Revisiting the depositional environment of the Neoproterozoic Callanna Group, South Australia

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Abstract

The Callanna Group was deposited around 800 million years ago (Ma) during an interval in Earth's history that saw a transition towards a more oxygenated atmosphere, increasing biodiversity among eukaryotic microfossils and climatic perturbations culminating in low-latitude glaciations. Previous researchers proposed that the Callanna basin was lacustrine and highly alkaline, which could provide important new insights into environmental cause-effect relationships at this time. To further interrogate these records, we examined standard biogeochemical proxies, including organic carbon and nitrogen isotopes, iron speciation, metal abundances and carbonate-associated sulfate. Much of the primary information has been lost because the rocks of the Callanna Group have experienced extensive metamorphism up to amphibolite facies and are altered by modern weathering. However, relics of these proxies, combined with sedimentological features, preserve evidence of redox stratification within this basin. Furthermore, our observations, in particular weakly fractionated nitrogen isotopes and abundant gypsum pseudomorphs, are incompatible with the interpretation of high alkalinity. The high salt content and occurrences of tidal indicators are most parsimoniously explained by frequent incursions of seawater. Thus, the Callanna Group cannot speak straightforwardly to environmental conditions in

non-marine habitats at this time. Lastly, the absence of a large carbon isotope anomaly indicates that these rocks do not correlate with the Bitter Springs Formation.

Keywords

Callanna Group; Neoproterozoic; evaporites; metamorphic alteration

1. Introduction

The early Neoproterozoic around 800 Ma is an important transitional interval in the evolution of life and environments on the early Earth. It shows an increasing diversification of eukaryotic microfossils (Knoll and Nowak, 2017), reveals perhaps the first indications of local or intermittent oxygenation of the deep ocean (Thomson et al., 2015), and it records a major inflection in the chromium isotope record of marine sediments, which may indicate a second rise of atmospheric oxygen after the Great Oxidation Event in the Paleoproterozoic (Planavsky et al., 2014; Cole et al., 2016). Further, fundamental changes at this time may have set the stage for Sturtian glacial event that followed at roughly 720 Ma. However, the cause-effect relationships among these events continue to be debated and require new constraints from the rock record.

With the aim of filling some of the critical gaps in understanding, we turned to the Callanna Group in South Australia, which has been dated to around 800 Ma (Section 2.1, reviewed by Preiss, 2000). The Curdimurka Subgroup of the Callanna Group has previously been interpreted as representing a non-marine depositional environment, because it contains mineral pseudomorphs that were interpreted as shortite—a sodium-calcium carbonate mineral that is only found in alkaline lakes (Rowlands et al., 1980). Furthermore, fluvial sedimentation has been documented from other parts of the Callanna Group (Preiss, 1987). If these interpretations are correct, then the Callanna Group could provide rare insights into a non-marine habitat at this critical time in Earth's history. So far very little geochemical work has been done on these rocks, largely because of a strong metamorphic overprint and alteration by modern oxidative weathering. Although the interpretive power of common biogeochemical proxies is certainly limited under these conditions, we present here new geochemical data, which in combination with sedimentological observations, provide new constraints on the depositional setting of the Curdimurka Subgroup. Our study

also highlights the possibility of extracting primary depositional information from rocks that are highly altered.

2. Geologic Setting

2.1. Tectonic setting and age constraints of the Callanna Group

The Callanna Group is the basal stratigraphic unit in the Adelaide Geosyncline (Figure 1a), which is the historic name of a Neoproterozoic rift basin located in South Australia (Preiss, 2000). At the time of deposition, South Australia was located at low latitude (McWilliams and McElhinny, 1980) and part of the Rodinia Supercontinent (Moores, 1991). The basin probably formed during incipient continental breakup, perhaps as a failed rift that opened toward the south (Von der Borch, 1980). Crustal thinning as a consequence of NE-SW-directed rifting created accommodation space for thick sedimentary packages in a northwesterly trending fault-bounded corridor that became the Adelaide Geosyncline (Preiss, 2000).

The Callanna Group is subdivided into the Arkaroola and Curdimurka subgroups (Preiss, 1987). Both are composed of siliciclastic sediments, carbonates, evaporites and minor volcanic flows but probably represent distinct phases of rifting. The depositional age of the Arkaroola Subgroup, which crops out primarily in the Peak and Denison Ranges and in the Mt. Painter region of the northeastern Flinders Ranges, is constrained to ~830 Ma, based on U-Pb and Sm-Nd dates obtained from intermediate volcanics and associated dolerite dykes (reviewed by Preiss, 2000). Precise dating of these rocks has been hindered by an amphibolite facies metamorphic overprint. The overlying Curdimurka Subgroup, which is the focus of this study, contains a thin tuff unit (Rook Tuff) that is dated to 802 ± 10 Ma (Fanning et al., 1986). The major outcrop areas of the Curdimurka Subgroup—from north to south—occur in the Peake and Denison Ranges, the Willouran Ranges, the Worumba Anticline and the Spalding Inlier, which may each represent tectonic sub-basins that were perhaps structurally isolated (Preiss, 1987). Samples for this study were collected from the Willouran Ranges—the type locality of the Curdimurka Subgroup—and from the Worumba Anticline. The two sections have been tentatively correlated, based on lithostratigraphic correspondences (Preiss, 1987).

Figure 1: (a) Map showing the assumed extent of sedimentation of the Curdimurka Subgroup of the Callanna Group in the Adelaide Geosyncline (yellow shading), redrawn from Preiss et al. (1993). Red stars mark outcrop localities of the Curdimurka Subgroup sampled for this study. Grey stars are other outcrop localities that were not sampled for this project. (b) Schematic of the lithostratigraphy of the Curdimurka Subgroup in the Willouran Ranges, after Preiss (1987). Blue shaded units are dominated by carbonate (mostly dolomite), light and medium grey shaded units are dominated by siliciclastic siltstone and sandstone. Dark grey denotes mud. Grainsize indicators (x-axis) denote mud, siltstone to fine sandstone (here slt) and medium to coarse sandstone (ss). Red stars mark major sampling localities; orange stars mark minor sampling sites. (c) Schematic of the lithostratigraphy of the Curdimurka Subgroup in the Worumba Anticline area. Symbols are as in panel b. We note that these stratigraphic columns are simplified and do not capture accurately the grainsize and position of specific features in the rock record.

2.2. Stratigraphy of the Curdimurka Subgroup

In the Willouran Ranges (Forbes et al., 1981; Preiss, 1987) the Curdimurka Subgroup is subdivided from oldest to youngest into the Dome Sandstone, the Rook Tuff (siltstone with porphyritic dacite lenses), the Dunns Mine Limestone, the Recovery Formation, the Hogan Dolomite, the Cooranna Formation and the Boorloo Siltstone (Figure 1b). In the Worumba Anticline, individual formations as described by Preiss (1987) include the Wirrawilka Beds, the Niggly Gap Beds, the Arkaba Hill Beds (possibly correlated with the Cooranna Fm in the Willouran Ranges), the Kirwan Siltstone (possibly comparable to the Boorloo Siltstone in the Willouran Ranges), the Waraco Limestone and the Worumba Dolomite Beds (Figure 1c). Generally speaking, the Curdimurka Subgroup can be described as cyclically alternating

siliciclastic and carbonate deposits, which may represent transgressive-regressive cycles (Preiss, 1987).

Many of the siltstone units display desiccation cracks, teepees and halite casts; nodular sulfate pseudomorphs occur in many of the carbonate beds throughout the Curdimurka Subgroup. Based on these observations and facies associations, Preiss (1987) interpreted the Curdimurka Subgroup as a coastal sabkha or playa lake environment that became progressively more restricted from south to north. A non-marine interpretation of the Willouran Ranges area was first proposed by Rowlands et al. (1980), who reported pseudomorphs after shortite—a sodium-calcium carbonate mineral ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) that is only found in alkaline lakes—from the Dunns Limestone and the Cooranna Formation in the Willouran Ranges. The shortite pseudomorphs were observed to alternate with pseudomorphs after gypsum.

According to this model, the Curdimurka Subgroup in the Willouran Ranges was deposited in a lacustrine setting similar to the modern East African rift valley, where alkaline saline lakes are common as a result of aqueous alteration of fresh volcanic rocks, followed by evapo-concentration of ions (Garrels and Mackenzie, 1967; Kempe and Kazmierczak, 2011). The presence of analgous alkaline lakes has been suggested for the Neoproterozoic Damara Belt in Namibia where similar mineralogical features were identified in a rift basin of roughly the same age as the early Adelaide Geosyncline (Porada and Behr, 1998). Hill and Walter (2000) argued in favour of the lacustrine model for the Curdimurka Subgroup in South Australia, because they found unusually light carbon isotope ratios ($\delta^{13}\text{C}_{\text{carb}}$ down to -9.5‰) in some carbonates, which they interpreted as recording oxidation of terrestrial biomass in the absence of a strong marine buffer of dissolved inorganic carbon (DIC). It should be noted, however, that such a buffer should be even stronger in an alkaline lake where DIC is more abundant than in seawater. Isotopically heavy carbonates up to +2‰, specifically in the Hogan Dolomite, were interpreted by Hill and Walter (2000) as reflecting a marine incursion into the basin, but given the coarse sampling resolution of their study, they were unable to identify regional consistencies.

To further investigate the environmental setting, we collected samples of carbonates and carbonaceous siltstones from the Willouran Ranges and Worumba Anticline areas. New sedimentological observations were paired with geochemical analyses. High-resolution

sections were collected from the Boorloo Siltstone, the Kirwan Siltstone and the Worumba Dolomite. Due to post-depositional deformation, metamorphic overprinting and modern weathering, it was difficult to obtain unaltered material. This study is therefore in part an attempt to 'see through' intense alteration to extract new environmental information about this setting during a key interval in Earth's history.

3. Materials and methods

3.1. Sampling

We conducted traverses in the Willouran Ranges area from the basal Dome Sandstone to the top of the Boorloo Siltstone. Most samples for geochemical analyses were collected from the Boorloo Siltstone, including the type section (Section 1 from 29.7264°S/137.9772°E to 29.7238°S/137.9821°E, locally known as Gum Creek) and three parallel sections separated by a few kilometers (section 2: 29.7187°S/137.9650°E to 29.7210°S/137.9661°E; section 3: 29.7129°S/137.9452°E to 29.713°S/137.9451°E; section 4: 29.7535°S/137.9798°E to 29.7559°S/137.9777°E). The four sections were correlated using the prominent carbonate ridges at the top of the Boorloo Siltstone as marker beds. The Boorloo Siltstone is stratigraphically variable and can be broadly subdivided into seven intervals at the type locality (Figure 2):

- I. 0-62 m: siltstone with sandstone interbeds of several dm in thickness. Wave ripples (symmetric, a few cm in scale here and elsewhere) and flaser bedding are common. Carbonate beds and calcareous sandstones at the scale of a few dm are present but rare.
- II. 62-107 m: interlaminated siltstone and shale with wave ripples and frequent dolomitic carbonate interbeds of a few dm in thickness. Some carbonate beds display wavy lamination, defined by siliciclastic laminae, but most beds are massive and fine crystalline (sparry). Several horizons have a sooty appearance, possibly reflecting pyrobitumen after hydrocarbon migration (Figure 3c and discussion below)
- III. 107 – 226 m: plane laminated siltstone with shale partings (Figure 3a). Sedimentary features indicative of current flow, wave action or exposure are absent.
- IV. 226 – 270 m: plane laminated black shale with minor siltstone laminae (Figure 4h), lacking other sedimentary features.

- V. 270 – 330 m: plane laminated siltstone grading upwards into a massive sandstone bed (roughly 310-330 m), which probably represents a single sand sheet as it contains no internal features.
- VI. 330 – 395 m: interlaminated siltstone and shale with minor sandstone interbeds of dm thickness. Frequent wave ripples.
- VII. 395 – 513 m: siltstone and shale with frequent thick (up to meter-scale) stromatolitic dolomite interbeds. The siltstone displays wave ripples and occasionally desiccation cracks indicating exposure (Figure 4g).

Figure 2: Stratigraphic data along the Boorloo Siltstone in the Willouran Ranges. Symbols for sedimentary features are as in Figure 1. Blue shading indicates carbonate. The four sections (1-4) are a few kilometres separated from each other along strike and were correlated by the prominent carbonate ridges at the top of the unit. The dashed line is the 5-point running mean.

Figure 3: Photomicrographs of samples in the Willouran Ranges and Worumba Anticline area. (a) Boorloo Stiltstone with shale laminae and minor carbonate; plane-polarized light. (b) Cubic hematite grains, likely after diagenetic pyrite, in the Kirwan Siltstone; crossed polarizers. (c) Monoclinic acicular quartz, likely pseudomorphs after diagenetic gypsum, within a matrix of sooty pyrobitumen in the basal Boorloo Siltstone; plane-polarized light. (d) Rosette fabric in quartz nodule within carbonate in the Hogan Dolomite; cross polarizers. (e) Inclusions with second-order birefringence, likely anhydrite, within nodular quartz, likely after gypsum or anhydrite, in the Worumba Dolomite; crossed polarizers. (f) Lenticular pseudomorph after gypsum, now quartz, within the basal Boorloo Siltstone; crossed polarizers.

Figure 4: Field photos of the Curdimurka Subgroup in the Willouran Ranges area. (a) 'Matchstick' texture of putative pseudomorphs after shortite in the Cooranna Fm, alternatively identified as pseudomorphs after barite. (b) Domal stromatolite from the Hogan Dolomite, a common morphology in several stratigraphic units. (c) Halite casts in siltstone from the Recovery Fm. (d) Wave ripples in siltstone slabs from the Recovery Fm. (e) Channel deposit (yellow dashed line) in the Dome Sandstone. Conglomeratic lag deposits are common at the bases of these channels. (f) Microbial carbonate with chert nodules after gypsum or anhydrite, reminiscent of chicken-wire fabric. (g) Desiccation cracks (white dotted lines) in the upper Boorloo Siltstone. (h) Plane laminated silty shale, partially calcareous, in the middle Boorloo Siltstone. (i) Herringbone cross-stratification in the Cooranna Fm, supported by 3-dimensional exposure of this outcrop.

Thus, broadly speaking, the section shows fining toward the middle; carbonates and wave ripples are restricted to the base and top. Oxidation trails, possibly after pyrite, are observed in many of the mudrocks. The carbonates are iron oxide stained (Figure 4b and 4f). Additional samples of carbonates and siltstones in the Willouran Ranges area were collected

from the Dunns Limestone (around 29.7479°S/137.9237°E), the Hogan Dolomite (around 29.7599°S/137.9584°E) and the Cooranna Formation (around 29.7548°S/137.9719°E). The carbonates commonly contain nodular and lenticular gypsum or anhydrite pseudomorphs (Figures 4f, 3f). A detailed stratigraphic description of these units is prohibited by the lack of continuous exposure. Our samples were taken from continuous meter-thick beds that stand proud above the more recessively-weathering calcareous mudstones above and below.

Figure 5: Field photos of the Curdimurka Subgroup in the Worumba Anticline area. (a) Nodular gypsum or anhydrite pseudomorphs in chicken-wire fabric within microbial carbonate of the Worumba Dolomite. (b) Stromatolitic carbonate with nodular gypsum or anhydrite pseudomorphs at the base in the Worumba Dolomite. (c) Plane-laminated Kirwin Siltstone.

In the Worumba Anticline, we targeted the most carbonaceous units, which are the Kirwan Siltstone (31.9036°S/138.6379°E to 31.9047°S /138.6371°E) and the Worumba Shale Member (31.8981°S/138.6334°E to 31.8994°S/138.6333°E). Both of these units consist of plane-laminated silty shales, often with alternating silt and shale laminae (Figure 5c). Sedimentary features indicative of wave action or current flow were not observed. Oxidation trails with cubic pits (Figure 3b), likely after pyrite, were observed in some samples, despite all efforts to sample below the modern weathering horizon. In addition to the mudstones, we collected ten fairly evenly spaced samples from the Worumba Dolomite over a stratigraphic interval of 3 m (around 31.8989° S/138.6342° E). The dolomite is wavy laminated and often stromatolitic (Figure 5b). It displays chicken-wire fabric with nodular gypsum or anhydrite pseudomorphs (now mostly quartz) of 1-2 cm in diameter (Figure 5a). The nodules often display an internal rosette fabric (Figure 3d), and some anhydrite is preserved (Figure 3e). The carbonate is stained with iron oxides.

3.2. Geochemical analyses

We used standard geochemical techniques at the University of Washington, Seattle, and at the University of California, Riverside (e.g. Stüeken et al., 2017a). First, outer surfaces were removed with a water-cooled rock saw. The rocks were then broken into sub-cm sized chips and subsequently washed with methanol, 2N HCl and DI-H₂O (18M Ω). The clean and dry chips were pulverized in a corundum puck mill, and the powder was stored in pre-combusted scintillation vials.

For bulk nitrogen and organic carbon analyses, a ~0.5 g aliquot of powder was decarbonated with 6N HCl at 60°C. The decarbonated powder was washed with DI-water, dried in a closed oven at 60°C and ultimately analysed by flash combustion in an elemental analyser (Costech) coupled to a gas source isotope ratio mass spectrometer (MAT253 Thermo Finnigan at UW). The isotopic ratios and elemental abundances were calibrated with in-house standards that had previously been calibrated to USGS-40 and USGS-41. Results are expressed in standard delta notation ($\delta = [R_{\text{sample}}/R_{\text{standard}} - 1] \cdot 1000$) relative to air for $\delta^{15}\text{N}$ and relative to VPDB for $\delta^{13}\text{C}_{\text{org}}$. Average reproducibility was 0.25‰ (1SD) for $\delta^{15}\text{N}$ and 0.07‰ for $\delta^{13}\text{C}_{\text{org}}$.

Iron speciation was determined by sequential extraction of iron phases from carbonates (Fe_{carb} , extracted with ammonium acetate), hematite (Fe_{Hem} , extracted with sodium dithionate), magnetite (Fe_{Mag} , extracted with ammonium oxalate), and pyrite (Fe_{Py} , extracted by chromium reduction) (Poulton and Canfield, 2005). For the first three phases, the extracted iron was measured in solution with an inductively coupled plasma mass spectrometer (Agilent 7500 at UCR). The calcium and magnesium concentrations of the ammonium acetate extract were used to approximate the total carbonate content of the samples (Stüeken et al., 2017a). The pyrite-bound iron was quantified by iodometric titration (Canfield et al., 1986). Highly reactive iron (Fe_{HR}) is defined as the sum of Fe_{Hem} , Fe_{Mag} , Fe_{Carb} and Fe_{Py} (Poulton and Canfield, 2005). The average reproducibility of iron measurements in replicate extractions was 13%, but this uncertainty does not alter our interpretation.

Carbonate-associated sulfate was extracted from carbonate samples following the procedure described by Planavsky *et al.* (2012). Roughly 5-10 g of powder were treated twice with a 10% NaCl solution to remove any potential gypsum phases that may have

formed during weathering of pyrite. The powder was then washed twice with DI-water and treated several times with 10% H₂O₂ overnight to remove pyrite as recommended by Wotte *et al.* (2012). H₂O₂ treatments were stopped when no more BaSO₄ precipitated in the extracted solution upon addition of BaCl₂. After another two DI-water rinses, the carbonate was mixed with 50-100ml of 4N HCl (excess to convert all carbonate to CO₂) and left to react until no more bubbling could be observed. The solution was then separated from the residual solids by filtration, and dissolved sulfate was precipitated as BaSO₄ after the addition of BaCl₂. The BaSO₄ was separated by filtration and washed with approximately 50ml of 1N HCl, followed by ~100ml of DI-water, and then dried overnight at 40°C. A small aliquot of the HCl solution containing the dissolved carbonate was analysed for sulfate concentrations by ICP-MS (Agilent 7500 at UCR). The BaSO₄ was analysed for sulfur isotope ratios by EA-IRMS (Costech EA, coupled to a Delta V Plus at UCR). A separate aliquot of each carbonate sample was subjected to chromium reduction to extract pyrite as Ag₂S for sulfur isotope analyses. The average reproducibility was 0.5‰ (1SD) for δ³⁴S, and values are expressed relative to VCDT as a reference standard.

For bulk elemental analyses, a 1g aliquot of each sample was sent to ALS Global for analysis by ICP-MS and ICP-OES, following a four-acid digestion with HNO₃, HClO₄, HF and HCl. Enrichment factors (EF) for redox-sensitive elements (X) relative to aluminium and bulk average crust were calculated as $EF = (X_{\text{sample}}/Al_{\text{sample}})/(X_{\text{crust}}/Al_{\text{crust}})$, using crustal abundances from Rudnick and Gao (2014).

4. Results

4.1. Iron speciation and redox-sensitive metals

The samples were noticeably depleted in pyrite (Table 1), although the black shales in particular have been described as pyritic by previous authors (Rowlands *et al.*, 1980; Preiss, 1987). Only two samples of the Boorloo Siltstone and one sample of the Worumba Shale Member contained pyrite above the detection limit of 0.1%. In the siliciclastic mudrocks, the ratio of highly reactive iron relative to total iron (Fe_{HR}/Fe_T) was mostly below the empirically defined oxic/anoxic threshold of 0.38 (Poulton and Canfield, 2011). Higher ratios were predominantly found in samples with more than 30% carbonate, where Fe_{HR}/Fe_T ratios exceeded 0.7 (Figure 6a). Those samples also displayed total Fe/Al ratios greater than

the continental average of 0.5 (Figure 6b), which is another empirically identified threshold for anoxic conditions (Lyons et al., 2003; Lyons and Severmann, 2006; Raiswell et al., 2019). It is important to note that the iron speciation proxy can also be applicable in carbonate-rich rocks with more than 0.5% Fe_T (Clarkson et al., 2014), which is fulfilled for these samples. The only sample that satisfies the iron criteria of euxinia (*i.e.*, anoxic conditions with free H₂S in the water column)—Fe_{HR}/Fe_T > 0.38 paired with Fe_{PY}/Fe_{HR} > 0.7 (Poulton and Canfield, 2011)—is the pyrite-bearing Worumba Shale sample (Figure 5c), which has a Fe_{HR}/Fe_T ratio of 0.82 and a Fe_{PY}/Fe_{HR} ratio of 0.84. The most abundant highly reactive iron phase in most of the samples was hematite extracted with the Na dithionate treatment (Figure 6d). Carbonate-bound iron was dominant in a few though not all carbonate-rich samples (Figure 5e). Magnetite constituted mostly less than 30% (Figure 6f).

Figure 6: Iron speciation data. Dashed lines mark empirically defined thresholds of anoxia ($Fe_{HR}/Fe_T > 0.38$ and $Fe_T/Al > 0.5$) and euxinia ($Fe_{PY}/Fe_{HR} > 0.7$) (Lyons et al., 2003; Poulton and Canfield, 2011). The high degree of modern oxidative weathering may have removed much if not all of the original pyrite, and sulfuric acid resulting from this process would likely have removed the Fe³⁺ from the host rock. Carbonates probably buffered this acidity, which could explain relative iron retention compared to carbonate-poor mudstones.

Concentrations of minor redox-sensitive metals (Table 2) were mostly close to crustal background (V, Cr) or depleted by a factor of 3-5 (Co, Ni, Cu, Zn, As). Rare outliers with enrichments above background levels are not systematic and show no covariance with pyrite content or total organic carbon.

4.2. Carbonate-associated sulfate and pyrite

Figure 7: Carbonate-associated sulfate isotope data. Marine range is taken from Grojan et al. (2000) and Canfield & Farquhar (2009).

Concentrations of carbonate-associated sulfate (CAS, Table 3) in our samples ranged from 273 ppm to 698 ppm (mean 439 ± 130 ppm) in the Worumba Dolomite and from <1 ppm to 142 ppm (mean $38 +53/-38$ ppm) in several scattered carbonates from the Willouran Ranges area. We were able to measure sulfur isotope ratios for samples with at least 2.5 ppm CAS and obtained $\delta^{34}\text{S}_{\text{CAS}}$ values of +17.5 ‰ to +20.9 ‰ (mean $+19.5 \pm 1.2$ ‰) in the Worumba Dolomite and +7.2 ‰ to +15.0 ‰ (mean $+11.4 \pm 2.8$ ‰) in the Willouran samples (Figure 7). Sulfur isotope data for trace amounts of pyrite (<0.1 ‰) contained in the same samples showed a range of -1.3 ‰ to +6.5 ‰ (mean $+1.1 \pm 2.5$ ‰) in the Worumba Dolomite and -14.6 ‰ to +17.3 ‰ (mean $+1.1 \pm 9.2$ ‰) in the Willouran samples. The Worumba samples are thus overall more uniform in their CAS content and isotopic composition. Minor amounts of pyrite (mostly <0.1%) extracted from carbonate-poor shales showed an isotopic composition of +15.1 ‰ for the only pyrite-bearing sample from the Worumba Shale Member and a range from -8.6 ‰ to +6.0 ‰ (mean -1.5 ± 8.0 ‰) in the

Willouran shales from the Boorloo Siltstone (Table 3). A few other scattered samples from the Willouran area show values from -12.4 ‰ to +15.5 ‰ for extracted pyrite.

4.3. Organic carbon and nitrogen isotopes and non-redox sensitive element ratios

4.3.1. Boorloo Siltstone. For the Boorloo Siltstone, we collected samples along four parallel stratigraphic sections. The results agree well among the sections and will thus be discussed jointly. $\delta^{15}\text{N}$ values (Table 4) show a negative excursion in the middle of the unit, starting from around +8 ‰ at the base, declining gradually to +3 ‰ at round 250m, and recovering quickly to values between +8 ‰ and +11 ‰ (Figure 2). This trend is vaguely mirrored by an excursion in $\delta^{13}\text{C}_{\text{org}}$, starting from values around -21 ‰, declining to -26 ‰, and returning to values around -20 ‰ near the top. The relatively higher values in both parameters are thus found in the carbonate-rich beds and in particular in the stromatolitic intervals at the top, whereas the black shale in the middle of the section records the lowest isotopic ratios.

The total organic carbon (TOC) content reaches 2.6 wt% near the base but is mostly below 0.4 wt% for the rest of the section. The basal organic-rich samples have a sooty, reflective appearance, resembling metamorphosed concentrates of hydrocarbons. These exceptionally organic-rich beds are traceable along strike for a few meters (extent of the outcrop), have a thickness of 1-2dm and are more massive in appearance than adjacent beds (see also Figure 3c). We therefore interpret these data as indicative of hydrocarbon migration and concentration in between carbonate beds. In contrast to TOC, total nitrogen (TN) concentration shows a peak of 240 ppm in the middle of the section, with lower values around 100 ppm and 50 ppm near the base and top, respectively.

As a consequence, there is only vague covariation between TN and TOC for a subset of samples. However, this lack of covariation is largely driven by the basal TOC-rich. Among all samples, the correlation coefficient (r^2) between TOC and TN is 0.07 (Figure 8b), but if samples above 1 wt% TOC and/or below 150 m are removed because of suspected pyrobitumen accumulation (Figure 3c), r^2 increases to 0.52 (Figure 8c). Molar ratios of organic carbon to total nitrogen (hereafter C/N) mirror the trend in TOC, with high values near the base (Figure 2). TOC content and C/N ratios are strongly correlated ($r^2 = 0.86$, Figure

8d), meaning that organic carbon is the main driver for large variations in C/N. If the basal organic-rich samples are excluded, r^2 drops to 0.47. Nitrogen isotopes are not correlated with C/N ratios ($r^2 = 0.001$, Figure 8a), but they show a (non-linear) inverse covariance with TN ($r^2 = 0.74$, Figure 8f). $\delta^{15}\text{N}$ and TN are not correlated with K/Al ratios ($r^2 = 0.13$ and 0.004, Figure 8e).

Figure 8: Scatter plots of nitrogen and related data in the Boorloo Siltstone. Panel c shows a subset of the data from panel b, excluding samples with more than 1% TOC and/or below 150 m where hydrocarbons may have migrated (Figure 3c).

Figure 9: Stratigraphic data along the Kirwan Siltstone (a) and the Worumba Shale Mbr (b) in the Worumba Anticline region. Both units are relatively monotonous siltstones with interlaminated dark shale.

4.3.2. Kirwan Siltstone and Worumba Shale Mbr. Neither the Kirwan Siltstone nor the Worumba Shale Member show any systematic stratigraphic variance in $\delta^{15}\text{N}$, TN, $\delta^{13}\text{C}_{\text{org}}$, TOC or C/N (Figure 9). Nitrogen isotope data are similar between the two sections ($+4.5 \pm 0.2 \text{ ‰}$ for the Kirwan Siltstone and $+4.6 \pm 0.4 \text{ ‰}$ for Worumba Shale Mbr), but the Kirwan Siltstone is enriched in TN ($355 \pm 36 \text{ ppm}$) compared to the Worumba Shale Member ($172 \pm 25 \text{ ppm}$). TOC levels are $0.2 \pm 0.1 \text{ wt\%}$ on average in both sections, but $\delta^{13}\text{C}_{\text{org}}$ is slightly heavier in the Worumba Shale Mbr ($-23.7 \pm 0.5 \text{ ‰}$) compared to the Kirwan Siltstone ($-26.8 \pm 0.5 \text{ ‰}$). In both sections, C/N ratios are strongly correlated with TOC ($r^2 = 0.96$ for the Kirwan Siltstone and 0.95 for the Worumba Shale Mbr; Figure 10c). We did not find strong correlations between nitrogen isotopes and C/N ratios ($r^2 < 0.4$ for both sections, Figure 10a) or TN contents ($r^2 < 0.4$ in both cases, Figure 10d), nor between TN and TOC (both $r^2 < 0.31$, Figure 10b). Also nitrogen abundances and isotope data are not correlated with K/Al ratios ($r^2 < 0.3$ and < 0.03 , respectively, for both sections, not shown).

Figure 10: Scatter plots of nitrogen data for the Kirwan Siltstone (blue diamonds) and the Worumba Shale Mbr (yellow triangles).

5. Discussion

5.1. Alteration by modern weathering

5.1.1. Iron speciation and redox-sensitive elements. We suspect that the scarcity of pyrite may largely be a consequence of modern oxidative weathering. Despite our efforts to dig deep into the outcrops, many samples displayed small oxidation trails, sometimes in cubic shapes, reminiscent of euhedral pyrite grains that may have formed during diagenesis with likely metamorphic overprints (Figure 3b). Oxidative loss of sulphide phases could also explain the depletion or lack of enrichment in redox-sensitive elements (V, Co, Ni, Cu, Zn, As).

Oxidation of pyrite-bound Fe^{2+} to Fe^{3+} would perturb the iron speciation proxy. If the Fe^{3+} is retained within the rock as iron oxides, the $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ ratio would drop, but the $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratio would stay constant. In this case, a sample that fell initially into the euxinic

category ($\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}} > 0.7$ and $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$, Poulton and Canfield, 2011) would appear ferruginous. If, however, some Fe^{3+} is lost during oxidation, $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ would drop together with $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$, and the sample would move towards the 'oxic' field in a $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ versus $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ crossplot. In our samples, it is noteworthy that the $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratio increases with carbonate content (Figure 6a), whereas the siliclastic shales have lower ratios of $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$. It is likely that pyrite oxidation in shales generated sulfuric acid, which mobilised Fe^{3+} and removed it from the system. In contrast, carbonate-rich samples may have buffered the acidity, leading to Fe^{3+} retention as iron oxides. This interpretation is consistent with the high ratios of diethionite-extracted iron to highly-reactive iron, where the former is assumed to represent mostly hematite-bound Fe^{3+} (*i.e.*, $\text{Fe}_{\text{HEM}}/\text{Fe}_{\text{HR}}$) (Figure 6d). The implications are that we are unable to infer redox conditions from iron speciation in the shale samples; however, the carbonates appear to record anoxic conditions at the time of deposition (Figure 6a). We cannot speak to the presence or absence of euxinia with this proxy due to the potential loss of pyrite, but the presence of gypsum/anhydrite nodular pseudomorphs with chicken-wire fabric and the lack of highly negative $\delta^{34}\text{S}$ values in pyrite suggest that sulfate was not totally consumed by microbial reduction in the water column, at least within the carbonate facies.

Carbonate-associated sulfate can also be affected by weathering. Gill *et al.* (2008) documented a significant drop in CAS concentrations during meteoric alteration of Pleistocene carbonates. However, the isotopic record appeared to have been buffered and was essentially unaltered. Oxidation of pyrite could potentially have created 'modern' sulfate phases during weathering; however, since we cleaned our samples thoroughly with NaCl solution and H_2O_2 (Wotte *et al.*, 2012), any such modern sulfate, along with residual pyrite, should have been removed from the rock prior to CAS extraction in the laboratory.

5.1.2. Organic carbon and nitrogen. Petch *et al.* (2000; 2005) showed that organic carbon is oxidized more slowly than pyrite during oxidative weathering, which is consistent with our observation that at least some organic carbon was still present in these rocks despite the loss of pyrite. However, TOC levels have likely been reduced, and organic carbon isotope ratios may have become heavier by 1-2 ‰ due to partial loss during weathering (Leythaeuser, 1973; Clayton and Swetland, 1978).

Oxidative weathering has also been shown to lower the nitrogen contents of rocks (Petsch et al., 2005), but the effects on nitrogen isotopes have to our knowledge not yet been tested. A previous study (Stüeken et al., 2017b) showed that the majority of the total nitrogen is contained in silicate minerals (Boorloo Siltstone 56-97%, n=3; Kirwan Siltstone ~96%, n=3; Worumba Shale Mbr 90-91%, n=2). Nitrogen can partition into silicate minerals as ammonium ions during diagenesis and metamorphism. Ammonium (NH_4^+) has the same charge as K^+ and a similar ionic radius, which allows it to substitute into K-rich minerals (Müller, 1977; Schroeder and McLain, 1998). We speculate that this silicate-bound ammonium fraction is relatively more resilient to oxidative weathering than organic-bound nitrogen, which could in part explain the high relative abundance of silicate-bound nitrogen in these rocks.

5.2. Diagenesis and metamorphism

Using H/C ratios of kerogen isotopes, it has been shown that the Boorloo Siltstone experienced lower amphibolite facies metamorphism ($\text{H/C} = 0.06\text{-}0.09$), whereas the Kirwan Siltstone and Worumba Shale Mbr ($\text{H/C} = 0.13\text{-}0.22$) have only been metamorphosed to greenschist facies (Stüeken et al., 2017b). Metamorphism can have significant effects on organic carbon and nitrogen isotopes. In both isotopic systems, the lighter isotope is volatilized more readily during metamorphic heating (e.g. Haendel et al., 1986; Bebout and Fogel, 1992; Boyd and Philippot, 1998; Palya et al., 2011). $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values thus tend to increase with metamorphic grade. For nitrogen, the effect is on the order of 1-2‰ for greenschist facies and 3-4‰ for amphibolite facies (reviewed by Thomazo and Papineau, 2013). Organic carbon isotopes increase by several permil during metamorphism, and this effect is enhanced in the presence of carbonates (Schidlowski, 1987). It is therefore likely that all our samples have been shifted to heavier isotopic values during regional metamorphism, and the effect was probably more significant in the Boorloo Siltstone than in the Kirwin Siltstone and Worumba Shale Mbr, because the former is of higher metamorphic grade (Stüeken et al., 2017b).

5.2.1. Nitrogen and carbon in the Boorloo Siltstone. The stratigraphic trends in the organic carbon isotope data may be an artefact of metamorphism, because the heavier values occur

in the more carbonate rich interval above 400 m (Figure 2), as would be expected with metamorphic isotopic equilibration between inorganic and organic carbon phases. However, although it is likely that our nitrogen data have also been pushed to heavier values, metamorphic volatilization probably cannot explain the stratigraphic variation in $\delta^{15}\text{N}$ across the Boorloo Siltstone as regional metamorphism should have affected the section as a whole. As noted above, $\delta^{15}\text{N}$ shows no covariance with C/N ratios, even though N tends to be lost more rapidly during metamorphism (Hayes et al., 1983). Nitrogen isotopes are instead correlated with TN contents (Figure 8f), where the highest TN contents occur in the black shale facies at around 250 m, which also shows a small peak in TOC. Thus, this correlation seems to be a primary feature. The shale facies likely started out more organic-rich and may have displayed lighter nitrogen isotope ratios as a consequence of redox stratification (further discussed in Section 5.3.2).

We can rule out significant post-depositional migration of ammonium across the section, as well as major input of detrital ammonium, because TN contents correlates with TOC but not with K/Al (Figures 8c, 8e). We note that the correlation between TN and TOC is only observed after excluding some samples from the basal Boorloo Siltstone (< 150 m) that show evidence of hydrocarbon migration in the form of abnormally high C/N ratios (Figure 2) and sooty organic carbon that is reminiscent of pyrobitumen (Figure 3c). Thus, while the basal part of the section may yield unreliable isotopic values, the transition from light $\delta^{15}\text{N}$ values in the middle black shale (~250 m) toward heavier values in the stromatolitic facies at the top (> 400 m, Figure 2) may be a primary relic of environmental conditions during the time of deposition (Section 5.3.2).

5.2.2. Nitrogen and carbon in the Kirwan Siltstone and Worumba Shale Mbr. Unlike the Boorloo Siltstone, the Kirwan Siltstone and the Worumba Shale Mbr are strikingly homogeneous in their TN content and isotopic composition. Another difference noted in a previous study (Stüeken et al., 2017b) is that the $\delta^{15}\text{N}$ value of the kerogen in the Kirwan Siltstone and Worumba Shale Mbr is further offset (by 3.9 ± 0.0 ‰ and 4.5 ± 0.4 ‰, respectively) from the $\delta^{15}\text{N}$ of the silicate-bound ammonium compared to the offsets in the Boorloo Siltstone (3.0 ± 0.1 ‰). Divergence in $\delta^{15}\text{N}$ between the two nitrogen phases is commonly observed with increasing regional metamorphic grade (Stüeken et al., 2017b) as

well as after metasomatic fluid alteration (Godfrey et al., 2013). In this case, the Boorloo Siltstone has a higher metamorphic grade (lower amphibolite facies) than the shales of the Worumba Anticline (greenschist facies). Hence, the relatively large nitrogen isotope offset between kerogen and silicates in the Kirwan Siltstone and Worumba Shale Mbr is perhaps not a metamorphic feature alone but may be evidence of metasomatic alteration. Such fluids could conceivably have homogenized the nitrogen contents and isotopic ratios within the two units.

As noted earlier (Section 5.1.2), ammonium released from the breakdown of organic matter during diagenesis partitions into K-rich minerals due to the similarity in ionic charge and size (Schroeder and McLain, 1998). For this reason it has been suggested that post-depositional ammonium migration may be linked to K-metasomatism, supported by correlations between TN and K contents in other datasets (Kump et al., 2011). We did not observe any such correlations in our samples (Section 4.3), which may indicate that ammonium and potassium migration were unrelated in this setting. Metasomatism with K-rich fluids is often explained by the breakdown of K-rich feldspars and clay minerals (reviewed by van de Kamp, 2016). In contrast, ammonium is primarily sourced from biomass during either diagenetic decay or metamorphic breakdown. Hence, ammonium migration could have occurred independently from K-metasomatism, and a correlation between the two elements is perhaps not necessarily to be expected.

The most likely ammonium source rocks in the Worumba Anticline are the shales sampled for this study, as they are the most organic rich units in this area. Hence, ammonium was probably released from the most organic-rich laminae and distributed relatively evenly across organic-poor beds via incorporation into clays. If so, no nitrogen would have been added from external sources, and hence the average isotopic composition of the shales may still approximate the primary isotopic composition with only a slight metamorphic overprint that would have pushed $\delta^{15}\text{N}$ heavier by 1-2‰ at greenschist facies.

5.2.3. Alteration of inorganic proxies. Metamorphism has been shown to have significant effects on iron speciation, where carbonate-bound iron can be transferred into silicates, making the rock appear, if anything, relatively more ‘oxic’ (Slotznick et al., 2018). The anoxic

(ferruginous or euxinic) conditions inferred from our carbonate samples are thus a reasonable interpretation.

Carbonate-associated sulfate can be strongly modified during diagenesis where in situ pyrite oxidation can lead to lower $\delta^{34}\text{S}_{\text{CAS}}$ values (Marenco et al., 2008), while diagenetic sulfate reduction can deplete porewater sulfate in ^{32}S , pushing $\delta^{34}\text{S}_{\text{CAS}}$ higher (Fike et al., 2015). We cannot rule out either of these effects. However, the presence of gypsum/anhydrite nodular pseudomorphs within the same carbonates in both outcrop areas (Figures 4f, 3d, 3e, 3f, 5a); the relatively small scatter in $\delta^{34}\text{S}_{\text{CAS}}$, in particular in the Worumba Dolomite and the moderately high CAS concentrations of several hundred ppm in many of the Worumba samples, compared to a few tens of ppm in some Neoproterozoic (e.g. Hurtgen et al., 2004) and Mesoproterozoic carbonates (e.g. Kah et al., 2004; Gellatly and Lyons, 2005), suggests that the water column was enriched in dissolved sulfate, probably as a result of evapo-concentration, and thus somewhat buffered against these diagenetic effects. Similar buffering has been described in modern sulfate-rich systems (Rennie and Turchyn, 2014).

5.3. Environmental interpretations

Despite extensive metamorphic alteration and modern weathering effects, a few environmental features can be inferred from the geochemical data, combined with sedimentary features.

5.3.1. Sedimentary features indicative of tidal action. Several sedimentary features noted in our field area provide evidence for the type of depositional setting. Most importantly, herringbone cross-beds as observed in the Cooranna Fm and flaser beds documented from the lower Boorloo Siltstone (see also Rowlands et al., 1980; Preiss, 1987) (Figure 4i) may suggest tidal influence during the deposition of these strata. Herringbone cross-stratification can be misidentified if it is only exposed in two dimensions (Awramik and Buchheim, 2009); however, the 3-dimensional exposure, which showed planar lamination on the orthogonal plane, supports our interpretation of bi-directional current flow, consistent with a tidally-influenced setting. Flaser bedding has been described from a lacustrine setting (Martin, 2000), but they are generally considered a hallmark of tidal influence on shallow marine

strata, reflecting frequent waxing and waning of depositional energy (Reineck and Wunderlich, 1968; Longhitano et al., 2012). Mud drapes in Archean and Mesoproterozoic strata have previously been used to infer marine conditions (Flannery et al., 2016; Stüeken et al., 2017a). Hence the wave-rippled sandstones with desiccation cracks and carbonates with gypsum pseudomorphs probably represent the intertidal to supratidal zone. If the basin was connected to the ocean, then the plane-laminated black shales and siltstones likely represent transgressive intervals. It would thus make sense if the Boorloo Siltstone were correlative with either the Kirwan Siltstone or the Worumba Siltstone Mbr, but our data cannot affirm this conclusion.

The basin likely also had a fluvial input, as evidenced by unidirectional current indicators (asymmetric ripples) and fluvial channel deposits in the basal Curdimurka Subgroup (Figure 4e, Preiss, 1987) and consistent with the observed trend in CAS isotope values. However, the abundant deposits of sulfate and halite evaporites (Figures 4c, 4f, 3d, 3e, 3f, 5a, 5b) were probably a result of frequent (daily or monthly) seawater incursions that replenished the salt content of the water column. Subsequent evaporation at low tide would have resulted in salt deposition on exposed surfaces and led to stagnant anoxic conditions in deeper waters. Collectively, our observations thus point to a marginal marine setting, perhaps akin to a sabkha.

5.3.2. Redox stratification. The relatively high Fe_{HR}/Fe_T ratios in carbonate-rich samples, where loss of reactive iron may have been minimized due to pH buffering (Section 5.1.1), may suggest anoxic conditions at the sediment-water interface, at least in this facies. We note that many of these carbonates contain gypsum/anhydrite nodular pseudomorphs with a chicken-wire fabric (Figure 4f, 3d, 5a) and are stromatolitic, which means that sulfate was stable in these environments and that these may have been sites of active O_2 production. However, these properties are not incompatible with the iron data. First, sulfate is thermodynamically stable in the presence of Fe^{2+} (Brookins, 1988), and so ferruginous anoxic conditions do not preclude the formation of gypsum precipitates within sediments under evaporitic conditions as suggested by the chicken-wire fabric. Second, the iron speciation proxy may only capture redox conditions within a few centimeters above the sediment-water interface. For example, it is possible that Fe^{2+} diffused upwards within

sediments during diagenesis and became trapped and concentrated in shallow-water carbonates. A similar process has been documented from modern settings (Raiswell et al., 2019). Hence surface waters were most like oxygenated.

However, deeper waters were probably anoxic as supported by the gradient in the nitrogen isotope data observed in the Boorloo Siltstone, where the black shales show relatively lighter values compared to the overlying carbonates (we exclude the basal strata from this discussion due to potential overprinting by hydrocarbon migration but note that they support the inferred trend). The amphibolite facies metamorphic overprint prohibits accurate reconstructions of primary $\delta^{15}\text{N}$ values, but if we assume an offset of 3-4‰, then the black shales and carbonates would fall around 0‰ and +6‰, respectively. Values near 0‰ are indicative of biological N_2 fixation (Zerkle et al., 2008; Zhang et al., 2014), which dominates in environments that are relatively depleted in fixed nitrogen. In contrast, positive values of around +6‰ are typically interpreted as evidence of nitrate assimilation, where the nitrate reservoir was isotopically fractionated by partial nitrate reduction to N_2 (denitrification) at an oxic/anoxic interface in the water column (Sigman et al., 2009; Ader et al., 2016; Stüeken et al., 2016). In other words, these data may indicate that there was a redoxcline and that nitrate was relatively more bioavailable in the stromatolitic carbonate facies, which probably represents shallower water. Occurrences of desiccation cracks in siltstones interlayered with the carbonate beds (Figure 4g) indicate that this facies was shallower than the black shales. Hence, the nitrogen data from the Boorloo Siltstone are broadly consistent with a redox stratified environment that was oxic and nitrate-rich in shallow waters but anoxic and nitrate-depleted at depth and offshore. A similar redox stratification in nitrate availability has been described from other Proterozoic basins (Stüeken, 2013; Koehler et al., 2017),

In the Kirwan Siltstone and Worumba Shale Member, reconstructed pre-metamorphic $\delta^{15}\text{N}$ values are around +2 to +3‰ (Section 5.2.2). These values are lower than in the modern ocean (around +5‰ to +6‰), where nitrate is the major nitrogen source (Tesdal et al., 2013). Similar values are found, for example, in some sedimentary intervals and suspended particulates in the modern Black Sea (Fuchsman and Murray, 2008; Fulton et al., 2012) and may indicate mixing between biomass from N_2 -fixing organisms (near 0‰) and nitrate-assimilating organisms (>3‰, Kipp et al., 2018). Hence nitrate was probably not

widely available in the water column during deposition of these siltstone beds, which may again be indicative of some level of redox stratification.

5.3.3. Geochemical indicators for a marine influence. The Callanna Basin, in particular the Curdimurka Subgroup, has previously been interpreted as an alkaline lake based on findings of pseudomorphs after shortite in several formations in the Willouran Ranges area (Rowlands et al., 1980). Our geochemical data do not support this interpretation and are instead more consistent with a marine influence. First, the $\delta^{34}\text{S}$ data of carbonate-associated sulfate in our samples are comparable to the range proposed for seawater sulfate at that time (+16‰ to +20‰, Gorjan et al., 2000, Figure 6; Canfield and Farquhar, 2009). Our data show a gradient from values around +20‰ in the Worumba Anticline to lower values around +11‰ in the Willouran Range. If these two sedimentary packages were roughly coeval (Preiss, 1987), then this gradient may indicate influx of seawater from the south with a composition around +18‰ that was perhaps mixing with some sulfate derived from crustal weathering (+6‰ today, Fike et al., 2015) towards the north, consistent with the proposed basin geometry (Preiss, 2000).

Second, our nitrogen isotope data are inconsistent with alkaline conditions. Sediments from known alkaline lakes typically display high $\delta^{15}\text{N}$ values, often up to 20‰ due to the formation and volatilization of NH_3 gas from NH_4^+ at $\text{pH} > 9$ (Collister and Hayes, 1973; Talbot and Johannessen, 1992; Lent et al., 1995; Menzel et al., 2013; Stüeken et al., 2019). Our data show no evidence of this process in any of the study sites. We did not analyse samples that contain putative shortite pseudomorphs, but we did sample from roughly the same interval and locations. Further, we note that the features illustrated by Rowlands et al. (1980) are unlikely to be this mineral. Shortite characteristically has wedge-shaped orthorhombic pyramidal crystals, not the elongate ‘match-stick’ habit with square cross-sections shown in our Figure 4a and their Figures 2a and 2b. We speculate that these are instead pseudomorphs after sulfate minerals. The highly alkaline conditions as proposed by Rowlands et al. (1980) are incompatible with the precipitation of gypsum, because alkaline waters are characterised by very low dissolved calcium concentrations due to extensive CaCO_3 precipitation, such that gypsum cannot reach saturation during evaporation (Garrels and Mackenzie, 1967; Stumm and Morgan, 1996). Hence, there is no evidence that this basin

was an alkaline lake. Instead, the combination of sedimentological and geochemical observations are most parsimoniously interpreted as reflecting a shallow marine basin, perhaps sabkha-like, that experienced occasional transgressions, leading to the deposition of plane-laminated black shales. Future trace element studies on the carbonate facies (e.g., Bolhar and van Kranendonk, 2007; Coffey et al., 2013) may be useful for testing this conclusion.

5.4 Comparison with the contemporaneous Bitter Springs Formation

The Callanna Group is roughly coeval with the Bitter Springs Formation in Central Australia (810-800 Ma), which is characterized by an extreme negative carbon isotope excursion of about 10‰ that is also seen in correlative marine basins worldwide (Halverson et al., 2005). In the canonical Bitter Springs section, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ values co-vary with a near-constant isotopic offset over several hundred meters of stratigraphy (Swanson-Hysell et al., 2010). In contrast, our organic carbon isotope data (Figures 2 and 8) fall around the global long-term average $\delta^{13}\text{C}_{\text{org}}$ value of -27‰ (Krissansen-Totton et al., 2015). More negative values would be expected if the Curdimurka Supgroup captured the Bitter Springs excursion. In the Boorloo Siltstone, Hill and Walter (2000) reported some $\delta^{13}\text{C}_{\text{carb}}$ values -7.5‰ and -7.1‰ from silty carbonates separated stratigraphically by about 300 meters, but these were bracketed by $\delta^{13}\text{C}_{\text{carb}}$ measurements of 0‰ to +1.5‰ and are thus best explained by diagenetic or metamorphic alteration. Hence, we see no expression of the Bitter Springs excursion at least in the intervals of the Curdimurka Subgroup investigated in this study, suggesting that they are not directly correlative with the Bitter Springs isotope anomaly. However, more detail geochronological work is needed to substantiate this conclusion. If the Curdimurka Subgroup is coeval to the Bitter Springs Formation, then the absence of a carbon isotope excursion may warrant further investigation.

6. Conclusion

The Callanna Group falls into a key interval in Earth history and could potentially provide novel insights into the evolution of life and environmental conditions at this time. The basin formed during continental rifting (Preiss, 2000) and has previously been interpreted as lacustrine and highly alkaline, based on observations of pseudomorphs after

shortite (Rowlands et al., 1980). Until now, little geochemical work had been done on these rocks to test this hypothesis, primarily due to the strong metamorphic overprint and alteration by modern weathering. Indeed, most pyrite appears to have been lost, limiting our ability to use proxies based on redox-sensitive trace elements. However, our analyses suggest that some primary environmental information can be extracted from such altered rocks. First, acid-buffering by carbonates appears to help with the retention of reactive iron despite oxidative weathering, such that $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratios are retained while $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ ratios drop. Hence signatures of anoxia can be preserved, even though the distinction between euxinic and ferruginous conditions becomes difficult. Second, relative trends in nitrogen isotopes may be preserved when absolute values are shifted by metamorphic overprint. Nitrogen stored in phyllosilicates is perhaps also more resistant to oxidative weathering than organic nitrogen species. Lastly, carbonate-associated sulfate (CAS) is extractable from rocks up to amphibolite facies metamorphic grade.

Despite the limitations of alteration, our data are thus overall suggestive of redox stratification and nitrate limitation in this basin. Oxidic conditions were probably limited to shallow waters. Furthermore, our data are inconsistent with the interpretation of an alkaline lake, because we found no evidence of ammonia volatilization resulting in very heavy nitrogen isotopes, which characterises such settings. We also note that high alkalinity is incompatible with the precipitation of sulfate evaporites, which are abundantly present as pseudomorphs in carbonate facies in the Curdimurka Subgroup. Instead, sedimentary features indicative of tidal activity and sulfur isotope ratios of carbonate-associated sulfate that are comparable to coeval seawater sulfate indicate that this basin had a marine connection and was frequently flooded by seawater. These rocks therefore provide little information about non-marine habitats on the Neoproterozoic Earth. Lastly, the absence of the characteristic Bitter Springs carbon isotope anomaly may indicate that the units investigated in this study are not directly correlative with the Bitter Springs Formation and can therefore not serve as an age constraint.

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