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Neoproterozoic Interglacial Geochemistry & Sedimentology of the Tapley Hill Formation in Kingsmill Creek, Arkaroola, South Australia

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

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NEOPROTEROZOIC INTERGLACIAL GEOCHEMISTRY & SEDIMENTOLOGY OF THE TAPLEY HILL FORMATION IN KINGSMILL CREEK, ARKARoola, SOUTH AUSTRALIA

GEOCHEMISTRY & SEDIMENTOLOGY OF THE TAPLEY HILL FORMATION IN KINGSMILL CREEK, ARKARoola, SOUTH AUSTRALIA

ABSTRACT

The break up of the Rodinian supercontinent seems to correspond with the commencement of the Sturtin glaciation which lasted for approximately 60 Ma. The Tapley Hill Formation is an interglacial succession of siliciclastic rocks, carbonaceous shales and carbonates deposited in a marine basinal setting before the onset of the Marinoan glacial period. The Kingsmill Creek section of the Tapley Hill Formation is of particular interest because of its lack of diagenesis and metamorphic overprinting. Over 240 rock samples were collected over 481 m. The samples were exposed to a range of geochemical analysis to look for major and trace elements and carbon and oxygen isotopes. Results confirmed that the Tapley Hill Formation was deposited in an open ocean environment under oxic to sub oxic conditions below wave base that resulted in the oxidation of organic matter. Detrital input was minimal and the rocks have preserved the primary seawater signature. A n inorganic carbon excursion at the base of the Tapley Hill Formation agrees with previous findings.

KEYWORDS

NEOPROTEROZOIC , TAPLEY HILL FORMATION, REDOX, INTERGLACIAL, SHALE, CARBONATE, GEOCHEMICAL

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INTRODUCTION

The Neoproterozoic era is a pivotal time in Earth's history which saw great tectonic upheavals including the breakup of the Rodinia supercontinent and the assembly of Gondwana, global climatic extremes and the evolutionary progression of life.

The Adelaide Rift Complex, which has previously been known as the Adelaide Geosyncline, is part of a large sedimentary super-basin in South Australia (Lloyd et al., 2020), which dates back to the Neoproterozoic, providing a geological record of around 300 million years of Earth's history. The development of the Adelaide Super-basin occurred as Laurentia began to rift off of Australia-East Antarctica. Sedimentation was thought to have begun from ca. 830 Ma (e.g. Preiss, 2000), but the relative timing of the transition from rift to drift is poorly constrained due to the lack of geochronological information. The main rifting phase is thought to have occurred between ca. 827–802 Ma (Fanning et al. 1986; Jenkins 1990; Wingate et al. 1998).

The Adelaide Rift Complex sedimentation, occurs in five main rift cycles and have been divided into three main supergroups (Preiss 2000), the Warrina Supergroup (Tonian), the Heysen Supergroup (Cryogenian and Ediacaran) and the Moralana supergroup (Cambrian). All available geochronological data for the Adelaide Rift Complex has been collated in Lloyd et al (2020). The Heysen Supergroup forms the basis for this study and encompasses all of the glacial interglacial and post-glacial sediments. The Heysen Supergroup, is further divided into the Umberatana and Wilpena Groups. The Umberatana Group, the main focus of this study, is part of an interglacial period constrained by two key and prominent global events, the Sturtian Glacial deposits at the base and the Marinoan glacial sequences marking the top.

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The warmer interglacial period between these events, saw the deposition of sediments that today form the Tapley Hill Formation. The Tapley Hill Formation is exposed along the Kingsmill Creek within the Arkaroola Wildlife Sanctuary, Northern Flinders Ranges, South Australia where it provides an ideal opportunity to obtain samples for study due to their accessibility and minimal deformation. The Tapley Hill Formation is described as a finely laminated, organic rich, grey to black siltstone/shale, often with carbonate layers, that represents deep water deposition over a period of approx. 30 Ma (Canfield et al., 2008) during the breakup of Rodinia c.720 Ma (Godderis et al., 2003).

The scientific value of black shales come from the wealth of data they often contain to enable the reconstruction of palaeomarine environments. These black shales are often enriched in redox sensitive metals such as molybdenum (Mo), vanadium (V), Chromium (Cr), Nickel (Ni), Cobalt (Co) and Copper (Cu). These metals are found as dissolved ions in oxic seawater but because of stratification within the water column, when they encounter deeper anoxic conditions, can precipitate out of the seawater thereby enriching the sediment below (Hall et al., 2020). These metal rich sediments are now routinely used as proxies to infer the oxygenation history of paleo-seawater both locally and globally (Pufahl & Hiatt, 2012).

The aim of this study is to discover what the oxygenation and redox status of interglacial seawater was during the Cryogenian period and what basin water redox conditions were at the time of deposition by analysing the geochemistry of carbonates and shales of the Tapley Hill Formation, using rare earth elements (REE) and trace

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elements to determine the connectivity of the basin to the open ocean. It also seeks to determine the productivity and biological activity at the time through carbon and oxygen isotope analysis. As a result, a high-resolution chemo-stratigraphic profile of the Tapley Hill Formation can also be achieved which aids in determining the depositional environment.

BACKGROUND AND GEOCHRONOLOGY**The Sturtian Glaciation**

Determining exactly when events occurred during the Cryogenian has proved somewhat difficult due to the general lack of dateable materials within these glacial deposits.

Gernon and Hicks (2016) suggest that the onset of the Sturtian glaciation coincided with the initial breakup of Rhodinia at ~720 Ma while Rooney et al., (2013) suggested a minimum constraining age of 662.4 ± 3.9 Ma from Re-Os dating and high-resolution Os and Sr isotope work on Rapitan Group rocks in northwest Canada which works well with the 658 Ma recorded from U–Pb SHRIMP ash bed from within the Merinjina Tillite (Fanning et al., 2008). Other geochronological constraints have been tabled by Lloyd et al., (2020) with a maximum depositional $^{206}\text{Pb}/^{238}\text{U}$ age of 654 ± 13 Ma. Some argue the Sturtian glaciation, which lasted for a period of around 60 Ma, ended abruptly when subaerial volcanic outgassing caused a major outgassing of carbon dioxide into Earth's atmosphere, leading to extreme global warming. The resulting transfer of atmospheric carbon dioxide to the ocean could explain a rapid precipitation of calcium carbonate. This is one explanation for the global appearance of cap carbonate deposits (Hoffman et al., 1998), however Williams and Gostin (2019) provide evidence of a lag

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time between the end of the Nantuo glaciation in south China and the precipitation of the cap carbonate, instead suggesting gradual rather than abrupt climatic changes.

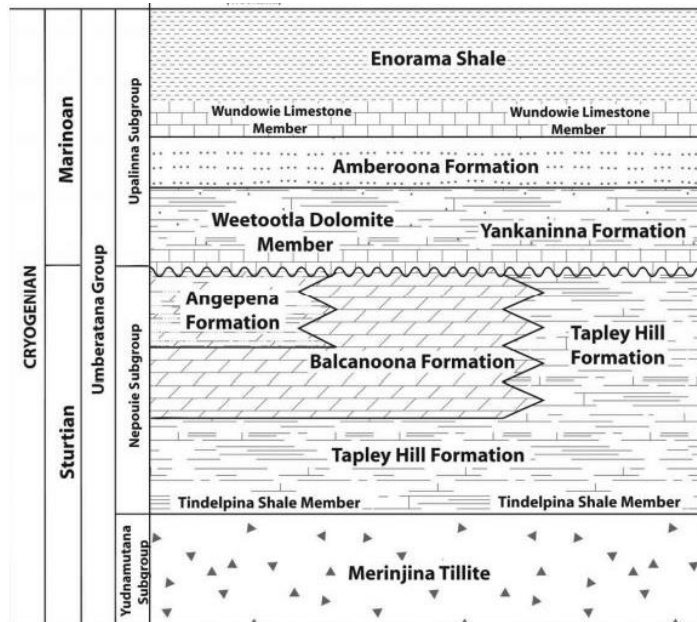


Figure 1 Stratigraphy of the Umberatana Group sediments in South Australia. Adapted from Fromhold & Wallace (2011)

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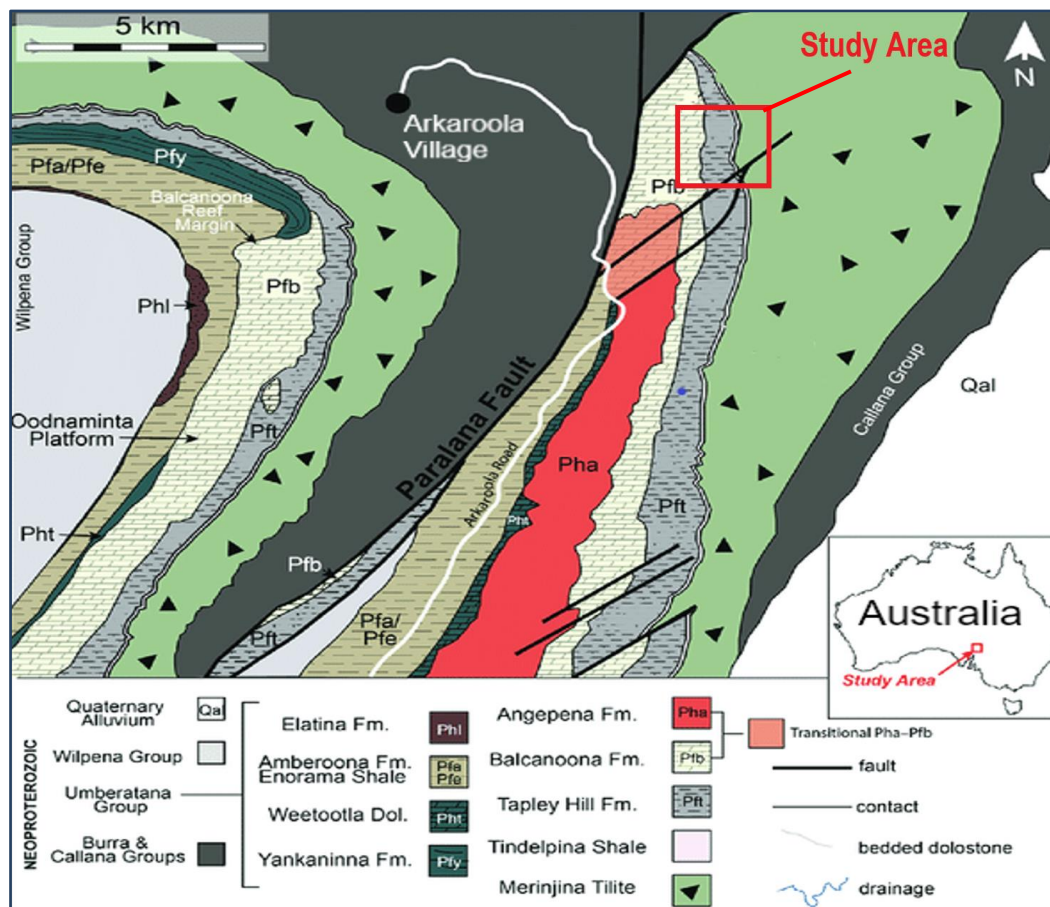


Figure 2 Geological map of Neoproterozoic strata near Arkaroola, South Australia and location of the study area. Adapted from O’Connell et al, 2020.

The Post Glacial Period

The Tapley Hill Formation forms a significant interglacial succession between the Sturtian and Marinoan glacial period and outcrops over a very wide area through the Mt. Lofty – Flinders Ranges, Stuart Shelf where more sandy facies predominate (Drexel et al., 1993). This unit gets its name from Tapley Hill, Adelaide where good exposures can be seen in road cuttings and was recognised by Walter Howchin in 1901 when he described the type locality glacial deposits in Sturt George (Howchin, 1908). It is described as a siltstone, grey to black, dolomitic and pyritic grading upwards to calcareous, thinly laminated, locally cross-bedded; Dolomite, grey, flaggy to massive; limestone conglomerate, intraformational; greywacke (Australian Stratigraphic Units

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Database (2019). The Tapley Hill Formation is an extensive marine transgression as melting icesheets rapidly filled the basin with sediment (Drexel et al., 1993). It has further been suggested that this sediment was discharged into an epicontinental basin, estimated to have been up to 300 km wide with access to the global ocean over a period of 30 Ma. (Canfield et al., 2008).

The Tapley Hill Formation exposed in Kingsmill Creek, Arkaroola Wildlife Sanctuary, northern Flinders Ranges (Fig 2) forms the main study area. Here the Tapley Hill Formation represents approximately 480 m thickness of exposed sediments.

Geochronology by Webb and Coats (1980) recorded a Rb–Sr whole rock isochron age of 750 ± 50 Ma for Tapley Hill Formation siltstone from the Stuart Shelf, however Priess (2000) suggests that this age is unlikely and maybe the result of a detrital mica and feldspar signature. The Tapley Hill formation seems to have been deposited in a period of approximately 10-15 Ma, and as previously mentioned, the basal Tindelpina Shale member was dated at 643 ± 2.4 Ma. (Kendall et al., 2006).

Previous work on the rocks exposed in Kingsmill Creek have mostly focussed on the overlying Balcanoona Formation and its stromatolitic reef system (Corkeron & Slezak, 2020; Hood & Wallace, 2014; Wallace et al., 2015) that form large dolomitic platforms with well preserved reef facies, which prograded into the basin over 15 km in extent (Wallace et al., 2015). They largely consist of ooidal–peloidal grainstones and stromatolites exhibiting various columnar, digitate, domal and planar forms (Wallace et al., 2015). Previous authors suggest that the Balcanoona Formation and the Tapley Hill Formation in Kingsmill Creek were deposited contemporaneously (Giddings &

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Wallace, 2009a) as the reefs prograded into open water to depths of up to 150 Metres (Wallace et al., 2015).

METHODS**SAMPLE COLLECTION**

During March 2020, field work was undertaken and 240 whole rock chip samples were collected from the Kingsmill Creek section of the Tapley Hill Formation. Samples were obtained at 2 metre intervals where possible from the top of the Merinjina Tillite to the base of the Balcanoona Formation, for a total of 481 m. Some breaks in the stratigraphy were due to poor or insufficient outcrops. The samples were placed in individual paper sample bags and grouped together into shale, carbonaceous shale or carbonate bags.

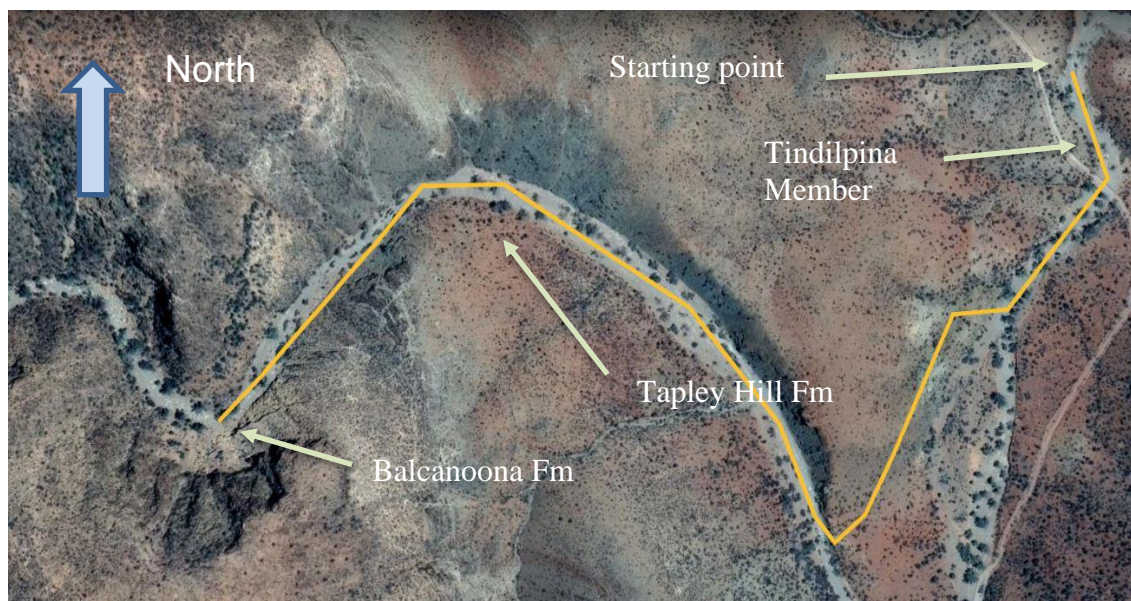


Figure 3 Google Earth satellite image of the study area showing route taken along Kingsmill Creek.

CRUSHING

One hundred samples were selected from the total number of samples at four to five metre spacings and prepared for to analyse for major and trace elements (including

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REE's) and carbon and oxygen isotopes in shales and carbonates. It was originally hoped to obtain data for nitrogen isotopes as well, but this did not eventuate. All chosen samples were reduced to a fine powder using an electric drill with tungsten carbide drill bits. Between each sample, the bit was cleaned using ethanol to ensure no cross contamination occurred. Approximately 100 mg of sample was obtained with 50 mg placed into plastic vials, one for isotopic and one for elemental analysis.

TREATMENTS**Carbonates**

Major and trace element (including REE's) analysis for were carried out on twenty one carbonate samples. Samples were determined to be carbonates based on their reaction to the application of 10% hydrochloric acid (HCl) to fresh surfaces during field work. All preparatory work for induced coupled plasma mass spectrometry (ICP-MS) was carried out in the University of Adelaide's Mawson Laboratories clean lab, with the final analysis being carried out by Adelaide Microscopy, University of Adelaide. The gas isotope ratio mass spectrometry (IRMS) analysis was performed at the University of Adelaide's Mawson.

Röhre, 10 ml centrifuge tubes were used but these were cleaned first to prevent possible contamination. This was achieved by placing 5 ml of 6 M HCl acid into each tube and placing on a heated element at 100 °C for 24 hrs. These were subsequently rinsed 3 times with MQ deionised water to remove any trace of acid and left to dry prior to leaching. Leaching was done in 3 stages to remove contaminant ions and to produce a leachate suitable for use in the mass spectrometer. Stage one involved removing any

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surface Rb-Sr ions by preparing a fresh 1M ammonium acetate solution. Then 2.7 ml of this solution was pipetted into each tube containing 75mg of sample and gently mixed and left alone for one hour before sonicating for 20 minutes and centrifuged for 10 minutes at 4000 rpm. The supernate was then disposed of taking care not to lose any solid residue. Stage two was designed to leach out Rb and Sr ions from within the crystal lattice and this was achieved by using 2.7 ml of a 0.2M acetic acid solution, mixing carefully, leaving for one hour, sonicating and centrifuging as before. Pouring off of the supernate, stage three was designed to leach metal ions from the residue with a further 2.7 ml of 0.2 M acetic acid solution, carefully mixing and leaving for one hour, sonicating for 30 minutes and centrifuged for 10 minutes at 4000 rpm. The supernate was then be poured out into cleaned Teflon beakers and placed on a hotplate to evaporate. The Teflon beakers were cleaned in a similar manner to the centrifuge tubes but were also soaked in 6 M nitric acid (HNO_3) for 48 hours at 170 °C before being rinsed three times with deionised water. The final preparation required was aimed at completely dissolving the dried residue. Firstly, 6 ml of 6 M HCl was added to the residue to help the conversion to chlorides and let stand overnight. This was then evaporated and 4.95 g of 2% HNO_3 to restrict partial dissolution of clays within the sample to produce an aliquot of 1:100. The supernatant was collected and digested with 2% HNO_3 again into aliquots of 1:1000, 1:10 000 and 1:100 000 dilutions for trace and major element analysis, respectively. The standards used were for the carbonate samples were JDo-1 and JLS-1. A calibration for matrix effects used standards prepared from multi-element stock standards solutions ranging from 0.3–300 $\mu\text{g/l}$. Accuracy was determined by a calibration curve established for five samples at concentrations of 0 ppb, 10 ppb, 20 ppb, 50 ppb, 100 ppb, 200 ppb and 500 ppb.

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To obtain inorganic carbon ($\delta^{13}\text{C}_{\text{carb}}$) and oxygen ($\delta^{18}\text{O}$) data for the carbonates, the same 20 carbonate samples and an additional seven randomly chosen calcareous shale samples were chosen for IRMS analysis. Untreated carbonate samples of 0.8 mg and calcareous shale samples of 5 mg were weighed out into glass vials with rubber seals. The vials were then placed into the Nu Horizon mass spectrometer and purged with helium. Then 8 drops of 1 M phosphoric acid was added and left for one hour to dissolve the solids. The samples were then analysed.

Shales and calcareous shales

A further 79 samples comprising 44 calcareous shale and 35 shale samples were also analysed by ICP-MS for major and trace elements (including REE's). Firstly, a 50 mg powdered sample was placed into pre-cleaned Teflon vials with screw lids. To this 2 ml of 7 M of HNO_3 was added followed by 4 ml of 48% (28 M) hydrofluoric acid (HF) to digest silica and clays and then was left on a hotplate for 48hrs. The liquid was then left to evaporate after which 6 ml of 6 M HCl was added and lefty overnight. This last step was then repeated. The samples were now ready for dilution to 1:100 then to 1:1000 into 5ml plastic vials with lids and the same procedure as per carbonates was used to produce aliquot samples for the ICP-MS. The standard used was SCo-1 for shales.

The Nu Horizon mass spectrometer was also used to obtain inorganic carbon ($\delta^{13}\text{C}_{\text{carb}}$) and oxygen ($\delta^{18}\text{O}$) data for the shales. The procedure used was the same as described for carbonate samples.

To obtain organic carbon ($\delta^{13}\text{C}_{\text{org}}$) isotope values, the shales required the removal of the inorganic carbonate fraction. This was performed by leaching a 50 mg powdered sample

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in 5 ml plastic vials with 6 M HCl and left on a hotplate overnight. The supernate was then carefully poured off and the residue left to dry. A test run was completed on a 10 mg sample on the elemental analyser-isotopic ratio mass spectrometer (EA-IRMS) under the supervision of Tony Hall. From the results of the test, it was possible to calculate the minimum required sample size based on the individual sample's carbon content. The powdered samples were then weighed out into foil caps the caps were carefully flattened and placed in a PerkinElmer Series II CHNS/O EA-IRMS carousel. Standards were used every 10 samples. The standard used was ST02 (C=71.09%; H=6.71%; N=10.36%; O= 11.84%).

The shales were also looked at for their total organic carbon (TOC) content. Again, some test samples were chosen to evaluate the minimum required sample size. Eight calcareous shale and four shale samples were chosen based on their darker colour compared to the other samples. Sample weights varied between 229 mg and 424 mg. Further drilling of the original rock sample was necessary to obtain the larger quantities. The samples were then analysed using the Source Rock Analyser (SRA).

OBSERVATIONS AND RESULTS**Descriptions of Main Stratigraphic Units**

Figure X represents 481 meters of stratigraphy within Kingsmill Creek, from the top of the Merinjina Tillite (Sturtian glacial rocks) to the base of the Balcanoona Formation (carbonate reef systems). The variability within the observed stratigraphy is summarised below. The full stratigraphic log can be located in appendix A

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STURTIAN GLACIAL SEQUENCES

The Merinjina Tillite

The Merinjina Tillite within Kingsmill Creek is defined by matrix supported, poorly bedded glacial diamictite with clasts of varying lithologies generally between 3cm and 1m in size.

POST GLACIAL SEQUENCES

Tapley Hill Formation

The base of the formation is a pale coloured micritic dolomite layer with a total thickness of 3 m on average. This layer exhibits an 'elephant skin' weathering pattern, and forms a number of beds approximately 10 cm thick. Upon exposure, the rock is a bluish brown colour, dense and somewhat crystalline. The transition between this layer and the overlying shale is poorly defined, with little outcrop observable. This is largely due to weathering and alluvial sediment cover. Because of this there is a 5.4 m gap in the stratigraphy here. Shale that is present, varies in colour between pale brown, khaki, beige and grey with >1 mm laminations. At 8.4 m, finely laminated shale with bedding between 2 and 10 cm is seen which grades into grey to black coloured mudstones and siltstones with <1 mm sized grains and fine yellow laminations. A 5 m thick section containing lenticular bedding occurs at 60 m. Interbedded within the mud and silt stones are carbonate beds sometimes greater than 30cm in thickness. These are often a blueish-grey colour, crystalline, homogeneous carbonates with the main variable being the presence or lack of laminations. The frequency of these beds increases up-section, with the thickest beds occurring towards the top of the section. Some crossbedding in shale was also observed at 425 m.

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Wavy textured layers, start to appear at around 343 metres and tend to form < 1 m layers between shale. The texture is accentuated by weathering whilst not as noticeable on freshly broken surfaces. At 406 metres these layers increased to nearly 4 m in thickness.

Balcanoona Formation

The Balcanoona formation is defined by thick blueish grey, blocky and crystalline dolomitic carbonate beds, some exhibiting stromatolitic structures. After 426 metres up section, only carbonates are observed with beds up to 20 metres thick. Asymmetrical ripple marks are observed at 432 metres and continued for 29 metres up section. Wavy carbonate beds become dominant as we near the base of the Balcanoona Formation. At 478 m and again at 480 m a 1 m thick, fine grained, pinkish sandstone bed is noted. The boundary between the Tapley Hill Formation and the Balcanoona Formation was determined by the first appearance (481 m) of very large blocks of stromatolitic carbonate rocks, some many metres across.

INTERPRETATION AND DISCUSSION

Geochemical data and stratigraphic observations made in the field enable a reconstruction of the interglacial paleoenvironment of the Tapley Hill Formation at Arkaroola. This section is structured to evaluate various aspects of this data and evaluate its significance and is set out under the following topics.

- Diagenesis
- Detrital Input

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- Paleoredox proxies
- Productivity
- Depositional environments
- Detrital Input

These have been further divided into two groups – carbonates and shales, as they contribute different information. The term, carbonate is used here in a generic sense to refer to crystalline calcium carbonate rocks, weakly laminated or not laminated at all, that reacted strongly to 10% HCl in the field. Calcareous shales are laminated siliciclastic rocks with slight to moderate reaction to 10% HCl and shales are defined as laminated mud rocks with no reaction to 10% HCl.

Effects of Diagenesis

Diagenesis is a process that produces degrees of physical and chemical changes in sediments post deposition. This usually involves lithification through compaction, heat, and pressure. Diagenesis is an important factor to consider when evaluating sedimentary rocks because the alteration can affect the primary geochemical signatures of these sediments. To ascertain the extent of any diagenesis, carbonate rocks must be treated differently to siliciclastic rocks such as shale. The reason for this is this is because carbonate rocks are formed mostly by precipitation and composed of different minerals and therefore their diagenetic signatures (Boggs Jr & Boggs, 2009). Another factor to consider is structural diagenesis which occurs near fault damage zones and cause substantial chemical alteration (Wu et al., 2019). The Paralana Fault system is a steeply dipping north -south striking fault occurring to the west of the study area which was active during the time the Tapley Hill Formation was being deposited. To the west of

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the fault, metamorphic grade reached amphibolite facies conditions while to the east of the fault it only reached greenschist facies (Weisheit et al., 2014). This makes the Tapley Hill Formation within the study area more significant because it is unlikely to have been subjected to structural diagenetic conditions. REE's need to be normalised to PAAS (post Archean Australian Shale) for both to provide a standard reference for comparison to average shale values. Pass values used in this study are taken from Nance & Taylor (1976) are given below.

DIAGENESIS IN CARBONATE SAMPLES

REEs are widely used as a test for determining the effects of diagenesis and metamorphism in both shales and carbonate rocks because they are generally less mobile than other elements (Toyama et al., 2019). Major and trace element excursions have likewise been used to detect diagenetic alteration of carbonate rocks. Carbonate data was normalised to Mg to counter effects of any dolomitisation. Other important

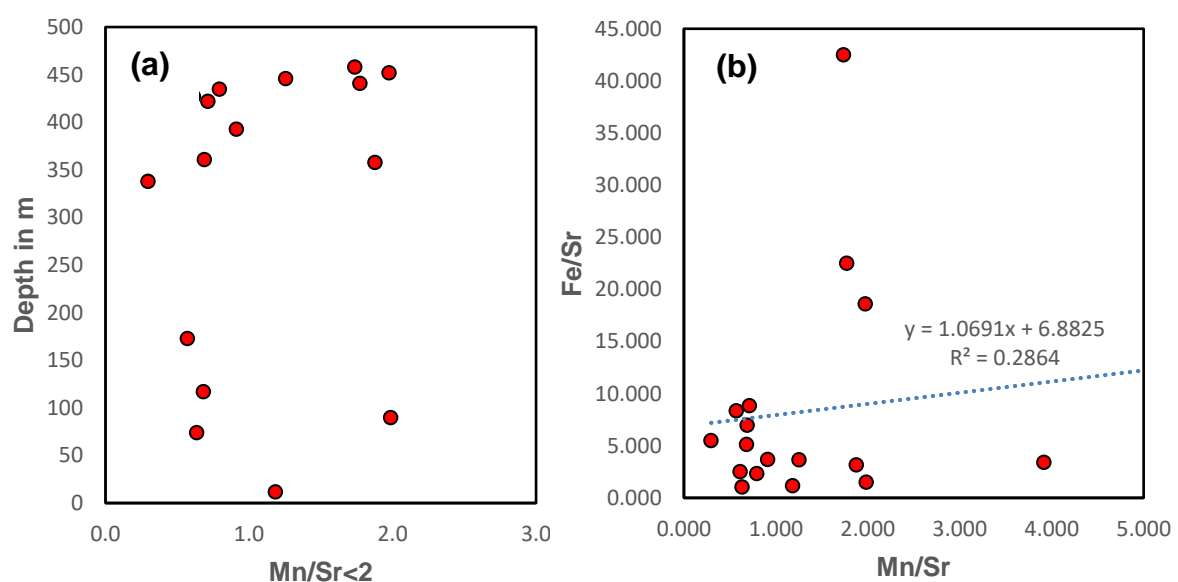


Figure 4. Mn/Sr used to assess diagenesis. alues are normalised to magnesium.

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indicators of diagenesis in carbonates include using Fe, Mg and Sr (Lindsay et al., 2005). Previous studies have used Mn/Sr values <2 as unaltered (Brand & Veizer, 1981) but others have suggested that values <10 are acceptable. Mn/Sr values >10 correlates with anomalous $\delta^{13}\text{C}$ values, which also suggest diagenetic alteration (Knoll et al., 1995). High strontium values are often an indication of diagenesis also. Toyama et al (2019), used strontium concentrations in carbonates <2500 ppm as being low and $\delta^{18}\text{O}$ values from -5 to -10‰ could preserve primary isotopic signatures. Tapley Hill samples contain less than 1000 ppm strontium. Figure 6 demonstrates a low level of diagenesis in carbonates. All carbonate samples returned a Mn/Sr value lower than 2 bar one which was taken as an outlier and excluded from the data (6a). There is no significant covariance between Mn/Sr and Fe/Sr which also suggests a low probability of diagenesis in carbonates.

DIAGENESIS IN SHALE AND CALCAREOUS SHALES

Shale is mostly formed from the settling out of fine detrital sediments and therefore the mineralogy is different to that of carbonate rocks and as such requires different measures

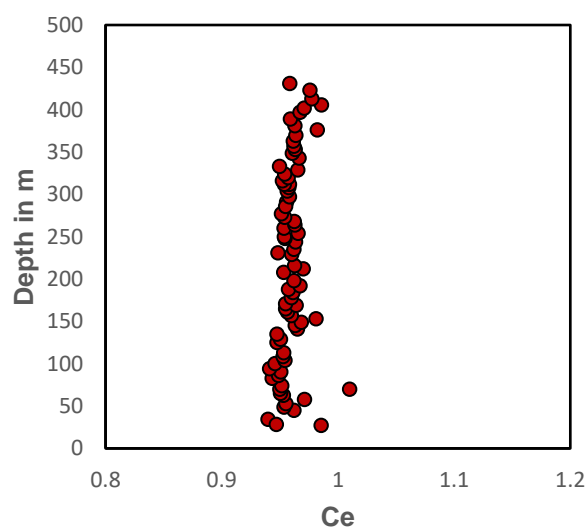


Figure 5. Cerium vs depth in both shale and calcareous shale samples. Values have been normalised to PAAS for diagenetic input. Values close to 1 represent original seawater

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to test for diagenesis. Cerium and europium are used as an accurate reflection of seawater chemistry and should plot close to 1. Positive Cerium anomalies are interpreted to indicate a lack of alteration and values plotting very close to 1 after normalising to

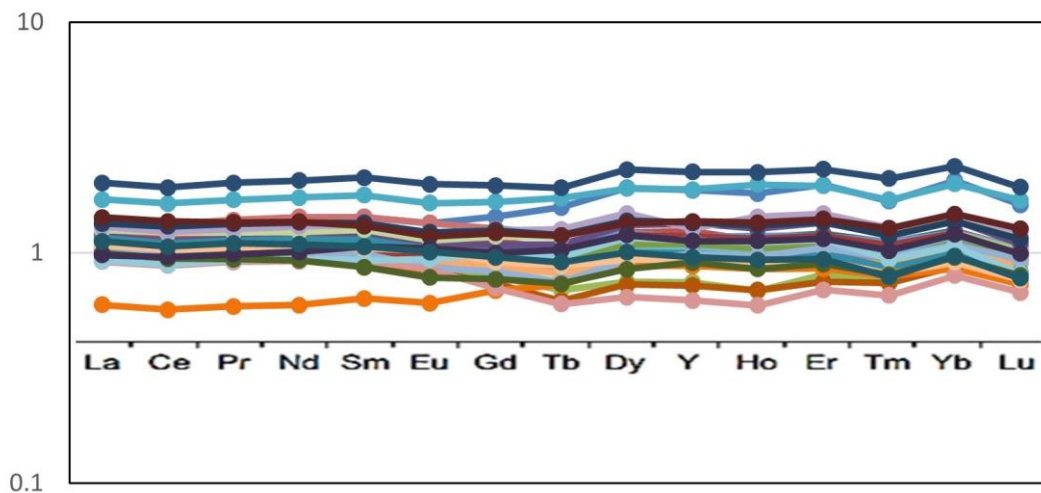


Figure 6. . Spider plot of REE values for 35 shale samples. REE's normalised to PAAS.

PAAS are interpreted as having been derived from primary sources and provide evidence against diagenesis in shales. The spider plot in Fig. 8 above shows very flat trends for REE's and no Ce or Eu anomalies in shales normalised to PAAS. This also is indicative of a negative response to diagenesis.

Of a minor but interesting note is the occurrence of several white antitaxial fibrous calcite veins up to 3 cm thick, observed cutting through shale beds exposed at 274 m in Kingsmill Creek. These veins are identical to the veins from the nearby Oopaminda Creek and described by Bons et al (2009) who raised the possibility of microbial life within the calcite veins . The veins formed at about 3–6 km below the surface at a temperature between 60–80C (Bons et al., 2009). The calcite is deemed to have been derived from carbonate within the host rocks and from external fluids moving through the sediments (Bons et al., 2009). It is possible that this is the result of movement along

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the Paralana Fault as the data gathered by Bons et al. supported a pre Delamerian age.

These veins seem to be very restricted to small areas and the fluid temperatures are not likely to have had any substantial diagenetic effects.

Depositional Environments**THE MERINJINA TILLITE**

The Merinjina Tillite forms the base of the Tapley Hill Formation and represents a period of global glaciation, known as the Sturtian. Deglaciation after the Sturtian seems to have been relatively rapid (Giddings & Wallace, 2009b) due to the sharp contact with the Tapley Hill Formation that overlies it. There is no evidence of any unconformity and there is an absence of any further glacial debris being deposited although Giddings and Wallace (2009) describes observing dropstones in the cap deposit within about 10 cm of its base.

THE TAPLEY HILL FORMATION

The Tapley Hill formation represents part of an interglacial sequence between the Sturtian and Marinoan glaciations. The initial post glacial sediments form what is commonly referred to in various literature as the Tindelpina Shale Member within the Tapley Hill Formation. It is believed to be a record of the maximum flooding of the transgression (McKirdy et al., 2001) as glacial icesheets melted and sea levels rose. The Tindelpina Shale is described by Sumartojo (1974) as a finely laminated, black carbonaceous pyritic shale approximately 60 meters thick and in places, a thin, yellowish-brown dolomite occurs at or near the base of this horizon. This description seems to aptly describe what is commonly termed a 'cap carbonate' deposit observed in

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this study directly overlying the Sturtian glacial deposits. These carbonate layers have been found worldwide (Giddings & Wallace, 2009b) overlying Neoproterozoic glacial deposits of a similar age and signifies the Sturtian glaciation was one of global significance. The Tindelpina Shale was not visibly observed as a distinguishable unit at the study site, nor was a distinct boundary between the Tindelpina Shale and the Tapley Hill Formation observed. It appears instead to be gradational and may extend to approx. 40-60 vertical metres above the Merinjina Tillite based on the rocks becoming darker in colour, occurring in beds 2 – 10 cm thick. Sample # C022 (53 m) was the closest sample to the Tindelpina Shale Member tested for TOC, but returned a value of 0.70 Wt.% which is in the lower range for organic carbon in shales (Jarvie, 1991). The increasingly calcareous and upper part of the Tapley Hill Formation reflects a shallowing of the basin waters leading to conditions favouring the establishment and growth of carbonate reef systems such as the Balcanoona Formation. The Tapley Hill Formation is generally homogenous with only minor variations in laminations and bedding thickness with very little crossbedding. The laminations are very fine where fine particles have been able to settle out in a low energy, deep-water depositional environment. This is supported by relatively high $\delta^{13}\text{C}$ but low $\delta^{18}\text{O}$ values that are suggestive of a deeper water column (García-Gallardo et al., 2017). Higher up stratigraphy some crossbedding can be observed possibly indicating a higher energy system and shallower water conditions. Closer to the Balcanoona Formation and detrital carbonate layers seem to suggest deposition near the slope margins of the reef complex where reef materials may be washing down into the shale sediments due to reef collapses above or perhaps storm events wreaking havoc on the reef and washing damaged material out to sea. There are also well-preserved asymmetrical ripple marks (450 m) in shales where waves are

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obviously created by wave action possibly indicating deposition in shallower and more sheltered back reef conditions. A beautiful cross section of the Tapley Hill shales showing lenticular bedding occurs at 60 metres in the stratigraphic column. This type of sedimentary structure is formed in a shallow marine intertidal zone where sand is being moved by wave action into oscillation ripples then as the tide recedes, mud or silt is deposited over them and the cycle is then repeated. (Reineck & Wunderlich, 1968). The Tapley Hill Formation is widespread throughout South Australia and depositional environments differ from location to location. At Kingsmill Creek, the data is suggestive of a deep but not anoxic basin water conditions based on trace metal values from the shales .

THE BALCANOONA FORMATION

The Balcanoona formation marks the top of the Tapley Hill Formation and there is a gradational change where the shales give way to more crystalline carbonate beds until the boundary of the reef system is met with. There is much detailed literature on the Balcanoona Formation at Arkaroola (Giddings et al., 2009; Giddings & Wallace, 2009a; Hood & Wallace, 2014; vS Hood et al., 2011; Wallace et al., 2015) which describes the remarkable well preserved structure of the reef complex and the fossilised reef organisms that built it. These reefs are a regional feature of Neoproterozoic interglacial time and are of world-wide interest. They have a comparable structure to modern day reefs such as the Great Barrier Reef off the east coast of Australia. The depositional environment here is probably not unlike conditions found today at places like Shark Bay in western Australia, where stromatolites are provided with a sheltered warm, shallow water environment yet still open to the sea. \

Paleoredox Proxies

In order to ascertain the redox conditions of the basin waters that the Tapley Hill sediments were being deposited into, redox sensitive elements are often used to interpret what the depositional environment of the basin and range from oxic to suboxic, anoxic

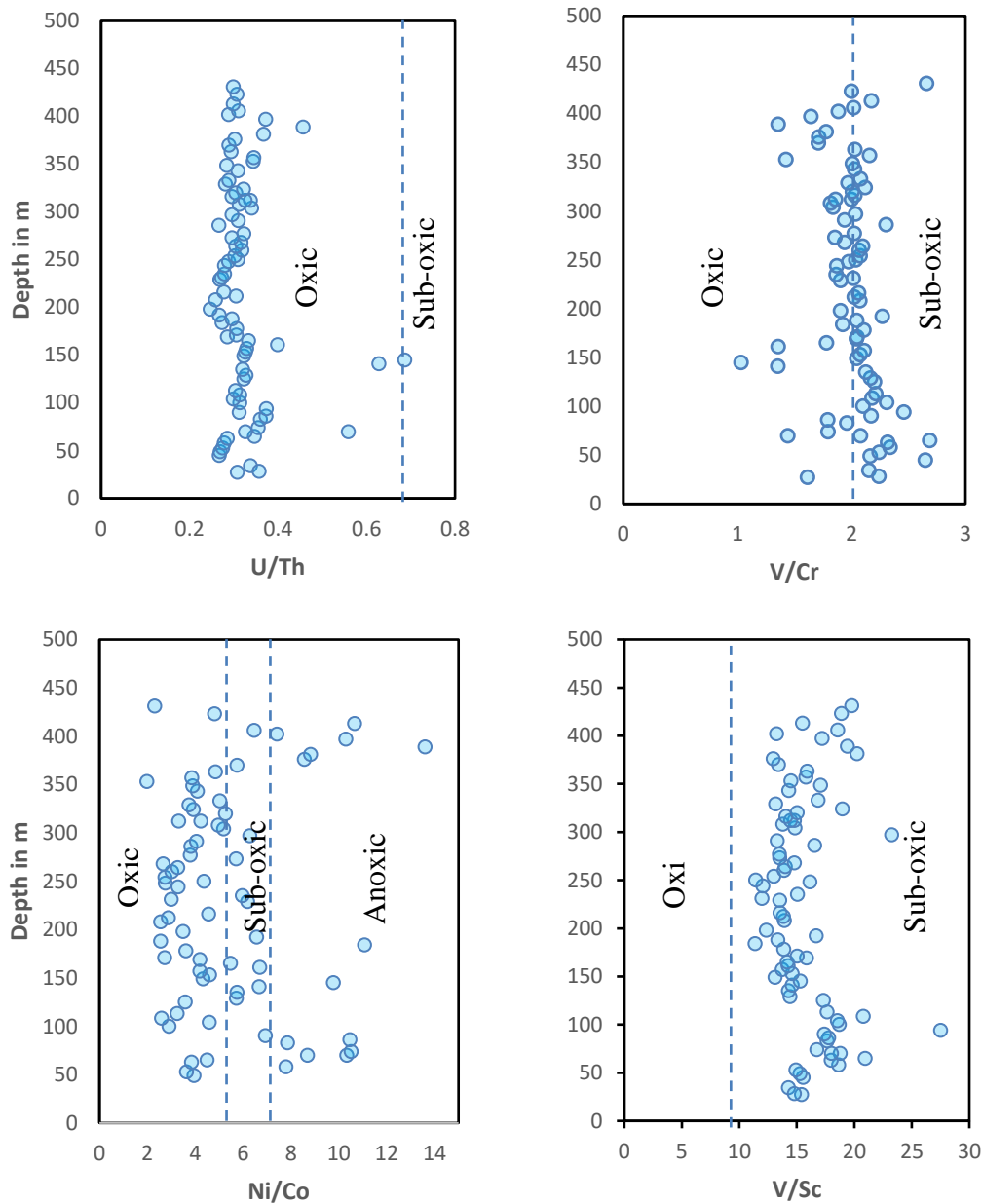


Figure 7. Chemostratigraphic profiles of redox sensitive trace element ratios normalised to aluminium for the Tapley Hill Formation. Vertical divisions represent the different redox zones. (McKirdy et al., 2011).

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or euxinic. Put simply it implies whether conditions were oxidising or reducing.

Elements used to determine this include trace such as Mo, V, Cr, Ni, Co, and U. These can be expressed as ratios together with other elements (Hua et al., 2013; Morford & Emerson, 1999; Pi et al., 2013; Reinhard et al., 2013; Tribovillard et al., 2006). Trace metals that are of seawater origin are incorporated into sediments in three ways (1) bound to organic matter, (2) incorporated in sulphide minerals (commonly pyrite) or (3) physically adsorbed onto the surface of minerals such as clays (Algeo & Maynard, 2004). If these metals are bound to buried organic carbon and sulphur (Xu et al., 2012) shales deposited in similar paleoredox conditions may have significantly different trace metal contents depending on the amount of organic carbon and sulphur buried with them (Algeo & Maynard, 2004). It is unclear as to what extent these proxies reflect the true depositional redox conditions or a result of materials they are being deposited with (Xu et al., 2012). Therefore, it is necessary to use more than one method to check that results are meaningful. Vanadium is useful as a proxy because under oxic conditions, vanadium occurs as V^{5+} vanadate oxyanions, while under anoxic conditions V^{5+} is reduced by both organic matter and hydrogen sulphide to V^{4+} (Cox et al., 2016). V can also be adsorbed onto clay minerals during deposition. Cr is thought to only be associated detrital materials and therefore not influenced by redox conditions, thus V/Cr values >2 are thought to indicate anoxic conditions while V/Cr ratios <2 infer oxic conditions (McKirdy et al., 2011; Mir, 2015).

Uranium is found in seawater in its oxidised state, U^{6+} mostly bound to dissolved carbonate ions (Cox et al., 2016). U correlates with oxygen penetration depth and is positively correlated with TOC content, even under euxinic conditions. U is enriched under both low oxygen and anoxic (sulphidic and ferruginous) conditions (Scott &

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Lyons, 2012). Likewise, the rare earth elements plus yttrium (REE+Y) consisting of seventeen elements, including yttrium and scandium, can also be used as redox proxies. Because these elements share similar chemical properties and a predictable pattern of behaviour when normalized to PAAS (post Archean Australian Shale), they are used consistently in evaluating water chemistry. Normalisation is a necessary practice as it removes the natural variations in absolute concentrations of REE+Y and allows a comparison with the rare earth composition of the upper crust, for which shale is a proxy (Pourmand et al., 2012; Tostevin et al., 2016). Cerium (Ce) and europium (Eu) are important proxies because they can exist in more than one oxidation state. Ce is often in the form of Ce^{3+} but oxidises to Ce^{4+} which being less soluble than Ce^{3+} remains in the sediment, with values of >0.10 labelled a positive Ce anomaly and reflecting oxic conditions while a Ce value <0.10 reflecting an anoxic environment or negative Ce anomaly (Mir, 2015). Eu is mainly used as a proxy to determine if the source of sediments was from seawater mixing with hydrothermal fluids or the result of chemical weathering resulting from the breakdown of plagioclase feldspar / clay minerals (Mir, 2015). A large Eu^* would indicate a hydrothermal input (Tostevin et al., 2016). Results (Fig. 7) provide evidence that the Tapley Hill shales at Kingsmill Creek were mostly deposited in oxic to suboxic conditions. This means that the basin must have been deep enough to be below wave base to deposit such fine particles but not deep enough to preclude oxygen. This is also borne out by the rather low TOC values (Fig X) due to oxidation.

Primary Productivity

A key focus of this study was to produce a more detailed evaluation of the carbon and oxygen isotope values contained within the Tapley Hill Formation at Arkaroola than had been accomplished before. The value of this is to provide insights into nutrient inputs, burial efficiency of organic matter, atmospheric CO₂ and O₂ both of which can impact climate and life.

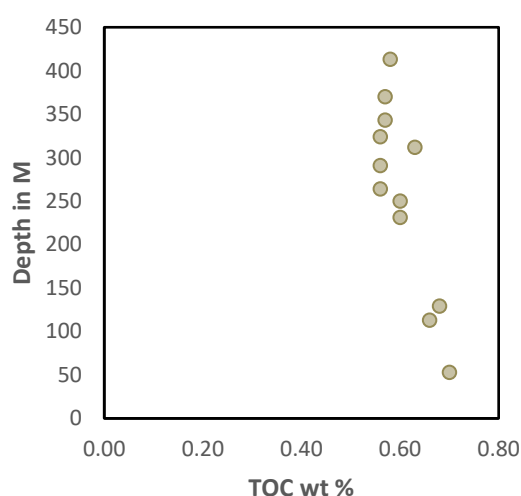


Figure 8. TOC of selected samples with Depth and Calcareous Shales

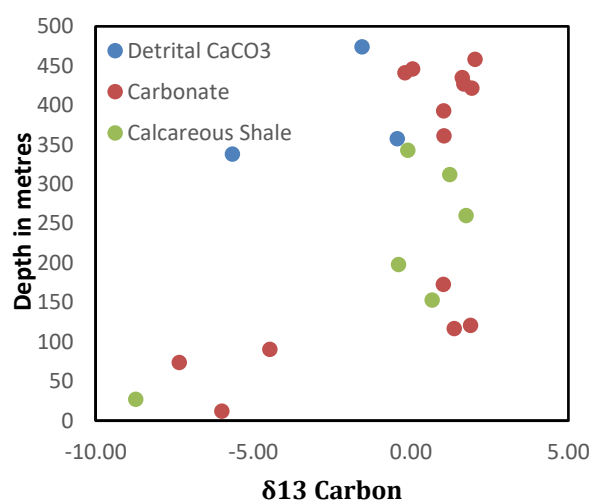


Figure 9. δ13C for carbonates and calcareous Shales

Global carbon cycle perturbations throughout Earth history are frequently linked to changing paleogeography, glaciation, ocean oxygenation, and biological innovation.

Swanson-Hysell et al (2010) as argued for a decoupling of organic carbon-isotope values between the Sturtian and Marinoan glacial events of the Cryogenian Period

(approximately 720 to 635 million years ago). They argue that organic carbon

remineralisation represents a negative climate feedback effecting the release of CO₂ and

preventing glaciation with the subsequent Marinoan glaciation being initiated when the

large dissolved organic carbon pool had decreased and no longer posed a negative

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feedback to global cooling. Figure data obtained from the study site do not support this and in fact do not show any decoupling.

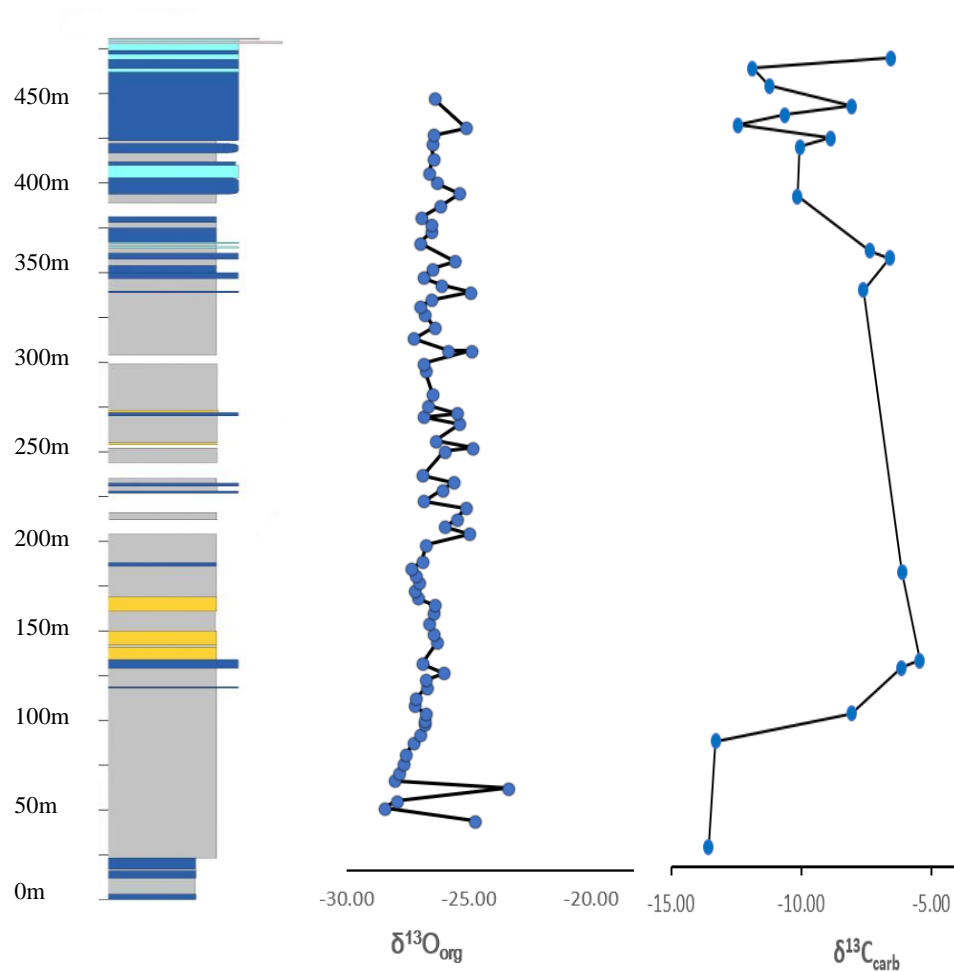


Figure 10. Stratigraphic log with values for organic & inorganic carbon in the Tapley Hill Formation. Note the excursion in inorganic carbon.

DETRITAL INPUT

The shales and calcareous shales of the Tapley Hill Formation are composed of fine silts, clays and organic matter. It is desirable to determine if the trace metals and REE+Y are being derived from inputs of terrestrial weathering or from precipitation from seawater reflecting, actual water geochemistry. A way of checking this is to cross-

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plot a given trace element against aluminium or titanium (Tribovillard et al., 2006) which are commonly detrital in origin and mostly immobile in the sediments (Calvert & Pedersen, 1993). If a good correlation is made with average shale values (PAAS) for the given element, it can be inferred that the trace element is mainly of detrital origin and not suitable paleoenvironmental interpretations. (Tribovillard et al., 2006).

Normalization to Al assumes that aluminium resides in siliciclastic materials (silt & clay) which do not contain trace elements of seawater but are of detrital origin (Xu et al., 2012).

CONCLUSIONS

The Tapley Hill Formation at Arkaroola represents an ideal window into the Neoproterozoic world. Geochemical analysis of the formation has enabled a better understanding the paleoenvironmental conditions after the Sturtian glacial period. The cap carbonate deposit on top of the glacials seem to suggest a dramatic climate change as the Earth thawed. As the Adelaide Super basin opened as a result of the rifting off of Rodinia, sediments that were to form the Tapley Hill Formation in Kingsmill Creek. As the basin filled it became shallower and allowed for the establishment of the carbonate reef systems of the Balcanoona Formation. Water depth was below wave base which allowed fine siliciclastic sediments to accumulate in oxic to sub oxic redox conditions while the basin remained open to the open ocean. These oxidising conditions did not allow for the preservation of organic carbon. The rocks in Kingsmill creek did not suffer from excessive diagenesis and therefore preserved the primary geochemistry of the seawater it was deposited in whilst the influence of detrital elements as a result of terrestrial weathering was minimal.

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Areas for further research include;

- The Mineralogy of the shales
- Access TOC on a larger range of samples
- More detailed examination of the Tindilpina shale section and cap carbonate – find better out crops and more detailed observations – looking for Bouma sequences or other structures in the cap carb.
- Geochronology – better age constraints on the Tapley Hill by looking for detrital zircons or tuffaceous layers within the shales.

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