W-dipping fault structures which extend deep into basement rock. This fault zone represents the Eastern border of the Adelaide Geosyncline where it borders the Curnamona Province (Brugger *et al.* 2005). The active section of the fault zone consists of a cluster of faults which have been active as reverse faults since the late Miocene (Wulser *et al.* 2011;Ingham 2012).



**Figure 2: Location of Uranium deposits within the Lake Frome Region and position relative to regional geology. Adapted from (Wulser et al. 2011)**

The Sandy sediments of the Lake Frome district host most of the major uranium deposits in the region, including the Pannikan (Figure 3), Pepegoona (Figure 4), Beverley and Honeymoon deposits. The Lake Frome area was originally a single sedimentary basin but has been divided into a series of sub-basins by the same tectonic activity which has uplifted the Mt Painter Domain (Wulser *et al.* 2011)

#### Regional geological history:

Rocks of the Mount Painter Domain were subjected to a series of metamorphic events in the Precambrian before being buried by an estimated 14 km of Adelaidean sediments over the space of 350 million years with sedimentation terminated by the Delamerian Orogeny in the Cambrian and Ordovician (Hill & Hore 2011). Metamorphism during the Delamerian was restricted to greenschist facies across most of the Flinders Ranges. The region around Mount Painter was however subjected to a much higher grade of metamorphism, reaching lower amphibolite in close proximity to the Mt Painter Inlier. This change in metamorphic facies

has been attributed to high heat production within the inlier (Brugger *et al.* 2005). At 440 Ma the region was subjected to a thermal event associated with the intrusion of mafics and S-type granites and generation of u-bearing fluids at 360 Ma. The Inliers have since been subjected to several periods of rapid uplift and erosion with an ice sheet covering the region during the Permian (Hill & Hore 2011).

During the Mesozoic the Frome Embayment was a major depocentre in the hinterland of the Eromanga Basin with sediments consisting mostly of braided fluvial gravels. During the Early Cretaceous sedimentation included marginal marine sediments, glacial tillites and organic rich silts, clays and sands. The Lake Eyre Basin formed during the Cenozoic as a depocentre associated with the Callabona Sub-basin. The Earliest Eocene sediments are quartz, kaolinite and organic-rich fluvial sediments which are followed by mid-Tertiary smectite-palygorskite-dolomite and organic-rich lacustrine sediments. Upper Cenozoic sediments contain a mixture of alluvial, colluvial, aeolian and lacustrine sediments (Hill & Hore 2011). Tectonic movement since the Tertiary has resulted in the division of the region surrounding Mt Painter into the Lake Eyre, Lake Torrens and Lake Frome basins, it has also resulted in the uplift of the Mount Painter Domain and the present topography of the Flinders Ranges. Tertiary sediments are capped by silcrete and duricrust which has resulted from deep chemical weathering (Brugger *et al.* 2005).

#### Stratigraphy:

The Eyre Formation consists of an upwardly fining sequence of mature sands interlayered with fine-grained silt and coarse-grained-gravels originating from a braided river environment, the formation itself is divided into upper and lower units with a period of non-deposition separating the two units (Skirrow 2009). The Eyre Formation is believed to have

been deposited in a tropic to sub-tropical environment with high rainfall supporting rainforest vegetation (Callen 1975). The Eyre Formation sands hosting the Pepegoona and Pannikan deposits are richer in carbonaceous material and pyrite than the Beverley sands which host the nearby Beverley deposit (Skirrow 2009). Eyre formation sands overlay a diamictite unit which overlies fractured basement rocks, possibly of the Mt Painter Inlier. Mineralisation occurs mostly at the contact between Lower Eyre Formation sands and the Diamictite unit, at a depth ranging from 150-200 m with an average of 180 m (Skirrow 2009)

#### Roll-Front Uranium Systems:

Both the Pannikan and Pepegoona are formed from the movement of meteoric water, where oxidising ground waters dissolve uranium which is transported till it reaches a reduced portion of the aquifer, often at a permeability boundary such as a change from massive sand to finer-grained material where reducing conditions are common (Hobday & Galloway 1999). The main reducing material within the Pannikan and Pepegoona deposits is pyrite which is replaced by uraninite during ore genesis (Ingham 2012). Roll front morphology is defined by the flow direction of ground-water which is controlled by regional topography at the time of formation and stratification of the host depositional system, as a result roll fronts form highly irregular ‘tongues’ of mineralisation with the largest concentrations of mineralisation at the tip of the ‘tongue’ (Hobday & Galloway 1999). In cross-section, roll front mineralisation forms a classic C-shape which concaves in the opposite direction to flow (Granger & Warren 1969; Hobday & Galloway 1999). Roll fronts will often have a region of elevated selenium associated with the mineralisation accumulating just behind the roll front (Granger & Warren 1969).

Mineralisation:

*Detrital phase:* The detrital mineralogy of the Lower Eyre Formation consists mostly of angular to sub-rounded quartz grains <0.5 mm in diameter, minor sub-rounded detrital feldspars ≥ 250 µm in size comprise the other framework mineral. Observed detrital minerals within the accessory phase include chalcopyrite, zircon, monazite, muscovite and ilmenite (Skirrow 2009). Kaolinite dominates the clay matrix although illite is also thought to be present, the matrix is organic-rich with small (1-2 µm) pyrite crystals.

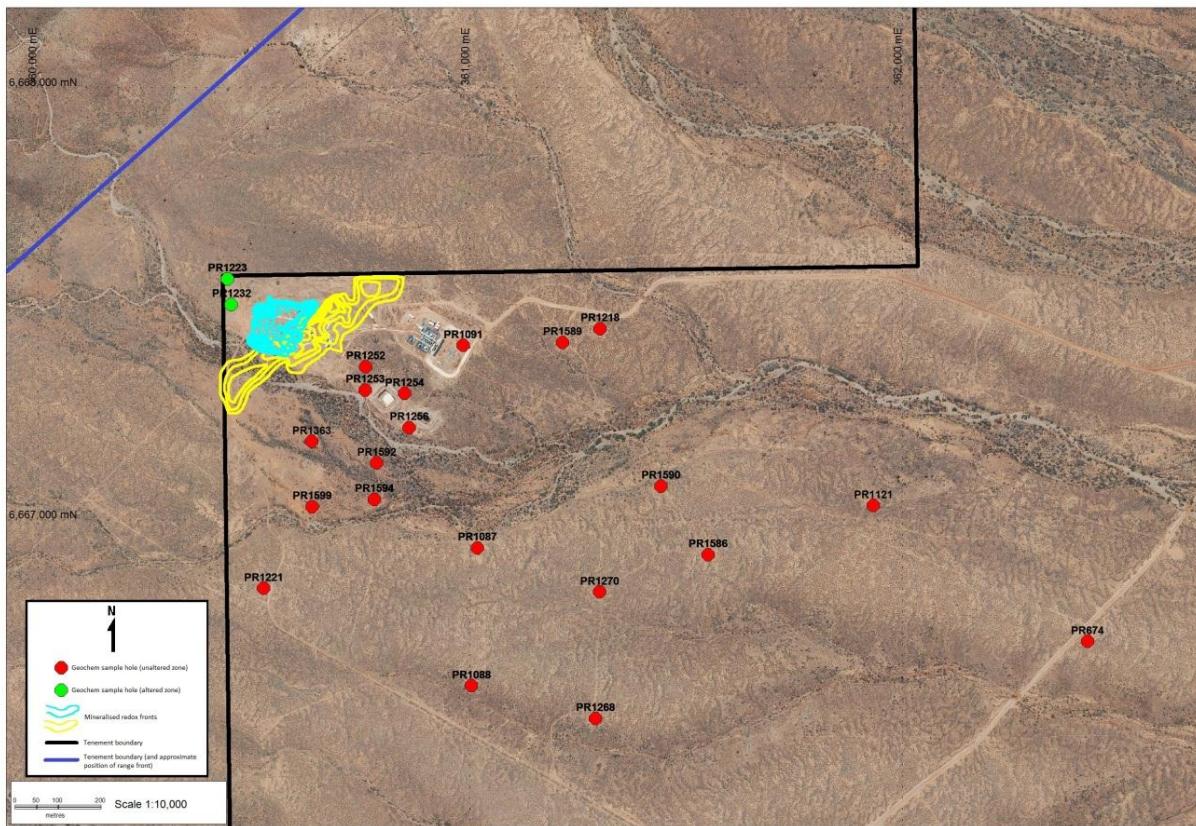
*Post-depositional phase:* Four phases of pyrite are described within the Eyre Formation (Skirrow 2009). The first phase formed either during deposition or shortly after and consisted of frambooidal aggregates, which are likely to have been bacterial in origin. Elemental analysis of frambooidal pyrite shows that trace elements are found in low abundance, this indicates that the supply of trace elements was restricted to the sandstone lithology alone (Ingham *et al.* 2014). This initial phase of pyrite growth has now been replaced by uraninite in mineralised zones. The second phase consists of euhedral pyrite growth which commonly forms a cement and overprints the initial phase. The timing of this phase of pyrite growth relative to uranium mineralisation is unclear, euhedral pyrite overprints frambooidal pyrite which has been replaced by uraninite indicating that uranium mineralisation occurred before the second phase of pyrite growth, however uraninite inclusions are also found within euhedral pyrite crystals.

It is suggested that either the uranium mineralisation was deposited in two separate events or alternatively, that pyrite formation and uranium mineralisation took place at the same time. The third phase of pyrite forms overgrowth rims on the euhedral pyrite and the final phase exists as tiny euhedral crystals within the matrix. The final two phases of pyrite postdate mineralisation (Skirrow 2009).  $^{34}\text{S}$  is low in the initial phase of pyrite growth. Such a feature

is characteristic of a biogenic sulphur source where bacteria preferentially reduce sulphate with the lighter sulphur isotope (Ingham *et al.* 2014). Pyrite growth in the three later phases is relatively  $^{34}\text{S}$ -rich which indicates formation in disequilibrium in an open system, a hydrothermal sulphur source is the likely explanation. Sulphur isotope ratios within the hydrothermal phases span an unusually large range. This is thought to reflect the mixing of several distinct sulphur sources and the preferential uptake of light sulphur isotopes by pyrite.

## APPROACH AND METHODOLOGY

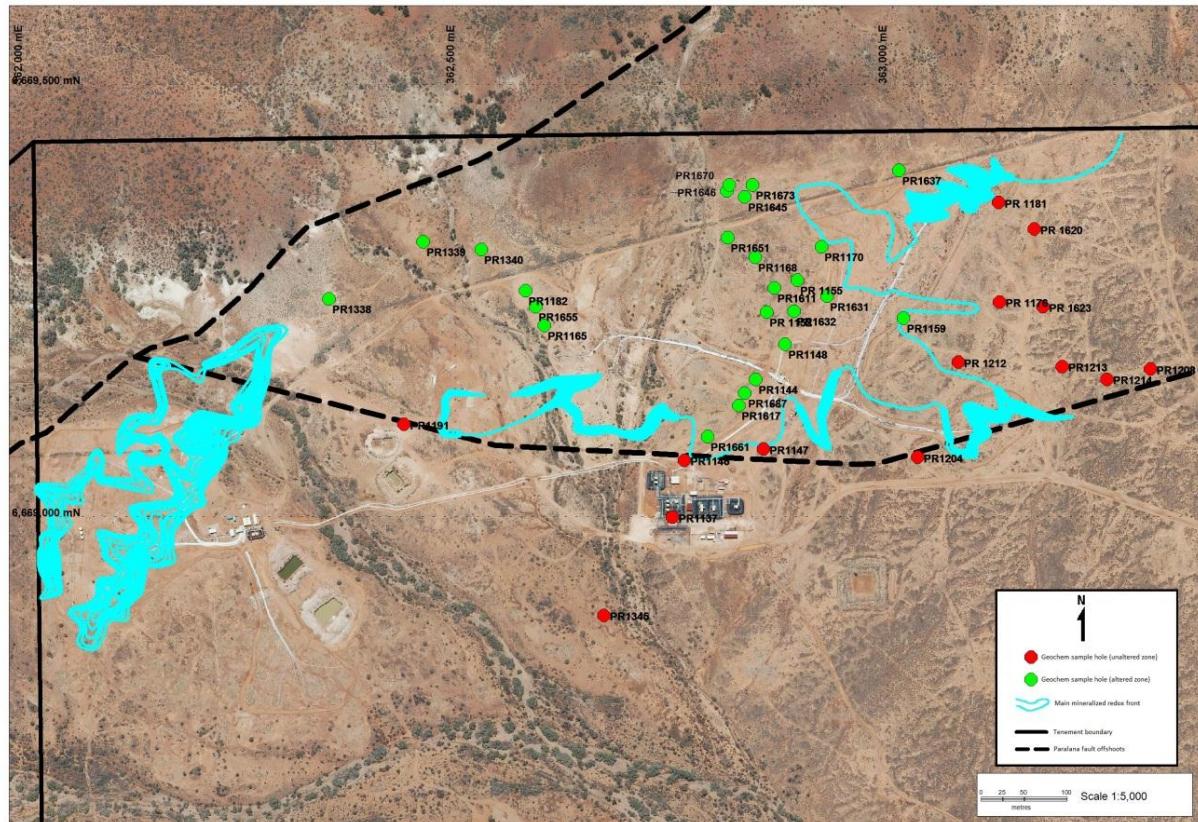
Chip sampling:



**Figure 3: Map of geochemical sampling holes within the Pannikan deposit overlayed on a satellite image of the surrounding region. The tenement boundary which represents the limit of data available for this study is outlined in black. Image courtesy of Heathgate Resources (2014)**

The samples used in this study consist of drill chips from rotary mud holes drilled during exploration and resource definition of the Pannikan and Pepegoona deposits. Samples are limited to the Eyre Formation which hosts uranium mineralisation in both roll fronts.

Drill chips were collected at 2 m-intervals during initial sampling, these samples were used to create composite samples of approximately 5 grams each over 8 m-intervals, with samples covering the full thickness of the Eyre Formation.



**Figure 4:** Map of geochemical sampling holes within the Pepegoona deposit, only main mineralised roll which was the target of this study is shown. Image courtesy of Heathgate Resources (2014).

Where possible samples were taken so that a complete profile of the mineralized zone from the unaltered zone in front of the mineralisation to a point as far up slope of the mineralisation as possible, however the nature of the original drilling program and the location of tenement boundaries restricted the availability of data. The location of the Pannikan and Pepegoona West ore-bodies at the edge of a tenement boundary prevented collection of data upstream from the roll front therefore data collection was focused on the region downstream of the roll. Sample collection from the Pepegoona East deposit was not restricted and a complete cross section of data was collected.

### X-Ray Florescence data

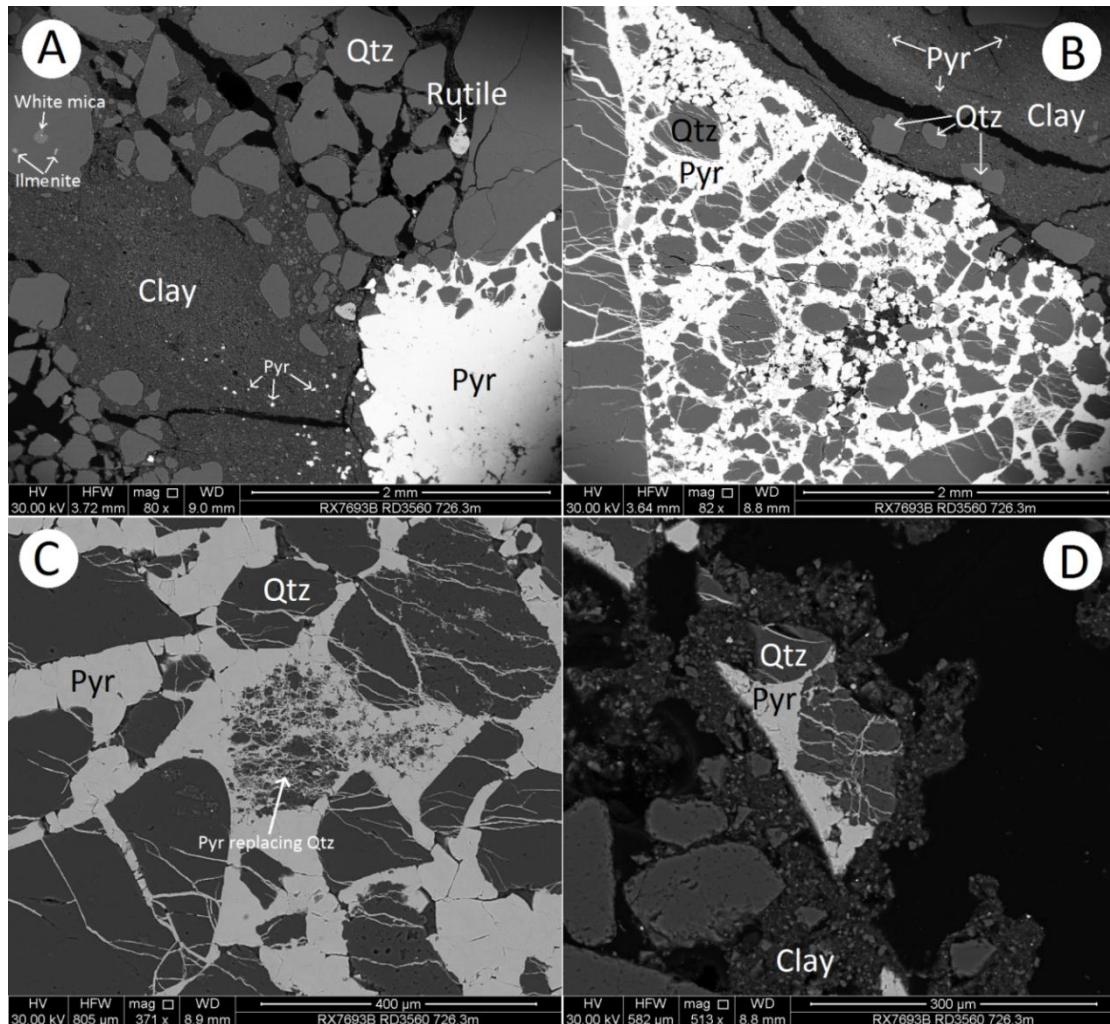
Geochemical data was collected using a portable XRF unit analysing samples from pre-existing drill-holes covering as large an area on and around the Pannikan and Pepegoona deposits as possible (detailed in Appendix A). Statistical analysis of this data was performed using Microsoft excel, with correlation between elements in front and behind each deposit used to infer changes in mineral species and deportment.

Optical and Scanning Electron Microscopy (SEM) in Back-Scattered Electron mode (BSE) were used in conjunction with Electron Probe Microanalysis (EPMA) of the sample set to link changes in the abundance of elements across the roll front with abundance and composition of minerals.

### Microscopy and microanalysis

A suite of 10 core samples was collected from the Pannikan deposit during a previous study (see Ingham *et al.* 2014), with a sample taken from each diamond hole drilled during exploration. These samples were set in epoxy resin and prepared as one-inch polished blocks for mineralogical and petrographic analysis. Of these samples 4 were chosen based on their position in front or well behind the mineralised zone and analysed using a quanta 450 scanning electron microscope. Optical and Scanning Electron Microscopy (SEM) was undertaken in Back Scattered Electron mode (BSE) to identify minerals within the samples. Energy-dispersive X-ray spectrometry was used to characterize the composition of minerals within the sample to identify carrier phases for the elements of interest. Diamond holes drilled within the Pepegoona deposit were drilled in close proximity to mineralisation and were not considered useful for this study.

## RESULTS

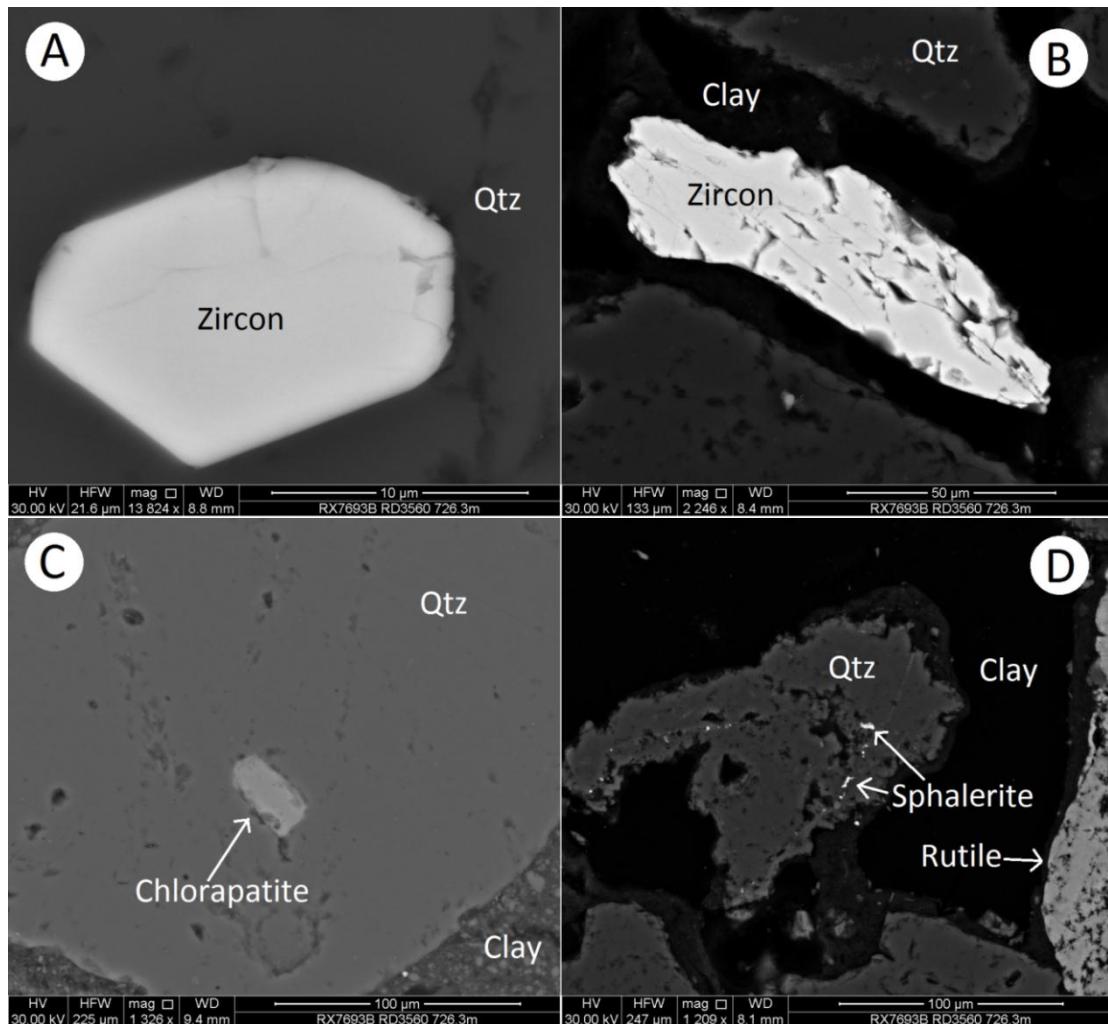


**Figure 5:** Back scatter electron images showing the relationship between pyrite, quartz and clays a) and b) boundary between quartz-pyrite zone and clay zone c) pyrite infill in quartz grains and replacement of quartz by pyrite d) pyrite and quartz grains in a clay matrix, suggesting transportation following an early phase of pyrite growth.

### Mineralogical and textural analysis of core samples

Sediments in the unaltered zone of the Pannikan deposit consisted of medium-grained sub-rounded quartz grains (>50%) frequently veined and overgrown by pyrite (Figure 5b-c) which constitutes around 20% of the sample, the matrix consists of fine-grained clay minerals. At least five phases of pyrite growth have been recorded within sediments of the region (Ingham *et al.* 2014). The quartz grains contain a diverse range of mineral inclusions

(Figure 6a-c-d) which could represent hosts for uranium and other elements of interest; these include zircon, chlorapatite, white mica, sphalerite and titanite. Titanium minerals represent a common accessory phase (Figure 7a-d) (<5% in total) with titanite and ilmenite represented in varying stages of deterioration.



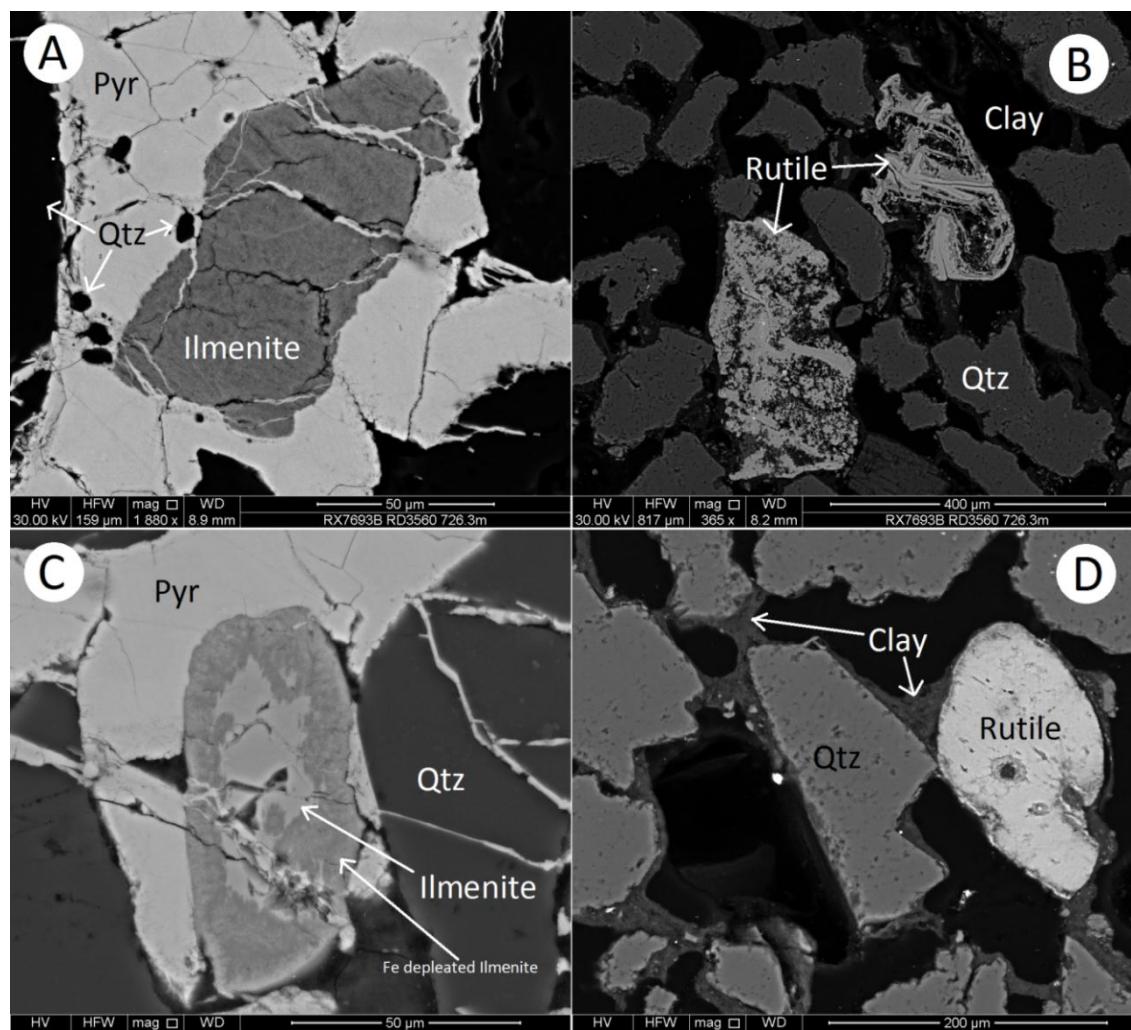
**Figure 6:** back scatter electron image showing accessory phases with the potential to host uranium in unaltered sediments a) hafnium-bearing zircon crystal within quartz grain b) detrital zircon within clay matrix c) chlorapatite in quartz grain d) sphalerite grains in an irregularly shaped quartz grain

#### Zircon [ $\text{ZrSiO}_4$ ]

Zircons (Figure 6a-b) are generally formed in granitic magmas but are durable enough to survive sedimentation and are a common component of sands. The crystal lattice of zircon is capable of including a range of high field strength incompatible elements including uranium,

thorium, hafnium, lead and other rare earth elements. Zircon can also contain trace amounts of Ti, Nb, P, Mn, Fe and Ba (Belousova *et al.* 2002) although these are not likely to be found in quantities exceeding a few hundred ppm.

Zircon is a potential host for U and Th in the unaltered zone.



**Figure 7: Back scatter electron images of titanium minerals in unaltered sediments: a) ilmenite grain within pyrite with pyrite veining b) decomposed rutile grains in clay matrix c) ilmenite grain with zone of iron depletion on outer rim d) tungsten-bearing rutile grain in clay matrix**



Apatite-group minerals (Figure 6c) are capable of hosting a diverse range of elements through substitution and structural distortion, including U, Th, As, Pb, Sr, V, P, Ca and Bi

(Pan & Fleet 2002). Chlorapatite will account for a small part of the calcium, phosphorous and chlorine within the samples and may also host some of the uranium, thorium and arsenic.

### Rutile ( $TiO_2$ )

Rutile (Figure 7b-d) is a common accessory mineral in metamorphic rocks but can also form in igneous rocks. Rutile is also highly resistant to weathering and often survives transportation to be included in clastic sediments. Aluminium, vanadium, chromium, iron, zirconium, niobium, tin, antimony, hafnium, tantalum, tungsten and uranium can substitute into the rutile structure (Meinholt 2010). While rutile will accept uranium into its structure it is not compatible with thorium, this is one of few situations where thorium is separated from uranium in high temperature systems and may result in significant variation from normal U/Th ratios where rutile hosts uranium (Klemme *et al.* 2005)

Rutile is a potential host for uranium, significant variation from normal U/Th ratios would be a strong indicator that this is the case.

### Ilmenite ( $FeTiO_3$ )

Ilmenite (Figure 7a-c) commonly forms in igneous rocks but is robust enough to survive sedimentation; its high specific gravity causes it to separate from lighter minerals both in magma chambers and in sedimentary systems.

Iron is commonly leached from ilmenite during weathering resulting in a breakdown of the crystal structure (Figure 7c), unweathered samples frequently contain 50%  $TiO_2$  while weathered samples can contain 70%  $TiO_2$  (Force 1991). Manganese, Mg, V, Nb and Cr can substitute for Fe and Ti within the crystal lattice, Al, Si, U, Th, P and Cr can be incorporated into ilmenite grains during weathering (Grey *et al.* 2005)

Ilmenite is a potential host for U, Th, V, Mn and Nb in the unaltered zone.

Table 1: Elemental abundance in the altered and unaltered zones of the Pepegoona deposit based on drill chip samples

	Pepegoona elemental abundance (ppm)																					
	Mo	Zr	Sr	U	Rb	Th	As	Zn	Fe	Cr	V	Ti	Ca	K	S	Ba	Nb	Bi	Al	Si	Cl	
<b>Unaltered zone (129 readings total)</b>																						
Average	6	207	17	14	19	22	6	32	6212	50	91	2373	1635	7469	2536	249	20	25	32303	283252	1469	
Median	5	175	15	10	19	18	5	18	5356	42	83	2346	881	7290	1806	130	16	20	33560	282043	1606	
Standard deviation	4	140	10	12	9	20	3	50	4127	22	74	1021	2462	2711	2137	480	14	25	10346	28135	756	
No of readings >LOD	59	139	139	125	139	137	42	117	139	32	132	139	136	139	137	108	135	126	139	139	139	
<b>Post roll front zone (202 readings total)</b>																						
Average	9	222	21	37	19	22	12	76	6864	55	106	2903	1641	5847	5836	206	20	26	28479	287796	1629	
Median	6	217	16	19	17	19	7	21	5059	44	92	2699	1099	5224	3610	130	20	23	27640	282428	1636	
Standard deviation	9	127	22	56	13	14	16	292	6620	29	83	1545	2790	3176	10508	243	11	16	10800	36650	811	
No of readings >LOD	143	202	202	196	201	193	115	160	202	50	196	202	199	202	200	143	190	166	202	202	202	
% change (average) unaltered to post roll	64%	3%	16%	140%	6%	-5%	107%	181%	-6%	-2%	14%	20%	3%	-19%	90%	-32%	2%	-3%	-12%	1%	13%	
% change (median) unaltered to post roll	21%	24%	8%	93%	-7%	8%	52%	15%	-6%	4%	11%	15%	25%	-28%	100%	1%	26%	16%	-18%	0%	2%	
redox sensitive elements																						
other elements of interest																						
elements which should be immobile																						
Thorium and bismuth (regarded as suspect)																						

Table 2: Elemental abundance in the Pannikan deposit based on XRF analysis of drill chip samples

	Pannikan elemental abundance (ppm)																				
	Mo	Zr	Sr	U	Rb	Th	As	Zn	Fe	Cr	V	Ti	Ca	K	S	Ba	Nb	Bi	Al	Si	Cl
<b>Unaltered zone (93 readings total)</b>																					
Average	3	239	20	9	28	18	5	46	8277	52	109	2524	1334	9978	1967	311	18	20	29669	278020	1924
Median	3	178	14	8	23	15	4	21	5883	45	98	2337	1157	9909	1337	194	16	15	28875	281528	2090
Standard deviation	2	242	16	5	18	13	3	80	6886	29	73	965	932	3508	2368	531	11	15	6787	28197	1004
No of readings >LOD	18	93	93	73	93	93	30	57	93	24	92	93	93	93	93	66	91	76	93	93	92
<b>Oxidised zone (17 readings total)</b>																					
Average	5	145	17	16	24	9	12	14	7473	32	74	2013	1065	7262	601	152	12	8	23772	274634	1385
Median	4	114	15	8	21	8	8	12	5692	32	71	1782	682	6772	540	155	10	6	23821	263965	1298
Standard deviation	2	79	14	18	12	4	11	7	6726	6	30	867	986	2549	332	53	7	5	5326	28648	506
No of readings >LOD	7	17	17	14	17	17	6	11	17	2	17	17	15	17	15	10	16	13	17	17	17
% change (average) unaltered to post roll	42%	-39%	-14%	67%	-15%	-50%	139%	-69%	-10%	-38%	-32%	-20%	-20%	-27%	-69%	-51%	-33%	-60%	-20%	-1%	-28%
% change (median) unaltered to post roll	31%	-36%	6%	-1%	-9%	-44%	89%	-41%	-3%	-29%	-27%	-24%	-41%	-32%	-60%	-20%	-36%	-61%	-18%	-6%	-38%
redox sensitive elements																					
other elements of interest																					
elements which should be immobile																					
Thorium and bismuth (regarded as suspect)																					

## DATA ANALYSIS

Data sets were divided between unaltered and altered zones based on location relative to the roll front. An estimation of minimum and maximum depth of mineralisation was made based on data within the mineralised zones. Readings outside this zone were excluded from the analysis.

Data was only included where measured concentrations were above the respective limit of detection. Elements which were present in fewer than 25% of samples were excluded from the dataset.

Differences between deposits:

The measured concentrations of the majority of elements decreased from the unaltered to oxidized zones of the Pannikan deposit. This change is unlikely to be the result of redox conditions and may have resulted from a change in sedimentary facies resulting in an increase in clay content downstream of the mineralized zone or a dilution effect caused by the introduction of silica upstream of the roll front. It should be noted that the altered zone of both deposits is likely to retain regions of unaltered material which were not conductive to fluid flow at the time of oxidation. The unaltered zone will also contain minor oxidation zones due to weathering in a period of non-deposition during formation of the Eyre Formation.

## ELEMENTS WHICH INCREASE ACROSS THE ROLL FRONT

Concentrations of Mo, U and As concentrations increase significantly from unaltered to oxidised zones in both deposits. Uranium, molybdenum and arsenic are strongly redox-sensitive elements (Hofmann 1999) and an increase in their abundance can be linked directly to the introduction of material by the oxidizing fluid.

## Uranium

The U concentration in the unaltered zone of the Pepegoona deposit is enriched relative to the Pannikan deposit. Sediments of the Pepegoona deposit contained an average of 14 ppm while Pannikan contained only 9 ppm. There was a significant change in concentration between the unaltered and oxidised zones with Pepegoona more than doubling to an average of 37 ppm, and Pannikan increasing to 16 ppm. The difference is, however not great enough to distinguish between the oxidised zone of the Pannikan deposit and the unaltered zone of the Pepegoona deposit based on U concentration alone.

## Molybdenum

The Mo concentration in the unaltered zone of the Pepegoona deposit is enriched relative to the Pannikan deposit, with the Pepegoona deposit containing an average of 6 ppm Mo while Pannikan contains an average of 3 ppm. The increase is however not as significant as for uranium; in the altered rocks, Pepegoona increased to 9 ppm while Pannikan increased to 5 ppm

The average crustal abundance of Mo is only 1-2 ppm, however it is heavily concentrated in oxygenated seawater and marine shales due to its redox sensitivity, the importance of Mo in organic systems meant that it is also concentrated in rocks with a high percentage of organic carbon (Reddy *et al.* 1997). Molybdenite ( $\text{MoS}_2$ ) is the most common mineral host for molybdenum and is generally found in rocks with a granitic composition. Molybdenite can also enter the crystal structure of pyrite (e.g. Ingham *et al.* 2014).

## Arsenic

Concentrations of As in the two deposits overlap statistically. Pepegoona had an average concentration of  $6 \pm 3$  ppm while Pannikan had an average concentration of  $5 \pm 3$  ppm.

Arsenic is generally found in low concentrations within igneous rocks (1-5 ppm) most of which is hosted by feldspars. Shales contain much higher concentrations of As (5-15 ppm), particularly if they are rich in carbonaceous material or sulphur (due to pyrite content). Sandstones typically have arsenic concentrations similar to igneous rocks (Onishi & Sandell 1954). The concentrations of As found in the unaltered zones of the two deposits are high for sandstone and are more typical of shales. Apatite and clay may host some of the As in altered sediments; pyrite however is likely to host most of it. The change in As concentrations between unaltered and oxidised sediments is significant and consistent between the two deposits with both increasing to an average of 12 ppm, an increase of 100% in both cases.

#### **ELEMENTS WHICH DECREASED ACROSS THE ROLL-FRONT:**

##### Potassium

Potassium concentrations decrease from an average of 7469 ppm to 5847 ppm in the Pepegoona deposit and from 9978 ppm to 7262 in the Pannikan deposit. Potassium is abundant in both deposits although Pannikan is slightly enriched relative to Pepegoona. Potassium is unlikely to be directly sensitive to redox conditions however it may be mobilized from clays by changes in pH (Hofmann 1999). Reduced concentrations may be the result of low pH, resulting from the oxidation of pyrite at the roll front.

##### Relatively immobile elements

Thorium and Ti tend to form minerals which are highly resistant to weathering, while Al forms part of the basic structure of clays. These elements are highly insoluble and their abundance in sediment is unlikely to vary significantly after deposition, this makes these elements or ratios involving them useful for correcting for inherent variations in sediment composition.

## GEOCHEMICAL DATA: PEPEGOONA EAST UNALTERED ZONE

Table 3: Correlation between elements in the unaltered zone of the Pepegoona East Deposit based on geochemical data

	<i>Mo</i>	<i>Zr</i>	<i>Sr</i>	<i>U</i>	<i>Rb</i>	<i>Th</i>	<i>As</i>	<i>Zn</i>	<i>Fe</i>	<i>Cr</i>	<i>V</i>	<i>Ti</i>	<i>Ca</i>	<i>K</i>	<i>S</i>	<i>Ba</i>	<i>Nb</i>	<i>Bi</i>	<i>Al</i>	<i>Si</i>	<i>Cl</i>
<i>Mo</i>	1.00																				
<i>Zr</i>	0.28	1.00																			
<i>Sr</i>	-0.14	0.43	1.00																		
<i>U</i>	0.64	0.22	0.04	1.00																	
<i>Rb</i>	0.09	0.54	0.50	0.10	1.00																
<i>Th</i>	0.26	0.43	0.17	0.15	0.32	1.00															
<i>As</i>	0.39	0.07	-0.21	-0.09	-0.16	-0.05	1.00														
<i>Zn</i>	0.11	0.21	0.32	0.02	0.06	0.05	0.11	1.00													
<i>Fe</i>	0.13	0.37	0.39	0.08	0.45	0.16	-0.13	0.11	1.00												
<i>Cr</i>	-0.08	0.26	-0.03	0.15	0.18	0.15	-0.34	0.13	0.03	1.00											
<i>V</i>	0.15	0.30	-0.02	0.00	0.14	0.33	0.14	0.01	0.05	0.25	1.00										
<i>Ti</i>	0.16	0.74	0.44	0.25	0.52	0.31	-0.07	0.13	0.51	0.01	0.29	1.00									
<i>Ca</i>	-0.15	0.11	0.60	-0.07	0.24	-0.08	-0.20	0.03	0.21	-0.05	-0.17	0.11	1.00								
<i>K</i>	0.17	0.55	0.28	0.11	0.72	0.42	-0.13	-0.04	0.58	-0.03	0.26	0.59	0.04	1.00							
<i>S</i>	0.30	-0.16	0.07	0.14	-0.24	-0.13	0.29	0.22	0.04	0.18	0.10	-0.07	-0.02	-0.38	1.00						
<i>Ba</i>	-0.07	0.11	0.57	-0.07	0.01	-0.14	-0.13	0.48	-0.01	0.08	0.53	0.02	0.16	-0.14	0.37	1.00					
<i>Nb</i>	0.38	0.80	0.24	0.28	0.53	0.45	0.14	0.08	0.30	0.11	0.27	0.69	-0.03	0.64	-0.26	-0.15	1.00				
<i>Bi</i>	0.24	0.38	0.15	0.21	0.25	1.00	-0.10	0.04	0.13	0.09	0.28	0.26	-0.07	0.36	-0.08	-0.16	0.40	1.00			
<i>Al</i>	0.19	0.34	-0.01	0.11	0.38	0.39	-0.02	-0.06	0.28	0.00	0.28	0.48	-0.36	0.65	-0.22	-0.23	0.48	0.31	1.00		
<i>Si</i>	-0.14	-0.33	-0.39	-0.02	-0.59	-0.22	-0.05	0.01	-0.59	0.11	-0.12	-0.52	-0.10	-0.69	0.09	0.02	-0.34	-0.14	-0.66	1.00	
<i>Cl</i>	0.25	-0.13	-0.48	-0.21	-0.24	0.13	0.36	-0.10	-0.29	0.26	0.43	-0.29	-0.41	0.00	-0.02	-0.12	-0.02	0.09	0.20	0.09	1.00

## Uranium

Uranium displays only a weak correlation (<0.30) with all elements except Mo (0.64) in the unaltered zone. The correlation between U and Ti (0.25) is stronger than with Th (0.15), indicating that rutile may host part of the uranium. The lack of strong correlation indicates, however, that multiple hosts for U are likely. The weak correlation with Zr (0.24) suggests that zircon hosts part of the uranium, particularly in the least-altered samples. The lack of a strong negative correlation with Si (quartz >70% of most samples) indicates that U is not exclusively found in the clay fraction and is probably also disseminated within some of the quartz grains. The strongest correlation other than Mo is with Nb (0.28), which is also a common component of rutile, brannerite and zircon.

## Molybdenum

Molybdenum has reasonably strong correlation with U (0.64), As (0.39) and Nb (0.38) in the unaltered zone. Molybdenum has weaker correlations with S (0.30) and Cl (0.25) which likely indicates the presence of molybdenite or other sulphides that can contain Mo such as pyrite; There is also weak correlation with Zr (0.28) and Th (0.26), which may indicate an association with zircon. As with U it is likely that Mo is hosted by a range of minerals. Molybdenum has positive correlation with both As and U, although As and U themselves display only a weak negative correlation (-0.09). This indicates that Mo is found in at least two phases, one associated with U, the other with As.

## Arsenic

Arsenic has strong correlation with Cl (0.36), chlorine is likely to be present as sodium salt (NaCl) suggesting that As may have been partly dissolved in pore water. Arsenic also correlates with Mo (0.39), possibly indicating that some of the molybdenum is dissolved in

water. The correlation with sulphur, which frequently forms minerals with arsenic, is relatively weak (0.29).

### Potassium

Potassium displays a strong negative correlation with Si (-0.69) and S (-0.38), indicating that it is unlikely to be found within quartz or pyrite. Potassium can be considered to be hosted almost exclusively within clay minerals. Positive correlations with Rb (0.72), Nb (0.64), Al (0.65), Sr (0.28), V (0.26) also support a close association with clays. Potassium also has strong correlation with Ti (0.59), Fe (0.58), Zr (0.55) and Th (0.42) which probably indicates the presence of zircon and ilmenite within the clay rich fraction.

### Uranium

The correlation between U and Mo is stronger in the altered zone (unaltered 0.64, altered 0.86). The correlation with Nb (unaltered 0.28, altered 0.48) also increases while Ti (unaltered 0.30, altered 0.22) decreases slightly. U now shows a correlation Rb (unaltered 0.13, altered 0.39) suggesting that U is more common within clays in the altered zone.

### Molybdenum

The correlation between Mo and, Zr (unaltered 0.28, altered 0.14), Th (unaltered 0.26, altered 0.04), As (unaltered 0.39, altered 0.13), S (unaltered 0.30, altered 0.17), Cl (unaltered 0.25, altered -0.09), and Nb (unaltered 0.38, altered 0.33) decreases in the altered zone while. Although the correlation between Mo and U (unaltered 0.64, altered 0.86) increased; there were no other strong increases in correlation. The lack of correlation with other elements suggests that Mo precipitating as an oxide or with another element which has not been analyzed. Interestingly, Mo appears to have a much stronger correlation with Cr (unaltered -0.08, altered 0.20) that cannot be readily reconciled with mineralogical observations.

## GEOCHEMICAL DATA: PEPEGOONA EAST ALTERED ZONE

Table 4: Correlation between elements in the altered zone of the Pepegoona East Deposit based on geochemical data

	<i>Mo</i>	<i>Zr</i>	<i>Sr</i>	<i>U</i>	<i>Rb</i>	<i>Th</i>	<i>As</i>	<i>Zn</i>	<i>Fe</i>	<i>Cr</i>	<i>V</i>	<i>Ti</i>	<i>Ca</i>	<i>K</i>	<i>S</i>	<i>Ba</i>	<i>Nb</i>	<i>Bi</i>	<i>Al</i>	<i>Si</i>	<i>Cl</i>
<i>Mo</i>	1.00																				
<i>Zr</i>	0.14	1.00																			
<i>Sr</i>	0.11	0.38	1.00																		
<i>U</i>	0.86	0.24	0.15	1.00																	
<i>Rb</i>	0.33	0.42	0.19	0.39	1.00																
<i>Th</i>	0.04	0.58	0.45	0.13	0.70	1.00															
<i>As</i>	0.13	-0.05	-0.05	0.02	-0.10	-0.10	1.00														
<i>Zn</i>	0.18	-0.05	-0.03	0.06	-0.05	0.04	0.05	1.00													
<i>Fe</i>	0.14	0.10	0.03	0.01	0.37	0.39	0.27	0.07	1.00												
<i>Cr</i>	0.20	-0.15	-0.20	0.01	-0.18	0.00	0.09	0.61	0.42	1.00											
<i>V</i>	0.13	0.32	0.18	0.10	0.12	0.17	0.27	0.12	0.01	0.16	1.00										
<i>Ti</i>	0.19	0.66	0.49	0.22	0.20	0.36	-0.03	0.00	0.05	-0.17	0.34	1.00									
<i>Ca</i>	0.04	0.04	0.09	-0.01	0.28	0.06	-0.11	-0.07	0.14	-0.24	0.03	0.03	1.00								
<i>K</i>	-0.04	0.32	0.08	-0.01	0.79	0.62	-0.14	-0.13	0.47	-0.32	-0.02	0.07	0.19	1.00							
<i>S</i>	0.17	-0.14	-0.07	0.05	-0.11	-0.08	0.40	0.24	0.64	0.66	0.12	-0.07	-0.03	-0.18	1.00						
<i>Ba</i>	0.04	0.13	0.11	0.00	-0.17	-0.17	0.27	0.15	-0.02	0.14	0.52	0.32	0.01	-0.25	0.06	1.00					
<i>Nb</i>	0.33	0.70	0.24	0.48	0.69	0.67	-0.11	-0.07	0.15	-0.23	0.12	0.39	0.07	0.49	-0.19	-0.14	1.00				
<i>Bi</i>	-0.07	0.47	0.43	0.01	0.59	0.99	-0.08	0.00	0.33	-0.03	0.15	0.26	0.03	0.53	-0.09	-0.17	0.55	1.00			
<i>Al</i>	0.12	0.27	0.11	0.19	0.52	0.54	0.01	0.10	0.21	-0.01	0.12	0.32	-0.07	0.49	-0.05	-0.15	0.32	0.45	1.00		
<i>Si</i>	-0.20	-0.21	0.02	-0.12	-0.50	-0.44	-0.12	-0.16	-0.59	-0.46	-0.04	-0.20	-0.10	-0.51	-0.34	0.17	-0.28	-0.35	-0.60	1.00	
<i>Cl</i>	-0.09	-0.06	-0.10	-0.10	-0.14	-0.04	-0.07	0.03	-0.35	0.01	0.22	-0.18	-0.11	-0.16	-0.16	-0.07	-0.01	-0.05	-0.09	0.19	1.00

## Arsenic

Correlation with Fe (unaltered -0.13, altered 0.27) increases significantly while As no longer correlates with Cl (unaltered 0.36, altered -0.07), indicating that As has been taken out of solution in a reaction involving Fe. Correlation with Mo (unaltered 0.39, altered 0.13) is now very weak.

The correlation with S has increased, (unaltered 0.29, altered 0.40), suggesting the presence of As within pyrite. The correlation with V (unaltered 0.14, altered 0.27), and Ba (unaltered -0.13, altered 0.27) increases, indicating a closer association with clays.

## Potassium

Potassium shows a significantly decreased correlation with Sr (unaltered 0.28, altered zone 0.08), Cr (unaltered -0.03, altered -0.32), V (unaltered 0.26, altered -0.02), Ba (unaltered -0.14, altered -0.25) and Ti (unaltered 0.59, altered 0.07), suggesting that clays host less K in the altered zone. The correlation with Al (unaltered 0.65, altered 0.49), Zr (unaltered 0.55, altered 0.32) and Nb (unaltered 0.64, altered 0.49) decreases but remain strong, possibly indicating variation in K concentrations dependent on clay mineral speciation. The correlation coefficient between K and Th increases from unaltered (0.42) to altered (0.62), probably indicating variation in the abundance of Th hosting minerals between clay types.

## Uranium

Uranium has strong correlation with Nb (0.67), Rb (0.65), K (0.49), Al (0.43) and V (0.40), indicating that clay minerals host a significant portion of uranium. The strong correlation with Th (0.64) suggests that separation due to selective inclusion in minerals has not occurred to the same extent as in Pepegoona, although the strong correlation with Ti (0.51) indicates

## GEOCHEMICAL DATA: PANNIKAN UNALTERED ZONE

Table 5: Correlation between elements in the unaltered zone of the Pannikan Deposit based on geochemical data

	<i>Mo</i>	<i>Zr</i>	<i>Sr</i>	<i>U</i>	<i>Rb</i>	<i>Th</i>	<i>As</i>	<i>Zn</i>	<i>Fe</i>	<i>Cr</i>	<i>V</i>	<i>Ti</i>	<i>Ca</i>	<i>K</i>	<i>S</i>	<i>Ba</i>	<i>Nb</i>	<i>Bi</i>	<i>Al</i>	<i>Si</i>	<i>Cl</i>
<i>Mo</i>	1.00																				
<i>Zr</i>	0.20	1.00																			
<i>Sr</i>	-0.22	0.31	1.00																		
<i>U</i>	-0.25	0.42	0.28	1.00																	
<i>Rb</i>	-0.09	0.26	0.54	0.65	1.00																
<i>Th</i>	0.25	0.84	0.46	0.64	0.59	1.00															
<i>As</i>	0.55	0.26	-0.01	0.21	0.40	0.43	1.00														
<i>Zn</i>	0.43	0.01	0.01	0.02	0.01	0.02	-0.12	1.00													
<i>Fe</i>	-0.11	0.18	0.84	0.22	0.50	0.33	0.15	0.01	1.00												
<i>Cr</i>	0.68	0.30	0.38	0.03	0.18	0.15	0.37	-0.01	0.42	1.00											
<i>V</i>	0.23	0.42	0.07	0.40	0.27	0.56	0.68	0.04	0.07	-0.03	1.00										
<i>Ti</i>	-0.05	0.54	0.72	0.51	0.54	0.67	0.20	0.13	0.62	0.33	0.36	1.00									
<i>Ca</i>	-0.41	0.11	0.80	0.14	0.42	0.19	-0.27	0.03	0.73	0.27	-0.10	0.56	1.00								
<i>K</i>	-0.02	0.19	0.65	0.49	0.80	0.52	0.31	0.04	0.62	0.19	0.25	0.65	0.49	1.00							
<i>S</i>	0.49	-0.18	-0.12	-0.21	-0.24	-0.17	0.03	0.13	0.12	0.27	-0.02	-0.09	0.05	-0.11	1.00						
<i>Ba</i>	-0.26	0.04	0.22	-0.04	-0.03	0.00	-0.12	-0.01	0.12	-0.11	0.09	0.13	0.15	-0.01	0.16	1.00					
<i>Nb</i>	0.01	0.71	0.40	0.67	0.55	0.90	0.40	-0.01	0.26	0.01	0.53	0.64	0.18	0.51	-0.28	-0.06	1.00				
<i>Bi</i>	0.28	0.82	0.47	0.58	0.55	0.99	0.42	0.01	0.38	0.56	0.47	0.67	0.21	0.44	-0.16	0.00	0.87	1.00			
<i>Al</i>	0.36	0.23	0.24	0.35	0.47	0.43	0.59	0.16	0.31	0.11	0.44	0.46	0.00	0.59	-0.01	-0.05	0.40	0.29	1.00		
<i>Si</i>	0.12	-0.43	-0.61	-0.28	-0.48	-0.51	-0.12	0.12	-0.56	-0.41	-0.20	-0.56	-0.47	-0.55	0.11	-0.02	-0.37	-0.52	-0.50	1.00	
<i>Cl</i>	0.34	-0.17	-0.59	-0.03	-0.21	-0.15	0.66	0.06	-0.46	-0.26	0.19	-0.41	-0.66	-0.30	-0.10	-0.30	-0.11	-0.21	0.07	0.25	1.00

that Ti-bearing minerals are still an important host. Uranium displays a weak correlation with Fe (0.22) and As (0.21) which may be due to the presence of both elements within clays. As with the Pepegoona deposit, U has a weaker than average negative correlation with Si (-0.28) indicating that a small amount of U is hosted within quartz.

### Molybdenum

Molybdenum has a strong correlation with S (0.49) and Cl (0.34), possibly indicating the presence of molybdenite and molybdenum chloride. Molybdenum also has strong correlation with Zn (0.43), Al (0.36) and Cr (0.68) which likely indicate the presence of molybdenum in clays. Molybdenum also has a strong correlation with As (0.55) which also appears to be hosted by clays. Molybdenum has negative correlation with Ca (-0.41), Ba (-0.26), U (-0.25) and Sr (-0.22) suggesting that it may be preferentially hosted by selected clay mineral species. Molybdenum has a weak positive correlation with Si (0.12) which indicates that some molybdenum may be hosted in sand grains, or absorbed on their margins.

### Arsenic

Arsenic has a strong correlation with V (0.68), Al (0.59), Mo (0.55), Th (0.43), Rb (0.40), Nb (0.40), Cr (0.37) and K (0.31), suggesting that most of the arsenic is hosted by clays. There is also a strong correlation with Cl (0.66) indicating that As is present in pore water. Arsenic displays a negative correlation with Ca (-0.27) which may, potentially, be blocking adsorption onto clays.

### Potassium

Potassium has a strong correlation with Rb (0.80), Ca (0.49), V (0.25), As (0.31), Th (0.52), U (0.49), Sr (0.65), Nb (0.51) and Al (0.59), suggesting that K is strongly controlled by clay abundance. A strong correlation with Ti (0.65) and Fe (0.62) probably suggests with the

presence of ilmenite within those clays. The negative correlation with Si (-0.55) and Cl (-0.30) indicates that K is not present in quartz or pore water.

Note: only 17 samples from the altered zone of the Pannikan deposit could be analyzed .

There also appears to be a change in sedimentary conditions resulting in an increase in silica content which likely impacts on results and correlations.

## Uranium

The negative relationship between U and Si is even weaker in the altered zone (unaltered -0.28, altered -0.05), the altered zone contains more silica than the unaltered zone and as a result much of the uranium is likely to be found in minerals within quartz or on mineral films along grain boundaries. The correlation between U and Al (unaltered 0.35, altered 0.04), Rb (unaltered 0.65, altered 0.19) and K (unaltered 0.49, altered -0.05) has significantly decreased, this indicates that clays host very little of the total uranium budget. Correlations with Ti (unaltered 0.51, altered -0.14) and Fe (unaltered 0.22, altered -0.17) are now negative indicating a lack of U- and Ti-bearing minerals in the altered zone. Correlation with As (unaltered 0.21, altered -0.44) and Ca (unaltered 0.14, altered -0.33) are also now strongly negative, which may indicate that U adsorption onto clays has been prevented by the presence of these elements. Correlation increased significantly with Mo (unaltered -0.25, altered 0.60) and Cl (unaltered -0.03, altered 0.31), both of which have positive correlation with silica suggesting that they may form minerals within quartz grains, correlation with chlorine may also indicate the presence of dissolved uranium. Correlation with V (unaltered 0.40, altered 0.47), Nb (unaltered 0.67, altered 0.46) and Th (unaltered 0.64, altered 0.45) remained stable possibly representing the small fraction of U adsorbed onto clays.

### Geochemical data: Pannikan altered zone

Table 6: Correlation between elements in the altered zone of the Pannikan Deposit based on geochemical data

	Mo	Zr	Sr	U	Rb	Th	As	Zn	Fe	Cr	V	Ti	Ca	K	S	Ba	Nb	Bi	Al	Si	Cl
Mo	1.00																				
Zr	-0.41	1.00																			
Sr	-0.49	0.88	1.00																		
U	0.60	-0.01	-0.15	1.00																	
Rb	-0.13	0.84	0.67	0.19	1.00																
Th	-0.11	0.71	0.45	0.46	0.87	1.00															
As	-	-0.52	-0.52	-0.44	-0.46	-0.66	1.00														
Zn	-0.89	0.25	0.27	-0.14	0.11	0.00	0.24	1.00													
Fe	-0.58	0.46	0.58	-0.17	0.35	0.14	0.00	0.88	1.00												
Cr	-	-	-	-	-	-	-	-	-	1.00											
V	-0.22	0.23	0.03	0.47	0.42	0.57	-0.02	0.69	0.41	-	1.00										
Ti	-0.54	0.72	0.82	-0.14	0.66	0.43	-0.53	0.50	0.77	-	0.30	1.00									
Ca	-0.70	0.66	0.83	-0.33	0.40	0.10	-0.22	0.62	0.70	-	-0.02	0.81	1.00								
K	-0.56	0.85	0.82	-0.05	0.83	0.65	-0.45	0.51	0.71	-	0.41	0.92	0.73	1.00							
S	-0.28	-0.26	-0.06	0.19	-0.29	-0.28	0.17	0.53	0.51	-	0.21	0.27	0.19	0.02	1.00						
Ba	-0.53	0.68	0.55	0.16	0.66	0.47	-0.81	0.20	0.20	-	0.15	0.59	0.47	0.57	-0.14	1.00					
Nb	0.03	0.76	0.50	0.46	0.92	0.95	-0.56	0.04	0.16	-	0.58	0.49	0.15	0.67	-0.22	0.62	1.00				
Bi	-0.15	0.64	0.27	0.36	0.85	0.95	-0.28	0.10	-0.06	-	0.51	0.18	-0.04	0.49	-0.46	0.37	0.92	1.00			
Al	-0.50	0.57	0.68	0.04	0.57	0.40	-0.43	0.51	0.72	-	0.34	0.82	0.65	0.83	0.22	0.49	0.37	0.04	1.00		
Si	0.34	-0.58	-0.37	-0.05	-0.65	-0.60	0.41	-0.54	-0.43	-	-0.63	-0.56	-0.29	-0.65	0.20	-0.56	-0.70	-0.65	-0.36	1.00	
Cl	0.80	-0.55	-0.75	0.31	-0.56	-0.34	0.36	-0.29	-0.60	-	-0.06	-0.79	-0.63	-0.73	-0.15	-0.33	-0.31	0.03	-0.75	0.20	1.00

### Molybdenum

Molybdenum has a strong positive correlation with Si in the altered zone (unaltered 0.12, altered 0.34), indicating that like uranium, much of the Mo is either hosted by minerals within quartz or on minerals forming on grain boundaries. Correlation between Mo and every major element except for Si, Cl (unaltered 0.34, altered 0.80), Nb (unaltered 0.01, altered 0.03), Rb (unaltered -0.09, altered -0.13) and Th (unaltered 0.25, altered -0.11) becomes strongly negative in the altered zone, probably indicating the presence of these elements within quartz. There is a very strong correlation between Mo and Cl which may be partly due to chlorapatite within quartz but may also indicate that Mo is found in solution together with sodium chloride.

### Arsenic

As with uranium and molybdenum, there is a significantly greater correlation between As and Si in the altered zone (unaltered -0.12, altered 0.41), which either represents As-bearing minerals hosted by quartz or formation of As-bearing minerals along quartz grain boundaries. Correlation with all other elements, with exception of Zn (unaltered -0.12, altered 0.24), S (unaltered 0.03, altered 0.17) and Cl (unaltered 0.66, altered 0.36) is now negative indicating that clay is not a major As-host in the altered zone. The persistent correlation with Cl suggests that As may still be present in pore water.

### Potassium

Potassium has a very strong negative correlation with Si (unaltered -0.55, altered -0.65) and is unlikely to be found in significant concentrations within quartz. Other significant correlations are found with Nb (unaltered 0.51, altered 0.67), Al (unaltered 0.59, altered 0.83), Sr (unaltered 0.65, altered 0.82), Th (unaltered 0.52, altered 0.65), Fe (unaltered

0.62, altered 0.71), V (unaltered 0.25, altered 0.41), Ti (unaltered 0.65, altered 0.92), Ca (unaltered 0.49, altered 0.73) and Rb (unaltered 0.80, altered 0.83), probably reflecting a decrease in abundance of clay instead of a real change in mineral speciation. Increased correlation with Ba (unaltered -0.01, altered 0.57), Zr (unaltered 0.19, altered 0.85) and Zn (unaltered 0.04, altered 0.51), suggests that zircon may be more common in the clay fraction than the quartz fraction in the altered zone. A strong negative correlation between K and Mo (unaltered -0.02, altered -0.56), U (unaltered 0.49, altered -0.05), As (unaltered 0.31, altered -0.45) and Cl (unaltered -0.30, altered -0.73) probably reflects their absence in the clay fraction.

### **SUMMARY:**

**Uranium** appears to be hosted by a combination of clays, Ti-minerals and minerals within quartz grains in the unaltered zones of both deposits. Clays appear to be more significant as hosts within the Pannikan deposit while Pepegoona appears to contain a greater abundance of U-bearing titanium minerals. Neither deposit has a single host for uranium in unaltered sediments.

In the altered zone of the Pannikan deposit, U appears to have had the greatest increase in the clay fraction of the samples with increased correlation with Al and Rb. In the Pepegoona East deposit it appears that the greatest increase in U concentrations was in the quartz-rich regions of the samples, this may be partly due to the increase in quartz between the unaltered and altered zones, however mineralisation is known to occur along quartz grain boundaries, a more likely explanation of the observed relationship.

As with uranium, **molybdenum** appears to have multiple hosts in the unaltered zones of both deposits including minerals within quartz grains, clays also appear to be a more significant host in the Pannikan deposit. In the altered zone of the Pepegoona East deposit, Mo has only a weak correlation with other elements, suggesting that Mo is dispersed throughout the sample and is likely to have mineralised in combination with another element which is not detectable using these methods (possibly oxygen). In the Pannikan deposit, Mo has a strong correlation with Si which suggests a similar behaviour to U, forming mineralisation along grain boundaries.

**Arsenic** has a strong correlation with Cl in the unaltered zone of the Pepegoona East deposit and is likely to be dissolved in water. In the Pannikan deposit arsenic has a strong correlation with Cl, indicating dissolved As but it also has strong correlation with minerals associated with clays. In the altered zone of the Pepegoona East deposit, As appears to be reacting with Fe, which removes As from solution and reduces correlation with Cl. In the Pannikan deposit, correlation with Si once again increases significantly, suggesting that arsenic is mineralizing around grains of quartz.

**Potassium** has a very strong link with clay elements in the unaltered zones of both deposits, clay is the likely host in both cases. Decreased K concentrations in the altered zone of the Pepegoona East deposit are linked to decreased correlation with some but not all of the elements associated with clays, this may indicate selective leaching from certain types of clay. At Pannikan, decreased K concentrations are hard to link to correlation data due to the silica increase, which may be partly responsible for the decreased concentration, however K decreases more significantly than other clay elements which suggests that identical processes impact on the two deposits.

## DISCUSSION

### URANIUM AS A PATHFINDER FOR URANIUM

Table 7: Geochemical alteration indicators based on changes in uranium concentration

	U	U/Th	U-(Th/3)	U/Zr*100	U/Ti*1000	U/Al*10000	U/K
<b>Pepegoona East</b>							
deposit specific critical value <sup>1</sup>	>26=altered	>1.7=altered	>21=altered	>13=altered	>8.5=altered	>6.5=altered	>4=altered
viable samples unaltered zone (out of 129)	115	115	115	115	115	115	115
viable samples altered zone (out of 202)	202	190	191	196	196	196	196
% unaltered identified as unaltered	95.65%	95.65%	94.78%	93.91%	94.78%	90.40%	93.91%
% altered identified as altered	33.67%	43.68%	35.60%	42.35%	35.71%	55.41%	45.41%
 <b>Pannikan</b>							
deposit specific critical value <sup>1</sup>	>20=altered	>0.80=altered	>7=altered	>10=altered	>7=altered	>4.5=altered	>1.5=altered
viable samples unaltered zone (out of 73)	73	73	73	73	73	73	73
viable samples altered zone (out of 17)	14	14	14	14	14	14	14
% unaltered identified as unaltered	95.89%	94.52%	97.26%	100.00%	95.24%	90.48%	94.52%
% altered identified as altered	21.43%	71.43%	35.71%	35.71%	35.71%	42.86%	35.71%
best fit critical value <sup>2</sup>	>23=altered	>0.95=altered	>6.5=altered	>10=altered	>5.5=altered	>4.5=altered	>2.5=altered
% unaltered identified as unaltered	98.63%	95.89%	90.41%	100.00%	85.71%	90.48%	97.26%
% altered identified as altered	21.42%	42.86%	42.86%	35.71%	35.71%	42.86%	21.43%

<sup>1</sup>The deposit specific critical value represents the optimum value for distinguishing between altered and unaltered sediments within a given deposit, with samples returning higher values interpreted as being altered. Values were selected with the aim of <5% probability of a false positive where possible.

<sup>2</sup>The best fit critical value represents a compromise between the deposit specific critical values, in most cases it is the average of the two values.

(U)

Uranium concentrations are elevated in the unaltered zones of both roll fronts relative to unaltered sediments. The increase in uranium concentrations alone can be used in exploration; however the accuracy is inhibited by variations in sediments composition. Uranium could be used independently to correctly identify 45.41% of altered samples in

the Pepegoona East deposit with 12.17% of unaltered samples misidentified. In the Pannikan deposit 21.42% of altered samples were correctly identified with only 1.37% of unaltered samples misidentified.

### (U/Th)

Uranium and thorium have similar chemical properties and very similar molecular weights (238.03 and 232.04, respectively) atomic radii and electron configurations (Adams *et al.* 1959). As a result, uranium and thorium tend to occur together in high temperature systems (Mernagh & Miezitis 2007). Uranium and thorium are incompatible elements which are far more abundant in the Earth's crust than in the mantle. Granitic magmas are often enriched in U and Th due to crustal recycling and fractionation, Palaeozoic intrusions from the Australian shield are often unusually high (Mernagh & Miezitis 2007). The abundance of Th at the Earth's surface is roughly triple that of uranium, however Th is rarely concentrated, making it harder to exploit (McDiarmid *et al.* 2001). The key difference between the two elements in terms of dispersion is the water solubility of U in its oxidised state (Zacharias *et al.* 2008). Thorium remains water-insoluble under oxidising conditions, only dissolving under extremely acidic conditions (McDiarmid *et al.* 2001). This property of uranium is key to the formation of roll fronts where oxidizing groundwaters dissolve uranium, forming mineralized zones where the aquifer meets a reduced environment. Host minerals for Th are often highly resistant to weathering as well as highly insoluble in water (Langmuir & Herman 1980), the ability of thorium to remain insoluble under changing oxidation states means that its distribution will be largely controlled by sedimentary processes.

Monazite represents the most significant Th-host in many systems however thorium can also be found in abundance in thorianite, thorite and thorogummite. Smaller amounts of thorium can be found in xenotime, fluorapatite, zircon, titanite and other accessory minerals. Thorium can often be enriched in the oxidised zones of U-Th mineral deposits due to the resistance of Th-bearing minerals to oxidation (Mernagh & Miezitis 2007).

The strong connection between uranium and thorium which is only usually broken under oxidising conditions makes their relative abundance a powerful exploration tool. Care should be taken in the presence of abundant rutile or brannerite which are capable of increasing the relative abundance of uranium in unaltered sediments. The ratio of U/Th is a very effective indicator of past redox conditions, although the unaltered sediments of Pepegoona East appear to have a higher average ratio than sediments of the Pannikan deposit.

The ratio of uranium to thorium correctly identifies 61.58% of altered samples in the Pepegoona East deposit with 19.13% of unaltered samples misidentified. In samples of the Pannikan deposit 42.86% of altered samples were correctly identified while 4.11% of unaltered samples were misidentified.

### Authigenic Uranium (U-(Th/3))

The link between U and Th can also be used to calculate the difference between expected detrital uranium concentration and actual uranium concentration. The results are likely to be very similar to U/Th but give a better indication of the numerical significance of anomalous values. In the Pepegoona East deposit 69.63% of altered samples were correctly identified using this method with 26.19% of unaltered samples misidentified. In the Pannikan deposit 42.86% of altered samples were correctly identified while 9.59% of unaltered samples were misidentified.

### (U/Zr), (U/Ti)

Zircon and titanium host at least part of the uranium and are present in the clay fractions of both deposits. Both elements are strongly controlled by sedimentary composition and can be used as a correction against changes in sediment composition.

In samples from the Pepegoona East deposit the ratio of uranium to zircon correctly identified 60.33% of altered samples with 16.95% of unaltered samples misidentified. In the Pannikan deposit 35.71% of altered samples were correctly identified with no unaltered samples incorrectly identified as altered.

The Ratio of uranium to titanium was slightly less effective, correctly identifying 70.82% of altered samples but incorrectly identifying 26.55% of unaltered samples. In samples from the Pannikan deposit 35.71% of altered samples were correctly identified while 14.29% of unaltered samples were misidentified.

### (U/Al), (U/K)

Aluminium and Potassium are strongly linked to the clay fraction of the samples, and as a result their changing abundance reflects sedimentary composition. Potassium appears to be depleted in the altered zone, which enhances change across the mineralised zone while also correcting for sediment composition. The ratio of uranium to aluminium positively identified 74.10% of altered samples and misidentified 23.16% of unaltered samples in the Pepegoona East deposit while 42.86% of altered samples in the Pannikan deposit with 9.52% of unaltered samples misidentified.

The ratio of uranium to potassium correctly identified 64.80% of altered samples in the Pepegoona East deposit while 13.04% of unaltered samples were misidentified. In the Pannikan deposit 21.43% of altered samples were correctly identified while only 2.74% of unaltered samples were misidentified.

## ARSENIC AS A PATHFINDER FOR URANIUM

Table 8: Geochemical alteration indicators based on changes in arsenic concentration

	As	As/Fe*1000	(As/Fe)/(Cl/As)*10000	As/Al*1000	As/K*1000
<b>Pepegoona East</b>					
deposit specific critical value <sup>1</sup>	>9=altered	>1.52=altered	>0.1=altered	>0.3=altered	>1.2=altered
viable samples unaltered zone (out of 129)	40	40	40	40	40
viable samples altered zone (out of 202)	115	115	115	115	115
% unaltered identified as unaltered	90%	91.53%	80.00%	85.00%	87.50%
% altered identified as altered	29.57%	42.67%	54.78%	43.48%	57.39%
best fit critical value <sup>2</sup>	>9=altered	>1=altered	>0.1=altered	>0.26=altered	>1=altered
% unaltered identified as unaltered	90%	77.97%	85.00%	79.66%	77.50%
% altered identified as altered	29.57%	59.33%	39.13%	42.00%	60.00%
<b>Pannikan</b>					
deposit specific critical value <sup>1</sup>	>9=altered	>1=altered	>0.1=altered	>0.23=altered	>0.93=altered
viable samples unaltered zone (out of 73)	30	30	29	30	30
viable samples altered zone (out of 17)	6	6	6	6	6
% unaltered identified as unaltered	93.33%	76.92%	93.10%	86.67%	93.33%
% altered identified as altered	50.00%	33.33%	50.00%	50.00%	50.00%
best fit critical value <sup>2</sup>	>9=altered	>1=altered	>0.1=altered	>0.26=altered	>1=altered
% unaltered identified as unaltered	93.33%	76.92%	82.76%	92.31%	93.33%
% altered identified as altered	50.00%	33.33%	50%	50.00%	50.00%

<sup>1</sup>The deposit specific critical value represents the optimum value for distinguishing between altered and unaltered sediments within a given deposit, with samples returning higher values interpreted as being altered. Values were selected with the aim of <5% probability of a false positive where possible.

<sup>2</sup>The best fit critical value represents a compromise between the deposit specific critical values, in most cases it is the average of the two values.

(As)

Arsenic concentrations are elevated in the unaltered zones of both roll fronts although the effect is weaker than with uranium. The average unaltered abundance of arsenic is fairly consistent between the two deposits with low variability. Unfortunately detection limits reduce the usefulness of arsenic as it is only detectable in around half the samples.

Using arsenic alone as an indicator of past redox conditions yields mixed results, the altered zone of the Pannikan deposit could be detected in 50% of altered samples with only a 6.67% chance of a false positive. In the Pepegoona East deposit only 29.57% of samples could be identified as altered with a 10% chance of a false positive.

#### (As/Fe)

Arsenic is a redox sensitive element which is present in small concentrations in ground water. Pyrite is capable of hosting large amounts of arsenic but will not accept arsenic into its structure after crystallisation (O'Day *et al.* 2004), which prevents accumulation of arsenic in unaltered sediments. Under oxidising conditions pyrite is converted into iron oxides which adsorb arsenic resulting in an increase in abundance over time.

Microbial re-reduction forces arsenic back into suspension but also results in the formation of pyrite which incorporates arsenic into its structure as it forms (Lowers *et al.* 2007). The increased concentration of arsenic in the newly formed pyrite will not change even after arsenic concentrations in the rest of the sediment decline. This process requires a rate of pyrite crystallisation which is more rapid than depletion of arsenic due to ground water flow (O'Day *et al.* 2004).

Using a ratio of As to Fe we can detect alteration in 42.67% of altered samples in the Pepegoona East deposit with an 8.47% chance of a false positive. The ratio doesn't work at all however in the Pannikan deposit where altered and unaltered sediments have the same probability of returning a positive reading, this may be due to an abundance of iron in minerals other than pyrite within the Pannikan deposit.

### (As, Fe and Cl)

The relationship between iron and arsenic can be diluted by the presence of iron-titanium minerals and clays, this can be compensated for using the relationship between arsenic and chlorine. Arsenic appears to be abundant in ground water in the unaltered zone, correlating strongly with chlorine which is likely to represent sodium salt. The ratio (As/Fe)/(Cl/As) is a measure of the abundance of arsenic relative to Fe and Cl which should indicate whether As predominantly found in the dilute or solid phase. This method can be used to positively identify 39.13% of altered samples in the Pepegoona East deposit with a 15% probability of false positives and 50% of altered samples in the Pannikan deposit with a 17.24% probability of a false positive.

### (As/K), (As/Al)

Arsenic is bound to clays in sediments of both deposits and as a result K and Al can be used to correct for variations within the sediments.

Using K as a correction positively identifies 60.00% of altered samples with a 22.5% probability of false positive in unaltered samples within the Pepegoona East deposit while 50% of altered samples could be correctly identified within the Pannikan deposit with a 6.67% chance of a false positive.

Using Al correctly identified 42% of altered samples in the Pepegoona East deposit with 20.34% of unaltered samples returning a false positive.

In the Pannikan deposit 50% of altered samples could be correctly identified with 7.69% of unaltered samples returning a false positive.

## MOLYBDENUM AS A PATHFINDER FOR URANIUM

Table 9: Geochemical alteration indicators based on changes in molybdenum concentration

	Mo	Mo/K*1000	Mo/Si*10000
<b>Pepegoona East</b>			
deposit specific critical value <sup>1</sup>	>7.5=altered	>1.8=altered	>0.4=altered
viable samples unaltered zone (out of 203)	54	54	54
viable samples altered zone (out of 314)	143	143	143
% unaltered identified as unaltered	88.89%	92.59%	94.44%
% altered identified as altered	43.36%	42.01%	20.98%
best fit critical value <sup>2</sup>			
% unaltered identified as unaltered	88.89%	81.48%	87.04%
% altered identified as altered	43.36%	62.94%	35.66%
<b>Pannikan</b>			
deposit specific critical value <sup>1</sup>	>7.5=altered	>0.6=altered	>0.27=altered
viable samples unaltered zone (out of 29)	18	18	18
viable samples altered zone (out of 17)	7	7	7
% unaltered identified as unaltered	94.44%	77.78%	94.44%
% altered identified as altered	28.57%	57.14%	28.57%
best fit critical value <sup>2</sup>			
% unaltered identified as unaltered	94.44%	100%	100.00%
% altered identified as altered	28.57%	14.29%	14.29%

<sup>1</sup>The deposit specific critical value represents the optimum value for distinguishing between altered and unaltered sediments within a given deposit, with samples returning higher values interpreted as being altered. Values were selected with the aim of <5% probability of a false positive where possible.

<sup>2</sup>The best fit critical value represents a compromise between the deposit specific critical values, in most cases it is the average of the two values.

(Mo)

Molybdenum is redox sensitive and increases in abundance across the roll front.

However the change in abundance between the altered and unaltered zones is less than either Uranium or Arsenic which along with the lack of association with other elements limits the usefulness of molybdenum as an alteration indicator.

Molybdenum by itself appears to be a reasonably effective pathfinder, 43.36% of altered samples could be positively identified in the Pepegoona East deposit with 11.11% of

unaltered samples giving positive readings. In the Pannikan deposit Molybdenum could be used to correctly identify 28.57% of altered samples with only 5.56% of unaltered samples giving positive readings.

#### (Mo/K), (Mo/Si)

Attempts to use insoluble elements to correct for sediment variation did not significantly improve accuracy, aluminium proved ineffective with Potassium and Silica were slightly better. Correction using Potassium was more effective than Silicon, positively identifying 62.94% of altered samples from the Pepegoona East deposit with 18.52% of unaltered samples giving false positive readings. 14.29% of altered samples in the Pannikan deposit were correctly identified with no false positives from the unaltered zone. Correction using silica correctly identified 35.66% of altered samples in the Pepegoona East deposit while 12.96% of unaltered samples were incorrectly identified.

### **PRACTICAL APPLICATION OF HANDHELD XRF**

The use of a handheld XRF device allows for rapid analysis of samples at minimal cost. However the technology should be used with caution. Use of a handheld XRF device may result in datasets which is less precise than would be achieved with conventional XRF technologies. Use of portable XRF will also restrict the range of elements which can be detected. Handheld XRF is also prone to software error as was the case with bismuth and thorium in this study, an issue which was only detected following statistical analysis of the complete data set.

## CONCLUSIONS

Oxidation of sediments in the Lake Frome basin results in geochemical changes which can be detected even after the system returns to a reduced state. The most significant changes relate to the concentrations of arsenic, uranium and molybdenum which are carried with the oxidising fluid and accumulate at the redox front. Large deviations from crustal U-Th ratio are a strong indicator of oxidation. Arsenic enrichment in pyrites can also indicate the influence of an oxidising fluid where pyrite is a major component of the sediment. Molybdenum concentrations are increased by inclusion in pyrite and adsorption onto clays.

The range of elements which could be surveyed has been restricted partially by the use of handheld XRF technology, and partially due to time constraints. Use of more conventional equipment or allowing for longer analysis times is likely to allow analysis of elements which are currently below detection limits. The geochemical dataset collected during this study suggested that lead, selenium and mercury may also be used as pathfinder if techniques could be refined enough to measure them, however these elements were rarely above detection limits which made it impossible to use them in this study.

The presence of clays within the system complicates geochemical data. Clays are capable of adsorbing a range of elements including pathfinder elements such as uranium, arsenic and molybdenum significantly increasing their abundance in the altered zone, elemental adsorption is however dependent on a range of factors including temperature, pH and the abundance of other elements. This could become a significant

factor in sediments outside the Eyre Formation which is predominantly sand, particularly in sediments such as the Namba Formation which hosts the Beverley deposit which is mostly silt.

This study has been limited to two deposits which has allowed comparisons to be made but would greatly benefit from data outside of the Pannikan and Pepegoona systems. Conclusions drawn from geochemical data in this study are based on geochemical relationships where possible but may be biased by the unique situation of each deposit, the Pannikan ore body in particular appears to have formed at a change in sedimentary facies which will have an impact on elemental composition and significantly change results. Analysis of a larger dataset including samples from varied deposits would enable more robust conclusions to be made without bias from localised geochemical variation.

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## REFERENCES

- ADAMS J. A., OSMOND J. K. & ROGERS J. J. 1959. The geochemistry of thorium and uranium. *Physics and Chemistry of the Earth* **3**, 298-348.
- BELOUSOVA E. A., GRIFFIN W. L., O'REILLY S. Y. & FISHER N. I. 2002. Igneous zircon: trace element composition as an indicator of source rock type. *Contributions to Mineral Petrology* **143**, 602-622.
- BRUGGER J., LONG N., MCPHAIL D. C. & PLIMER I. 2005. An active amagmatic hydrothermal system: The Paralana hot springs, Northern Flinders Ranges, South Australia. *Chemical Geology* **222**, 35-64.
- CALLEN R. A. 1975. Stratigraphy, sedimentology and Uranium deposits of tertiary rocks: Lake Frome area, South Australia. bachelor of science thesis, Department of Earth and Environmental Science, University of Adelaide (unpubl.).
- FORCE E. R. 1991. *Geology of Titanium-mineral Deposits*. The Geological Society of America, Inc.
- GRANGER H. C. & WARREN C. G. 1969. Unstable sulfur compounds and the origin of roll-type uranium deposits. *Economic Geology* **64**, 160-171.
- GREY I., MACRAE C., SILVESTER E. & SUSINI J. 2005. Behaviour of impurity elements during the weathering of ilmenite. *Mineralogical Magazine* **69**, 437-446.
- HILL S. M. & HORE S. B. 2011. Key insights into range-front mineral system expression and evolution from regolith and long-term landscape history, NE Flinders Ranges. *Mesa Journal* **63**, 20-31.
- HOBDAY D. K. & GALLOWAY W. E. 1999. Groundwater processes acid sedimentary uranium deposits. *Hydrogeology Journal* **7**, 127-138.
- HOFMANN B. A. 1999. Geochemistry of Natural Redox Fronts - a review. *National Cooperative for the Disposal of Radioactive Waste*.
- INGHAM E. 2012. Pyrite in the Pepegoona, Pepegoona West and Pannikan uranium deposits, Lake Eyre Basin, S.A.: implications for regional uranium exploration. Honours Degree in Geology thesis, Faculty of Science, University of Adelaide (unpubl.).
- INGHAM E. S., COOK N. J., CLIFF J., CIOBANU C. L. & HUDDLESTON A. 2014. A combined chemical, isotopic and microstructural study of pyrite from roll-front uranium deposits, Lake Eyre Basin, South Australia. *Geochimica et Cosmochimica Acta* **125**, 440-465.

- KLEMME S., PROWATKE S., HAMETNER K. & GUNTHER D. 2005. Partitioning of trace elements between rutile and silicate melts: Implications for subduction zones. *Geochimica et Cosmochimica Acta* **69**, 2361-2371.
- LANGMUIR D. & HERMAN J. S. 1980. The mobility of thorium in natural water at low temperatures. *Geochimica et Cosmochimica Acta* **44**, p.1753 to 1766.
- LOWERS H. A., BREIT G. N., FOSTER A. L., WHITNEY J., YOUNT J., UDDIN N. & MUNEEM A. 2007. Arsenic incorporation into authigenic pyrite, bengal basin sediment, Bangladesh. *Geochimica et Cosmochimica Acta* **71**, 2699-2717.
- MCDIARMID M. A., GAITENS J. M. & SQUIBB K. S. 2001. Uranium and Thorium. *Patty's Toxicology*, pp, 769-813, John Wiley & Sons, Inc.,
- MEINHOLD G. 2010. Rutile and its applications in earth sciences. *Earth-Science Reviews* **102**, 1-28.
- MERNAGH T. P. & MIEZITIS Y. 2007. *A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources* Australia G. Geoscience Australia, Canberra.
- NEUMANN N., SANDIFORD M. & FODEN J. 2000. Regional geochemistry and continental heat flow: implications for the origin of the South Australian heat flow anomaly. *Earth and Planetary Science Letters* **183**, 107-120.
- O'DAY P. A., VLASSOPOULOS D., ROOT R. & RIVERA N. 2004. The influence of sulphur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proceedings of the National Academy of Sciences of the United States of America* **101**, 13703-13708.
- ONISHI H. & SANDELL E. B. 1954. Geochemistry of arsenic. *Geochimica et Cosmochimica Acta* **7**, 1-38.
- PAN Y. & FLEET M. E. 2002. Compositions of the Apatite-Group Minerals: Substitution Mechanisms and Controlling Factors. *Reviews in Mineralogy and Geochemistry* **48**, 13-49.
- REDDY K. J., MUNN L. C., WANG L., SMITH K. S., BALISTRERI L. S., SMITH S. M. & SEVERSON R. C. 1997. *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.
- SKIRROW R. G. 2009. Uranium ore-forming systems of the Lake Frome region, South Australia: Regional spatial controls and exploration criteria. *Geoscience Australia Record* **2009/40**, p.151.
- WHITBREAD M. A. 2002. Ratio analysis of bulk geochemical data: tracking ore-related cryptic alterations by modelling mineral changes. In Roach I. C. ed.

*Regolith and Landscapes in Eastern Australia*, pp, 133-135, Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME).

WULSER P. A., BRUGGER J., FODEN J. & PFEIFER H. R. 2011. The Sandstone-Hosted Beverley Uranium Deposit, Lake Frome Basin, South Australia: Mineralogy, Geochemistry, and a Time-Constrained Model for Its Genesis. *Economic Geology* **106**, 835-867.

ZACHARIAS J., ADAMOVIC J. & KONECNY P. 2008. The Uraninite-Pyrite Association, a Sensitive Indicator of Changes in Paleofluid Composition: An Example from the Ohre (Eger) Graben, Bohemian Massif, Czech Republic. *The Canadian Mineralogist* **46**, 1159-1172.

## **APPENDIX 1: XRF DEVICE SPECIFICATIONS AND SAMPLING EQUIPMENT**

See attached

#### XRF specifications and sampling equipment:

The accuracy and repeatability of XRF measurements has been shown to be greatly reduced by moisture content and grain size (Laiho & Peramaki 2005). Moisture content is unlikely to be an issue due to storage of the samples in a ventilated shed for a period exceeding a year. Each sample was pulverised using a glass rod and a ceramic bowl to the finest powder possible and any large pieces which could not be crushed were removed, the result was a set of samples with a fine enough grain to avoid sampling bias. Samples were placed in a plastic sampling cup with a 4.0 $\mu$ m prolene film viewing window, through which readings were taken.

A XL3tGOLDD+ model Niton Portable XRF unit was used with a Niton Portable test stand. The XRF unit was tested with a SiO<sub>2</sub> blank as well as one of several standards issued by the manufacturer when the machine was initial turned on and again before turning the machine off.

## **APPENDIX 2: GEOCHEMICAL DATA**

See Attached







Hole Name	Easting	Northing	Depth (m)	Mo	Zr	Sr	U	Rb	Th	As	Zn	Fe	Cr	V	Tl	Ca	K	S	Ba	Nb	Bi	Al	Si	Cl		
PR1232	360447.5	6667499	258	260		113.73	9.40	6.24	16.11	8.20	11.28	5482.44		72.74	1420.98	165.75	6772.31		56.70	7.01	5.84	22293.94	305075.16	1298.17		
PR1232	360447.5	6667499	260	262	3.30	73.99	8.08	7.87	13.27	8.59	16.15	5691.84		70.55	1096.40		4791.92			5.85	5.33	23127.09	310194.25	1330.94		
PR1232	360447.5	6667499	262	264	8.40	109.67	8.66	66.85	20.96	9.14	10.47	4662.22		81.24	1196.34	229.08	5330.31	931.85		12.63	5.95	24359.15	308789.63	2029.89		
PR1232	360447.5	6667499	264	266		61.56	3.98	12.30	7.51	4.97		2293.89		59.18	1519.37		5284.30	653.70		2.87		21955.54	311284.97	2042.66		
PR1223	360438.2	6667558	206	208		111.05	6.48	5.83	15.80	6.63		2014.66		43.25	1307.80	681.61	4529.14	539.88		8.33		12182.16	263965.09	2277.27		
PR1223	360438.2	6667558	266	268		86.28	5.26		4.98	4.63		2636.97		58.96	1066.72	573.70	4246.71	784.62				19067.36	281626.84	1892.04		
PR1223	360438.2	6667558	242	248		107.59	17.53	2.44	18.54	6.41	1.85	4.55	2903.40		29.00	2310.89	1146.20	6272.90	737.72	158.84	7.35	2.10	22176.39	302531.77	1131.38	
PR1223	360438.2	6667558	258	264		63.22	9.84	3.00	18.18	3.95	33.80	12.67	4232.33		32.73	1263.22	941.33	4717.47	595.02	102.96	4.57	4.10	18131.80	318990.04	1130.52	
PR1223	360438.2	6667558	210	212	5.85	126.48	15.01	44.07	32.62	14.08		5029.31		139.53	2570.86	541.83	7973.97	854.80		23.42	12.63	23821.32	244884.13	1242.41		
PR1223	360438.2	6667558	208	210	3.42	241.47	14.82		43.39	14.24		6691.90		117.57	2096.72	656.58	8945.74	252.24	238.88		23.80	14.34	24189.43	231623.89	1532.55	
PR1223	360438.2	6667558	262	264		88.52	8.09		6.75	5.34		16.58	6818.90		79.02	1200.80	395.29	4671.68	311.71		4.98		18420.96	260229.50	1937.91	
PR1223	360438.2	6667558	214	216	3.96	212.34	16.60	26.03	43.02	15.86		6954.02		92.09	2167.78	603.37	10111.68	276.41	129.14	21.89	17.20	24830.85	238315.89	1275.59		
PR1223	360438.2	6667558	264	266	7.83	132.49	16.73	6.96	30.37	8.43		10.15	7073.97		92.36	1782.27	734.98	7314.83	240.08	102.06	13.08	6.42	24669.25	256910.11	1617.18	
PR1223	360438.2	6667558	234	240		297.31	48.16	12.80	38.54	12.80	4.58	8.33	8144.19		48.48	2814.70	1413.96	9381.65	364.94	189.16	20.05	12.26	26320.44	280890.36	614.07	
PR1223	360438.2	6667558	250	256		133.79	20.21	8.29	27.44	8.07	9.17	12.34	9011.06		52.48	2853.18	1269.88	9076.74	494.28	187.35	9.92	4.00	32863.43	258172.23	766.74	
PR1223	360438.2	6667558	226	232		335.49	53.06	10.62	41.32	11.50	7.69	21.67	16418.35	37.77	71.13	3697.29	4091.72	12803.85	438.48	209.27	18.70	10.39	32604.60	247410.27	782.95	
PR1223	360438.2	6667558	266	272	1.79	175.09	29.05	5.75	26.18	7.45	15.21	29.59	30975.19		26.42	118.92	3858.10	2527.87	11234.80	1540.80	150.53	10.47	4.83	33117.05	247876.01	635.65

