



## Sedimentology, chemostratigraphy, and stromatolites of lower Paleoproterozoic carbonates, Turee Creek Group, Western Australia

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### ABSTRACT

The ca. 2.45–2.22 Ga Turee Creek Group, Western Australia, contains carbonate-rich horizons that post-date earliest Proterozoic iron formations, bracket both Paleoproterozoic glaciogenic beds and the onset of the Great Oxidation Event (GOE), and predate ca. 2.2–2.05 Ga Lomagundi-Jatuli C-isotopic excursion(s). As such, Turee Creek carbonate strata provide an opportunity to characterize early Paleoproterozoic carbonate sedimentation and carbon cycle dynamics in the context of significant global change. Here, we report on the stratigraphy, sedimentology, petrology, carbon isotope chemostratigraphy, and stromatolite development for carbonate-rich successions within the pre-glacial part of the Kungarra Formation and the postglacial Kazput Formation.

Kungarra carbonate units largely occur as laterally discontinuous beds within a thick, predominantly siliciclastic shelf deposit. While this succession contains thin microbialite horizons, most carbonates consist of patchy calcite overgrowths within a siliciclastic matrix. C-isotopic values show marked variation along a single horizon and even within hand samples, reflecting spatially and temporally variable mixing between dissolved inorganic carbon in seawater and isotopically light inorganic carbon generated via syn- and post-depositional remineralization of organic matter.

In contrast, the Kazput carbonates consist of subtidal stromatolites, grainstones, and micrites deposited on a mixed carbonate–siliciclastic shelf. These carbonates exhibit moderate  $\delta^{13}\text{C}$  values of  $-2\%$  to  $+1.5\%$  and likely preserve a C-isotopic signature of seawater. Kazput carbonates, thus, provide some of the best available evidence that an interval of unexceptional C-isotopic values separates the Lomagundi-Jatuli C-isotopic excursion(s) from the initiation of the GOE as inferred from multiple sulfur isotopes (loss of mass independent fractionation). The Kazput Formation also contains unusual, m-scale stromatolitic buildups, which are composed of sub-mm laminae and discontinuous, convex upward lenticular precipitates up to a few mm in maximum thickness. Laminae, interpreted as microbial mat layers, contain quartz and clay minerals as well as calcite, whereas precipitate lenses consist of interlocking calcite anhedral, sometimes showing faint mm-scale banding. These cements formed either as infillings of primary voids formed by

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gas emission within penecontemporaneously lithified mats, or as local seafloor precipitates that formed on, or within, surface mats. It is possible that both mechanisms interacted to form the unique Kazput stromatolites. These microbialites speak to a distinctive interaction between life and environment early in the Paleoproterozoic Era.

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## 1. Introduction

Lower Paleoproterozoic sedimentary rocks record a number of first-order changes in the Earth system, including globally extensive ice sheets, one or more extreme states of the carbon cycle characterized by uniquely high  $\delta^{13}\text{C}$  in carbonates, and the initial accumulation of oxygen in the atmosphere and surface oceans (Akin et al., 2013; Asael et al., 2013; Bekker and Holland, 2012; Bekker et al., 2004, 2013; Farquhar et al., 2000; Fralick et al., 2011; Hoffman, 2013; Konhauser et al., 2011; Lyons et al., 2012, 2014; Melezhik and Fallick, 2010; Partin et al., 2013; Planavsky et al., 2012, 2014; Pufahl and Hiatt, 2012; Pufahl et al., 2010, 2011; Reinhard et al., 2013; Scott et al., 2014; Swanner et al., 2014; and references therein). Co-occurring global glaciation, carbon isotopic variation, and redox change also characterize Neoproterozoic rocks, and for this younger interval, carbonate strata have played an important role in both recording key events and providing context for the interpretation of these events (e.g., Halverson and Shields-Zhou, 2011; Johnston et al., 2012). Detailed analyses of platform and shelf carbonates are available for Neoproterozoic successions [e.g., the Campbellrand/Malmani subgroups of the Transvaal Supergroup, South Africa; (Knoll and Beukes, 2009; and references therein)] and younger Paleoproterozoic rocks (e.g., 2 Ga platform carbonates of the Slave Province, Canada; (Hotinski et al., 2004)). To date, however, relatively few studies have focused on lower Paleoproterozoic carbonates, despite their potential importance in understanding early Paleoproterozoic evolution and environmental change.

The ca. 2.45–2.22 Ga Turee Creek Group, exposed in the Hamersley Range of Western Australia, conformably overlies earliest Paleoproterozoic iron formations, predates the ca. 2.2 Ga onset of the Lomagundi-Jatuli C-isotopic excursion(s), and hosts carbonate and glacially-influenced strata that record onset of the Great Oxidation Event (GOE) (Bekker et al., 2004; Martin et al., 2013; Van Kranendonk and Mazumder, 2015). Thus, these carbonates provide an opportunity to characterize the response of early Paleoproterozoic carbonate deposition and carbon cycle dynamics to significant global change, including the GOE and glaciation. Here, we report on the stratigraphy, sedimentology, carbonate petrology, carbon isotope chemostratigraphy, and stromatolite development in two closely spaced sections of the Kazput Formation of the upper Turee Creek Group. We also report lithological and isotopic data from three parallel stratigraphic sections from the older Kungarra Formation of the lower Turee Creek Group. Together, these data place carbonate strata of the Turee Creek Group in the context of profound global change following the early oxygenation of Earth's surface environments.

## 2. Geologic setting

The Turee Creek Group of the Mount Bruce Supergroup is the youngest sedimentary succession within the Hamersley Basin of the Pilbara Craton (Trendall, 1990). Turee Creek Group rocks conformably overlie iron formations of the Hamersley Group and sit unconformably beneath sedimentary and volcanic deposits of the Wyloo Group (Fig. 1) (Horwitz, 1982; Thorne, 1990; Thorne and Seymour, 1991; Trendall, 1969; Trendall et al., 1983). Initial research suggested conformable relationships throughout the Proterozoic stratigraphy of Western Australia (e.g., Trendall

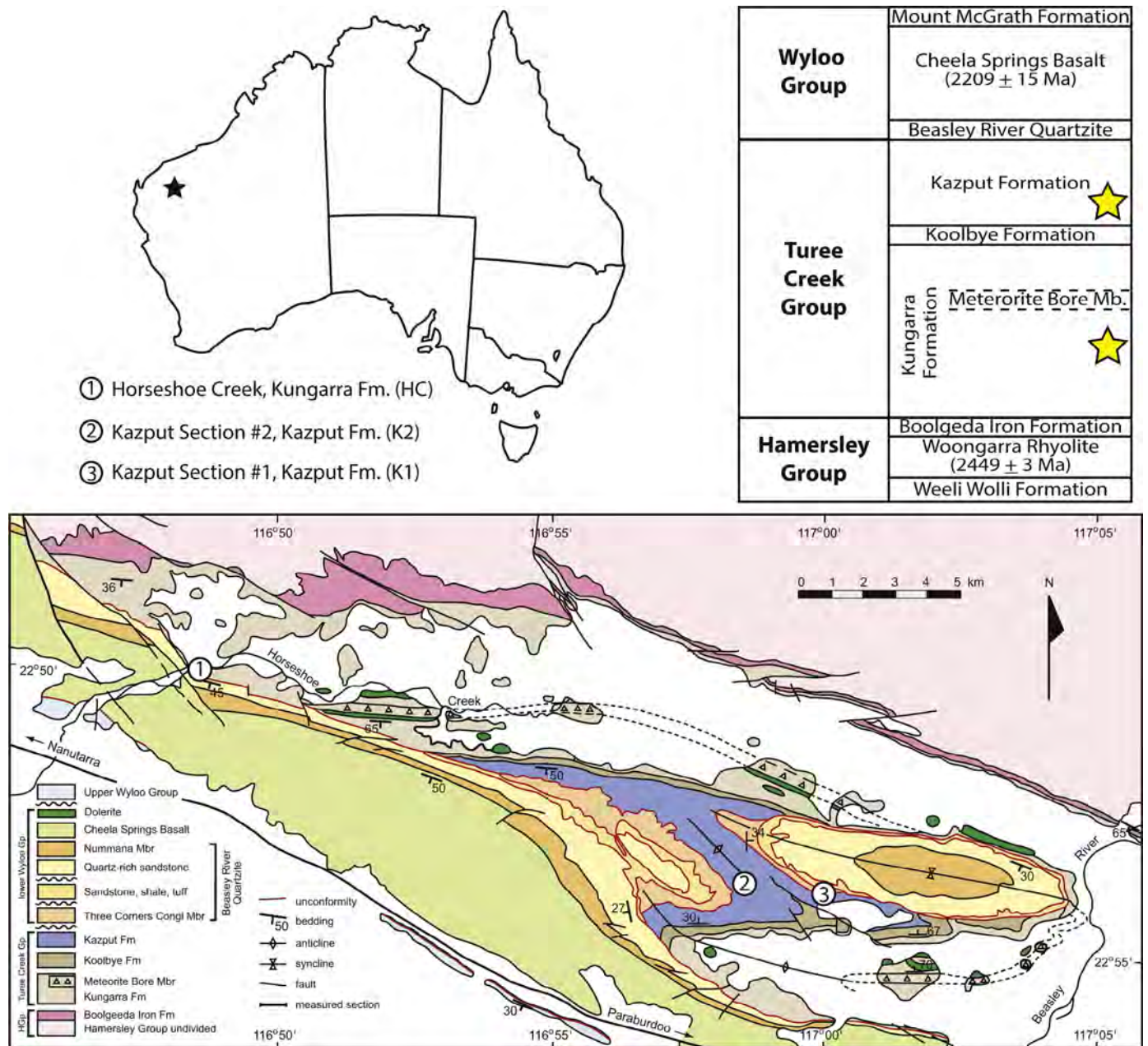
and Blockley, 1970), but continuing stratigraphic and geochronological studies have since identified significant unconformities and deformational events that point to a protracted, but episodic, depositional history spanning more than 330 Myr (Martin et al., 2000; and references therein).

Palinspastic reconstructions and basin analysis of upper Hamersley Basin and lower Wyloo Group stratigraphy led Horwitz (1982) to propose a post-Hamersley depositional feature, called the McGrath Trough, that reflects flexural subsidence driven by peripheral or retroarc foreland basin development (Horwitz, 1982; Krapež, 1996; Martin, 1999; Martin et al., 2000; Powell and Horwitz, 1994). The foreland-related tectonostratigraphic sequence most likely involves the Turee Creek and lower Wyloo groups (Martin et al., 2000); however, some authors have argued that it only involves the Turee Creek Group (e.g., Blake and Barley, 1992; Krapež, 1996) or both the Turee Creek and entire Wyloo groups (e.g., Thorne and Seymour, 1991; Tyler and Thorne, 1990). More recently, Van Kranendonk et al. (2015) suggested the Turee Creek Group was deposited in an intracratonic basin. Regardless of McGrath dynamics, the 3–4 km thick Turee Creek Group records rapid lateral facies change (e.g., Martin et al., 2000 and references therein).

The Turee Creek Group consists, in stratigraphic order, of the Kungarra (including the glaciogenic Meteorite Bore Member), Koolbye, and Kazput Formations (Fig. 1) (Thorne et al., 1995; Trendall, 1979, 1981). It is bracketed in age by the  $2449 \pm 3$  Ma Woongarra Rhyolite (Barley et al., 1997) near the top of the underlying Hamersley Group and the  $2209 \pm 15$  Ma Cheela Springs Basalt (Martin et al., 1998) low in the unconformably overlying Wyloo Group succession (Fig. 1). Müller et al. (2005) reinterpreted the Cheela Springs date as a reflection of provenance rather than crystallization age, but their U–Pb age on baddeleyite of  $2208 \pm 15$  Ma for diorite sills that cut the Turee Creek Group provides an essentially indistinguishable minimum age constraint. The Kungarra Formation of the Turee Creek Group is further constrained to be younger than ca. 2420 Ma, based on U–Pb ages of detrital zircons in the Meteorite Bore Member (Takehara et al., 2010). Turee Creek Group strata record a broad shallowing-upward profile from deep-water banded iron formation (the Boolgeeda Iron Formation of the underlying Hamersley Group), through fine-grained siliciclastic deposits of the Kungarra Formation, to fluvial and shallow marine strata of the Koolbye and Kazput Formations.

Although detailed correlation with other Paleoproterozoic successions is challenging, Turee Creek Group strata record two events that guide interbasinal correlation. First, Williford et al. (2011) documented mass independent sulfur isotope fractionation, a proxy for the near-absence of environmental oxygen (Farquhar et al., 2000), in the lower part of the Meteorite Bore Member of the Kungarra Formation. On this basis, the authors suggested that the lower glaciogenic unit of the Meteorite Bore Member, locally in contact with the Boolgeeda Iron Formation, was deposited during the final stages of the GOE, when oxygen levels were still low enough for the development of MIF-S, but sufficiently high for oxidative weathering of continental sulfides and significant sulfur isotope fractionation.

The glacial character of the Meteorite Bore Member and a second recently discovered unit of glacial diamictite in the Kungarra Formation provide a means of correlation to other Paleoproterozoic



**Fig. 1.** Geographic, stratigraphic, and geological location of the studied sections. Upper left: location of study area in Australia (star). Upper right: stratigraphic context for the Turee Creek Group; stars indicate stratigraphic horizons of studied sections. Bottom: geological map of the Hardey Syncline from [Martin et al. \(2000\)](#); numbered circles indicate studied localities.

basins ([Martin, 1999](#); [Trendall, 1976](#); [Van Kranendonk and Mazumder, 2015](#)). [Martin \(1999\)](#) and [Van Kranendonk et al. \(2012\)](#) pointed to analogous basin histories of the South African Transvaal Supergroup and the Canadian Huronian Supergroup on the basis of similar ca. 2.45 Ga felsic magmatic events followed by glacial episodes and mafic magmatism at ca. 2.2 Ga. [Hoffman \(2013\)](#) suggested a similar global correlation scheme based on the assumption that the GOE, as marked by the disappearance of MIF-S, was a unique event connected in time to a Snowball Earth event ([Kirschvink et al., 2000](#)). By this reasoning, disparate sedimentary rocks may be correlated by a single tie point, even though some regions record three glacial events and others only record two. Thus, while it is difficult to assign an exact age to the Turee Creek Group, the glacial history of these strata generally enables broad correlation to the timing of the Great Oxidation Event ([Van Kranendonk and Mazumder, 2015](#)).

### 3. Methods

Fieldwork for this project was conducted as part of the 2012 Advanced Geobiology Course sponsored by the Agouron Institute. Five stratigraphic sections were measured and sampled from three sites in the Hardey Syncline: the Horseshoe Creek locality of [Lindsay and Brasier \(2002\)](#) (Fig. 1, three sections at site 1) and two Kazput Formation localities, K1 and K2, on the southwest and northeast limbs of a small NNW-SSE-trending anticline in the central part of the Syncline (Fig. 1, sites 2 and 3). The Horseshoe Creek strata were previously described by [Lindsay and Brasier \(2002\)](#) as Kazput Formation, but regional mapping places this section below the Meteorite Bore Member and is thus part of the Kungarra Formation (Fig. 1) ([Martin et al., 2000](#); [Van Kranendonk, 2010](#); [Van Kranendonk et al., 2015](#)).



At Horseshoe Creek, three parallel stratigraphic columns were measured through ~120 m of the Kungarra Formation to determine patterns of lateral facies change and geochemical variation (HC1, HC2, and HC3). The first Kazput section was measured through roughly 140 m of sedimentary rocks on the west-southwestern limb of the anticline (locality K1), and the second section is a composite stratigraphic column measured across two ridges (roughly 100 m apart) on the southwestern limb of the anticline (localities K2A, K2B, and K2C). Although the K1 and K2 localities are within a few kilometers of each other, their exact correlation is uncertain due to differing facies development and structural complications.

Rock samples were collected from each measured section at roughly 1–3 m intervals for geochemical and petrological analysis; samples were cut using a diamond saw, and made into thin sections for petrographic analysis. Thin section blanks were then micro-drilled following methods of Kaufman et al. (1990) to obtain fresh powder. Blanks were commonly drilled several times if multiple lithologies or microfacies were present in a single thin section.

Carbonate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for 225 Kazput and 125 Kungarra samples were measured on a VG Optima dual inlet mass spectrometer fed by an Isocarb preparation device in the Harvard University Laboratory for Geochemical Oceanography (see supplementary data). Approximately 1 mg of carbonate powder was dissolved in a common anhydrous phosphoric acid ( $\text{H}_3\text{PO}_4$ ) bath kept at 90 °C for eight minutes. Carbon dioxide gas was purified cryogenically and measured against an in-house reference gas. No dolomite corrections were applied to the data. Analytical uncertainty was  $\pm 0.1\%$  (sample:standard ratio of 8:1); results are reported on a Vienna Pee Dee Belemnite scale.

Two samples were additionally analyzed using a scanning electron microscope (SEM) with an attached electron dispersive spectrometer (EDS). These small-scale analyses are employed to visualize and compare textures of the two carbonates, as well as to provide a high-resolution map of the stromatolitic laminae from the Kazput Formation. A representative sample from the Kungarra Formation (from 16.25 m in section HC3) and a stromatolite from the Kazput Formation (KAZS1), were photographed using backscatter detector imaging to highlight compositional contrasts on a Zeiss 1550VP Field Emission SEM in the California Institute of Technology Geological and Planetary Sciences Division Analytical Facility. An Oxford INCA Energy 300 EDS system was utilized to produce elemental color maps of key elements [Si, Ca, C, Fe, Al, Mg] and these maps were superimposed on backscatter images to highlight different minerals. Elemental analyses have relative accuracy of better than 5%.

## 4. Results: sedimentology, facies analysis, and petrography

### 4.1. Kungarra Formation at Horseshoe Creek

Three parallel stratigraphic sections (HC1, HC2, and HC3) were measured from the Horseshoe Creek locality; as these sections were only a few hundred meters apart they are shown as a composite section in Fig. 2. The lower ~73.5 m consists of variably exposed, monotonous gray-green siltstone and shale with occasional thin (<10 cm) lenticular or planar beds of very fine- to fine-grained quartz-rich lithic arenites. These sandstone intervals are locally erosive and host parallel-lamination or occasional very fine ripple cross-lamination with abundant shale partings. Some of the more massive siltstone intervals are locally interspersed with starved ripples of very-fine grained sandstone, but many of the sedimentary structures in the siltstones are masked by a pervasive penetrative cleavage.

Numerous discontinuous limestone-bearing beds, 3–70 cm thick, occur sporadically within the massive siltstone and shale

units. Many of these carbonate beds are broadly nodular or irregular in geometry and locally grade into pure siltstone, both vertically and laterally. Some carbonate-rich horizons essentially mimic starved ripples and other sedimentary structures characteristic of surrounding siliciclastic beds (Fig. 3A), consistent with post-depositional diagenetic carbonate precipitation. A diagenetic origin for these discontinuous layers is also supported by petrographic observations and microscale SEM-EDS mapping (Figs. 3C and 4). For example, evidence for diagenetic carbonate emplacement includes both the restriction of these Kungarra carbonates to lenses and thin layers intermixed with detrital grains (Figs. 3C and 4) and the distribution within these lenses of patchy carbonate in overgrowth and cement-filling textures within a matrix of silt-sized quartz grains, clay minerals, and rare other silicates (Figs. 3C and 4). Fig. 4 shows a representative carbonate layer (green) that includes many detrital silicate grains (orange). A diagenetic origin for many Kungarra carbonates is consistent with major element abundances reported by Lindsay and Brasier (2002); on average, Ca and Mg together make up less than 15% by weight of sampled lithologies, requiring that carbonates are a subordinate component of the samples.

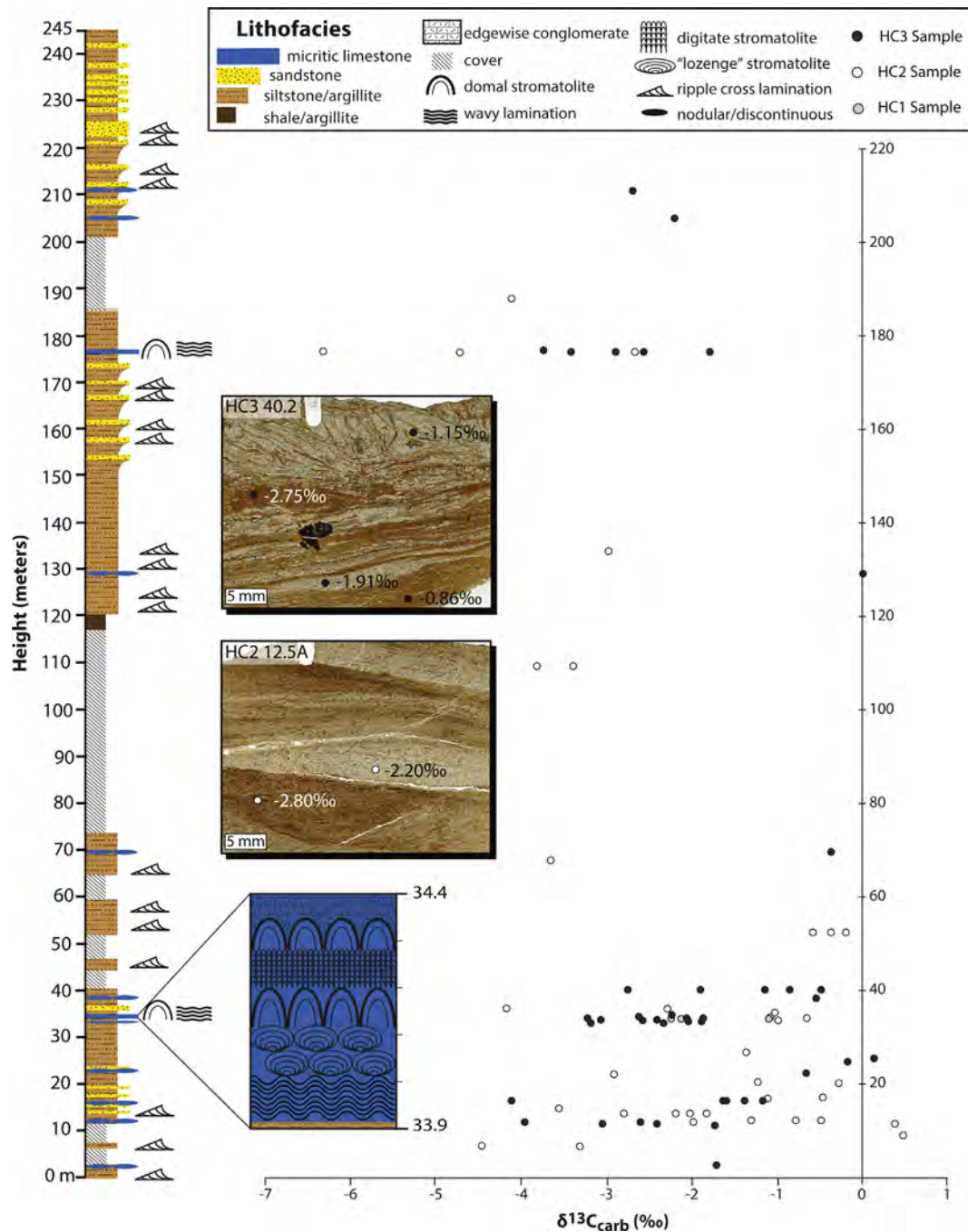
A few limestone beds from the Kungarra Formation are more continuous, relatively pure, and either irregularly laminated or clearly stromatolitic. In particular, a distinct stromatolite unit occurs from ~33.9 to 34.4 m in section HC3, which progresses from ~10 cm of brown-yellow-colored irregular crinkly lamination with interstitial micrite fill into ~25 cm of discrete ~70 cm wide elongate stromatolites. These structures are draped by peach-colored dolomicrite and transition into two distinct layers of brownish-white ~15–30 cm thick domal stromatolites (Fig. 3B) separated by a horizon of 1–4 cm wide and ~10 cm tall, high-inheritance digitate stromatolites. The upper 2–5 cm of the stromatolitic interval is irregular, with local rip-up clasts. Laterally, this stromatolitic interval becomes poorly developed; at section HC2, only the irregular carbonate laminae and small domal stromatolites occur (Fig. 3B), and at section HC1 this unit becomes indistinguishable from other thin carbonate units. The only other location in this section with similar stromatolitic features occurs at ~176 m; however, this microbial unit is poorly developed and much thinner (~10 cm). Unlike the carbonate overgrowths in the siltstone units, these carbonate units were likely primary (although they have since been recrystallized). Thus the carbonate-rich units at Horseshoe Creek reflect both original carbonate sediments as well as later carbonate overgrowths of siliciclastics.

The upper ~172 m of the Horseshoe Creek section broadly coarsens upwards into a siliciclastic succession dominated by very fine- to fine-grained sandstone. These strata generally transition from green-gray siltstone and argillite with abundant starved ripples, parallel lamination, ripple cross-lamination, and minor carbonate horizons into a succession dominated by very thin- to thin-bedded quartz-rich lithic arenite and sublitharenite with abundant shale partings. One can distinguish clear smaller-scale 1–5 m thick coarsening upwards packages of siltstone and shale into very-fine to fine-grained sandstone, which are superimposed on the broader coarsening upwards sequence on the formation scale.

### 4.2. Kazput Formation, NW Hardey Syncline

#### 4.2.1. Kazput Section #1 (K1)

The K1 section (Figs. 5A and 6) was measured on the NE-dipping flank of a NNW-SSE-striking anticline in the southeastern part of the Hardey Syncline (locality 3 on Fig. 1). The base of this section is covered by alluvium, so its relationship to the underlying Koolbye Formation is unclear. The section begins with a prominent bench of dark gray parallel-laminated limestone, about 1.5 m thick (Fig. 5B), that is overlain by ~6 m of

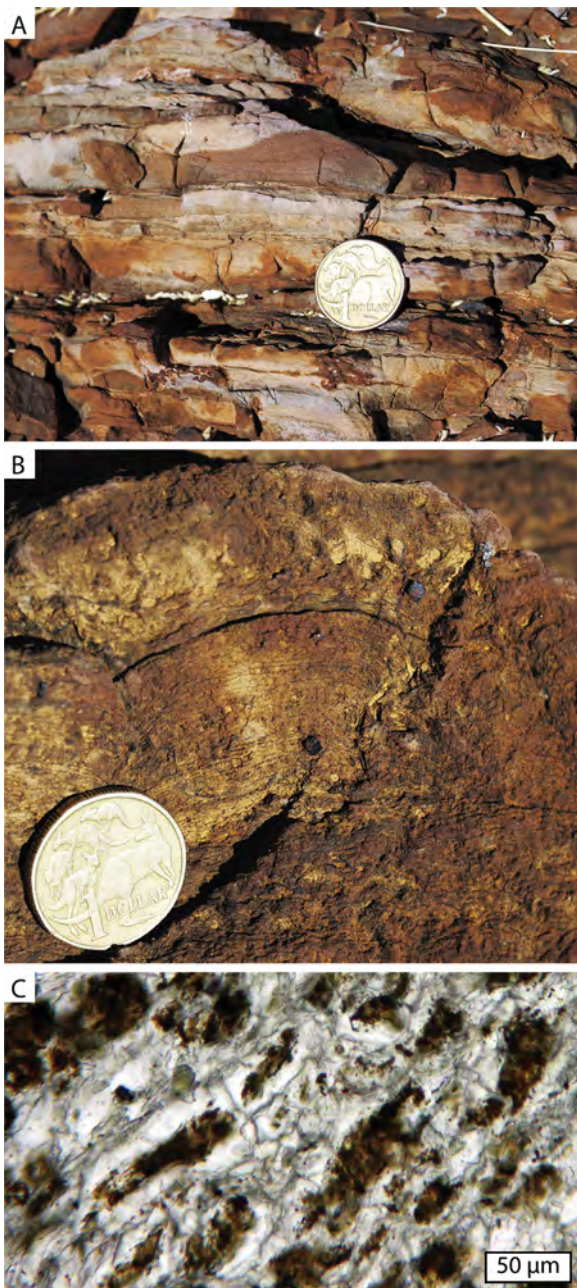


**Fig. 2.** Litho- and chemostratigraphy of the Kungarra Formation section at Horseshoe Creek (composite section of stratigraphic columns HC1, HC2, and HC3). The stratigraphic interval between 33.9 m and 34.4 m has been enlarged to show the succession of stromatolitic textures (interpreted to be of microbial origin). Inset images are photomicrographs (plane polarized light) of the Kungarra carbonates; sample HC2 12.5A is from 13.8 m and HC3 40.2 is from 40.2 m. Dots in inset images indicate microsampling locations and their carbon isotope values.

sandy limestone with evidence for soft-sediment deformation. The carbonate strata become increasingly sand-rich and dolomitic upsection until, by ~16.5 m, they are dominated by medium-bedded brown dolomitic sandstone. The outcrop then disappears into cover for ~30 m, but thin-bedded, often calcareous, sandstone horizons are occasionally visible in subcrop (Fig. 5A). Continuous outcrop reappears at 52.5 m, again consisting of interbedded finely laminated calcareous sandstone and brown dolograinstone. The overlying 30 m consists of brown-weathering (white on fresh surface), coarsely recrystallized dolomite with no visible sedimentary structures. At 86.8 m the recrystallization fabric disappears and dolostone displays crinkly lamination and roll-up structures

that resemble microbially influenced sedimentary structures. In addition, interbedded chert-replaced rip-ups and intraformational conglomerates occur with other indicators of traction load deposition, including ripple and trough cross-stratified dolograinstone, channelized grainstone, and thin channelized sandstone lenses (Fig. 5C). Starting at 116.7 m, the section becomes dominated by wavy laminated dolomite, with abundant pisoids and oncoids (up to a cm in diameter), and domal stromatolites up to 30–50 cm wide. A small fault cuts the section at ~127.5 m rendering thickness measurements of the uppermost part of the succession less reliable. At a minimum, an additional 10 m of small conical stromatolites, oncoids, and massive gray dolomite cap the section. Pervasive





**Fig. 3.** Kungarra Formation carbonates at Horseshoe Creek. (A) Pinkish-white micritic limestone interbedded with reddish-brown fine-grained sandstone forming starved ripples, Australian dollar for scale (25 mm diameter). (B) Close up of stromatolites from roughly 34.2 m in stratigraphic height, Australian dollar for scale. (C) Petrographic view of the domal stromatolite layer (sample HC3 34.3, 34.3 m in stratigraphic height), showing overgrowths of calcite on micritic carbonates stained by iron oxides (note scale bar). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

recrystallization of Kazput Formation carbonates dominates petrographic fabrics, but the interlocking calcite euhedra still preserve mm-scale features such as bedding lamination, coated grains, and ooids.

#### 4.2.2. Kazput Section #2 (K2)

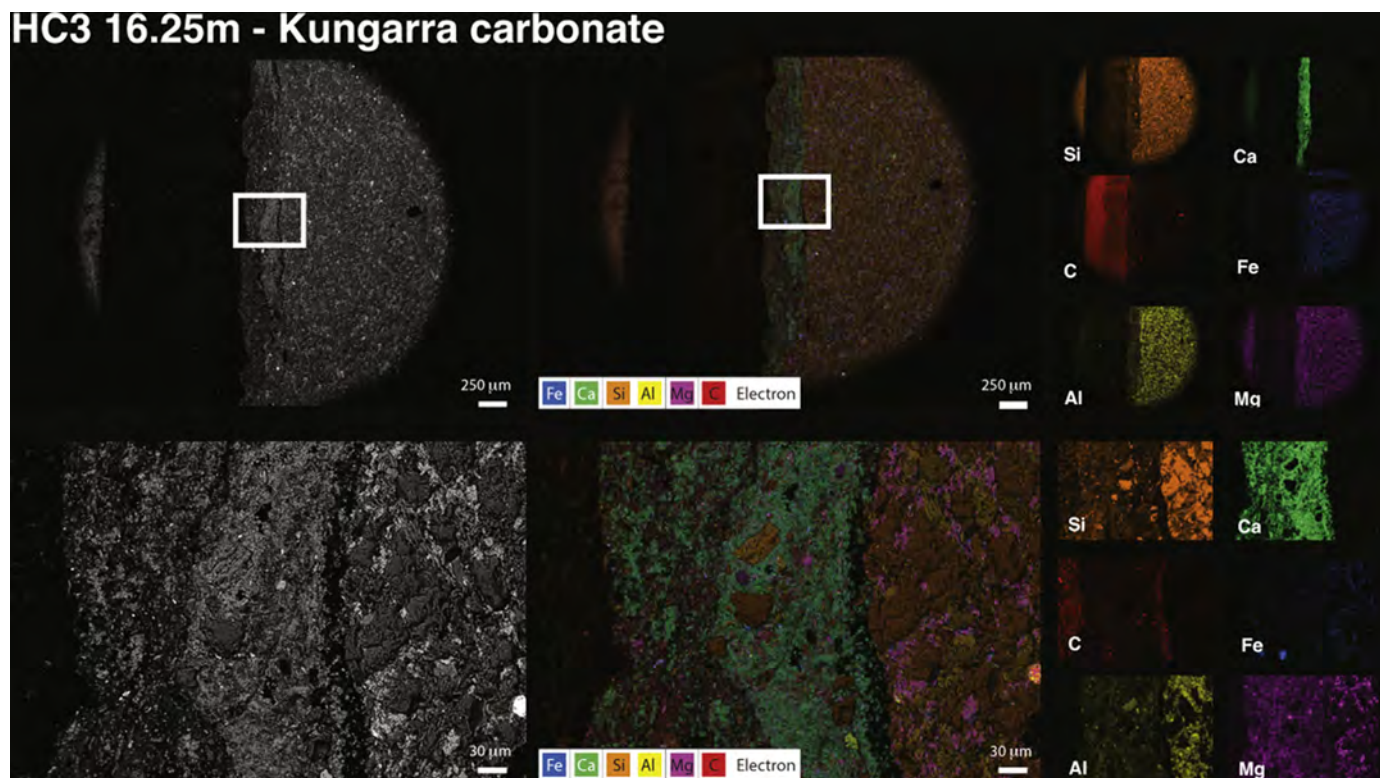
The K2 composite section (Figs. 7A, 8 and 9) was measured on the SW-dipping flank of the anticline in the central part of the Hardey Syncline (Locality 2 on Fig. 1). The K2 section includes two ridges (Fig. 7A) separated by a small valley filled by alluvial material

(likely the surficial expression of a fault), so the stratigraphy is represented herein as a composite section (K2A, K2A2, and K2B–K2C; Figs. 8 and 9).

The basal portion of section K2A (Fig. 8) consists of highly fractured and oxidized maroon and olive green siltstone and shale subcrop exposed in a small, south-flowing dry creek bed at the core of the anticline. Fine-grained deposits transition upsection into ~18 m of olive green to dark gray, parallel laminated to ripple cross-laminated micritic limestone with locally-abundant silt and very fine-grained quartz sand. The basal carbonate-rich strata are thinly bedded and record discrete mm- to cm-scale alternations between massive and laminated beds that resemble the discrete Bouma C–E subdivisions of distal turbidites. The central ~6 m of these more carbonate-rich strata are dominated by pure olive green siltstone with minor detrital carbonate, and the upper 5–6 m of these strata record the local development of hummocky cross-stratification and occasional stoss-preservational ripple cross-lamination in the silty limestone deposits. The upper ~45 m of section K2A consists of a broad coarsening-upwards package of olive green to dark gray siltstone and argillite and minor thin-bedded light brown very-fine- to fine-grained quartz sandstone (Fig. 7B). The sandstone beds generally display evidence for subtle scouring of underlying siltstone and argillite intervals and the units are dominated by hummocky and swaley cross-stratification. Sedimentary structures in the siltstone and argillite strata are difficult to discern due to a pervasive penetrative cleavage, but they occasionally contain thin (<5 cm thick) stringers of nodular and planar micritic limestone. The silica- and carbonate-cemented sandstones of the Kazput Formation can generally be classified as quartz-rich sublitharenites (Martin et al., 2000), but they are mostly dominated by moderately sorted and subrounded to angular monocrystalline quartz sand with minor lithics, chert, and a pervasive chloritic matrix.

Since the upper part of section K2A was exposed on a prominent dip slope that projected into a small, faulted alluvial valley, a parallel section was measured to the northwest on the other side of the structure, section K2A2 (Fig. 8). A ~6 m thick package of pure olive green siltstone was used to trace the section over the projected small fault horizon. This section begins with ~17 m of dark gray-green siltstone and argillite that progressively becomes increasingly carbonate rich. Thin (2–3 cm thick) stringers of nodular to stratiform, silty micritic limestone thicken upsection into parallel-laminated and ripple cross-laminated beds up to 10 cm thick. These silty limestone deposits are abruptly overlain by ~4 m of peach-orange to blue-gray-colored fine-grained dolostone with abundant ripple cross-lamination and minor detrital silt and quartz sand. Locally, there are thin (<20 cm) horizons with irregular and wavy lamination that resemble microbial carbonates. The upper portion of this small section becomes heavily dolomitized, although there are multiple horizons with crenulated or wavy laminae and intervals of detrital silt and quartz sand that form discrete lenses and stringers within the carbonate laminae. A massive, light bluish-gray colored dolostone horizon was used to trace this section over to section K2B.

Section K2B forms the base of a large hill and K2B/C comprises over 65 m of interbedded carbonate and siliciclastic deposits with some evidence for synsedimentary slumping and faulting (Figs. 7A, D and 9). The lowermost 21 m of K2B strata are composed of silty to fine-grained sandy limestone with mm-scale parallel lamination, ripple cross-lamination, and low-angle bedding truncations (Fig. 7B) interbedded with two carbonate-dominated units: (a) fine-grained micritic limestones with wavy laminae, crenulated laminae, and small slumps from syn-sedimentary faults; and (b) finely-laminated silty to sandy carbonates with low angle hummocky and swaley cross stratification (Fig. 7C). The wavy laminated carbonates often form thin (up to a few cm) stromatolites, which can follow relict topography (Fig. 10B) or become contorted,



**Fig. 4.** Elemental map of Kungarra Formation limestone (sample HC3 16.25 from 16.25 m in stratigraphic height); top images are the entire sample, and the bottom images are close up views of the boxed area. On the left are SEM images, on the right are false color representations of the elemental maps, and the middle images are a composite image of the SEM images and elemental maps. Note that the calcium (calcite) only manifests in rare lenses with abundant detrital minerals, suggesting that it is not primary carbonate but rather diagenetic. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

folded, or faulted (syn-sedimentary). These cm-scale stromatolite layers become thicker and well developed higher in the section. Above the interbedded silty and stromatolitic carbonates is a thick (~15 m) interval of well-sorted, fine- to medium-grained sandstone, in decimeter-scale beds with ripple and hummocky cross-stratification.

A similar succession of silty and stromatolitic carbonates capped by thick sandstone occurs again in the K2C section; however, the internal structure of the silty carbonate is more massive than those lower in the section. Higher in the section (around 45 m), the stromatolitic units develop into thick, well-defined, meter-scale stromatolite domes (Fig. 10). These large stromatolites are commonly contorted and occasionally cut by neptunian dykes (e.g. Fig. 10E). Interbedded with and above the large stromatolitic domes are wave-rippled and hummocky cross-stratified silty sandstones. Beds are often amalgamated, making bedding thickness difficult to discern. A further silty sandstone at the top of the section is distinguished by carbonate intraclasts one centimeter to several meters in length and typically rounded or tabular in shape (Fig. 9). The clasts consist of stromatolites and other carbonate lithologies observed lower in the section, as well as recrystallized oolitic grainstones that broadly link the two measured Kazput sections.

## 5. Results: carbon isotope chemostratigraphy

### 5.1. Kungarra carbonates

Lindsay and Brasier (2002) reported carbon isotopic abundances for 22 carbonate samples distributed through an estimated 250 m of stratigraphy at Horseshoe Creek, reported as Kazput Formation but now known to belong to the Kungarra Formation. Their  $\delta^{13}\text{C}$

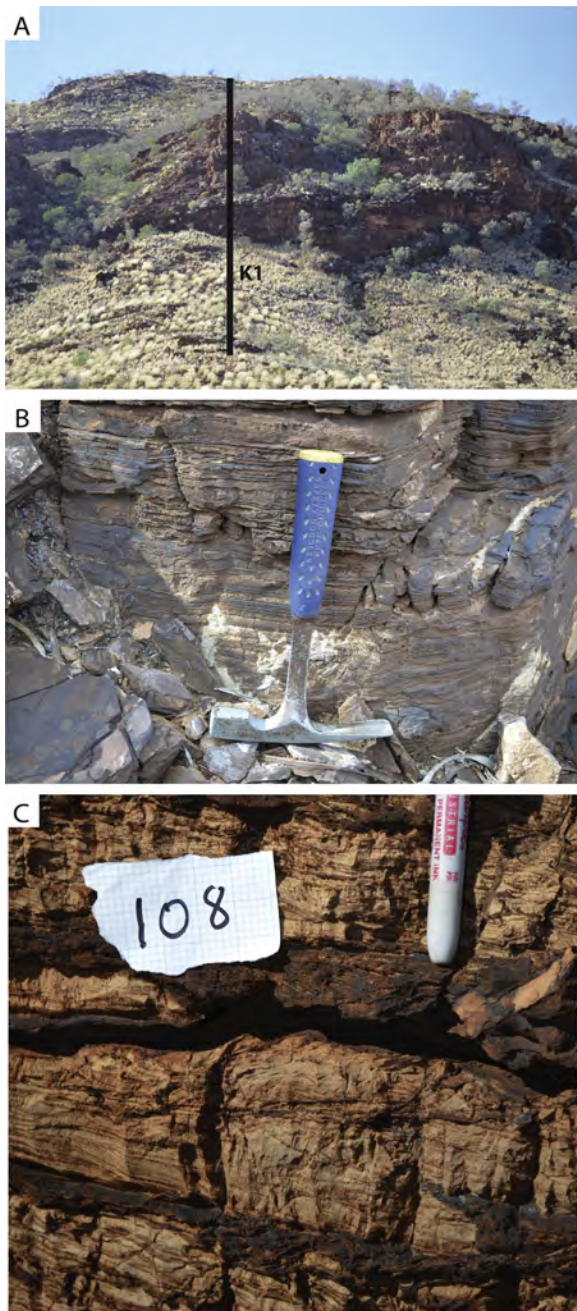
values ranged from  $-6$  to  $+2$ ‰, varying in sawtooth fashion through the reported section. Our larger sample set ( $n = 125$ ) is consistent with measurements by Lindsay and Brasier (2002);  $\delta^{13}\text{C}$  values for Kungarra carbonates at Horseshoe Creek exhibit a wide range of isotopic values, from  $-6.3$ ‰ to  $+0.5$ ‰, with no strong stratigraphic trend (Fig. 2). The  $\delta^{18}\text{O}$  values for the same samples range from  $-6.15$ ‰ to  $-1.61$ ‰, again with no strong trend (see supplemental data). In contrast to Lindsay and Brasier (2002), our denser sampling coverage across multiple spatial scales enables us to detect variations in the carbon isotope results of up to 2‰ between lighter (more carbonate) and darker (less carbonate) layers within a single hand sample, as much as 4‰ between samples from closely spaced sections at a single stratigraphic horizon, and equally strong variation between samples spaced stratigraphically only centimeters to a few meters apart (Fig. 2, supplemental data).

### 5.2. Kazput carbonates

All  $\delta^{13}\text{C}$  values measured for Kazput carbonates in the Hardey Syncline ( $n = 252$ ) fall between  $-4.5$ ‰ and  $+2$ ‰, and all but a stratigraphically constrained subset lie between  $-0.5$ ‰ and  $+1.5$ ‰ (Figs. 6, 8 and 9). These results are consistent with reconnaissance analyses by Bekker et al. (2002).  $\delta^{18}\text{O}$  values range from  $-8.13$ ‰ to  $-16.63$ ‰, with most values falling between  $-15.5$ ‰ and  $-16.5$ ‰ (see supplemental data).

At the base of section K1 (Fig. 6),  $\delta^{13}\text{C}_{\text{carb}}$  values are low (around  $-4$ ‰); whereas the last data point before the prominent covered interval is more moderate at  $0.7$ ‰. Above the covered interval,  $\delta^{13}\text{C}_{\text{carb}}$  values are again depleted ( $-3$ ‰) but quickly return to values between  $0$  and  $1$ ‰ for the remainder of the section (Fig. 6). The  $\delta^{13}\text{C}_{\text{carb}}$  signature of section K2 begins much like that of K1, with negative values ( $-2.5$ ‰ to  $-1.2$ ‰) in the lowermost 10 m





**Fig. 5.** Lithologies of the Kazput Formation in Hardey Syncline section K1. (A) Overview of stratigraphy, section K1 begins in the thin-bedded limestones in the foreground, the base of the cliff is at 53 m elevation in the stratigraphic column (Fig. 6), and the measured section continues up the gully on the left. (B) Close-up of thin-bedded limestones at the base of the K1 section, hammer for scale. (C) Cross-stratified grainstones with abundant bed-parallel silicification at meter 108 in the K1 section, Sharpie tip for scale.

(K2A, Fig. 8) followed by values that fluctuate around 0‰ (K2A and K2A2, Fig. 8). Higher in the section (K2B and K2C), C-isotopic values generally fluctuate between ca. 0.5 and 1.5‰, with a few more negative values interspersed through the sections (Fig. 9). Variations of up to 1‰ among carbonate intraclasts at the top of the section likely reflect the heterogeneous stratigraphic levels from which the intraclasts and carbonate blocks were sourced.

Petrographic subsampling of stromatolites at 46–47 m of K2C shows limited isotopic variation among microfacies, with stromatolitic carbonates slightly heavier than the carbonate-rich clastics

that overlie the stromatolites (Fig. 9). As might be predicted when ambient waters are strongly oversaturated with respect to calcite and aragonite (Bergmann et al., 2013), carbonates within stromatolites differ little from encompassing laminae in both their carbon and oxygen isotope values (Fig. 9). The analyzed Kazput carbonates do not record the extreme  $^{13}\text{C}$  enrichment that defines the younger Lomagundi-Jatuli event.

## 6. Results: Kazput stromatolites

The most notable sedimentary features of the Kazput carbonates are m-scale domal stromatolites in section K2B/C (Fig. 10). These stromatolites appear to have nucleated on erosional surfaces within underlying siliciclastic units and were, in turn, episodically buried by further influx of sands that locally display hummocky cross-stratification. The resulting microbialites can be as thin as a centimeter (Fig. 10B), suggesting only a limited time for accretion between inundation events, to as much as 1.5 m thick (Fig. 10A).

Two fabrics make up the Kazput stromatolites (see Section 7.3 for genetic interpretations): wavy to crenulated siliciclastic laminae, 30–400  $\mu\text{m}$  thick, that are continuous on the scale of a single dome, and interbedded, convex upward, lenticular carbonates that are generally discontinuous on a mm to cm-scale and are common or absent in alternating zones (Fig. 10). The discrete fabrics are clear in both optical microscopic view (Fig. 11) and in elemental maps using SEM (Fig. 12). Lamina-rich zones tend to be <1 cm to about 2 cm thick, whereas zones rich in lenticular carbonate vary from <1 cm to, more commonly, 10–15 cm thick. Because silicate laminae are more resistant to erosion than carbonate lenses, the broad mesoscale fabric of the stromatolites is best observed on weathered surfaces; lamina-rich zones are darker brown and more resistant, carbonate-rich zones are gray or lighter tan and more recessive (Fig. 10). For the most part, lenticular carbonates occur within 5–15 mm long convex-upward mini-domes bounded by laterally linked laminae that tend to be continuous across the surfaces on which they occur. In some layers, lenses extend laterally for several cm along bedding planes (Fig. 10D); however, these occurrences are rare. Most of the stromatolitic structures are irregular, and some show evidence of plastic deformation (folds and slumps). At a few horizons, however, more or less regular, laterally linked columns develop either locally (Fig. 10F) or across a stromatolitic dome surface (Fig. 10D); columns are 5–8 cm wide and 2–10 cm high.

At the microscopic scale, laminae contain an admixture of several minerals, including equant calcite anhedral, 10–25  $\mu\text{m}$  in maximum dimension; quartz silt; clay minerals (commonly chloritized, but also including Mg-rich species); and small opaque euhedra, probably originally diagenetic pyrite, but now altered to iron oxides (Figs. 11 and 12). While clays can form authigenically within microbialites (Konhauser and Urrutia, 1999; Léveillé et al., 2000) the presence of abundant fine-grained quartz grains and other detrital material indicates the incorporation of suspension load siliciclastics, even when traction load sands were absent. Organic carbon inclusions also occur sporadically throughout the K2 stromatolites; these appear as black spots on the composite elemental map or red spots on the carbon map in Fig. 12.

Lenticular units generally consist of interlocking calcite anhedral 25–100  $\mu\text{m}$  in maximum dimension. Pyrite, reduced carbon, and clay minerals also occur in these zones, although at low abundances (Fig. 12). The coarsely crystalline carbonates reflect pervasive diagenetic and/or metamorphic recrystallization, but mm-scale banding is preserved locally (Fig. 11C). Crystals are smaller in these banded carbonates, generally less than 25  $\mu\text{m}$ , and discrete zones are defined by both larger and smaller crystals (lighter and darker



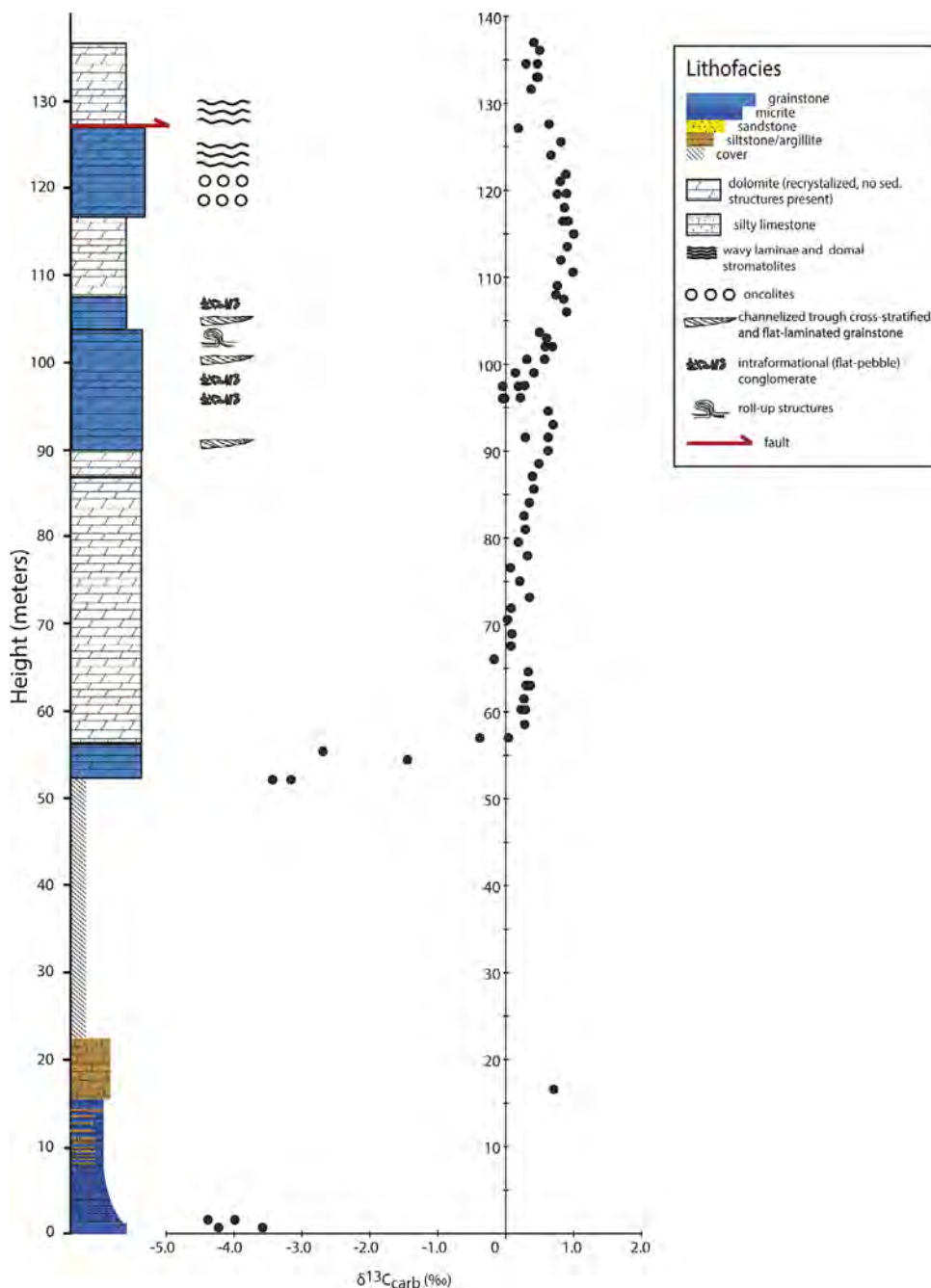


Fig. 6. Litho- and chemostratigraphy of the Kazput Formation at section K1.

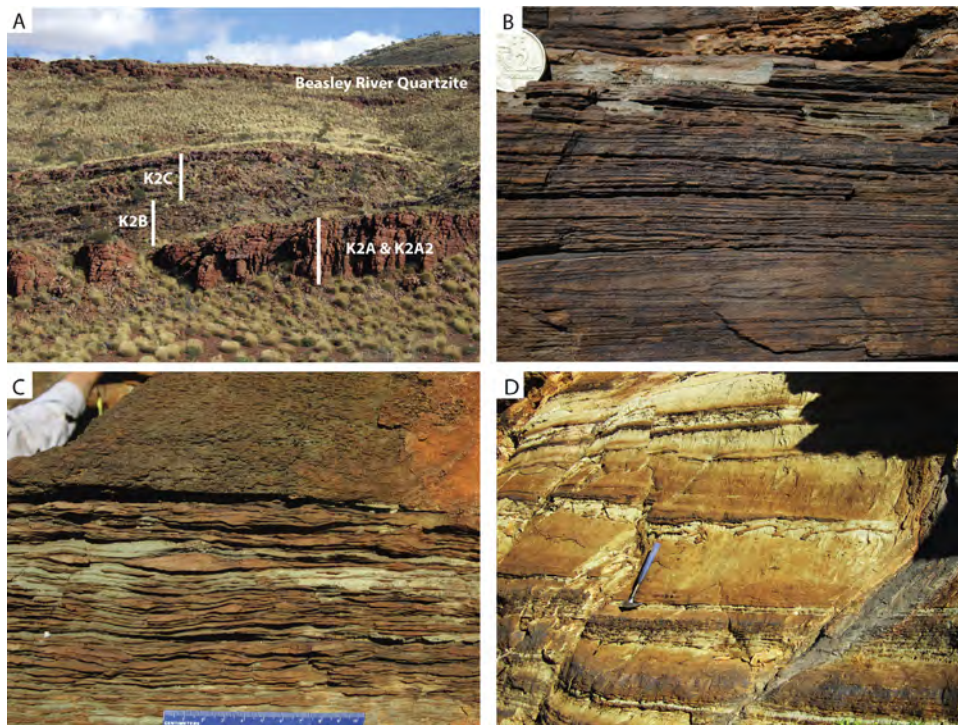
zones in Fig. 11C), as well as a faint tendency for smaller crystals to be oriented along laminae surfaces.

The stromatolites form irregular, m-scale domes on flat-lying surfaces or arches over relict seafloor relief; local reorientation and folding indicate slumping during or shortly after accretion. Like the smaller scale fabrics, at the decimeter to meter scale these stromatolitic domes are variable in shape, but heritability is much higher. The domes are capped by and often interbedded with hummocky cross-stratified sandstones. Clastic-filled neptunian dykes occur sporadically through the section (Fig. 10E). The dykes typically cut at a high angle through the undeformed stromatolite layers, but can run parallel to lamination in cement-poor intervals. In aggregate, these features are plausibly explained by a composite structure that combined rigid penecontemporaneous cements with more plastic silt- and clay-rich laminae, as discussed below.

## 7. Discussion

### 7.1. Kungarra carbonates

Broadly, Kungarra Formation strata record a major coarsening upwards sequence from banded iron formation and starved basin deposits of the underlying Boolgeeda Iron Formation through glaciomarine deposits of the Meteorite Bore Member and finally into tidal flat, beach, and fluvial deposits of the overlying Koolbye Formation (Mazumder et al., 2015). The measured Horseshoe Creek section (Fig. 2) captures a small component of this broad coarsening upwards trend. The abundance of fine-grained suspension deposits interbedded with starved ripple and planar ripple cross-laminated sandstone intervals most likely represents subtidal deposition between storm and fair weather wave base. This is



**Fig. 7.** Lithologies of the Kazput Formation in Hardey Syncline section K2. (A) Overview of stratigraphy, showing where individual subsections were measured. (B) Fine grained, parallel-laminated facies in section K2A, Australian dollar for scale (25 mm diameter). (C) Section K2B; silty to (fine) sandy carbonates with small-scale ripples in the lower half of the photo and mm-scale laminations in the upper half. Blue ruler at the bottom of the photo is 10.5 cm long. (D) Interbedded sandy carbonates and fine-grained carbonates with wavy to stromatolitic laminae (section K2B); rock hammer for scale.

consistent with the limited development of stromatolites. The lack of directly overlying shoreface deposits suggests that deposition was predominantly in an offshore setting, although the increase in sandstone intervals and the broad coarsening upwards trend in the upper ~25 m of the measured section is diagnostic of progradation. Given these features, we suggest these strata were largely deposited in a prodeltaic or mid-outer shelf environment, broadly consistent with the interpretations of previous workers (Krapež, 1996; Martin et al., 2000; Van Kranendonk et al., 2015).

As noted above, Lindsay and Brasier (2002) sampled the carbonate-bearing rocks at Horseshoe Creek, and the highly variable carbon isotope values were interpreted to indicate pronounced carbon cycle variation in the aftermath of the GOE. However, regional mapping has shown that the strata in question lie stratigraphically beneath the Meteorite Bore Member and so are properly assigned to the Kungarra Formation (Krapež, 1996; Martin et al., 2000; Van Kranendonk et al., 2015). Furthermore, stratigraphic field relationships and detailed petrology both suggest that most of these Kungarra carbonates formed during diagenesis, and the marked C-isotopic variation recorded in these rocks confirms this interpretation (Figs. 2–4).  $\delta^{13}\text{C}$  values of  $-6\text{‰}$  are unusual for carbonates of any age and commonly reflect the incorporation of isotopically light carbon into diagenetic carbonates precipitated within sediments (Irwin et al., 1977). Within Lindsay and Brasier's (2002) plotted stratigraphic column,  $\delta^{13}\text{C}$  values commonly vary by several per mil from one sample to the next. Our more detailed data set enables us to document large carbon isotopic variations (up to  $4\text{‰}$ ) within hand samples and between samples from the same stratigraphic horizon (Fig. 2). Such fine-scale spatial and temporal variation is essentially impossible to accommodate in terms of primary C-isotopic signatures reflecting global seawater chemistry.

Arguably, the isotopic variation observed at individual horizons in the lower Kungarra Formation of the Horseshoe Creek section reflects diagenetic carbonate precipitation from pore fluids in which dissolved inorganic carbon (DIC) sourced from seawater

was variably mixed with inorganic carbon generated by the remineralization of isotopically light organic matter. In this case, the most positive isotope results represent values closest to the dissolved inorganic carbon (DIC) in seawater. Alternatively, if these units underwent episodic subaerial exposure in the Paleoproterozoic, meteoric waters may have altered the isotopic composition of the strata during early diagenesis. Regardless, the isotopic values from the measured Kungarra Formation from the Horseshoe Creek section by and large do not represent the original isotopic composition of seawater during the time of deposition.

## 7.2. Kazput carbonates

Similar to the underlying Kungarra Formation, the ~750 m thick Kazput Formation records a complex depositional history heavily influenced by local syndepositional tectonism (Krapež, 1996; Martin et al., 2000; Thorne and Tyler, 1996; Thorne et al., 1995). Numerous cm to dm scale syndepositional normal faults in K2B and K2C indicate the occurrence of active extensional tectonism during Kazput sedimentation. Furthermore, the large stromatolitic clasts and rip-ups (including m-scale rafts that are clearly transported) in the uppermost K2 facies likely represent seismically-generated breccias (seismites) or the erosion of locally uplifted strata. Given the limited stratigraphic range of this study within the Turee Creek Group, it is difficult to provide more context to the greater basinal or tectonic setting of these strata.

Given previous descriptions of the basal Kazput succession as a starved basin marked by distinct carbonate rhythmites (e.g., Krapež, 1996), the Kazput sections described here appear to lie relatively close to the base of the formation. The parallel-laminated and turbiditic silty limestone units that mark the base of the two measured sections suggest a relatively quiet-water environment. At both localities, the rocks quickly transition upsection into fine-grained siliciclastic units with abundant evidence for storm-generated bedforms, indicative of higher energy/shallower



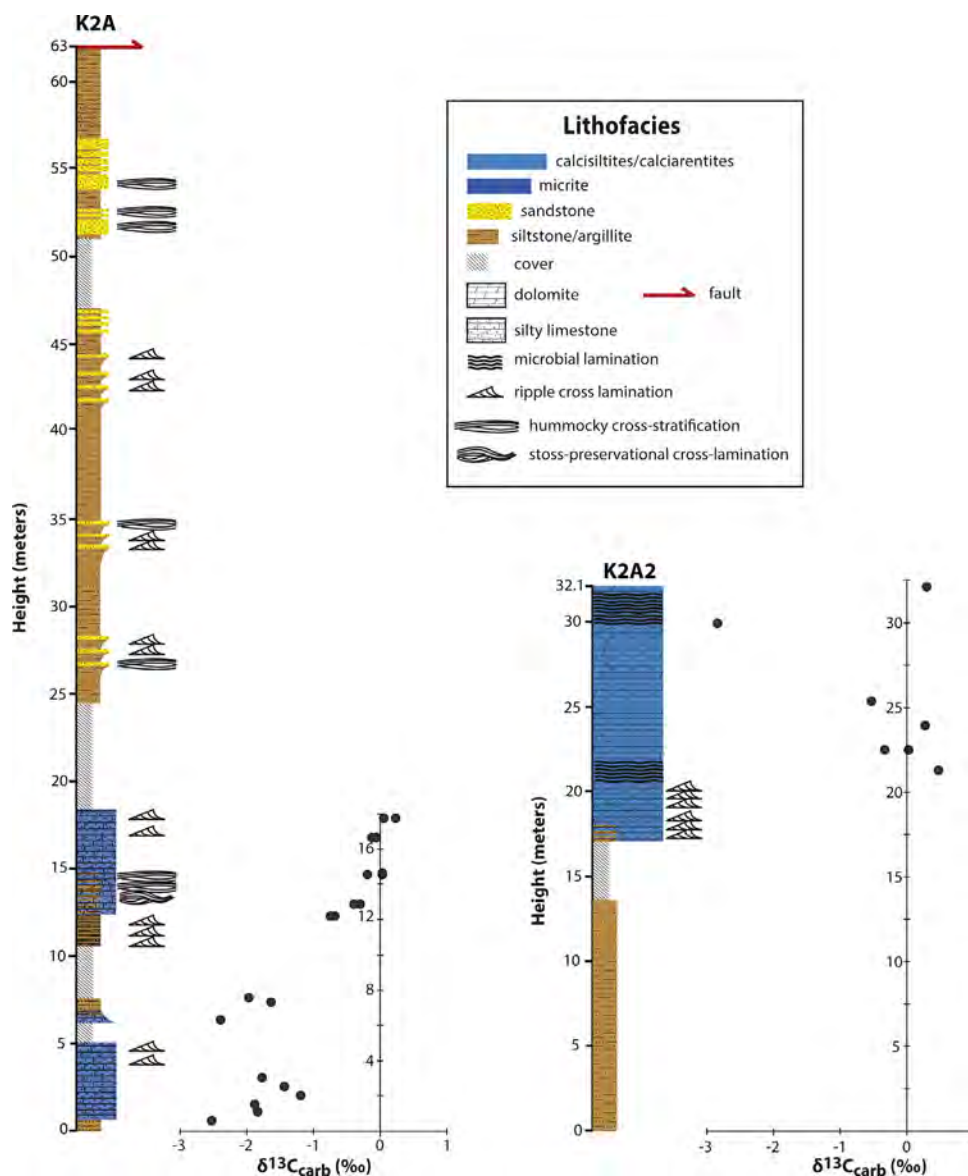


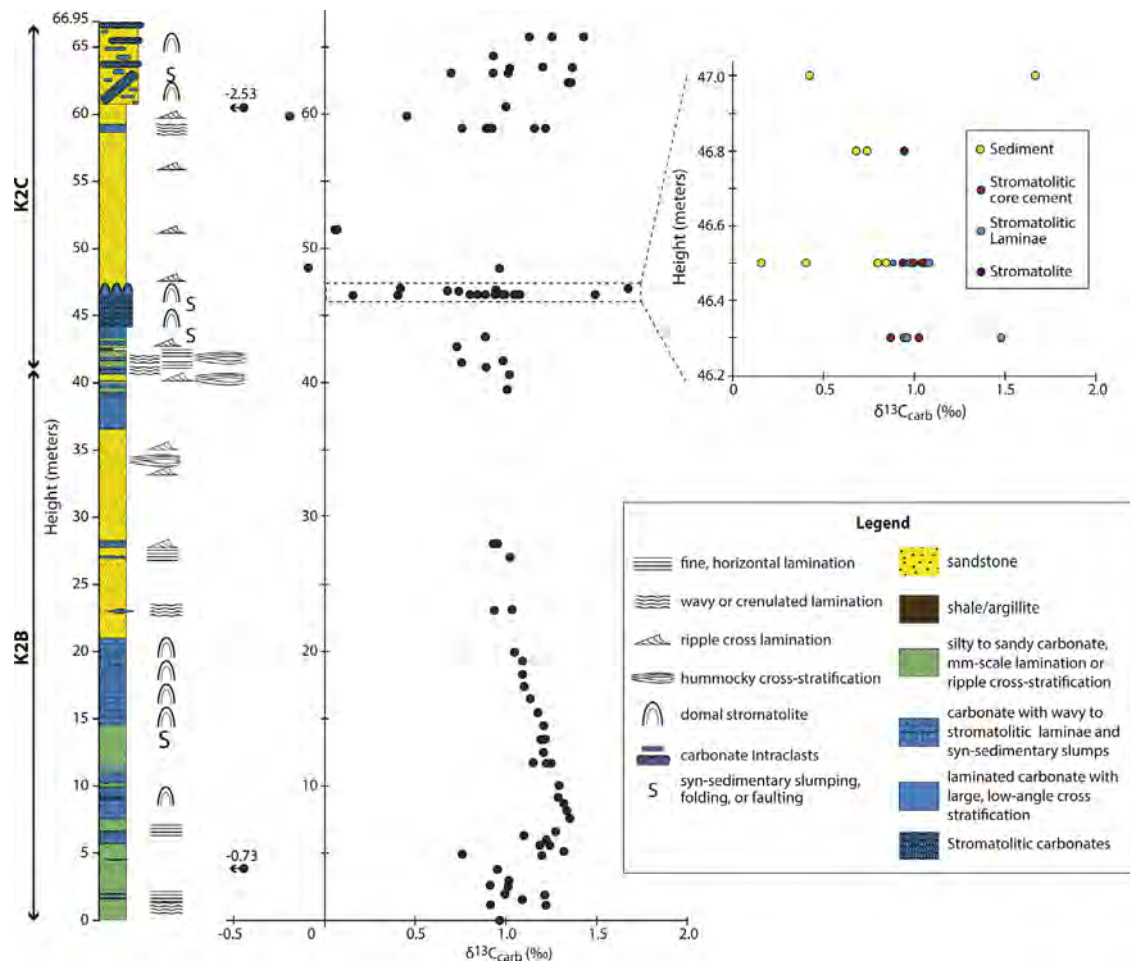
Fig. 8. Litho- and chemostratigraphy of the Kazput Formation at sections K2A and K2A2. Note that K2A2 sits stratigraphically above the K2A section.

water conditions. The remainder of the measured sections can be interpreted as a broad shallowing upward succession of mixed carbonate and siliciclastic strata. The abundance of fine-grained shale and siltstone interbedded with hummocky and swaley cross-stratification in the central part of the sections suggests subtidal deposition on a storm-dominated shelf between storm and fair weather wave base. The establishment of this subtidal shelf setting was relatively short-lived because both Kazput sections record relatively abrupt shoaling into shallow-water shoreface and platformal settings. This is clearly evidenced by the deposition of thick peritidal to subtidal platformal carbonate dominated by ooids, oncoids, and coarse dolograins in section K1 (Fig. 6) and a more complex mixed sandstone-stromatolitic limestone sequence in section K2 (Figs. 8 and 9).

The striking difference in siliciclastic composition between the upper portions of the two parallel sections (K1 and K2) is problematic; however, given the complexity and heterogeneity of along-strike facies and possible proximity to a shoreline, it is reasonable to conclude that their differences are primarily due to proximity to siliciclastic point sources, such as nearby deltaic systems. In fact, section K2 preserves many of the hallmarks of

high sedimentation rates in a tectonically active basin, such as thick sequences of stoss-preservational ripple cross-lamination and abundant syndepositional dykes and soft-sediment deformation. The intimate association of unique stromatolite morphologies and abundant trough cross-stratified sandstone intervals in the upper K2 interval also suggests deposition in a shoreface setting subject to periodically high sedimentation rates. We note that carbonate lithologies differ between sections K1 and K2, with stromatolite development limited to the latter. We cannot rule out the possibility that the two sections are not strictly coeval, but prefer to interpret these facies as contemporaneous expressions of carbonate deposition in a spatially heterogeneous and rapidly developing basin.

Unlike the results from the Kungarra Formation carbonates, the Kazput isotope data are interpreted to indicate dominantly primary seawater values. The agreement of values from closely spaced samples and the consistent trends suggest that diagenetic overprinting of the isotopic signal was minimal. Furthermore, no petrographic results suggest secondary calcite overgrowths, which are clearly documented in the Kungarra carbonates (Fig. 3). Thus, the C-isotopic values of  $-1$  to  $-3\text{‰}$  in lowermost Kazput carbonates



**Fig. 9.** Litho- and chemostratigraphy of Kazput Formation at sections K2B and K2C. Expanded section in upper right highlights geochemical results from stromatolite microsampling.

could record transiently low  $\delta^{13}\text{C}$  in contemporaneous seawater. Above this horizon, however, values hover between 0.5‰ and 1.5‰ through the remainder of the succession.

### 7.3. Kazput stromatolites

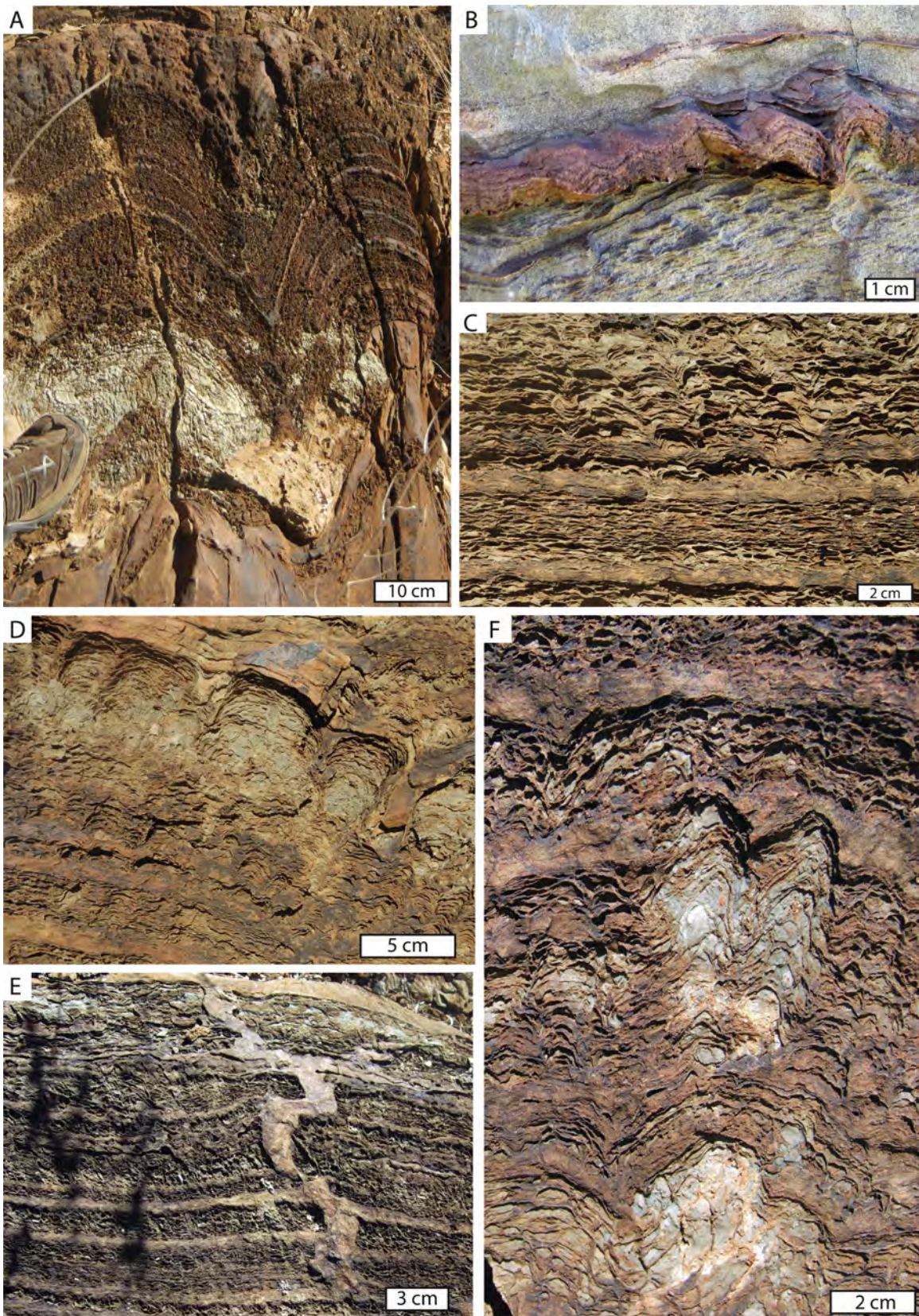
The striking m-scale stromatolite domes of the Kazput Formation (Fig. 10) exhibit features that are typically associated with microbial carbonates, but are unique in containing such an abundance of lenticular calcite precipitates. Laminae in these structures are interpreted as the sedimentary manifestation of mat-building microbial communities. Beyond their general similarity to laminae observed in stromatolites throughout the Proterozoic Eon, a mat origin is supported by at least four observations: (1) the irregular and commonly distorted surfaces of laminae indicate formation by materials that were both coherent and flexible; (2) quartz silt and, very likely, clay minerals within laminae indicate the trapping and binding of introduced materials; (3) laminae contain a higher concentration of reduced carbon than associated microfabrics, consistent with an origin as mats; and (4) laminae contain localized high concentration of (originally) pyrite, suggesting decay within mats via microbial sulfate reduction. The microbial mats likely nucleated on sandy substrates, forming wrinkled mats (wrinkle structures or laminae) and cm-scale stromatolites (Fig. 10B); larger structures resulted from protracted growth between episodes of sand deposition. Based on petrographic and elemental analysis, the quartz silt and clay minerals that are found within the

stromatolites indicate that suspension load siliciclastics were continuously deposited on mat surfaces during stromatolite growth.

An outstanding question is the extent to which the lenticular carbonates found between laminae formed on, or just beneath, mat surfaces or filled primary voids formed by gas emission within mats. Gas-generated voids occur sporadically throughout the Proterozoic stromatolite record. Their formation generally requires strong but flexible mats populated by filamentous microorganisms, gas generation (e.g., oxygenic photosynthesis, decomposition of organic matter, or methanogenesis), and seawater that is strongly oversaturated with respect to calcium carbonate minerals (e.g., Knoll et al., 2013; Mata et al., 2012). Indeed, primary voids in Archean stromatolites have been interpreted as prima facie evidence for oxygenic photosynthesis at 3 Ga (Bosak et al., 2009, 2010). The carbonate precipitates do not crosscut microbial laminae, eliminating dissolution and subsequent in-filling as an explanation for the observed textures.

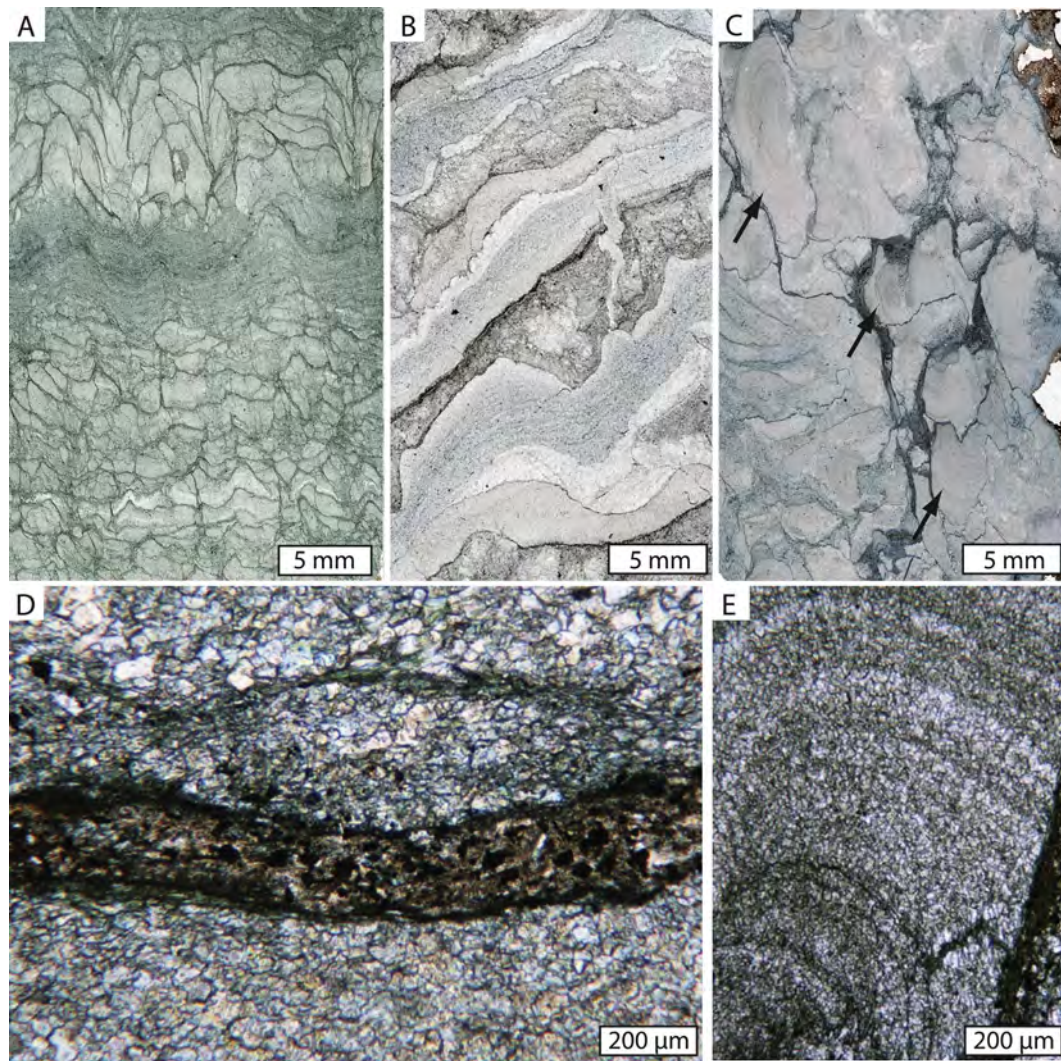
Given that the Kazput stromatolites lie within rocks deposited stratigraphically after the GOE, all aforementioned requirements for the formation and preservation of primary voids appear to have been met locally. The irregular, convex upward morphology of laminae is consistent with this interpretation, as is the orientation of zoned cements in some stromatolites (Fig. 11C and E). However, the lateral extent of discrete cement horizons that occasionally contain clay, pyrite, and reduced carbon flecks also supports the alternative interpretation that the cements are seafloor precipitates formed on or within surface mats (e.g., Fig. 11B). In fact, the two interpretations are not mutually exclusive; if the





**Fig. 10.** Kazput stromatolites. (A) Large domal stromatolites forming over relict topography at 47 m stratigraphic height (in section K2C). (B) Thin stromatolite layer within fine-grained micritic limestones; note the eroded base on which the stromatolite accreted. (C) Alternating layers of siliciclastic lamina-rich (resistant) and carbonate-rich (recessive) layers within the larger stromatolites; note the weathering difference between units. (D) Top layers of domal stromatolites from K2C (47 m), note the alternating layers of siliciclastic lamina-rich and carbonate-rich layers. The stromatolites on the top layer formed much larger (>5 cm), more cement-rich structures than earlier layers. (E) Synsedimentary neptunian dyke through stromatolite layers, dark patches are shadows from vegetation on the outcrop. (F) Domal stromatolites growing into microdigitate stromatolites within cement-rich intervals of the large domal stromatolites in K2C.





**Fig. 11.** Petrographic textures of Kazput stromatolites (all plane polarized light). (A) Alternating siliciclastic lamina-rich and discontinuous carbonate-rich layers of large domal stromatolites from section K2C (47 m, sample K2C 5.5B2); (B) unusually continuous carbonate-rich layers in section K2C (65.7 m, sample K2C 31.8 m); (C) microstructure of a transported and rolled up stromatolite, showing the local preservation of fine banding in lenticular carbonate precipitates highlighted by arrows (63.4 m, sample K2C 28.6); (D) detail of a siliciclastic-rich lamina in a small stromatolite containing quartz, pyrite, and clay minerals, with carbonate-rich areas above and below (sample K2C 28.5); (E) close up of (C) highlighting the faint banding within the carbonate fabric of the deformed stromatolite (63.4 m sample K2C 28.6).

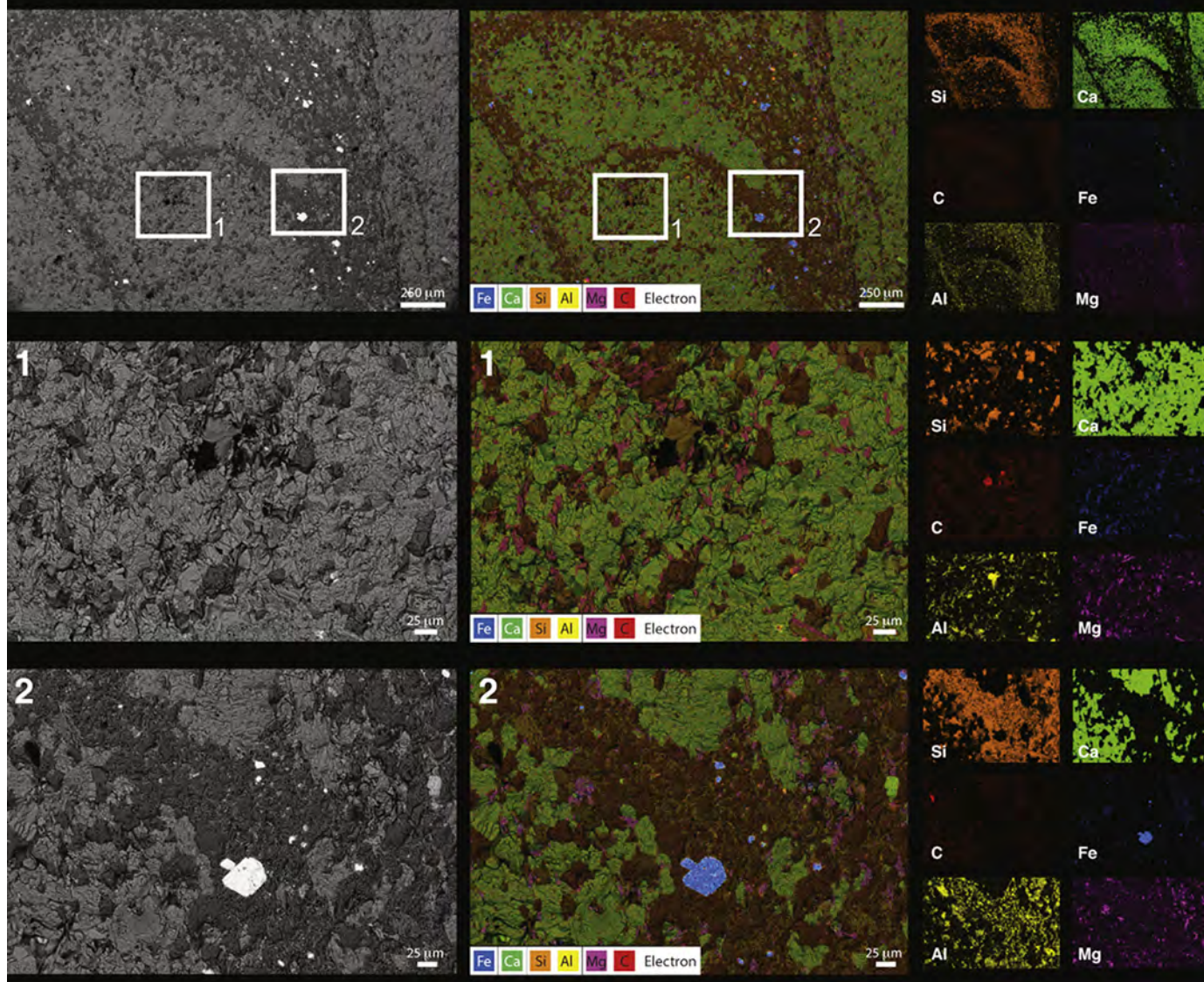
waters that bathed the Kazput bioherms were strongly supersaturated with respect to calcium carbonate, both void-forming and cementing processes may have been operating during stromatolite accretion.

Stromatolites are found widely in late Archean and Paleoproterozoic carbonates, with particularly good descriptions of macro- and microstructure available for late Archean microbialites from the Gamohaan and Frisco formations of the Campbellrand/Malmmani succession, South Africa (Sumner, 1997), and lower Paleoproterozoic carbonates from the Fennoscandian Shield (McLoughlin et al., 2013). What differentiates the Kazput stromatolites from most of these (and essentially all younger Proterozoic) structures is their abundance of lenticular carbonate. Microdigitate stromatolites, some of them small microbial structures and others stacked crystal fans (Grotzinger and Knoll, 1999), are particularly widespread in Paleoproterozoic carbonate successions (Medvedev et al., 2005). These structures formed widely across shallow shelves and platforms and reflect a high degree of oversaturation with respect to calcium carbonate minerals. Thus, they are relevant to the interpretation of the Kazput structures, but differ in lacking the regular interlamination of microbial laminae and precipitates described here.

Perhaps the closest approximation of the composite laminar–lenticular Kazput fabric is found in cusped microbialites from the Campbellrand/Malmmani succession (Sumner, 1997) and elsewhere in late Archean carbonates (e.g., Hofmann and Masson, 1994; Riding et al., 2014). In these structures, void spaces that originated by the draping of pliant mats across vertical microbial “tent poles” were filled penecontemporaneously by carbonate cement (Sumner, 1997). Locally, stromatolites in the  $2720 \pm 5$  Ma Tumbiana Formation, Fortescue Group, Western Australia, also contain thin, irregular patches of carbonate precipitates, interpreted as lake-floor precipitates (Flannery and Walter, 2012; Lepot et al., 2008, 2009). The Kazput and Tumbiana stromatolites do share some similarities, such as the weathering profile (prominent laminae and recessive cements) and the  $\mu\text{m}$ -scale banded carbonate domes within carbonate-rich layers; however, there are important distinctions between the two. Kazput stromatolites do not contain halite pseudomorphs, nor is there evidence for the penecontemporaneous erosion of carbonate precipitates, as is clearly evident in the Tumbiana stromatolites (Lepot et al., 2008, 2009). Furthermore, the Kazput stromatolite cements are largely discrete (mm- to cm-scale) lenses and typically do not form thick, continuous cement laminae as in the



## KAZS1 - Kazput carbonate



**Fig. 12.** Elemental map of Kazput Formation stromatolitic carbonates (sample KAZS1, 47 m height in section K2C); top row is an image of the entire sample, and the middle and bottom rows are close up views of boxes 1 and 2 respectively. Left column are SEM images, right column images are false color representations of the elemental maps, and the middle illustrations are composite images of the elemental and SEM maps. Note, unlike the Kungarra Fm. (Fig. 4), calcium (calcite) is the dominant mineral with quartz and aluminosilicates occurring with high relative abundance in stromatolitic laminae. Small iron oxide grains (blue in false color maps) occur throughout the Kazput section but are concentrated in silicate-rich laminae (orange in false color maps). There are also organic carbon inclusions throughout the section (see second row); they appear as black spots in the composite figure and are highlighted in red on the carbon (C) elemental map. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Tumbiana examples. These examples underscore the importance of macroscopic carbonate precipitates in generating fabrics within late Archean/early Paleoproterozoic stromatolites; nonetheless, the specific alternation of particle-binding mats and lenticular carbonate precipitates is, to the best of our knowledge, a unique feature of Kazput stromatolites in the Hardey Syncline, reflecting a potentially time-limited interaction between the evolving biota and its physical surroundings.

### 7.4. Chemostratigraphic comparisons

Few carbon isotopic data are available for carbonates that unambiguously lie above Paleoproterozoic iron formations but below glaciogenic rocks. Samples from the poorly dated Boxelder Creek Formation, South Dakota (Bekker et al., 2003a) and Polisarka

Sedimentary Formation in drill cores from the Kola Peninsula, Russia (Brasier et al., 2013), span a range of  $-6\%$  to  $1\%$ . Carbonates of the Gandarela Formation, Brazil, are isotopically similar, but cannot be placed unambiguously relative to Paleoproterozoic ice ages. Post-glacial marbles of the Paleoproterozoic Sauser Group, India, also show C-isotopic values of  $-3.1\%$  to  $+2.6\%$  above a moderately negative basal interval ( $-4.4\%$  to  $-7.4\%$ ) interpreted as a cap carbonate (Mohanty et al., 2015). The most positive C-isotopic values for Kungarra carbonates are consistent with the values reported from other basins, but the uncertainties introduced by diagenetic carbonate precipitation limit what the Kungarra samples can add to discussions about the post-BIF, pre-GOE carbon cycle.

On the basis of limited data, Karhu and Holland (1996) hypothesized that the strongly positive carbon isotopic excursion called the Lomagundi-Jatuli event began ca. 2.2 Ga. Even now, isotopic

data are sparse for successions younger than GOE onset/glaciogenic rocks but older than 2200 Ma. Martin et al. (2013) summarized available radiometric constraints on the Lomagundi-Jatuli event, concluding that the event began between  $2306 \pm 9$  Ma and  $2221 \pm 5$  Ma and ended between  $2106 \pm 8$  and  $2057 \pm 1$  Ma, for a maximum duration of  $249 \pm 9$  million years and a minimum duration of  $128 \pm 9.4$  million years. The new data presented herein are consistent with these age constraints, and provide no evidence for strongly positive Lomagundi-Jatuli  $\delta^{13}\text{C}$  values during deposition of the measured Kazput sections. We recognize, however, that our sections represent a limited proportion of the time interval between Paleoproterozoic ice ages and events commencing at 2200 Ma; regionally, Kazput carbonates are separated from the Cheela Springs basalt and its intrusive counterpart ( $2209 \pm 15$  Ma; Martin et al., 1998) by thick siliciclastic deposits and a major unconformity (Fig. 1). Thus, while these new data demonstrate that the interval between the GOE onset/glacials and 2200 Ma includes a time where the seawater DIC isotopic composition was unperturbed and similar to modern isotopic values, we cannot rule out the possibility that it also includes short intervals of positive C-isotopic excursions, which are not recorded in the analyzed Kazput Formation sections.

Kazput carbonates are isotopically similar to those of well-developed carbonates in the Gandarela Formation, Brazil, where 163 samples show values near 0‰ (Bekker et al., 2003b; Maheshwari et al., 2010). The Gandarela carbonates (Babinski et al., 1995) lie stratigraphically above major BIF and below carbonates that show Lomagundi-type  $^{13}\text{C}$  enrichment, but the regional stratigraphy contains no glacial diamictites; Bekker et al. (2003b) cite a Pb–Pb date of  $2420 \pm 19$  Ma for Gandarela carbonates, but this does not appear in Martin et al.'s (2013) review due to the low confidence in the interpretation of Pb–Pb carbonate dates in Proterozoic successions. The well-studied Duitschland Formation, dated indirectly at  $2316 \pm 7$  Ma by Re–Os on black shale of the possibly correlative Rooihogte–Timeball Hill Formation (Hannah et al., 2004), bears  $^{13}\text{C}$  enrichments up to 10.1‰ in its upper part (Bekker et al., 2001). However, the Moodraai Dolomite (diagenetic age of  $2394 \pm 26$  Ma, based on carbonate-bound Pb), also in South Africa, appears to have no isotopic anomalies, with  $\delta^{13}\text{C}$  values of 0.5–1‰, more similar to those of the Kazput Formation (Bau et al., 1999). Clearly, tighter radiometric constraints will be necessary to validate interbasinal correlations and accurately reconstruct early Paleoproterozoic carbon cycle dynamics.

## 8. Conclusions

This study provides new litho- and chemostratigraphic data for carbonate-bearing intervals of the 2.45–2.22 Ga Turee Creek Group, Western Australia, which spans a pivotal time in Earth history after the deposition of global banded iron formation and across the GOE. Field relationships, petrography, elemental mapping, and C-isotope values reveal that most Kungarra carbonates in the pre-glacial lower part of the Turee Creek Group formed during syndepositional or post-depositional diagenesis; therefore, the abundant and highly negative C-isotopic values within these rocks cannot be interpreted in terms of global carbon cycle dynamics, as previously assumed by Lindsay and Brasier (2002).

In contrast, carbonates from the lower part of the uppermost Kazput Formation of the Turee Creek Group—which sits in a globally under-sampled interval above Paleoproterozoic glacial deposits and below an unconformity constrained by the ~2.2 Ga Cheela Springs Basalt and associated sills—do appear to record the C isotopic composition of seawater DIC, with consistent  $\delta^{13}\text{C}$  values of  $-2$  to  $+1.5$ ‰. As the lower parts of the Kazput Formation likely represent a relatively brief time interval, it strengthens a growing

body of evidence indicating that the initial geochemical signature of the GOE and the exceptionally positive values of the Lomagundi-Jatuli isotope excursion(s) are separated by one or more intervals of normal C isotopic composition.

The moderate C-isotopic values of Turee Creek Group carbonates strengthen the argument that the complex set of processes that drove the onset of the GOE did not include anomalously high proportional rates of organic carbon burial. Of course, as others have noted (e.g., Lyons et al., 2014; and references therein), it is not required that the increase in Paleoproterozoic oxygen concentrations was limited to the brief interval marked by the end of mass-independent S isotope fractionation, nor that oxygen change was monotonic (Canfield, 2014; Canfield et al., 2013; Lyons et al., 2014). Instead, the MIF-S signature might reflect an interval of atmospheric oxygen accumulation that was neither large nor rapid but crossed an important threshold. One would expect  $p\text{O}_2$  to continue to rise during the Lomagundi-Jatuli event (e.g., Bekker and Holland, 2012; Kump et al., 2011; Rasmussen et al., 2013), but any increase in oxygen levels driven by extensive organic carbon burial postdates the MIF-S boundary, very likely by tens of millions of years (see also Martin et al., 2013).

Beyond the perspective on Paleoproterozoic carbon cycle dynamics provided by the stable carbon isotopic data, Turee Creek Group carbonates host unusual, if not unique, stromatolites that are geobiologically informative. Notably, Kazput stromatolites contain a high volume of precipitated carbonate—indeed, more abundant than the siliciclastic-rich laminae in many horizons (Fig. 10). As noted above, this reflects locally abundant seafloor precipitates and/or penecontemporaneous filling of primary voids formed by microbial gas release. The most comparable structures are precipitate-rich cuspete Archean microbialites from South Africa (Sumner, 1997) and late Archean Tumbiana stromatolites from Western Australia (Flannery and Walter, 2012; Lepot et al., 2008, 2009). Whatever their proper mechanistic interpretation, the Kazput Formation stromatolites in the Hardey Syncline are morphologically distinct, reflecting a potentially time-limited interaction between the evolving biota and its physical surroundings.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.precamres.2015.05.021>



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