Gulf of Nuna: Astrochronologic correlation of a Mesoproterozoic oceanic euxinic event

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ABSTRACT
The ca. 1.4 Ga Velkerri and Xiamaling Formations, in Australia and the north China craton, respectively, are both carbonaceous shale deposits that record a prominent euxinic interval and were intruded by ca. 1.3 Ga dolerite sills. These similarities raise the possibility that these two units correlate, which would suggest the occurrence of widespread euxinia, organic carbon burial, and source rock deposition. Paleomagnetic data are consistent with Australia and the north China craton being neighbors in the supercontinent Nuna and thus permit deposition in a single large basin, and the putative stratigraphic correlation. However, lack of geochronological data has precluded definitive testing. The Xiamaling Formation has been shown to exhibit depositional control by orbital cycles. Here, we tested the putative correlation with the Velkerri Formation by cyclostratigraphic analysis. The Velkerri Formation exhibits sedimentological cycles that can be interpreted to represent the entire hierarchy of orbital cycles, according to a sedimentation rate that is consistent with Re-Os ages. Comparison of the inferred durations of the euxinic intervals preserved in both the Xiamaling and Velkerri Formations reveals a nearly identical ~10-m.y.-long oceanic euxinic event. This permits the interpretation that the two hydrocarbon-rich units were deposited and matured in the same basin of Nuna, similar to the Gulf of Mexico during the breakup of Pangea.

INTRODUCTION
Reconstructing the redox evolution of the Precambrian oceans and atmosphere is crucial to improve our understanding of the evolution of early life and increasing marine ecosystem complexity. Besides the need for accurate estimates of ancient water-column chemistry in a range of depositional environments, paleoredox reconstructions are most insightful for understanding the evolution of life if they are based on as many coeval sections, basins, and continents as possible. Although geochemical tools exist to reconstruct ancient seawater redox chemistry and track the rise of oxygen through time (Lyons et al., 2014), the identification of correlative strata across different Proterozoic basins and continents is challenging due to increasing uncertainty in plate tectonic reconstructions and correlation tools with increasing age. The identification of widespread euxinia (anoxic seawater with free hydrogen sulfide), such as oceanic anoxic events, is achieved in Proterozoic sections with biostratigraphy (Cocconi et al., 2006), which may be available in some Proterozoic successions, but is not refined enough for precise correlations. Just as in Phanerozoic strata, sequence stratigraphy can be used to precisely correlate sections across Proterozoic basins (Kunzmann et al., 2020), but as separate basins have different tectonic histories, stratigraphic sequences from two basins are unlikely to be precisely time equivalent (Catuneanu, 2019). If available, carbon isotopes can be very useful if significant isotopic variation is recorded in the studied succession. A further complication in identifying widespread euxinia in Proterozoic oceans is the general lack of reliable deep time geochronology. U-Pb dating of zircon in interbedded tuffs is ideal, but tuffs are rarely available. U-Pb dating of baddeleyite in crosscutting mafic dikes and sills is precise, but it only constrains the minimum depositional age, whereas U-Pb dating of detrital zircon only constrains the maximum depositional age. Stratigraphic sequences rich in organic carbon can also be dated with Re-Os geochronology, as has been done with particular success for some Mesoproterozoic organic-rich shales (Rooney et al., 2010; Sperling et al., 2014); however, outstanding concerns, such as insufficient precision, exist.

Astrochronology or cyclostratigraphy, i.e., the stratigraphic record of orbitally forced paleoclimatic change according to Milankovitch theory, which states that orbital variations influence incoming solar radiation, has become a central tool in the calibration of the Phanerozoic time scale (Gradstein et al., 2012). Despite pioneering work constraining Earth’s ancient rotation rate (Williams, 2000), the potential for cyclostratigraphy in Proterozoic time has only begun to be explored (Zhang et al., 2015; Gong et al., 2017; Bao et al., 2018). Orbital climate forcing in the ca. 1.4 Ga Xiamaling Formation of the north
China craton (hereafter simply referred to as “North China”) has been demonstrated with cyclostratigraphy and independently confirmed with U-Pb geochronology (Zhang et al., 2015). This unit was deposited partly under euxinic conditions (Zhang et al., 2016; Diamond et al., 2017). As the ca. 1.4 Ga Velkerri Formation in the McArthur Basin of Australia was also deposited partly under euxinic conditions (Cox et al., 2016), this represents a unique opportunity to test the existence of a widespread oceanic euxinic event in the Proterozoic by astrochronologic correlation of successions from two different continents.

**STRATIGRAPHIC FRAMEWORK**

The Velkerri Formation of the Roper Group (McArthur Basin) in northern Australia (Fig. 1A) contains up to 8% total organic carbon, corresponding to a clear euxinic interval (Cox et al., 2016). It represents one of the largest Precambrian hydrocarbon resources and a potentially large unconventional gas play (Jackson et al., 1986; Revie and Edgoose, 2015). Re-Os ages from the Velkerri Formation (Kendall et al., 2009) overlie, within uncertainty, with U-Pb ages (isotope dilution–thermal ionization mass spectrometry method on zircon) from multiple tuffs from the Velkerri Formation (Kendall et al., 2009) overlying the top of the Lower Velkerri Formation, the target of our high-resolution study (Fig. 1A), is a thinly laminated mudstone with organic matter content and grain-size variation deposited at or below storm-wave base (Fig. 1C). Re-Os ages from the top and the bottom of the Velkerri Formation (Altrel2 core, (15°55′24.96″S, 133°47′11.75″E) suggest a sediment accumulation rate (i.e., postcompaction rock accumulation rate) of 0.339 cm k.y.⁻¹ (Fig. 1; Kendall et al., 2009). However, this would be less than the ~0.5 cm k.y.⁻¹ sedimentation rate of the well-dated and lithologically similar Xiamaling Formation (Zhang et al., 2015). Also, since the Velkerri Formation is substantially thicker, one would expect it to have been deposited faster, not slower. Taking into account the large geochronologic uncertainties on both Re-Os ages (1417 ± 29 Ma and 1361 ± 21 Ma), sedimentation could have been as fast as 3.17 cm k.y.⁻¹. Thus, the faster end of the sedimentation rates, deemed feasible by extant Re-Os ages, sets the parameter space for exploring if significant spectral peaks of the Velkerri Formation correlate with known Milankovitch cycles or not, and whether astrochronologic correlation with the euxinic Xiamaling Formation is likely.

**METHODS**

Standard cyclostratigraphic procedures were used and are described in further detail in the Supplemental Material. Magnetic susceptibility, used herein, is one of the more successful proxies used in astrochronology, including for the lithologically similar Xiamaling Formation (Zhang et al., 2015). High-resolution magnetic susceptibility measurements were performed on.

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**Figure 1. Potential stratigraphic correlation between coeval ca. 1.4 Ga black shale deposits in (A) Australia (Velkerri Formation) and (B) the north China craton (Xiamaling Formation). Globe inset shows present-day locations of both basins. Geochronology: Australia (Abbott et al., 2001; Kendall et al., 2009; Yang et al., 2020) and north China craton (Gao et al., 2007; Yang et al., 2012; Su et al., 2010; Zhang et al., 2015). (C) Thinly laminated mudstone from studied interval in core Tarlee3 (McArthur Basin, Australia, 15°37′56.74461″S, 132°49′33.53895″E). Scale bar indicating sedimentation rate was estimated by this study.**
flush, flat surfaces of the TarleeS3 core (McAr
thur Basin, Australia, 15°37'56.74461''S, 132°49'33.53895''E; Figs. 1A and 1C) using a Terraplus KT-10 handheld meter. Spanning ∼32.5 m of the organic-rich Velkerri Formation, 682 measurements were taken (Table S1 in the Supplemental Material), for an average sampling spacing of ∼5 cm, sufficient to resolve cycles on the decimeter scale. The data were detrended in preparation for time-series analysis (Fig. S1; Table S2).

We conducted time-series analysis on the magnetic susceptibility record using the fast-Fourier transform (FFT) method (Muller and MacDonald, 2000) in order to test for the presence of any significant cycles. We evaluated the significance of the FFT spectral peaks using a Monte Carlo routine to simulate noise (Muller and MacDonald, 2000), and we interpreted spectral peaks rising above the 95% confidence level as statistically significant. Spectral peaks identified in the stratigraphic domain (meters) were converted into the time domain (k.y.) using a prescribed sediment accumulation rate. In the time domain, the target periods were the Milankovitch cycles of precession (∼20 k.y.), obliquity (∼41 k.y.), and eccentricity (∼100 k.y. and ∼405 k.y.; Laskar et al., 2004), which by the ca. 1.4 Ga age of our strata, are thought to have been faster at ∼14 k.y. (precession) and ∼23 k.y. (obliquity; Fig. S2; Berger and Loutre, 1994). Eccentricity (short and long) is thought to be essentially stable through geologic time (Laskar et al., 2004), and therefore it represents a critical chronometer to identify in deep time cyclostratigraphy. The sediment accumulation rate that yielded the smallest net misfit between observed and theoretical target cycles was selected, similar to the “average spectral misfit” method (Meyers and Sageman, 2007).

RESULTS

Numerous cycles of statistical significance emerged from our study of the Velkerri Formation, and reasonable correlation to orbital cycles was possible. In fact, the Velkerri Formation yielded all known Milankovitch cycles, including precession, obliquity, and both short and long eccentricity (Fig. 2). Only the long-term 1.2 and 2.4 m.y. modulations of obliquity and eccentricity, respectively, were not identified, but these cycles are too long to resolve given the length of our record. The net spectral misfit of Velkerri cycles when compared to theoretical orbital cycles was ∼1 k.y. (Fig. 2). This estimate excluded the long eccentricity cycle, which, although identified, had a poorly resolved wavelength, since only two of the long cycles were present given the length of the record. We note that of the two obliquity bands identified, the longer cycle exhibited more spectral power.

Figure 2. Time-series analysis of the Velkerri Formation (TarleeS3 core; McArthur Basin, Australia, 15°37'56.74461''S, 132°49'33.53895''E). (Top) Fast-Fourier transform (FFT) results. Inset compares observed cycles to predicted bandwidths for orbital cycles at this age (Fig. S2 [see footnote 1]). (Bottom) Band-pass filters of significant cycles identified with FFT. See Figure S2 for raw data.
Despite the theoretical expectation that it should be weaker. Nonetheless, there is precedent in younger rocks for strong power in the longer obliquity band, which may relate to the way in which the forcing is rectified as environmental change under similarly euxinic conditions (Mitchell et al., 2008).

The sediment accumulation rate implied by this orbital correlation (4 cm k.y. \(^{-1}\)) is very close to the more reasonable maximum constraint (3.17 cm k.y. \(^{-1}\)) from Re-Os geochronology (Kendall et al., 2009), particularly when those constraints would be wider if the \(^{187}\)Re decay constant were included in the age uncertainties. Furthermore, the rate is faster than that of the thinner Xiamaling Formation (Zhang et al., 2015). Regularity of cyclicity through the section of all cycles identified suggests we cannot refute the null hypothesis of broadly constant sedimentation.

The Velkerri magnetic susceptibility data passed perhaps one of the most diagnostic tests for orbital forcing: precession modulated by eccentricity. Due to its effect on Earth’s equinoxes, eccentricity affects insolation largely due to its amplitude modulation of precession. Thus, the eccentricity signal is usually extracted from the amplitude modulation of the precession signal (Mitchell et al., 2008). Indeed, the bandpass filter covering the eccentricity band (both short and long eccentricity) closely resembles the amplitude modulation of the band-pass filter of the presumed precessional signal (Fig. 2). In summary, we found that the origin of magnetic susceptibility cycles in the Velkerri Formation are best explained by orbital forcing based on: (1) the close matches with all Milankovitch cycles and modulations when assuming sediment accumulation rates consistent with independent geochronology; (2) the reasonable implied sediment accumulation rate; and (3) the striking evidence for eccentricity-modulated precession.

Thermal susceptibility experiments revealed the formation of magnetic minerals during heating with peaks of 300–400 °C and ~450–580 °C, which we interpret as magnetite/titanomagnetite and siderite, respectively (Fig. S4). Cooling indicated the presence of pure magnetite and, potentially, iron sulfides unblocking at ~320 °C. These observations imply that variability in detrital magnetite in these clastic sediments due to changes in climate and weathering patterns is therefore the most likely mechanism for recording orbital forcing, which is consistent with sedimentological observations of varying proportions of silt and organic matter (Fig. 1C). Additionally, iron sulfides are also consistent with euxinic oceanographic conditions.

**DISCUSSION**

Our Velkerri Formation results suggest the promise of astrochronology as a tool for analyses in the McArthur Basin specifically and more generally highlight its potentially powerful application in Proterozoic successions worldwide. The coeval and similarly organic-rich and euxinic Xiamaling Formation of North China suggests these units are potentially correlative (Fig. 1) and together record widespread euxinia. Since both the Xiamaling Formation and the Velkerri Formation have been studied cyclostratigraphically and have astrochronologic age models, we tested whether their euxinic intervals represent the same duration, supporting stratigraphic correlation. Two high-resolution, organic carbon–rich, euxinic core records of the entire middle Velkerri Formation are assumed to have similar sedimentation rates as the core studied here. Stratigraphic thicknesses were converted to time using sedimentation rates of 5 m m.y. \(^{-1}\) (Xiamaling) and 40 m m.y. \(^{-1}\) (Velkerri), and then the Velkerri euxinic intervals were shifted within Re-Os absolute age uncertainty to best match the well-dated Xiamaling euxinic interval. A coherent ~10-m.y.-long (7–12.5 m.y. from range of individual cores) peak in TOC burial and euxinia is apparent in both areas (Fig. 3B). The supposition that Australia and North China were neighbors in Mesoproterozoic time is thus consistent with our data, independently corroborating previous correlation of the coeval Derim Derim and Yanliao dolerite complexes (Fig. 1; Zhang et al., 2017), as well as previous paleogeographic reconstruction of the two continents (Fig. 3A; Ding et al., 2020).}

Cox et al. (2016) noted that the protracted period of peak organic carbon burial and euxinia was likely due to tectonic forcing and enhanced nutrient supply rather than eustasy. Both astrochronologic age models in Australia and North China, corroborated by precise U-Pb ages in the latter, confirm a long~10 m.y. duration for peak organic carbon burial and euxinia that cannot be explained by Milankovitch-driven eustasy. Most continents were close to the equator due to the equatorial position of supercontinent Nuna at that time (Fig. 3A; Evans and Mitchell, 2011; Ding et al., 2020). Thus, the peaking of organic carbon burial and the oceanic euxinic event at this age can be explained by the increased continental weathering and sediment accumulation rates in the tropics. Longer than most eustatic changes, the ~10-m.y.-long euxinic event was likely controlled by tectonic and geodynamic drivers (e.g., true polar wander that could move continents in and out of the tropics in such a time scale). The occurrence of synchronous euxinia on different continental margins and thus an “oceanic euxinic event,” i.e., a period of euxinia and enhanced organic carbon burial, on a potentially more global scale can be tested by future studies in basins beyond the Gulf of Nuna.
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