Isotope Constraints on Intra-Basin Correlation and Depositional Settings of the Mid-Proterozoic Carbonates and Organic-Rich Shales in the Greater McArthur Basin, Northern Territory, Australia

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SUMMARY

The Greater McArthur Basin in northern Australia forms the world's oldest potential unconventional gas play. It comprises Paleo- to Mid-Proterozoic sedimentary successions (i.e., the McArthur and Limbunya Groups) dominated by carbonate rocks (i.e., dolostones) deposited in various shallow marine to more restricted lagoonal and sabkha/playa evaporitic environments, while the associated organic-rich shales (i.e., the Barney Creek and Fraynes Formations) likely formed in relatively deeper and/or redox stratified depositional settings.

Here we use a multi-proxy approach based on the isotope tracers of carbon ($\delta^{13}C$) and strontium ($^{87}Sr/^{86}Sr$), and selected paleo-redox proxies (cerium anomalies: Ce/Ce*) to further constrain (i) temporal and spatial changes in the paleo-depositional environments and redox-structure of the basin, and also (ii) to test the applicability of the above isotope proxies for intra-basin correlations in the Greater McArthur Basin. This study presents the first continuous high-resolution $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ isotope records acquired from two drill cores: LV09001 and Manbulloo-S1 (located more than 400 km from each other), which intersected the above Proterozoic carbonate and organic-rich sedimentary sequences (i.e., the Barney Creek and Fraynes Formations, dated at ~1640 ± 5 million years) deposited in the central and western parts of the basin, respectively.

Importantly, our composite isotope trends from the Greater McArthur Basin (based on data from LV09001 and Manbulloo-S1) show consistent and systematic variations in the carbonate-based $\delta^{13}C$, $^{87}Sr/^{86}Sr$ and Ce/Ce* proxy records that are tightly coupled to changes in the local depositional environments, the latter interpreted as oscillations between relatively open marine (suboxic to anoxic) and more restricted (anoxic to euxinic) conditions. Overall, our results indicate coherent basin-wide isotope patterns with characteristic isotope anomalies during the purported basin restriction (i.e., the deposition of organic-rich shales) the measured $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ trends shift to isotopically lighter and more radiogenic values, respectively. These coherent isotope trends acquired from LV09001 and Manbulloo-S1 cores thus supports the proposed connectivity of the central and western parts of the basin, and the suitability of our multi-proxy isotope approach for future intra-basin correlation studies in the Greater McArthur Basin.

Key words: McArthur Basin; Proterozoic; Depositional Environments; Redox; Isotopes; Carbon, Strontium; Chemostratigraphy

INTRODUCTION

Geological Settings

The McArthur Basin contains extensive sedimentary packages up to 10 km thick, ranging in ages from the Paleo- to Mid-Proterozoic. The five lithologically distinct packages, as described by Rawlings (1999), are separated by regional unconformities (Ahmad *et al.*, 2013) associated with inversion events (Betts *et al.*, 2014). Previous work within other coeval basins have discovered that the sedimentary succussions from Rawlings (1999) have stratigraphic correlations relating to the Birrindudu Basin and Tomkinson Province, with the extent of the deposition referred to as the Greater McArthur Basin (Close, 2014). This intracratonic sedimentary superbasin formed by lithospheric tilting and transpressional rifting, casued by subduction and magmatic arc processes in Central Austalia (Scott *et al.*, 2000). The low oxygen conditions in the coeval Proterozoic ocean-atmosphere system allowed for organic rich black shales to develop, and despite its long geological history spaning more than 1.5 billion years (Byr), the Greater McArthur Basin has experienced generally low degree of post depositional alteration, which in turn allowed excellent preservation of these oldest hydrocarbon reservoirs and the associated primary isotope signature recorded in the coeval carbonate/shale sequences (Bullen 2017; Giulliano 2016; Fennel *et al.*, 2005).

Research Aims and Sampling Sites

Here we apply a novel multi-proxy geochemical approach based on the carbon (δ^{13}C) and strontium (^{87}Sr/^{86}Sr) isotope tracers, coupled with trace element paleo-redox proxies (Cerium anomalies: Ce/Ce*, Mo and U concentrations), to further constrain (i) temporal and spatial changes in the redox structure and paleo-depositional environments of the Greater McArthur Basin, and also (ii) to evaluate the potential of the above isotope tracers for the chemostratigraphy and intra-basin correlations. The Mid-Proterozoic sedimentary record of the Greater McArthur Basin (including the McArthur and Birrindudu Basins, presumably linked in the subsurface) is dominated by carbonate rocks (i.e., dolostones) deposited in various shallow marine to more restricted lagoonal and sabkha/playa evaporitic environments, while the associated organic-rich shales (i.e., the Barney Creek and Fraynes Formations) likely formed in relatively deeper and/or redox stratified depositional settings.

For the purpose of this study we focused on the analysis of two tentatively correlated drill cores, LV09001 and Manbulloo-S1 (see Figure 1), intersecting the above Mid-Proterozoic (~1640 ±5Ma) organic-rich shales and dolomites in the McArthur and Birrindudu Basins, respectively. These cores were sampled at a relatively high-resolution with the aim to generate and compare the first continuous high-resolution C and Sr isotope records, and trace element paleo-redox patterns, from the Mid-Proterozoic sedimentary sequences across the Greater McArthur Basin.
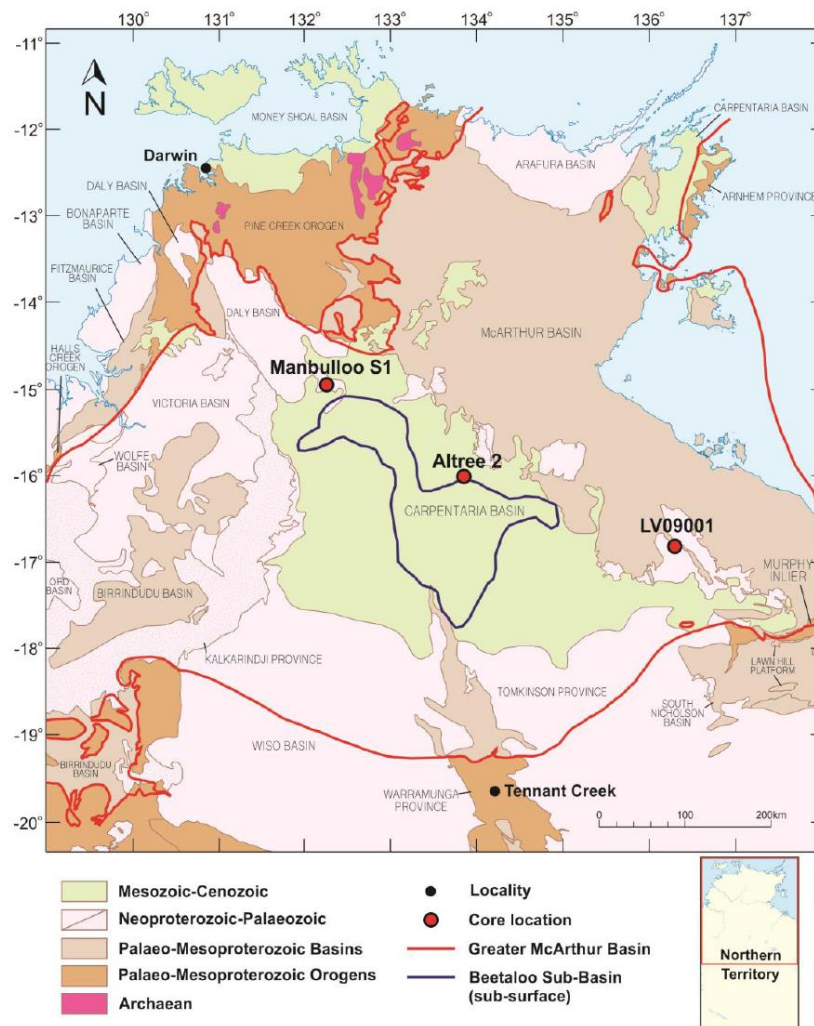
Figure 1. Geological map of the Northern Territory, showing all major basins and outlining the known extent of the Greater McArthur Basin (Close, 2015) and Beetaloo Basin. The cores analysed in this study are: LV00901 and Manbulloo-S1, which are located more than 400 km from each other (after Bullen 2017).

METHOD AND RESULTS

Selection and Sampling of Drill Cores

The Manbulloo-S1 and LV09001 cores, which form the basis for this study, show no obvious evidence of major post-depositional alteration, and these cores contain a complete and undisturbed record of the major lithological formations relevant to this study. A total of 215 samples were sampled from Manbulloo S1 core, and 120 samples from LV09001, at the NTGS core facility in Darwin. Typically, the samples (quarter cores) were collected with a resolution of between 3-10 meters, although this was increased to 20 cm for intervals with the organic rich zones (i.e., Fraynes and Barney Creek Fms). Variation of resolution was dependent on key lithological boundaries, and proximity to any obvious local diagenetic alteration or occurrences of secondary veins.

Carbon Isotope (δ^{13}C) Analysis of Carbonates

A selection of 230 carbonate-rich samples were mirco-drilled along bedding planes, and the rock powders were precisely weighed (ca. 0.5-1 mg) and placed into 1 mL glass septa vials. The vials were purged with helium, and phosphoric acid (ca. 10 drops, 1M) was added. The ratio of the isotopic composition from the resultant gas (CO_2) was measured using a Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) at the University of Adelaide. The standards used were ANU P3 (aragonite shell), UAC-1 and CO-8, and the carbonate-associated C isotope ratios (δ^{13}C) are expressed in per mil (‰) relative to Pee Dee Belemnite (PDB) using the following equation:

$$\delta^{13}\text{C (‰)} = [(^{13}\text{C}/^{12}\text{C}_{SAMPLE})/(^{13}\text{C}/^{12}\text{C}_{STANDARD})-1] \times 1000$$

Strontium Isotope (^{87}Sr/^{86}Sr) Analysis of Carbonates

A selection of 60 carbonate-rich samples were mirco-drilled along bedding planes, and the rock powder (ca. 0.5 mg) was washed with ammonium acetate (1.5 mL, 1 M) to remove any loosely bound cations (Bailey, McArthur, Prince, & Thirlwall, 1999). The resulting powder was washed and dried, and the leached with dilute ammonium acetate (2 x 1.5 ml, 10% w/w). The use of a weak acid minimizes the partial dissolution of any clays within the sample (Bailey *et al.*, 1999; Helverson & Théou-Hubert, 2014). The original sample was reconcentrated using high purity nitric acid (3.5 M) and the strontium was separated using ion chromatography in polyprep columns containing Eichrom Sr resin SPS (extended method is described in Bullen 2017). The purified Sr fraction (ca. 800 ng of Sr) was loaded onto outgassed Rhenium filaments, and the carbonate-associated ^{87}Sr/^{86}Sr ratio was measured using an Isotopx Phoenix Thermal Ionisation Mass Spectrometer (TIMS), operating in double collector dynamic measurement mode. The reproducibility at two standard error was better than 0.000005. Standards used throughout this procedure were JDO-1 and SRM 987.

Trace Element Analysis and Cerium anomalies (Ce/Ce*) Data

Carbonate leachates prepared for ^{87}Sr/^{86}Sr ratio analysis were also measured for their elemental composition. A fraction of the leachate was diluted with nitric acid (2%) into aliquots of ca. 1:2000 and ca. 1:100,000 dilutions. These solutions were used to determine elemental concentrations using an Agilent 8900x (QQQ) Inductively Coupled Plasma Mass Spectrometer (ICP-MS). An internal standard (Indium) was mixed with the samples to compensate for any potential matrix effects. A calibration curve was established (5 samples, 0-500 ppb) and several blanks were used throughout the sampling. Plasma conditions are shown in extended methods, Appendix A. The standard used was JDO-1.
Cerium anomalies (Ce/Ce*), the deviation of the concentration of Ce relative to the Lanthanum (La) and Praseodymium (Pr), were calculated from this trace element data using the following equation (see also Bullen 2017*):*

$$\text{Ce*}_{SN} = \text{Ce}_{SN}/\sqrt{\text{La}_{SN} \text{ x Pr}_{SN}}$$

Where SN denotes that the elemental concentration normalised to the Post Archean Australian Shale (PAAS).

**Geochemical and Isotope Trends from Manbulloo-S1 and LV09001 Cores**

The measured stable carbon isotope (δ^{13}C) and radiogenic strontium isotope (^{87}Sr/^{86}Sr) trends, from Manbulloo-S1 and LV09001 cores, are presented in Figure 2, which also shows proposed correlations between these two cores based on the acquired isotope trends. Note that intervals dominated by the deposition of organic-rich shales (Fraynes and Barney Creek Fms.) show systematic shifts to lower δ^{13}C and more radiogenic (higher) ^{87}Sr/^{86}Sr, and these shifts have been documented in both cores.
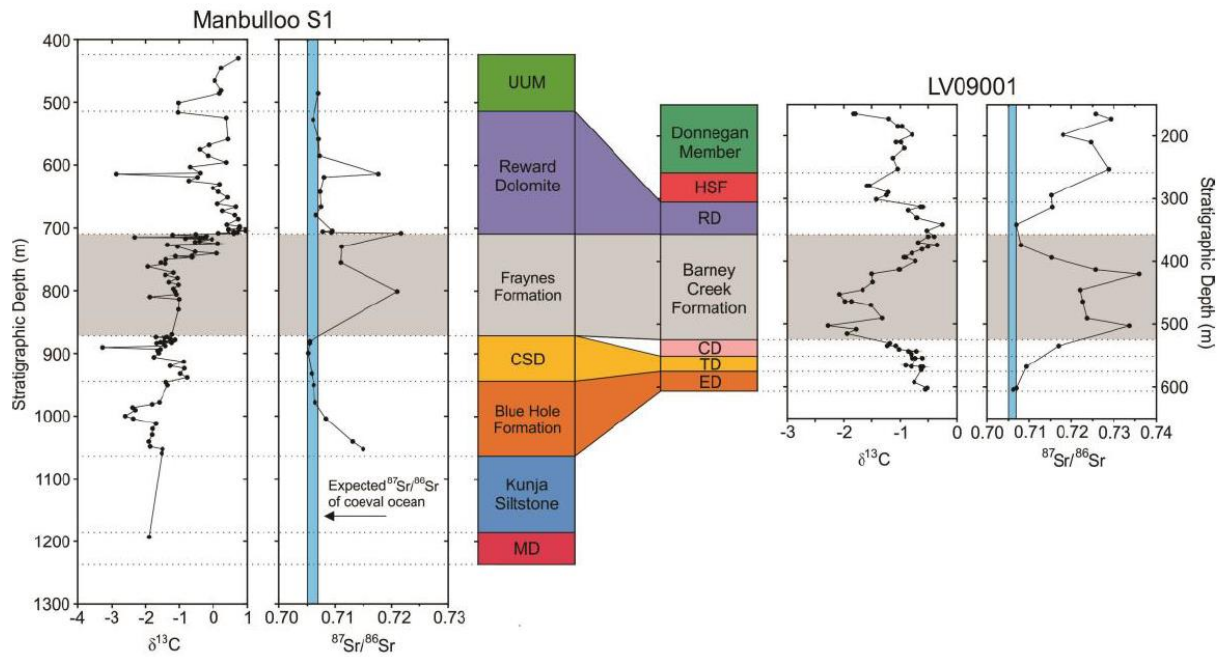
Figure 2. Comparison of high-resolution C and Sr isotope trends from the Manbulloo-S1 and LV09001 cores, from the Greater McArthur Basin, showing systematic shifts in measured $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ values during the deposition of presumably correlated organic-rich shales (Fraynes and Barney Creek Fms.) and carbonates (Reward Dolomites). After Bullen (2017), and Giuliano (2016).

Evidence for Chemical and Redox Stratification of the McArthur Basin: Comparisons to Modern Black Sea

Previous studies have shown evidence that stratification was present in the late Proterozoic McArthur Basin water column (Johnston *et al.*, 2008), along with abundant organic matter production and preservation (Giuliano, 2016; Bullen, 2017). Accordingly, it can be assumed that the conditions present in the modern day and redox-stratified Black Sea could be in some way analogous to the conditions during the deposition of the Proterozoic organic-rich shales in the McArthur Basin, especially with respect to chemical, redox and salinity stratification. However, with such comparisons one has to keep in mind the marked differences between the modern and mid-Proterozoic levels of free O_2 in the atmosphere. A comparison of selected isotope and redox signatures ($\delta^{13}C$ and Ce/Ce* anomalies) measured from Manbulloo-S1 sedimentary archives (rock samples from drill core) and the modern Black Sea (water samples) is illustrated in Figure 3.
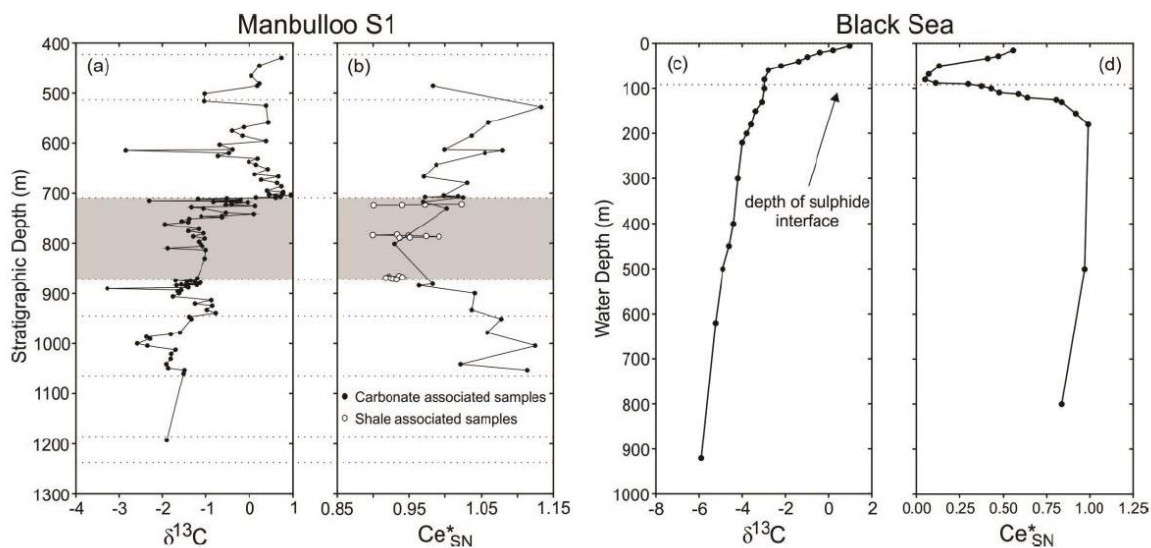
Figure 3. Comparison of carbonate-associated $\delta^{13}C$ and Ce/Ce* trends from the Manbulloo-S1 core and the same parameters measured across the water column in the Black Sea (after Bullen, 2017). The grey rectangle in plots (a) and (b) shows the position of organic-rich shales (Fraynes Fm.). Black Sea data are from Fry *et al.* (1991) and German *et al*. (1991). After Bullen (2017)

The purported restrictive event that occurred during the deposition of the Fraynes and Barney Creek Formations could lead to the deviation away from the coeval 'normal' marine $\delta^{13}C$ values (i.e., shifts to more negative values), but this does not explain why negative $\delta^{13}C$ values persisted also below the deposition of the Fraynes Formation from Manbulloo core (which however was not observed in $\delta^{13}C$ data from LV09001 core, intersecting the correlative Barney Creek Fm.). Because the $\delta^{13}C$ of precipitated carbonates is believed to closely approximate the C isotope composition of the DIC pool (Halverson *et al.*, 2010), and the $\square^{13}C$ of DIC pool in redox-stratified basins is expected to systematically decrease with depth (Fry *et al.*, 1991), it can be assumed that the depth of the water column can also control the $\delta^{13}C$ value of precipitated carbonates in the McArthur Basin. The Ce* data fits in with this interpretation, as the values throughout the Fraynes Formation resemble the trend seen at the sulphide interface in the Black Sea (German, 1991). In other words, the stratigraphic and systematic changes in $\delta^{13}C$ and Ce* trends recorded in the Fraynes Formations and overlying Reward Dolomite (i.e., data from Manbulloo core, Figure 3a, b) are consistent with the progressive shallowing of the depositional environment (using Black Sea water column data as an analogue, see Figure 3c, d). The absolute values from this comparison only conforms to the $\delta^{13}C$ data, as Ce/Ce* is a redox sensitive tracer controlled by the oxygen concentrations in the ocean-atmosphere system, which were significantly lower during the Proterozoic compared to present day values.

In contrast, the Black Sea shows a notable $\delta^{13}C$ isotopic trend with the DIC becoming more negative with depth (Fry *et al.*, 1991). This negative trend is due to the remineralisation of the isotopically light organic matter at the water-sediment interface and the subsequent release of such isotopically light DIC into the water column, which in turn causes the observed $\delta^{13}C$ gradient of the Black Sea with depth, caused by a lack of vertical mixing associated with salinity stratification. Also, German *et al.* (1991) observed that the Ce/Ce* anomalies in the Black Sea water column are not static, but display variation with respect to the depth or position of the redoxcline, with the most negative values occurring at depth of the oxic-anoxic interface (see also Figure 3d).
For the Mid-Proterozoic, the $\delta^{13}C$ of carbonate precipitated from seawater has a values typically near 0‰ PDB (Strauss *et al.*, 1992). Such anticipated normal 'seawater' $\delta^{13}C$ values are observed throughout the upper half of the core (i.e., in dolomites deposited above the Fraynes Formation). In contrast to this, exclusively negative $\delta^{13}C$ values are observed in the lower half of the core, including the organic-rich Fraynes Formation (Figure 3a). The transition from negative to positive $\delta^{13}C$ values is abrupt, and coincides with the transition from organic rich dolomitic shales (i.e., Fraynes Fm.) to pure dolomites of the Reward Formation.

Strontium Isotope Constraints ($^{87}Sr/^{86}Sr$) on the Restriction of the Greater McArthur Basin

Strontium isotopes are used in the reconstruction of paleo-depositional environments because they track relative contributions of old continental material with radiogenic $^{87}Sr/^{86}Sr$ ratios and unradiogenic hydrothermal Sr sources in the ocean and/or coastal marine systems. Due to the long residence time of Sr in the ocean it is considered to be well mixed in open marine systems, consequently, deviations in $^{87}Sr/^{86}Sr$ ratios to more radiogenic values are considered indicative of basin restriction (Kuznetsov *et al.*, 2010), in which the input of strontium becomes dominated from continental sources.
Based on the observed carbonate-associated $^{87}Sr/^{86}Sr$ trend from the Manbulloo-S1 and Lv09001 cores, a shift to more radiogenic values and away from the anticipated Paleoproterozoic seawater $^{87}Sr/^{86}Sr$ signature (Kuznetsov *et al.*, 2010) is observed during the deposition of the Fraynes and Barney Creek Formations (Figure 2). This isotopic shift to non-marine and more radiogenic Sr isotope signatures would be consistent with a transient basin restriction (with respect to an open ocean) during the deposition of these organic-rich shales in the Greater McArthur Basin. Together these consistent results from two different paleo-depositional sites recorded in Manbulloo and LV09001 cores would suggest that such purported restrictive event was a basin-wide phenomena which inhibited the flow and exchange of waters between the coeval global ocean and the Greater McArthur Basin during the deposition of the Fraynes and Barney Creek Formations.

Implications for Isotope Chemostratigraphy and Intra-Basin Correlations

The comparison between the data sets from the Manbulloo-S1 and the LV09001 cores show many similarities and systematic changes for the $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ isotope tracers (Figure 2). The $^{87}Sr/^{86}Sr$ ratio is more continentally influenced during the deposition of both the Fraynes Fm and Barney Creek Formations, suggesting a basin-wide restriction with respect to an open ocean. In contrast, immediately above and below the deposition of these organic-rich dolomitic shales, the $^{87}Sr/^{86}Sr$ ratio of sediments reflects the anticipated mid-Proterozoic paleo-seawater (see also blue vertical boxes in Figure 2), which in turn point to an active exchange of water masses between the McArthur basin and the coeval open ocean, suggesting cessations of those restricted conditions. Moreover, the $\delta^{13}C$ is more negative within the Fraynes and Barney Creek Formations, while trending to more positive values within the overlying unit of Reward dolomites. The main disagreement between the data sets from Manbulloo-S1 and LV09001 cores is noted in the Limbunya Package (i.e., Manbulloo core), where $\delta^{13}C$ values recorded in the Campbell Springs Dolomite and Blue Hole Formation are negative, despite the $^{87}Sr/^{86}Sr$ data indicating that the basin had open access to the ocean. The two plausible ways to interpret such variations observed in the studied cores are that there was either (i) a local effect which allowed the two areas to record independent signals (e.g., differences in primary productivity, the isotope composition of dissolved inorganic carbon DIC pool), or that (ii) the water depth of carbonate deposition at the Manbulloo site was deeper (relative to LV09001 site), which would translate to more negative $\delta^{13}C$ values of the local DIC pool, and thus precipitated carbonates.

CONCLUSIONS

Using stable and radiogenic isotope tracers (δ^{13}C and ^{87}Sr/^{86}Sr), major and trace elemental concentrations (including REEs), and organic carbon data (TOC) from the Manbulloo-S1 and LV09001 cores, the paleo-depositional and redox conditions within the Greater McArthur Basin (i.e., Limbunya and McArthur Groups) have been further constrained. Changes in trace element concentrations (i.e., cerium anomalies, Ce/Ce*) coupled with the total organic carbon (TOC) data, suggests prevailing anoxic conditions with a transient euxinia during the deposition of the organic-rich shales in the basin (i.e., Fraynes and Barney Creek Fms). Pronounced and systematic isotopic anomalies in δ^{13}C and ^{87}Sr/^{86}Sr proxies, associated with the deposition of the above organic-rich shales, indicate that the Greater MacArthur Basin was not connected with the coeval global ocean during the deposition of Fraynes and Barney Creek Formations, and thus experienced a basin restriction coupled with a redox-stratification. However, ^{87}Sr/^{86}Sr values from the conformably overlying and underlying dolomitic units (i.e., Reward or Teena Dolomites, respectively) yielded the Sr isotope signatures consistent with the mid-Proterozoic seawater, suggesting that the Greater McArthur Basin was communicating at some level with an open ocean during these times. Importantly, our comparisons of the equivalent stratigraphic units from Manbulloo-S1 and LV09001 cores suggest the existence of basin-wide Sr and C isotope patterns, which in turn have the potential for future isotope chemostratigraphy studies and the intra-basin correlations in the Greater McArthur Basin.

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