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Constraints on the origin and relative timing of the Trezona $\delta^{13}C$ anomaly below the end-Cryogenian glaciation

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ABSTRACT

The Neoproterozoic Era was punctuated by the 'Sturtian' (~710 million years ago) and 'Marinoan' (~635 million years ago) low-latitude glaciations. Carbonates preceding the younger Marinoan glacial succession record an ~18‰ negative shift in the $\delta^{13}C$ of carbonate around the world. This 'Trezona' isotopic anomaly is the largest $\delta^{13}C$ shift in Earth history and its origin and timing remain controversial. The $\delta^{13}C$ anomaly could record a dramatic reorganization of Earth's carbon cycle and be linked causally to the initiation of Marinoan ice-house conditions. Alternatively, the $\delta^{13}C$ anomaly might record secondary fluid alteration following carbonate deposition. Here we document dropstones within the carbonate sediments immediately below the Marinoan glacial diamictite in South Australia. Advancing ice sheets caused soft-sediment deformation of the beds below the glacial diamictite, as well as subglacial erosion of the carbonates beneath, showing that the Trezona $\delta^{13}C$ values must have been acquired *before* glaciation. Although these stratigraphic relationships do not provide a specific mechanism to explain the Trezona $\delta^{13}C$ anomaly, they do require that the nadir of the Trezona $\delta^{13}C$ anomaly was recorded prior to local glacier advance and long before late-stage burial diagenesis could have occurred. Furthermore, the $\delta^{13}C$ recovery in the Trezona Formation toward 0‰ was synchronous with the appearance of icebergs in the tropics.

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1. Introduction

Neoproterozoic carbonate carbon isotope records are characterized by two features unique to the era: 1) prolonged periods with high carbonate $\delta^{13}C$, and 2) short-term departures to negative $\delta^{13}C$ values. The Cryogenian (~710–635 Ma) $\delta^{13}C$ record exhibits increasing $\delta^{13}C$ after the Sturtian ice age, a +8‰ plateau, and finally an 18‰ negative shift in $\delta^{13}C$ preceding the Marinoan glaciation. This preglacial negative $\delta^{13}C$ 'Trezona' anomaly, named after its discovery in the Trezona Formation (Fm) of South Australia (McKirdy et al., 2001), gradually recovers from $\delta^{13}C$ of −10‰ towards 0‰ before the overlying glacial deposit. This trend likely represents a globally synchronous signal as it is recorded in carbonates on five continents (Halverson et al., 2005; Hoffman et al., 2002; Kaufman et al., 1997; McKirdy et al., 2001; Miller, 2008; Narbonne et al., 1994; Xiao et al., 2004) and always occurs stratigraphically above the +8‰ plateau and below the Marinoan glacial deposit. The glacial deposit has been correlated between continents using the overlying sedimentologically and geochemically distinct 'cap' carbonate sequences. An ash within the Marinoan glacial deposit in Namibia yielded an U–Pb age of 635.5 ± 0.6 Ma (Hoffmann et al., 2004), while an ash within the Marinoan cap carbonate in South China contained zircons dated at 635.2 ± 0.6 Ma using the U–Pb system (Condon et al., 2005). The Trezona $\delta^{13}C$ anomaly is comparable in magnitude to an anomaly that precedes the Sturtian glaciation on three cratons (>716.5 ± 0.24 Ma (Halverson et al., 2005; Macdonald et al., 2010)), as well as to the younger Shuram $\delta^{13}C$ excursion on five continents (full recovery dated at ~551 Ma, South China (Condon et al., 2005)) where $\delta^{13}C$ shifts from +4 to −12‰ before gradually recovering to positive values again (Burns and Matter, 1993; Calver, 2000; Kaufman et al., 2007; McFadden et al., 2008; Melezhik et al., 2008). Despite these similarities with the Trezona $\delta^{13}C$ anomaly, the goal of this paper is not to correlate the anomaly between continents or compare the $\delta^{13}C$ profile to other similar Neoproterozoic $\delta^{13}C$ anomalies. Instead, we document the Trezona $\delta^{13}C$ anomaly recorded on one continent across one basin and use stratigraphic relationships to evaluate the relative age of the $\delta^{13}C$ variability and glaciation.

The origin of such a large global isotopic shift remains contentious: does the anomaly represent a significant perturbation to the carbon cycle reflected in the global oceanic dissolved inorganic carbon (DIC) from which limestones are derived (Halverson et al., 2002; Pavlov et al., 2003; Schrag et al., 2002; Swanson-Hysell et al., 2010), or does it reflect diagenetic alteration of the limestones by porewaters (Derry, 2010a,b,c; Knauth and Kennedy, 2009; Swart and Kennedy, 2012)? Proponents of a primary DIC or early diagenesis origin interpret the close association of the Trezona $\delta^{13}C$ anomaly below M0arinoan glacial deposits

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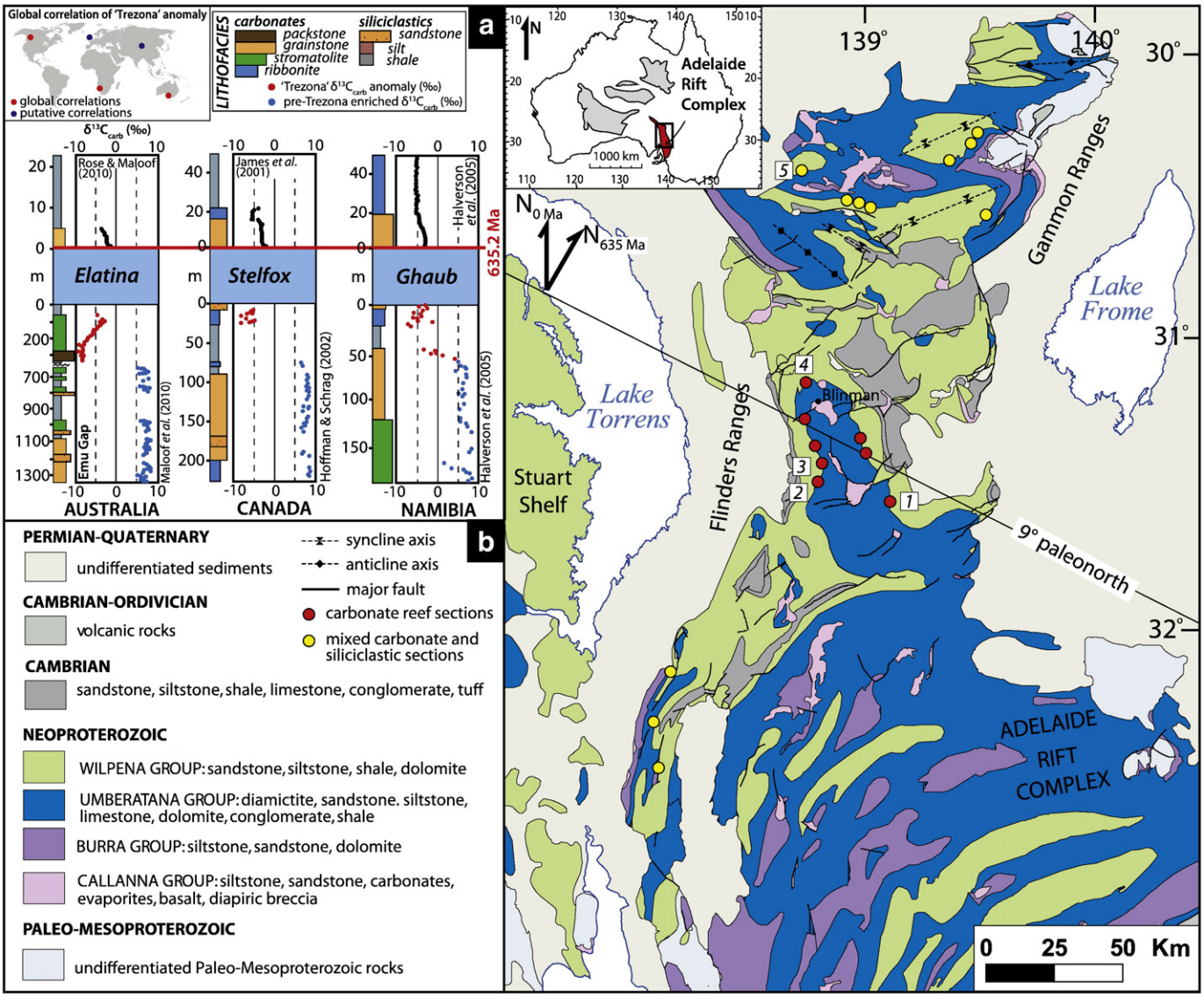


Fig. 1. (a) Inset: world map showing locations of Cryogenian interglacial successions that record the Trezona $\delta^{13}C$ anomaly: South Australia (McKirdy et al., 2001), northern Namibia (Halverson et al., 2005; Miller, 2008), northern Canadian cordillera (Hoffman et al., 2002; Kaufman et al., 1997; Narbonne et al., 1994), northwest China (Xiao et al., 2004), and Scotland (Prave et al., 2009). Simplified representative stratigraphic sections that record the large (~18‰) Trezona isotopic anomaly observed beneath the Elatina (Australia), Stelfox (Canada), and Ghaub (Namibia) glacial sediments. The Trezona anomaly recorded in limestones across the Adelaide Rift Complex (ARC), South Australia, is younger than a 659.7 Ma tuffaceous horizon in the Wilyerpa Fm (SHRIMP U–Pb zircon age), just above the Appila (Sturtian) diamictite (Fanning, 2006), and older than the ~635 Myr old Nuccaleena Fm 'cap dolostone', which has been correlated to U–Pb zircon-dated ashes within the Marinoan glacial deposit and cap dolostone in Namibia (Hoffmann et al., 2004) and China (Condon et al., 2005), respectively. (b) Inset: map illustrating the Neoproterozoic basins in Australia (gray) with the Adelaide Rift Complex (ARC) highlighted in red. Simplified geological map (adapted from Preiss and Robertson, 2002) of the study area within the ARC. Locations of measured stratigraphic sections are denoted by red dots (carbonate reef sections) and yellow dots (mixed carbonate-siliciclastic sections). Sections discussed in this paper are labeled with numbered squares (1. Emu Gap, 2. Elatina Creek, 3. Trezona Bore, 4. Mooloolo, and 5. Punches Rest). The orientation of paleonorth and paleolatitude depicted on the map are from paleomagnetic results measured in the Elatina Fm of the central Flinders Ranges (Sohl et al., 1999).

worldwide as evidence for a causal relationship between the two (Pavlov et al., 2003; Schrag et al., 2002; Swart and Kennedy, 2012). However, due to erosional unconformities truncating the upper recovering $\delta^{13}C$ trend (Halverson et al., 2002), no observation has constrained the timing of the Trezona $\delta^{13}C$ anomaly to the onset of the Marinoan glaciation.

There are five published hypotheses for the origin and timing of large-scale Neoproterozoic $\delta^{13}C$ excursions that can be applied to the Trezona $\delta^{13}C$ anomaly: (1) limestone $\delta^{13}C$ was reset during deep (>1 km) burial diagenesis by warm, CO_2-charged brines (Derry, 2010a,b; Grotzinger et al., 2011); (2) $\delta^{13}C$ records diagenetic alteration of shallowly-buried limestones associated with CO_2-charged brines rising from deeper overpressured reservoirs that were fractured during rapid deglacial sea level rise (Derry, 2010c); (3) $\delta^{13}C$ was altered during meteoric diagenesis and sea level drawdown during ice age initiation (Knauth and Kennedy, 2009; Swart and Kennedy, 2012); (4) $\delta^{13}C$ records changes in DIC either as a cause or consequence of the transition into a low-latitude glaciation (Pavlov et al., 2003; Schrag et al., 2002; Swanson-Hysell et al., 2010; Tziperman et al., 2011); and (5) $\delta^{13}C$ records primary changes in global oceanic DIC significantly before the onset of glaciation (Halverson et al., 2002).

The abundance of chemical sediments and broad range of pre- and syn-glacial paleo-environments and water depths across the Adelaide Rift Complex (ARC), South Australia, offer a unique opportunity to constrain the timing of the $\delta^{13}C$ anomaly relative to deposition of

the Trezona Fm and ensuing glaciation. In particular, the Trezona Fm includes outer shelf–slope stratigraphy that records continuous submarine deposition and $\delta^{13}C$ evolution while shallow carbonate platforms are subaerially exposed globally during glacial eustatic fall. Across the ARC, the Trezona Fm is preceded by the older Etina Fm and Enorama Fm and is overlain by the Elatina Fm. The Etina Fm consists of shallow marine sandstone, oolites and microbial reefs. The base of the Enorama Fm shale marks a major flooding surface, followed by a gradual coarsening and shoaling-upward sequence that culminates in intraclastic limestone breccias, stromatolite bioherms, oolitic grainstones and siltstones of the Trezona Fm. This carbonate succession consists of cm to m-scale parasequences that show no evidence of subaerial exposure. The Trezona Fm packstones contain putative skeletal fossil debris that onlap and drape the stromatolite bioherms and have been interpreted as the first sponge-grade metazoan body fossils (Maloof et al., 2010). Detailed mapping and 19 measured stratigraphic sections show that the pre- and syn-glacial facies record a progressive deepening towards the north of the ARC (Fig. 1). The pre-glacial Trezona Fm equivalent in the south is a thick, dark red, mud-cracked sandstone and siltstone deposit with medium-coarse grit lenses (Yaltipena Fm; Fig. 2b,c). These sediments inter-finger with nearshore channelized grainstones, stromatolite reefs, and limestone breccias in the central region (Fig. 2a), and transition to stormy outer shelf carbonate ribbonites and gray–green calcareous shales in the north. The overlying glacigenic Elatina Fm transitions from marine sands in the south, to ice-contact tillites in the central region (Fig. 2g,h), and debris flows and turbidites in the north. In this paper, we present paired sedimentological and geochemical evidence from the ARC that constrain the recovery from the Trezona $\delta^{13}C$ isotopic nadir to be synchronous with the appearance of icebergs in the tropics. These new observations constrain the timing of the $\delta^{13}C$ trend, and thus, rule out hypotheses 1, 2 and 5, and allow us to evaluate hypotheses 3 and 4 for the origin of the Trezona $\delta^{13}C$ anomaly.

2. Methods

2.1. $\delta^{13}C$ methods

Carbonates were sampled at ~1.0 m resolution whilst measuring 5 stratigraphic sections from across the ARC. Clean dolostones and limestones without siliciclastic components, secondary veining or cleavage were targeted. A total of 1042 samples were slabbed and polished perpendicular to bedding and 5 mg of powder were micro-drilled from individual laminations for isotopic analysis. At the University of Michigan Stable Isotope Laboratory, all powders were heated to 200 °C to remove volatile contaminants and water. Samples were then placed in individual borosilicate reaction vessels and reacted at 76 °C with 3 drops of H_3PO_4 in a Finnigan MAT Kiel I preparation device coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer. $\delta^{13}C$ and $\delta^{18}O$ data were acquired simultaneously and are reported in the standard delta notation as the ‰ difference from the VPDB standard. Measured precision was maintained at better than 0.1‰ (1σ) for both $\delta^{13}C$ and $\delta^{18}O$. At Princeton University, all carbonate powders were heated to 110 °C to remove water. Samples were then placed in individual borosilicate reaction viles and reacted at 72 °C with 5 drops of H_3PO_4 in a GasBench II preparation device coupled directly to the inlet of a Thermo DeltaPlus continuous flow isotope ratio mass spectrometer. $\delta^{13}C$ and $\delta^{18}O$ data were acquired simultaneously and are reported in the

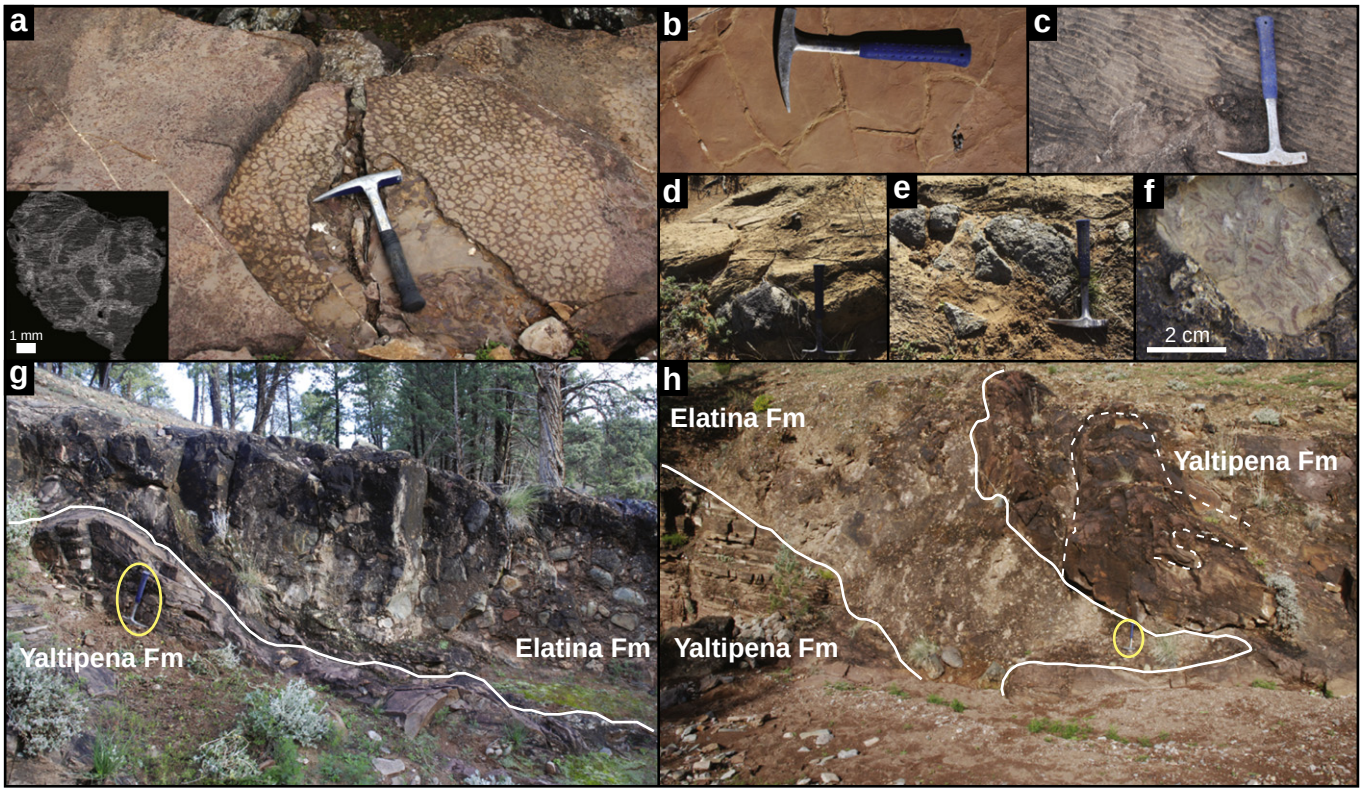


Fig. 2. (a) Outcrop of the Trezona Fm showing putative skeletal morphologies in fossil debris onlapping and draping a stromatolite bioherm (under the 30 cm long hammer) (Maloof et al., 2010). A 3D reconstruction of one such fossil is shown in the inset image. (b–c) Mudcracked siltstone and symmetric micro-wave ripples, Yaltipena Fm at Trezona Bore (Section [3], Figs. 1b and 3a), indicating intermittent subaerial exposure and very shallow water respectively. (d–e) Granitoid clasts within microbialite bioherm of the Trezona Fm at Punches Rest (Section [5], Figs. 1b and 3a). (f) Trezona Fm fossiliferous packstone clast within the glacial diamictite of the Elatina Fm. (g) Elatina Fm diamictite resting unconformably on tidal flat sandstone of the Yaltipena Fm as a result of ice-contact deposition, Trezona Bore. (h) Sub-glacial push structure lying unconformably on the Yaltipena Fm (right of image) at Trezona Bore. Note hammer for scale. The scoured basal contact and contorted diamictite beds indicate local ice-contact deposition and sub-glacial push structures.

standard delta notation as the ‰ difference from the VPDB standard. Precision and accuracy of data are monitored through analysis of 21 standards which are run for every 59 samples. Measured precision is maintained at better than 0.1‰ (1σ) for both $\delta^{13}C$ and $\delta^{18}O$.

2.2. Geochronology methods

Zircon separates were prepared using standard crushing, heavy liquid, and isodynamic separation techniques. To minimize any potential sampling bias, an aliquot of between 500 and >2000 zircons from the bulk separate were mounted (without hand picking) directly into a 25 mm diameter epoxy resin disc and polished. All zircons were mapped using a cathodoluminescence imaging system attached to a FEI Q400 FEG scanning electron microscope (SEM) housed at the University of California, Santa Barbara. The SEM was operated at 10 kV accelerating voltage and a beam current of 0.5 nA. The cathodoluminescence images revealed simple concentric zonation in the majority of zircons that were targeted (Fig. S1).

Zircons were analyzed for U, Th and Pb isotopes using a Laser Ablation Multi-Collector Inductively Coupled Plasma Mass Spectrometer (LA-MC-ICPMS) system housed at the University of California, Santa Barbara. Instrumentation consists of a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK) and a 193 nm ArF laser ablation system (Photon Machines, San Diego, USA). Analytical protocol is similar to that described by (Cottle et al., 2009a, b, c). U–Th–Pb analyses were conducted for 15 s each using a spot diameter of 24 μm, a frequency of 4 Hz and 1.2 J/cm^2 fluence (equating to crater depths of approximately 4 μm). U–Th–Pb data from 5 samples were collected over 4 days of continuous instrument operation. A primary reference material, '91500' zircon (1065.4 ± 0.6 Ma $^{207}Pb/^{206}Pb$ ID-TIMS age and 1062.4 ± 0.8 Ma $^{206}Pb/^{238}U$ ID-TIMS age (Wiedenbeck et al., 1995)) was employed to monitor and correct for mass bias as well as Pb/U and fractionation. To monitor data accuracy, a secondary reference zircon 'GJ-1' (608.5 ± 0.4 Ma $^{207}Pb/^{206}Pb$ ID-TIMS

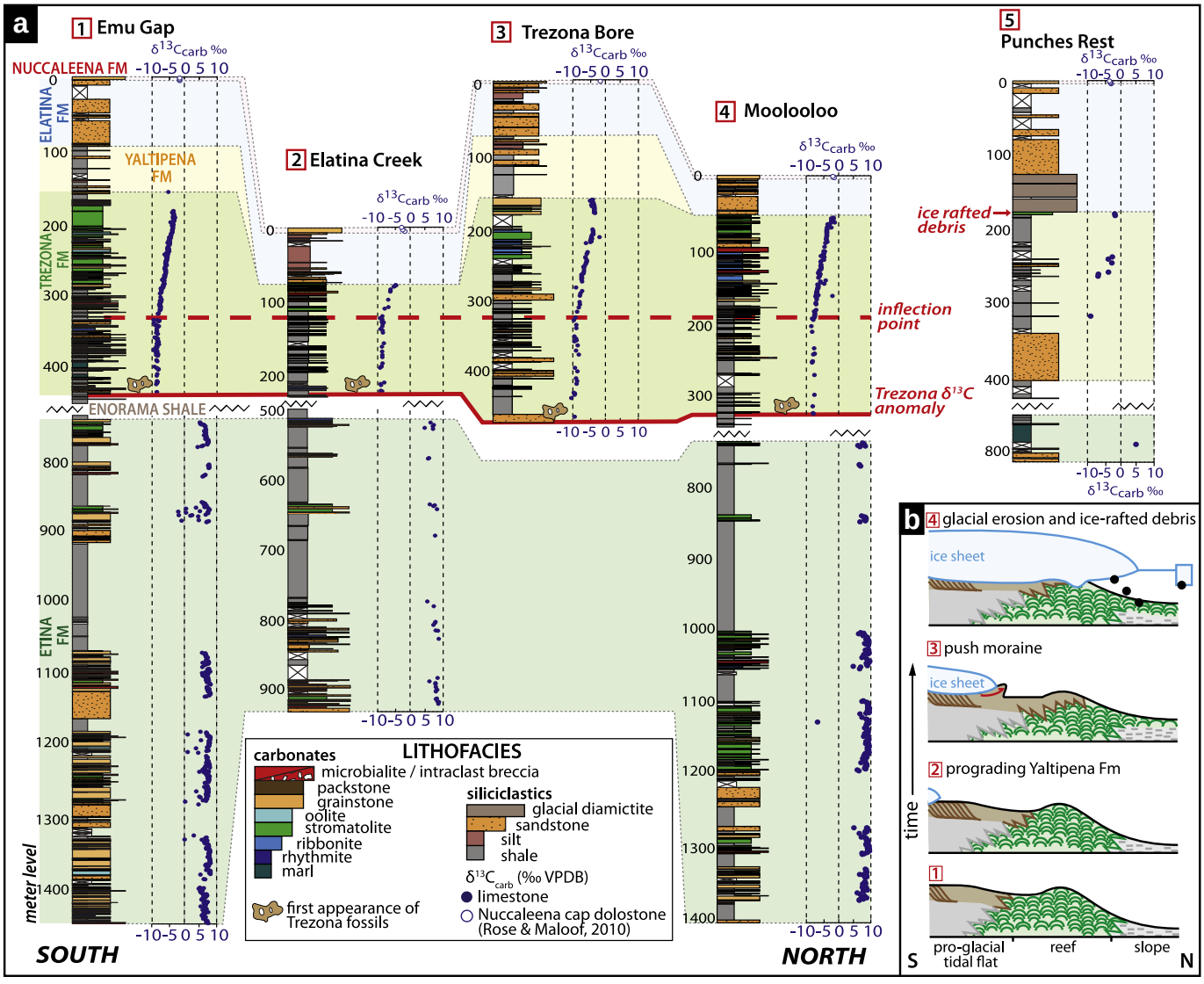


Fig. 3. (a) Selection of stratigraphic sections from the central anticline of the ARC (numbered to correspond with Fig. 1). The stratigraphic sections were drafted using MatStrat software (Lewis et al., 2011). Pre-glacial $\delta^{13}C$ data within the Etina and Trezona Fms are denoted by blue circles and $\delta^{13}C$ data within the post-glacial Nuccaleena Fm cap dolostone are denoted by white circles (Rose and Maloof, 2010). All sections are hung from a datum chosen at the inflection point at the base of the recovery from the Trezona negative $\delta^{13}C$ anomaly. The Yaltipena Fm progressively thins until it is missing entirely at the Elatina Creek section (Elatina Creek, [2]). Differential glacial erosion truncated the Yaltipena Fm during the ice advance. Furthermore, the $\delta^{13}C$ data indicate truncation of the Trezona Fm's reproducible carbon isotopic trend, thereby quantifying the degree and lateral variability of glacial erosion. Note that the Enorama Fm consists of shale with no associated $\delta^{13}C$ data and therefore has been omitted from the stratigraphic sections for clarity. (b) Schematic depositional model for the central anticline and northern region of the ARC, showing ice-contact deformation of the Yaltipena Fm and glacial truncation of the Trezona Fm in the central fold, and synchronous deposition of dropstones within stromatolites in the uppermost Trezona Fm to the north.

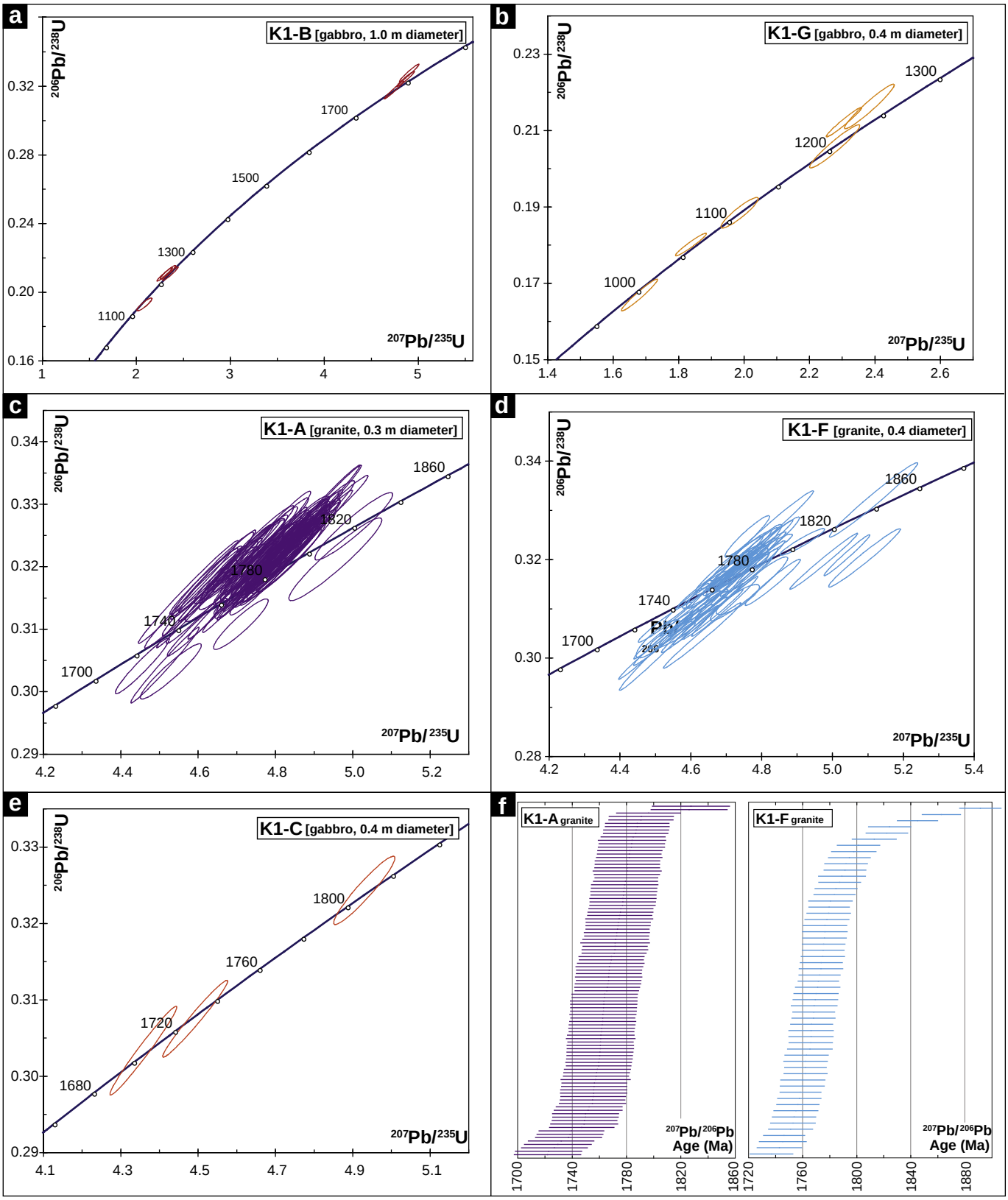
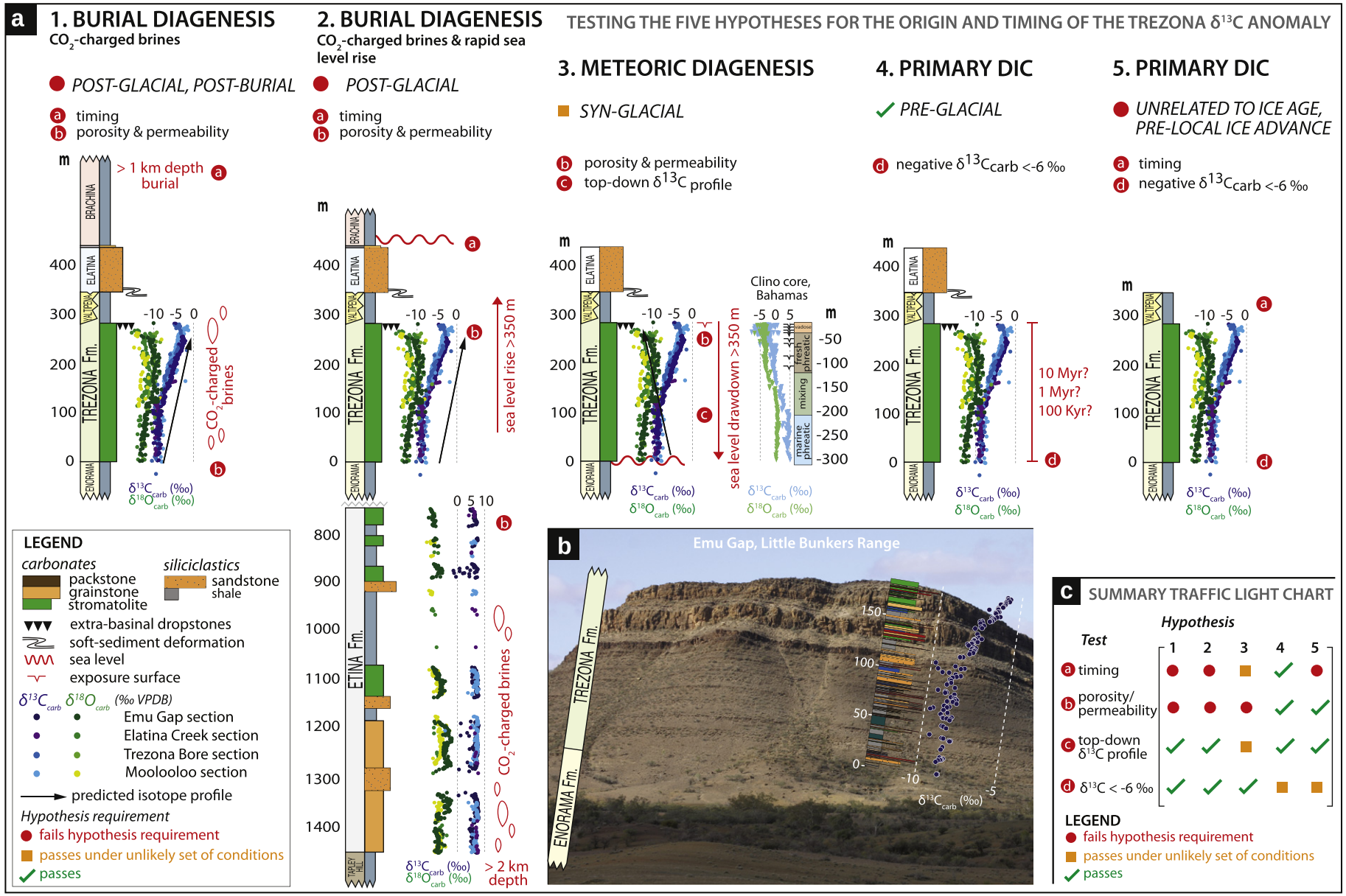


Fig. 4. U–Pb concordia diagrams for five ice-rafted clasts in the top of the Trezona Fm carbonate platform. We interpret the average of the concordant zircons to approximate the crystallization age of the clast. (a–b) Two gabbro clasts (K1–B and K1–G) are ~1000 Ma and ~1140 Ma, whilst two granite clasts (K1–A and K1–F) and a gabbro clast (K1–C) record ~1780 Ma and ~1700 Ma crystallization ages, respectively (c–e). These ages all can be derived from west and north regions of the Australian continent, respectively. (f) $^{207}Pb/^{206}Pb$ dates for single-grain zircons from granite clasts, color-coded to samples in c and d. All uncertainties are 2σ.


a
1. BURIAL DIAGENESIS
CO2-charged brines
POST-GLACIAL, POST-BURIAL
a timing
b porosity & permeability
> 1 km depth burial
CO2-charged brines
2. BURIAL DIAGENESIS
CO2-charged brines & rapid sea level rise
POST-GLACIAL
a timing
b porosity & permeability
sea level rise >350 m
TESTING THE FIVE HYPOTHESES FOR THE ORIGIN AND TIMING OF THE TREZONA δ13C ANOMALY
3. METEORIC DIAGENESIS
SYN-GLACIAL
b porosity & permeability
c top-down δ13C profile
sea level drawdown >350 m
Clino core, Bahamas
vadose
fresh phreatic
mixing
marine phreatic
4. PRIMARY DIC
PRE-GLACIAL
d negative δ13Ccarb <-6 ‰
10 Myr?
1 Myr?
100 Kyr?
5. PRIMARY DIC
UNRELATED TO ICE AGE, PRE-LOCAL ICE ADVANCE
a timing
d negative δ13Ccarb <-6 ‰
BRACHINA
ELATINA
WALTEMA
TREZONA Fm.
ENORAMA
ETINA Fm.
TARCEY HILL
δ13Ccarb (‰)
δ18Ocarb (‰)
> 2 km depth
LEGEND
carbonates
packstone
grainstone
stromatolite
siliciclastics
sandstone
shale
extra-basinal dropstones
soft-sediment deformation
sea level
exposure surface
δ13Ccarb δ18Ocarb (‰ VPDB)
Emu Gap section
Elatina Creek section
Trezona Bore section
Mooloolo section
predicted isotope profile
Hypothesis requirement
fails hypothesis requirement
passes under unlikely set of conditions
passes
b
Emu Gap, Little Bunkers Range
c
SUMMARY TRAFFIC LIGHT CHART
Hypothesis
Test
1 2 3 4 5
a timing
b porosity/ permeability
c top-down δ13C profile
d δ13C < -6 ‰
LEGEND
fails hypothesis requirement
passes under unlikely set of conditions
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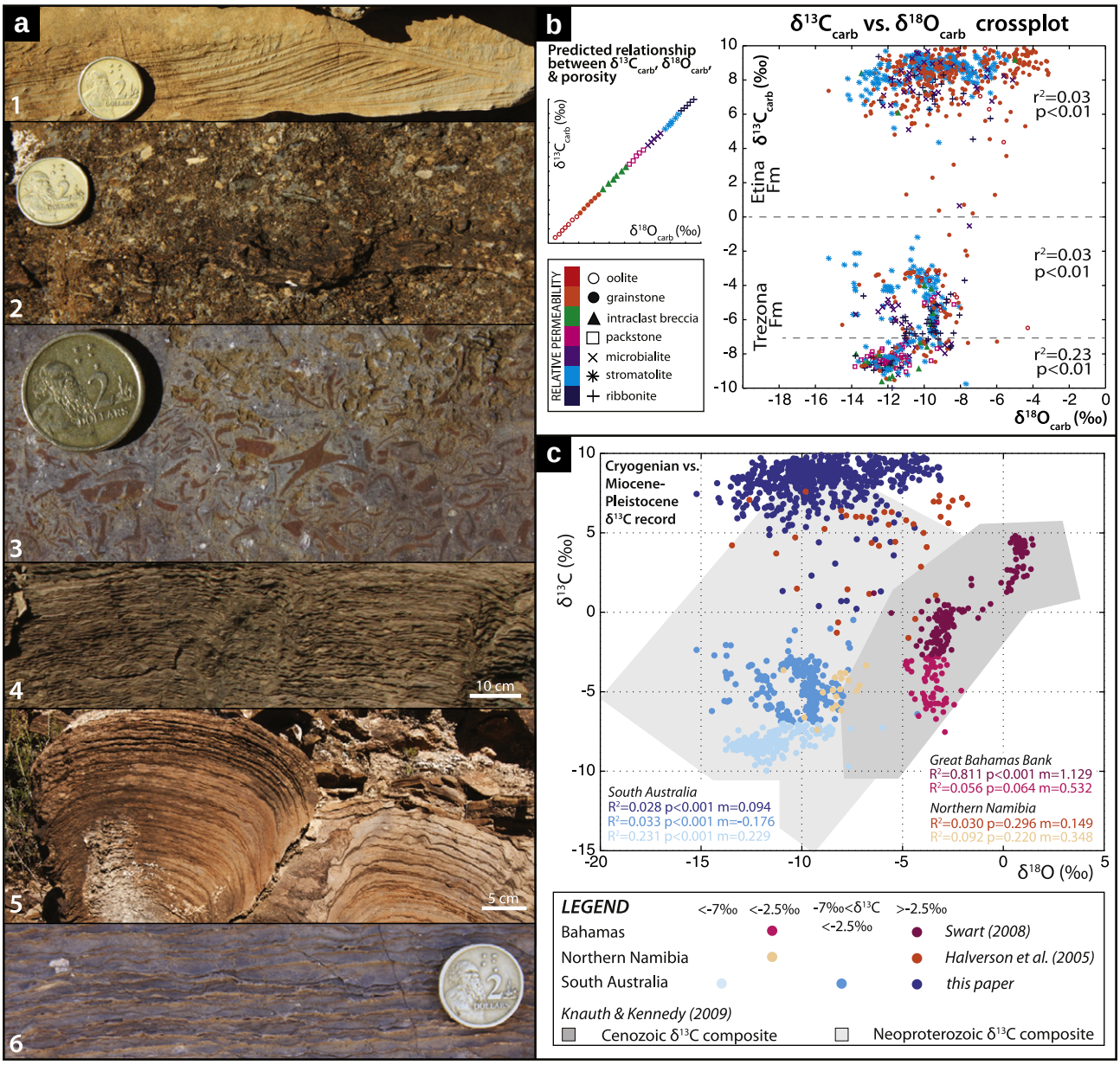

Fig. 6. (a) Field photos showing the predominant lithofacies within the Trezona Fm: (1) grainstone; (2) intraclast breccia; (3) packstone; (4) microbialite; (5) stromatolite; and (6) ribbonite. Diameter of coin is 20.5 mm. (b) Crossplot showing $\delta^{18}O$ vs. $\delta^{13}C$ data for the Trezona and Etina Fms from the Emu Gap, Elatina Creek, Trezona Bore, and Mooloolo sections with data color-coded by facies and relative permeability (Figs. 1b and 3a [1–4]. If diagenetic fluid-rock interactions control the $\delta^{13}C$–$\delta^{18}O$ in the Trezona Fm, $\delta^{13}C$ and $\delta^{18}O$ should be most negative in the most permeable sediments, and should become less altered (although not necessarily with a linear relationship) in less permeable units. (c) A crossplot comparing $\delta^{18}O$–$\delta^{13}C$ for the Cryogenian 'Trezona' $\delta^{13}C$ anomaly in South Australia (this paper) and northern Namibia (Halverson et al., 2005), and the Miocene–Pleistocene Clino core record, Great Bahamas Bank (Swart, 2008). Light colors represent $\delta^{13}C$ <−2.5‰ and dark colors for $\delta^{13}C$ >−2.5‰. The Trezona Fm (South Australia) is further divided into $\delta^{13}C$ <−7.0% (pale blue) and $\delta^{13}C$ >−7.0‰ (mid blue). The dark and light gray shaded regions represent Cenozoic and Neoproterozoic $\delta^{18}O$–$\delta^{13}C$ data composites, respectively (Knauth and Kennedy, 2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

age (Jackson et al., 2004) and 601.7 ± 1.3 Ma $^{206}Pb/^{238}U$ ID-TIMS age) was analyzed concurrently (once every 5–7 unknowns) and mass bias- and fractionation-corrected based on measured isotopic ratios of the primary reference material. Analyses of the GJ-1 secondary reference zircon during the analytical period yield a weighted mean $^{206}Pb/^{238}U$ age of 603.9 ± 0.6 Ma, MSWD = 0.9. Data reduction, including corrections for

Fig. 5. (a) Schematic diagram illustrating the five hypotheses for the origin and timing of the Trezona $\delta^{13}C$ anomaly. Hypotheses 1–2 propose that late-stage burial diagenesis generated CO_2-charged brines that reset the $\delta^{13}C$ values (Derry, 2010a; Derry, 2010b; Derry, 2010c; Grotzinger et al., 2011). Hypothesis 3 proposes that $\delta^{13}C$ values were altered during early meteoric diagenesis associated with glacio-eustatic sea level drawdown (Knauth and Kennedy, 2009; Swart and Kennedy, 2012). Data from the Clino core of the Great Bahama Banks provides a modern analog of a carbonate platform that has experienced pervasive meteoric diagenesis (Swart, 2008). Note that the recovery from the nadir of the Trezona $\delta^{13}C$ anomaly toward positive $\delta^{13}C$ values spans hundreds of meters (except where truncated) and is restricted to beneath the glacial surface. In contrast, the thin layer of positive $\delta^{13}C$ values at the top of Clino core and other Plio-Pleistocene cores are recorded within the post-glacial Holocene (Swart and Kennedy, 2012). Hypotheses 4–5 suggest that the $\delta^{13}C$ values record primary changes in DIC, either as a cause, consequence, or coincidental with the transition into a low-latitude glaciation (Halverson et al., 2002; Pavlov et al., 2003; Schrag et al., 2002; Swanson-Hysell et al., 2010). The problems with each hypothesis are highlighted by red circles labeled a–d and are referred to in the main text. The Trezona $\delta^{13}C$ data are from the four measured sections in the central Flinders region overlain on each other, illustrating the reproducibility across the ARC. (b) Laterally continuous outcrop of a stromatolite reef within the Trezona Fm exposed along the Little Bunkers Range (Fig. 1b [1]). The detailed Emu Gap stratigraphic section and associated $\delta^{13}C$ isotope data are overlaying the outcrop (Fig. 3a [1]). (c) A summary traffic light matrix illustrating which of the five hypotheses fail the fewest tests.

baseline, instrumental drift, mass bias, down-hole fractionation and age calculations was carried out using Iolite version 2.1.2 (Paton et al., 2010). All reported uncertainties are quoted at the 95% confidence or 2σ level and include contributions from the external reproducibility of the primary reference material for the $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios. The complete dataset is presented in SOM, Table 2.

3. Results

Five new field observations constrain the origin and timing of the Trezona anomaly as a signal that was recorded in carbonates prior to burial, and whose recovery was concurrent with the onset of the ice age. *First*, in the northern ARC, isolated rounded ~0.2–1.0 m diameter granite and gabbro clasts are incorporated within the upper 2 m of a Trezona Fm stromatolite bioherm that records the highest $\delta^{13}C$ following the Trezona anomaly (Punches Rest; Fig. 2d, e and 3a [5]). This ice-rafted debris requires overlying icebergs in water possibly no deeper than the photic zone during terminal carbonate deposition on the outer shelf. The boulder horizon probably does not represent a debris flow sourced from an active salt diapir (Lemon, 2000) because: (1) three sections measured along the Punches Rest syncline show that this boulder horizon is the only one within the ~300 m thick Trezona Fm; (2) the single horizon occurs <2 m below the first Elatina Fm diamictites that contain similar boulders; (3) microbialite growth around the clasts appears continuous, without evidence of a high-energy erosion surface or winnowing of any associated finer debris; and (4) in map view, the nearest diapir cross-cuts the Etina Fm but only impinges on the lowermost ~50 m of the Trezona Fm, ~5 km south of the horizon. This observation suggests that during the deposition of the upper Trezona Fm and Elatina Fm, the nearby diapirs were not emergent or obviously active. However, some of the clasts within the horizon may have originated from a more distal diapir that was eroded and transported by the ice sheet.

Zircons from five of the ice-rafted clasts were dated by U–Pb LA-ICPMS to constrain the source of the debris (Fig. 4). Two gabbro clasts contain ~1000–1140 Ma igneous zircons, consistent with an Australian intra-continental source in the Musgrave Block, Northampton Inlier and/or Albany-Frazier Province (Fig. 4a, b). Similarly, granite and gabbro clasts with ~1780 Ma crystallization ages may have been sourced from the Mt. Painter Block, Stuart Shelf basement and/or Peak and Denison Inliers (Fig. 4c–e). Alternatively, these clasts could originate from the Grenville and Yavapai–Mazatzal provinces, respectively, of Laurentia and/or East Antarctica that abutted Australia for the previous 300 My (Karlstrom and Bowring, 1988; Goodge et al., 2008). The m-scale diameter of some boulders is consistent with an intra-continental origin, with ice potentially covering at least the southern half of Australia. However, the Li et al. (2008) paleogeographic reconstruction of the break up of Rodinia does not exclude the clasts being debris delivered to the tropics by sea ice prior to substantial ice sheet growth, sea level fall, and subaerial exposure of the Trezona Fm.

Together, the remaining field observations constrain the Trezona anomaly to be a syn-depositional $\delta^{13}C$ signal recorded in carbonates. *Second*, a scoured basal contact and contorted diamictite beds at the base of the Elatina Fm at the Trezona Bore section (Fig. 3a [3]) indicate local ice-contact and sub-glacial push structures formed during an ice advance (Lemon and Gostin, 1990) (Fig. 2g, h). Associated soft-sediment deformation of the Yaltipena Fm silts below the diamictite suggests the silts were unlithified and were rucked up during glaciation by overriding ice, and that even the basal Trezona Fm was only shallowly (<300 m) buried. *Third*, local glacial erosion variably truncates the Yaltipena Fm, such that this formation is entirely missing in parts of the central Flinders anticline (Fig. 3a [2], [4]). *Fourth*, local glacial erosion also truncates the carbon isotope records in the Trezona Fm across the ARC. All stratigraphic sections across the ARC show a dramatic shift in $\delta^{13}C$ from +9‰ to −9‰ within the Enorama Fm, before recovering towards 0‰ within the overlying Trezona Fm. The upper ~15 m of the Trezona Fm typically record a ~1‰ decline in $\delta^{13}C$, with an increase in scatter and a decrease in mean $\delta^{18}O$ values. However, these characteristics are truncated in the Elatina Creek and Mooloolloo sections, where the advancing ice incised through the Yaltipena Fm into the Trezona Fm (Fig. 3a [2], [4]). *Fifth*, ~20 cm sub-angular limestone packstone clasts of the Trezona Fm, which contain the distinctive skeletal fossil debris (Maloof et al., 2010), are present as clasts within the Elatina Fm diamictite near Punches Rest (Fig. 2f and 3a [5]). Observations 3–5 indicate that differential glacial erosion removed the unlithified Yaltipena Fm and locally incised the carbonate platform at least 150 m during ice advance. Collectively, all five new observations support the idea that deposition of the upper Trezona Fm and recovery from the 18‰ $\delta^{13}C$ anomaly were contemporaneous with local glaciation. In light of the new sedimentological and geochemical evidence from the ARC, we evaluate the five published hypotheses for the origin and timing of the Trezona $\delta^{13}C$ anomaly.

4. Discussion

4.1. Post-glacial burial diagenesis

High-temperature (>100 °C) fluid–rock interactions during burial are a potential secondary diagenetic origin for highly negative and co-varying carbonate $\delta^{13}C$ and $\delta^{18}O$ (Derry, 2010a,b,c) (Hypotheses 1 and 2) (Fig. 5a [1], [2]). A recent hypothesis suggests that the Ediacaran-age Shuram $\delta^{13}C$ anomaly and covarying $\delta^{13}C$–$\delta^{18}O$ can be explained with a two component mixing model combining high pCO_2, low $\delta^{13}C$ fluid developed from interaction with organic matter at depth, and high $\delta^{18}O$ basinal brine (Derry, 2010a,b,c). Minimal $\delta^{13}C$–$\delta^{18}O$ covariation occurs within the carbonate grainstones of the Etina Fm that underlie the Enorama Fm ($r^2 = 0.03$, $p < 0.01$) (Fig. 6a–c). $\delta^{13}C$–$\delta^{18}O$ covariation within the Trezona Fm is restricted to $\delta^{13}C$ values <−7‰ in the lowermost ~150 m of the Trezona anomaly within individual sections and is of unknown origin (Fig. 6b, c). However, geological observations 1–5 are inconsistent with a burial diagenetic origin for the Trezona $\delta^{13}C$ anomaly because the $\delta^{13}C$ signal must have been recorded in sediment prior to glaciation.

Any burial diagenesis hypothesis requires that organic-rich sediments reach temperatures >60 °C for thermal cracking reactions to generate hydrocarbons and release CO_2-rich fluids that alter overlying carbonates during upward fluid migration (Seewald, 2003). Hypothesis 1 proposes that additional sedimentary overburden above the Trezona Fm helped generate such CO_2-charged brines (Fig. 5a [1]). Hypothesis 2 also calls upon hydrocarbon migration, but suggests that ^{13}C-depleted brines were released during post-glacial sea level rise when hydrostatic over-pressure caused the reservoir seal to fracture, leading to a global diagenesis event (Derry, 2010c) (Fig. 5a [2]). The Enorama Fm shale underlying the Trezona Fm is the only viable source of ^{13}C-depleted carbon, since the very permeable Etina Fm grainstones below remain at +10‰ (Fig. 5a [1]). Hypotheses 1 and 2 demand that the Trezona $\delta^{13}C$ anomaly was recorded diagenetically either after the glaciation, or after burial under >1 km of overlying sediments. However, the Trezona $\delta^{13}C$ anomaly and the then unlithified Yaltipena Fm are variably truncated across the carbonate platform, indicating that the isotope signature was acquired in the carbonates before interfingering siliciclastics were lithified, before erosional ice advance, and long before significant burial of the Enorama Fm.

4.2. Syn-glacial meteoric diagenesis

Meteoric diagenetic alteration associated with sea level drawdown and subaerial exposure during the Marinoan ice age has been proposed as an origin for the Trezona $\delta^{13}C$ anomaly (Knauth and Kennedy, 2009; Swart and Kennedy, 2012) (Hypothesis 3, Fig. 5a [3]). Flat-topped, shallow-water carbonate platforms can become exposed to $\delta^{13}C$- and $\delta^{18}O$-depleted meteoric water during sea-level fall, leading to depth-dependent variation in $\delta^{13}C$ and $\delta^{18}O$ beneath the subaerial carbonate

exposure surface (Allan and Matthews, 1982). These isotopically-depleted meteoric fluids would become progressively heavier with depth as they mix with relatively isotopically-enriched marine porewaters below the new syn-glacial base level (Allan and Matthews, 1982). Such a trend would be duplicated in altered carbonates, with the most enriched and covarying $\delta^{13}C$–$\delta^{18}O$ near the base of the altered stratigraphy within the meteoric-marine mixing zone (Moore, 2001; Swart and Eberli, 2005) (Fig. 5a [3c]). This pattern is observed in the Clino core of the Great Bahama Bank, which has undergone periodic subaerial exposure during the glacial–interglacial cycles of the Plio-Pleistocene. For a single period of exposure to be sufficient to alter hundreds of meters of stratigraphy, the meteoric influx must be exceptionally ^{13}C-depleted. Terrestrial biomass, with $\delta^{13}C$ values that are >20‰ lower than primary carbonate values, provides the main source of organic matter in the Bahamas, as primary marine organic matter within the carbonates is typically <0.5% (Knauth and Kennedy, 2009).

In general, the Trezona Fm represents a single shoaling upward sequence that lacks evidence for subaerial exposure in either physical or sequence stratigraphic analysis (Figs. 2 and 3). The one exception to this pattern is the impressive glacial erosional surface that truncates the top of the Trezona Fm. Any meteoric alteration along this surface would need to be synchronous with the accumulation of enough land-ice somewhere on the globe to cause sea level to fall and expose the platform, but before local glaciers truncated the $\delta^{13}C$–$\delta^{18}O$ profile on the carbonate platform during deposition of the Elatina Fm (Fig. 5a [3]). In contrast to the Great Bahama Bank data, where the uppermost carbonates record the most negative $\delta^{13}C$ values, the Trezona Fm records a profile with the most depleted and covarying $\delta^{13}C$–$\delta^{18}O$ values near the base of the altered stratigraphy, ~200 m below the truncation surface (Fig. 5a [3]). To create the complete observed Trezona $\delta^{13}C$ profile by meteoric diagenesis would require a sea level drawdown of ~5–200 m, where high freshwater recharge rates and low hydraulic conductivity values for the Trezona carbonates would lead to smaller required sea level drops (Budd and Vacher, 1991) (Fig. 5a [3]). The carbonate reef of the Trezona Fm is approximately 35 km wide and is restricted to the central anticline of the ARC with laterally equivalent silt-dominated facies towards the north and south (Fig. 1). Thus, the resulting freshwater lens could have penetrated ~350 m deep into this paleo-island and generated a marine mixing zone within the organic carbon-rich Enorama shales, leading to highly depleted $\delta^{13}C$ values and $\delta^{13}C$–$\delta^{18}O$ covariation at the base of the Trezona Fm. It is therefore possible that growth of just a Greenland-sized ice sheet somewhere in the world could have stimulated meteoric diagenesis through the entire thickness of the Trezona Fm. However, if such a small sea level change is sufficient for extreme diagenetic alteration of a 300 m thick column of rock, why is such dramatic $\delta^{13}C$ modification not more pervasive in the rock record? The underlying Etina Fm has evidence of periodic exposure, has a similar island geometry, and also is underlain by organic-rich shales and silts of the Tapley Hills Fm, but the $\delta^{13}C$ values remain +10‰. To explain the Trezona anomaly by meteoric diagenesis, one would have to find evidence that the carbonates were particularly disposed to $\delta^{13}C$ alteration, due either to the peculiar nature of their organic carbon content or to the oxidizing power of porewaters at the time (Grotzinger et al., 2011).

Diagenesis models (Hypotheses 1–3) also predict that the severity of physical and isotopic alteration should scale with the permeability and porosity of each unit. Primary porosity and permeability are a function of grain size and shape, degree of sorting, and sedimentation rate indicative of each lithofacies (Beard and Weyl, 1973). Following recrystallization and porosity reduction, the distribution of secondary porosity and permeability is controlled by the original lithofacies because fluid migration still preferentially occurs along grain boundaries (Moore, 2001). Therefore, diagenesis models predict spatially variable, grain size-dependent $\delta^{13}C$ (Fig. 5a [1b, 2b, 3b]). However, Trezona Fm $\delta^{13}C$ and $\delta^{18}O$ show no lithofacies-dependent trends (Fig. 6b, c), and the Trezona $\delta^{13}C$ anomaly is reproducible with minimal scatter at 1 cm, 1 km and 100 km scales, despite being recorded in a wide range of carbonate lithofacies across 45,000 km^2 (Fig. 6a).

4.3. Pre-glacial primary dissolved inorganic carbon

The Trezona $\delta^{13}C$ anomaly could record changes in oceanic DIC at the time of sedimentation (Hypotheses 4–5, Fig. 5a [4], [5]). Similar to South Australia, the Trezona anomaly in northern Namibia spans 30–50 m of predominantly shallow, platform-facies carbonates (Halverson et al., 2002; Miller, 2008). A simple thermal subsidence model accounting for glacial erosion suggested that the start of the negative $\delta^{13}C$ anomaly preceded glacioeustatic sea level fall by ~1 Myr (Halverson et al., 2002; Halverson et al., 2005; Hoffman, 2011) (Hypothesis 5). Ice-rafted debris in the upper Trezona $\delta^{13}C$ recovery requires synchroneity between the recovery of $\delta^{13}C$ to 0‰ and the glaciation (Fig. 5a [5a]. Together, these observations imply that the isotopic nadir predates the growth of significant land ice, but that the Trezona anomaly did not significantly predate glaciation.

5. Conclusions

Does the nadir of the Trezona $\delta^{13}C$ anomaly record a primary signal of global ocean DIC as a cause or a consequence of the transition into low-latitude glaciation, or are the two events completely unrelated? The former hypothesis is favored because a primary DIC origin fails the fewest geological and isotopic tests (Pavlov et al., 2003; Schrag et al., 2002; Swanson-Hysell et al., 2010). To achieve very negative primary $\delta^{13}C$ values below the long-term mantle input (~−6‰), additional inputs of ^{13}C-depleted material are required. Determining the duration of the Trezona $\delta^{13}C$ anomaly (negative shift and recovery) is critical to constraining the size and isotopic composition of the requisite reservoir of light carbon, to differentiate between sources such as methane (Bjerrum and Canfield, 2011; Pavlov et al., 2003; Schrag et al., 2002), dissolved organic carbon (Fike et al., 2006; Rothman et al., 2003; Swanson-Hysell et al., 2010; Tziperman et al., 2011) or remineralized particulate organic matter (Higgins and Schrag, 2006), and to evaluate the influence of such an event on the global carbon cycle and climate.

Sedimentological and geochemical constraints require that the $\delta^{13}C$ anomaly was recorded in carbonate sediments prior to local glacial erosion, thus ruling out any late-stage burial diagenesis hypothesis. While the meteoric diagenesis hypothesis can be made consistent with the new timing constraints presented here, it is inconsistent with the lack of permeability-dependent diagenetic indicators. We favor a primary DIC origin for the $\delta^{13}C$ signal, with the recovery from the global $\delta^{13}C$ Trezona anomaly synchronous with the first debris-laden icebergs in the tropics.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.12.027.

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