The palaeoenvironmental context of the Trezona anomaly in South Australia: Do carbon isotope values record a global or regional signal?

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Funding information
Australian Research Council, Grant/Award Number: DP120100104, LP120200086

ABSTRACT

The composite δ¹³C record of Neoproterozoic carbonates is characterized by large magnitude (<18‰ Vienna Pee Dee Belemnite) swings that have been interpreted to record (a) changes in dissolved inorganic carbon in sea water driven by a carbon cycle with different boundary conditions, (b) pervasive diagenetic alteration or (c) local controls similar to those active in Cenozoic platformal successions. A sedimentological study of the Trezona Formation in the Flinders Ranges of South Australia was conducted to determine the palaeoenvironmental context of the Trezona anomaly, one of the most widely recognized examples of a Neoproterozoic mega-exursion that occurs beneath glaciogenic sediments of the Marinoan ice age (ca 635 Ma). Stratigraphic mapping identified an unconformity at its base separating it from the shelf deposits of the underlying Enorama Shale. The lower Trezona Formation is dominantly calcareous mudstone with mudcracks, channels, and mud chip and algal flake breccias interpreted to record exposure and desiccation on mudflats, shallow pools and lagoons. A marked increase in microbial carbonate and oolites in the upper Trezona Formation records a relative decline of mud input that terminates with karst. The Trezona Formation is thus interpreted to have been deposited in shallow, localized, salt withdrawal basins on the exposed shelf creating a mosaic of poorly connected lagoons and (alkaline) lakes that were intermittently restricted or isolated from the sea. Variations in δ¹³C and δ¹⁸O correspond with facies changes and reflect locally evolving depositional conditions influenced by sills and channels that shifted the sea water to freshwater balance. This restricted setting and range of δ¹³C values is more similar to Cenozoic platformal deposits (ca 12‰) than the muted (ca 3‰) global sea water variation recorded in pelagic sediments. The anomalous δ¹³C values in the Trezona Formation may instead provide constraints on the changing terrestrial biosphere directly preceding the evolution and rapid expansion of metazoon life.

KEYWORDS

carbon isotopes, chemostratigraphy, diagenesis, lacustrine carbonates, Neoproterozoic
INTRODUCTION

Stratigraphic patterns of $\delta^{13}C$ variation in Neoproterozoic carbonate successions are widely used as a record of global sea water change in dissolved inorganic carbon (DIC) that provides a recognizable signal able to be correlated between basins (Knoll, Hayes, Kaufman, Swett, & Lambert, 1986). Neoproterozoic sedimentary successions contain large magnitude $\delta^{13}C$ variations ($-12^{\circ}C$ to $+10^{\circ}C$) with values as depleted as $-9^{\circ}C$ extending over hundreds of metres of section (Halverson, Hoffman, Schrag, Maloof, & Rice, 2005). The recurrence of these anomalies in multiple basins and their association with glaciogenic sediments has been used to suggest that these excursions record perturbations in the global carbon cycle linked to the ice ages of the Cryogenian (Hoffman & Schrag, 2002) and potentially to the first appearance of animals in the fossil record (Maloof et al., 2010). The fact that variations of similar magnitude are not evident in the oceans after the Cambrian imply carbon cycling processes unique to this period of time (Bristow & Kennedy, 2008; Derry, 2010b; Melezhk, Fallick, & Pokrovsky, 2005; Rothman, Hayes, & Summons, 2003).

There is an ongoing debate as to the synchronity and the degree that post-depositional alteration played in these anomalous $\delta^{13}C$ values (Derry, 2010a; Grotzinger, Fike, & Fischer, 2011; Klaebe, Kennedy, Jarret, & Brocks, 2017; Klaebe, Smith, Fairchild, Fleming, & Kennedy, 2017; Knauth & Kennedy, 2009; Rose et al., 2012; Swanson-Hysell et al., 2010; Swart & Kennedy, 2012). Less has been said about how representative sampled material is of the open ocean $\delta^{13}C$ value versus how much it records local isotopic gradients and influences from processes that are not time related (Fanton & Holmden, 2007; Higgins et al., 2018; Holmden, Creaser, Muehlenbachs, Leslie, & Bergstrom, 1998; Husson, Higgins, Maloof, & Schoene, 2015; Klaebe, Smith, et al., 2017; Panchuk, Holmden, & Kump, 2005; Swart, 2008; Swart & Eberli, 2005; Swart & Kennedy, 2012). The assumption that particular samples record an open marine $\delta^{13}C$ value is fundamental to the use of these records as a constraint for the global carbon cycle and their utility as a correlation tool because it connects values to the isotope mass balance of the ocean atmosphere system. Independent of subsequent diagentic alteration, $\delta^{13}C$ values of carbonates do not always record a globally representative sea water value but can record local influences and vary spatially across carbonate depositional environments (Panchuk et al., 2005; Swart, 2008).

Identifying the open marine affinity of Precambrian $\delta^{13}C$ values is challenging compared to Cenozoic deep sea pelagic sediments (Higgins et al., 2018; Swart, 2008; Swart & Eberli, 2005; Swart & Oehlert, 2018). The Cenozoic record is compiled from pelagic carbonate shells that are ecologically constrained to well-mixed open marine waters that are isotopically homogenous (Zachos, Pagani, Sloan, Thomas, & Billups, 2001). These sediments accumulate as a relatively continuous succession on ocean crust at great water depths with little chance of exposure, erosion or alteration during sea-level fall (Berger & Vincent, 1986; Maslin & Swann, 2005; Ravizza & Zachos, 2003). Biostratigraphic dating allows $\delta^{13}C$ features to be compared between locations to determine if values from any given stratigraphic anomaly represent a synchronous event present in other basins or reflect local influences or diagentic alteration. In successions older than the Jurassic, deep sea records are lost through subduction. Sea water $\delta^{13}C$ values are thus compiled from less complete successions preserved on continental crust in intracratonic or marginal basins. Since these basins are comparatively shallow, the temporal continuity of carbonate records is interrupted by siliciclastic cycles, depositional hiatuses or erosion. Exposure to meteoric fluids associated with sea-level fall can lead to the addition of meteoric carbonate cements in interstitial porosity and recrystallization of carbonate minerals in fluids with different $\delta^{13}C$ and $\delta^{18}O$ values (Allan & Matthews, 1982; Swart & Eberli, 2005; Swart & Oehlert, 2018). Pore-fluid interactions during early marine diagenesis may result in stratigraphic $\delta^{13}C$ and $\delta^{18}O$ variation that is both systematic and unrelated to global DIC (Ahm, Bjerrum, Blättler, Swart, & Higgins, 2018; Higgins et al., 2018). Studies have also demonstrated laterally variable $\delta^{13}C$ values that in any given section may be distinct from global sea water (Holmden et al., 1998; Panchuk et al., 2005; Patterson & Walter, 1994).

Unlike the Palaeozoic, there are no lithologies in Precambrian sediments that are ecologically constrained to open marine conditions and can be targeted during sampling. Many carbonate analyses are conducted on fine-grained carbonates in the form of (dolo)micrite, or marl that lack direct evidence of environmental origin (Grotzinger & James, 2000) and often have a component of cement forming after deposition. Carbonate allochths like stromatolites and ooids are less ambiguous, forming equally in restricted, lacustrine or marine environments and Precambrian sediments lack a diagnostic biota to distinguish between these settings. The lack of preserved ocean crust means the vast majority of carbonates comprising the Precambrian $\delta^{13}C$ record come from recrystallized limestone and dolomite deposited in shallow, periodically exposed, carbonate ramps and platforms in intracratonic settings (Martin, 1995) that the lack high-resolution biostratigraphic information useful in determining the synchrony of isotopic features.

The broad stratigraphic reproducibility within and between basins of Neoproterozoic $\delta^{13}C$ features has provided confidence that they record a shared (marine) origin and are thus time significant features. Cenozoic shallow water successions, however, also show reproducible $\delta^{13}C$ excursions comparable to those in the Neoproterozoic in
magnitude (>10%) stratigraphic thickness, continuity and global persistence (Swart, 2008; Swart & Eberli, 2005; Swart & Kennedy, 2012). Biostratigraphic information indicates that these features are not coincident and do not agree with the widely accepted deep sea pelagic record of δ¹³C but rather record a combination of local environmental, mineralogical and diagenetic influences (Swart, 2008). This contrast between shallow and deep marine δ¹³C records emphasizes the importance of determining a palaeoenvironmental setting consistent with the inferred origin of δ¹³C.

In order to better understand the palaeoenvironmental influence on a prominent Neoproterozoic δ¹³C excursion, we conducted a sedimentological study on the Trezona Formation. The Trezona Formation houses an increase in δ¹³C values up-section from −9‰ to −1‰ termed the Trezona anomaly that lies stratigraphically below Marinoan-aged (ca 635 Ma) glaciogenic deposits in the section containing the Global Boundary Stratotype Section and Point (GSSP) for the Ediacaran Period in South Australia (Knoll, Walter, Narbonne, & Christie-Blick, 2006). The Trezona anomaly is reproducible across the central Flinders Ranges and serves as a standard stratigraphic feature used to correlate Neoproterozoic successions in Namibia, NW Canada and the north Atlantic region (Halverson et al., 2005; McKirdy et al., 2001). The goal of this work was to understand the δ¹³C values in the context of the depositional setting with an emphasis on recognizing exposure surfaces and establishing water depth to identify periods of restriction or isolation from the open ocean. The intent of the study was to determine if the depositional constraints allowed a sea water interpretation independent of any question about diagenetic influence on δ¹³C values. These results show deposition occurred on mudflats and within intermittently connected shallow ponds and lagoons responding to local (salt withdrawal influenced) subsidence on a regionally exposed shelf. Connection to the ocean was probably intermittent allowing δ¹³C values to be modified by runoff and evaporation.

2 | GEOLOGICAL SETTING

The Trezona Formation is preserved in the Flinders Ranges of South Australia (Figure 1) as a mixed siliciclastic and carbonate deposit. While there are no direct radiometric age constraints from the Trezona Formation, it underlies the Marinoan-aged glacial unit and the GSSP for the Ediacaran Period providing a minimum age of ca 635 Ma (Knoll et al., 2006). It occurs stratigraphically above a thick succession of carbonate, sandstone and shale overlying glaciogenic sediments of the Sturtian ice age (Wilyerpa Formation) with a post-glacial Re-Os date of 643 ± 2 Ma (Kendall, Creaser, & Selby, 2006). The Trezona Formation typically comprises a lower marl and carbonate-cemented mudstone interval with limestone mudclast and algal flake storm beds and intraclastic deposits that pass upwards into oolite shoals and microbial bioherms. The formation has a bulls-eye isopach thickness pattern with a maximum thickness of ca 450 m focused on the central Flinders Ranges (Figure 1; Preiss, 1987). Successive stratigraphic units thin and wedge out laterally beneath overlying units resulting from syn-depositional salt withdrawal during the deposition of Trezona Formation sediments (Lemon, 1988). These once salt cored diapiric structures are exposed in cross-section by subsequent folding and exhumation during the Delamerian Orogeny (ca 514–500 Ma, Foden, Elburg, Dougherty-Page, & Burtt 2006). Periods of active salt movement are evident during deposition of the Trezona Formation and underlying Etina Formation, and are identified by erosional surfaces over the diapiric high, topographically influenced facies changes adjacent to the diapir (Figure 1c), extruded diapiric breccias, mass flows and thickening of sediment layers in the adjacent salt withdrawal mini-basins (Dalgaro & Johnson, 1968; Lemon, 1988; McKirdy et al., 2001). The Trezona Formation is now limited to the region of salt withdrawal that occurred in the Neoproterozoic in the central Flinders Ranges and is not present elsewhere in the Adelaide Fold Belt (Preiss, 1987).

The depositional environment for the Trezona Formation has been interpreted as shallow platformal, lagoonal, tidal, restricted marine or lacustrine. Preiss (1987) interpreted a lagoonal to lacustrine setting based on its limited distribution, evidence of shallow water depths and local exposure. Lemon (1988) interpreted deposition in the lower portion in a very shallow periodically exposed lagoonal to tidal environment that deepened slightly up-section forming a shallow, often restricted and exposed, platform. He noted the topographic effects of diapirs that controlled current directions, barrier bar position, sediment composition and the distribution of lagoons. McKirdy et al. (2001) studied the geochemical variation of palaeokarst horizons arguing for the retention of primary δ¹³C values based on the limited difference between δ¹³C in karst and background carbonates. Singh (1986, 1987) studied the diagenetic history of the Trezona Formation at the micron scale, identifying high Sr concentration in portions of the upper carbonate interval indicative of initial aragonite precipitation in oolites. Singh (1986) also demonstrated extensive meteoric phreatic and burial cements influencing stable isotope values. Rose et al. (2012) argued that periods of exposure and porosity within the Trezona Formation were insufficient for meteoric waters to reset δ¹³C values and interpreted an open marine origin for δ¹³C values. All studies have recognized an unconformity at the base of the Marinoan-aged glacial deposits of the Elatina Formation (Figure 2), with a second unconformity beneath the red-bed arkosic silt and sandstone of the Yaltipena Formation in the central Flinders Ranges (Lemon & Reid, 1998).
Rose et al. (2012) proposed the offshore deposits of the Amberooana Siltstone in the northern Flinders Ranges to be possible lateral equivalents of the Trezona Formation and suggested these formed a conformable transition to glacial sediments of the Elatina Formation. The unconformities separating the Trezona Formation beneath the Yaltipena and Elatina formations in addition to a basal Trezona unconformity and exposure surfaces throughout the formation described here, suggest that deposition of the Trezona Formation may have been more closely related to episodic localized salt tectonics in the central Flinders Ranges (Lemon, 1988) than a single glacio-eustatic shallowing cycle beginning with the underlying Enorama Shale as proposed by McKirdy et al. (2001).

3 | METHODS

All samples analysed in this study were collected during logging of nine stratigraphic sections of the Trezona Formation in the Flinders Ranges in South Australia. Limestones and carbonate-cemented siltstone samples were collected, with limestones >95% calcite in composition used to construct $\delta^{13}C$ profiles (Figure 2). Samples were slabbcd and ca 15 mg subsamples were collected from individual textures and laminations using a dentist drill. The petrography of the samples was studied in 50 thin sections to determine depositional and diagenetic components. Stable isotope ($\delta^{13}C$ and $\delta^{18}O$) measurements were performed on ca 0.8 mg powders using continuous-flow isotope ratio mass spectrometry. Measurements were made on an Analytical Precision AP2003 at the University of Melbourne (mean analytical precision for $\delta^{13}C$ and $\delta^{18}O$ is $\pm 0.03\%e$ and $\pm 0.07\%e$, respectively) and on a Nu Horizon CF-IRMS at the University of Adelaide (mean analytical precision for $\delta^{13}C$ and $\delta^{18}O$ is $\pm 0.1\%e$). Samples were digested in 105% phosphoric acid at 70°C and mass spectrometric measurements were made on evolved CO$_2$ gas following the method of Spötl and Vennemann (2003). Results were normalized to the Vienna Pee Dee Belemnite scale using internal working standards.

4 | SEDIMENTOLOGY OF THE TREZONA FORMATION

4.1 | Base contact

New field observations identify a regionally unconformable contact separating the deeper water (non-calcareous)
siltstone and fine sandstone of the Enorama Shale from the predominantly calcareous mudstone deposited in shallow water and mudflats at the base of the Trezona Formation. At Angorichina Station, the siltstone of the Enorama Shale is sharply overlain by a 10 m thick interval of laminated to cross-stratified micaceous and feldspathic sandstone that is in turn overlain by the typical calcareous mudstone comprising the lower Trezona Formation (Figures 3 and 4a,b). Similarly, at Enorama Creek, stromatolitic carbonate and interbedded calcareous mudstone sharply overlies the (non-calcereous) siltstone of the Enorama shale (Figure 4d). A third locality at Bulls Gap shows a distinctive 30 cm thick interval of massive, poorly structured feldspathic and quartz coarse sandstone (Figure 4d) exposed for ca 50 m laterally. Fragments of shale from the underlying unit are incorporated into the base of the unit as tabular to elongate clasts up to 6 cm, and are aligned parallel to the original bedding plane showing no evidence of channelization or clast reworking as is typical of intraclastic facies in the Trezona Formation (Figure 4e). In some examples, tabular fragments pass laterally into preserved lamination, indicating that fragmentation took place in situ, consistent with the development of a soil horizon or regolith. These observations suggest that the basal Trezona Formation in the Flinders Ranges overlies a sequence boundary, representing a depositional cycle following exposure and erosion at the top of the Enorama Shale.

4.2 | Lower mudstone unit of the Trezona formation

The Trezona Formation can be subdivided into two distinctive stratigraphic intervals that vary in relative thickness away from the central zone of salt withdrawal (Figures 1 and 2) and record conditions of shallow water, exposure and local erosion. These are a lower unit comprising interbedded siliciclastic and carbonate facies, and an upper unit that is almost exclusively carbonate. The lower Trezona Formation comprises 150–200 m of laminated fissile calcite-cemented mudstone with ca 5–15 cm bedding-parallel sparry-calcite concretions and discrete resistant beds of dolomite-cemented siltstone often preserving 1–2 cm thick ripple cross-beds (Figure 5a). Figure 5b shows the 5–15 cm thick beds of intraformational mud and algal flake breccias, microbial mats, red arkosic silt and sandstone beds, and rare oolitic packestones that are interbedded at 1–5 m intervals within laminated calcareous mudstone (Figure 5b). Mudflake breccia is often confined to sharp-based lensoidal beds that thin laterally over tens of metres, preserve clast-rosettes, and are capped by 0.5–2 cm thick (dolo)micritic drapes. These features are consistent with erosion of microbial mounds and mud beds as mud chips and algal flake breccias during storms with deposition in channels (Figure 5b). The micritic drapes themselves preserve mud cracks (Figure 5c,d) that penetrate downward into mudclast conglomerates, indicating that the mudstone
was deposited in a mudflat or as overbank deposits that were periodically subaerially exposed and desiccated. These same beds correspond to the hieroglyphic limestone of Mawson (1938) and were reinterpreted in some places by Maloof et al. (2010) as early sponge fossils. Discontinuous, low-relief (<30 cm) stromatolite mounds (Figure 5e,f) overlie intraclastic and siliciclastic substrates or thin (ca 15 cm) laminites. Desiccation of this material probably provided conspicuous algal flakes that were reworked locally into mudflake breccia, and occasionally fill the space between discrete domes. Red-coloured, poorly sorted, angular, micaceous and feldspathic silt to fine sandstone is commonly trough cross-laminated and occurs within sharp-based lenses up to 45 cm thick with local evidence of synsedimentary slumping (Figure 5g,h). These sandstone beds occur intermittently within the calcareous mudstone-dominated lower Trezona Formation (Figure 2), and are the coarsest grained siliciclastic component present in the Trezona Formation until the base of the overlying Yaltipena Formation. Resistant carbonate units form prominent outcropping beds within recessive mudstone, and typically comprise stacks of polymict intraformational conglomerate beds with decimetre-scale bedforms that are often draped by calcareous mudstone along depositional reactivation surfaces. Clasts comprise bladed mud flakes, subangular to subrounded mud fragments, and ooids, that are mineralogically and texturally similar to local bedded units. Individual beds thin laterally over hundreds of metres but are not apparently confined to channels and occasionally act as a substrate for stromatolite domes.

The sediments within the lower Trezona Formation indicate deposition in shallow water conditions and mudflats with intermittent exposure and disturbance by storms or currents. Channels filled by feldspathic sand suggest a direct or nearby fluvial supply of siliciclastic sediment. These features are not evident in the underlying Enorama Shale, which is characterized by persistent finely laminated non-calcareous siltstone and occasional centimetre-scale fine sandstone beds with local evidence for hummocky cross-stratification interpreted by McKirdy et al. (2001) to record storm-related deposition on a shelf.

4.3 | Upper carbonate unit of the Trezona Formation

The upper carbonate unit overlies the lower mudstone unit in all sections. The base is transitional and defined by an abrupt increase in the bed thickness and relative percentage of microbial and grainstone carbonate (Figure 2). Microbial limestones occur as laminated mats accumulating in <15 m thick stacks, with circular domes up to 1 m wide and ca 50 cm of synoptic relief (Figure 6a). Stromatolites also occur as ca 3–5 cm wide columnar forms (Figure 6b). Oolitic (locally pisolithic) and intraclastic shoals form 1–12 m thick beds that sharply overlie microbial carbonates (Figure 6c). These resistant beds form laterally continuous strike ridges and cap the top of mudstone and stromatolite cycles laterally traceable over several kilometres. The upper carbonate unit varies in stratigraphic thickness from 150 to 200 m where subsidence was influenced by salt withdrawal.
in the Trezona, Bunkers Range and Angorichina Station while in sections to the north at Warraweena and Glass Gorge, respectively, and lacks grainstone shoal deposits (Figure 2). These sections do not show the cycles of calcareous mudstone to stromatolitic bioherms evident in the southern sections.

### 4.4 Upper contact

The contact between the Trezona Formation and overlying glaciogenic sediments of the Elatina Formation is variable across the Flinders Ranges. At Warraweena, microbial carbonates are capped by heavily dolomitized stromatolitic carbonate showing karst features such as collapse-fill breccias (Figure 6d). Karst features are also reported at multiple levels at Bulls Gap (Lemon, 1988; McKirdy et al., 2001). Karst is sharply overlain by massive feldspathic sandstone beds with gritty-quartz lenses and pebble-clasts comprising the basal Elatina Formation (Figure 6e). Similarly, a sharp contact between carbonate and similar massive, feldspathic, pebble-bearing sandstone occurs at Glass Gorge and Angorichina Station. In Glass Gorge, this unit contains lon-estones of probable glacial origin and underlies the Nuc-caleena Formation cap-carbonate. In the thickest sections of the Trezona Formation adjacent to the Oraparinna and Eno-rama diapirs, a sequence of red-bed siltstones and sandstones comprising the Yaltipena Formation abruptly overlies the carbonate beds of the upper Trezona Formation (Lemon & Reid, 1998). The lower contact of the Yaltipena Formation is marked by a karst collapse breccia exposed in the Trezona Range identifying a sequence boundary at the

![Figure 4](image_url)

**Figure 4** (a and b) Outcrop of basal Trezona Formation unconformity at Angorichina Station. Arkosic trough cross-bedded sandstone lies in sharp contact (dashed line) with continuous non-calcareous shales of the Enorama Formation. The first Trezona Formation carbonates occur within 10 m of this boundary. (c) Outcrop of basal unconformity at Enorama Creek preserved as an abrupt step from continuous shales to stromatolitic carbonates. (d and e) Putative palaeo-soil horizon defining the base of the Trezona Formation at Bulls Gap. Following >75 m of continuous non-calcareous shale deposition, the basal Trezona Formation unconformity here is characterized by bedding-parallel fragments of shale in an arkosic matrix, consistent with in situ weathering of the Enorama Shale rather than sedimentary brecciation and transport. Immediately above this horizon is a typical lower Trezona Formation limestone mudclast conglomerate (e)
top of the Trezona Formation (Figure 6d). To the North, this sequence boundary merges with the erosion surface beneath the Elatina Formation where the Yaltipena Formation is not present. The lower interval of the Yaltipena Formation is comprised of laminated mudstone and angular feldspathic fine-grained sandstone that coarsens upwards into medium-grained, red-coloured, cross-laminated sandstone. Casts of rain drop impressions (Figure 6f), pseudomorphs after halite and mudcracks (Figure 6g) indicate subaerial exposure. Coarse-grained and gritty sandstone occurs within channel-shaped beds that often preserve basal mudclast conglomerates and trough crossbedding indicating a fluvial origin (Lemon & Reid, 1998).

4.5 | Palaeoenvironmental synthesis

Following a fall in sea-level that exposed the offshore shelf deposits of the Enorama Shale, calcareous muds accumulated in shallow depressions surrounding the Oraparinna and Enorama diapirs as mudflats, lagoonal and/or lacustrine environments depending on access to channels opening to the sea. Microbial carbonates formed as thin mats on the fringes of ponded areas where intermittent emergence resulted in desiccation and formation of mudflake conglomerate deposited in shallow channels and between stromatolite mounds during storms. Micritic grains precipitated in carbonate supersaturated conditions in the water column.
and were deposited as draping muds from suspension following storm events. Intraclastic and oolitic shoals formed within areas of slightly deeper water such as in ponds, channels and between microbial mounds. Red-bed arkosic sands introduced by fringing fluvial systems accumulated in channels that cut through mudflats. While these channels might have been influenced by tidal reworking if connected to the sea, no direct tidal evidence was identified in this study. Localized deepening within lagoons or reduced mud supply resulting from a changing shoreline position or redirection of siliciclastic feeder systems allowed microbial communities to form interconnected mounds with greater synoptic relief in the upper carbonate unit, while oolitic shoals accumulated in channels and acted as a substrate for new domes. Isolation from sea water or freshwater sources, or drying through greater rates of evaporation, led to dissolution and karst collapse at the top of the Trezona Formation. Further changes in fluvial channels, or drying of the region, resulted in the remaining accommodation space being filled by fluvial and deltaic sediments of the Yaltipena Formation.

4.6 Controls on spatial distribution

The Trezona Formation was deposited over a spatially limited region in a bulls-eye isopach thickness pattern (Figure 1) centred around the areas of maximum salt withdrawal adjacent to the Oraparina and Enorama diapirs (Preiss, 1987). Facies variations suggest local topographic highs and subsidence during deposition of the Trezona Formation.

FIGURE 6 Facies of the Upper Trezona Formation: (a) Micrite and laminated microbial mats in the upper Trezona Formation, Angorichina Station. (b) Stromatolitic bioherms in plan-view from the upper Trezona Formation, Bulls Gap. (c) Pisolitic limestone from the upper Trezona Formation, Angorichina Station. (d) Uppermost karst directly below the Yaltipena Formation, Trezona range with sand infilling downward from overlying Yaltipena Formation. (e) Massive feldspathic sands at the base of the Elatina Formation, Glass Gorge. (f) Rain drop impression casts in non-calcareous mudstones of the Yaltipena Formation, Bulls Gap and (g) Mudcracks in the Yaltipena Formation, Bunkers Range. Lens cap is 37 mm in diameter.
Formation (Lemon, 1988) with erosion associated with the unconformity beneath the Yaltipena Formation (Lemon & Reid, 1998). Subsequent subglacial erosion beneath the sub-Elatina Formation unconformity (McKirdy et al., 2001; Rose et al., 2013), also probably reduced the lateral extent of the Trezona Formation by removing some parts of the upper carbonate facies as well as the Yaltipena Formation in the northern sections on the edge of the sub-basin. Sohl, Christie-Blick, and Kent (1999) reported evidence for plastic deformation in the upper Yaltipena Formation interpreted to result from subglacial ice dragging (north of Trezona Bore). This evidence temporally links deposits of the Yaltipena Formation with glacial deposits of the Elatina Formation (Rose et al., 2012). The regional extent of the sub-Yaltipena and sub-Elatina erosion is unclear. The Trezona Formation is thinner in the northern sections, and shows an abbreviated upper carbonate facies lacking the mudstone to stromatolitic bioherm cycles evident in the southern sections. This variation in thickness, however, may be due to syn-sedimentary thickening in space created by salt withdrawal adjacent to the diapirs rather than erosional truncation beneath the Yaltipena and Elatina formations. In support of this is a similar distribution and thinning to the north in the underlying Eina Formation that does not have an erosional surface at its top and is also spatially limited by diapir-related subsidence (Figure 1; Lemon, 1988; Preiss, 1987). Secondly, the complete $\delta^{13}C$ profile from $-9%e$ to $-2%e$ in the southern sections is also present in the thinner northern sections suggesting limited truncation, assuming the stratigraphic pattern in $\delta^{13}C$ values predates erosion.

### 4.7 | Geochemical variation in the Trezona formation

The lower mudstone unit of the Trezona Formation shows a consistent $\delta^{13}C$ value of ca $-8%e$ within carbonate grains (mud flake breccia, microbial laminites and micrite) through $>150$ m in the five sections analysed. Co-occurring siltstone with interstitial carbonate cements show $\delta^{13}C$ and $\delta^{18}O$ values that are ca $4%e$ heavier than adjacent allochems and are similar to the range of values in the upper carbonate unit. Carbonate siltstone values show a positive relationship between $\delta^{13}C$ and $\delta^{18}O$ in all sections with up to $R = 0.9$ (Figure 7).

The boundary with the upper carbonate-rich lithofacies defines an inflection point in $\delta^{13}C$ values in all sections, with values becoming progressively heavier to ca $-1%e$ at the top of the section. The shift in $\delta^{13}C$ values coincides with the boundary between the lower mudstone and upper carbonate-rich lithofacies even where the upper lithofacies is thin and represents only a small proportion of the total thickness. While the Glass Gorge and Warraweena sections show a much thinner upper carbonate unit, they still show the full range of the stratigraphic shift in $\delta^{13}C$ values apparent in locations to the south and record the highest $\delta^{13}C$ values measured in this study (Figure 2).

The $\delta^{18}O$ values show systematic variation of $>3%e$ in the Trezona, Bunkers and Angorichina sections, with heavier values within the upper carbonate unit, that ultimately decline towards the top of the formation (Figure 8). Inflection points in $\delta^{18}O$ values occur at the base of the lithological transition from mudstone to stromatolite bioherms and coincide with changes in the relationship between $\delta^{18}O$ and $\delta^{13}C$ values. Three different trends between $\delta^{13}C$ and $\delta^{18}O$ values of carbonate grains (as opposed to diagenetic textures) coincide with different stratigraphic intervals (Figure 8). The lower mudstone unit shows a positive relationship ($R = 0.82$). The first prominent (thick) carbonate band shows no relationship followed by a positive relationship in the second interval ($R = 0.71$) with reversal to a negative relationship in the last interval ($R = 0.74$; Figure 8). This pattern is evident in the Angorichina Station, Bunkers Range and Trezona Range sections. No relationship is evident in the Glass Gorge and Warraweena sections where only a single carbonate cycle at the top of the formation is present. In these sections, $\delta^{18}O$ is largely invariant.

### 4.8 | Environmental and stratigraphic context of $\delta^{13}C$ values

Past studies have considered $\delta^{13}C$ values in the Trezona Formation as either a record of secular sea water variation (open marine) or the result of diagenetic alteration (McKirdy et al., 2001; Rose et al., 2012; Singh, 1986). Here the possibility is considered that $\delta^{13}C$ values in carbonate allochems retain a primary origin but record the effects of restriction and/or modification by local processes such as evaporation or dilution by freshwater.

The deposition of the Trezona Formation and its $\delta^{13}C$ record have been generalized as the upper interval of a shallowing-upward cycle starting at the base of the Enorama Shale (McKirdy et al., 2001; Rose et al., 2012) and ending with erosion at the base of the glaciogenic deposits of the Elatina Formation. In detail, the Trezona Formation represents its own sea-level cycle beginning with an exposed shelf at the top of the Enorama Shale and ending with erosion beneath the Yaltipena Formation. When compared to the shelf-wide and blanket-like deposits of the Enorama Shale, the Trezona Formation was spatially variable and regionally restricted to the sub-basin surrounding the Oraparina and Enorama diapirs. The inability to trace cycles and facies laterally more than several kilometres, evidence for periodic exposure, and the limited spatial extent of the Trezona Formation in general indicates deposition at or near base level and localized subsidence and
sediment supply. Deposition thus likely occurred in a mosaic of poorly connected lagoons, isolated ephemeral (alkaline) lakes and sediment starved regions behind barrier bars. The increase in microbial bioherm size and continuity in the upper Trezona Formation records a reduction in silt and mud delivery allowing prolonged formation of carbonate environments and less disturbance of biohermal microbial communities. Variations in input/output flow, sills and banks influencing connectivity to sea water likely lead to the interruption of marine connections, changing the sea water to freshwater balance, affecting rates of evaporation and consequently influencing $\delta^{13}C$ and $\delta^{18}O$ values in restricted water bodies include carbonate saturation, rates of evaporation and organic matter degradation, the composition of input waters as riverine and groundwater discharge, and the fractionating effects of locally prolific phototrophic communities (Hinga, Arthur, Pilson, & Whitaker, 1994; Horton, Defliese, Tripati, & Oze, 2015; Talbot, 1990). These effects manifest themselves when sea-level falls and marginal basins become shallower and more restricted, with connections to the sea becoming more toruous resulting in an increasing influence of meteoric water. The covariation of $\delta^{13}C$ and $\delta^{18}O$ values is commonly used to identify the effects of evaporation and mixing in these types of lacustrine or restricted environments (Talbot, 1990). The covariation between $\delta^{13}C$ and $\delta^{18}O$ values poses a dilemma. Either values record a strong meteoric influence on both isotope systems and the carbon values are unreliable as indicators of initial DIC in the overlying water column, or they retain a primary DIC value in which the two isotope systems shift together. This latter possibility is incompatible with preservation of sea water values because C and O have a different residence time in the ocean and thus $\delta^{13}C$ and $\delta^{18}O$ values do not covary, whereas covariation is common in restricted or lacustrine water (Horton et al., 2015; Talbot, 1990).

Changes in water composition through time may account for the changes in slope between $\delta^{13}C$ and $\delta^{18}O$ that are linked to the stratigraphic variation in the Trezona Formation (Figure 8). Sediment composition, shifts from calcite to aragonite, diagenetic textures, and evidence of shallowing and exposure can also be linked to changes in sea-level across platforms and ramps that become restricted and develop isotopic gradients (Gischler & Lomando, 2005; Swart & Eberli, 2005). Sea-level fall changes base level and redirects fluvial feeder systems basinward resulting in bypass of marginal basins trapped on the former shelf. The reduction in mud, silt and sand favours chemical and biological sedimentation in marginal basins and Oehlert, 2018). These Cenozoic values are not considered to record the DIC content of sea water because these isotopic features are shown to be asynchronous within a given basin and in conflict with coeval and demonstrably open marine $\delta^{13}C$ values (Swart & Eberli, 2005). Large magnitude variability in Phanerozoic carbonate $\delta^{13}C$ records occur in shallow marginal (Gischler & Lomando, 2005; Gischler, Swart, & Lomando, 2007; Swart & Eberli, 2005), intracratonic (Ludvigson et al., 2004; Panchuk et al., 2005; Saltzman, 2002), and non-marine (Bade, Carpenter, Cole, Hanson, & Hesslein, 2004; Klaebe, Kennedy, et al., 2017; Talbot, 1990) environments where carbon isotope gradients exist both laterally across basins and vertically as ambient water chemistry shifts systematically in response to changing local hydrological and environmental conditions through time. Controls on water column $\delta^{13}C$ and $\delta^{18}O$ values in restricted water bodies include carbonate saturation, rates of evaporation and organic matter degradation, the composition of input waters as riverine and groundwater discharge, and the fractionating effects of locally prolific phototrophic communities (Hinga, Arthur, Pilson, & Whitaker, 1994; Horton, Defliese, Tripati, & Oze, 2015; Talbot, 1990). These effects manifest themselves when sea-level falls and marginal basins become shallower and more restricted, with connections to the sea becoming more toruous resulting in an increasing influence of meteoric water. The covariation of $\delta^{13}C$ and $\delta^{18}O$ values is commonly used to identify the effects of evaporation and mixing in these types of lacustrine or restricted environments (Talbot, 1990). The covariation between $\delta^{13}C$ and $\delta^{18}O$ values poses a dilemma. Either values record a strong meteoric influence on both isotope systems and the carbon values are unreliable as indicators of initial DIC in the overlying water column, or they retain a primary DIC value in which the two isotope systems shift together. This latter possibility is incompatible with preservation of sea water values because C and O have a different residence time in the ocean and thus $\delta^{13}C$ and $\delta^{18}O$ values do not covary, whereas covariation is common in restricted or lacustrine water (Horton et al., 2015; Talbot, 1990).

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FIGURE 7 Scatterplot of $\delta^{13}C$ versus $\delta^{18}O$ values measured in calcareous mudstones from the lower Trezona Formation at Glass Gorge, Angorichina Station and the Bunkers Range

5 | DISCUSSION

The magnitude and relationship between $\delta^{13}C$ and $\delta^{18}O$ values within the Trezona Formation are unlike any Phanerozoic carbonates deposited in open marine settings. The $\delta^{13}C$ variability in the Cenozoic pelagic record, for example fluctuates by less than 3‰ (Shackleton, 1987; Zachos et al., 2001). The Trezona anomaly is, however, comparable with the range and stratigraphic pattern of $\delta^{13}C$ values in Cenozoic settings with similar lithologies (Higgins et al., 2018; Swart & Kennedy, 2012; Swart & Oehlert, 2018). These Cenozoic values are not considered to record the DIC content of sea water because these isotopic features are shown to be asynchronous within a given basin and in conflict with coeval and demonstrably open marine $\delta^{13}C$ values (Swart & Eberli, 2005). Large magnitude variability in Phanerozoic carbonate $\delta^{13}C$ records occur in shallow marginal (Gischler & Lomando, 2005; Gischler, Swart, & Lomando, 2007; Swart & Eberli, 2005), intracratonic (Ludvigson et al., 2004; Panchuk et al., 2005; Saltzman, 2002), and non-marine (Bade, Carpenter, Cole, Hanson, & Hesslein, 2004; Klaebe, Kennedy, et al., 2017; Talbot, 1990) environments where carbon isotope gradients exist both laterally across basins and vertically as ambient water chemistry shifts systematically in response to changing local hydrological and environmental conditions through time. Controls on water column $\delta^{13}C$ and $\delta^{18}O$ values in restricted water bodies include carbonate saturation, rates of evaporation and organic matter degradation, the composition of input waters as riverine and groundwater discharge, and the fractionating effects of locally prolific phototrophic communities (Hinga, Arthur, Pilson, & Whitaker, 1994; Horton, Defliese, Tripati, & Oze, 2015; Talbot, 1990). These effects manifest themselves when sea-level falls and marginal basins become shallower and more restricted, with connections to the sea becoming more toruous resulting in an increasing influence of meteoric water. The covariation of $\delta^{13}C$ and $\delta^{18}O$ values is commonly used to identify the effects of evaporation and mixing in these types of lacustrine or restricted environments (Talbot, 1990). The covariation between $\delta^{13}C$ and $\delta^{18}O$ values poses a dilemma. Either values record a strong meteoric influence on both isotope systems and the carbon values are unreliable as indicators of initial DIC in the overlying water column, or they retain a primary DIC value in which the two isotope systems shift together. This latter possibility is incompatible with preservation of sea water values because C and O have a different residence time in the ocean and thus $\delta^{13}C$ and $\delta^{18}O$ values do not covary, whereas covariation is common in restricted or lacustrine water (Horton et al., 2015; Talbot, 1990).
restricted lagoons increasing carbonate deposition, similar to the transition in to the upper unit of the Trezona Formation.

Most carbon isotope studies of Precambrian successions focus on an a) open marine or b) diagenetic origin for $\delta^{13}C$ values, with few explicitly considering the effects of restriction or local depositional influences on $\delta^{13}C$ values. In more recent settings that show similar depositional conditions to the Trezona Formation, $\delta^{13}C$ values diverge from open marine values in sabkha environments on the Persian Gulf that flood during sea-level highstand (Evans, Schmidt, Bush, & Nelson, 1969), the Great Bahamas Bank that records excursions varying between $-10\%e$ and strongly positive values of $>+5\%e$ (Melim, Swart, & Maliva, 2001; Melim, Westphal, Swart, Eberli, & Munnecke, 2002; Swart & Eberli, 2005), the modern South Australian coast line with Coorong lakes (Von der Borch, Lock, & Schwebel, 1975) and the range of lacustrine carbonate environments that rely on freshwater inputs over sea water and record systematically evolving $\delta^{13}C$ profiles (Bade et al., 2004; Talbot, 1990). In the absence of diagnostic fossil evidence for restricted/non-marine conditions in Precambrian sediments, sedimentary evidence and the stratigraphic context of individual sections can be used to determine the depositional setting. Features that indicate periods of restriction, evaporation and subaerial exposure such as salt deposits,
desiccation and palaeokarst are, not surprisingly, also a feature of Precambrian carbonate-bearing successions (Calver, 2000; Day, James, Narbonne, & Dalrymple, 2004; Halver-son, Hoffmann, Schrag, & Kaufman, 2002; Halverson, Maloof, & Hoffman, 2004; Hill, Aroui, Gorjan, & Walter, 2000; Kenny & Knauth, 2001). Compiled curves of sea water δ13C values likely include some of these intervals which could account for anomalies from sea water.

Stable isotopic values also suggest systematic differences between the major facies shifts observed in the Trezona Formation that reflect locally changing depositional environments. Highly depleted and covariant δ13C and δ18O values may reflect variable degrees of post-depositional alteration (Ahm et al., 2018; Dyer, Maloof, & Higgins, 2015; Higgins et al., 2018; Quinn, 1991; Swart & Eberli, 2005) but they are characteristic features of lakes with negative water balances (Talbot, 1990). In the context of the lower Trezona Formation where δ13C values are consistently −8‰ to −9‰, either of these interpretations can be applied to a non-marine basin fed dominantly by terrestrial groundwater systems as would be predicted by a model where marine connections are severed. Persistent brackish conditions with a significant freshwater content are consistent with depleted δ13C and δ18O values as meteoric fluids charged with terrestrially sourced organic acids carried the bulk of the dissolved carbon into the basin that subsequently precipitated as cements in mudstones and fluvial sands, and as primary limestones. The relationship between δ13C and δ18O values with different slopes between successive cycles could identify diagenetic alteration from different fluids but could also record different degrees of restriction influencing water chemistry in a series of restricted or isolated water bodies with the greatest meteoric input at the base and the greatest marine influence at the top (Figure 8).

The Trezona Formation, while ambiguous as a tracer for global-scale perturbations to the Earth’s carbon cycle, may demonstrate that an extensive photosynthetic terrestrial biomass existed coeval with its deposition. If δ13C values have not been substantially altered by diagenesis and these deposits record DIC from a meteoric source to carbonate precipitated in isolated, restricted or lacustrine ponds as results suggest here, values as depleted as −9‰ imply a terrestrial source of organic acids. A Neoproterozoic expansion of terrestrial photosynthesizing communities has been considered based on molecular (Heckman et al., 2001), palaeontological (Kennedy & Droser, 2011), mineralogical (Kennedy, Droser, Mayer, Pevear, & Mrofka, 2006) and isotopic (Knauth & Kennedy, 2009) lines of evidence, but may in the case of the Trezona Formation be expanded to an association of more complex metazoans and non-marine environments (Maloof et al., 2010). Understanding the nature of δ13C variations in restricted basins like the Trezona Formation may thus contribute significantly to answering the question of the conditions necessary for the profound evolutionary steps that characterize the Neoproterozoic record.

6 CONCLUSIONS

The pre-Marinoan (ca 635 Ma) Trezona Formation records δ13C values on the order of −9‰ interpreted to record a global change in carbon cycling. A basal sequence boundary indicated by palaeosol/regolith and fluvial deposits separates the Trezona Formation from underlying deep-water shelf siliciclastics. Fluvial sediments and mudcracks in carbonate-cemented mudstones identify deposition in a shallow to mudflat depositional environment through the lower Trezona Formation which records sustained δ13C values of −9‰. A gradual vertical increase in δ13C values from −9‰ to −2‰ occurs synchronously with an abrupt change in lithofacies from interbedded mudstones and limestones to stacked microbial and grainstone carbonates in the upper interval of the formation. A positive linear covariation of δ13C and δ18O values in lower the Trezona Formation shows varying slopes with successive cycles indicating co-evolution of the isotopic composition of a series of restricted water masses. The recorded vertical trend in δ13C values is similar in shape and magnitude to Pliocene-aged carbonate platform sediments altered by meteoric fluids during diagenesis, and with modern alkaline lakes, but is difficult to explain as a primary oceanographic signal. The systematic variation of isotopic data, indicators of shallow water to subaerial exposure, and the limited spatial distribution of the Trezona Formation (<200 km²) describes a restricted marine to non-marine depositional environment. The δ13C variation recorded in the Trezona Formation is thus more consistent with δ13C patterns of alteration common to coastal or lacustrine carbonates responding to exposure and sea-level variation rather than a shift in global biogeochemical dynamics.

ACKNOWLEDGEMENTS

A. Corrick, M. Rollog and R. Drysdale are thanked for fieldwork and analytical contributions. Linda Kah and a second anonymous reviewer are thanked for their helpful comments. This work was supported by Australian Research Council grants DP120100104 and LP120200086 awarded to Kennedy.

CONFLICT OF INTEREST

The authors have no conflict of interest to declare.
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**How to cite this article:** Klaebe R, Kennedy M. The palaeoenvironmental context of the Trezona anomaly in South Australia: Do carbon isotope values record a global or regional signal? *Depositional Rec.* 2019;5:131–146. https://doi.org/10.1002/dep2.60