

A combined chemical, isotopic and microstructural study of pyrite from roll-front uranium deposits, Lake Eyre Basin, South Australia

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Abstract

The common sulfide mineral pyrite is abundant throughout sedimentary uranium systems at Pepegooona, Pepegooona West and Pannikan, Lake Eyre Basin, South Australia. Combined chemical, isotopic and microstructural analysis of pyrite indicates variation in fluid composition, sulfur source and precipitation conditions during a protracted mineralization event. The results show the significant role played by pyrite as a metal scavenger and monitor of fluid changes in low-temperature hydrothermal systems.

In-situ micrometer-scale sulfur isotope analyses of pyrite demonstrated broad-scale isotopic heterogeneity ($\delta^{34}\text{S} = -43.9$ to $+32.4\text{‰VCDT}$), indicative of complex, multi-faceted pyrite evolution, and sulfur derived from more than a single source. Preserved textures support this assertion and indicate a genetic model involving more than one phase of pyrite formation. Authigenic pyrite underwent prolonged evolution and recrystallization, evidenced by a genetic relationship between archetypal framboidal aggregates and pyrite euhedra. Secondary hydrothermal pyrite commonly displays hyper-enrichment of several trace elements (Mn, Co, Ni, As, Se, Mo, Sb, W and Tl) in ore-bearing horizons. Hydrothermal fluids of magmatic and meteoric origins supplied metals to the system but the geochemical signature of pyrite suggests a dominantly granitic source and also the influence of mafic rock types. Irregular variation in $\delta^{34}\text{S}$, coupled with oscillatory trace element zonation in secondary pyrite, is interpreted in terms of continuous variations in fluid composition and cycles of diagenetic recrystallization. A late-stage oxidizing fluid may have mobilized selenium from pre-existing pyrite. Subsequent restoration of reduced conditions within the aquifer caused ongoing pyrite re-crystallization and precipitation of selenium as native selenium.

These results provide the first qualitative constraints on the formation mechanisms of the uranium deposits at Beverley North. Insights into depositional conditions and sources of both sulfide and uranium mineralization and an improved understanding of pyrite geochemistry can also underpin an effective vector for uranium exploration at Beverley North and other sedimentary systems of the Lake Eyre Basin, as well as in comparable geological environments elsewhere.

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1. INTRODUCTION

The resistate mineral pyrite is the most common sulfide mineral and an important component in a variety of ore-bearing mineral assemblages (Bowles et al., 2011). Arsenian

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pyrite is the main host for Au in Carlin-type deposits and other refractory Au deposits (Reich et al., 2005), and framboidal pyrite may also host economic concentrations of Ti (Zhou et al., 2005). Provided that complete recrystallization does not occur, pyrite is able to record its evolution by preserving patterns of intra-crystal morphological, chemical and isotopic zoning. This ubiquitous refractory mineral commonly contains measurable and often high levels of trace elements either hosted within the crystal lattice or as sub-micrometer- to nano-scale inclusions (Huston et al., 1995; Cook et al., 2009; Ciobanu et al., 2012). Data derived from the study of pyrite also provides insights into conditions present during ore formation (e.g., Large et al., 2007, 2009; Sung et al., 2009; Cook et al., 2009; Koglin et al., 2010; Reich et al., 2013) and will potentially assist in the development of new exploration vectoring strategies.

Pyrite is commonly found associated with uranium ore deposits in sedimentary settings where it acts as a reductant (Scott et al., 2007) and is generally considered to have been derived from the reduction of sulfates in ore-bearing solutions (Granger and Warren, 1969; Min et al., 2005a; Jaireth et al., 2008). All models for the genesis of sediment-hosted uranium deposits require the presence of pyrite, organic carbon or other reductant in the host rock prior to mineralization (Granger and Warren, 1969; Min et al., 2005a).

Pyrite is a common constituent of the uranium ores in the hydrothermal systems at the Beverley uranium deposits, South Australia, and throughout the sedimentary systems of the encompassing Lake Frome region (Brugger et al., 2005; Skirrow, 2009; Wülser et al., 2011). The sandstone-hosted uranium deposits of Pepegooona, Pepegooona West and Pannikan, which make up the study area at Beverley North, also contain pyrite, for which little previous detailed textural and chemical characterizations have been made to date. These uranium deposits were discovered in 2009 by Heathgate Resources and lie approximately 8 km NNW of the well-established Beverley uranium mine (Heathgate Resources, 2012; Märten et al., 2012).

This study provides the first comprehensive dataset on pyrite from the Pepegooona, Pepegooona West and Pannikan uranium deposits. Microtextural analysis and *in-situ* microanalysis on a suite of pyrite-bearing samples from across the three deposits provide preliminary constraints on the depositional conditions and sources of ore-bearing fluids for the deposits at Beverley North. This new information is important not only for deciphering the geological history of the deposits, but also indicates the considerable potential that pyrite mineral data has in development of innovative strategies for uranium exploration in the broader sedimentary systems of the Lake Frome region. The results also carry significance for understanding the role played by pyrite as a metal scavenger and monitor of fluid changes in low-temperature hydrothermal systems.

2. GEOLOGICAL SETTING

In the Lake Frome region (Fig. 1), sedimentary rocks of the Eromanga and Lake Eyre Basin unconformably overlie the Palaeoproterozoic basement and are bound to the west by the northern Flinders Ranges (Stoian, 2010). The

northern Flinders Ranges, directly adjacent to the Beverley North study area, host metamorphic inliers of the Mount Painter Domain (MPD), emplaced in the Neoproterozoic Adelaidean sedimentary sequences (Idnurm and Heinrich, 1993). The Mount Painter and Mount Babbage Inliers which make up the MPD (Brugger et al., 2005) comprise heat-producing granites and uplifted Proterozoic (~1590 Ma) metasedimentary, granitic and metabasaltic basement rocks (Stoian, 2010; Brugger et al., 2011; Wülser et al., 2011).

The MPD was pervasively deformed and metamorphosed up to amphibolite facies during the Delamerian Orogeny (~514–490 Ma; Foden et al., 2006). Felsic magmatism at the end of the Delamerian (~440 Ma), resulted in emplacement of granites with localized U and Th enrichment, with U reaching ~110 ppm in some localities (Neumann et al., 2000; Elburg et al., 2003; Wülser et al., 2011). This uranium is the proposed source of the secondary uranium mineralization in the adjacent Lake Frome region (Hore and Hill, 2010; Brugger et al., 2011; Wülser et al., 2011).

The eastern margin of the MPD is defined by the Paralana Fault Zone (PFZ), part of a regional fault network initiated in the early Palaeozoic. The PFZ is broadly defined by a series of NE–SW trending, W-dipping structures which extend to the surface from the basement (Brugger et al., 2011; Wülser et al., 2011; Märten et al., 2012). The fault network has been active since the late Miocene and is currently active as a cluster of reverse faults (Wülser et al., 2011). The PFZ also hosts the Paralana Hot Springs (PHS), a heat flow regime active since the late Palaeozoic. The regime is controlled by hydrothermal circulation of meteoric water through radiogenic MPD rocks which are undergoing rapid uplift (Neumann et al., 2000; McLaren et al., 2002; Skirrow, 2009; Brugger et al., 2011). Low-temperature epithermal activity, limited by low rainfall, continues in the PHS and the current shallow groundwater is considered a relic of the palaeofluids responsible for uranium mineralization in the Lake Frome region (Brugger et al., 2005, 2011; Skirrow, 2009).

The Lake Frome region, to the east and north of the Mount Painter Domain, hosts a thick sequence of sedimentary rocks deposited in a number of sub-basins (Table 1), which unconformably overlies the Proterozoic basement (Wülser et al., 2011).

The Beverley North uranium deposits, hosted by organic-rich terrestrial sandstones of the Eocene Eyre Formation, lie approximately 500 m from the eastern escarpment of the northern Flinders Ranges, at a depth of ca. 200–260 m (Fig. 2; Walker, 1999; Lambert et al., 2005; Jaireth et al., 2008; Hill and Hore, 2011; Märten et al., 2012). The depositional age of the host Eocene Eyre Formation constrains the maximum age of uranium mineralization to <55 Ma (Skirrow, 2009).

The Eyre Formation was deposited as the basal unit of the Lake Eyre Basin, which unconformably overlies the Frome Embayment; the southernmost portion of the Cretaceous Eromanga Basin. A ~30–50 Ma hiatus in deposition at the end of the Cretaceous is associated with extensive weathering and resulted in the widespread disconformities

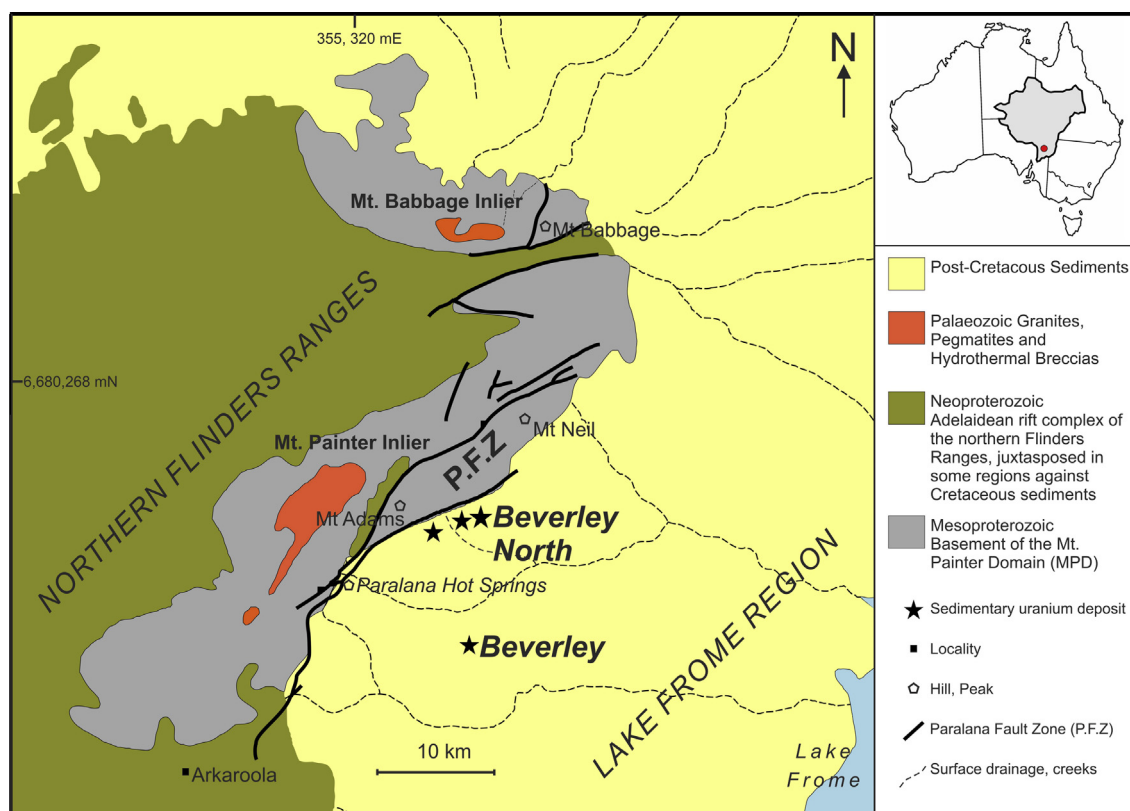


Fig. 1. Location of the Beverley North uranium deposits in the context of the regional geology of the Lake Frome Region. Inset shows the location of the study area in the southern-most portion of the Lake Eyre Basin. Adapted from Wülser et al. (2011). Grid coordinates follow UTM grid, MGA Zone 54, GDA 94.

between the basins (Skirrow, 2009; Wülser et al., 2011). Sedimentation continued in the interior, non-marine Lake Eyre Basin until the late Oligocene when widespread gentle folding caused uplift and division into sub-basins. The Beverley North region is encompassed by the Callabonna Sub-basin, broadly known as the Lake Frome region (Skirrow, 2009; Hore and Hill, 2010).

The location of the Beverley North deposits in intra-cratonic sedimentary basins adjacent to highly-deformed igneous and metamorphic terrains indicates a complex and multi-faceted evolution. The geometries of epigenetic uranium deposits are primarily controlled by the permeability of strata and the distribution of chemical traps in the environment for dissolved uranium (Hobday and Galloway, 1999). Other known uranium deposits of the Lake Frome region (Beverley, Honeymoon, Oban and Gould's Dam) are associated with Eocene to Miocene palaeochannels and palaeovalleys which are characterized by carbonaceous and pyritic sands intercalated with clays and gravels (Skirrow, 2009; Jaireth et al., 2010). Although the Beverley North deposits are hosted by similar sedimentary environments, a palaeochannel setting for them has not yet been established (Jaireth et al., 2010).

Märten et al. (2012) characterizes the sandstone-hosted uranium deposits of Beverley North as a series of stacked roll-front deposits which are likely a result of prolonged migration of oxidizing fluids through the sedimentary

environment. In general, sandstone-hosted roll-front deposits reflect the down-dip fluid flow of oxidized groundwater carrying dissolved uranium, within a confined sandstone aquifer (Galloway, 1978; Min et al., 2005a,b; Jaireth et al., 2008). Uranium-bearing minerals precipitate at redox fronts defined by the presence of reducing agents such as organic matter and pre-ore pyrite.

Primary uranium dissolution, transport from the source in the Mt. Painter Inlier and subsequent deposition likely occurred via low-temperature, slightly acidic and oxidizing groundwaters (Hore and Hill, 2010; Brugger et al., 2011; Wülser et al., 2011). Palaeo-aquifers similar to the currently active Paralana Hot Springs were the likely source of oxidized groundwater which precipitated uranium into the stratigraphic column where sufficiently reduced conditions existed (Pirlo and Giblin, 2004). Coeval ore-stage pyrite and other reduced minerals were formed as a result of repeated dissolution and reprecipitation of pre-ore minerals during groundwater flow down aquifer gradients (Pirlo and Giblin, 2004; Wülser et al., 2011).

3. METHODOLOGY

Thirty six core samples were collected from the Beverley North deposits (Fig. 2b). These are representative of different ore horizons, host formations and redox systems, whilst optimizing pyrite content wherever possible. The samples

Table 1
Stratigraphic Summary of the Lake Frome Region.

Cenozoic	Quaternary	Lake Eyre Basin	Current Deposition Willawortina Fm.	Terrestrial aeolian and alluvial erosion of the uplifted northern Flinders Ranges is currently causing the deposition of sediments in a variety of environments such as; claypans, dunes, playas and alluvial fans Deposited during the late Cenozoic to Plio-Pleistocene uplift and exposure of the Mount Painter Domain, the Willawortina Fm is characterized by coarse siliciclastics from braided fans and fine sands and clays from lacustrine settings
	Miocene		Namba Fm.	Deposited in Miocene lacustrine, alluvial and other low relief environments, the Namba Fm is characterised by angular immature sands and silts with minor conglomerates, black carbonaceous clays and green grey clays with some dolomites and lignite. The formation disconformably overlies the Eyre Fm. and is commonly capped by silcrete in the Lake Frome area
	Late Palaeocene - Eocene		Eyre Fm.	The Eyre Formation was deposited as the basal unit of the Lake Eyre Basin as a result of ongoing tectonic subsidence in the late Palaeocene to middle Eocene. Two major stages of deposition occurred (~55–49 Ma and ~45–37 Ma) resulting from basin subsidence associated with the uplift of the northern Flinders Ranges to the west. Depositional environments were dominantly fluvial and lacustrine and the Eyre Fm. is found in S–N palaeochannels, throughout the region, which commonly incise underlying stratigraphic units. The formation is characterized by pyritic carbonaceous mature sands of very fine to pebble grain size and is regionally capped by silcrete lenses
Mesozoic	Cretaceous	Eromanga Basin	Bulldog Shale	Deposited in a late Cretaceous, non-marine setting, the Bulldog Shale forms the uppermost unit of the Eromanga Basin. This widespread unit is a blue-gray silty, bioturbated clay mudstone with abundant organic matter
			Cadna-owie Fm.	The Cretaceous Cadna-owie Formation represents a transitional depositional environment from terrestrial to marine conditions. It is a fine-grained unit of pale grey siltstone and sandstone with minor carbonaceous claystone intervals Proterozoic Basement

Data from [Skirrow \(2009\)](#), [Stoian \(2010\)](#), [Hore and Hill \(2010\)](#), [Hill and Hore \(2011\)](#) and [Wülser et al. \(2011\)](#).

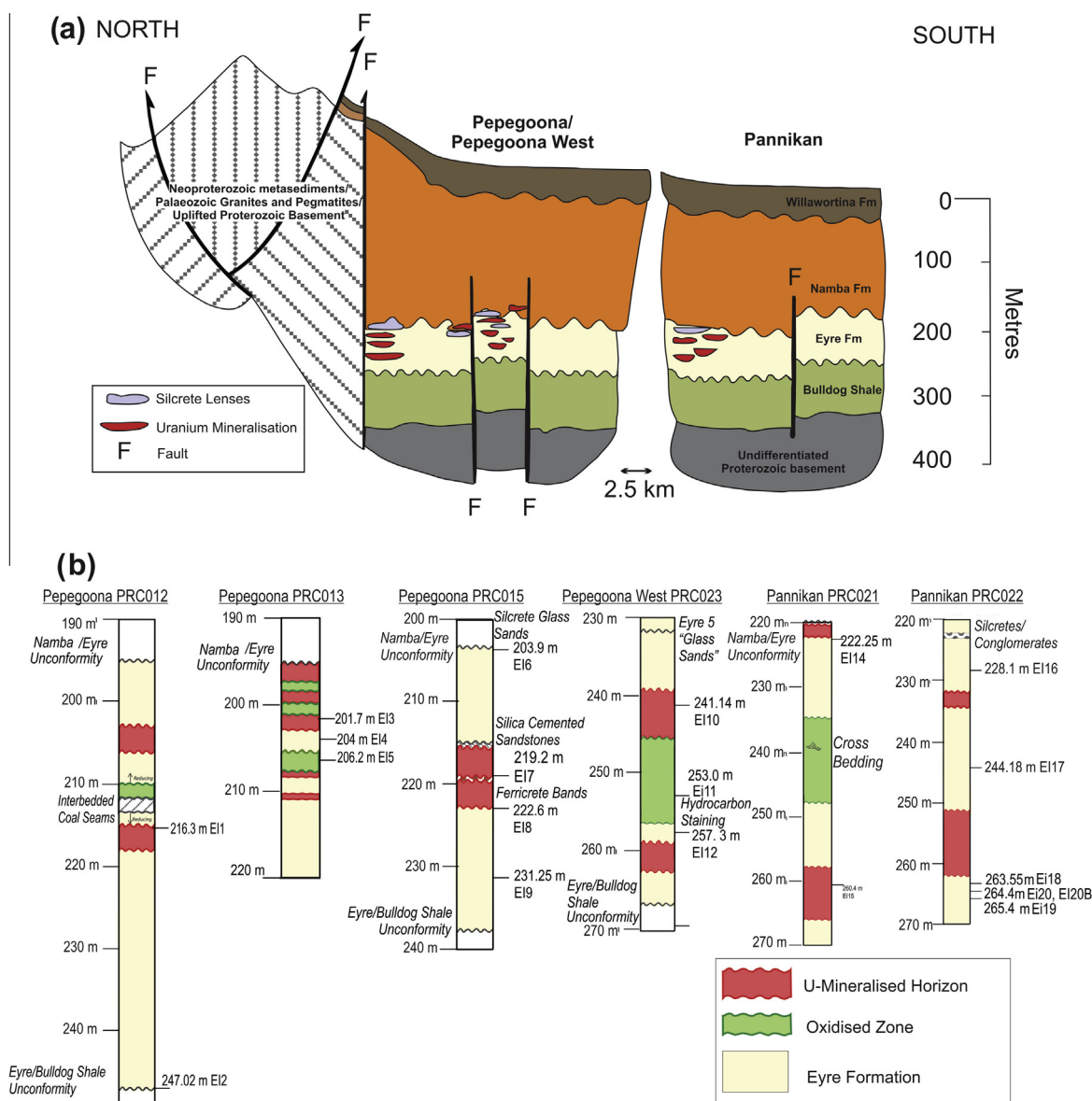


Fig. 2. (a) Schematic cross-section of the stratigraphy of the Lake Frome region hosting the sandstone-hosted uranium deposits of Pepegoona, Pepegoona West and Pannikan. The stacked, roll-front deposits are hosted by the Eocene Eyre Fm. (adapted from [Heathgate Resources, 2012](#)). (b) Stratigraphic logs of selected sampled intersections of drill core, showing the principal sample locations relative to the U-mineralized horizons.

were set in epoxy resin and prepared as one-inch polished blocks for mineralogical and petrographic analysis.

Optical and scanning electron microscopy (SEM) in back-scattered electron mode (BSE) were used to characterize pyrite morphology, document significant textural and mineralogical relationships, particularly between pyrite and the U-bearing minerals and Fe-(Ti)-oxides present. The SEM used (Philips XL-30) was equipped with an energy-dispersive X-ray spectrometer to aid mineral characterization.

Laser-ablation inductively-coupled mass spectrometry (LA-ICP-MS; [Ridley and Lichte, 1998](#)) was used to provide trace element concentrations in pyrites from various

localities and horizons, as well as distinct morphological types. Generally the grains analyzed by LA-ICP-MS were coarse-grained and whenever possible free from visible inclusions of other minerals. Details of analytical methods, standards and calibration are given in [Appendix A](#). LA-ICP-MS element mapping of approximately 0.5 cm²-sized areas of pyrite focused on areas of zonation to gain two-dimensional images of trace element partitioning within grains.

In-situ sulfur isotope analyses by secondary-ion-mass spectrometry (SIMS) were carried out using an IMS 1280 ion microprobe at the Centre for Microscopy Characterisation and Analysis at the University of Western Australia.

General analysis conditions and data reduction protocols follow those of Farquhar et al. (2013) and are presented in detail in Appendix A. Briefly, $^{33}\text{S}/^{32}\text{S}$ and $^{34}\text{S}/^{32}\text{S}$ ratios were measured using triple Faraday Cup detectors, a 20 keV Cs^+ primary ion beam focused to an $\sim 10\ \mu\text{m}$ spot, and 10 keV extraction voltage. Since $^{33}\text{S}/^{32}\text{S}$ ratios fell within the uncertainty of the mass dependent fractionation line (Farquhar and Wing, 2003), only $^{34}\text{S}/^{32}\text{S}$ ratios are reported here. $^{34}\text{S}/^{32}\text{S}$ ratios are reported in δ notation where:

$$\delta^{34}\text{S}_{\text{‰}} = 1000 \left(^{34}\text{S}/^{32}\text{S}_{\text{unk}} / ^{34}\text{S}/^{32}\text{S}_{\text{VCDT}} - 1 \right)$$

where $^{34}\text{S}/^{32}\text{S}_{\text{unk}}$ signifies the $^{34}\text{S}/^{32}\text{S}$ of an unknown sample and $^{34}\text{S}/^{32}\text{S}_{\text{VCDT}}$ signifies the $^{34}\text{S}/^{32}\text{S}$ value for the international standard VCDT. Sulfur isotope data are summarized in Table 2. All analyses are presented in the order they were obtained, in Appendix B.

Selected pyrite grains from seven samples were taken across the deposits to test for variations in $\delta^{34}\text{S}$ and characterize the isotope signatures of the morphologically distinct types of pyrite. Variations in the trace element concentration and $\delta^{34}\text{S}$ signatures were used to identify geochemical trends which may impact on understanding of ore genesis.

Nano-scale compositional characterization and high-resolution imaging of pyrite and other minerals in two polished ore blocks was carried out using a focused ion beam–scanning electron microscope (FIB–SEM) system following procedures outlined by Ciobanu et al. (2011).

4. RESULTS

4.1. Morphological and textural observations

Intercalation of oxidized and reduced sandstones with siltstone and clay-rich siltstones is prevalent throughout the Beverley North mineralized systems. Both pyrite and uranium-bearing minerals were found to be ubiquitously present proximal to reduced and/or clay-rich zones. Pervasive hydrocarbon staining, evident in hand samples, was observed across these reduced zones and is likely due to the proximity of the porous host sandstone to the hydrocarbon-rich Eromanga Basin.

Samples are predominately medium- to coarse-grained ($>1\ \text{mm}$, rarely up to as much as 2–3 mm), matrix-supported, sub-rounded quartz sandstones with accessory minerals prevalent throughout the matrix. A consistent mineral assemblage is observable across all pyrite-bearing samples: quartz ($\geq 50\ \text{vol.}\%$), pyrite ($\geq 30\ \text{vol.}\%$), $\pm$ U-bearing minerals ($\leq 10\ \text{vol.}\%$), $\pm$ ilmenite ($\leq 5\ \text{vol.}\%$), $\pm$ rutile ($\leq 5\ \text{vol.}\%$) $\pm$ minor clay minerals, zircon, hematite and sphalerite. Samples containing negligible pyrite (EI21–37) are predominantly composed of quartz ($\geq 80\ \text{vol.}\%$), ilmenite ($\leq 15\ \text{vol.}\%$) and rutile ($\leq 5\ \text{vol.}\%$) $\pm$ pyrite + hematite.

Pyrite displays a range of morphologies, and for the purposes of this study, these were categorized as: (i) framboidal; (ii) euhedral and cubic; (iii) cement; and (iv) infill and overgrowth. Specific morphologies do not appear exclusive to any particular deposit or horizon.

Framboidal pyrite is the most widespread morphological type of pyrite observed throughout the sample suite (Fig. 3). Framboids ($\sim <10\ \mu\text{m}$) are dominated by densely-

packed, spherical aggregates of sub-micrometer-sized pyrite crystals (Fig. 3a), and are found in clusters of up to several hundred individual framboids. Discrete framboids are observed in a range of sizes (commonly between 5 and 50 μm) and the idiomorphic microcrystals within framboids are highly uniform in both size and shape (Fig. 3b).

Framboidal aggregates throughout the samples are comparable with those documented by Wilkin and Barnes (1997), although within this study we extended this characterization to include a range of more hypidiomorphic pyrite spheroids, which likely share similar formation processes (Fig. 3c). These hypidiomorphic framboids lack the porosity associated with microcrystal aggregations in classic framboidal pyrite and are typically found both in isolated clusters and coexisting with archetypal framboids (Fig. 3c). No specific framboid morphologies were observed exclusively within any particular horizon or deposit but they are frequently seen intergrown with U-bearing minerals in samples from the ore-bearing horizons (Fig. 3c and d).

Cubic and euhedral pyrites vary widely in morphology across the sample suite (Fig. 4). Fine-grained cubic pyrites often appear as discrete grains, with associated U-bearing minerals at grain margins (Fig. 4a). In some instances, porous euhedral grains display evidence of multi-stage pyrite growth. Both spheroidal nuclei (Fig. 4b) and porous xenomorphic overgrowths between more coherent pyrite growth stages (Fig. 4c) are observed. Some euhedral grains also appear associated with framboidal growth. These are identifiable by the appearance of porous microcrystals within the center of grains (Fig. 4d). Anhedral pyrite grains are common in samples where massive pyrites are observed but also coexist with idiomorphic cubic pyrite or as single grains within the matrix. Similar to other pyrite morphologies, anhedral pyrite grains were observed intergrown with cemented pyrite.

Cement pyrite is the most abundant type of pyrite throughout the sample suite and occurs primarily as a matrix-forming mineral in the host sandstones. The appearance and growth of cement pyrite appears varied, with petrographic and SEM analysis confirming the presence of texturally homogenous, crystalline and xenomorphic cement growth (Fig. 5). A limited number of samples display micro-scale compositional zoning within the crystalline pyrite cement (Fig. 5a). The textural homogeneity of the cement pyrite is strongly influenced by local variation in porosity.

Infill textures characterize a sub-type of pyrite that is commonly seen pervasively fracturing sub-rounded quartz grains and/or overprinting porous cement pyrite (Fig. 5b). This pyrite generation is also seen bounding intergrowths of porous pyrite cement and archetypal framboids (Fig. 5c), and infilling micro-fracturing in other minerals, notably Fe–(Ti)-oxides (Fig. 5d).

Micro-fracturing and overprinting of quartz grains and texturally homogenous pyrite cement by hematite and native selenium was observed in one sample (EI11; PRC015, Pegoona) (Fig. 6). The zone of oxidized sandstone from which this sample was taken displayed a prevalent, visible yellow sulfur-staining on the drill core. Hematite and native

Table 2
Summary of data obtained during *in-situ* sulphur isotope analysis.

Sample No.	Pyrite morphology		δ^{33}_{CDT}	Uncertainty	2s	δ^{34}_{CDT}	Uncertainty	2s
<i>Pepegoona</i>								
EI3	Framboidal	Min	−22.72	0.09	0.19	−43.87	0.11	0.21
		Max	−21.80	0.15	0.29	−42.17	0.16	0.32
		Mean ($n = 10$)	−22.14	0.11	0.23	−42.88	0.13	0.26
		Std dev	0.32	0.02	0.04	0.64	0.02	0.04
EI7	Framboidal	Min	−17.47	0.12	0.23	−34.11	0.08	0.16
		Max	−15.36	0.17	0.34	−29.87	0.21	0.41
		Mean ($n = 4$)	−16.40	0.15	0.30	−31.88	0.15	0.30
		Std dev	0.86	0.03	0.05	1.74	0.06	0.12
<i>Pepegoona West</i>								
EI11 (assoc with native Se)	Cement	Min	13.46	0.08	0.16	25.97	0.07	0.14
		Max	16.67	0.18	0.37	32.40	0.27	0.53
		Mean ($n = 16$)	15.16	0.12	0.24	29.45	0.14	0.28
		Std dev	0.95	0.03	0.06	1.84	0.05	0.09
EI12	Porous cement	Min	−7.55	0.09	0.17	−14.96	0.12	0.23
		Max	13.86	0.15	0.30	27.01	0.18	0.36
		Mean ($n = 20$)	5.64	0.12	0.25	10.73	0.13	0.27
		Std dev	7.30	0.02	0.03	14.29	0.01	0.03
<i>Pannikan</i>								
EI15	Cement, anhedral and framboidal	Min	−20.72	0.09	0.18	−40.18	0.08	0.15
		Max	13.66	0.21	0.43	26.28	0.34	0.68
		Mean ($n = 10$)	−3.27	0.12	0.25	−6.74	0.16	0.31
		Std dev	11.22	0.04	0.08	21.81	0.07	0.14
EI19	Massive cement	Min	−2.50	0.07	0.14	−5.07	0.10	0.21
		Max	−1.68	0.12	0.24	−3.68	0.12	0.25
		Mean ($n = 14$)	−2.26	−1.26	−0.26	−4.54	1.74	2.74
		Std dev	0.21	0.02	0.03	0.36	0.01	0.01
EI20	Cubic, euhedral and overgrowth	Min	−5.82	0.07	0.15	−11.62	0.05	0.11
		Max	11.46	0.22	0.44	22.19	0.27	0.53
		Mean ($n = 20$)	6.89	0.11	0.22	13.18	0.12	0.24
		Std dev	4.64	0.04	0.07	9.08	0.06	0.11

δ Ratios represent a per mil deviation from the universal standard; *troilite* from the Canyon Diablo Meteorite (CDT) (0.00‰) (Farquhar and Wing, 2003).

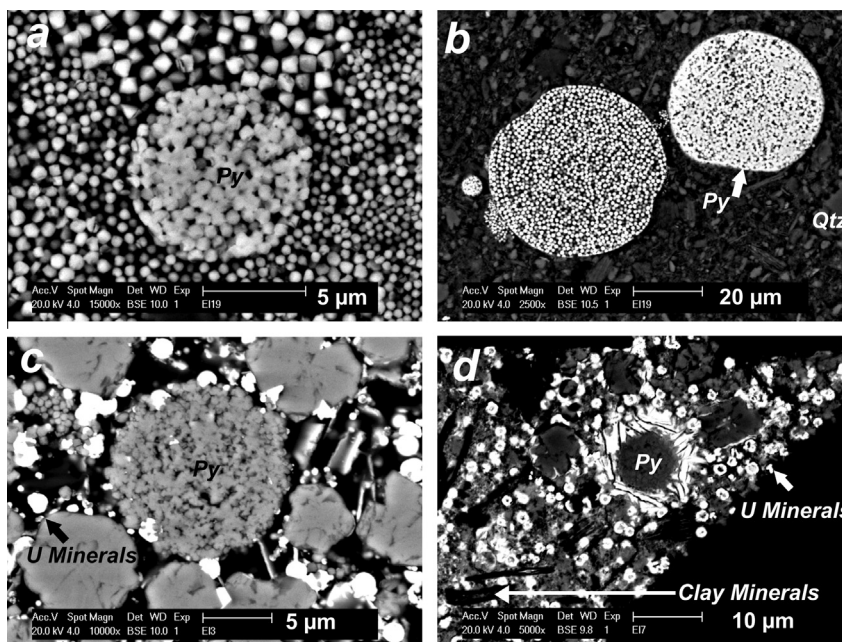


Fig. 3. Back-scattered electron images showing the occurrence of framboidal pyrite (Py). (a) An ordered spherical aggregate of sub-micrometer-sized pyrite crystals displays archetypal framboid morphology and is surrounded by disordered pyrite micro-crystals of likely similar provenance. (b) Discrete framboidal pyrite aggregates (Py) displaying large size variation hosted by a matrix of fine-grained quartz (Qtz). (c) Archetypal pyrite framboid (Py) in close proximity to more hypidiomorphic framboid types, which despite being more irregular retain a somewhat spherical shape. Rounded U-bearing minerals are commonly intergrown with both framboid morphologies. (d) Similar rounded U-bearing minerals associated with framboidal pyrite (Py) and clay minerals.

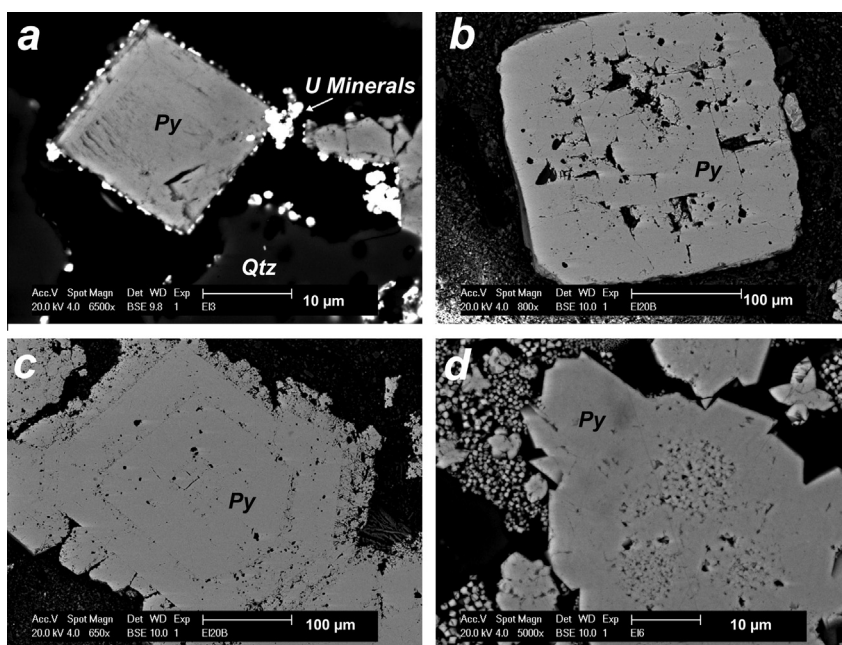


Fig. 4. Back-scattered electron images of euhedral and cubic pyrite (Py) grains. (a) Fine-grained cubic pyrite associated with U-bearing nodules predominately at grain edges. Qtz – quartz. (b) Porous cubic pyrite with clear multi-stage growth around a spheroidal nucleus. (c) Texturally-zoned euhedral pyrite with porous xenomorphic overgrowth at grain boundaries and between phases of more coherent pyrite growth. (d) Porous framboidal pyrite overgrown by euhedral pyrite.

selenium are pervasive throughout the sample, and appear to be genetically linked. Hematite is precipitated within fracture

zones and displays massive infill morphology, commonly juxtaposed against pyrite and late-stage native selenium

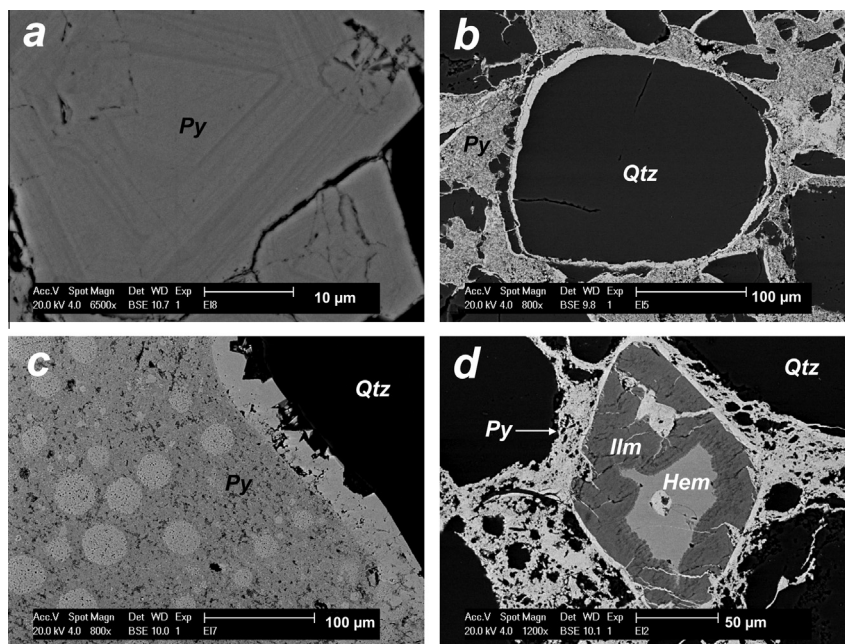


Fig. 5. Back-scattered electron images of cement and infill pyrite (Py) morphologies. (a) Compositionally zoned, crystalline pyrite cement. (b) Pervasive pyrite infills fractures in sub-rounded quartz (Qtz) grains with highly porous cement pyrite in the matrix. (c) Porous pyrite cement intergrown with archetypal framboidal pyrite and also associated with pervasive crystalline, euhedral pyrite infills. (d) Pyrite infilling porous space and fractured euhedral ilmenite (Ilm) and hematite (Hem).

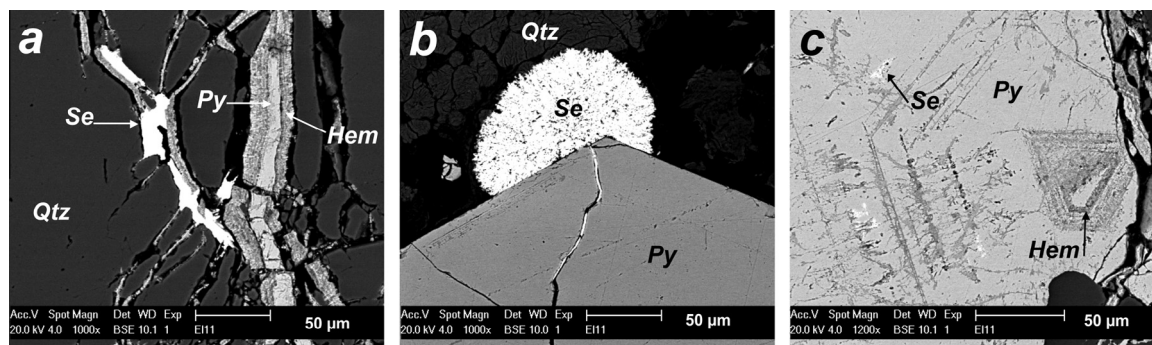


Fig. 6. Back-scattered electron images displaying pervasive precipitation of late-stage native selenium (Se) and hematite (Hem) throughout sample EI11. (a) Native selenium (Se) within micro-fractures in quartz (Qtz) where precipitation of pyrite (Py) and associated hematite (Hem) has occurred. (b) Crystalline native selenium growth in porous sandstone, associated with micro-fracturing and infill of pyrite. (c) Native selenium observed within pyrite cement. This occurrence also occurs proximal to septian replacement textures of pyrite by hematite in visually homogeneous pyrite cement.

(Fig. 6a). Native selenium is also observed as an accumulation of porous, feathery and bladed grains (Fig. 6b). Both minerals form septian textures (Schwartz, 1951), which appear as oscillatory deterioration patterns within the otherwise texturally homogenous cement pyrite (Fig. 6c).

Uranium-bearing minerals (dominantly uraninite with minor brannerite) most commonly occur as very fine-grained, nodule-like minerals overgrowing framboidal pyrite (Figs. 3d and 7a). Porous cement textures and intergrowths along pyrite cement boundaries are also commonly observed, with clay minerals as accessories in these assemblages (Fig. 7b and c).

Ilmenite and rutile are common throughout all samples but are most prevalent in samples from oxidized zones and

those which contain negligible pyrite. Coarse sub- and euhedral ilmenite and rutile appear to have undergone significant deterioration, fracturing and breakdown; linear and boxwork textures and pyrite infill of fractures are common. Hematite with relic framboidal textures was observed in oxidized sandstones; rare intergrowths of ilmenite with hematite were also observed.

4.2. Sulfur isotopic compositions

Results of *in-situ* sulfur isotope analysis are summarized in Table 2. The $\delta^{34}\text{S}$ values are broadly heterogeneous, ranging from -43.8 to $+32.4\text{‰}$ (avg. 2.79‰). Within this unusually broad range of values, distinct populations are

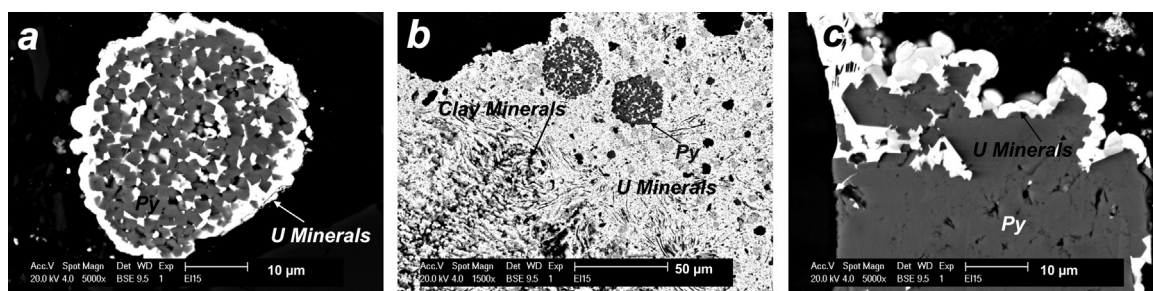


Fig. 7. Back-scattered electron images of fine-grained U-bearing minerals. (a) U-bearing minerals (uraninite and minor brannerite) intergrown with porous framboidal pyrite (Py). (b) Porous cement intergrown with pyrite (Py) and clay minerals. (c) Uranium minerals (dominantly uraninite) overgrowing margins of pyrite grains (Py).

nevertheless recognized. These correlate to some extent, although never exclusively, with pyrite morphology. Fig. 8, in which $\delta^{34}\text{S}$ is plotted against $\delta^{33}\text{S}$, demonstrates the large variation in isotopic values both within individual grains and among samples from the same horizon or deposit.

The spread of all framboid $\delta^{34}\text{S}$ data ranges between -43.8‰ and -18.3‰ . The $\delta^{34}\text{S}$ values for the morphologically-distinct framboidal pyrite populations (samples EI3 and EI7) show discrete, ^{34}S -depleted populations in relatively tight clusters for each sample.

Sulfur isotope data recorded from other morphological type of pyrite (cement, cubic and porous overgrowths; Ta-

ble 2), display a broader and more enriched range of $\delta^{34}\text{S}$ (Fig. 8). Some samples (EI12, EI15 and EI20) display large ranges in $\delta^{34}\text{S}$, whereas others (EI11 and EI19) form tight groups on Fig. 8. Despite this isotopic complexity, and the large $\Delta^{34}\text{S}$ of 65.0‰ , these S-isotope compositions in these samples are all enriched relative to framboidal pyrite.

Analyses of homogenous pyritic cement in sample EI11, in which BSE images showed secondary overprinting by hematite and native selenium, plot as a tight cluster of highly $\delta^{34}\text{S}$ -enriched points (mean $+29.45\text{‰}$; standard deviation 1.84‰).

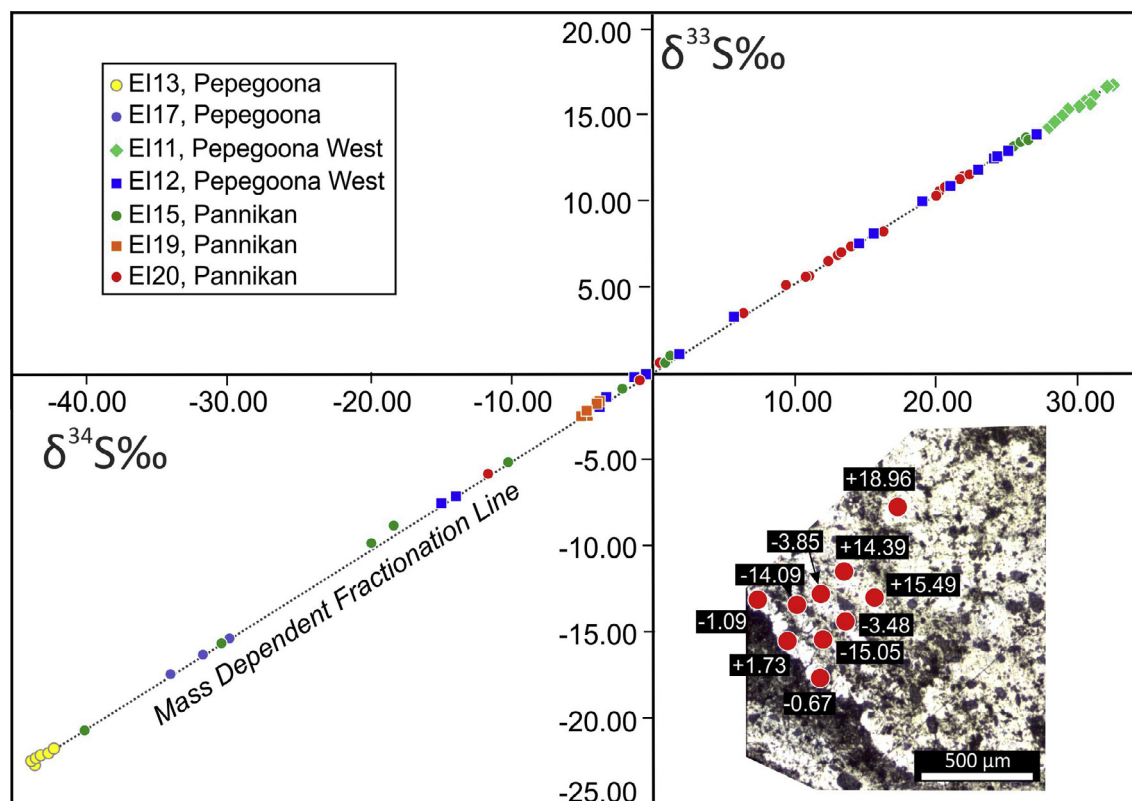


Fig. 8. $\delta^{34}\text{S}$ values are displayed against $\delta^{33}\text{S}$ values for each individual analysis. This plot can be used to extract information about the source of the sulfur. Despite the limited number of analyses per sample, a large variation of sulfur isotope compositions were recorded. Fit to the mass-dependent fractionation line indicates that all sulfur isotope fractionation was carried out by mass-dependent fractionation processes (Ono et al., 2006). Inset shows the large variation in $\delta^{34}\text{S}$ values recorded across individual pyrite bands from sample EI12.

The highly heterogeneous pyrite matrix in sample EI12, in which a prevalent colloform banding is observed (Fig. 8a), has $\delta^{34}\text{S}$ ranging from -14.95‰ to 26.27‰ , with each band giving a discrete, narrow range of $\delta^{34}\text{S}$ values but no systematic isotopic gradient across the banding.

4.3. Minor and trace elements in pyrite

LA-ICP-MS trace element analysis of pyrite in 19 samples indicated a broad variation in the trace element compositions. Significant non-uniform elevations of V, Cr, Mn, Co, Ni, As, Se, Mo, Sb, Ba, W and Tl are observed throughout the sample suite (Table 3).

Pyrite is broadly enriched in arsenic that was measured at elevated levels in 15 of the 19 samples analyzed by LA-ICP-MS methods. Whilst typically present at ~ 500 – 600 ppm, As reaches $16,000$ ppm in pyrite in some samples. No arsenopyrite was observed. These concentration ranges were corroborated by electron probe microanalysis. Strong positive correlations exist between As and Co, Sb and Tl, when data is transformed on a logarithmic scale (Table 4).

The correlation coefficients between Co and Ni, V and W, and As and Sb (Fig. 9) are among the highest in the dataset, with Pearson's r values of 0.88 , 0.89 and 0.82 , respectively. The correlation between As and Sb (Fig. 9c) highlights the significantly higher concentrations of both elements in the Pepegooona and Pepegooona West deposits relative to the Pannikan deposit. Data from the Pepegooona and Pepegooona West deposits show a range of trace element concentrations across five orders of magnitude, and whilst some low values are comparable with those from the Pannikan deposit, their median concentrations exceed those in the latter.

Within the Pannikan deposit, variation in trace element concentration in pyrite is observed. Trace elements, and in particular As, Co and Ni, are elevated in pyrite from core PRC021 relative to those from PRC022 (Fig. 10). This trend appears to reflect locations within the oxidized cell of the roll-front deposit. Samples taken from closer to the dominant mineralized zone are consistently more enriched in trace elements than their more distant counterparts.

Corresponding patterns are observed when the full dataset is viewed in terms of the spatial relationship with mineralization throughout the three deposits. Pyrite in samples taken from zones hosting uranium mineralization are consistently more enriched in a significant number of trace elements than pyrites hosted by other stratigraphic horizons (Fig. 11). This trend is most prevalent for Tl (Fig. 11a), which rarely exceeds background concentrations (≤ 50 ppm) in samples from outside the mineralized horizons but systematically attains concentrations of ~ 500 – 1300 ppm in pyrite associated with uranium mineralization (Table 3).

Nickel and to some extent Co, which are strongly correlated across all horizons, show additional enrichments in samples from the mineralized horizons (Fig. 11b). Both commonly reach ~ 800 – 2000 ppm in ore-bearing horizons but average only ~ 150 ppm in zones barren of U. Arsenic, V and Sb also display hyper-enrichment in pyrite from zones of uranium mineralization (Fig. 11a and c).

Limited minor trace element enrichment is also observable in pyrite in samples taken proximal (<2 vertical meters) to zones of U mineralization (Table 2). These elevations are not uniform across the LA-ICP-MS dataset, however; As, V, Co, Ni, Mo and Sb display only moderate enrichments in the proximal zones (Fig. 11a–c).

The apparent exception to these trends is sample EI11 taken from within the roll-front at Pepegooona West, which contains abundant hematite and native selenium (Fig. 6d). Pyrite in this sample is enriched in As, Se, Mo, Sb and W but is not from, or proximal to a mineralized horizon. Enrichment in Se (mean ~ 2663 ppm) is noteworthy as Se concentrations are limited in other samples analyzed.

LA-ICP-MS element mapping of pyrite grains from samples EI3, EI7, EI8, EI11 and EI12 also demonstrated irregular trace element enrichment across all pyrite morphologies. The map of pyrite from sample EI7 (Fig. 12) shows that framboidal pyrite hosts limited trace element concentrations relative to the surrounding and intergrown pyrite morphologies. Framboids are markedly depleted in As, Co, Ni, Mn, Sb, Tl and V, although a limited gradational zoning of As, Co and Ni toward framboid margins was apparent. In contrast, the surrounding porous pyrite cement is enriched in all these elements. Late-stage pyrite forming veinlets in the cement is enriched in both Mo and As.

The pyrite cement mapped in sample EI11 (Fig. 13) shows distinct oscillatory zoning with respect to As, Mo, Sb and Tl. The septian zone of deterioration (visible on Fig. 6c) is highly enriched in Co, Ni, As, Se, Mo, Tl, V and W, and trace element enrichment in the surrounding pyrite appears focused around this “nucleic” zone. The element maps highlight the strongly crystalline nature of the pyrite cement, which is not apparent from optical or scanning electron imaging.

The colloform-banded pyrite cement in sample EI12 was also mapped for minor and trace elements (Fig. 14). The colloform banding is readily picked out by orders of magnitude variation in As, Al, Co, Fe, Ga, Mn, Mo, Ni, Sb, Tl and Zn concentrations across the bands and is indicative of fluctuation in fluid composition during pyrite formation. It is interesting to compare these maps with the marked sulfur isotope variation across the same area noted above.

4.4. Nanoscale characterization of pyrite cement

One sample with pyrite-cemented sandstone was chosen for FIB-SEM study with the aim of better understanding relationships between pyrite textures and uranium mineralization. Pyrite textures in the cement are varied and reflect different cycles of pyrite growth. Fibrolitic textured pyrite (possibly itself representing a regrowth of framboidal pyrite or maybe pseudomorphic replacement of marcasite?) is surrounded by overgrowths of pyrite zoned with respect to As (Fig. 15a). Framboids are also present and, in some cases, contain small volumes of U-bearing minerals within them (Fig. 15b). Most U minerals, however, occur either concentrated in the matrix surrounding the framboids (Fig. 15c) or within domains in which clay minerals and organic material are present (Fig. 15d). In the latter, the U minerals are typ-

Table 3
Summary of LA-ICP-MS trace element data for pyrite (ppm).

		V	Cr	Mn	Co	Ni	As	Se	Mo	Sb	Ba	W	Ti
Pepegona	E11 (216.3m)												
	Min	8.4	3.5	97	5.8	13	276	33	25	30	271	10	154
	Max	2082	1317	434	835	1401	1054	285	-	83	16517	2568	243
	Mean	446	275	240	238	352	553	126	111	31	4116	560	204
	Std Dev	915	582	129	344	591	309	100	181	34	6990	1123	39
	E12 (247.1m)												
	Min	0.98	bdl	4.7	bdl	bdl	4.7	bdl	0.64	0.28	133	1.6	0.59
	Max	19	7.2	27	4.8	7.3	571	2.4	15	5.4	329	41	25
	Mean	8.4	3.0	13	1.1	2.5	139	1.4	4.4	1.6	232	17	6.3
	Std Dev	7.5	2.6	7.7	1.5	2.6	171	0.60	4.2	1.4	69	15	7.5
	E13 (201.7m)												
	Min	32	bdl	3.7	159	75	2773	191	107	241	15	15	186
	Max	3853	1308	180	635	780	16903	944	351	869	3429	3300	1337
	Mean	1566	211	72	342	409	12091	461	225	563	1113	1370	895
	Std Dev	1184	428	63	170	237	4957	259	64	165	1018	1028	400
	E14 (204.0m)												
	Min	37	bdl	13	66	24	176	18	11	1.9	81	16	24
	Max	533	437	335	269	344	333	103	90	10	14473	761	43
	Mean	170	104	88	153	115	274	44	37	4.9	5684	230	35
	Std Dev	206	187	138	86	131	59	35	31	3.2	7131	305	9.1
E16 (203.9m)													
Min	3.1	bdl	2.0	11	20	298	42	15	1.6	8.4	1.5	11	
Max	221	375	8.2	181	350	1259	319	123	29	447	50	62	
Mean	73	86	3.7	139	90	992	101	39	7.0	206	13	36	
Std Dev	72	125	2.0	54	93	276	86	33	8.2	179	16	13	
E17 (219.2m)													
Min	23	1.8	23	400	229	659	bdl	10	3.9	170	0.67	130	
Max	152302	454	8228	12085	12122	57295	482	2576	12523	30589	125202	1521	
Mean	429	4.0	49	1129	803	4240	23	46	166	401	248	326	
Std Dev	53697	159	2892	3986	4065	19101	163	895	4373	10676	44179	443	
E18 (222.6m)													
Min	1.2	bdl	4.2	0.6	6.4	140	bdl	16	0.33	6.3	0.24	3.5	
Max	229	31	32	291	253	1921	7.5	488	15	1625	8.2	57	
Mean	39	7.5	9.9	52	71	580	3.5	122	4.1	151	2.1	15	
Std Dev	65	8.4	7.2	75	66	542	1.7	127	4.2	397	2.2	14	
E19 (231.3m)													
Min	0.34	bdl	2.6	bdl	0.40	2.1	bdl	4.0	0.32	8.9	0.32	0.02	
Max	3.2	4.1	141	125	153	1953	51	293	126	230	3.4	130	
Mean	1.3	1.1	15	27	56	292	9.4	122	19	128	1.9	29	
Std Dev	0.7	0.9	35	39	51	532	14	84	40	80	1	42	
Pepegona West	E111 (253.0m)												
	Min	0.36	bdl	1.4	0.34	bdl	22	8.7	2.6	0.45	13	2.5	1.0
	Max	487	5.8	14	410	51	1301	36432	935	688	288	466	136
	Mean	77	1.3	7.2	70	12	407	2663	270	63	88	65	29
	Std Dev	106	1.4	3.3	96	15	329	7620	222	133	50	98	34
	E112 (257.2m)												
	Min	0.08	bdl	10	3.0	5.3	24	bdl	0.59	2.7	12	0.22	1.7
	Max	5.7	2.4	187	262	699	450	12	43	103	388	2.4	94
	Mean	2	1.1	73	107	207	184	3.5	17	31	224	1.6	44
	Std Dev	1.6	0.7	60	98	210	118	4	14	31	151	0.7	31
	E113 (269.1m)												
	Min	0.56	bdl	1.2	0.23	1.2	25	1.9	1.4	0.11	12	0.02	4.3
	Max	11	5	32	79	141	602	3.2	25	2.8	1468	1.3	297
	Mean	1.8	1.1	6.3	25	40	214	2.2	7.8	1.1	184	0.4	46
	Std Dev	3.2	1.4	9.6	26	42	167	0.4	7.5	1	452	0.4	90
Pannikan		V	Cr	Mn	Co	Ni	As	Se	Mo	Sb	Ba	W	Ti
	E114 (222.5m)												
	Min	43	bdl	15	48	35	86	bdl	26	1.9	290	101	18
	Max	640	285	140	281	1566	359	914	667	15	23443	788	53
	Mean	144	95	47	133	290	221	167	119	5.4	6524	242	31
	Std Dev	204	106	43	79	523	82	305	222	4.5	8225	259	12
	E115 (260.4m)												
	Min	0.81	bdl	15	2.8	37	25	bdl	0.32	0.09	57	0.09	285
	Max	94	3.9	27	3949	3233	550	58	59	4.2	170	227	529
	Mean	12	1.1	21	569	532	165	8	12	0.7	95	35	415
	Std Dev	29	1.1	4.2	1219	988	162	18	23	1.3	33	73	81
	E116 (228.1m)												
	Min	0.99	bdl	12	2.2	1.3	12	bdl	4.8	0.21	39	1.6	11
	Max	59	128	170	174	106	51	28	225	3.1	610	49	140
	Mean	20	20	60	39	27	27	8.7	54	1.2	191	16	55
	Std Dev	19	44	55	62	36	12	10	70	1.1	192	16	44
	E117 (244.2m)												
	Min	1.45	bdl	700	0.21	1.3	156	984	52	0.40	45	0.56	11
	Max	37	30	1356	100	503	496	1736	109	4.2	234	11	232
	Mean	11	9	982	38	123	281	1291	75	1.6	134	3.3	85
Std Dev	15	13	267	42	214	137	348	21	1.5	86	4.4	90	
E118 (263.6m)													
Min	0.48	bdl	4.9	0.11	0.35	0.51	bdl	bdl	bdl	8.2	0.27	0.16	
Max	44	109	151	8.3	52	87	6.5	3.9	1.3	236	28	6.1	
Mean	12	17	36	2	10	38	1.7	1.5	0.3	99	8	2.1	
Std Dev	15	34	48	2.7	16	37	1.7	1.6	0.4	93	10	2.5	
E119 (265.4m)													
Min	bdl	bdl	2.5	1.1	6.3	238	2.4	4.9	3.8	5.1	bdl	6.1	
Max	5.5	237	47	6.5	34	608	23	16	17	627	0.73	50	
Mean	1.5	27	10	3.1	16	353	7.3	8.0	6.6	152	0.1	14	
Std Dev	2.0	74	13	1.9	9.7	138	6.2	3.0	4.2	188	0.2	13	
E120 (264.4m)													
Min	0.71	bdl	11	0.7	0.38	1.1	bdl	bdl	bdl	18	1.9	0.29	
Max	33	11	161	38	108	140	3.2	40	0.72	461	13	4.3	
Mean	6.7	2.6	57	4.9	17	49	1.9	7.8	0.2	101	4.3	1	
Std Dev	9.7	3.1	55	12	33	44	0.5	13	0.2	129	3.5	1.3	
E120B (264.4m)													
Min	0.87	bdl	4.5	0.14	0.51	bdl	bdl	bdl	bdl	35	1.6	0.1	
Max	4.7	1.2	34	4.5	11	26	bdl	2.3	0.91	128	3.1	1.5	
Mean	2.7	0.7	18	1.7	4.1	9.3	1.8	0.6	0.2	68	2.4	0.4	
Std Dev	1.7	0.4	13	1.8	4.4	11	0.2	0.9	0.3	38	0.6	0.5	

Ore-bearing horizons (shaded grey) show hyper-enrichment of a range of elements and moderate elevations are observed in samples proximal (<2 m) to ore zones (striped grey). 'bdl' represents values below detection limits and practices outlined by [Winderbaum et al. \(2012\)](#) were followed.

^a The mean of E17 was recalculated without extreme outlier values to show a more representative value of the dataset.

Table 4

Pearsons coefficients of the LA-ICP-MS trace element data for pyrite ($n = 194$) after logarithmic transformation.

	V	Cr	Mn	Co	Ni	As	Se	Mo	Sb	Ba	W	Tl
Cr	0.5											
Mn	0.34	0.26										
Co	0.63	0.38	0.23									
Ni	0.49	0.41	0.35	0.88								
As	0.56	0.37	0.11	0.70	0.64							
Se	0.59	0.27	0.20	0.54	0.30	0.54						
Mo	0.49	0.27	0.07	0.55	0.38	0.59	0.60					
Sb	0.56	0.29	0.18	0.68	0.55	0.82	0.63	0.67				
Ba	0.63	0.51	0.47	0.44	0.45	0.32	0.31	0.35	0.41			
W	0.89	0.46	0.37	0.52	0.35	0.41	0.57	0.46	0.51	0.67		
Tl	0.45	0.26	0.33	0.72	0.71	0.76	0.42	0.42	0.67	0.35	0.34	

Note: In the creation of this table, values which were <mdl in the dataset were halved to facilitate their inclusion in statistical calculations so as to approximate the correct spread of data; they do not make any significant changes to inter-element correlations.

Bold entries are correlation coefficients >0.7.

ically embedded between lamellae of the clay minerals. Both domains feature high porosity.

The U-bearing phases are typically rounded crystals, either single (as within the framboids for example; Fig. 15e), or as aggregates or clusters of individual grains, as within the clay minerals (Fig. 15f). Cross-section imaging of the two U-rich domains shows that U-bearing minerals are typically sub-micrometer in scale and are deposited around larger pyrite domains, of some tens of μm in size, such as framboids (Fig. 15g). Textures recording small-scale replacement reactions are observable at boundaries between such coarser domains and the fine-grained pyrite matrix (Fig. 15h). New-formed pyrite may be no more than 100–200 nm in diameter (Fig. 15i). A commonly observed, ‘artichoke-like’ texture between pyrite and/or U minerals and clay minerals (Fig. 15j) is characteristic of this nano-scale pyrite cement hosting U minerals. This is suggestive of simultaneous growth of pyrite and clay minerals during U deposition.

In detail (Fig. 15k), the U minerals within such domains display a concentric, ring- or atoll-like texture in which a relatively U-poor core is enclosed by a rim zone richer in U. EDAX data confirmed the presence of uraninite and brannerite but could not provide unequivocal proof that coffinite is also present. At the smallest observable scale, there is evidence of resorption of the core and trapping of clay minerals among the U minerals (Fig. 15l).

The study clearly shows several aspects of interest at the sub-500 nm-scale. Firstly, there is a close relationship between the presence of clay minerals, pyrite and uranium. Secondly, the presence of brannerite can be related to processes of dissolution and reprecipitation of the Ti-(Fe)-oxides that are occasionally observed within the pre-existing pyrite cement. Thirdly, the scale of textural features in the cement is much smaller than observed elsewhere in the pre-existing pyrite matrix. The latest-formed matrix pyrite (e.g., Fig. 15i) is <100 nm in size, well below that of the framboids, and probably formed at the same time as U mineralization. Finally, there is strong evidence of cycles of dissolution–reprecipitation reaction that affected pyrite and clay minerals during precipitation of U-bearing miner-

als. Organic matter occurs within the same domains and may play a redox role in defining the larger scale fluid-infiltration processes. The distribution of U minerals, however, is not necessarily tied to such organic matter. Instead, uranium deposition appears closely linked to the presence of clay minerals.

5. DISCUSSION

The uranium-bearing ore systems of Pepegooona, Pepegooona West and Pannikan are the products of prolonged and evolving hydrothermal flow of uranium-enriched fluids in the Lake Frome Region that is likely continuing to the present day (Skirrow, 2009; Wülser et al., 2011).

The mineralogy and geochemistry of the ores reflects a superimposition of a succession of hydrothermal fluids onto an already lithologically-varied sequence of sedimentary rocks. The location of U mineralization is controlled by the interplay between sediment permeability, direction of fluid flow and the proportion of reducing components, such as carbonaceous matter and sulfides in the host rock (Skirrow, 2009).

Given this complexity, many factors likely influenced the pyrite morphology, trace element geochemistry, and isotopic signatures of pyrite across the region. The practicability of any vectoring approach to exploration using the trace element chemistry of pyrite depends on understanding both the cause and expression of this variation at a range of scales. The data generated in this study is intended to assist understanding of the hydrothermal systems, the sources of ore components and the controls on ore genesis in the regional sedimentary basins. Importantly, the dataset was obtained using site-specific methods, allowing information to be correlated not only with geological position but also with textures and grain morphology at the microscopic scale.

The high variance in analytical datasets can reduce the usefulness of the mean values in characterizing the population (Dawson and Sinclair, 1974; Ryall, 1977), and the relatively small size of the sample set influences its value for petrogenetic interpretation (e.g., Winderbaum et al.,

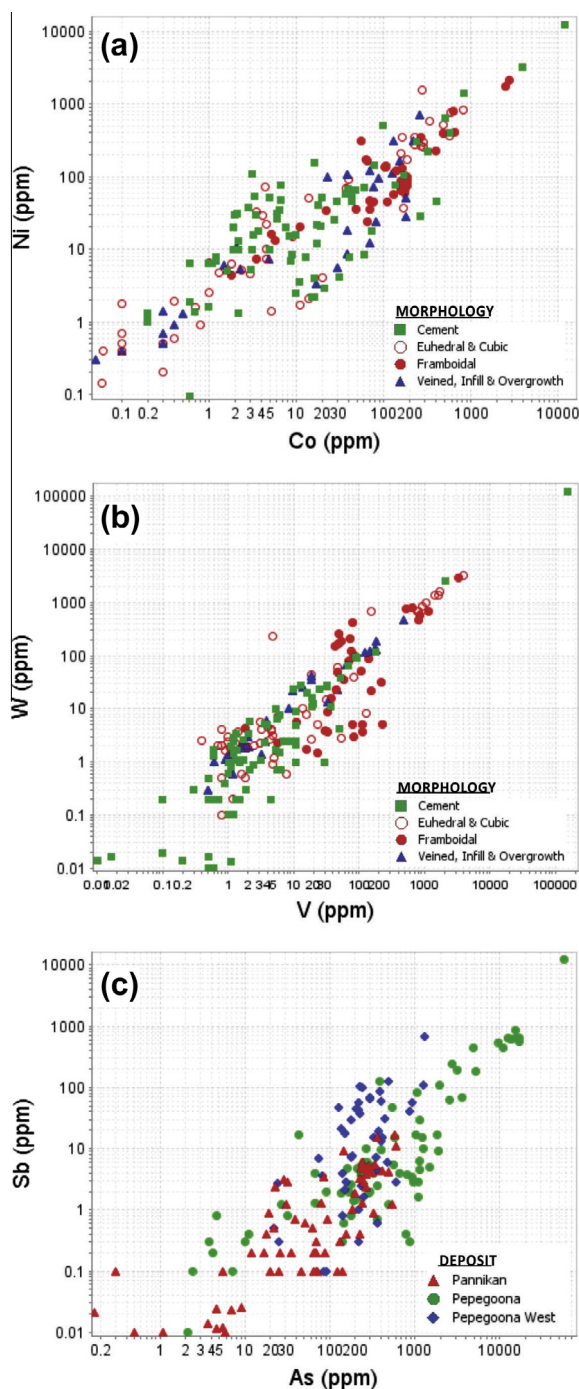


Fig. 9. Inter-element plots displaying strong positive correlations across 5 orders of magnitude, between the trace elements (a) Co and Ni, (b) V and W and (c) As and Sb. Plots (a) and (b) demonstrate that these strong linear relationships appear independent of pyrite morphology. Plot (c), which still displays a linear relationship between the trace elements, demonstrates a broad trend towards greater enrichment in pyrites from the Pepegooona and Pepegooona West deposits relative to the Pannikan deposit.

2012). Whilst these considerations likely contribute to the apparent variance across the datasets, the inherent variability within the open system which has undergone protracted mineralization must be taken into account.

5.1. Sulfur sources

The widespread presence of sulfur in nearly all natural environments has established sulfur isotope systematics as an effective geochemical tracer of past geological and environmental processes (Bendall et al., 2006). The two most abundant isotopes of sulfur (^{32}S and ^{34}S), along with less common isotopes (^{33}S and ^{36}S), are used to provide information on sulfur source and precipitation mechanisms (Warren, 1972; Johnston, 2011). Moreover, *in-situ* analytical techniques, allowing high-resolution analysis of the smallest areas within complex pyrite crystals, give insight into the complex interplay of biological and chemical processes that occurs in sediments during sulfide precipitation (Kohn et al., 1998).

Depletion or enrichment of heavy sulfur isotopes (^{34}S and ^{36}S) in a sample reveals information about biogeochemical processes, hydrothermal fluid sources and sediment diagenesis (Butler et al., 2004; Ono et al., 2006; Johnston, 2011). Major changes in sulfur isotope ratios during the deposition of ore and gangue minerals indicate a systematic change in the redox conditions of the fluid during ore deposition (Fleming and Bekken, 1995). These chemical variations make it possible to trace out mechanisms of transport, concentration and local precipitation during ore genesis (Fleming and Bekken, 1995; Hoefs, 2009).

As demonstrated by Fig. 8, the $\delta^{34}\text{S}$ compositions of pyrite are highly variable (-43.8 to $+32.4$ ‰). Such large scale heterogeneity is commonly observed in sulfur isotope datasets obtained from sedimentary pyrite (e.g., Kohn et al., 1998), as sulfur isotope fractionation and the consequent partitioning of light stable isotopes in mineral forming systems is driven by temperature, bacterial reduction, pH and reservoir effects (Fleming and Bekken, 1995; Ohmoto and Goldhaber, 1997; Ulrich et al., 2011). The overall discordance of data at the regional scale is suggestive of at least two sources of sulfur involved in pyrite formation.

The distinct populations observable within the broad dataset correlate to some extent, although not exclusively with pyrite morphology and inferred mineral paragenesis. Where different phases of sulfides occur in close petrographic context, *in-situ* sulfur isotope analysis is capable of sufficient spatial resolution to address these textural variations (Ulrich et al., 2011).

Isotopic ratios from morphologically-distinct framboidal pyrites display discrete and largely ^{34}S -depleted populations (-43.8 ‰ to -18.3 ‰). This ^{34}S depletion in framboidal pyrites is characteristic of a biogenic sulfur source (Schwarcz and Burnie, 1973; Raiswell, 1982; Seal, 2006) with minor differences in the clustered isotopic ratios from different samples likely reflecting diversity during reduction processes (Schwarcz and Burnie, 1973; Butler et al., 2004; Seal, 2006). Sulfate-reducing bacteria preferentially select sulfate with light sulfur (Chambers and Trudinger, 1979), and organic material in the sedimentary systems supplies the energy for sulfate reduction (Warren, 1972; Beier and Feldman, 1991).

Relative to framboidal pyrite, the remaining highly heterogeneous dataset, which represents a range of pyrite morphologies, displays relative ^{34}S enrichment. These values are

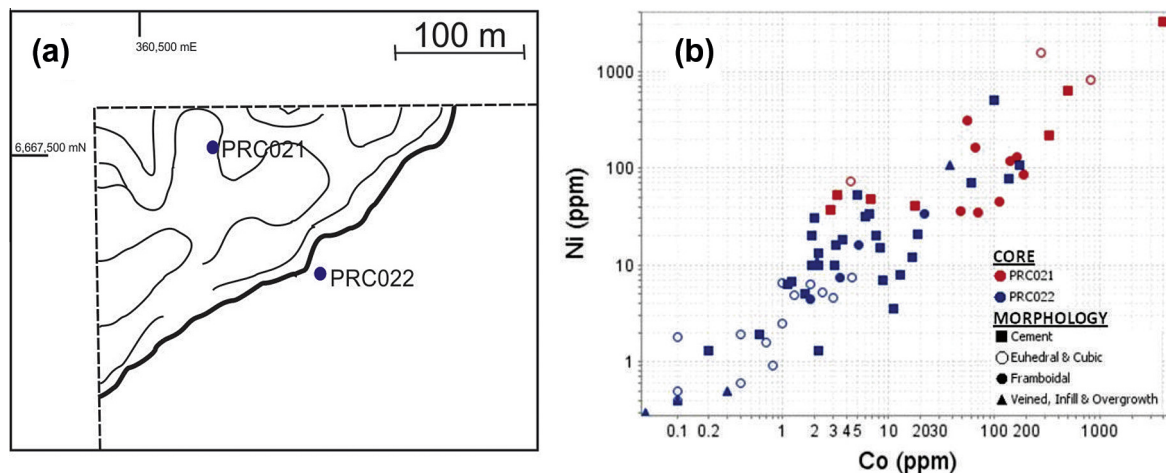


Fig. 10. Intra-deposit variation in trace element enrichment is apparent within the Pannikan deposit. (a) Simplified location map for cores PRC021 and PRC022 from which the samples were taken. Core PRC021 intersects the roll-front system; PRC022 was taken in front of the oxidized zone. (b) Inter-element plot showing trace element variation in pyrites from the Pannikan deposit in terms of core location. The plot demonstrates how pyrites from core PRC021 appear consistently more enriched in Co and Ni than pyrites from core PRC022.

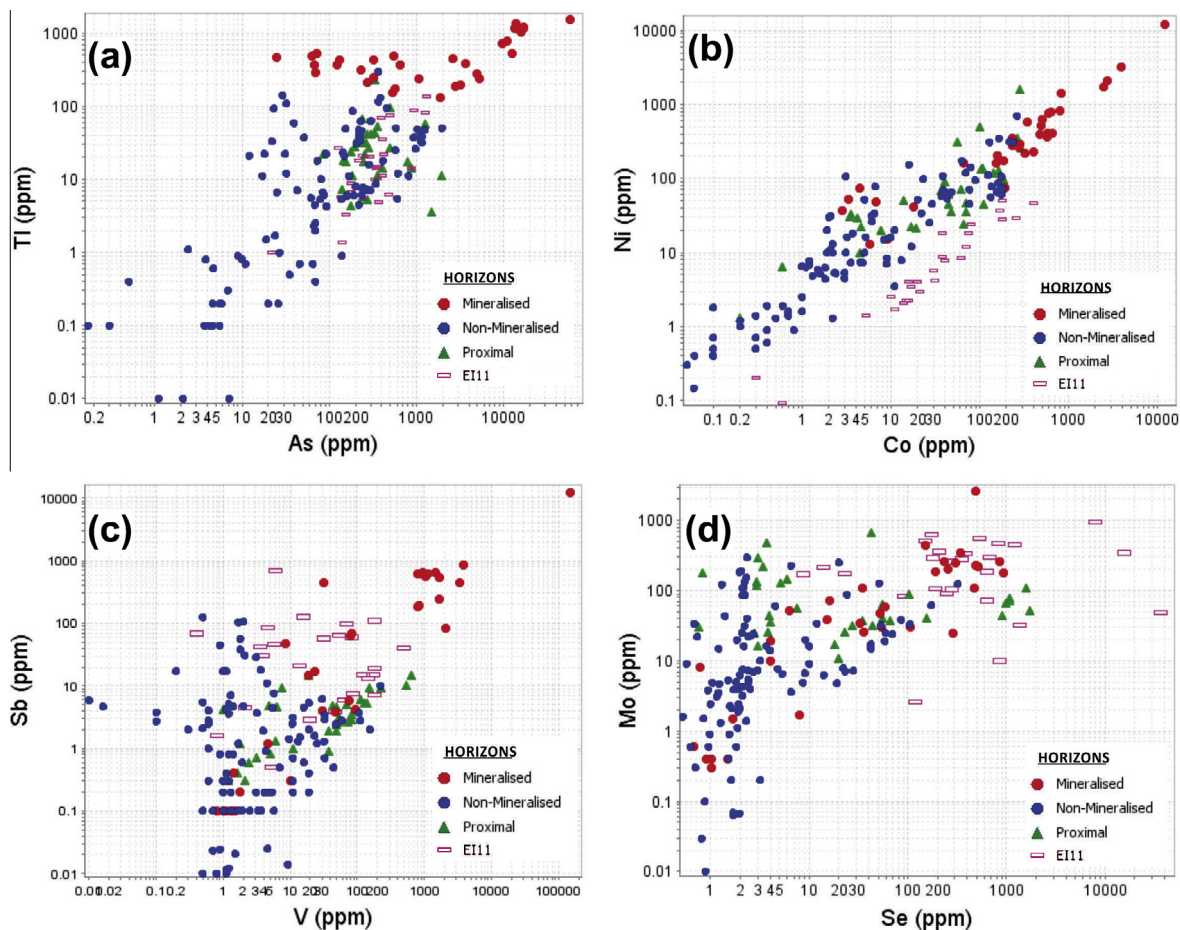


Fig. 11. Inter-element plots of (a) As and Tl, (b) Co and Ni and (c) V and Sb demonstrate consistent trace element enrichment in pyrites from ore-bearing horizons relative to their non-mineralized counterparts. Pyrite from zones proximal to ore-bearing horizons consistently display a more moderate enrichment which often falls just below levels seen in the mineralized horizons. Sample EI11 appears as an exception to these trends, as this non-mineralized sample shows enrichment in terms of (c) V and Sb and (d) Se and Mo. The plot of Se against Mo further demonstrates the non-conformity of sample EI11 to the horizon-related trends. Pyrite in this sample is significantly enriched in both Se and Mo; enrichment in these elements is much more limited and non-uniform in pyrite of other samples.

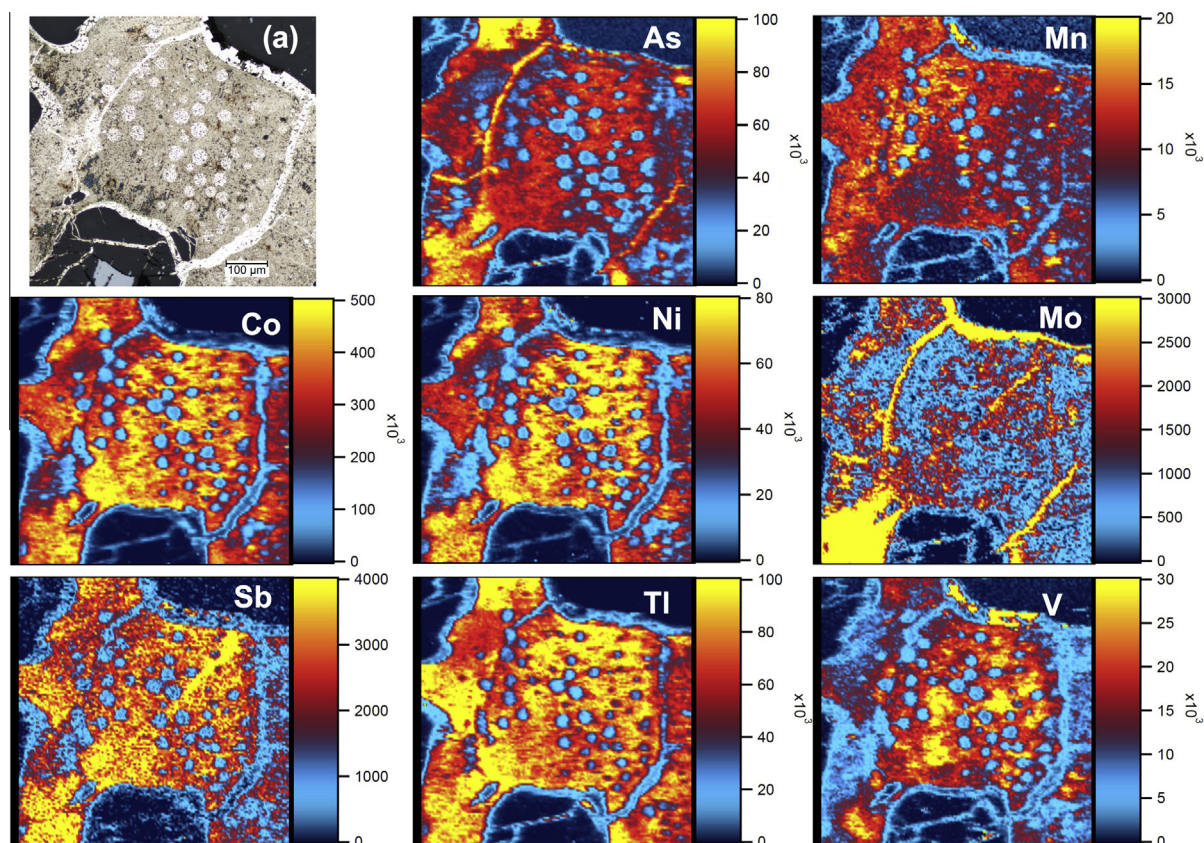


Fig. 12. LA-ICP-MS element maps of an intergrowth of porous cement, framboidal and pyrite infilling fractures, from sample EI7 (Pepegoona). (a) Petrographic image of mapped pyrite zone demonstrates the observed textural relationship between the authigenic framboids, an overgrowth of porous pyrite cement and a late-stage pyrite infill of fractures. Framboids show limited enrichment of As, Sb, Co, Ni and Tl relative to the adjacent pyrite morphologies. Minor zonation is observable within framboids in terms of As and Ni. Porous cement is enriched in terms of As, Sb, Co, Ni and Tl. Infill pyrite is enriched in As, Mo and somewhat Co, Ni and Tl. Scales are in counts-per-second.

indicative of pyrite mineralization developed in disequilibrium in an open system (Seal, 2006) and point primarily towards a hydrothermal sulfur source (Thode et al., 1953; Kohn et al., 1998).

Progressive ^{34}S enrichment due to the preferential uptake of lighter sulfur isotopes by pyrite and the mixing of two or more major sources of sulfur during late-stage diagenesis appear likely mechanisms to produce the broad range of $\delta^{34}\text{S}$ values observed in the hydrothermal pyrites (Warren, 1972; Beier and Feldman, 1991). In this case the mixing of sulfur from discrete sources was likely caused by an interaction between the intrusive rocks of the nearby Mt. Painter Domain granites (displaying $\delta^{34}\text{S}$ values close to zero; Ohmoto and Goldhaber, 1997) and sediments containing ^{34}S -rich sulfur such as evaporites throughout the Lake Eyre Basin (Ohmoto and Goldhaber, 1997; Wülser et al., 2011). Migrating hydrothermal fluids of meteoric and magmatic origin likely facilitated these interaction processes.

In addition, these hydrothermal pyrites often appear to be texturally homogenous, with only minor variations in alteration patterns and porosity; however, intragranular isotopic variations are common throughout the dataset (e.g., EI12 and EI15). These irregular ratios show little to

no systematic variation by grain habit or morphology, and hint at influences by complex fluid mixing processes.

Sulfur isotopic data recorded across the colloform banding in pyrite cement (sample EI12) also highlights the non-systematic nature of the sulfur isotopic signatures in the hydrothermal pyrite. Whereas each discrete pyrite band appears to have a representative isotopic signature, the absence of any identifiable regular or progressive variation again supports a model of complex fluid mixing processes occurring during protracted hydrothermal mineralization.

5.2. Pyrite evolution

Textural characterization of the discrete pyrite morphologies, as defined above, give insight into the apparent relationships between pyrite type and their genetic evolution.

Framboidal pyrite, observed throughout the sample suite is comparable with the distinct aggregates described by Wilkin and Barnes (1997) and may be classified as authigenic in nature. The widespread preservation of framboidal pyrite throughout the samples is likely dependent on (i) isolation of the framboids from the influence of the external diagenetic environment, and (ii) the interruption of supply

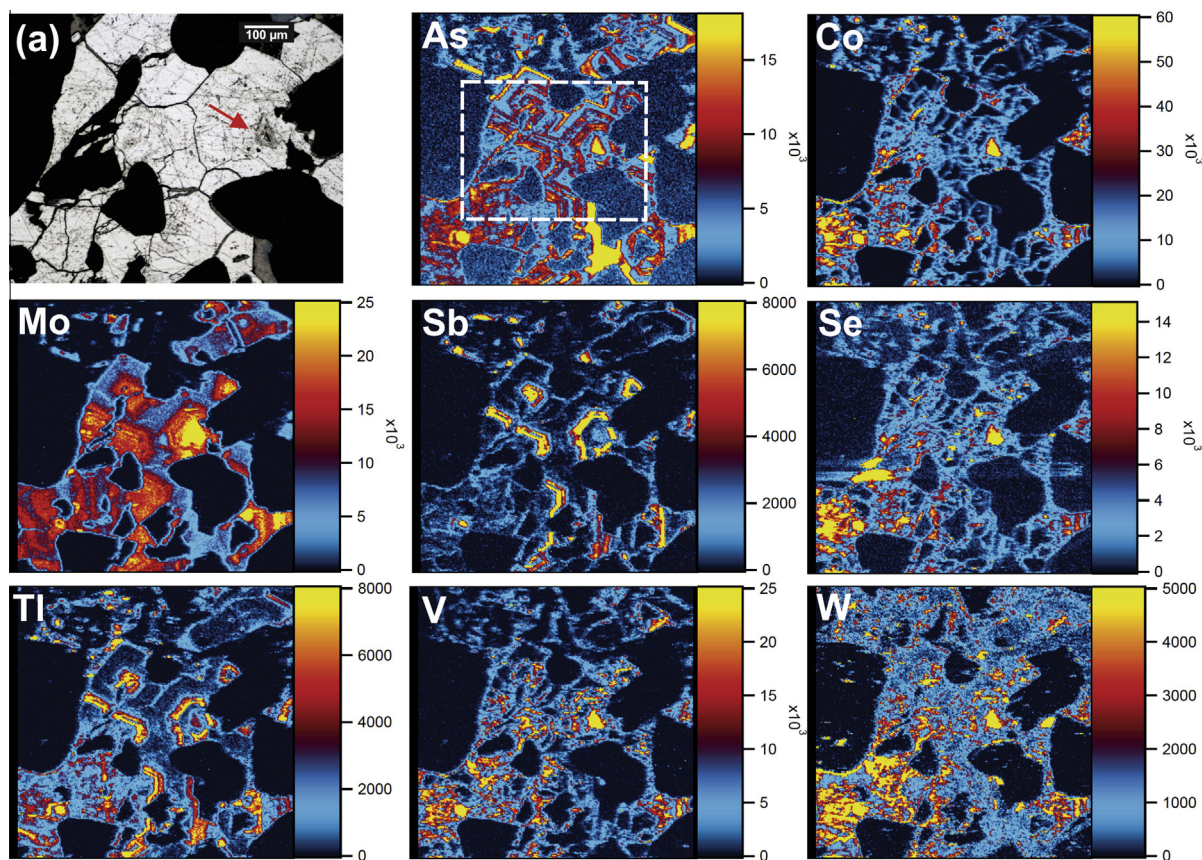


Fig. 13. LA-ICP-MS element maps of sample EI11 (Pepegoona West) displaying a highly crystalline nature of cement. (a) Petrographic image of massive pyrite cement on which the analysis was conducted. This image correlates with the dashed box in the map of As. The cement displays some septian deterioration textures, indicated by the arrow which is associated with replacement by hematite. These patterns appear to be nucleic zones for trace element partitioning as they are highly enriched in As, Co, Mo, Tl, Se and V. Arsenic displays strong zonation, which correlates with an enrichment in Sb and Tl. Molybdenum displays a gradient of enrichment centred around the nucleic zones. Cobalt, V, W and Se (and Ni, not shown) show similar gradient patterns of trace element enrichment. Scales are in counts-per-second.

of at least one essential compound in the mineralizing fluid (Fe and/or H_2S) (Sawlowicz, 1993).

Both LA-ICP-MS spot analysis and element mapping show that framboidal pyrite is poorly endowed in trace elements relative to other morphological types of pyrite (Figs. 9–14). This limited enrichment, and some minor zoning with respect to As, Co and Ni at the margins of framboidal aggregates, indicates that the trace elements supplied to the system during authigenic growth were likely supplied by the sandstone host lithology alone. This apparent supply during growth, and the presence of Fe-oxide minerals with relic framboidal textures in oxidized sandstones, makes it unlikely that detrital deposition of pyrite into the host sandstone occurred.

Framboidal pyrite is not restricted to sedimentary environments and has been observed outside early diagenetic environments (e.g., Scott et al., 2009 and references therein). Sawlowicz (1993) commented on a possible genetic relationship between framboidal and euhedral pyrite. The author considers framboidal pyrite to exist in a metastable state on which different mechanisms act to result in a homogenization of framboids into euhedral crystals. This transformation process is a result of a trend to minimize surface energy (Sawlowicz, 1993). Observation of different

phases of framboidal pyrite in the present study (Fig. 4) is considered indirect evidence for such a hypothesis. The transformed pyrite will then show variations in chemical properties resulting from inherited trace element and isotopic signatures. The massive cubic pyrites with porous centers (Fig. 5c) are seemingly consistent with this hypothesis and show both negligible trace element enrichment and a mixed sulfur isotope signature possibly as a result of diagenetic recrystallization during transformation of framboids to euhedra.

Protracted hydrothermal pyrite precipitation and possible late-stage diagenetic recrystallization of pyrite cements and overgrowths are evident not only from textural observations but also from the element maps of samples EI7 and EI11 (Figs. 12 and 13).

The role of porosity in pyrite cements is highlighted by the zones of lower Fe mapped in sample EI7 (Fig. 12). This lack of purity is commonly attributed to intergrowths of pyrite with other minerals. However the FIB–SEM imaging showing the simple assemblage of pyrite + clay minerals + U minerals (Fig. 15) in the cements makes it likely that the persistent trace element enrichment measured in the porous pyrite is attributable to the penetration of hydrothermal fluids into the sedimentary systems.

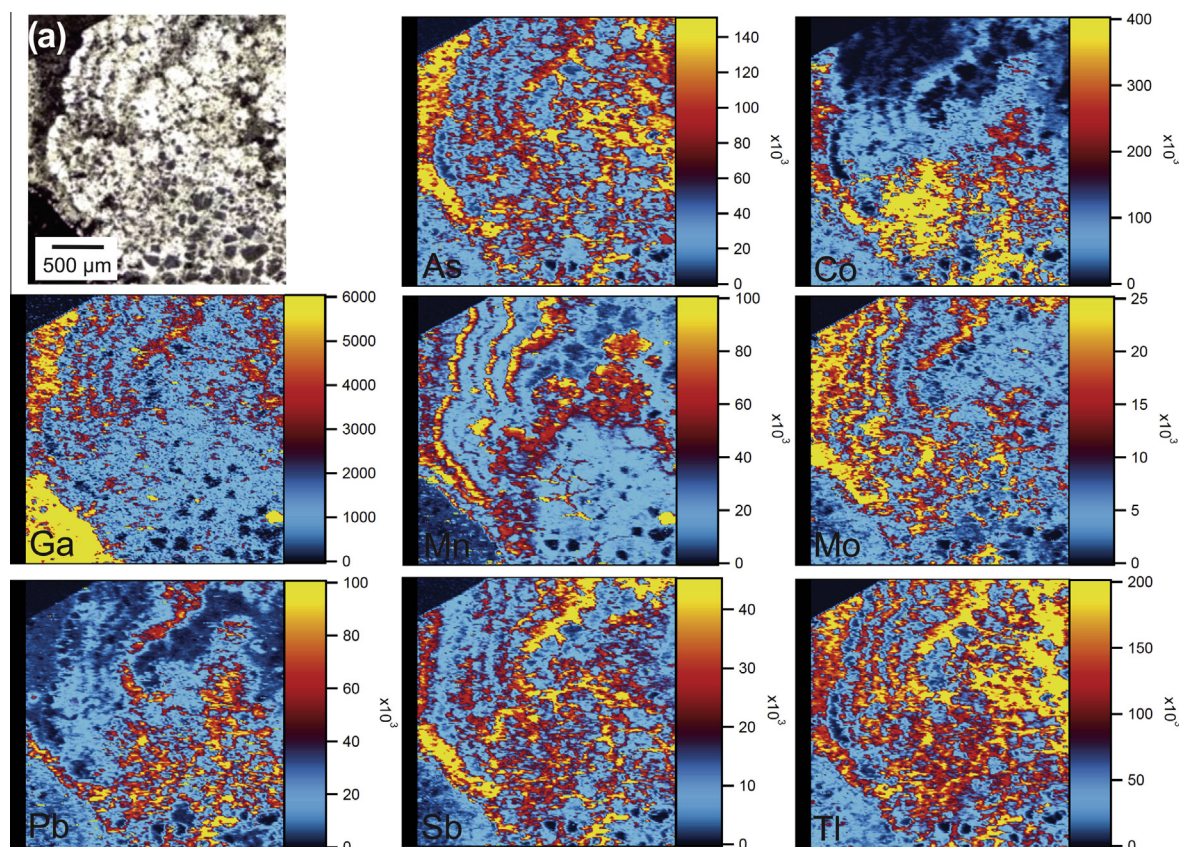


Fig. 14. LA-ICP-MS element maps of sample EI12 (Pepegoona West) displaying the association of trace elements with colloform banding in pyrite. (a) Petrographic image of mapped pyrite demonstrates the large variation in pyrite across a small area, with colloform banding being present at the boundaries of pyrite mineralization and more cemented pyrite being present towards the centre. The dashed box on the image delineates the boundaries to which element mapping was conducted. Enrichment in the colloform bands of the pyrite appears mainly in the Mn map, whilst As, Ga, Mo, Sb and Tl appear predominately enriched in the impure pyrite matrix observed between the better defined colloform bands. As, Co, Ni, Sb and Tl are also elevated in the cemented pyrite matrix. Scales are in counts-per-second.

Compositional zoning within the texturally homogenous pyrite cement mapped in sample EI11 (Fig. 14) demonstrates an evolution of hydrothermal fluid composition and/or variation in physiochemical conditions of sulfide precipitation throughout formation of hydrothermal pyrite (Belcher et al., 2004).

5.3. Trace element behavior

The non-uniform enrichment of trace elements in pyrite occurs across all of the uranium deposits at Beverley North. The large standard deviations of individual trace element datasets, as outlined in Table 3, reflect variability in the textural homogeneity of pyrite, and the development of porosity and possibly also inclusions of discrete minerals.

Pyrite of different morphologies, and in all deposits, is broadly enriched in As above background levels. Arsenic is generally considered to be incorporated into the pyrite lattice by substitution of reduced As^{-1} for sulfur (Savage et al., 2000; Lowers et al., 2007). Neumann et al. (2013) have recognized higher valence states (+III, +V) in As from framboidal pyrite in recent sediments of the Baltic Sea and interpreted the results in terms of dysoxic formation conditions. Confirmation of As valence state in pyrite from Bev-

erley North is beyond the scope of the present study but we nevertheless speculate that mixed valence states may be present, particularly in pyrite zoned with respect to As content and S-isotope signature.

The enrichment of trace elements in pyrite in the Pepegoona and Pepegoona West deposits relative to pyrite from the Pannikan deposit is likely an influence of fluid flow through sandstone beds and the geometry of both active and palaeoaquifers within the regional sedimentary systems. Fluid properties and flow directions would likely be modelled on the general trend of Eocene palaeochannels to the south of the deposits and the distance of each deposit from the U-rich source rocks of the Mt. Painter Inlier (Skirrow, 2009). These influences on hydrothermal fluid properties are a likely partial cause of the inter-deposit variations.

The intra-deposit variation at Pannikan, evidenced by the correlation between As, Co and Ni (Fig. 11), is associated with the location of the drillhole intersections in the roll-front deposit. Interpretation of deposit models and roll-front morphology shows that core PRC021 intersects the roll-front system whilst core PRC022 is located in front of the oxidizing system where hydrothermal fluids have not extensively penetrated. Hence, the relatively barren pyrite

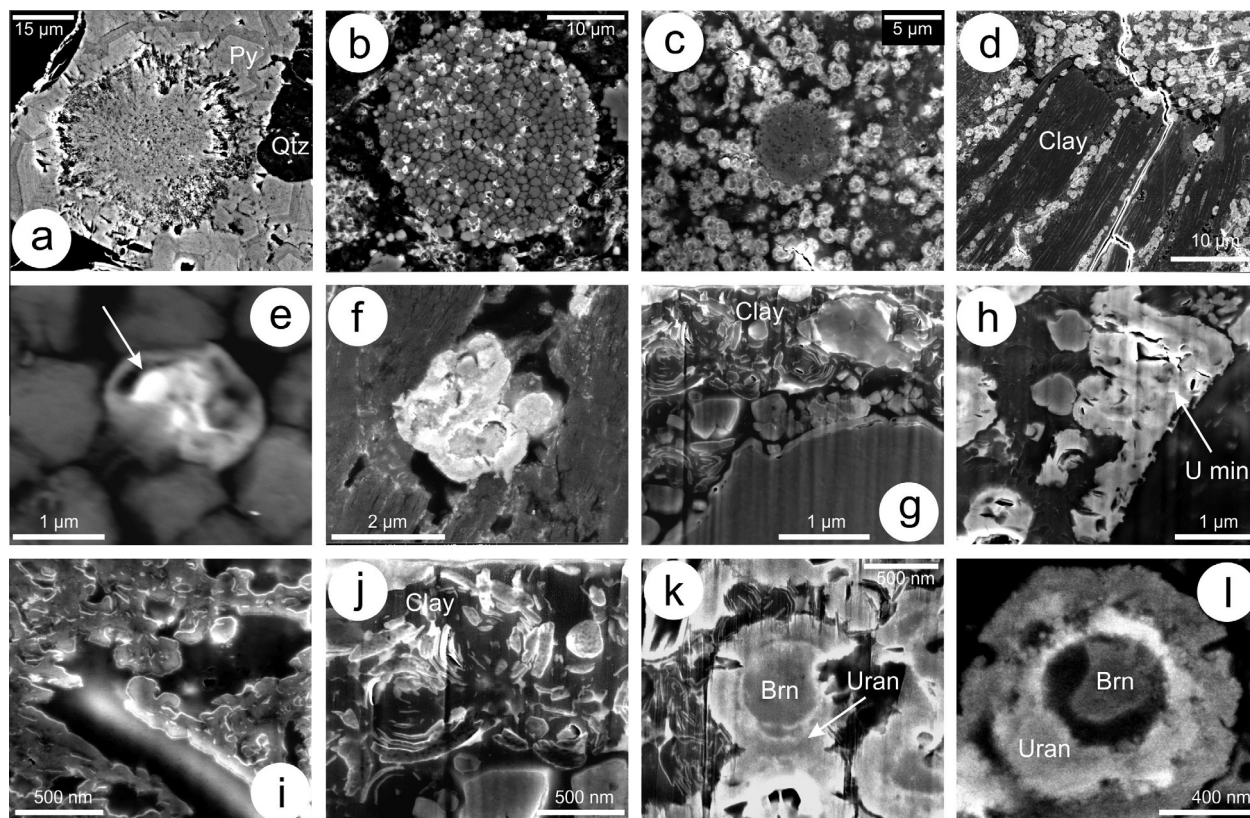


Fig. 15. FIB-SEM images demonstrate the nano-scale complexity within the samples. (a) Fibrolitic textured pyrite (Py), hosted by texturally-zoned pyrite cement, interpreted to indicate possible recrystallization processes; (b) porous, framboidal pyrite hosting intergrowths of U-bearing minerals (uraninite and minor brannerite, brighter on the images); (c) U minerals intergrown in porous matrix with framboidal pyrite (Py); (d) and associated with clay minerals and organic matter; (e) rounded U minerals resemble the grain habit of adjacent pyrite microcrystals; (f) aggregates of rounded U mineral grains with (g) cross-section imaging of these minerals displaying their association with pyrite and clay minerals and (h) the replacement textures between pyrite, clay and U mineral domains; (i) porous pyrite intergrowths also commonly seen as (j) rosette textures intergrown with phyllosilicate and U minerals; (k) the rounded U mineral grains display concentric intra-grain zonation and are increasingly U-rich toward grain edges; (l) grain edges of U minerals are also intergrown with clay minerals. Qtz – quartz.

observed in samples from PRC022 is a result of the lack of protracted hydrothermal flow at that location.

Enrichment in a large number of geochemically unrelated trace elements (e.g., Co, Ni, W, Mo, Sb, Tl, Se, As, and V) in pyrite from ore-bearing horizons is likely a result of input into the mineralizing hydrothermal fluids from multiple sources. Cobalt and nickel are commonly associated with fluids derived from a mafic source or have been leached from a source rock containing these elements (Goldschmidt, 1954; Clark et al., 2004). Likewise, W and Mo are commonly enriched in fluids from a granitic source (Blevin et al., 1996), and Sb, Tl, As and V are representative of an influence from organic-rich black shales (Brumsack, 2006). Within the geological setting of the Beverley North deposits, all three components are present.

On the same note, broad-scale enrichment of Co, Ni and As in pyrite of different morphological types indicates that these elements may have originated from different sources. The limited enrichment of these elements in authigenic pyrites indicates leaching from the host lithologies, whilst their hyper-enrichment in hydrothermal pyrite of ore-bearing horizons is indicative of continued compositional vari-

ation of the hydrothermal fluids during the progressive evolution of the deposits.

Given these trends, it is interesting to note an apparent negligible relationship between $\delta^{34}\text{S}$ values and samples from mineralized horizons. Of the samples analyzed from ore-bearing horizons, two showed significant ^{34}S depletion, which was interpreted as a result of the presence of morphologically-distinct framboidal pyrite in these samples. Analyses made on the third ore-bearing sample comprised a range of pyrite morphologies and displayed a significantly wider variance in $\delta^{34}\text{S}$ (-40.8‰ to $+26.3\text{‰}$), with one framboidal pyrite aggregate in this sample displaying the largest ^{34}S depletion in the entire dataset.

Comparable, heterogeneous but nevertheless positive ^{34}S signatures in samples taken from non-mineralized horizons would suggest that there is no direct relationship between $\delta^{34}\text{S}$ isotopic composition and U mineralization. Conversely, it appears that there exists a more consistent relationship between pyrite morphology and sulfur source.

Furthermore, the colloform pyrite banding (EI12) shows large variation in trace element enrichment across the textures (Fig. 14). The greatest enrichment is typically asso-

ciated with the ‘cleanest’ zones free of intergrowths with clays and other minerals. When these enrichments are considered relative to the highly heterogeneous sulfur isotope results taken across the same zone of pyrite cement (Fig. 8), we may infer that the trace element enrichment is independent of the sulfur source (i.e., most metals were derived from a range of different sources). In such a scenario, it is likely that the trace element enrichment in pyrite within the mineralized horizons was inherited from both the (epigenetic) fluid transporting uranium into the basin and from the proximal sedimentary rocks.

5.4. Late stage mineralization

The observation of native selenium in sample EI11 (Pepegoona West) provides insight into late-stage mineralization processes (Fig. 6). Native selenium is a rare mineral only recognized in a dozen or so localities around the world, many of them sandstone-hosted U-bearing ore systems (Simon et al., 1997; Zhu et al., 2012). The mobility and bioavailability of selenium in the environment is strongly dependent on redox transformations, and it may be mobilized into fluids at very-low temperatures (Johnson et al., 1999; Zhu et al., 2004, 2012; Chen et al., 2006). In this instance, the ubiquitous pyrite in the Beverley North system may have supplied Se during (re)-crystallization and associated release of incorporated elements. Pyrite is known for its capacity to control the geochemical behavior and occurrence of selenium in both reducing and oxidizing environments (Howard, 1977).

The localized occurrence of native selenium is likely a result of oxidation of Se-bearing pyrite, followed by mobilization and subsequent reduction of Se oxy-anions (selenate and selenite) by microorganisms in the presence of Fe²⁺-bearing minerals such as Fe-oxides or pyrite (Garbisu et al., 1996; Zhu et al., 2004, 2012; Chen et al., 2006).

The oxidation of the pyrite cements and subsequent re-precipitation likely caused the significant compositional zonation observed in terms of trace element enrichment (Fig. 12). Trace element enrichment appears to nucleate from distinct zones of hematitic alteration, with Se almost exclusively enriched in these areas. Marked enrichment also occurs in As, Co, Ni, V, Mo, Sb and W; all of these were likely introduced to the system by protracted stages of hydrothermal activity.

Precipitation of native selenium and associated hematite is a late-stage event in the genesis of the Beverley North deposits. Inflow of Se-rich hydrothermal fluids was facilitated by the porosity of the sandstone, leading to pervasive micro-fracturing and infilling pre-existing mineral assemblages and precipitating native selenium. We envisage a scenario in which late-stage oxidizing fluid may have mobilized selenium from pre-existing pyrite, or possibly another Se-bearing mineral (although we note that none have been observed). Subsequent restoration of reduced conditions within the aquifer caused precipitation of selenium as native selenium and pyrite re-crystallization. Hixon and Powell (2012) invoke such changes in redox conditions to account for selenium mineralogy in *in-situ* leach recovery operations.

Sulfur isotopic compositions taken from associated pyrite cement displayed a tight cluster of $\delta^{34}\text{S}$ ($\sim +29.5\%$) values, the highest of the dataset (Fig. 8). This clustering provides further evidence for the final-stage character of the oxidizing fluids associated with secondary mineral precipitation. It is conceivable that the oxidizing fluid had some effect on inherited $\delta^{34}\text{S}$ values either as a result of primary inhomogeneity in the pyrite or due to fractionation during dissolution and preferential incorporation of heavier isotopes (^{34}S) during diagenetic recrystallization.

6. CONCLUDING REMARKS

The study has revealed that pyrite displays textural and geochemical complexity at a variety of scales. The results are a contribution towards a preliminary and very broad genetic model for the deposition of the sandstone-hosted uranium deposits of Pepegoona, Pepegoona West and Pannikan. The most important outcome is the identification of the compositional, textural and chemical heterogeneity of pyrite throughout the ore-bearing systems at every scale. Textural and chemical interpretations of the discrete morphological types of pyrite highlight the protracted and possibly ongoing nature of the evolution of the ore systems and further the ability to track trace element behavior in pyrite grains which have undergone multiple stages of mineralization. All observations reinforce the interpretation that this is a long-lived and continually evolving hydrothermal system and that paragenetic observations reported here represent just one ‘snapshot’ view.

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APPENDIX A. METHODOLOGY

A.1. Sampling and sample preparation

A total of 36 samples (each $\sim 4 \times 4$ cm in size) was collected from six drill cores from the Pepegoona, Pepegoona West and Pannikan U deposits; six samples were selected from each core based on Heathgate Resources company reports. Sampling targeted an accurate representation of the mineralization, contacts with underlying and overlying formations, oxidized and reduced zones as well as non-mineralized sections whilst aiming to optimize pyrite content where possible. Due to their unconsolidated nature, samples were kept frozen to retain competency until prepared as 1-inch-diameter polished blocks set in epoxy resin.

A.2. Electron probe microanalysis (EPMA)

Quantitative compositional data for pyrite to corroborate concentrations of minor elements and ascertain Fe con-

centrations to be used as an internal standard for LA-ICP-MS were obtained using a CAMECA SX-51 microprobe with wavelength-dispersive spectrometers (Adelaide Microscopy, University of Adelaide). The instrument was operated at an accelerating voltage of 20 kV and beam current of 40 nA. Standards, X-ray lines and approximate minimum detection limits (mdl; wt.%) are: FeS₂ (S K α) 0.12; almandine (Fe K α) 0.07; cobalt metal (Co K α) 0.0478; pentlandite (Ni K α) 0.052; ZnS (Zn K α) 0.113; Bi₂Se₃ (Se L α ; Bi M α) 0.093 and 0.123; Ag₂Te₃ (Ag L α) 0.112; PbS (Pb M α) 0.173; CuFeS₂ (Cu K α) 0.078; cadmium metal (Cd L α) 0.194; Sb₂S₃ (Sb L α) 0.082; and GaAs (As L α) 0.21.

A.3. Laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS)

LA-ICP-MS spot analysis of pyrite was undertaken using an Agilent HP-7500 Quadrupole ICPMS instrument (Adelaide Microscopy, University of Adelaide). The instrument is equipped with a New Wave UP-213 Nd:YAG laser ablation system equipped with MeoLaser 213 software. Data reduction was performed using Glitter software (GEMOC, 2005). Eligibility of grains of pyrite for ablation was determined by SEM and petrographic analysis, aiming to determine the presence of inclusions and other textures such as fractures or intergrowths that might affect the quality of the trace element data. A total of 194 spots were ablated using a consistent spot size diameter of 40 μ m. The laser system was operated at pulse rates of 5 Hz, and 75% power level; laser energy was typically 6–9 J/cm², giving an ablation rate of approximately 1.5 μ m/s. Suitable pyrite grains were analyzed for the following isotopes: ²³Na, ²⁹Si, ³³S, ³⁴S, ⁴³Ca, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷⁵As, ⁸²Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁸⁴W, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi. The total analysis time was 90 s (30 s background measurement with laser off, and 60 s analysis with the laser on).

Calibration was performed using the Mass-1 reference standard (Wilson et al., 2002). The raw analytical data for each spot analysis is plotted as a line graph and the integration times for background and sample signal selected. The counts are then corrected for instrument drift (standards were run after each five unknown samples). Data reduction was undertaken using Glitter software (GEMOC, 2005) and used Fe as the internal standard for pyrite. Data was converted to ppm concentration values using Fe as an internal standard with Fe values as measured by electron probe. Data for Na, Si, Cu, Zn, Ga, Ag, Cd, In, Sn, Te, Ir, Au, Hg, Pb and Bi are excluded from the tables in this work as measured concentrations for these elements rarely exceed mdl values. Reproducibility and precision were generally concordant with other LA-ICP-MS analyses of sulfides in our laboratory. We do, however, note some drop off in reproducibility when analyzing smaller grains, those which are very finely intergrown, or compositionally zoned at a scale below that of the LA-ICP-MS spot diameter. We acknowledge that, although every effort has been made to maximize the quality of the LA-ICP-MS data throughout this study, the requirement of relatively large sampling volumes to give ppm-level sensitivity has forced a degree of

compromise. Mean one-sigma errors (relative%) are as follows: V 5.5, Cr 6.8, Mn 5.1, Co 4.3, Ni 6.4, As 5.4, Se 12.1, Mo 9.0, Sb 12.3, Ba 20.7, W 8.0, Tl 10.2. Typical precision was around 5–6% for Co and Ni and better than 10% for other elements, except for Se, Sb (~15%) and Ba (20–25%).

A.4. LA-ICP-MS Element Mapping

LA-ICP-MS mapping of approximately 0.5 cm² areas of pyrite was conducted using a Resonetics M-50-LR 193-nm Excimer laser microprobe coupled to an Agilent 7700cx Quadrupole ICP-MS housed at Adelaide Microscopy, University of Adelaide. This new-generation laser system permits high spatial resolution matched by sensitivity of low (sub-ppm) element concentrations. Imaging was performed by ablating sets of parallel line rasters across the sample using a 5 μ m beam size, line spacing of 5 μ m and 5 μ m/s scan speed at a laser frequency of 10 Hz and 0.003 dwell time for all elements. Redeposition during mapping was minimized by pre-ablating each line prior to data collection. Identical rasters were done on standard MASS-1, at the start and end of each mapping run to correct for instrumental drift.

Images were compiled and processed using the program Iolite (e.g., Woodhead et al., 2007) developed by the Melbourne Isotope Group at University of Melbourne (Paton et al., 2011). Iolite is an open source software package for processing ICP-MS data, and is an add-in for the data analysis program Igor developed by WaveMetrics.

A.5. SIMS analysis of sulfur isotopes

Ion microprobe analysis for sulfur isotopes in pyrite was undertaken on the Cameca IMS 1280 instrument located at the Centre for Microscopy, Characterisation and Analysis (CMCA), The University of Western Australia. Analysis was performed *in-situ* using the same polished blocks on which other analyses were performed. Representative samples were selected based on petrographic, SEM and LA-ICP-MS trace element analysis. Samples were chosen to be representative of the various deposits, different horizons, and differing morphological pyrite types encountered during sampling. Samples were prepared by cutting small (<5 mm²) portions of the polished ore blocks and mounting them in epoxy resin with the in-house Son-1 pyrite standard. Three to four samples were used in each mount and the pyrite grain mounts were imaged and Au-coated (~30 nm) before analysis was carried out.

A 1 nA Cs⁺ stationary primary beam was focused to a 10 μ m spot size with an impact energy of 20,000 V, resulting in an average sample emission 7.5×10^8 counts per second for ³²S. Triple Faraday cup collectors were used and data reduction protocols generally followed that of Farquhar et al. (2013). In all cases NMR regulation was used, an electron gun was used for charge compensation, and ³²S, ³³S, and ³⁴S were measured using Faraday cup detectors. A 1 nA focused primary beam was used to pre-sputter the analysis area for 10 s after which automatic secondary centering and 16 $\times$ 4 s analysis cycles were performed. Other conditions include a 133 $\times$ magnification between sample stage and Field aperture (FA), 75 μ m entrance slit, 4000 μ m FA, 400 μ m

contrast aperture, a 40 eV energy window with a 5 eV offset to the high energy side, and 500 μm exit slits.

Raw measured $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ ratios were converted to the delta notation of $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$, respectively by normalizing to Vienna Cañon Diablo Troilite (VCDT) values. Uncertainties were propagated using standard methods that incorporated internal precision of individual measurements, external precision of bracketing standard analyses, uncertainty of the standard reference value relative to VCDT, and uncertainty associated with drift correction coefficients (where applied). Details are provided in (Farquhar et al., 2013). Since all $\delta^{33}\text{S}$ analyses fell within uncertainty of the mass dependent fractionation line, the results are not reported here. Eight to ten unknowns were bracketed by two to five Son-1 pyrite in-house standards which were cast in the center of each sample mount to correct for instrumental mass fractionation (IMF) and drift. Propagated internal precisions for $^{34}\text{S}/^{32}\text{S}$ measurements averaged

0.13% (1 SD). The external precision of the Son-1 pyrite standard analyses over two analytical sessions was 0.11% (1 SD, $n = 31$).

A.6. Focused ion beam–scanning electron microscopy

A FEI-Helios nanoLab DualBeam focused ion beam–scanning electron microscope was used for high-resolution cross-section imaging of pyrite cement and contained U-bearing and host minerals. The methodology of Ciobanu et al. (2011) was followed. Operating conditions were 30 kV for ion milling and 20 and 5 kV for normal and immersion mode imaging, respectively, using the electron beam.

APPENDIX B. SULFUR ISOTOPE ANALYSIS DATASET

Sample	Pyrite morphology	^{32}S (cps) ¹	$^{34}\text{S}/^{32}\text{S}$ ²	$\delta^{34}\text{S}_{\text{‰}}$ (VCDT)	2σ ³
<i>Analytical session 1</i>					
Son-2	-	7.56	0.044242		0.23
Son-3	-	7.54	0.044234	1.42	0.23
Son-4	-	7.57	0.044239	1.35	0.23
Son-5	-	7.52	0.044230	1.15	0.24
EI11-1	Cement, assoc. native Se	7.52	0.045541	30.83	0.25
EI11-2	Cement, assoc. native Se	7.41	0.045459	28.96	0.27
EI11-3	Cement, assoc. native Se	7.54	0.045476	29.35	0.29
EI11-4	Cement, assoc. native Se	7.33	0.045602	32.20	0.14
EI11-5	Cement, assoc. native Se	7.46	0.045553	31.11	0.27
EI11-6	Cement, assoc. native Se	7.48	0.045515	30.24	0.25
EI11-7	Cement, assoc. native Se	7.52	0.045615	32.49	0.24
EI11-8	Cement, assoc. native Se	7.35	0.045523	30.41	0.27
son-6	-	7.51	0.044231	1.16	0.23
son-7	-	7.52	0.044241	1.40	0.24
EI11-9	Cement, assoc. native Se	7.60	0.045422	28.14	0.25
EI11-10	Cement, assoc. native Se	7.66	0.045435	28.42	0.23
EI11-11	Cement, assoc. native Se	7.39	0.045436	28.46	0.40
EI11-12	Cement, assoc. native Se	7.51	0.045515	30.23	0.27
EI11-13	Cement, assoc. native Se	7.59	0.045329	26.03	0.13
EI11-14	Cement, assoc. native Se	7.60	0.045337	26.21	0.35
EI11-15	Cement, assoc. native Se	7.55	0.045529	30.55	0.26
EI11-16	Cement, assoc. native Se	7.38	0.045457	28.91	0.53
son-8	-	7.47	0.044225	1.04	0.25
son-9	-	7.56	0.044243	1.45	0.27
EI3-1	Framboidal	7.44	0.042318	-42.13	0.26
EI3-2	Framboidal	7.31	0.042280	-42.99	0.31
EI3-3	Framboidal	6.07	0.042242	-43.84	0.32
EI3-4	Framboidal	7.51	0.042312	-42.26	0.21
EI3-5	Framboidal	7.31	0.042257	-43.51	0.21
EI3-6	Framboidal	3.45	0.042272	rejected	-
EI3-7	Framboidal	2.64	0.042315	rejected	-
EI3-8	Framboidal	6.56	0.042305	-42.42	0.23
EI3-9	Framboidal	6.87	0.042283	-42.92	0.27
EI3-10	Framboidal	7.26	0.042297	-42.60	0.21
EI3-11	Framboidal	7.12	0.042313	-42.23	0.31
EI3-12	Framboidal	6.77	0.042248	-43.71	0.21
son-10	-	7.35	0.044234	1.23	0.23
son-11	-	7.33	0.044236	1.29	0.23
EI12-1	Porous cement	6.82	0.044432	5.71	0.36
EI12-2	Porous cement	7.35	0.044256	1.74	0.27

EI12-3	Porous cement	7.32	0.044120	-1.35	0.28
EI12-4	Porous cement	7.49	0.045244	24.09	0.23
EI12-5	Porous cement	7.21	0.045252	24.28	0.28
EI12-6	Anhedral	7.38	0.045371	26.98	0.27
EI12-7	Anhedral	7.37	0.045344	26.37	0.27
EI12-8	Porous cement	7.26	0.045283	24.98	0.26
EI12-9	Porous cement	7.38	0.045190	22.87	0.26
EI12-10	Porous cement	7.11	0.045105	20.97	0.23
EI12-11	Porous cement	7.20	0.045338	26.22	0.25
EI12-12	Porous cement	7.48	0.045017	18.96	0.22
son-12	-	7.35	0.044237	1.31	0.25
son-13	-	7.37	0.044235	1.26	0.23
son-14	-	7.31	0.044236	1.28	0.28
EI12-13	Porous cement	7.36	0.044815	14.39	0.26
EI12-14	Porous cement	7.42	0.044864	15.50	0.25
EI12-15	Porous cement	7.32	0.044009	-3.85	0.25
EI12-16	Porous cement	7.33	0.044026	-3.48	0.26
EI12-17	Porous cement	7.47	0.043557	-14.09	0.23
EI12-18	Porous cement	7.40	0.043515	-15.05	0.28
EI12-19	Porous cement	7.53	0.044131	-1.09	0.23
EI12-20	Porous cement	7.21	0.044150	-0.67	0.26
EI7-1	Framboidal	7.10	0.042772	-31.85	0.38
EI7-2	Framboidal	6.94	0.042668	-34.22	0.25
EI7-3	Framboidal	7.09	0.042855	-29.98	0.41
EI7-4	Framboidal	7.15	0.042770	-31.90	0.15
Son-15	-	7.23	0.044228	1.10	0.24
Son-16	-	7.24	0.044238	1.33	0.28
Son-17	-	7.26	0.044238	1.33	0.25
Son-18	-	7.31	0.044240	1.39	0.25
<i>Analytical session 2</i>					
Son-3	-	7.87	0.044238	1.12	0.24
Son-4	-	7.93	0.044239	1.15	0.26
Son-5	-	7.96	0.044245	1.29	0.23
EI19-1	Massive cement	7.98	0.043986	-4.59	0.22
EI19-2	Massive cement	7.87	0.043965	-5.07	0.22
EI19-3	Massive cement	8.04	0.044026	-3.68	0.21
EI19-4	Massive cement	8.01	0.043991	-4.46	0.24
EI19-5	Massive cement	8.08	0.044004	-4.18	0.23
EI19-6	Massive cement	8.09	0.044009	-4.07	0.20
EI19-7	Massive cement	8.03	0.043985	-4.61	0.25
EI19-8	Massive cement	8.09	0.043987	-4.56	0.22
EI19-9	Massive cement	8.29	0.043984	-4.63	0.21
EI19-10	Massive cement	8.08	0.043984	-4.63	0.22
EI19-11	Massive cement	7.90	0.043972	-4.90	0.22
EI19-12	Massive cement	7.94	0.043981	-4.70	0.21
son-6	-	7.90	0.044250	1.40	0.24
son-7	-	7.95	0.044248	1.36	0.25
EI19-13	Massive cement	7.95	0.043977	-4.78	0.21
EI19-14	Massive cement	8.02	0.043979	-4.75	0.22
EI20-1	Cubic	8.21	0.044604	9.40	0.42
EI20-2	Overgrowth	6.63	0.044212	0.53	0.22
EI20-3	Cubic	8.04	0.045071	19.98	0.11
EI20-4	Overgrowth	8.02	0.044668	10.85	0.53
EI20-5	Cubic	7.79	0.045146	21.68	0.13
EI20-6	Cubic	8.02	0.045169	22.18	0.31
EI20-7	Euhedral	7.92	0.044764	13.02	0.11
EI20-8	Euhedral	8.10	0.045096	20.55	0.24
EI20-9	Overgrowth	7.99	0.045081	20.21	0.27
EI20-10	Overgrowth	6.75	0.045101	20.66	0.30
son-8	-	8.02	0.044247	1.33	0.24
son-9	-	8.05	0.044248	1.35	0.25
EI20-11	Euhedral	8.33	0.045157	21.91	0.21
EI20-12	Euhedral	8.12	0.044675	11.01	0.17
EI20-14	Overgrowth	8.02	0.045157	21.92	0.23

EI20-15	Cubic	8.00	0.044148	-0.90	0.13
Son-8R	Overgrowth	8.06	0.044246	1.31	0.27
Son-9R	Overgrowth	8.11	0.044250	1.40	0.26
EI20-17	Overgrowth	7.91	0.044470	6.37	0.14
EI20-18	Overgrowth	7.92	0.044804	13.94	0.28
EI20-19	Overgrowth	7.88	0.044736	12.39	0.26
EI20-20	Overgrowth	3.59	0.043675	-11.62	0.41
EI20-21	Overgrowth	7.98	0.044903	16.18	0.23
EI20-22	Overgrowth	7.57	0.044776	13.29	0.17
Son-10	-	8.07	0.044244	1.25	0.25
Son-11	-	8.02	0.044243	1.23	0.24
EI15-1	Cement	8.13	0.045320	25.61	0.23
EI15-2	Cement	7.96	0.043736	-10.23	0.26
EI15-3	Cement	8.06	0.042413	-40.18	0.23
EI15-4	Cement	8.02	0.044092	-2.17	0.36
EI15-5	Cement	8.07	0.042840	-30.50	0.28
EI15-6	Anhedral	7.34	0.043309	-19.90	0.68
EI15-7	Anhedral	8.00	0.044221	0.74	0.38
EI15-8	Anhedral	8.03	0.045349	26.28	0.28
EI15-9	Cement	7.97	0.044245	1.29	0.26
EI15-12	Framboidal	2.93	0.043379	-18.33	0.15
Son-12	-	7.65	0.044238	1.12	0.28
Son-13	-	7.66	0.044242	1.21	0.25
Son-14	-	7.65	0.044246	1.31	0.23
Son-15	-	7.60	0.044244	1.26	0.25

Sample derivation: EI3, EI7 – Pepogoona; EI11, EI12 – Pepegooona West; EI15, EI19, EI20 – Pannikan.

¹ Average intensity of ³²S signal in counts per second $\times 10^8$.

² Drift corrected ³⁴S/³²S prior to IMF calibration.

³ Two-sigma propagated uncertainty on individual measurements.

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