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Geochemical analysis of the regolith of Kangaroo Island: Using portable XRF to identify geochemical signatures to distinguish lithogeochemical horizons and vectors toward mineralization.

Thesis submitted in accordance with the requirements of the University of Adelaide for an Honours Degree in Geology

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Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

GEOCHEMICAL ANALYSIS OF THE REGOLITH OF KANGAROO ISLAND: USING PORTABLE XRF TO RECOGNIZE GEOCHEMICAL SIGNATURES AND TO DISTINGUISH LITHOGEOCHEMICAL HORIZONS AND VECTORS TOWARD MINERALIZATION.

GEOCHEMICAL ANALYSIS OF THE REGOLITH AND COVER SEQUENCE OF KANGAROO ISLAND, SA.

ABSTRACT

Mineralisation overlain by extensive cover can be identified through the geochemical signature dispersed through the surrounding regolith. This project aimed to use portable XRF (pXRF) analysis to increase the understanding of the regolith geochemistry in the proximity of the Cygnet-Snelling Shear Zone (CS-SZ), Kangaroo Island. The shear zone is significant as it hosts several potentially economic deposits including the Bonaventura Copper (Cu) deposit as well as the Dewrang and Kohinoor Lead – Zinc (Pb-Zn) prospects. By using pXRF analysis at 2m intervals on drill hole transects taken from the vicinity of the CS-SZ it was hoped to be able to discern known pathfinder elements associated with Cu, Pb and Zn mineralisation
The data collected from these transects can be used to develop a model of the regolith sequence lithogeochemistry, and to determine which elements can be reliably analysed by pXRF within a regolith sequence such as that seen on Kangaroo Island.
The study has also attempted to identify any geochemical signatures associated with Cu, Zn or Pb mineralisation, their spatial extent and potential as geochemical vectors towards mineralisation.

KEYWORDS

Kangaroo Island, Cygnet-Snelling Shear Zone, geochemical, regolith, lithogeochemistry, exploration, mineralization,.

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INTRODUCTION

The challenge faced by mineral explorers today is that most deposits that are exposed at the Earth's surface or shallowly buried (<30 m) have been found. With the average depth of discovery in Australia now 79 m (Schodde 2014), mineral explorers are increasingly required to use innovative techniques to gain an understanding of the prospectivity of deeply buried bedrock, and then to efficiently identify and test potentially mineralised targets.

Cover sequence rocks and weathering horizons that overlie mineralisation are now being seen as a medium that should be utilised and not discarded, as has been previous practice. In particular, the geochemistry of the cover sequence, or regolith, is being recognised as preserving geochemical pathfinder elements that can be used to vector towards mineralisation (Anand et al. 2000, Poustie et al. 2006, Anand et al. 2010). This is particularly effective where geochemistry can be linked with lithology, palaeotopography and landscape evolution
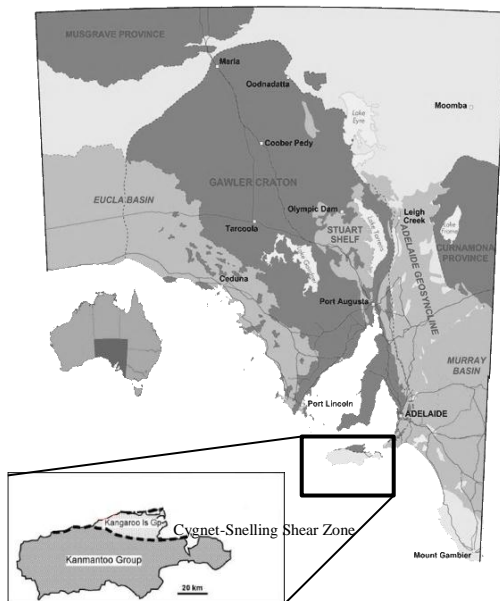
Figure 1: Map of South Australian geological provinces showing the Gawler Craton and its association with Kangaroo Island (highlighted).
Inset: Location of the Cygnet-Snelling Shear Zone on Kangaroo Island.
(Modified after Parker (1990) pir.sa.com.au)

(Anand 2014).

The Gawler Craton, South Australia (Figure 1) is prospective for many types of mineralisation (Belperio et al. 1998) and is known to host several world class mineral deposits (Sheard MJ 2008) including the giant Olympic Dam FeO-Cu-Au-REE-U deposit, the Challenger Au deposit and zircon-rich mineral sands.

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The abundance of cover over the majority of the state has led to the use of different methods of exploration to discover and explore for mineralisation. (Poustie et al. 2006) Kangaroo Island, South Australia marks the southern boundary of the Gawler Craton (Figure. 2); (Belperio et al. 1993). The Gawler Craton is buried at about 3-4km south of the Cygnet-Snelling Shear Zone (CS-SZ). Mineralisation is hosted within the CS-SZ, and includes the Bonaventura Cu deposit (Schwartz 2006). The mineralised basement rocks are extensively overlain by 20 to 60m of cover, mostly consisting of Tertiary laterites and Quaternary alluvial deposits (Gum et al. 2008)

This paper aims to increase the understanding of the geochemistry of the cover sequence over Kangaroo Island, particularly in the proximity of the CS-SZ. Portable XRF (pXRF) data collected from the cover sequence and the top ~1m of fresh basement rocks from a series of N-S trending drill hole transects across the CS-SZ are used to constrain the lithogeochemistry using elemental relationships. The methods used in this study are aimed to be able to identify lithogeochemical horizons and if the relationships between major and pathfinder elements within these horizons can be used as geochemical vectors toward potential mineralisation, with a focus on Cu, Pb and Zn anomalies. It is hoped that the results of this project can be used by explorers to create three dimensional models based on the known movement of elements through a regolith profile. This modelling technique can be a valuable exploration tool in areas of buried mineralisation, resulting in lower costs and allowing for more accurate and precise drilling.

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GEOLOGICAL SETTING

Much work has been done in the Olympic Domain of the Gawler Craton in South Australia (Figure 2) where mineralised basement rocks are overlain by extensive cover sequences and regolith. Previous sampling of cover sequence geochemistry has been successful in providing vectors towards mineralisation of the underlying basement (Butt et al. 2000).
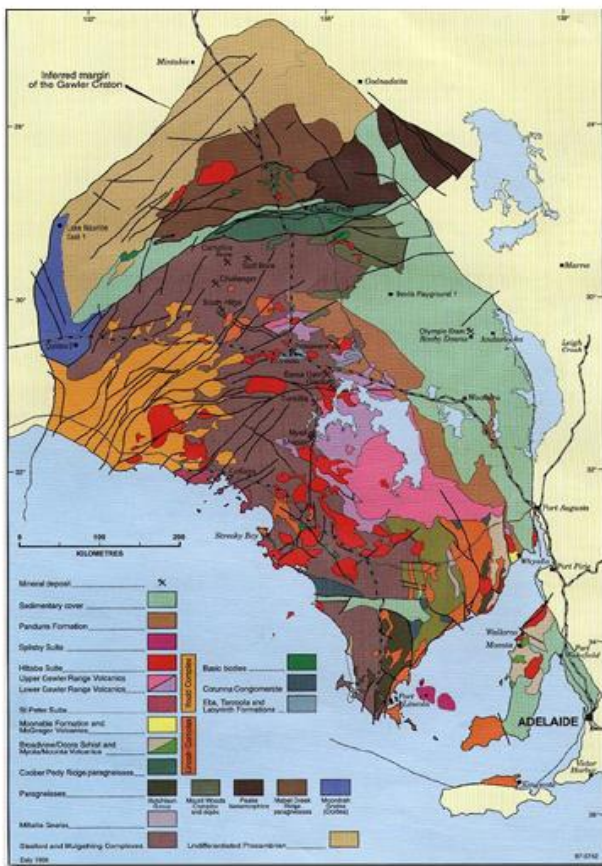
Figure 2: Geology of the Gawler Craton, South Australia. Modified after Forbes et al. (2011).

The Gawler Craton is an ancient crystalline shield, comprising Archaean to Mesoproterozoic metasediments, volcanics and granites (Hand et al. 2007). Mesoproterozoic igneous rocks, including the Gawler Range Volcanics and the co-magmatic Hiltaba suite granites, intrude and overlie the older Archean sequence (Parker 1990). Overlying the basement are gently dipping to flat-lying strata of the Stuart Shelf, which range in age from Mesoproterozoic to Neoproterozoic (Adelaidean) (Preiss 2000).

The Mesoproterozoic red-beds of the Cariewerloo Basin and the Neoproterozoic Stuart Shelf sediments cover the basement to depths in excess of 1000 m (Reeve et al. 1990). Kangaroo Island lies at the southernmost margin of the Gawler Craton (Figure 2).

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The basement geology of Kangaroo Island is dominated by two Cambrian age rock packages; the Kangaroo Island group in the north and the Kanmantoo Group to the south (Flottmann et al. 1995). These rock packages are separated by the Cygnet-Snelling Shear Zone (CS-SZ) (Figure 3).

To the north of the CS-SZ, the Kangaroo Island Group is considered a part of the widespread Early to Mid-Cambrian Stansbury Basin (Belperio et al. 1998) which overlies the southernmost known extension of the Gawler Craton (Belperio et al. 1993). These sediments were deposited as a platformal sequence (Gravestock 1995) and comprise lower greenschist facies siltstones, shales and fine grained sandstones deposited within a shallow water, shelf environment (Flottmann et al. 1995).

To the south of the CS-SZ, deeper water sediments of the Cambrian Kanmantoo Basin are preserved. The Kanmantoo group comprises fine – grained greywackes and are intruded by syn- to post-tectonic magmas causing localised partial melting (Foden et al. 2002). These rock packages have undergone high temperature – low pressure metamorphism to upper greenschist/lower amphibolite facies (Jenkins et al. 1992).

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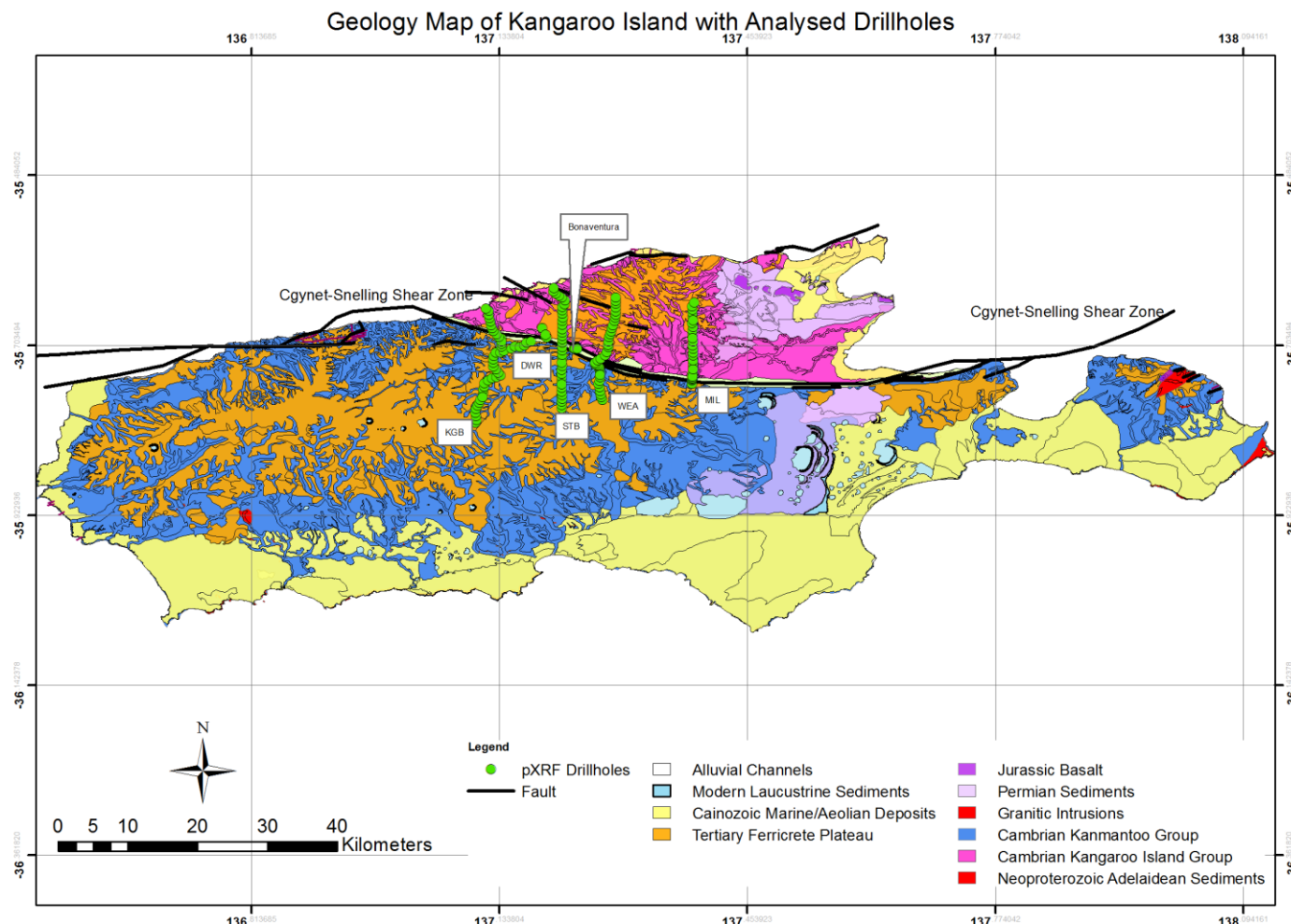
Figure 3: Geological map of Kangaroo Island showing labelled drill hole transects and their position in relation to the east-west trending Cygnet Snelling shear zone (CS-SZ). Also shown is the distinction between Kangaroo Island sequence stratigraphy to the north of the CS-SZ and the Kanmantoo group, south of the CS-SZ. The tertiary ferricrete group presents one of the major impediments to exploration and can be seen extensively covering the island and transecting both units. This cover overlies the Cambrian sequences in which mineralisation is known to be hosted. The historic Bonaventura working, known to host Cu mineralisation is labelled (Modified after Fairclough et al. 2009)

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The boundary between the northern and southern zones is the Cygnet-Snelling Shear

Zone (CS-SZ). The CS-SZ is an east-west trending, north vergent zone of

anastomosing mylonitised meta-sedimentary rocks (Flottmann et al. 1995). The CS-SZ

is a deep crustal feature, interpreted to coincide at depth with the Southern margin of the

Gawler Craton (Belperio 1996). Gold and base metal occurrences are preserved along

much of the CS-SZ, including at Grainger's Mine (Cu, Au) and the Bonaventura

Prospect (Pb-Zn) (Figure 4).
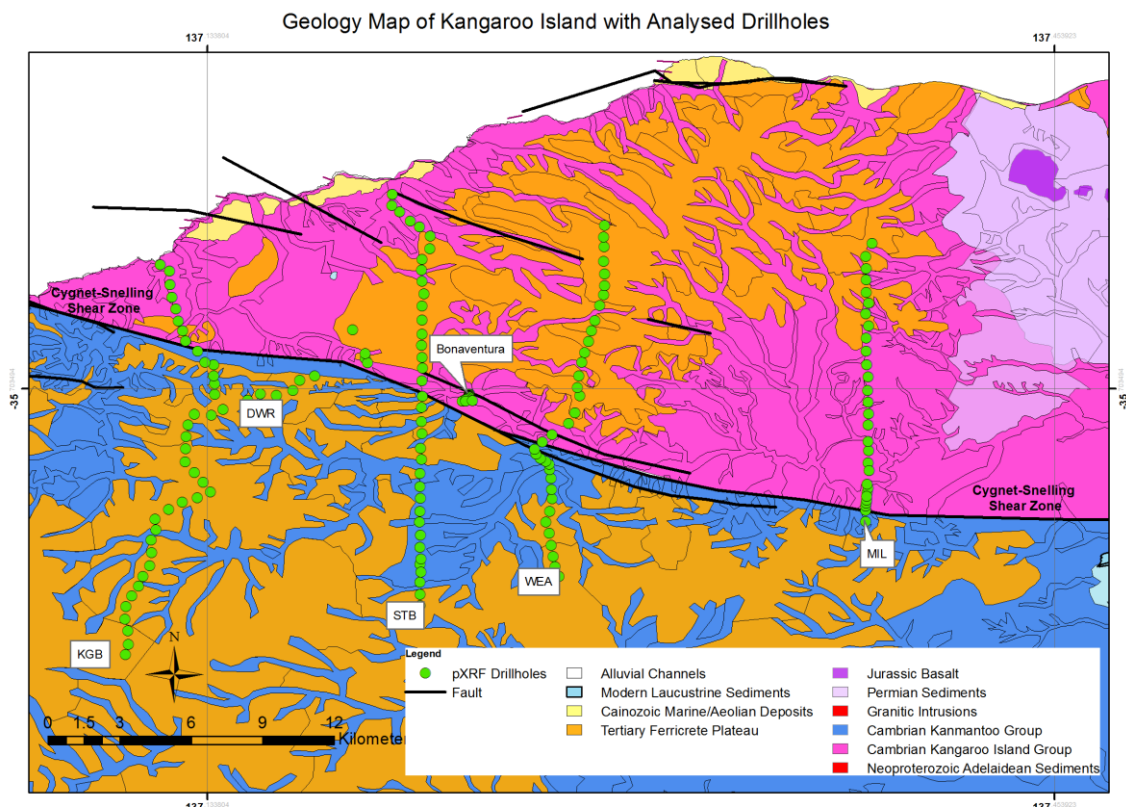
Figure 4: Expanded view of study area showing individual drill hole locations and their position in relation to the CS-SZ. This figure also shows the drill hole position relative to differing stratigraphic units. The GRA holes were taken from the area of the historic workings of Grainger's Mine, prospective for Cu and Au. The Bonaventura mine also seen in this figure is a known Cu deposit, which is also prospective for Pb and Zn. (Schwarz 2006) (Modified after Fairclough, 2008)

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The Kanmantoo and Kangaroo Island Groups were deformed and metamorphosed during the ca. 514 – 490 Ma Delamerian Orogeny (Flottmann et al. 1995, Foden et al. 2006). Deformation associated with orogenesis resulted in the development of a series of east-west trending, north vergent thrust faults that delineate the interpreted southern boundary of the Gawler Craton (Belperio 1996) During this event the Kanmantoo Group sediments were thrust over the Kangaroo Island group (Flottmann et al. 1995).
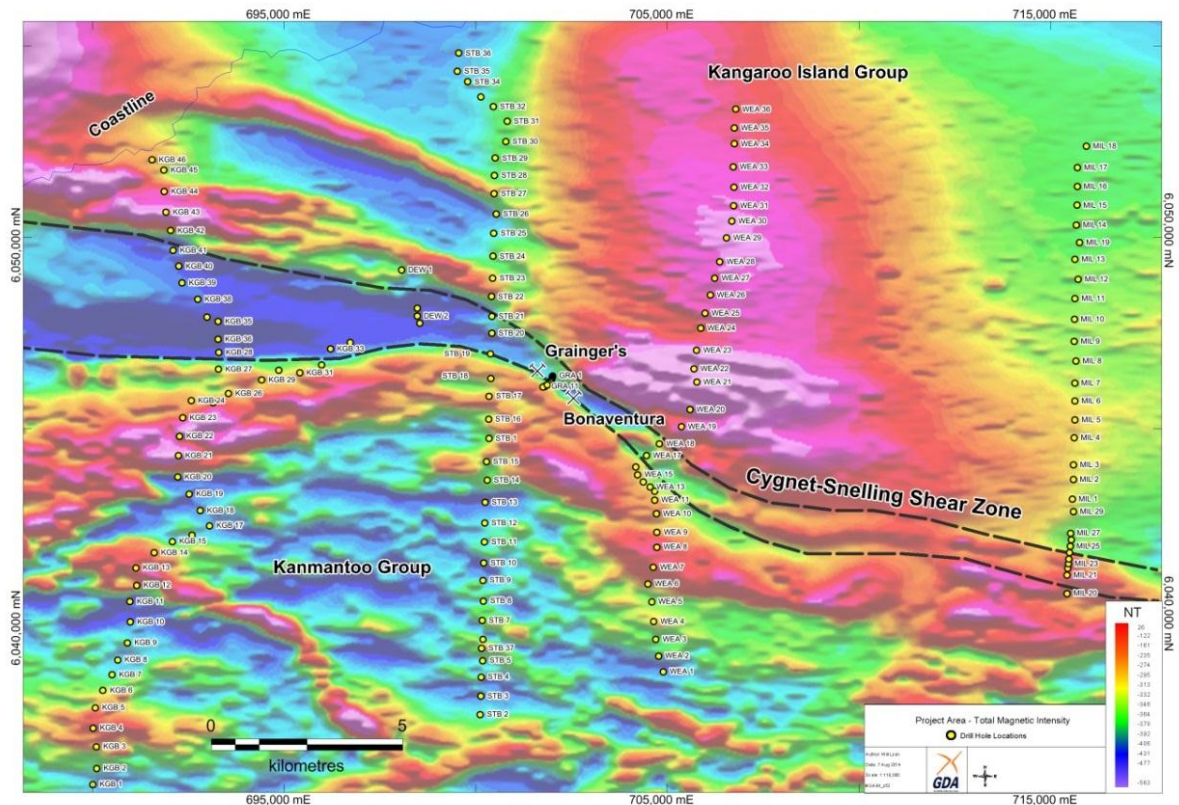
Figure 5: TMI map showing magnetic boundaries of the Cygnet-Snelling Shear zone. The boundaries of the shear zone are bounded by a magnetic low, seen here within the dashed lines. This map also shows the position of the drill holes with relation to the shear zone and other magnetic features. (TMI image from Monax Mining Pty Ltd)

The basement rocks of Kangaroo Island are overlain by highly weathered and iron indurated regolith (Stoate et al. 2012). This encompasses everything from the fresh bedrock up to the surface, and includes weathered to highly weathered bedrock as well as the iron indurated material. There is some confusion as to the protolith of the

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indurated materials, however field evidence (Stoate et al. 2012) suggests that it is part of

the deep weathering sequence of the Kanmantoo. Thickness of regolith is up to 60m

(Gum et al. 2008) with the possible options being that it is part of the weathered

Kanmantoo sequence or part of an Eocene deposition from the St Vincent Basin (S.

Hill, pers. comm. 2014).

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METHODS

Logging

Each sample was logged according to lithology recorded by SADME geologist at the time of drilling. Each 2m section was assigned a lithology from the geologist logs of SADME Kangaroo Island drilling report (Appendix B). The lithologies logged included: sandstone, siltstone, clay, metasandstone and metasiltstone.

The colour of each crushed sample was also recorded prior to analysis (Figure 6)

BROWN (Soil)

RED (Ferruginised zone)

ORANGE (Mottled Zone)

WHITE (Saprolite/Pallid Zone)

YELLOW (Saprolite)

PURPLE (Saprock/Fresh Rock)

GREY (Saprock/Fresh Rock)

Figure 6: Crushed sample colour. The pattern Brown → Grey was often seen as holes increased in depth.

Portable XRF geochemistry

Samples were taken from open file access aircore drill holes that are stored at the Department of State Development (DSD) core storage facility at Thebarton, Adelaide.

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Drill holes were selected based on their proximity to the CS-SZ (Figure 2) and known mineralisation in the area.

Each sample is a composite of a 2m interval of drilling. Approximately 30g of sample from each available interval was taken and crushed to minimise issues of heterogeneity associated with varying grain-size and blebby or nuggetty mineralisation.

The crushed samples were then used for portable X-ray fluorescence (pXRF) analysis using an Olympus X-5000 portable XRF and following the procedure outlined by Fisher et al. (2013). Analyses were run in mining plus and soil modes to capture the broadest possible range of elements at the best detection limits. The beam time used on each analysis was 60 seconds, allowing for maximum exposure to ensure that analytical precision was maintained (Fisher et al. 2011). Blanks and standards were run at the beginning and end of each data collection session. Standards were again run after every 20 unknowns. Standards used were OREAS certified reference materials (CRMs) 901, 902 and 904, that are representative of sediment Cu hosted deposits (Appendix A).

Laboratory whole rock geochemistry

Fifteen samples that were analysed by pXRF were also used for laboratory whole rock geochemical analysis. Samples were analysed at Genalysis Laboratories in Adelaide, South Australia using standard XRF and ICP-MS procedures. Representative data is given in Table 2. These results were used to give an accurate indication of the correction values for the pXRF data.

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Modelling

The data was then interrogated using the Reflex ioGAS software. Each element was run through the program to determine any patterns in the sequences. Both major and trace elements were included in the ioGAS data analysis.

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Table 1: Major element data lab vs pXRF

ELEMENTS		Al_2O_3	MgO	P_2O_5	SiO_2	K_2O	CaO	Fe_2O_3	Ti
UNITS		Wt%	Wt%	Wt%	Wt%	ppm	ppm	Wt%	ppm
4291	Lab	11.58	0.97	0.27	74.43	4.58	2644.39	2.95	4076.66
DEW-1 28-30	Lab	3.79	0.08	0.02	91.82	1.56	214.41	1.63	1258.97
DEW-1 56-57	Lab	11.68	0.36	0.05	77.66	2.57	1286.46	2.46	1978.38
GRA-14 4-5	Lab	10.49	0.31	X	78.65	3.07	357.35	3.35	2398.04
GRA-4 15-16	Lab	11.72	0.93	0.02	76.09	3.44	714.7	2.65	3716.96
KGB-1 4-6	Lab	14.76	0.3	0.03	75.49	1.39	142.94	2.32	3776.91
KGB-15 16-17	Lab	11.45	1.08	0.09	76.75	1.78	1786.75	2.9	2697.79
KGB-29 10-12	Lab	17.02	0.4	0.05	70.64	2.09	142.94	2.25	6174.95
MIL1 20-22	Lab	16.26	1.7	0.12	63.63	3.92	1643.81	5.62	4856.03
MIL19 8-10	Lab	14.2	0.33	0.12	70.28	3.27	857.64	4.5	4496.32
MIL28 21-22	Lab	12.84	0.86	0.17	68.43	3.18	3430.56	8.1	4136.61
STB1 5.5-7.5	Lab	14.14	0.84	0.19	69.66	3.48	857.64	5.32	2817.69
4291	pXRF	11.33	N/A	0.26	73.18	5.09	0	3.39	4946.3
DEW-1 28-30	pXRF	12.11	N/A	0.20	78.78	3.02	0	2.39	2842.3
DEW-1 56-57	pXRF	15.70	N/A	N/A	70.94	3.18	303.7	3.35	3493.9
GRA-14 4-5	pXRF	8.508	N/A	N/A	69.95	3.28	0	3.95	3873.6
GRA-4 15-16	pXRF	12.43	N/A	N/A	71.33	3.65	0	3.42	5899
KGB-1 4-6	pXRF	24.53	N/A	N/A	66.89	2.51	0	2.78	6395.2
KGB-15 16-17	pXRF	7.827	N/A	N/A	82.09	2.18	0	2.88	3315.3
KGB-29 10-12	pXRF	26.43	N/A	N/A	74.43	3.92	0	3.16	10457.5
MIL1 20-22	pXRF	15.43	N/A	N/A	63.22	3.95	0	7.18	5441.9
MIL19 8-10	pXRF	20.29	N/A	N/A	67.90	3.37	0	7.10	6304.3
MIL28 21-22	pXRF	16.09	N/A	N/A	61.65	4.22	1940.8	6.05	5387.8
STB1 5.5-7.5	pXRF	10.77	N/A	N/A	67.21	4.18	0	5.24	4387

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Table 2: Trace element data lab vs pXRF

ELEMENTS		Bi	Cr	As	Cu	Ni	Pb	Rb	S	Sr	U	V	W	Zn	Zr
UNITS		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4291	Lab	0.44	57	46.2	16	23	1599	245.3	5673	24	3.89	77	2	8318	396
DEW-1 28-30	Lab	0.04	0	4.7	3	4	17	37.1	X	35.4	1.65	X	X	7	723
DEW-1 56-57	Lab	0.07	29	4	X	6	10	85.7	X	75.4	4.93	34	X	8	191
GRA-14 4-5	Lab	0.24	35	5.9	4	6	9	113.4	X	47.7	1.75	41	3	4	207
GRA-4 15-16	Lab	0.11	33	6.7	5	13	246	114.2	420	107.2	3.15	52	3	216	327
KGB-1 4-6	Lab	0.15	56	3.6	X	4	33	38.9	92	46.9	1.99	58	X	4	294
KGB-15 16-17	Lab	0.1	36	3.2	7	12	16	79.4	X	123.1	2.65	47	X	35	430
KGB-29 10-12	Lab	0.15	81	4.9	2	3	65	87.3	99	71.5	3.43	86	2	8	788
MIL1 20-22	Lab	1.75	91	6.6	68	40	19	203.5	283	118.2	5.85	109	3	136	225
MIL19 8-10	Lab	0.16	55	3.9	3	4	20	111.3	X	126.5	3.15	75	3	11	367
MIL28 21-22	Lab	0.39	77	9.1	10	39	18	190.1	198	32.9	3.69	92	2	19	207
STB1 5.5-7.5	Lab	0.23	47	6.6	4	14	18	181.7	X	138.2	2.31	51	X	27	224
4291	pXRF	93.5	87		10	24	1239	251.1	1651	33.7	12	88	222	7443	457
DEW-1 28-30	pXRF	21.3	81	5	8.9	4.8	10.5	45.3	52	58.4	6	59.7	1	7	907.2
DEW-1 56-57	pXRF	31.4	49	4.7	1.9	7.4	5.2	89.4	77	106	12	54.8	7	7.1	235.6
GRA-14 4-5	pXRF	41.7	52	2.3	4.1	9.2	4.7	109.9	5	60	4	71.5	8	2.5	177.6
GRA-4 15-16	pXRF	55.2	76		7.5	13.4	150.7	113.2	80	140	3	86	7	159	387.5
KGB-1 4-6	pXRF	45.4	95	5.8	2.4	1.3	21.2	41.4	33	64.9	4	93	6	3.8	406.2
KGB-15 16-17	pXRF	36.5	43	4.4	5	5.4	8.7	54.8	28	212	8	42.8	5	16.2	574.3
KGB-29 10-12	pXRF	167.6	117	9.4	6.1	6.1	45.7	100.3	45	96	10	109	7	7.4	1229.2
MIL1 20-22	pXRF	67.2	166	11.2	87	54	6.2	188.2	121	173	18	112	23	138	292.6
MIL19 8-10	pXRF	85.6	121	9.4	4.7	3.6	12.4	118.3	-42	226	9	110	8	11	529.7
MIL28 21-22	pXRF	56.9	87	9.1	19.7	54	0.5	188.3	157	36.5	9	88	-1	15.6	227.6
STB1 5.5-7.5	pXRF	51.7	98	4.8	2.6	20.6	11.4	169.2	32	175	7	107	3	23.1	239.1

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RESULTS

Major elements

Geochemical data from pXRF analysis shows that Si and Al are the dominant major elements in the samples. Across all samples, the average concentrations of SiO_2 and Al_2O_3 were 75 wt% and 16.6 wt% respectively. Sample DEW1 28-30 (Table 1) shows unusually elevated concentrations of SiO2 (91.82 wt%) and unusually low Al_2O_3 (3.79 wt%) in the lab data analysis.

Average concentrations of Al_2O_3 from samples within the shear zone were 13.78 wt%. Averages of all other samples was 17.3 wt%.

Lower levels of SiO_2 and Al_2O_3 were present in several of the samples logged as metasandstones (Appendix B) and plot together on a Si:Al plot (Figure 7).
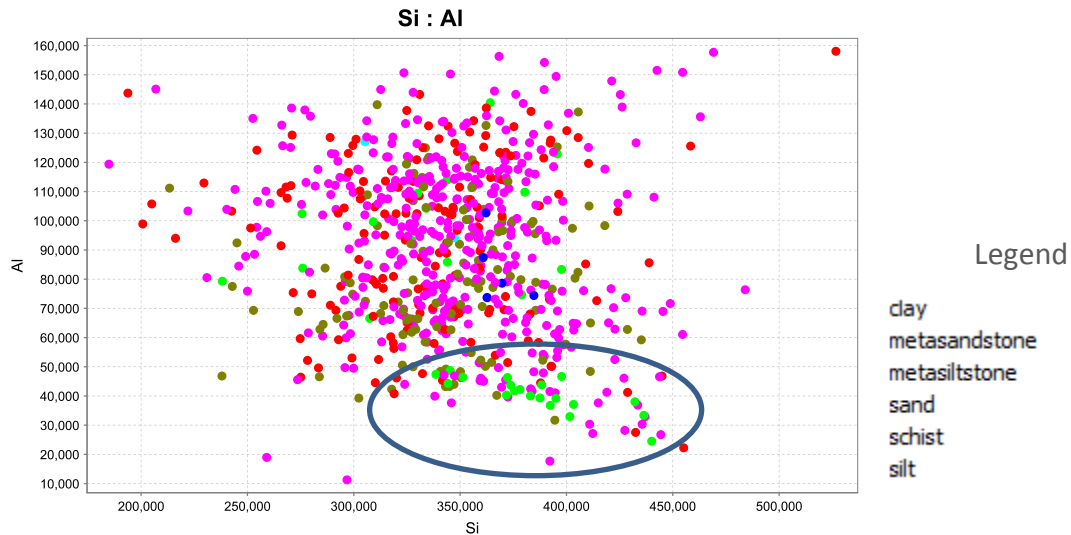
Figure 7: Silica vs Aluminium plot coloured according to geologists' logs showing metasandstones plotting in low Al section of graph. (Appendix B).

Elevated S (>200ppm) was seen in holes 4281-4297 and holes WEA 15 and GRA 6.

The average concentration of S across all samples was 16.3 ppm.

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Hole WEA15 returned S at 1503 ppm at 13m. These samples with elevated S tend to be from within the shear zone (Figure 8). Average concentration of S from samples within the shear zone is 42.9 ppm. The average concentration of S over all other samples is 12.3 wt%
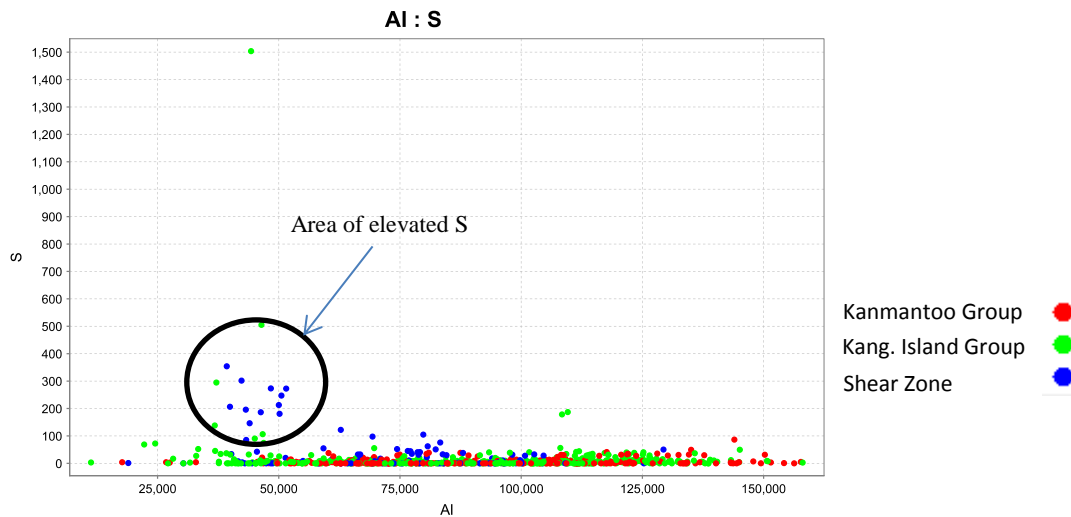
Figure 8: **Al:S plot showing elevated levels of Sulphur in samples from predominantly within the shear zone and Kangaroo Island Group sediments. Kanmantoo Group shows very little elevated S.**

Of the other major elements, Mg and Na analyses were not included in the pXRF sampling modes used. Ca and P data returned inconsistent reading across the sample range.

Transition and post transition elements are dominated by Fe_2O_3 with elevated levels (> 5%) in over half the sampled holes.

Samples taken from the top 0-6m had an average Fe_2O_3 concentration of 5.6 wt%, the top 0-2m of holes averaged 6.9 wt%.

Concentrations of Ti were variable across all samples. High Ti (>0.64 wt%) found in many samples across a broad range of depths, the highest being in hole KGB30 at 3.2 wt%.

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Trace elements

Zn levels in holes 4280-4297 was found to be above crustal abundance at anomalous levels between up to 24142ppm in sample 4297 from 85m.

Samples from deeper than 10m returned elevated concentrations of Zn, the average concentration between 10m and above mineralized depth was 48.1ppm. Samples from within the CS-SZ (Figure 5) from these depths had an average concentration of 84.6 ppm.

Pb also shows anomalous levels in holes 4280-4297 with all holes returning Pb at >1000ppm. Elevated Pb (>100ppm) was seen in the deeper sections of each hole and often in close proximity to the CS-SZ.

Non mineralized samples indicated three populations of Pb, Pb+Zn and Zn, up to 800 ppm Pb and 950ppm Zn (Figure 20).

Cu levels are low in most samples but show above average levels at several points along transect MIL, north of the shear zone in Kangaroo Island Group sediments. Holes 4280-4297 showed varied Cu levels, the highest being in hole 4297 returning 199ppm Cu at 85m.

Elevated W in many holes of the study ranged from 2.46ppm to 457ppm. There is no discernible pattern related to W distribution.

Samples taken from greater than ten metres depth show a trend towards elevated Rb levels (>150ppm) when compared to the average of 117.9ppm over all samples. These samples also tend to display elevated K_2O (>3.0 wt%).

K_2O and Rb levels in the samples taken from the top 0-10m of all drill holes averaged 2.3 wt% and 63 ppm respectively. Low levels of As (<5ppm) were returned from holes 4279-4292 and most GRA holes (Figure 5).

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Table 3: Combined elemental averages for drill hole depth.

DEPTH	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Zr	Sb	W	Pb	Bi	Th	U	Ba
0-2m	92433.3	325506.8	57.8	12.5	18045.1	594.9	4331.1	6.4	57.6	39.1	48173.2	16.1	2.8	31.8	13.6	59.2	36.5	324.6	2.2	10.4	35.4	61.0	27.8	5.7	299.9
2-4m	87990.0	338116.4	307.1	9.9	20334.3	335.1	4164.1	7.5	62.0	43.0	38640.0	19.1	2.1	49.5	8.4	67.4	52.8	399.2	1.7	11.2	48.0	56.7	21.8	5.5	631.0
4-6m	90697.6	344510.8	269.4	14.7	19497.3	431.6	4136.0	8.7	70.4	72.0	36343.2	11.5	5.0	340.4	8.0	88.8	48.0	352.7	2.2	15.3	37.0	56.8	24.5	6.5	488.3
6-8m	90643.0	350611.3	497.7	11.0	21784.4	253.7	4052.4	8.0	63.5	64.6	33572.2	9.8	3.6	36.3	8.6	99.5	53.7	417.9	2.3	12.8	40.3	51.9	29.1	7.4	502.9
8-10m	90123.2	356859.4	674.1	5.6	21972.2	438.1	4183.9	9.5	77.6	69.1	30759.7	10.6	5.0	27.4	9.2	105.7	65.1	554.4	2.7	7.9	44.2	54.7	27.0	9.3	528.3
10-12m	90169.9	332906.9	1081.5	20.5	18828.8	539.0	4012.0	9.0	71.8	77.8	43100.3	18.0	6.4	33.2	8.6	123.1	63.2	374.0	2.2	12.4	156.2	59.2	25.2	9.2	525.8
12-14m	90592.1	351930.8	574.9	34.9	24748.5	464.4	3805.0	8.2	65.7	77.6	34499.1	11.2	10.0	41.4	8.6	121.5	63.8	305.7	2.5	8.6	47.3	55.4	27.2	8.0	532.0
14-16m	87557.7	348176.0	1138.5	13.2	26144.3	670.2	4031.7	11.4	98.5	153.2	34030.3	16.9	15.7	57.7	9.6	143.5	85.3	429.9	2.3	9.9	340.3	53.6	35.3	9.0	510.6
16-18m	90574.0	350826.7	1134.7	8.5	25197.0	762.1	4191.1	8.8	82.0	151.8	36803.7	14.9	10.3	44.2	9.8	140.6	88.5	302.4	3.9	14.8	54.3	35.7	32.2	7.5	322.6
18-20m	93647.2	354921.8	307.8	10.9	25077.7	555.8	4849.8	8.5	75.3	109.7	31952.6	20.8	7.4	40.7	7.9	129.6	76.6	232.7	3.0	9.8	188.5	69.2	27.5	7.4	461.2
20-22m	81816.0	354054.8	642.4	4.2	23792.2	813.5	3781.1	8.8	81.0	176.6	38642.6	27.9	9.2	61.4	7.3	122.7	93.5	581.3	1.7	10.1	25.5	33.7	35.4	6.6	346.5
22-24m	83020.1	341846.0	1696.4	0.6	22933.0	256.0	4893.9	7.7	73.9	119.9	39485.0	18.4	7.6	54.4	7.5	143.3	102.7	526.7	1.0	23.5	20.6	34.4	21.7	8.0	313.1
24-26m	87906.3	353607.4	186.4	15.4	22820.6	123.2	3991.7	8.4	69.8	90.1	32437.5	8.3	14.0	117.5	7.0	144.3	100.7	825.6	2.8	2.8	1159.9	39.7	29.5	8.5	356.3
26-28m	88885.8	367646.7	63.3	6.4	19145.6	0.0	3009.8	6.5	59.8	50.5	30226.4	4.1	6.2	8.3	6.0	74.6	61.5	399.1	1.2	2.6	24.3	38.0	26.1	5.6	409.8
30-40m	94894.2	362719.5	307.0	15.2	26801.6	237.2	4159.0	7.3	58.6	55.3	28340.3	10.8	9.8	76.4	6.3	125.7		497.8	2.2	5.2	980.1	85.2		7.9	509.9
40-50m	96711.5	363126.2	216.0	11.0	27901.1	301.1	4526.0	7.4	57.8	67.9	36042.2	14.4	8.9	76.5	7.6	121.6		487.2	1.7	7.0	672.6	88.5		9.3	535.3
50-60m	92274.5	359876.5	267.2	9.5	25261.9	695.9	4060.1	7.1	55.4	103.9	39227.7	20.5	6.3	69.6	12.8	102.9		445.1	1.7	7.6	382.6	66.0		9.3	505.2
60-86m	48535.7	352913	2680.1	202.5	33629.2	3579.7	3372.7	8.1	60.4	341.7	42523.5	41.4	29.9	14945.3	15.1	208.8		339.3	5.5	236.1	1897.6	88.9		13.7	659.0

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DISCUSSION

Lithology analysis

The results of the pXRF analysis were initially compared against the known lithologies, logged by government geologists in the late 1980s (Appendix B). When these lithological categories were used in a silica vs aluminium plot there were no discernible patterns between sands, silts and clays. These lithologies would expect to separate out into three separate groups as sandstones will generally have a higher Si content while clays will have a higher Al content (Tucker 2009). Packages logged as metasandstones, usually from within the CS-SZ, tended to group at the low aluminium end of the scale (Figure 7). Many of these samples were logged by SADME geologists as containing mica (Appendix B). These micas are likely a result of hydrous deformation within the shear zone, creating a low grade metamorphic environment where Al depletion is expected (Rolland et al. 2003). In the surrounding regolith, Al has remained relatively immobile. The Si:Al plots were coloured according to sample colour, depth and their rock unit. These plots also showed no clear discernible pattern (Figure 9).

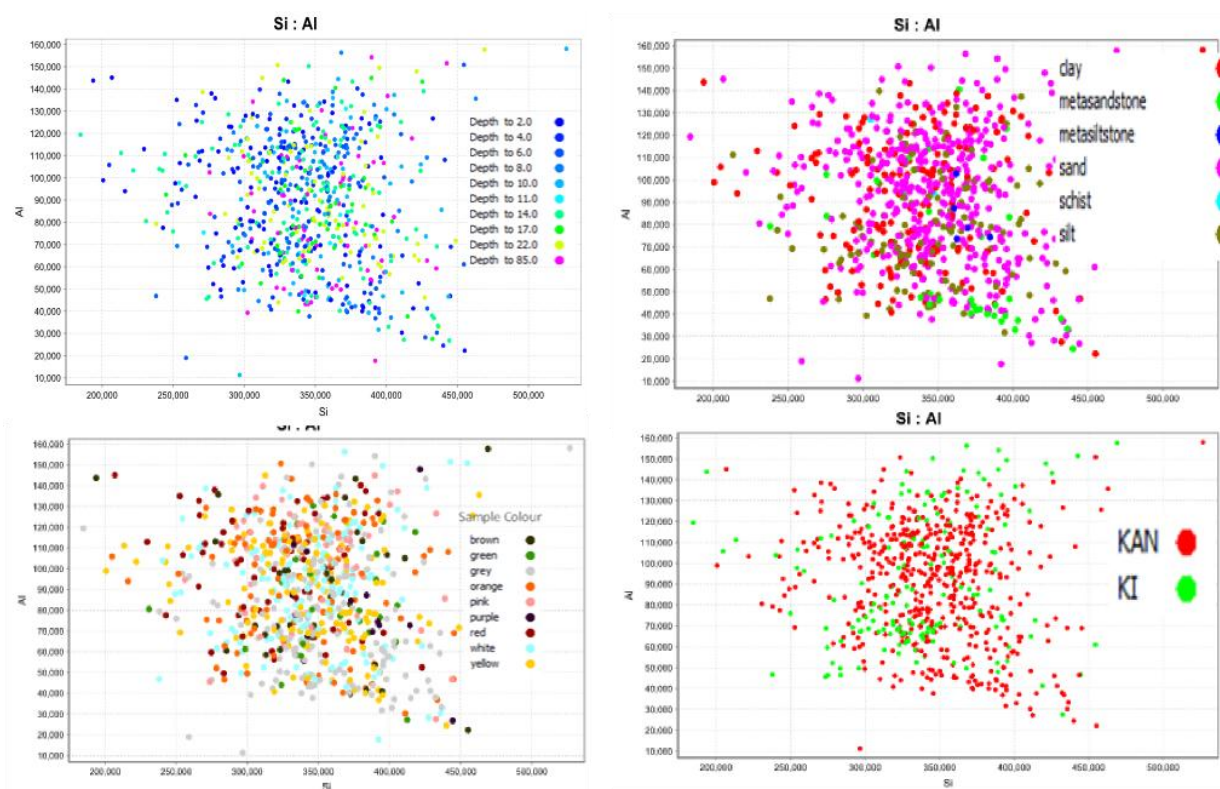Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

Figure 9: Si:Al relationship of all samples A) Depth; B) Lithology; C) Sample Colour; D) Rock Unit

Colour analysis

In certain regolith profiles such as the lateritic profile of Kangaroo Island, colour can be

used to identify certain lithological boundaries (Pain 2008).

Well developed in situ profiles typically display reddish, orange and yellow-brown

colouration in an upper mottled zone, where Fe induration causes red colouration

grading to white or cream in leached saprolite (Figure 10). Yellow-brown and orange

zones appearing lower in the profile can indicate old redox fronts—generally related to

palaeo or perched water tables (McDonald et al. 1998). Goethite dominance is indicated

by yellow and brown colours, while hematite dominance appears as purplish, red and

pink shades. Mixtures typically result in different orange hues (Pain 2008).

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The transition from weathered rock to fresh rock is usually marked by a change from coloured to more neutral hues (e.g. brown or orange hues to grey, green grey, purple grey): commonly close to, or just below, the active redox front (Pain 2008) .

This general colouration pattern could be seen in many samples.
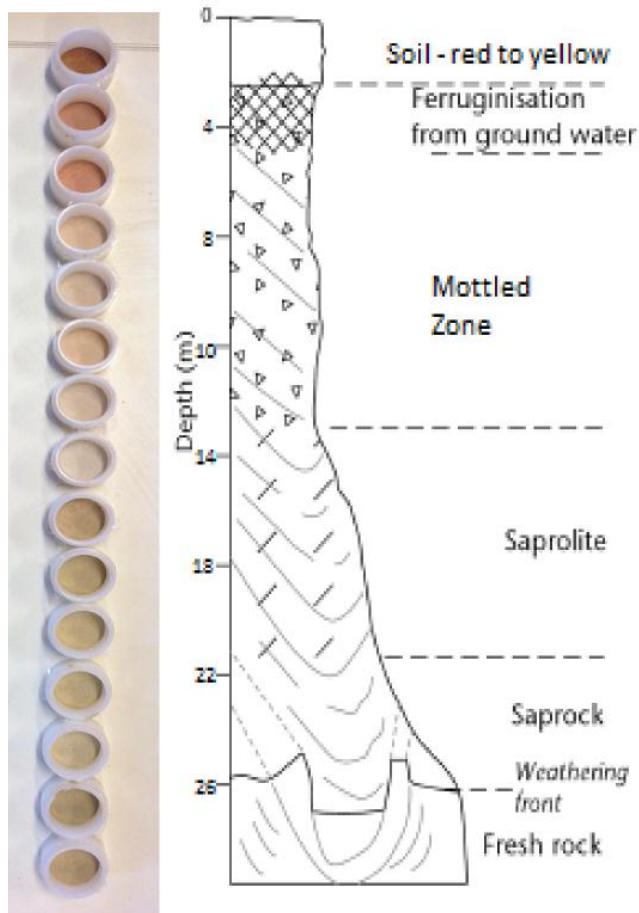
Figure 10 – Typical drill hole section of prepared samples against a regolith profile similar to that seen on Kangaroo island (modified from Scott et al 2009).

The red/orange rock is generally found in the top 0-6m of the holes then a white, pallid zone from 10-15m, often followed by a yellow/orange zone and at times another redder zone which would often overlie the bottom of the hole or a green/purple-grey, fresh rock sample (Figure 10). As such, each crushed sample was assigned its own colour

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(Figure 6). This colour pattern was consistent over many of the drill holes; however was not always the case. This is due to a number of factors including variation in primary lithology, variation in weathering processes and surface erosion.
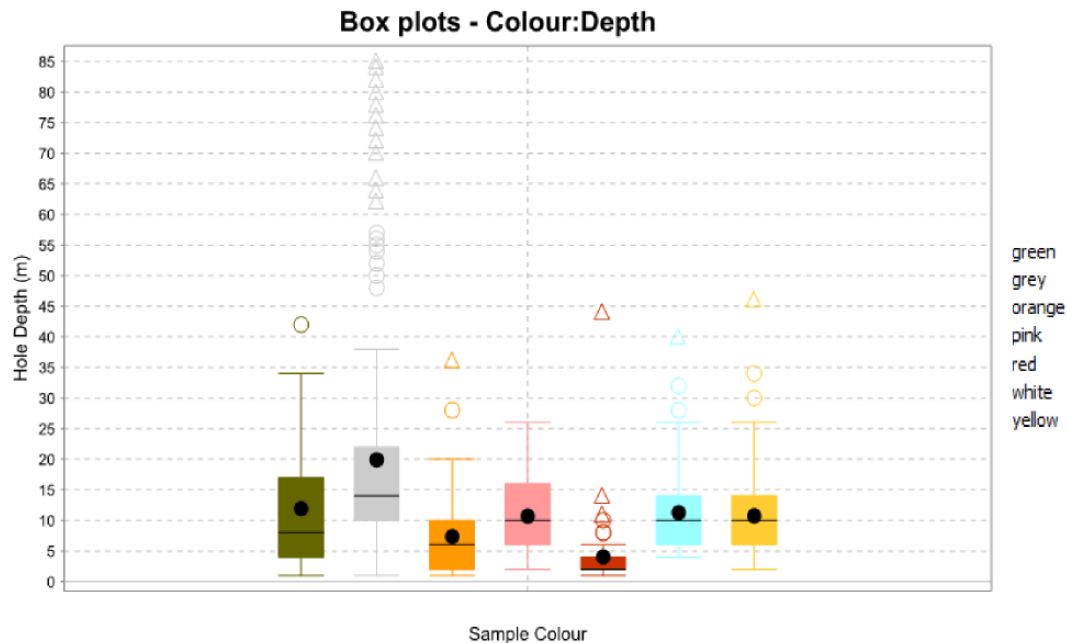

Figure 11: Box plots showing different colour units and their mean depths. Red and orange material plots in the shallow region between 0-10m, grey material, generally fresh rock, plots deeper. White coloured material plots between 5-10m and the yellow lithology also plots in this region.

Major elements

The results plotted using the crushed sample colour (Figure 6) initially showed a similar scattered pattern to that of the logged lithologies on the Si:Al plot. Here, many of the grey samples which were often found as fresh rock, or nearer to the bottom of the hole plotting around the low aluminium and medium to high silica section of the scale. On further analysis of the data it was found that Ti:Al (Figure 9) demonstrated a broad linear trend, possibly explained by mineralogical control. High Titanium could be indicating high rutile or ilmenite levels within a sequence while high Aluminium could indicate the presence of clays.

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.
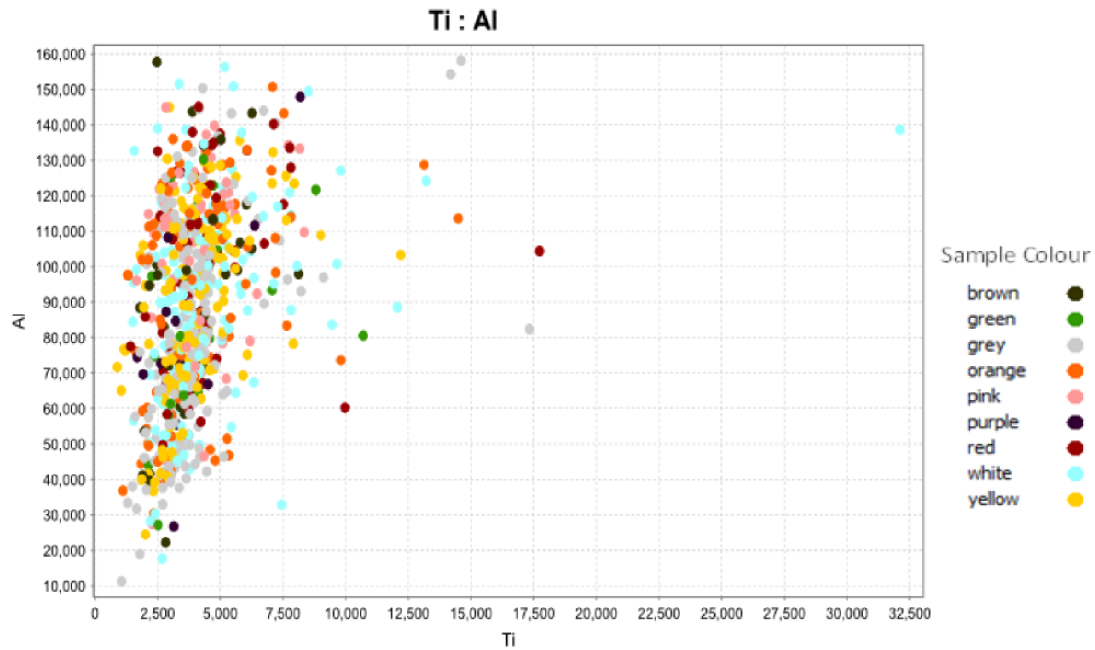
Figure 12: Ti vs Al shows a broadly positive linear trend. Many of the grey samples are plotting at the lower end of the scale while many of the red/orange samples show elevated Al:Ti. Units are in PPM.

Rubidium substitutes for Potassium in micas and feldspars and a high Rb:K usually indicates less weathered material and /or less altered K enrichment. Fresh rock samples from deeper in the profile show a higher Rb:K ratio while the more weathered material (ferruginised) in the top 0-5m of the profile show a lower Rb:K ratio (Figure 13). This can be attributed to loss of soluble ion K to solution (Taylor et al. 2001). Some K may remain due to saturation.

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.
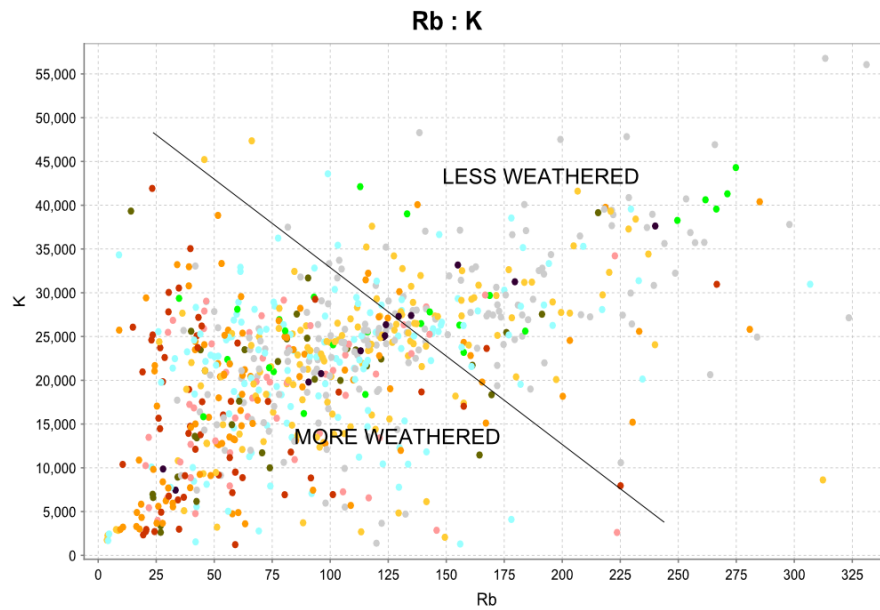
Figure 13: Rb:K plot indicating sample colours. Ferruginised samples plotting at the low K and low Rb section of the plot. Fresh rock samples grey, green are plotting in the higher Rb:K zone.

This high Rb can also be seen in samples taken from within the shear zone (Figure 14) as more mica is present due to the low grade metamorphism associated with the shear zone. Many of the samples logged by SADME geologists had the presence of micas in the samples (Appendix B).

Figure 14: Probability plot for Rubidium indicating higher levels of Rb within the shear zone

25

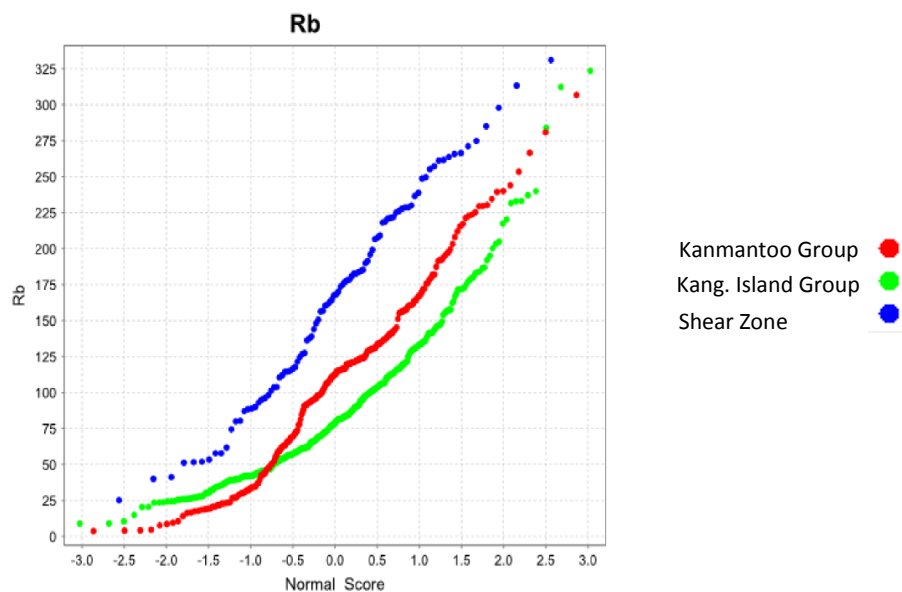Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

Lithogeochemistry

On average, the elemental dispersion of Fe was consistent with that of a typical lateritic profile. The concentration of Fe_2O_3 is highest in the top 0-5m of the profile (Figure 15).
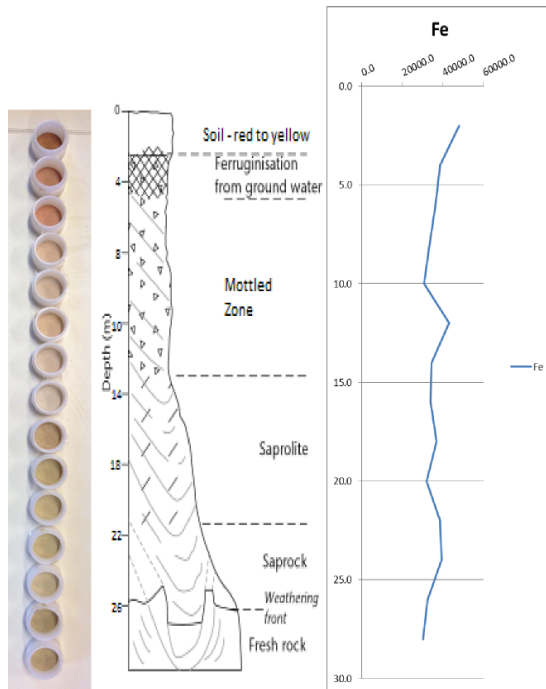
Figure 15: Average levels of Fe with relation to hole depth shows reduction in Fe from 0-10m as the ferruginised zone becomes before increasing towards the base of the mottled zone. It remains steady through the saprolite/saprock zone.

As depth increases, Si and Al become more abundant in the profile. This indicates a mottled zone, generally rich in goethite, hematite and clays. The higher levels of Al indicate the presence of clays, while the increase in Si with depth is from weathering resistant quartz becoming concentrated in the profile (Scott et al. 2009). The saprolite (pallid) zone (between 5-20m) contains silicate minerals in various stages of breakdown. Silica levels are variable due to the presence of quartz veins. As depth increases Si associations increase as the material becomes less weathered and the primary fabric of the host rock is reintroduced into the profile.

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.
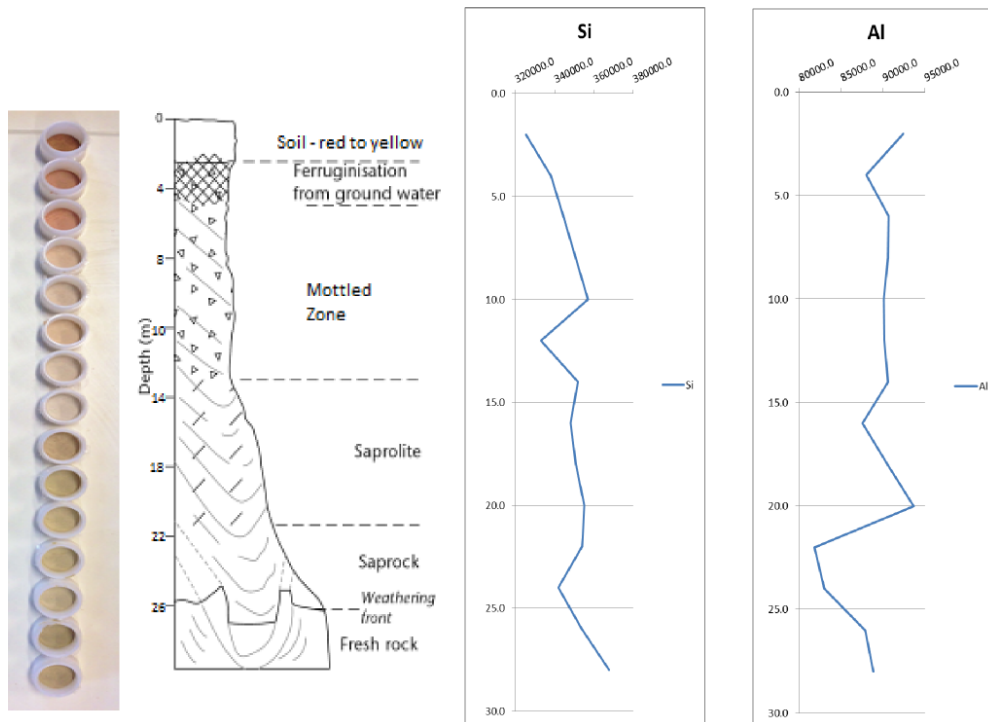
Figure 16: Silica and Aluminium against depth show increasing Si with depth before a sharp decrease in Si levels in the pallid zone between 10-15m. Al drops sharply after 20m.

Mineralisation

Samples numbered 4287-4299 were from a known area of Pb-Zn mineralisation from drilling conducted by Monax Mining Pty Ltd. These samples were from much deeper in the profile (up to 85m), and well into the basement material. It is from these samples that the study was aimed to discern Pb and Zn pathfinder elements within the surrounding regolith material. In the mineralised samples the results show a relationship between Pb+Zn and S (Figure 19). Mineralisation comprises galena (PbS)-sphalerite (ZnS) and is supported by these results which show a linear trend between Pb+Zn and S.

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.
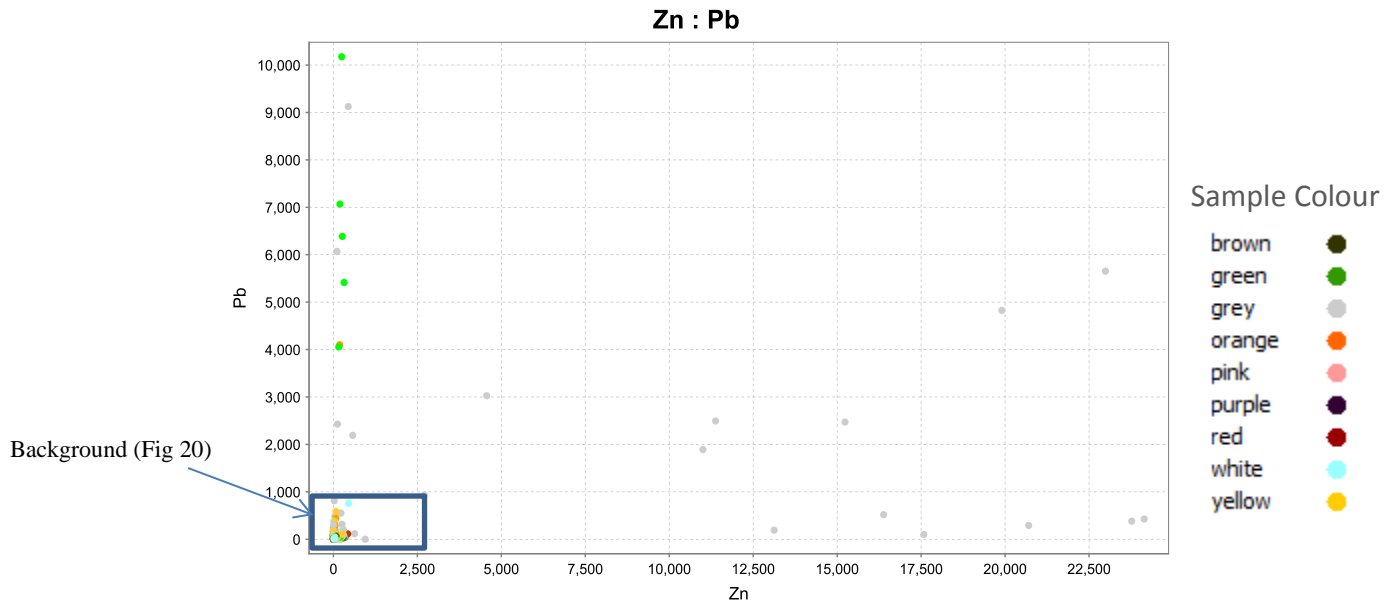
Figure 17: Three populations of mineralisation. High Zn, low Pb; High Pb, Zn and High Pb, low Zn

These samples also showed low As (Figure 18), particularly in the high Pb holes.
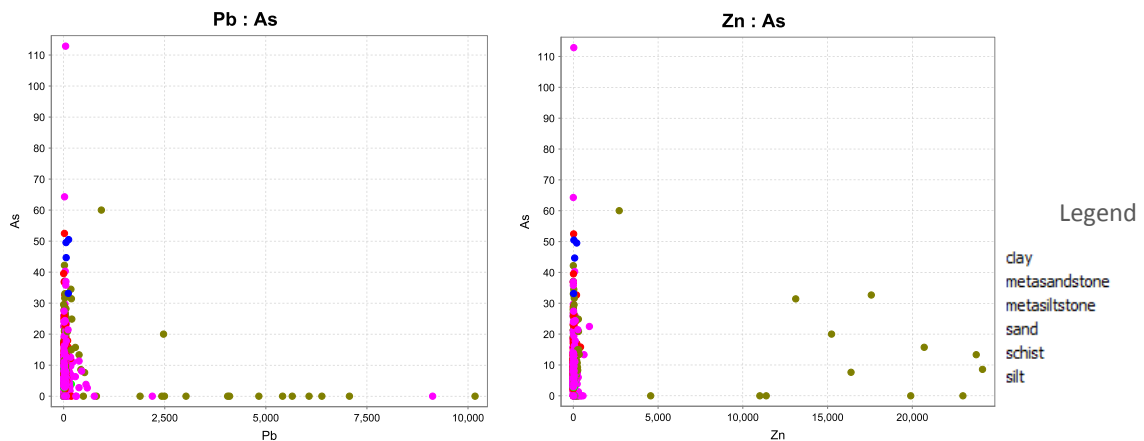
Figure 18: As:Pb + Zn showing low levels of As in mineralised samples coloured by lithology.

The results from the mineralised holes and the lack of pathfinder elements in the

surrounding rock show similarities to exploration models for Mississippi Valley Style

deposits outlined by Dorling et al (1996) whereby mineralisation is stratabound and

hosted in faults and hydrothermal cavities. If the fluid associated with mineralisation is

focussed within the shear zone, there will be no distinguishable distal signature in the

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

surrounding rock. This may explain the lack of pathfinder elements in the surrounding

rock units.

Diamond core samples show that the mineralisation is not widespread and there is no

substantial evidence to suggest large scale fluid movement throughout the mineralised

zone (G. Swain, pers. comm. 2014). Localised fluid movement is explained by smaller

networks of quartz veins and sphalerite - galena alteration within the basement rocks.
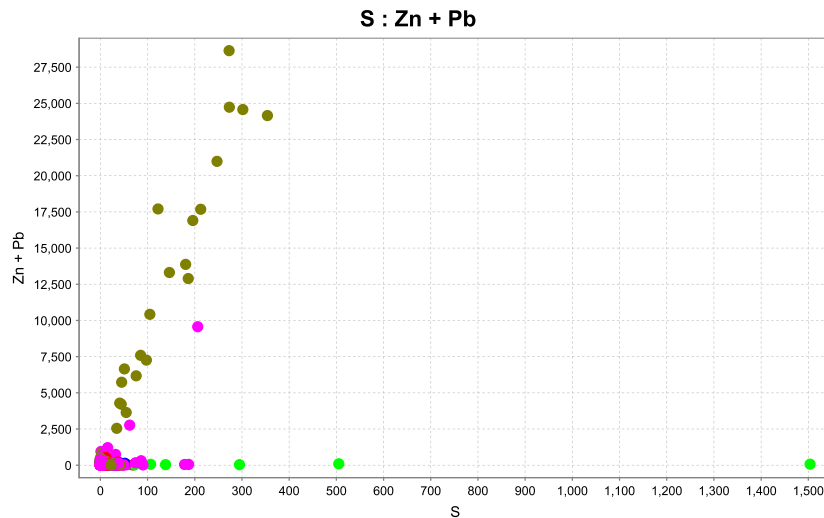
Figure 19: Showing correlation between Zn+Pb and S.

Pathfinder Elements

Elements commonly associated with high or anomalous Pb-Zn-Ag and Cu

concentrations include the target elements themselves and pathfinder elements such as

As, Hg and Sb. Negative indicators Mn, Ba, Co and Ni oxidize and adsorb into Fe

oxides in ferruginous regolith profiles. There is minimal data for several of these

elements due to the detection limits of the pXRF (Appendix B).

Arsenic in particular can be used in recognising primary and secondary halos in areas of

sulphide mineralisation (Boyle et al. 1973). As depletion can be seen in associated with

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anomalous Pb and Zn (Figure 18) particularly in holes 4279-4290 and GRA holes. This

however may also be related to peak interference of elements occurring in the pXRF

itself (Appendix C).
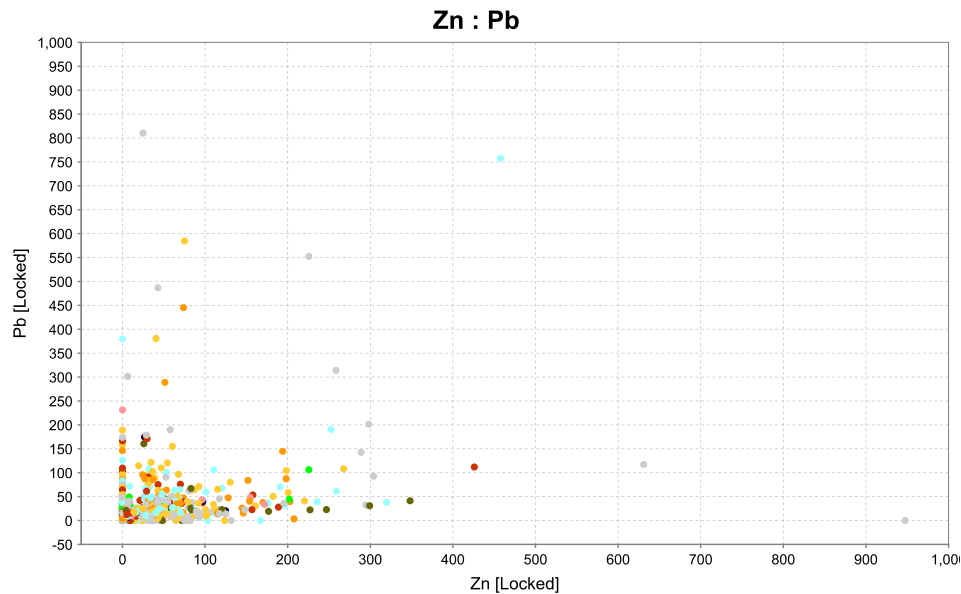
Figure 20: Pb:Zn ratio of background material showing a similar population distribution of elevated Zn, Zn+Pb and Pb predominantly within the grey coloured samples.

Non-mineralised samples

Background data came from samples above the level of mineralisation in holes 4279-

4297, between 0-30m.

pXRF limitations

Sample preparation

One of the main limitations when conducting a study of this type was homogeneity in

the preparation of the samples. For example, when a sample contains high levels of

quartz (which is likely as quartz is more resistant to weathering), it becomes very hard

to manually crush and therefore larger grains of quartz are incorporated into the crushed

sample. If this section was to be analysed, it would likely return very high silica in

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comparison with the rest of the sample. This is one potential explanation for the large

abundance of silica across all samples. The same can be said for ferruginised samples,

where Fe induration has caused hard Fe nodules to form. These discrepancies can be

seen in the differences between the lab analyses (Table 2 & 3), where samples were

crushed down to several microns against the manual crushing of this study. This also

has implications for repeatability of the prepared specimens if they are to undergo

further comparative testing.

Limits of detection

An important consideration in XRF analysis is the capability of an instrument to detect

whether an element is present or not in a specimen. It is an objective of pXRF analysis

to determine with defined statistical certainty that a given element is present if its

concentration is greater than a certain limit. This limit is the limit of detection.

Certain geological settings and mineralisation styles will produce varying types and

abundances of certain elements proven to be, in certain abundances and combinations,

known vectors towards mineralisation. In this study, initially work was undertaken to

search for typical Cu pathfinders such as Antinomy, however it was soon apparent that

certain elements vital to the study could not be relied upon due to their low detection

limits.

Peak Interference

The W:Zn data initially showed a linear trend (Figure 17) however when the pXRF data

was analysed against the lab data it was found that the level of W in the pXRF data was

significantly higher than that of the lab data (Table 3).

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Every element has a unique set of emission peaks; the area under these peaks is proportional to the concentration of the element. Since an element is never on its own there can be multiple emission peaks from different elements that overlap or one element's emission peak may swamp or influence the emission peak of another element (Figure 21). It is in this situation that the instrument will use the lower energy emission peaks to calculate the element concentrations, and when these peaks have low intensity there can be accuracy issues. As with any analytical method, we must be wary of elements whose concentrations are equal to or several times the detection limit (Appendix C).
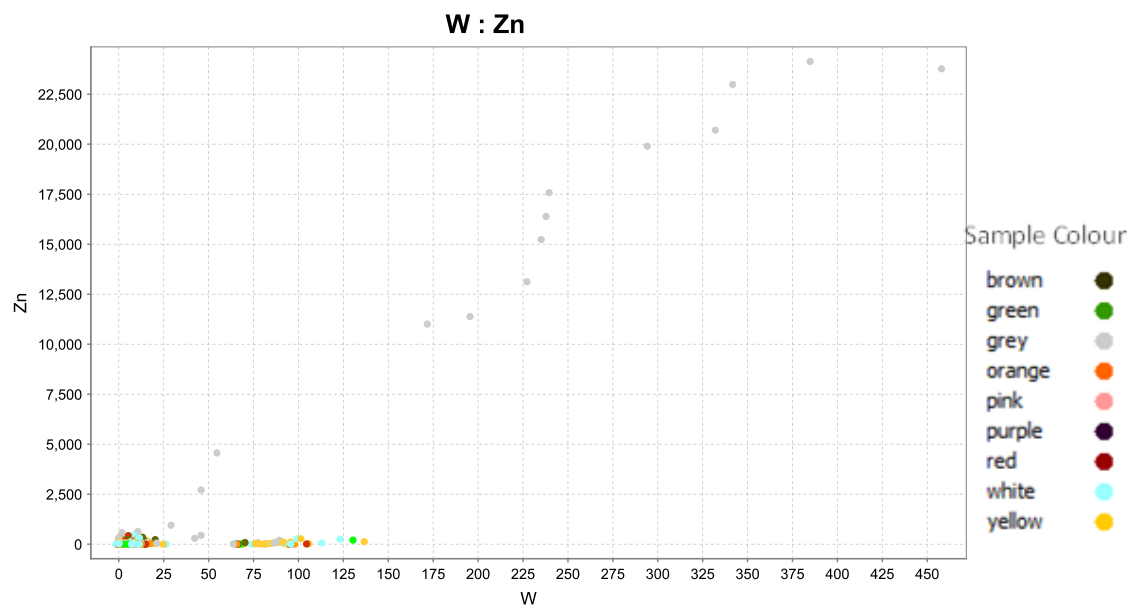

Figure 21: Linear trend of W:Zn in high Zn samples

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CONCLUSIONS

Using pXRF to sample the regolith surrounding mineralisation has been known to work and has been used successfully in many exploration programs however the usefulness for finding prospective mineralisation in this particular area seems to be quite low. The alteration associated with this style of mineralisation seems to be negligible and as a result, analysis of associated distal signatures of elements has proven to be inconclusive. The study has, however still increased the knowledge of the geochemistry of Kangaroo Island in that it is clear that there is no obvious movement of elements through the regolith, suggesting mineralisation is contained within the shear zone.

When using these technologies the importance of knowing the landscape and the regolith cannot be understated. The logged data from the study area and the pXRF data did not correlate suggesting problems with either the logging or the sampling itself. There were some associations, suggesting that with more precise sampling techniques and logging data, a more accurate lithogeochemical analysis can be produced. Overall, there is much work to be done on improving this exploration method in areas such as the Cygnet Snelling Shear Zone in order to confidently identify vectors towards mineralisation.

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ACKNOWLEDGMENTS

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APPENDIX A – METHODS

The samples used for this study were selected from open fill access air core drill holes that are stored at the DMITRE core storage facility at Glenside. These samples were extremely old and in most cases in their original calico bags which had become cemented (Figure 1).
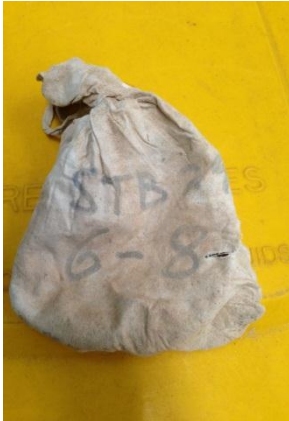
Figure 1: Original bagged sample from DMITRE storage facility
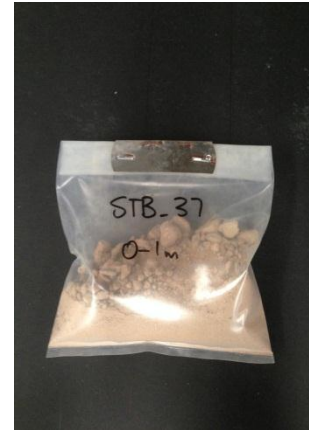
Figure 2: Crushed, rebagged and relabelled sample

Each of these samples was crushed using a rubber mallet, rebagged and relabelled (Figure 2).

Each sample represents a 2m composite, taken from the cover sequence above the basement and the first 1-2m of basement (where available). A representative sample of the composites was taken and placed in a 30mL container (Figure 3) and was then used for XRF analysis using the Olympus Innov-X 5000 portable XRF (Figure 5).

Figure 3: 30mL container of powdered rock, labelled with drill hole and depth, ready for transfer to pXRF plastic cup for analysis

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Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

The 30mL sample containers were ordered according to drill hole and depth and photographed against a black background to record colour changes across potentially differing lithologies.

A plastic teaspoon was used to remove a representative sample (including any aggregates) into a ceramic mortar and pestle where the rock was crushed into a fine powder. The powder was transferred into a pXRF plastic sample holder with a polypropylene X-ray film base (Figure 4) to a depth of >1mm. The mortar and pestle and plastic spoon were then cleaned with methylated spirits and excess powdered rock discarded between each sample.

Figure 4: Assembled pXRF sample holder showing X-ray film base.

A desktop portable Olympus X-5000 XRF (Figure 5) was used to collect whole rock geochemical data. Analyses were done using two modes, mining plus and soils mode, to maximise the number of elements with lowest possible detection limits for which data could be collected.

Beam count times of 60 seconds were used for each mode, this is the optimum beam count time based on experiments carried out by Morris (2009), using a Niton pXRF and Hall et al. (2011) using several pXRF models. Optimisation of the beam time is required to ensure that analytical precision is maintained while also allowing rapid data collection (Fisher et al. 2011).

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

Figure 5: Olympus X-5000 portable XRF.

Blanks and standards were run at the beginning and end of each data collection session, with the standards being run after every 20 samples. By analysing an SiO2 blank a multiple times, averaging the concentrations of elements detected, and repeating the process with the sample container material between the instrument and the SiO2 blank any additions can be identified. These can be subtracted from all results prior to correction for instrument bias or analytical drift (Fisher et al 2013).

Standards used were OREAS certified reference materials (CRMs) 901, 902 and 904. These are representative of sediment copper hosted deposits. Detailed geochemistry of each standard can be found at www.pxrfs.com.au.

The raw whole rock geochemical data was calibrated against the standards. Results from the two instrument modes were compared and data with calibration factors closest to 1 were used. Instrument drift was calculated from the standards analysed throughout each day. The data was then interrogated using ioGAS and modelled using Leapfrog software.

Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

APPENDIX B – SADME LOGGING DATA (EXAMPLE)

Full version available at:

https://sarigbasis.pir.sa.gov.au/WebtopEw/ws/samref/sarig1/image/DDD/RB9100023.pdf

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                                    A-50

xxx chlorite ± Fe infilled joint.
Miller's Road
Hole No:  MIL 25                      Date Drilled: 17.1.90
    0 - 5.0 core bit                  Logged by WSM

Quaternary :
    0    0.8    Lt brown clay-sand, & some Fe ind sandstone.
Kanmantoo Group :
  0.8    4.0    Lt orange-brown fine sandstone, trace of black mins, & trace of coarse
                muscovite on partings, some lt Fe staining & rare ind, faint laminae
                0.5 to 1.5mm with diffuse margins dip 20'.
                Rare lt grey weathered siltstone.
                Some vertical Fe stained joints, & one chlorite? infilled joint dips
                70'.
  4.0    5.0    Lt brownish grey v fine to fine sandstone, trace of black mins, & faint
                layering dips 30'; minor red-brown Fe stained fractures at 4.7m.
  5.0           End of Hole.


Miller's Road
Hole No:  MIL 26                      Date Drilled: 17.1.90
    0 - 7.0 core bit             .     Logged by WSM

Quaternary :
    0    0.5    Brown clay-sand.
  0.5    2.1    ", grey, & some basement rock fragments.
Kanmantoo Group :
  2.1    4.6    Lt grey clay-silt, finely foliated (dips 0 to 20'), trace of black mins,
                & some pale Fe mottling, & partially weathered lt grey siltstone.
                Lt orange Fe stained intersecting joints, dip 30 to 70' from 3 to 4m.
  4.6    4.8    Purplish grey siltstone/v fine sandstone, faintly laminated, some
                orange-brown Fe staining or induration.
  4.8    7.0    Lt grey to pale grey-brown v fine sandstone, faint laminae & parting
                dip 40' with muscovite & biotite on parting, rare Fe staining on joints
                and laminae, & some thin Fe stained zones.
                Some lt purplish brown to cream siltstone from 5.5 to 6m.
  7.0           End of Hole.


Miller's Road
Hole No:  MIL 27                      Date Drilled: 17.1.90
    0 - 5.0 core bit          .        Logged by WSM

Quaternary :
    0    0.3    Pale grey-brown fine sand.
  0.3    0.5    Grey/orange/red-orange laminated or mottled clay.
  0.5    1.2    Grey/orange/red-orange finely laminate clay-sand.
Kanmantoo Group :
  1.2    2.0    Pale grey finely foliated siltstone, lt orange brown Fe staining on
                laminae & joints.
  2.0    3.0    ", & abundant muscovite (& biotite?) on partings 2-4mm, & rare thin
                <0.5mm anastomosing quartz veins.
  3.0    4.0    Brownish grey metasiltstone, rare faint laminae, & Fe staining &
                muscovite on partings.
  4.0    5.0    ", laminae (slight colour & hardness variation, no mineral or
                textural variation ) & parting dip 45'.
                Faint schistosity (micro tensional shears/fractures) dip 55'.
  5.0           End of Hole.




E00317
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Geochemical analysis of the regolith and cover sequence of Kangaroo Island, SA.

APPENDIX C: X-5000 LIMITS OF DETECTION

OLYMPUS®
Your Vision, Our Future

LIMITS OF DETECTION (LODS)

X-5000 Portable XRF Analyzer

LODs, reported in PPM unless otherwise noted, are optimal.

Element of Interest	X-5000 3-Beam Soil Ta Tube, SDD
Mg	Not Available
Al	1.40%
Si	0.50%
P	380
S	90
Cl	33
K	18
Ca	17
Ti	2
Cr	2
V	1
Mn	2
Fe	4
Ni	4
Cu	3
Zn	2
As	2
Se	1
Rb	1
U	2
Sr	1
Zr	1
Th	2
Mo	1
Ag	1
Cd	2
Sn	3
Sb	4
Ba	20
Hg	3
Pb	2
La	30
Ce	45
Pr	75
Nd	90
Pm	130
Sm	150

Measurements were taken in air for 120 seconds per beam.

Standards used were in a clean, homogenous SiO_2 matrix without interfering elements.

NOTE:
Common, well-known inter-element interferences for environmental real-world soil samples are as follows:
» High levels of Fe can interfere with measurements of low levels of Cr
» High levels of Pb can interfere measurements of with low levels of As

The determination of detection limits for all methods of analysis depend on numerous factors including the instrumentation and its settings, the standards that are utilized to determine the limits of detection, and the actual working samples analyzed.

The LOD's reported here are based on the X-5000 portable XRF analyzer with a large area SDD; automatically selected kV-uA-Filter settings; SiO_2 blank measurements; Compton normalization; 120 seconds measurement time; standards that are pure elemental oxides, and NIST standards with some common soil matrices. All measurements were done in air.

These parameters allow the determination of the best LOD's for the X-5000 being calibrated. Actual working samples may contain interfering elements that the hardware settings or selection of analyte lines do not correct for; therefore, the actual working LOD's for "real-world" samples may be higher than those determined with the interference-free standards.

Limits of Detection for portable XRF instrumentation are typically determined using well defined and easily reproduced parameters:

Optimized hardware settings
» X-ray tube target material
» Power (kV, uA)
» Filters
» Background subtraction and/or normalization

Measurement times
» 60 to 120 seconds depending on the element of interest

Interference-free standards
» Standards used to determine instrumentation detection limits typically do not contain anything that introduces other variables, such as interfering elements, unless the hardware settings used eliminate or significantly reduce the interference.

LIMITS OF DETECTION

For Mg analysis, please contact your local Olympus Innov-X representative. The X-5000 is available with alternative x-ray tube options for light element optimized analysis.

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