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Great Oxidation Event, Global glaciation, Paleoproterozoic, Turee Creek basin, Western Australia

Discussion

Comment on "Correlation of the stratigraphic cover of the Pilbara and Kaapvaal cratons recording the lead up to Paleoproterozoic Icehouse and the GOE" by Andrey Bekker, Bryan Krapež, and Juha A. Karhu, 2020, Earth Science Reviews, https://doi.org/10.1016/j.earscirev.2020.103389

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1. Introduction

The re-interpretation by Bekker et al. (2020) of the chronology of the Turee Creek Basin suggests that its C- and S-isotope records span only 2.45 to 2.42 Ga, instead of ~ 2.45 to 2.20 Ga, with significant implications for our understanding of the earliest rise of atmospheric oxygen. The comparison they made between the sedimentary and geochemical records of the Pilbara and Kaapvaal cratons is indeed important, as our knowledge of the Great Oxidation Event (GOE) is thus far dominated by evidence from one craton, the Kaapvaal, partly because of its geochronologic constraints. Meanwhile, for the Pilbara, the interpretation by Bekker et al. (2020) preempts other published works on the stratigraphic sequence, geochronology, geochemistry and geotectonic setting for the Turee Creek Group (Thorne and Seymour, 1991; Tyler and Thorne, 1990; Powell and Horwitz; 1994; Powell et al. 1999; Martin, 1999, 2020; Martin and Morris, 2010; Martin et al. 1998, 2000; Mazumder and Van Kranendonk, 2013; Mazumder et al. 2015; Van Kranendonk and Mazumder, 2015; Van Kranendonk et al. 2015; Caquineau et al. 2018; Philippot et al. 2018; Killingsworth et al. 2019; Chen et al. 2019). The problem with understanding the geochronology of Turee Creek has been a lack of absolute age constraints, with recent progress in that regard (Caquineau et al. 2018; Philippot et al. 2018) being dismissed by this new study, which instead relies on a sequence stratigraphy approach that i) requires assumption of a specific basinal setting for the deposition of the Turee Creek sequence and ii) considers C isotope regional chemostratigraphy of carbonate rocks as a paleo-indicator of unequivocal global significance.

In order to help the reader evaluate the efficacy of the new interpretation by Bekker et al. (2020), we compare the main arguments constraining their geochronologic model against recent significant evidence published for the Turee Creek Basin. These are: 1) robust U-Pb and Re-Os geochronological

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data from the Meteorite Bore Member refuting any correlation with the Makganyene Formation, and 2) the occurrence of four glacial horizons that parsimoniously correlate with other glacial successions in the Huronian, Eastern Transvaal, and Griqualand West basins. Other lines of argument such as the rate of sedimentation, C-isotope chemostratigraphy and conjoint occurrence of detrital pyrite with strong hydrothermal imprint throughout the Turee Creek sedimentary successions will also be addressed.

2. A tale of too many unknowns?

The scenario considered by Bekker et al. (2020) for the Turee Creek is a short-lived basin of less than 30 Myr duration between about 2.45 and 2.42 Ga ago, followed by a ~420 Myr sedimentary gap comprising two orogenies, the Turee Creek (~ 2403 Ma) and the Ophtalmian (~2152 Ma) orogenies, and bookended by the Horseshoe Basin at about 2.0 Ga (Figure 1). This interpretation proposed by Blake and Barley, (1992), Krapež (1996, 1997, 1999), Müller et al. (2005) and Krapež et al. (2017) arises from a lack of detrital zircons younger than 2.42 Ga. Such a model makes severe restrictions on viable tectonic and chrono-stratigraphic correlations with other Paleoproterozoic basins. For example, despite evidence for multiple glacial units in the Turee Creek Group (Figure 1), Bekker et al. (2020) consider the Meteorite Bore Member (MBM) as representing its sole glacial event, which they correlate to the Makganyene glaciation whose minimum age is constrained by the 2426 ± 3 Ma Ongeluk Formation (Gumsley et al. 2017). Then, they reconcile their model with the geological and geochronological record of the Turee Creek Basin by casting doubt on the new ages published by Caquineau et al. (2018) and Philippot et al. (2018), and by defining a new volcanic unit above the MBM to correlate with the Ongeluk Formation. Their newly defined unit, the "Bubbawalyee Formation", consists of dismembered blocks of mafic volcanics of unknown age located at the top of the Turee Creek Syncline in the easternmost part of the Turee Creek Basin (see Figure 5 of Krapež et al. 2017). According to Müller et al. (2006) "there is no exposures of basalt in the core of the Turee Creek Syncline and only float of dolerite". While some studies (Tyler and Thorne, 1990; Thorne and Seymour, 1991; Martin et al. 1998, 2000; Martin, 2020; Martin and Morris, 2010) assign the Beasley River Quartzite and overlying mafic blocks in the Turee Creek Syncline to the Wyloo Group, others (Müller et al. 2005; 2006; Krapež et al. 2017) have argued that the Beasley River Quartzite could belong to the Turee Creek Group because it was not deformed during initial folding of the Turee Creek Group. In summary, it is presently impossible to correlate the floating blocks of their Bubbawalyee Formation to the Ongeluk Formation without more substantial geologic, geochronological and geochemical evidence. In addition, it is worth noting that the Ongeluk volcanics is specific to the Griqualand West Province and has not been reported in other Paleoproterozoic provinces so far, including the Turee Creek, Huronian and Eastern Transvaal basins.

3. Age of the Turee Creek Basin

3.1. Constraints from detrital zircon U-Pb geochronology

The argument used by Bekker et al. (2020) to reject the zircon U-Pb analyses that yielded an age of 2340±22 Ma (Caquineau et al. 2018) is: "Based on the data-filtering criteria for SHRIMP U-Pb detrital zircon geochronology used by Krapež et al. (2017), all of those analyses would be rejected as they either fall outside 5% of Concordia or were measured on zircon grains with more than 450 ppm U." A first problem with that statement is that it invokes a data-filtering criteria used for SHRIMP U-Pb analyses although the data of Caquineau et al. (2018) were obtained by LA-ICPMS. A second issue is that the only sentence referring to this data-filtering procedure found in Krapež et al. (2017) is: "Only data for analyses with common Pb up to 1% (based on 206 Pb) and discordance up to 5% were accepted". We fully agree with that point, which could be completed by the rejection of zircon with high U contents (>1000 ppm) and structureless dark CL images, both being combined with

discordance and common Pb to characterize metamict grains. A third issue is that discussion of the 450 ppm U limit is not found anywhere in Krapež et al. (2017) and, more worrisome, that about 10% of the zircons published therein are above this threshold limit of 450 ppm U, with extreme values as high as 2258 ppm U. To understand this 450 ppm U limit, we investigated the references (Nelson, 1997; Buick et al. 2003; Fielding et al. 2017; Pickard, 2003; Rasmussen et al. 2005; Krapež et al. 2000) mentioned by Bekker et al. (2020). The Fielding and Rasmussen studies deal with monazite and xenotime U-Pb dating, not zircon. These studies identified two regional thermal events in the southern Pilbara Craton at 2430-2400 Ma and 2215-2145 Ma but none at 2.32 Ga. Pickard does not mention U content limits and uses the same standard data-filtering of Krapež et al. (2017). The Nelson (1997) and Krapež et al. (2000) studies deal with strongly recrystallized and hydrothermallyaltered zircons from the Eastern Goldfield Province of the Yilgarn Craton that experienced several orogenic cycles, regional metamorphism up to the upper amphibolite facies, and pervasive fluid circulation leading to massive ore deposits. According to Krapež et al. (2000) "Nelson noted that analyses of zircon grains from the Eastern Goldfields Province that have values of U >350 ppm yield spuriously young radiogenic ages suggesting Pb loss by diffusion" with no further detail. This is an observation restricted to one case study of the Eastern Goldfield Province, not a tested data-filtering criterion. Buick et al. (2003) showed that some zircons with high U contents between 550 and 3090 ppm are highly discordant with apparent young ages scattered about two trend lines, which extrapolate to Concordia intersections that do not have geochronological significance. This last, more serious, scenario is at odd with the two 98% confidence Concordia ages obtained by Caquineau et al. (2018) as discussed below.

We agree with Bekker et al. (2020) that several discordant zircons used by Caquineau et al. (2018) are reflected in the relatively large uncertainty of the 2340 \pm 22 Ma maximum age obtained for the MBM. However, two out of the six zircons used to constrain this age are 98% concordant, yielding concordia ages of 2357 \pm 10 Ma (grain T2-332/01) and 2376 \pm 13 Ma (grain T2-272/A-7), respectively. These two grains contain 554 \pm 110 ppm and 620 \pm 120 ppm of uranium, respectively, which is not significantly different from the 450 ppm U threshold invoked by Bekker et al. (2020). The oscillatory-zoned texture of grain T2-272/A-7 shown in figure 6 of Caquineau et al. (2018) argues against a metamictized crystal lattice. Importantly, raw data allow calculating 206 Pb/ 204 Pb ratios of 15,000 and higher, so only minor common Pb occurs. In addition, 206 Pb and 238 U counts are about 1.3 Mcps and 2.2-2.4 Mcps, respectively. This indicates that both isotopes were recorded in counting mode, which rules out a biased determination of the ACF analog/counting conversion factor of the Thermo Element XR. Consequently, the two zircon grains at 2357 \pm 10 Ma and 2376 \pm 13 Ma are unquestionable, making the 2340 \pm 22 Ma age proposed for the MBM robust for chronostratigraphic reconstructions of the Turee Creek Group.

3.2. Constraints from Re-Os geochronology

Another issue at debate is whether the Re-Os age obtained on pyrite separates and bulk mudstone matrix of the MBM reflects a sedimentation age (Philippot et al. 2018; this issue) or a reequilibration age associated with late-stage fluid infiltration processes that would have pervasively affected the Turee Creek Basin. First, there is a contradiction in the claim of Bekker et al. (2020) that detrital pyrite in the Turee Creek sequence (their Figure 2) could survive resetting of geochemical proxies during secondary fluid circulation because pyrite is sensitive to fluid processes and would be an early phase to experience dissolution and recrystallisation during regional metamorphism at about 300°C (Rasmussen et al. 2005). To be conclusive, such a contradiction would require examination of critical textural and geochemical relationships that are not presented, and simply do not exist. Meanwhile, Philippot et al. (2018) provides a six-page description of the texture and trace element (Co, Ni, Cu, Zn) compositions of the different pyrite types in Turee Creek sediments. Petrographic analyses showed the majority of the pyrites have textures indicative of a syngenetic

(formed within water column) or early diagenetic (crystallized below sediment-water interface) origin. Trace element analyses of more than 900 pyrite grains unequivocally argue for a sedimentary origin for the different types of pyrites measured for S-isotope compositions and Re-Os dating, with inter-element ratios within composition limits defined for sedimentary pyrites, and no evidence for secondary hydrothermal fluid re-equilibration. For example, a syngenetic microbial sulfate reduction origin of the Boolgeeda Iron Formation pyrites is further evident in mm-scale horizons showing Δ^{33} S \sim 0‰ and strongly negative (<30‰) δ^{34} S compositions arguing for microbial sulfate reduction. Additional support against late-stage pervasive fluid circulation in the MBM and Kazput carbonates is found in their bimodal distribution of coupled N and C isotopes, which has been interpreted as reflecting a change in the sedimentary N-budget from a biomass dominated by N2-fixers to NO3assimilating microorganisms, and thus a coeval increase of O2 concentration in the water column during deposition of the Kazput carbonates (Chen et al. 2019). Furthermore, the strongly negative δ^{18} O (-19.5%) and mildly positive Δ^{33} S (+1.5%) combination carried by microscopic barium sulfates present in Kazput carbonates has led Killingsworth et al. (2019) to argue for the role of oxidative weathering in a continental glacial environment, ruling out post-depositional fluid processes or a detrital origin for those sulfates.

The argument of Bekker et al. (2020) that the 2312.7 ± 5.6 Ma Re-Os isochron does not date deposition of the MBM, but instead dates high-temperature hydrothermal alteration processes, comes from recent U-Pb dating of monazite and xenotime that grew in bedding-parallel veins in 2.63–2.5 Ga shales along the southern Pilbara Craton (Rasmussen et al. 2020). Despite evidence that this study deals with different rock types in a different geological context and that there is no pervasive network of quartz-calcite-chlorite-bearing veins in the Turee Creek sedimentary successions, the effect of a younger fluid-rock interaction process would have added Re and radiogenic Os to the sediments. Considering the different stages of re-equilibration obtained by Rasmussen et al. (2020) at 2.40, 2.30, 2.20, 2.10, 2.05 and 1.66 Ga, it is expected that repeated cycles of hydrothermal alteration would have resulted in a large degree of scatter in the Re–Os isochron plot. The data obtained by Philippot et al. (2018) show a well-defined isochron, however, which strongly argues against multiple stages of hydrothermal alteration.

Bekker et al. (2020) further raise the issue of the initial ¹⁸⁷Os/¹⁸⁸Os of the Re-Os isochron in Philippot et al. (2018) as being suprachondritic and higher than that of Hannah et al. (2004), and thus indicative of late-forming pyrite that would not be appropriate for dating the time of deposition or early diagenesis. While the initial 187 Os/ 188 Os value of 0.149 ± 0.008 reported by Philippot et al. (2018) is slightly more radiogenic than that of the mantle/extraterrestrial value (187 Os/188 Os~0.11; Shirey and Walker, 1998), it is in good agreement with values (from -0.37 to +0.5) reported for black shales deposited between 2.7 and 2.3 Ga (Anbar et al. 2007; Yang et al. 2009; Sekine et al. 2011; Cabral et al. 2013; Kendall et al. 2013). For example, the initial Os of 0.149 \pm 0.008 lies within the range (0.12-0.43, average of 0.23±0.08) reported by Sekine et al. (2011) for the glacial diamictites of the Bruce Formation of the Huronian Basin, but is significantly lower than the Os initial composition (up to ca. 0.8) recorded in the overlying Espanola Formation. This sharp increase in initial Os was interpreted for an increased delivery of radiogenic Os to the ocean at deglaciation onset. As the deep ocean was essentially anoxic during the early Paleoproterozoic, the dissolved Os delivered via rivers would have been reduced to immobile Os over a short time interval. In such a case, most of the delivered Os would have accumulated within shallow-marine settings. Facies analysis of the Kungarra Formation (Van Kranendonk et al. 2015) indicates that it comprises a falling-stage systems tract at the base overlain by two glacial cycles (also interpreted as falling-stage systems tracts) associated with the MBM. In contrast, during the same period, the 2.316 Ga lower Timeball Hill Formation (Hannah et al. 2004), was deposited in a deep-marine setting (Coetzee et al. 2006). In this context, continental Os would have remained depleted because of the short residence time of Os in an anoxic ocean. This would have resulted in the non-radiogenic, hydrothermal Os in the Timeball

Hill Formation reported by Hannah et al. (2004) that contrasts with the 187 Os/ 188 Os reported in Philippot et al. (2018).

3.3 Constraints from sedimentation rates and C-isotope systematics

Two additional points of criticism were addressed by Bekker et al. (2020) concerning the age constraints published on the Turee Creek Group: i) sedimentation rates, and ii) the inconsistency in palaeoenvironmental indicators from the Turee Creek Group and the upper Huronian Supergroup.

Evaluation of sedimentation rates for the Turee Creek Basin is subject to large uncertainties due to the occurrence of contrasting lithologies, multiplicity of chronostratigraphic models and diversity of sedimentary unconformities reported in the literature (see Martin, 2020 for a review). Nevertheless, the sedimentation rates discussed by Philippot et al. (2018) were evaluated using the lithostratigraphy model of Van Kranendonk et al. (2015). Proposed sedimentation rates are not significantly different from the one estimated for the underlying Hamersley Basin (Trendal et al. 2004). These estimates are far from being set in stone and may be reconsidered in light of new observations and factual data published in the coming years.

The absence of a positive excursion of C-isotopes in the Kazput carbonates similar to that reported from the 2.3 Ga Gordon Lake carbonates of the Huronian Basin (Bekker et al. 2006), is a central argument used by Bekker et al. (2020) to support their chronostratigraphic scenario. However, with the exception of the short duration post-Lomagundi C-isotope excursion reported by Bekker et al. (2016) in the 2.03 Ga old Wooly Dolomite, the lack of significantly positive C-isotope data from the Turee Creek Basin can be easily explained by i) its lack of carbonates within the ~2.2-2.06 Ga Lomagundi time interval, and ii) the positive C-isotope excursion recorded in the Gordon Lake Formation may have local, rather than global chronostratigraphic significance, as it is restricted to the Huronian Basin and not yet observed in other Paleoproterozoic basins. Specifically, recent studies have shown that the connection between C-isotope excursions in the rock record and the redox budget of the Earth's surface may not be as simple as previously thought as it could be strongly affected, on a regional scale, by secondary (i.e. disconnected from the global surficial carbon budget) processes such as pervasive authigenic carbonate precipitation during early diagenesis (Schrag et al. 2013) or localized, biologically-mediated, water column methane cycling (Cadeau et al. 2020). Clearly, such concerns point out the need for balanced interpretations of Paleoproterozoic $\delta^{13}C_{carbonate}$ records.

4. Correlations with other Paleoproterozoic basins

Figure 1 illustrates the main divergence between the model proposed by Bekker et al. (2020) and this study. Like in the Kaapvaal Craton and Huronian Supergroup, at least four glacial diamictite horizons have been identified in the Turee Creek Basin. The oldest of those diamictites, the Boolgeeda diamictites (Martin et al. 1998; Philippot et al. 2018), are located in the Boolgeeda Iron Formation that has now been reported in four different outcrops along strike by Martin (2020), who renamed it the Cave Hill Member. This glacial interval, defined as the circle #1 in Figure 1, can be correlated with the Makganyene diamictites in South Africa and the Ramsay Lake in North America. Altghough Bekker et al. (2020) correlate the Koegas and Boolgeeda iron formations, they refute the interpretation that the Boolgeeda diamictites could be an equivalent of the Makganyene Formation, arguing that the two successions were deposited in shallow (Koegas) versus deep (Boolgeeda) water environments. However, in contrast to Bekker et al. (2020) claim, the Boolgeeda Formation evolved from deep ferruginous water environment to more oxic shallow water settings as indicated by periodic venue of detrital and sulfate-rich sediments derived from continental weathering (Warchola et al. 2018). Furthermore, Polteau et al. (2006) showed that the upper part of the Koegas iron

formations (Rooinekke Formation), like the Boolgeeda Iron Formation, were interleaved with glacial lenses and debrites, which they interpreted to reflect the onset of glacial conditions prior to the development of the main Makganyene glacial episode.

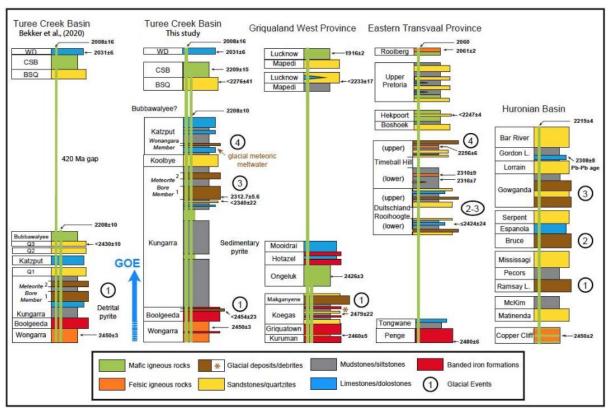


Figure 1. Stratigraphic correlations are shown between Western Australia, South Africa, and North America basins for the early Paleoproterozoic 2.5 to 2.0 Ga time interval. All ages are in millions of years (Ma). For the Turee Creek Basin, the chronostratigraphy suggested by Bekker et al. (2020) is compared against the age constraints and suggested stratigraphy (Van Kranendonk et al. 2015; Caquineau et al. 2018; Philippot et al. 2018; Martin, 2020) synthesized here but based on the prior work of Caquineau et al., 2018 and Philippot et al., 2018. Four glacial diamictite units are noted in the Turee Creek Basin that compose three glacial events (numbered 1, 3, and 4), which can be tentatively correlated across cratons. The record of sulfate carrying a "glacial meteoric meltwalter" signal at the base of the Kazput Formation is from Killingsworth et al. (2019). Between West Australia and South Africa, it is suggested that the Boolgeeda and Koegas formations, respectively, correlate with each other and formed in a similar type of environment (see text). Note the occurrence of glacial debrites at the top of the Koegas Formation indicated by an asterisk (*; Rooinekke Formation; Polteau et al. 2006), which correlates well with the Boolgeeda diamictites.

The second glacial event comprises the two glacial horizons forming the Meteorite Bore Member. Owing to age constraints, this interval, noted #3, can be correlated with the two glacial horizons forming the Gowganda Formation in the Huronian Basin and the Duitschland and/or Rooihoogte intervals in South Africa (the question remains as to whether the Duitschland and Rooihoogte formations are time equivalents (Martini, 1979) or distinct events (Erikson, 1988; Cheney and Winter, 1995). Although Bekker et al. (2020) refer to the one sentence rebuttal of Cheney and Winter (1995) namely "Martini's (1979) suggestion that the Rooihoogte might be equivalent to the Duitschland Formation seems unlikely because chert breccia, which marks the unconformity below the Pretoria Group (TII), occurs below the Rooihoogte but above the non-BIF-bearing Duitschland" to advocate that they represent different stratigraphic horizons, we have considered here that the original claim of Martini (1979) is supported by numerous new evidence, which can be summarized as follows: i) Duitschland and Rooihoogte formations occupy the same stratigraphic position with the same upper (Timeball Hill) and lower (Tongwane/Penge) contacts (Coetzee, 2001), ii) they record

similar depositional sequences, cycles, and environments (Coetzee, 2001; Warke and Schröder, 2018), iii) both have major intraformational unconformities associated with the loss of sulfur-MIF (Guo et al., 2009; Luo et al., 2016); iv) both have similar detrital zircon populations (Schröder et al., 2016; Zeh et al., 2020). However, as emphasized by Bekker et al. (2020), precise geochronological data are needed to fully clarify this issue, with which we agree.

The fourth glacial event noted #4 represents four separate outcrops of glacial diamictites recently identified and named the Wonangara Member by Martin (2020, Figure 20 d-f) at the base of the Kazput Formation, that can be correlated with the glacial horizon of the Timeball Hill Formation. The Wonangara glacial horizon corroborates the recent study of Killingsworth et al. (2019) who showed that sulfates from the Kazput carbonates record a likely glacial meltwater signal inherited during continental weathering, which, like sulfate evaporites in the Gordon Lake carbonates, implies oxidative weathering processes under oxygenated atmospheric conditions.

5. Conclusions

The opportunity Bekker et al. (2020) provided for clearing up some concerns about recent age constraints on the Turee Creek Basin is appreciated. The geochronological models proposed for the Eastern Transvaal-Criqualand West Basin (Gumsley et al. 2017) and the Turee Creek Basin (Philippot et al. 2018) are in good agreement. In both cases, and in contrast to the short-duration model starting at about 2.32 Ga advocated by Bekker et al., (2004), the increase in atmospheric oxygen occurs as early as 2.45 Ga (see Warke et al. (2020) for similar conclusions reached on the Fennoscandian Shield) and either fluctuates for a couple of hundreds of millions years (Gumsley et al. 2017) or establishes at a level above the threshold for MIF-S production and preservation in the rock record as indicated by the occurrence of a homogeneous MIF-S signal of ~1‰ throughout the Turee Creek sequence, which has been attributed to the weathering of anomalous pyrite on land and transport of riverine sulfate carrying a mean value of Δ^{33} S ~1‰ in the ocean (Philippot et al. 2018). In this model, local disappearance of this S-MIF signal is attributed to changes in the conditions of deposition (shallow vs deep water, proximity from the continent, occurrence/absence of ice sheets) rather than reflecting global fluctuations of the atmospheric oxygen content with time. The central role of regional conditions of deposition can also account for the episodic and random distribution of carbonates showing strongly positive C-isotope compositions as recorded in the 2.0 Ga old Wooly Dolomite (Turee Creek Basin), the 2.3 Ga old Gordon Lake Formation (Huronian Basin) or the 2.31 to 2.42 Ga old Duitschland carbonate (Eastern Transvaal Province). Further studies can thus rely on the robust recent age determinations for Paleoproterozoic Western Australia to assist in the important work of global tests, across cratons, of the various biogeochemical models describing the Earth system controls on, and responses to, the initial rise of Earth's atmospheric oxygen.

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