



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

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Sedimentology, chemostratigraphy, and stromatolites of lower Paleoproterozoic

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39 ABSTRACT

40 The ca. 2.45–2.22 Ga Turee Creek Group, Western Australia, contains carbonate-41 rich horizons that postdate earliest Proterozoic iron formations, bracket both 42 Paleoproterozoic glaciogenic beds and the onset of the Great Oxidation Event (GOE), 43 and predate ca. 2.2–2.05 Ga Lomagundi-Jatuli C-isotopic excursion(s). As such, Turee 44 Creek carbonate strata provide an opportunity to characterize early Paleoproterozoic 45 carbonate sedimentation and carbon cycle dynamics in the context of significant global 46 change. Here, we report on the stratigraphy, sedimentology, petrology, carbon isotope 47 chemostratigraphy, and stromatolite development for carbonate-rich successions within 48 the pre-glacial part of the Kungarra Formation and the postglacial Kazput Formation. 49 Kungarra carbonate units largely occur as laterally discontinuous beds within a 50 thick, predominantly siliciclastic shelf deposit. While this succession contains thin 51 microbialite horizons, most carbonates consist of patchy calcite overgrowths within a 52 siliciclastic matrix. C-isotopic values show marked variation along a single horizon and 53 even within hand samples, reflecting spatially and temporally variable mixing between 54 dissolved inorganic carbon in seawater and isotopically light inorganic carbon generated 55 via syn- and post-depositional remineralization of organic matter. 56 In contrast, the Kazput carbonates consist of subtidal stromatolites, grainstones, 57 and micrites deposited on a mixed carbonate-siliciclastic shelf. These carbonates exhibit moderate δ^{13} C values of -2‰ to +1.5‰ and likely preserve a C-isotopic signature of 58 59 seawater. Kazput carbonates, thus, provide some of the best available evidence that an 60 interval of unexceptional C-isotopic values separates the Lomagundi-Jatuli C-isotopic

61 excursion(s) from the initiation of the GOE as inferred from multiple sulfur isotopes (loss

62 of mass independent fractionation). The Kazput Formation also contains unusual, m-scale 63 stromatolitic buildups, which are composed of sub-mm laminae and discontinuous, 64 convex upward lenticular precipitates up to a few mm in maximum thickness. Laminae, 65 interpreted as microbial mat layers, contain quartz and clay minerals as well as calcite, 66 whereas precipitate lenses consist of interlocking calcite anhedra, sometimes showing 67 faint mm-scale banding. These cements formed either as infillings of primary voids 68 formed by gas emission within penecontemporaneously lithified mats, or as local seafloor 69 precipitates that formed on, or within, surface mats. It is possible that both mechanisms 70 interacted to form the unique Kazput stromatolites. These microbialites speak to a 71 distinctive interaction between life and environment early in the Paleoproterozoic Era. 72

73 Keywords: Turee Creek Group; Kazput Formation; Kungarra Formation; Great
74 Oxidation Event; stromatolite; Lomagundi-Jatuli Event.

75

76 **1. Introduction**

77 Lower Paleoproterozoic sedimentary rocks record a number of first-order changes 78 in the Earth system, including globally extensive ice sheets, one or more extreme states of the carbon cycle characterized by uniquely high δ^{13} C in carbonates, and the initial 79 80 accumulation of oxygen in the atmosphere and surface oceans (Akin et al., 2013; Asael et 81 al., 2013; Bekker and Holland, 2012; Bekker et al., 2004, 2013; Farguhar et al., 2000; 82 Fralick et al., 2011; Hoffman, 2013; Konhauser et al., 2011; Lyons et al., 2012, 2014; 83 Melezhik and Fallick, 2010; Partin et al., 2013; Planavsky et al., 2012, 2014; Pufahl and 84 Hiatt, 2012; Pufahl et al., 2010, 2011; Reinhard et al., 2013; Scott et al., 2014; Swanner et

| 85 | al., 2014; and references therein). Co-occurring global glaciation, carbon isotopic |
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| 86 | variation, and redox change also characterize Neoproterozoic rocks, and for this younger |
| 87 | interval, carbonate strata have played an important role in both recording key events and |
| 88 | providing context for the interpretation of these events (e.g., Halverson and Shields-Zhou, |
| 89 | 2011; Johnston et al., 2012). Detailed analyses of platform and shelf carbonates are |
| 90 | available for Neoarchean successions [e.g., the Campbellrand/Malmani subgroups of the |
| 91 | Transvaal Supergroup, South Africa; (Knoll and Beukes, 2009; and references therein)] |
| 92 | and younger Paleoproterozoic rocks [e.g., 2 Ga platform carbonates of the Slave |
| 93 | Province, Canada; (Hotinski et al., 2004)]. To date, however, relatively few studies have |
| 94 | focused on lower Paleoproterozoic carbonates, despite their potential importance in |
| 95 | understanding early Paleoproterozoic evolution and environmental change. |
| 96 | The ca. 2.45–2.22 Ga Turee Creek Group, exposed in the Hamersley Range of |
| 97 | Western Australia, conformably overlies earliest Paleoproterozoic iron formations, |
| 98 | predates the ca. 2.2 Ga onset of the Lomagundi-Jatuli C-isotopic excursion(s), and hosts |
| 99 | carbonate and glacially-influenced strata that record onset of the Great Oxidation Event |
| 100 | (GOE) (Bekker et al., 2004; Martin et al., 2013; Van Kranendonk and Mazumder, 2015). |
| 101 | Thus, these carbonates provide an opportunity to characterize the response of early |
| 102 | Paleoproterozoic carbonate deposition and carbon cycle dynamics to significant global |
| 103 | change, including the GOE and glaciation. Here, we report on the stratigraphy, |
| 104 | sedimentology, carbonate petrology, carbon isotope chemostratigraphy, and stromatolite |
| 105 | development in two closely spaced sections of the Kazput Formation of the upper Turee |
| 106 | Creek Group. We also report lithological and isotopic data from three parallel |
| 107 | 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.

111

112 **2. Geologic Setting**

113 The Turee Creek Group of the Mount Bruce Supergroup is the youngest 114 sedimentary succession within the Hamersley Basin of the Pilbara Craton (Trendall, 115 1990). Turee Creek Group rocks conformably overlie iron formations of the Hamersley 116 Group and sit unconformably beneath sedimentary and volcanic deposits of the Wyloo 117 Group (Fig. 1) (Horwitz, 1982; Thorne, 1990; Thorne and Seymour, 1991; Trendall, 118 1969; Trendall et al., 1983). Initial research suggested conformable relationships 119 throughout the Proterozoic stratigraphy of Western Australia (e.g., Trendall and 120 Blockley, 1970), but continuing stratigraphic and geochronological studies have since 121 identified significant unconformities and deformational events that point to a protracted, 122 but episodic, depositional history spanning more than 330 Myr (Martin et al., 2000; and 123 references therein). 124 Palinspastic reconstructions and basin analysis of upper Hamersley Basin and

125 lower Wyloo Group stratigraphy led Horwitz (1982) to propose a post-Hamersley

126 depositional feature, called the McGrath Trough, that reflects flexural subsidence driven

127 by peripheral or retroarc foreland basin development (Horwitz, 1982; Krapež, 1996;

128 Martin, 1999; Martin et al., 2000; Powell and Horwitz, 1994). The foreland-related

tectonostratigraphic sequence most likely involves the Turee Creek and lower Wyloo

130 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).

137 The Turee Creek Group consists, in stratigraphic order, of the Kungarra 138 (including the glaciogenic Meteorite Bore Member), Koolbye, and Kazput formations 139 (Fig. 1) (Thorne et al., 1995; Trendall, 1979, 1981). It is bracketed in age by the 2449 ± 3 140 Ma Woongarra Rhyolite (Barley et al., 1997) near the top of the underlying Hamersley 141 Group and the 2209 ± 15 Ma Cheela Springs Basalt (Martin et al., 1998) low in the 142 unconformably overlying Wyloo Group succession (Fig. 1). Müller et al. (2005) 143 reinterpreted the Cheela Springs date as a reflection of provenance rather than 144 crystallization age, but their U-Pb age on baddeleyite of 2208 ± 15 Ma for diorite sills 145 that cut the Turee Creek Group provides an essentially indistinguishable maximum age 146 constraint. The Kungarra Formation of the Turee Creek Group is further constrained to be 147 younger than ca. 2420 Ma, based on U-Pb ages of detrital zircons in the Meteorite Bore 148 Member (Takehara et al., 2010). Turee Creek Group strata record a broad shallowing-149 upward profile from deep-water banded iron formation (the Boolgeeda Iron Formation of 150 the underlying Hamersley Group), through fine-grained siliciclastic deposits of the 151 Kungarra Formation, to fluvial and shallow marine strata of the Koolbye and Kazput 152 formations.

153 Although detailed correlation with other Paleoproterozoic successions is 154 challenging, Turee Creek Group strata record two events that guide interbasinal 155 correlation. First, Williford et al. (2011) documented mass independent sulfur isotope 156 fractionation, a proxy for the near-absence of environmental oxygen (Farquhar et al., 157 2000), in the lower part of the Meteorite Bore Member of the Kungarra Formation. On 158 this basis, the authors suggested that the lower glaciogenic unit of the Meteorite Bore 159 Member, locally in contact with the Boolgeeda Iron Formation, was deposited during the 160 final stages of the GOE, when oxygen levels were still low enough for the development 161 of MIF-S, but sufficiently high for oxidative weathering of continental sulfides and 162 significant sulfur isotope fractionation.

163 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 164 165 correlation to other Paleoproterozoic basins (Martin, 1999; Trendall, 1976; Van 166 Kranendonk and Mazumder, 2015). Martin (1999) and Van Kranendonk et al. (2012) 167 pointed to analogous basin histories of the South African Transvaal Supergroup and the 168 Canadian Huronian Supergroup on the basis of similar ca. 2.45 Ga felsic magmatic 169 events followed by glacial episodes and mafic magmatism at ca. 2.2 Ga. Hoffman (2013) 170 suggested a similar global correlation scheme based on the assumption that the GOE, as 171 marked by the disappearance of MIF-S, was a unique event connected in time to a 172 Snowball Earth event (Kirschvink et al., 2000). By this reasoning, disparate sedimentary 173 rocks may be correlated by a single tie point, even though some regions record three 174 glacial events and others only record two. Thus, while it is difficult to assign an exact age 175 to the Turee Creek Group, the glacial history of these strata generally enables broad

176 correlation to the timing of the Great Oxidation Event (Van Kranendonk and Mazumder,177 2015).

178

179 **3. Methods**

180 Fieldwork for this project was conducted as part of the 2012 Advanced 181 Geobiology Course sponsored by the Agouron Institute. Five stratigraphic sections were 182 measured and sampled from three sites in the Hardey Syncline: the Horseshoe Creek 183 locality of Lindsay and Brasier (2002) (Fig. 1, three sections at site 1) and two Kazput 184 Formation localities, K1 and K2, on the southwest and northeast limbs of a small NNW-185 SSE-trending anticline in the central part of the Syncline (Fig. 1, sites 2 and 3). The 186 Horseshoe Creek strata were previously described by Lindsay and Brasier (2002) as 187 Kazput Formation, but regional mapping places this section below the Meteorite Bore 188 Member and is thus part of the Kungarra Formation (Fig. 1) (Martin et al., 2000; Van 189 Kranendonk, 2010; Van Kranendonk et al., 2015). 190 At Horseshoe Creek, three parallel stratigraphic columns were measured through 191 ~120 m of the Kungarra Formation to determine patterns of lateral facies change and 192 geochemical variation (HC1, HC2, and HC3). The first Kazput section was measured 193 through roughly 140 m of sedimentary rocks on the west-southwestern limb of the 194 anticline (locality K1), and the second section is a composite stratigraphic column 195 measured across two ridges (roughly 100 m apart) on the southwestern limb of the 196 anticline (localities K2A, K2B, and K2C). Although the K1 and K2 localities are within a 197 few kilometers of each other, their exact correlation is uncertain due to differing facies 198 development and structural complications.

199Rock samples were collected from each measured section at roughly 1–3 m200intervals for geochemical and petrological analysis; samples were cut using a diamond201saw, and made into thin sections for petrographic analysis. Thin section blanks were then202microdrilled following methods of Kaufman et al. (1990) to obtain fresh powder. Blanks203were commonly drilled several times if multiple lithologies or microfacies were present204in a single thin section.

Carbonate δ^{13} C and δ^{18} O values for 225 Kazput and 125 Kungarra samples were 205 206 measured on a VG Optima dual inlet mass spectrometer fed by an Isocarb preparation 207 device in the Harvard University Laboratory for Geochemical Oceanography (see 208 supplementary data). Approximately 1 mg of carbonate powder was dissolved in a 209 common anhydrous phosphoric acid (H₃PO₄) bath kept at 90°C for eight minutes. Carbon 210 dioxide gas was purified cryogenically and measured against an in-house reference gas. 211 No dolomite corrections were applied to the data. Analytical uncertainty was $\pm 0.1\%$ 212 (sample:standard ratio of 8:1); results are reported on a Vienna Pee Dee Belemnite scale. 213 Two samples were additionally analyzed using a scanning electron microscope 214 (SEM) with an attached electron dispersive spectrometer (EDS). These small-scale 215 analyses are employed to visualize and compare textures of the two carbonates, as well as 216 to provide a high-resolution map of the stromatolitic laminae from the Kazput Formation. 217 A representative sample from the Kungarra Formation (from 16.25 m in section HC3) 218 and a stromatolite from the Kazput Formation (KAZS1), were photographed using 219 backscatter detector imaging to highlight compositional contrasts on a Zeiss 1550VP 220 Field Emission SEM in the California Institute of Technology Geological and Planetary 221 Sciences Division Analytical Facility. An Oxford INCA Energy 300 EDS system was

- 222 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%.

225

4. Results: Sedimentology, facies analysis, and petrography

227 *4.1. Kungarra Formation at Horseshoe Creek*

228 Three parallel stratigraphic sections (HC1, HC2, and HC3) were measured from 229 the Horseshoe Creek locality; as these sections were only a few hundred meters apart 230 they are shown as a composite section in Fig. 2. The lower \sim 73.5 m consists of variably 231 exposed, monotonous grey-green siltstone and shale with occasional thin (<10 cm) 232 lenticular or planar beds of very fine- to fine-grained quartz-rich lithic arenites. These 233 sandstone intervals are locally erosive and host parallel-lamination or occasional very 234 fine ripple cross-lamination with abundant shale partings. Some of the more massive 235 siltstone intervals are locally interspersed with starved ripples of very-fine grained 236 sandstone, but many of the sedimentary structures in the siltstones are masked by a 237 pervasive penetrative cleavage.

238 Numerous discontinuous limestone-bearing beds, 3–70 cm thick, occur 239 sporadically within the massive siltstone and shale units. Many of these carbonate beds 240 are broadly nodular or irregular in geometry and locally grade into pure siltstone, both 241 vertically and laterally. Some carbonate-rich horizons essentially mimic starved ripples 242 and other sedimentary structures characteristic of surrounding siliciclastic beds (Fig. 3A), 243 consistent with post-depositional diagenetic carbonate precipitation. A diagenetic origin 244 for these discontinuous layers is also supported by petrographic observations and 245 microscale SEM-EDS mapping (Figs. 3C, 4). For example, evidence for diagenetic

246 carbonate emplacement includes both the restriction of these Kungarra carbonates to 247 lenses and thin layers intermixed with detrital grains (Figs. 3C, 4) and the distribution 248 within these lenses of patchy carbonate in overgrowth and cement-filling textures within 249 a matrix of silt-sized quartz grains, clay minerals, and rare other silicates (Figs. 3C, 4). 250 Figure 4 shows a representative carbonate layer (green) that includes many detrital 251 silicate grains (orange). A diagenetic origin for many Kungarra carbonates is consistent 252 with major element abundances reported by Lindsay and Brasier (2002); on average, Ca 253 and Mg together make up less than 15% by weight of sampled lithologies, requiring that 254 carbonates are a subordinate component of the samples. 255 A few limestone beds from the Kungarra Formation are more continuous, 256 relatively pure, and either irregularly laminated or clearly stromatolitic. In particular, a 257 distinct stromatolite unit occurs from ~33.9–34.4 m in section HC3, which progresses 258 from ~10 cm of brown-yellow-colored irregular crinkly lamination with interstitial 259 micrite fill into ~ 25 cm of discrete ~ 70 cm wide elongate stromatolites. These structures 260 are draped by peach-colored dolomicrite and transition into two distinct layers of 261 brownish-white ~15–30 cm thick domal stromatolites (Fig. 3B) separated by a horizon of 262 1-4 cm wide and ~ 10 cm tall, high-inheritance digitate stromatolites. The upper 2-5 cm 263 of the stromatolitic interval is irregular, with local rip-up clasts. Laterally, this 264 stromatolitic interval becomes poorly developed; at section HC2, only the irregular 265 carbonate laminae and small domal stromatolites occur (Fig. 3B), and at section HC1 this 266 unit becomes indistinguishable from other thin carbonate units. The only other location in 267 this section with similar stromatolitic features occurs at ~176 m; however, this microbial 268 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 sincebeen recrystallized). Thus the carbonate-rich units at Horseshoe Creek reflect both

271 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

274 generally transition from green-grey siltstone and argillite with abundant starved ripples,

275 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.

281

282 4.2. Kazput Formation, NW Hardey Syncline

283 *4.2.1. Kazput Section #1 (K1)*

284 The K1 section (Figs. 5A, 6) was measured on the NE-dipping flank of a NNW-285 SSE-striking anticline in the southeastern part of the Hardey Syncline (locality 3 on Fig. 286 1). The base of this section is covered by alluvium, so its relationship to the underlying 287 Koolbye Formation is unclear. The section begins with a prominent bench of dark grey 288 parallel-laminated limestone, about 1.5 m thick (Fig. 5B), that is overlain by ~6 m of 289 sandy limestone with evidence for soft-sediment deformation. The carbonate strata 290 become increasingly sand-rich and dolomitic upsection until, by ~16.5 m, they are 291 dominated by medium-bedded brown dolomitic sandstone. The outcrop then disappears

292 into cover for ~ 30 meters, but thin-bedded, often calcareous, sandstone horizons are 293 occasionally visible in subcrop (Fig. 5A). Continuous outcrop reappears at 52.5 m, again 294 consisting of interbedded finely laminated calcareous sandstone and brown 295 dolograinstone. The overlying 30 m consists of brown-weathering (white on fresh 296 surface), coarsely recrystallized dolomite with no visible sedimentary structures. At 86.8 297 m the recrystallization fabric disappears and dolostone displays crinkly lamination and 298 roll-up structures that resemble microbially influenced sedimentary structures. In 299 addition, interbedded chert-replaced rip-ups and intraformational conglomerates occur 300 with other indicators of traction load deposition, including ripple and trough cross-301 stratified dolograinstone, channelized grainstone, and thin channelized sandstone lenses 302 (Fig. 5C). Starting at 116.7 m, the section becomes dominated by wavy laminated 303 dolomite, with abundant pisoids and oncoids (up to a cm in diameter), and domal 304 stromatolites up to 30-50 cm wide. A small fault cuts the section at ~127.5 m rendering 305 thickness measurements of the uppermost part of the succession less reliable. At a 306 minimum, an additional 10 m of small conical stromatolites, oncoids, and massive grey 307 dolomite cap the section. Pervasive recrystallization of Kazput Formation carbonates 308 dominates petrographic fabrics, but the interlocking calcite euhedra still preserve mm-309 scale features such as bedding lamination, coated grains, and ooids.

310

311 *4.2.2 Kazput Section #2 (K2)*

The K2 composite section (Figs. 7A, 8, 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, 9).

317 The basal portion of section K2A (Fig. 8) consists of highly fractured and 318 oxidized maroon and olive green siltstone and shale subcrop exposed in a small, south-319 flowing dry creek bed at the core of the anticline. Fine-grained deposits transition 320 upsection into ~18 m of olive green to dark grey, parallel laminated to ripple cross-321 laminated micritic limestone with locally-abundant silt and very fine-grained quartz sand. 322 The basal carbonate-rich strata are thinly bedded and record discrete mm- to cm-scale 323 alternations between massive and laminated beds that resemble the discrete Bouma C-E 324 subdivisions of distal turbidites. The central ~6 m of these more carbonate-rich strata are 325 dominated by pure olive green siltstone with minor detrital carbonate, and the upper 5-6326 m of these strata record the local development of hummocky cross-stratification and 327 occasional stoss-preservational ripple cross-lamination in the silty limestone deposits. 328 The upper \sim 45 m of section K2A consists of a broad coarsening-upwards package of 329 olive green to dark grey siltstone and argillite and minor thin-bedded light brown very-330 fine- to fine-grained quartz sandstone (Fig. 7B). The sandstone beds generally display 331 evidence for subtle scouring of underlying siltstone and argillite intervals and the units 332 are dominated by hummocky and swaley cross-stratification. Sedimentary structures in 333 the siltstone and argillite strata are difficult to discern due to a pervasive penetrative 334 cleavage, but they occasionally contain thin (< 5 cm thick) stringers of nodular and planar 335 micritic limestone. The silica- and carbonate-cemented sandstones of the Kazput 336 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

338

monocrystalline quartz sand with minor lithics, chert, and a pervasive chloritic matrix.

339 Since the upper part of section K2A was exposed on a prominent dip slope that 340 projected into a small, faulted alluvial valley, a parallel section was measured to the 341 northwest on the other side of the structure, section K2A2 (Fig. 8). A ~6 m thick package 342 of pure olive green siltstone was used to trace the section over the projected small fault 343 horizon. This section begins with ~ 17 m of dark grey-green siltstone and argillite that 344 progressively becomes increasingly carbonate rich. Thin (2–3 cm thick) stringers of 345 nodular to stratiform, silty micritic limestone thicken upsection into parallel-laminated 346 and ripple cross-laminated beds up to 10 cm thick. These silty limestone deposits are 347 abruptly overlain by ~4 m of peach-orange to blue-grey-colored fine-grained 348 dolograinstone with abundant ripple cross-lamination and minor detrital silt and quartz 349 sand. Locally, there are thin (<20 cm) horizons with irregular and wavy lamination that 350 resemble microbial carbonates. The upper portion of this small section becomes heavily 351 dolomitized, although there are multiple horizons with crenulated or wavy laminae and 352 intervals of detrital silt and quartz sand that form discrete lenses and stringers within the 353 carbonate laminae. A massive, light bluish-grey colored dolostone horizon was used to 354 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, 9). The lowermost 21 m of K2B strata are composed of silty to fine-grained sandy limestone with mm-scale parallel lamination, ripple crosslamination, and low-angle bedding truncations (Fig. 7B) interbedded with two carbonate-

360 dominated units: a) fine-grained micritic limestones with wavy laminae, crenulated 361 laminae, and small slumps from syn-sedimentary faults; and b) finely-laminated silty to 362 sandy carbonates with low angle hummocky and swaley cross stratification (Fig. 7C). 363 The wavy laminated carbonates often form thin (up to a few cm) stromatolites, which can 364 follow relict topography (Fig. 10B) or become contorted, folded, or faulted (syn-365 sedimentary). These cm-scale stromatolite layers become thicker and well developed 366 higher in the section. Above the interbedded silty and stromatolitic carbonates is a thick 367 $(\sim 15 \text{ m})$ interval of well-sorted, fine- to medium-grained sandstone, in decimeter-scale 368 beds with ripple and hummocky cross-stratification.

369 A similar succession of silty and stromatolitic carbonates capped by thick 370 sandstone occurs again in the K2C section; however, the internal structure of the silty 371 carbonate is more massive than those lower in the section. Higher in the section (around 372 45 m), the stromatolitic units develop into thick, well-defined, meter-scale stromatolite 373 domes (Fig. 10). These large stromatolites are commonly contorted and occasionally cut 374 by neptunian dykes (e.g. Fig. 10E). Interbedded with and above the large stromatolitic 375 domes are wave-rippled and hummocky cross-stratified silty sandstones. Beds are often 376 amalgamated, making bedding thickness difficult to discern. A further silty sandstone at 377 the top of the section is distinguished by carbonate intraclasts one centimeter to several 378 meters in length and typically rounded or tabular in shape (Fig. 9). The clasts consist of 379 stromatolites and other carbonate lithologies observed lower in the section, as well as 380 recrystallized oolitic grainstones that broadly link the two measured Kazput sections. 381

382 **5. Results:** *Carbon isotope chemostratigraphy*

383 5.1. Kungarra carbonates

| 384 | Lindsay and Brasier (2002) reported carbon isotopic abundances for 22 carbonate |
|-----|--|
| 385 | samples distributed through an estimated 250 m of stratigraphy at Horseshoe Creek, |
| 386 | reported as Kazput Formation but now known to belong to the Kungarra Formation. |
| 387 | Their δ^{13} C values ranged from -6 to +2‰, varying in sawtooth fashion through the |
| 388 | reported section. Our larger sample set $(n = 125)$ is consistent with measurements by |
| 389 | Lindsay and Brasier (2002); δ^{13} C values for Kungarra carbonates at Horseshoe Creek |
| 390 | exhibit a wide range of isotopic values, from -6.3‰ to +0.5‰, with no strong |
| 391 | stratigraphic trend (Fig. 2). The δ^{18} O values for the same samples range from -6.15‰ to - |
| 392 | 1.61‰, again with no strong trend (see supplemental data). In contrast to Lindsay and |
| 393 | Brasier (2002), our denser sampling coverage across multiple spatial scales enables us to |
| 394 | detect variations in the carbon isotope results of up to 2‰ between lighter (more |
| 395 | carbonate) and darker (less carbonate) layers within a single hand sample, as much as 4‰ |
| 396 | between samples from closely spaced sections at a single stratigraphic horizon, and |
| 397 | equally strong variation between samples spaced stratigraphically only centimeters to a |
| 398 | few meters apart (Fig. 2, supplemental data). |
| | |

399

400 *5.2. Kazput carbonates*

401 All δ^{13} C values measured for Kazput carbonates in the Hardey Syncline (n = 252)

402 fall between -4.5‰ and +2‰, and all but a stratigraphically constrained subset lie

- 403 between -0.5‰ and +1.5‰ (Figs. 6, 8, 9). These results are consistent with
- 404 reconnaissance analyses by Bekker et al. (2002). δ^{18} O values range from -8.13% to -
- 405 16.63‰, with most values falling between -15.5‰ and -16.5‰ (see supplemental data).

| 406 | At the base of section K1 (Fig. 6), $\delta^{13}C_{carb}$ values are low (around -4‰); whereas |
|-----|---|
| 407 | the last data point before the prominent covered interval is more moderate at 0.7‰. |
| 408 | Above the covered interval, $\delta^{13}C_{carb}$ values are again depleted (-3‰) but quickly return to |
| 409 | values between 0 and 1‰ for the remainder of the section (Fig. 6). The $\delta^{13}C_{carb}$ signature |
| 410 | of section K2 begins much like that of K1, with negative values (-2.5% to -1.2%) in the |
| 411 | lowermost 10 m (K2A, Fig. 8) followed by values that fluctuate around 0‰ (K2A and |
| 412 | K2A2, Fig. 8). Higher in the section (K2B and K2C), C-isotopic values generally |
| 413 | fluctuate between ca. 0.5 and 1.5‰, with a few more negative values interspersed |
| 414 | through the sections (Fig. 9). Variations of up to 1‰ among carbonate intraclasts at the |
| 415 | top of the section likely reflect the heterogeneous stratigraphic levels from which the |
| 416 | intraclasts and carbonate blocks were sourced. |
| 417 | Petrographic subsampling of stromatolites at 46–47 m of K2C shows limited |
| 418 | isotopic variation among microfacies, with stromatolitic carbonates slightly heavier than |
| 419 | the carbonate-rich clastics that overlie the stromatolites (Fig. 9). As might be predicted |
| 420 | when ambient waters are strongly oversaturated with respect to calcite and aragonite |
| 421 | (Bergmann et al., 2013), carbonates within stromatolites differ little from encompassing |
| 422 | laminae in both their carbon and oxygen isotope values (Fig. 9). The analyzed Kazput |
| 423 | carbonates do not record the extreme ¹³ C enrichment that defines the younger |
| 424 | Lomagundi-Jatuli event. |
| 425 | |
| 426 | 6. Results: Kazput stromatolites |

427 The most notable sedimentary features of the Kazput carbonates are m-scale
428 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 crossstratification. 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
meters thick (Fig 10A).

434 Two fabrics make up the Kazput stromatolites (see Section 7.3 for genetic 435 interpretations): wavy to crenulated siliciclastic laminae, 30 to 400 μ m thick, that are 436 continuous on the scale of a single dome, and interbedded, convex upward, lenticular 437 carbonates that are generally discontinuous on a mm to cm-scale and are common or 438 absent in alternating zones (Fig. 10). The discrete fabrics are clear in both optical 439 microscopic view (Fig. 11) and in elemental maps using SEM (Fig. 12). Lamina-rich 440 zones tend to be <1 cm to about 2 cm thick, whereas zones rich in lenticular carbonate 441 vary from <1 cm to, more commonly, 10–15 cm thick. Because silicate laminae are more 442 resistant to erosion than carbonate lenses, the broad mesoscale fabric of the stromatolites 443 is best observed on weathered surfaces; lamina-rich zones are darker brown and more 444 resistant, carbonate-rich zones are grey or lighter tan and more recessive (Fig. 10). For 445 the most part, lenticular carbonates occur within 5-15 mm long convex-upward mini-446 domes bounded by laterally linked laminae that tend to be continuous across the surfaces 447 on which they occur. In some layers, lenses extend laterally for several cm along bedding 448 planes (Fig 10D); however, these occurrences are rare. Most of the stromatolitic 449 structures are irregular, and some show evidence of plastic deformation (folds and 450 slumps). At a few horizons, however, more or less regular, laterally linked columns

451 develop either locally (Fig. 10F) or across a stromatolitic dome surface (Fig 10D);
452 columns are 5–8 cm wide and 2–10 cm high.

453 At the microscopic scale, laminae contain an admixture of several minerals, 454 including equant calcite anhedra, $10-25 \mu m$ in maximum dimension; guartz silt; clay 455 minerals (commonly chloritized, but also including Mg-rich species); and small opaque 456 euhedra, probably originally diagenetic pyrite, but now altered to iron oxides (Figs. 11, 457 12). While clays can form authigenically within microbialites (Konhauser and Urrutia, 458 1999; Léveillé et al., 2000) the presence of abundant fine-grained quartz grains and other 459 detrital material indicates the incorporation of suspension load siliciclastics, even when 460 traction load sands were absent. Organic carbon inclusions also occur sporadically 461 throughout the K2 stromatolites; these appear as black spots on the composite elemental 462 map or red spots on the carbon map in Figure 12. 463 Lenticular units generally consist of interlocking calcite anhedra 25–100 µm in 464 maximum dimension. Pyrite, reduced carbon, and clay minerals also occur in these zones, 465 although at low abundances (Fig. 12). The coarsely crystalline carbonates reflect 466 pervasive diagenetic and/or metamorphic recrystallization, but mm-scale banding is 467 preserved locally (Fig 11C). Crystals are smaller in these banded carbonates, generally 468 less than 25 µm, and discrete zones are defined by both larger and smaller crystals 469 (lighter and darker zones in Fig 11C), as well as a faint tendency for smaller crystals to be 470 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. Clasticfilled 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.

481

482 **7. Discussion**

483 7.1 Kungarra carbonates

484 Broadly, Kungarra Formation strata record a major coarsening upwards sequence 485 from banded iron formation and starved basin deposits of the underlying Boolgeeda Iron 486 Formation through glaciomarine deposits of the Meteorite Bore Member and finally into 487 tidal flat, beach, and fluvial deposits of the overlying Koolbye Formation (Mazumder et 488 al., 2015). The measured Horseshoe Creek section (Fig. 2) captures a small component of 489 this broad coarsening upwards trend. The abundance of fine-grained suspension deposits 490 interbedded with starved ripple and planar ripple cross-laminated sandstone intervals 491 most likely represents subtidal deposition between storm and fair weather wave base. 492 This is consistent with the limited development of stromatolites. The lack of directly 493 overlying shoreface deposits suggests that deposition was predominantly in an offshore 494 setting, although the increase in sandstone intervals and the broad coarsening upwards 495 trend in the upper ~ 25 m of the measured section is diagnostic of progradation. Given 496 these features, we suggest these strata were largely deposited in a prodeltaic or mid-outer

497 shelf environment, broadly consistent with the interpretations of previous workers

498 (Krapež, 1996; Martin et al., 2000; Van Kranendonk et al., 2015).

499 As noted above, Lindsay and Brasier (2002) sampled the carbonate-bearing rocks 500 at Horseshoe Creek, and the highly variable carbon isotope values were interpreted to 501 indicate pronounced carbon cycle variation in the aftermath of the GOE. However, 502 regional mapping has shown that the strata in question lie stratigraphically beneath the 503 Meteorite Bore Member and so are properly assigned to the Kungarra Formation 504 (Krapež, 1996; Martin et al., 2000; Van Kranendonk et al., 2015). Furthermore, 505 stratigraphic field relationships and detailed petrology both suggest that most of these 506 Kungarra carbonates formed during diagenesis, and the marked C-isotopic variation recorded in these rocks confirms this interpretation (Figs 2–4). δ^{13} C values of -6‰ are 507 508 unusual for carbonates of any age and commonly reflect the incorporation of isotopically 509 light carbon into diagenetic carbonates precipitated within sediments (Irwin et al., 1977). Within Lindsay and Brasier's (2002) plotted stratigraphic column, δ^{13} C values commonly 510 511 vary by several per mil from one sample to the next. Our more detailed data set enables 512 us to document large carbon isotopic variations (up to 4‰) within hand samples and 513 between samples from the same stratigraphic horizon (Fig. 2). Such fine-scale spatial and 514 temporal variation is essentially impossible to accommodate in terms of primary C-515 isotopic signatures reflecting global seawater chemistry. 516 Arguably, the isotopic variation observed at individual horizons in the lower 517 Kungarra Formation of the Horseshoe Creek section reflects diagenetic carbonate 518 precipitation from pore fluids in which dissolved inorganic carbon (DIC) sourced from 519 seawater was variably mixed with inorganic carbon generated by the remineralization of

| 520 | isotopically light organic matter. In this case, the most positive isotope results represent |
|-----|--|
| 521 | values closest to the dissolved inorganic carbon (DIC) in seawater. Alternatively, if these |
| 522 | units underwent episodic subaerial exposure in the Paleoproterozoic, meteoric waters |
| 523 | may have altered the isotopic composition of the strata during early diagenesis. |
| 524 | Regardless, the isotopic values from the measured Kungarra Formation from the |
| 525 | Horseshoe Creek section by and large do not represent the original isotopic composition |
| 526 | of seawater during the time of deposition. |
| 527 | |
| 528 | 7.2. Kazput carbonates |
| 529 | Similar to the underlying Kungarra Formation, the ~750 m thick Kazput |
| 530 | Formation records a complex depositional history heavily influenced by local |
| 531 | synsedimentary tectonism (Krapež, 1996; Martin et al., 2000; Thorne and Tyler, 1996; |
| 532 | Thorne et al., 1995). Numerous cm to dm scale synsedimentary normal faults in K2B and |
| 533 | K2C indicate the occurrence of active extensional tectonism during Kazput |
| 534 | sedimentation. Furthermore, the large stromatolitic clasts and rip-ups (including m-scale |
| 535 | rafts that are clearly transported) in the uppermost K2 facies likely represent seismically- |
| 536 | generated breccias (seismites) or the erosion of locally uplifted strata. Given the limited |
| 537 | stratigraphic range of this study within the Turee Creek Group, it is difficult to provide |
| 538 | more context to the greater basinal or tectonic setting of these strata. |
| 539 | Given previous descriptions of the basal Kazput succession as a starved basin |
| 540 | marked by distinct carbonate rhythmites (e.g., Krapež, 1996), the Kazput sections |
| 541 | described here appear to lie relatively close to the base of the formation. The parallel- |
| 542 | laminated and turbiditic silty limestone units that mark the base of the two measured |
| | |

543 sections suggest a relatively quiet-water environment. At both localities, the rocks 544 quickly transition upsection into fine-grained siliciclastic units with abundant evidence 545 for storm-generated bedforms, indicative of higher energy/shallower water conditions. 546 The remainder of the measured sections can be interpreted as a broad shallowing upward 547 succession of mixed carbonate and siliciclastic strata. The abundance of fine-grained 548 shale and siltstone interbedded with hummocky and swaley cross-stratification in the 549 central part of the sections suggests subtidal deposition on a storm-dominated shelf 550 between storm and fair weather wave base. The establishment of this subtidal shelf 551 setting was relatively short-lived because both Kazput sections record relatively abrupt 552 shoaling into shallow-water shoreface and platformal settings. This is clearly evidenced 553 by the deposition of thick peritidal to subtidal platformal carbonate dominated by ooids, 554 oncoids, and coarse dolograinstone in section K1 (Fig. 6) and a more complex mixed 555 sandstone-stromatolitic limestone sequence in section K2 (Figs. 8, 9). 556 The striking difference in siliciclastic composition between the upper portions of 557 the two parallel sections (K1 and K2) is problematic; however, given the complexity and 558 heterogeneity of along-strike facies and possible proximity to a shoreline, it is reasonable 559 to conclude that their differences are primarily due to proximity to siliciclastic point 560 sources, such as nearby deltaic systems. In fact, section K2 preserves many of the 561 hallmarks of high sedimentation rates in a tectonically active basin, such as thick 562 sequences of stoss-preservational ripple cross-lamination and abundant synsedimentary 563 dykes and soft-sediment deformation. The intimate association of unique stromatolite 564 morphologies and abundant trough cross-stratified sandstone intervals in the upper K2 565 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.

571 Unlike the results from the Kungarra Formation carbonates, the Kazput isotope 572 data are interpreted to indicate dominantly primary seawater values. The agreement of 573 values from closely spaced samples and the consistent trends suggest that diagenetic 574 overprinting of the isotopic signal was minimal. Furthermore, no petrographic results 575 suggest secondary calcite overgrowths, which are clearly documented in the Kungarra 576 carbonates (Fig. 3). Thus, the C-isotopic values of -1 to -3‰ in lowermost Kazput carbonates could record transiently low δ^{13} C in contemporaneous seawater. Above this 577 578 horizon, however, values hover between 0.5‰ and 1.5‰ through the reminder of the 579 succession.

580

581 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 lensoidal 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

589 materials that were both coherent and flexible; (2) guartz silt and, very likely, clay 590 minerals within laminae indicate the trapping and binding of introduced materials; (3) 591 laminae contain a higher concentration of reduced carbon than associated microfabrics, 592 consistent with an origin as mats; and (4) laminae contain localized high concentration of 593 (originally) pyrite, suggesting decay within mats via microbial sulfate reduction. The 594 microbial mats likely nucleated on sandy substrates, forming wrinkled mats (wrinkle 595 structures or laminae) and cm-scale stromatolites (Fig 10B); larger structures resulted 596 from protracted growth between episodes of sand deposition. Based on petrographic and 597 elemental analysis, the quartz silt and clay minerals that are found within the 598 stromatolites indicate that suspension load siliciclastics were continuously deposited on 599 mat surfaces during stromatolite growth.

600 An outstanding question is the extent to which the lenticular carbonates found 601 between laminae formed on, or just beneath, mat surfaces or filled primary voids formed 602 by gas emission within mats. Gas-generated voids occur sporadically throughout the 603 Proterozoic stromatolite record. Their formation generally requires strong but flexible 604 mats populated by filamentous microorganisms, gas generation (e.g., oxygenic 605 photosynthesis, decomposition of organic matter, or methanogenesis), and seawater that 606 is strongly oversaturated with respect to calcium carbonate minerals (e.g., Knoll et al., 607 2013; Mata et al., 2012). Indeed, primary voids in Archean stromatolites have been 608 interpreted as prima facie evidence for oxygenic photosynthesis at 3 Ga (Bosak et al., 609 2009, 2010). The carbonate precipitates do not crosscut microbial laminae, eliminating 610 dissolution and subsequent in-filling as an explanation for the observed textures.

611 Given that the Kazput stromatolites lie within rocks deposited stratigraphically 612 after the GOE, all aforementioned requirements for the formation and preservation of 613 primary voids appear to have been met locally. The irregular, convex upward 614 morphology of laminae is consistent with this interpretation, as is the orientation of zoned 615 cements in some stromatolites (Fig. 11C, E). However, the lateral extent of discrete 616 cement horizons that occasionally contain clay, pyrite, and reduced carbon flecks also 617 supports the alternative interpretation that the cements are seafloor precipitates formed on 618 or within surface mats (e.g., Fig. 11B). In fact, the two interpretations are not mutually 619 exclusive; if the waters that bathed the Kazput bioherms were strongly supersaturated 620 with respect to calcium carbonate, both void-forming and cementing processes may have 621 been operating during stromatolite accretion. 622 Stromatolites are found widely in late Archean and Paleoproterozoic carbonates, 623 with particularly good descriptions of macro- and microstructure available for late 624 Archean microbialites from the Gamohaan and Frisco formations of the 625 Campbellrand/Malmani succession, South Africa (Sumner, 1997), and lower 626 Paleoproterozoic carbonates from the Fennoscandian Shield (McLoughlin et al., 2013). 627 What differentiates the Kazput stromatolites from most of these (and essentially all 628 younger Proterozoic) structures is their abundance of lenticular carbonate. Microdigitate 629 stromatolites, some of them small microbial structures and others stacked crystal fans 630 (Grotzinger and Knoll, 1999), are particularly widespread in Paleoproterozoic carbonate 631 successions (Medvedev et al., 2005). These structures formed widely across shallow 632 shelves and platforms and reflect a high degree of oversaturation with respect to calcium 633 carbonate minerals. Thus, they are relevant to the interpretation of the Kazput structures,

but differ in lacking the regular interlamination of microbial laminae and precipitatesdescribed here.

636 Perhaps the closest approximation of the composite laminar-lenticular Kazput 637 fabric is found in cuspate microbialites from the Campbellrand/Malmani succession 638 (Sumner, 1997) and elsewhere in late Archean carbonates (e.g., Hofmann and Masson, 639 1994; Riding et al., 2014). In these structures, void spaces that originated by the draping 640 of pliant mats across vertical microbial "tent poles" were filled penecontemporaneously 641 by carbonate cement (Sumner, 1997). Locally, stromatolites in the 2720 ± 5 Ma 642 Tumbiana Formation, Fortescue Group, Western Australia, also contain thin, irregular 643 patches of carbonate precipitates, interpreted as lake-floor precipitates (Flannery and 644 Walter, 2012; Lepot et al., 2008, 2009). The Kazput and Tumbiana stromatolites do share 645 some similarities, such as the weathering profile (prominent laminae and recessive 646 cements) and the µm-scale banded carbonate domes within carbonate-rich layers; 647 however, there are important distinctions between the two. Kazput stromatolites do not 648 contain halite pseudomorphs, nor is there evidence for the penecontemporaneous erosion 649 of carbonate precipitates, as is clearly evident in the Tumbiana stromatolites (Lepot et al., 650 2008, 2009). Furthermore, the Kazput stromatolites cements are largely discrete (mm- to 651 cm-scale) lenses and typically do not form thick, continuous cement laminae as in the 652 Tumbiana examples. These examples underscore the importance of macroscopic 653 carbonate precipitates in generating fabrics within late Archean/early Paleoproterozoic 654 stromatolites; nonetheless, the specific alternation of particle-binding mats and lenticular 655 carbonate precipitates is, to the best of our knowledge, a unique feature of Kazput

stromatolites in the Hardey Syncline, reflecting a potentially time-limited interactionbetween the evolving biota and its physical surroundings.

- 658
- 659 7.4. Chemostratigraphic comparisons

660 Few carbon isotopic data are available for carbonates that unambiguously lie 661 above Paleoproterozic iron formations but below glaciogenic rocks. Samples from the 662 poorly dated Boxelder Creek Formation, South Dakota (Bekker et al., 2003a) and 663 Polisarka Sedimentary Formation in drill cores from the Kola Peninsula, Russia (Brasier 664 et al., 2013), span a range of -6‰ to 1‰. Carbonates of the Gandarela Formation, Brazil, 665 are isotopically similar, but cannot be placed unambiguously relative to Paleoproterozoic 666 ice ages. Post-glacial marbles of the Paleoproterozoic Sauser Group, India, also show C-667 isotopic values of -3.1‰ to +2.6‰ above a moderately negative basal interval (-4.4‰ to 668 -7.4‰) interpreted as a cap carbonate (Mohanty et al., 2015). The most positive C-669 isotopic values for Kungarra carbonates are consistent with the values reported from 670 other basins, but the uncertainties introduced by diagenetic carbonate precipitation limit 671 what the Kungarra samples can add to discussions about the post-BIF, pre-GOE carbon 672 cycle.

673 On the basis of limited data, Karhu and Holland (1996) hypothesized that the 674 strongly positive carbon isotopic excursion called the Lomagundi-Jatuli event began ca. 675 2.2 Ga. Even now, isotopic data are sparse for successions younger than GOE 676 onset/glaciogenic rocks but older than 2200 Ma. Martin et al. (2013) summarized 677 available radiometric constraints on the Lomagundi-Jatuli event, concluding that the 678 event began between 2306 ± 9 Ma and 2221 ± 5 Ma and ended between 2106 ± 8 and

679 2057 ± 1 Ma, for a maximum duration of 249 ± 9 million years and a minimum duration 680 of 128 ± 9.4 million years. The new data presented herein are consistent with these age constraints, and provide no evidence for strongly positive Lomagundi-Jatuli δ^{13} C values 681 682 during deposition of the measured Kazput sections. We recognize, however, that our 683 sections represent a limited proportion of the time interval between Paleoproterozoic ice 684 ages and events commencing at 2200 Ma; regionally, Kazput carbonates are separated 685 from the Cheela Springs basalt and its intrusive counterpart (2209 ± 15 Ma; Martin et al., 686 1998) by thick siliciclastic deposits and a major unconformity (Fig. 1). Thus, while these 687 new data demonstrate that the interval between the GOE onset/glacials and 2200 Ma 688 includes a time where the seawater DIC isotopic composition was unperturbed and 689 similar to modern isotopic values, we cannot rule out the possibility that it also includes 690 short intervals of positive C-isotopic excursions, which are not recorded in the analyzed 691 Kazput Formation sections.

692 Kazput carbonates are isotopically similar to those of well-developed carbonates 693 in the Gandarela Formation, Brazil, where 163 samples show values near 0‰ (Bekker et 694 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 ¹³C 695 696 enrichment, but the regional stratigraphy contains no glacial diamictites; Bekker et al. 697 (2003b) cite a Pb-Pb date of 2420 ± 19 Ma for Gandarela carbonates, but this does not 698 appear in Martin et al.'s (2013) review due to the low confidence in the interpretation of 699 Pb-Pb carbonate dates in Proterozoic successions. The well-studied Duitschland 700 Formation, dated indirectly at 2316 ± 7 Ma by Re-Os on black shale of the possibly correlative Rooihoogte-Timeball Hill Formation (Hannah et al., 2004), bears ¹³C 701

enrichments up to 10.1‰ in its upper part (Bekker et al., 2001). However, the Mooidraai Dolomite (diagenetic age of 2394 ± 26 Ma, based on carbonate-bound Pb), also in South Africa, appears to have no isotopic anomalies, with δ^{13} C values of 0.5 to 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.

708

709 8. Conclusions

710 This study provides new litho- and chemostratigraphic data for carbonate-bearing 711 intervals of the 2.45–2.22 Ga Turee Creek Group, Western Australia, which spans a 712 pivotal time in Earth history after the deposition of global banded iron formation and 713 across the GOE. Field relationships, petrography, elemental mapping, and C-isotope 714 values reveal that most Kungarra carbonates in the pre-glacial lower part of the Turee 715 Creek Group formed during syndepositional or post-depositional diagenesis; therefore, 716 the abundant and highly negative C-isotopic values within these rocks cannot be 717 interpreted in terms of global carbon cycle dynamics, as previously assumed by Lindsay 718 and Brasier (2002). 719 In contrast, carbonates from the lower part of the uppermost Kazput Formation of 720 the Turee Creek Group — which sits in a globally under-sampled interval above 721 Paleoproterozoic glacial deposits and below an unconformity constrained by the ~2.2 Ga 722 Cheela Springs Basalt and associated sills — do appear to record the C isotopic

723 composition of seawater DIC, with consistent δ^{13} C values of -2 to +1.5‰. As the lower

724 parts of the Kazput Formation likely represent a relatively brief time interval, it

725 strengthens a growing body of evidence indicating that the initial geochemical signature 726 of the GOE and the exceptionally positive values of the Lomagundi-Jatuli isotope 727 excursion(s) are separated by one or more intervals of normal C isotopic composition. 728 The moderate C-isotopic values of Turee Creek Group carbonates strengthen the 729 argument that the complex set of processes that drove the onset of the GOE did not 730 include anomalously high proportional rates of organic carbon burial. Of course, as others 731 have noted (e.g., Lyons et al., 2014; and references therein), it is not required that the 732 increase in Paleoproterozoic oxygen concentrations was limited to the brief interval 733 marked by the end of mass-independent S isotope fractionation, nor that oxygen change 734 was monotonic (Canfield, 2014; Canfield et al., 2013; Lyons et al., 2014). Instead, the 735 MIF-S signature might reflect an interval of atmospheric oxygen accumulation that was 736 neither large nor rapid but crossed an important threshold. One would expect pO_2 to 737 continue to rise during the Lomagundi-Jatuli event (e.g., Bekker and Holland, 2012; 738 Kump et al., 2011; Rasmussen et al., 2013), but any increase in oxygen levels driven by 739 extensive organic carbon burial postdates the MIF-S boundary, very likely by tens of 740 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

cuspate Archean microbialites from South Africa (Sumner, 1997) and late Archean

749 Tumbiana stromatolites from Western Australia (Flannery and Walter, 2012; Lepot et al.,

750 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.

753

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1035 **Figure captions**

1036 Figure 1. Geographic, stratigraphic, and geological location of the studied sections.

1037 Upper left: Location of study area in Australia (star). Upper right: stratigraphic context

1038 for the Turee Creek Group; stars indicate stratigraphic horizons of studied sections.

- 1039 Bottom: Geological map of the Hardey Syncline from Martin et al. (2000); numbered
- 1040 circles indicate studied localities.

1041

1042 Figure 2. Litho- and chemostratigraphy of the Kungarra Formation section at Horseshoe

1043 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

1045 succession of stromatolitic textures (interpreted to be of microbial origin). Inset images

are photomicrographs (plane polarized light) of the Kungarra carbonates; sample HC2

1047 12.5A is from 13.8 m and HC3 40.2 is from 40.2 m. Dots in inset images indicate

1048 microsampling locations and their carbon isotope values.

1049

1050 Figure 3. Kungarra Formation carbonates at Horseshoe Creek. A) Pinkish-white micritic

1051 limestone interbedded with reddish-brown fine-grained sandstone forming starved

1052 ripples, Australian dollar for scale (25 mm diameter). B) Close up of stromatolites from

1053 roughly 34.2 m in stratigraphic height, Australian dollar for scale. C) Petrographic view

1054 of the domal stromatolite layer (Sample HC3 34.3, 34.3m in stratigraphic height),

showing overgrowths of calcite on micritic carbonates stained by iron oxides (note scalebar).

| 1058 | Figure 4. Elemental map of Kungarra Formation limestone (sample HC3 16.25 from |
|------|--|
| 1059 | 16.25m in stratigraphic height); top images are the entire sample, and the bottom images |
| 1060 | are close up views of the boxed area. On the left are SEM images, on the right are false |
| 1061 | color representations of the elemental maps, and the middle images are a composite |
| 1062 | image of the SEM images and elemental maps. Note that the calcium (calcite) only |
| 1063 | manifests in rare lenses with abundant detrital minerals, suggesting that it is not primary |
| 1064 | carbonate but rather diagenetic. |
| 1065 | |
| 1066 | Figure 5. Lithologies of the Kazput Formation in Hardey Syncline section K1. A) |
| 1067 | Overview of stratigraphy, section K1 begins in the thin-bedded limestones in the |
| 1068 | foreground, the base of the cliff is at 53 m elevation in the stratigraphic column (Fig. 6), |
| 1069 | and the measured section continues up the gully on the left. B) Close-up of thin-bedded |
| 1070 | limestones at the base of the K1 section, hammer for scale. C) Cross-stratified |
| 1071 | grainstones with abundant bed-parallel silicification at meter 108 in the K1 section, |
| 1072 | Sharpie tip for scale. |
| 1073 | |
| 1074 | Figure 6. Litho- and chemostratigraphy of the Kazput Formation at section K1. |
| 1075 | |
| 1076 | Figure 7. Lithologies of the Kazput Formation in Hardey Syncline section K2. A) |
| 1077 | Overview of stratigraphy, showing where individual subsections were measured. B) Fine |
| 1078 | grained, parallel-laminated facies in section K2A, Australian dollar for scale (25 mm |
| 1079 | diameter). C) Section K2B; silty to (fine) sandy carbonates with small-scale ripples in the |
| 1080 | lower half of the photo and mm-scale laminations in the upper half. Blue ruler at the |
| | |

| 1081 | bottom of the photo is 10.5 cm long. D) Interbedded sandy carbonates and fine-grained |
|------|---|
| 1082 | carbonates with wavy to stromatolitic laminae (section K2B); rock hammer for scale. |
| 1083 | |
| 1084 | Figure 8. Litho- and chemostratigraphy of the Kazput Formation at sections K2A and |

1085 K2A2. Note that K2A2 sits stratigraphically above the K2A section.

1086

1087 Figure 9. Litho- and chemostratigraphy of Kazput Formation at sections K2B and K2C.

1088 Expanded section in upper right highlights geochemical results from stromatolite

1089 microsampling.

1090

1091 Figure 10. Kazput stromatolites. A) Large domal stromatolites forming over relict

1092 topography at 47 m stratigraphic height (in section K2C). B) Thin stromatolite layer

1093 within fine-grained micritic limestones; note the eroded base on which the stromatolite

1094 accreted. C) Alternating layers of siliciclastic lamina-rich (resistant) and carbonate-rich

1095 (recessive) layers within the larger stromatolites; note the weathering difference between

1096 units. D) Top layers of domal stromatolites from K2C (47 m), note the alternating layers

1097 of siliciclastic lamina-rich and carbonate-rich layers. The stromatolites on the top layer

1098 formed much larger (>5 cm), more cement-rich structures than earlier layers. E)

1099 Synsedimentary neptunian dyke through stromatolite layers, dark patches are shadows

1100 from vegetation on the outcrop. F) Domal stromatolites growing into microdigitate

1101 stromatolites within cement-rich intervals of the large domal stromatolites in K2C.

1102

1103 Figure 11. Petrographic textures of Kazput stromatolites (all plane polarized light). A)

1104 Alternating siliciclastic lamina-rich and discontinuous carbonate-rich layers of large

domal stromatolites from section K2C (47 m, sample K2C 5.5B2); B) Unusually

1106 continuous carbonate-rich layers in section K2C (65.7 m, sample K2C 31.8m); C)

1107 Microstructure of a transported and rolled up stromatolite, showing the local preservation

1108 of fine banding in lenticular carbonate precipitates highlighted by arrows (63.4 m, sample

1109 K2C 28.6); D) Detail of a siliciclastic-rich lamina in a small stromatolite containing

1110 quartz, pyrite, and clay minerals, with carbonate-rich areas above and below (Sample

1111 K2C 28.5); E) Close up of Fig. 11C highlighting the faint banding within the carbonate

1112 fabric of the deformed stromatolite (63.4 m sample K2C 28.6).

1113

1114 Figure 12. Elemental map of Kazput Formation stromatolitic carbonates (sample KAZS1,

1115 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

1117 images, right column images are false color representations of the elemental maps, and

1118 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.

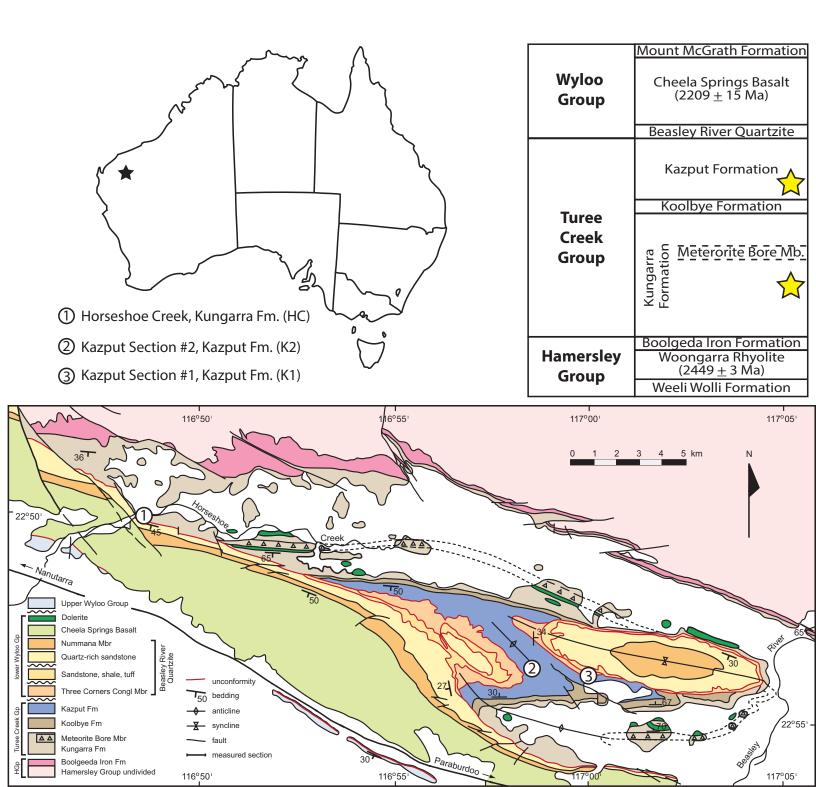
1121 Small iron oxide grains (blue in false color maps) occur throughout the Kazput section

1122 but are concentrated in silicate-rich laminae (orange in false color maps). There are also

1123 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.

1125



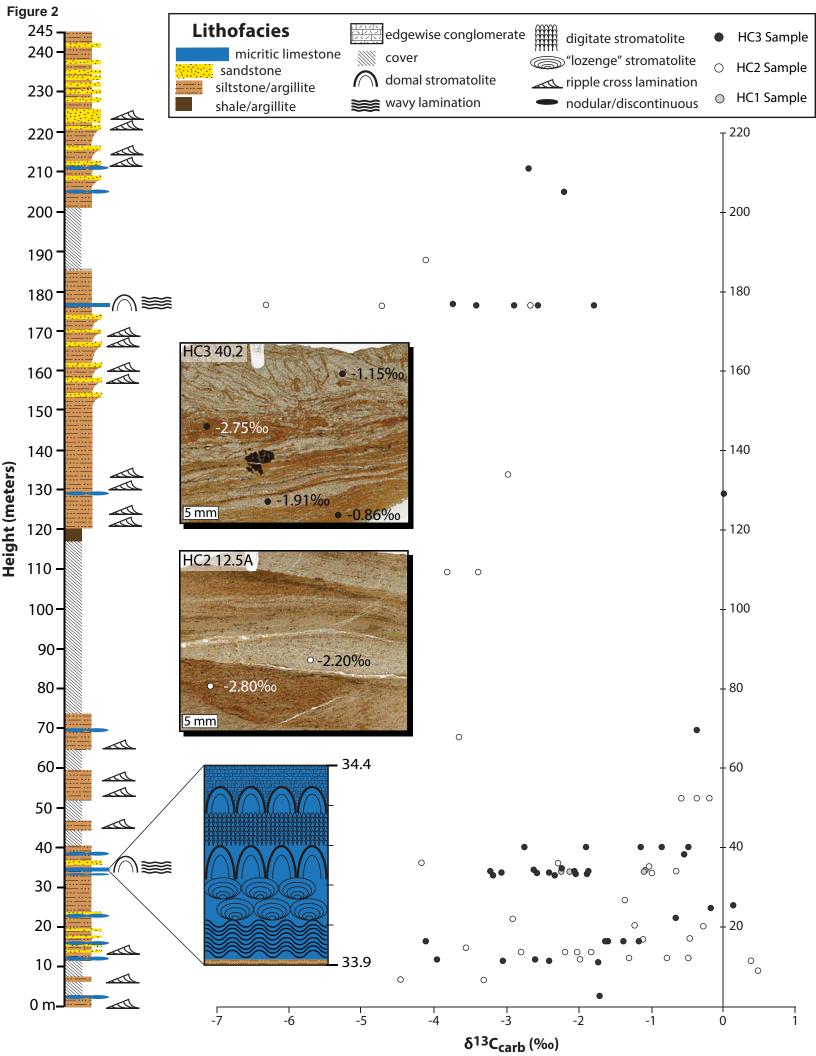


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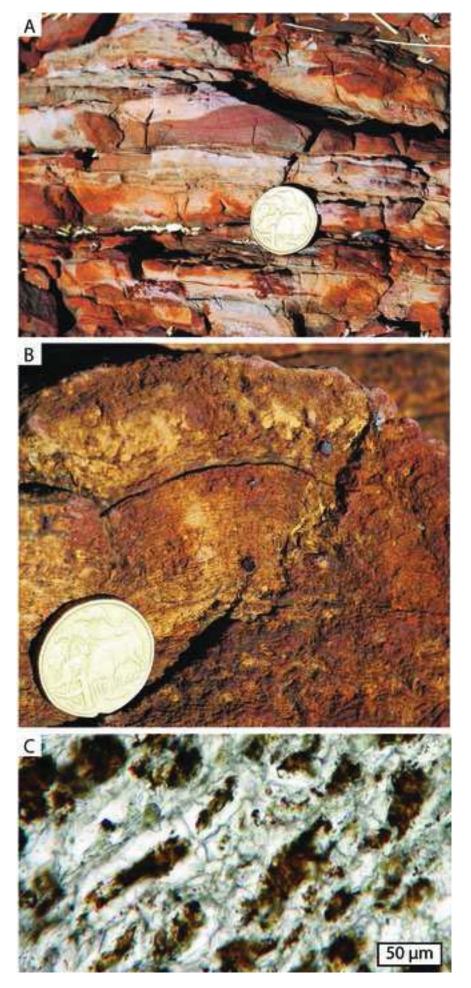
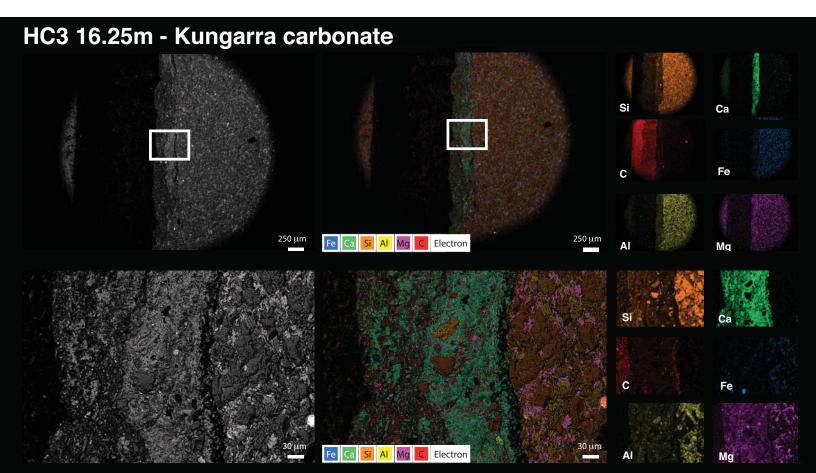
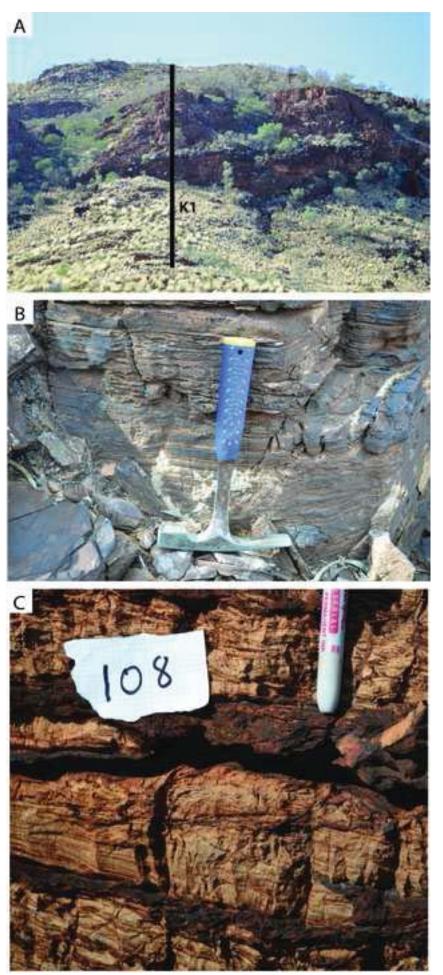
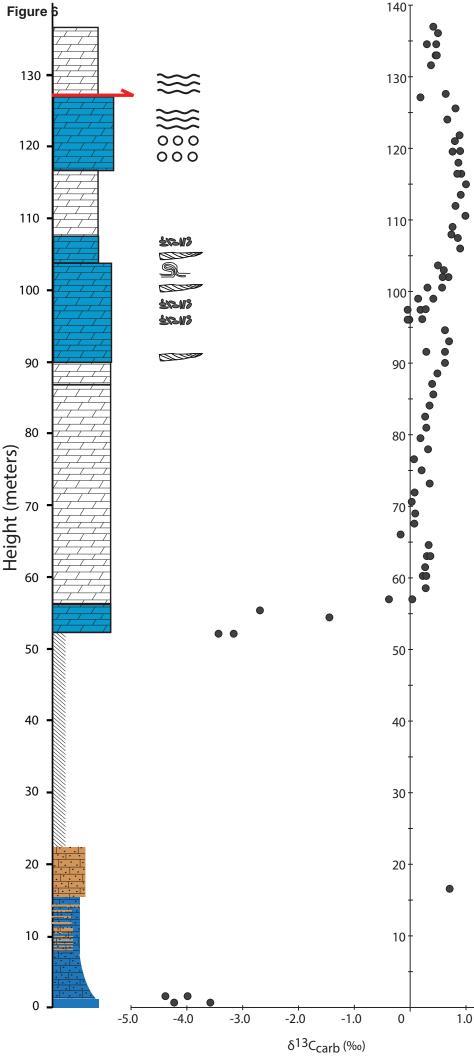
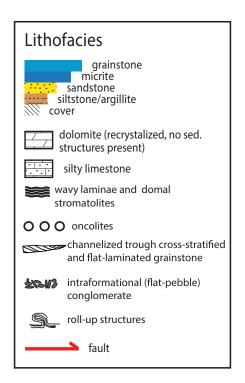


Figure 4



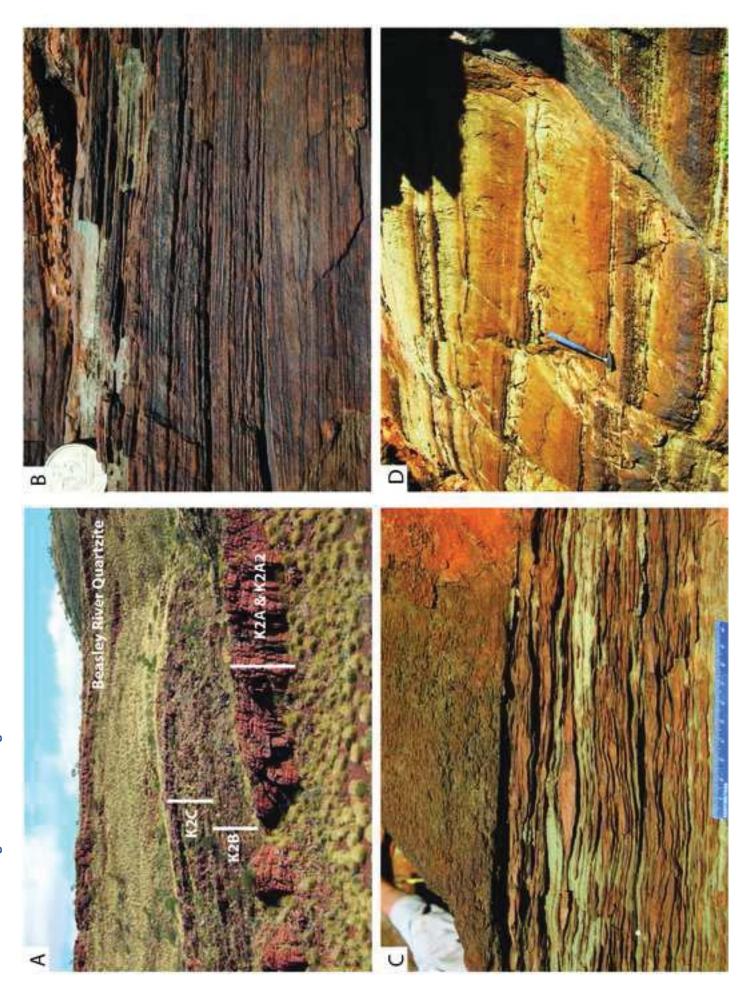


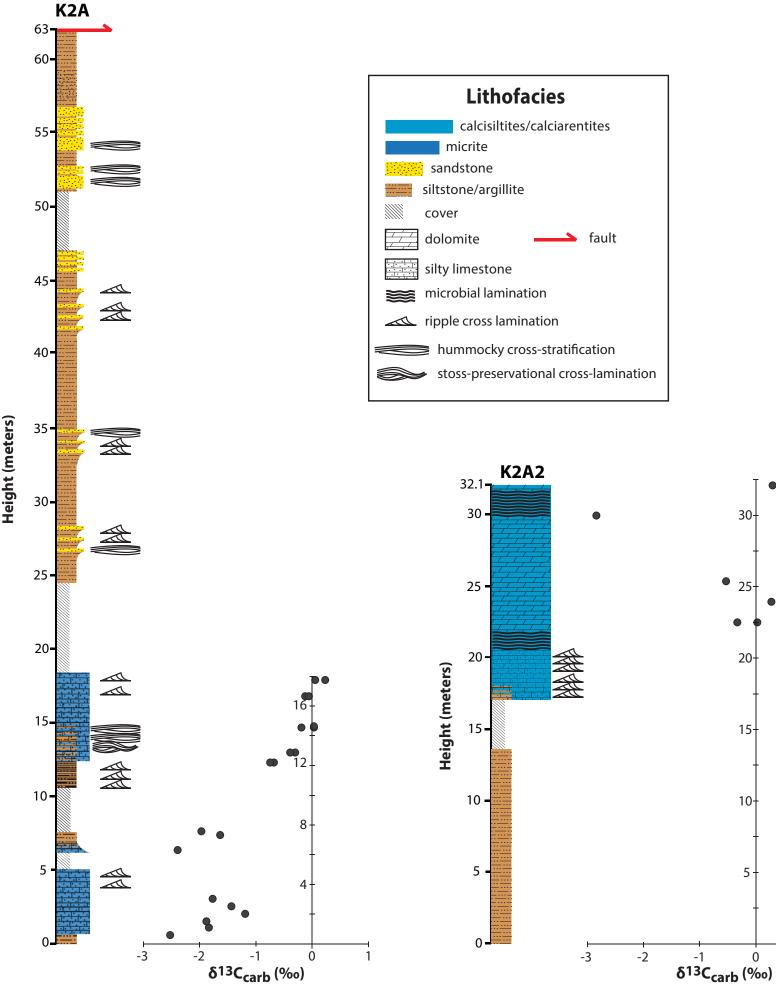




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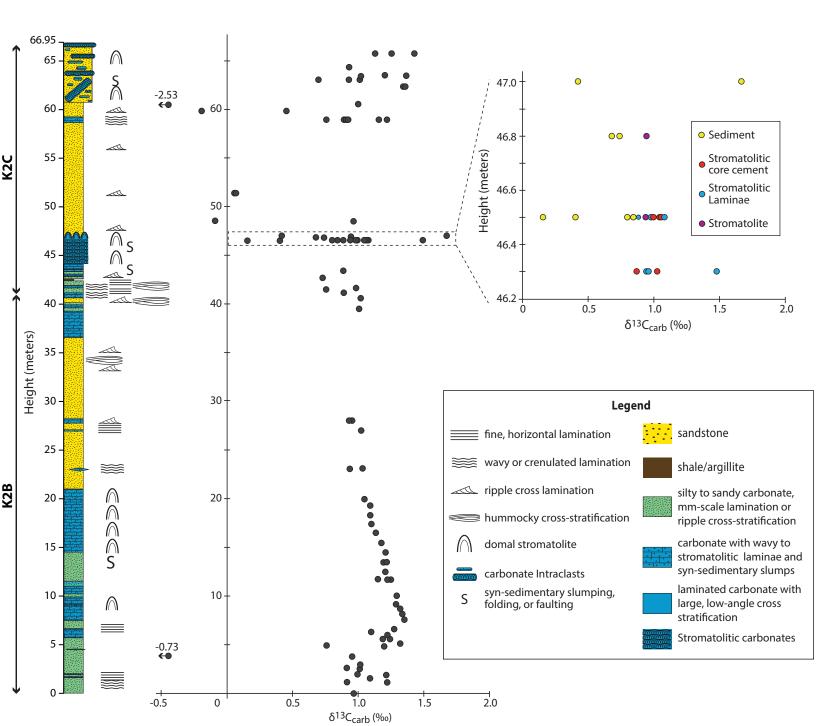
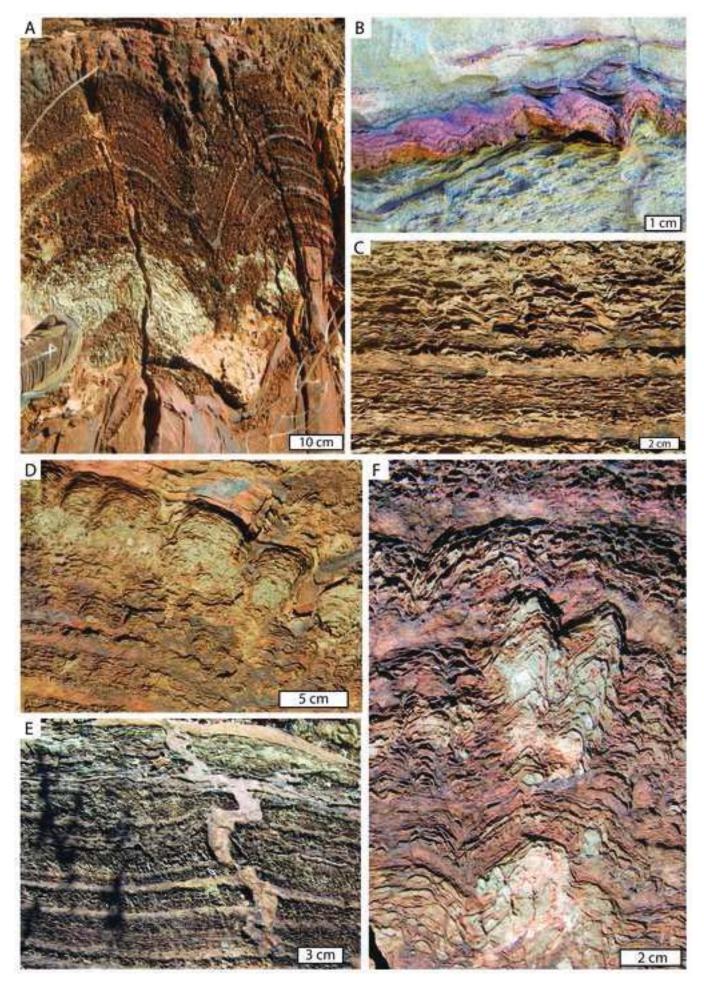
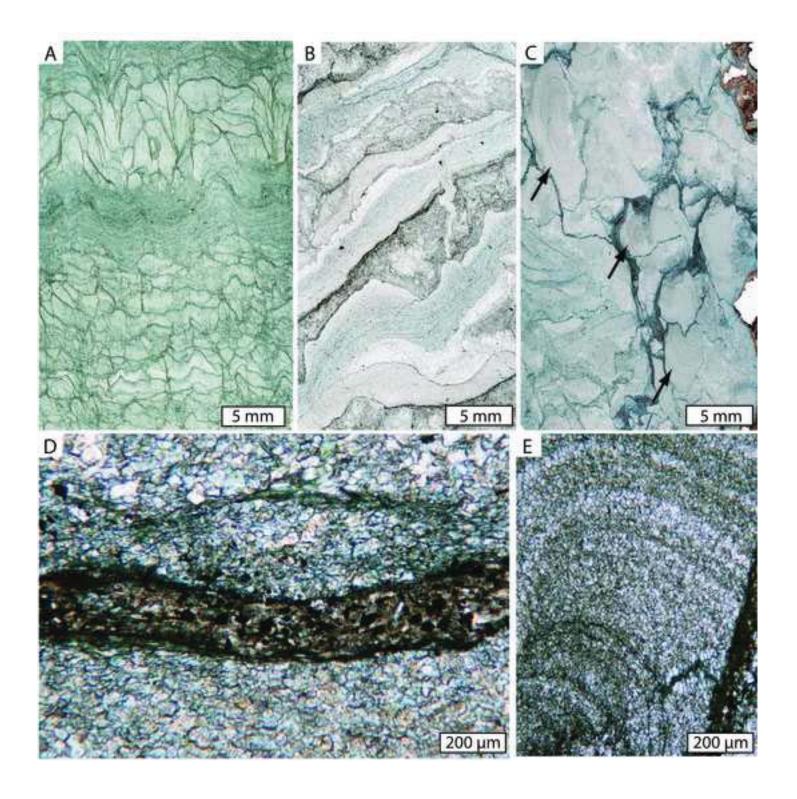


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KAZS1 - Kazput carbonate

