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Primitive Os and 2316 Ma age for marine shale: implications for Paleoproterozoic glacial events and the rise of atmospheric oxygen

Judith L. Hannah[a,*], Andrey Bekker[b,1], Holly J. Stein[a,2], Richard J. Markey[a,3], Heinrich D. Holland[b,4]

[a]AIRIE Program, Department of Geosciences, Colorado State University, Fort Collins, CO 80523-1482, USA
[b]Department of Earth and Planetary Sciences, 20 Oxford Street, Harvard University Cambridge, MA 02138, USA

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Abstract

Re–Os dating of synsedimentary to early diagenetic pyrite from carbonaceous shale that straddles the boundary between the Rooihoogte and Timeball Hill formations, Transvaal Supergroup, South Africa, provides a precise isochron age of 2316±7 Ma (±4 statistical uncertainty if error on decay constant is excluded) and a chondritic initial $^{187}Os/^{188}Os$ ratio of 0.1121±0.0012. These units were deposited between what are interpreted as the second and third of three Paleoproterozoic global glacial events, and thus provide minimum and maximum ages, respectively, for these events. The Rooihoogte Formation is correlative with the Duitschland Formation, which records previously undated carbon isotope excursions. Because the pyrite samples show no evidence of mass independent fractionation of sulfur and have highly negative $\delta^{34}S$ values, the rise of atmospheric oxygen most likely began prior to 2.32 Ga. The chondritic initial $^{187}Os/^{188}Os$ ratio requires that primitive hydrothermal sources of Os dominated the Os budget of seawater at 2.32 Ga. Os is mobile only under oxidizing conditions. Therefore, the chondritic initial $^{187}Os/^{188}Os$ ratio may reflect atmospheric oxygen levels too low to introduce sufficient riverine flux of dissolved radiogenic Os to offset the primitive hydrothermal/magmatic flux. Even if atmospheric oxygen levels had increased significantly by 2.32 Ga,

* Corresponding author. Tel.: +1 970 491 5661; fax: +1 970 491 6307.
E-mail addresses: jhannah@cnr.colostate.edu (J.L. Hannah), a.bekker@gl.ciw.edu (A. Bekker), hstein@cnr.colosate.edu (H.J. Stein), rmarkey@cnr.colostate.edu (R.J. Markey), holland@eps.harvard.edu (H.D. Holland).
[1] Current address: Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, USA. Tel.: +1 202 478 7974; fax: +1 202 478 8901.
[2] Tel.: +1 970 491 5661; fax: +1 970 491 6307.
[3] Tel.: +1 970 491 3789; fax: +1 970 491 6307.
[4] Tel.: +1 617 495 5892; fax: +1 617 495 8839.

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anoxic conditions throughout the Archean most likely limited Os enrichment in Archean marine shales, so that their subsequent exposure and weathering was unable to provide a significant amount of radiogenic Os to Paleoproterozoic seawater.

Keywords: osmium; atmospheric oxygen; Paleoproterozoic; glaciation; Transvaal supergroup

1. Introduction

Paleoproterozoic sedimentary successions record dramatic paleoenvironmental changes in the exosphere between 2.45 and 2.22 Ga [1,2], including: (1) the rise of atmospheric oxygen, (2) compressional tectonism on the margins of the oldest recognized supercontinent, Kenorland, and an accompanying superplume event in the interior and on the periphery of the supercontinent at 2.48–2.42 Ga, and (3) a glacial epoch with three documented glaciations extending to low latitudes, two of which are recognized in South Africa. Precise ages are lacking worldwide to constrain these critical events and to test correlations between Paleoproterozoic basins. We show that Re–Os dating of synsedimentary or early diagenetic pyrite in carbonaceous shales can place chronologic markers in key stratigraphic successions. Moreover, the initial $^{187}Os/^{188}Os$ ratio of the pyrite records seawater composition, and thus also reflects changing environmental factors that control riverine input of dissolved Os from the continents.

The Re–Os age of 2.32 Ga for the Rooihoogte-Timeball Hill formations in the Transvaal Basin, South Africa, has several important implications. First, the same pyrite samples used for Re–Os analyses lack mass independent fractionation (MIF) of sulfur isotopes and have highly negative $\delta^{34}S$ values [2]. If mass difference were the only cause of fractionation of sulfur isotopes, $\delta^{33}S$ should be about one half $\delta^{34}S$ in the same sample. MIF results in $\delta^{33}S$ values that differ significantly from that prediction. This requires an alternative fractionation process, most likely photodissociation of sulfur species in the atmosphere [3]. Thus, these data require oxidative atmospheric conditions by 2.32 Ga, earlier than previously documented. Second, the dated units lie between the second and third Paleoproterozoic glacial events, providing significantly tighter age constraints and aiding correlation with events on other continents. Third, the Rooihoogte Formation is correlative with the Duitschland Formation, which reveals a negative $\delta^{13}C$ excursion in the cap carbonate above a basal diamictite marking the second glacial event of the Paleoproterozoic glacial epoch, and a highly positive $\delta^{13}C$ excursion in carbonates near the top of the formation below the third glacial event—both previously undated. Finally, the age provides new constraints on the regional geology, as the entire sequence was previously constrained only between 2480 and 2222 Ma [1].

Carbonaceous shales are good candidates for Re–Os geochronology because they are likely to be hydrologically sealed and because they provide a reducing environment that immobilizes Re and Os. Whole rock Re–Os dating of carbonaceous shales has seen modest success, though uncertainties are, with one exception [4], relatively large (±3% or more; [5–7]). Scatter of isotopic data may result from either spatial variability in initial $^{187}Os/^{188}Os$ ratios [5,7–10], or variable time of isotopic closure in hydrologically open systems [9]. For example, Re and Os in pyrites from relatively permeable sandstones of the Late Jurassic Morrison Formation, Colorado, remained mobile for at least 60 my after deposition [9]. Morrison pyrites from a restricted sample volume (ca. 10 cm diameter) yield an 83.1±5.7 Ma isochron (initial $^{187}Os/^{188}Os$= 0.817±0.005) for the time of hydrologic closure, whereas variable ages and initial ratios are obtained for pyrites taken only a few meters apart. Thus, precise geochronology requires both hydrologic closure and closely spaced samples to assure homogeneity of the initial isotopic ratio.

Yet another factor to be considered is the possibility of contributions of Os with variable initial $^{187}Os/^{188}Os$ from detrital material. This can be avoided by analyzing synsedimentary or early diagenetic pyrite, since Re and Os will co-precipitate with the pyrite from pore waters. Previous Re–Os results for pyrite from Phanerozoic black shales support the stricture that samples must be taken in close proximity. The first such study, based on sulfide samples taken several hundred km apart, produced scatter of the isotopic data about a 560 Ma reference line [11], whereas, in a subsequent study of the same unit, six out of seven sulfide samples from a single mine pit defined a 541±16 Ma isochron [12]. Our results, based on Paleoproterozoic samples collected less than 3 m apart, show that pyrites taken in close stratigraphic and along-strike proximity have the same initial $^{187}Os/^{188}Os$ ratios yet a sufficient spread in the Re/Os ratio to yield a precise isochron.

The initial $^{187}Os/^{188}Os$ ratio in marine carbonaceous shale reflects seawater composition at the time of deposition or early diagenesis. Under present atmospheric conditions, about 80% of seawater Os is derived from the continents, with the balance from extraterrestrial or hydrothermal sources [13]. Modern seawater has a $^{187}Os/^{188}Os$ ratio of about 1 [13,14], slightly below the average composition of currently eroding upper continental crust [15]. Several studies document spatial or temporal excursions in seawater $^{187}Os/^{188}Os$ resulting from local input of low $^{187}Os/^{188}Os$ hydrothermal fluid [13,16,17], large impacts of extraterrestrial material [18], and variable rates of chemical weathering [5,19–22]. Most important is oxidative weathering of sulfidic, carbonaceous sedimentary rocks, a key reservoir for crustal Re, and therefore of radiogenic ^{187}Os [6,18,23,24]. Given the short residence time of Os in seawater (probably less than 12 ky), excursions caused by impacts or local hydrothermal events are unlikely to persist for more than a few 100 ky [18]. Our results yield a chondritic initial $^{187}Os/^{188}Os$ ratio for Paleoproterozoic seawater, documenting near complete absence of ^{187}Os input from the continents at that time.

2. Geologic setting and pyrite paragenesis

The Rooihoogte Formation and the conformably overlying Timeball Hill Formation of the Pretoria Group, South Africa (Figs. 1 and 2), overlie a prominent karstified unconformity on the Late Archean Malmani carbonate platform and the 2480±6 Ma Penge Iron Formation [25]. The units below the unconformity were folded and deeply eroded after an unnamed compressional event before deposition of the Rooihoogte and the correlative Duitschland formations. Several lines of evidence suggest that the units below the unconformity are older than the rise of atmospheric oxygen: (1) early diagenetic pyrite of the Gamohaan Formation, Campbellrand Subgroup, correlative with the Malmani Subgroup, carries a strong MIF signal [3]; (2) shallow-water iron formations of the Griqualand West Basin, which are slightly younger than the Penge Iron Formation, are reduced and lack a Ce anomaly [26,27]; (3) $\delta^{34}S$ values of early diagenetic pyrites from these units cluster near 0‰ V-CDT and have a narrow range [28,29]; (4) detrital uraninite and pyrite grains are present in the Black Reef Quartzite [30].

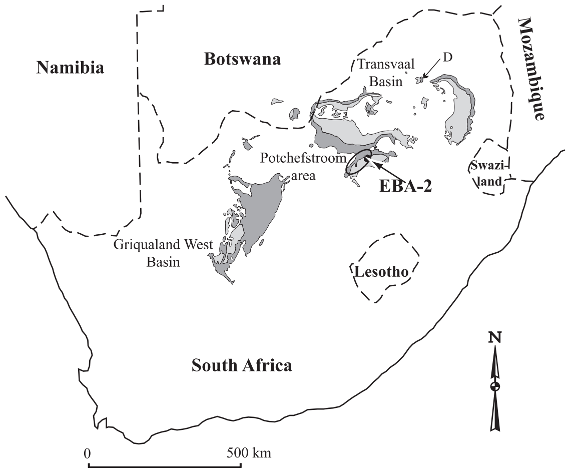

Fig. 1. Map of early Paleoproterozoic sedimentary successions of South Africa, showing distribution of the Chuniespoort (dark grey) and Pretoria (light grey) groups in the Transvaal structural basin and Ghaap (dark grey) and Postmasburg (light grey) groups in the Griqualand West structural basin (after Coetzee [32]). Units in both structural basins accumulated in the same depositional basin. 'D' indicates the location of the Duitschland Formation exposures. Samples used in this study are from drill hole EBA-2 in the Potchefstroom area.

The Rooihoogte Formation and the overlying Timeball Hill Formation contain evidence for the rise of atmospheric oxygen; the pyrites lack MIF of S isotopes and have highly negative $\delta^{34}S$ values [2], and shallow-water hematitic oölites and pisolites occur in the upper Timeball Hill Formation [31]. The Duitschland Formation, which is preserved only in the northeastern part of the Transvaal Basin (Fig. 1), is a time equivalent of the Rooihoogte Formation based on their equivalent stratigraphic positions with respect to the unconformity and the Timeball Hill Formation. Both units contain basal glacial diamictite, quartzite in the middle, and chert breccia at the top [32]. The carbonates of the lower Duitschland Formation record a negative $\delta^{13}C$ excursion immediately above the glacial diamictite, whereas carbonates of the upper Duitschland Formation, above a prominent sequence boundary, have $\delta^{13}C$ values as high as +10.1‰ V-PDB [1]. Similar negative $\delta^{13}C$ values are found in carbonates above the middle of three glacial diamictites of the Huronian and Snowy Pass supergroups, ON and WY [33], but a positive $\delta^{13}C$ excursion has not yet been recognized in any other succession at the same stratigraphic level. The age of both excursions is constrained only between 2.45 and 2.22 Ga.

The Timeball Hill Formation contains glacial diamictite at the top that is correlative with the Makganyene Diamictite in the Griqualand West Basin (Fig. 2). A major unconformity separates the Makganyene Diamictite from the underlying units, as time-equivalents of the Rooihoogte and Timeball Hill formations are missing in the Griqualand West Basin. In the Transvaal Basin, the contact between the glacial diamictite of the Timeball Hill Formation and the underlying shale is gradational [32]. Based on paleomagnetic data for the Ongeluk andesite, low latitude glaciation has been inferred for the Makganyene Diamictite [34]. Highly negative carbon isotope values of carbonates of the overlying Mooidraai Dolomite and Fe- and Mn-deposits of the Hotazel Formation have been related to ocean composition in the aftermath of the Paleoproterozoic Snowball Earth [35].

Based on detailed sedimentologic studies, the Rooihoogte and Timeball Hill formations were deposited in the deltaic part of a basin open to the ocean on the southwest [32,36–38]. Volcanic contributions are found only in the extreme southwestern part of the basin, about 27 km from the sampled drill core (Fig. 1), where the 5-m-thick Bushy Bend Lava occurs within the upper Rooihoogte Formation [32]. The formations are sandwiched between two glacial diamictites, one at the base of the Rooihoogte Formation [32], the other at the top of the Timeball Hill Formation [32,39]. These two glacial diamictites are considered correlative with the middle and the upper of three glacial diamictites in the early Paleoproterozoic Huronian Supergroup, ON [1]. The units have been affected by lower greenschist facies metamorphism [32].

Pyrite is confined to extremely organic-rich, finely laminated shale layers and displays demonstrably syndepositional–early diagenetic textures (Fig. 3). It occurs as nodules (Fig. 3A and B), mineralized microbial mats (Fig. 3C and D), disseminated grains, and laminated seams up to several centimeters thick. Where nodules with radial, bladed crystals (spherulites) are closely packed, they form a substrate for layers of fibrous pyrite crystals (Fig. 3A). The spherulites probably consisted initially of marcasite. Laminae in the shale bend around nodules, indicating that the nodules predate compaction (Fig. 3B). Microbial mats (Fig. 3D) and microbial mat rip-ups (Fig. 3C)

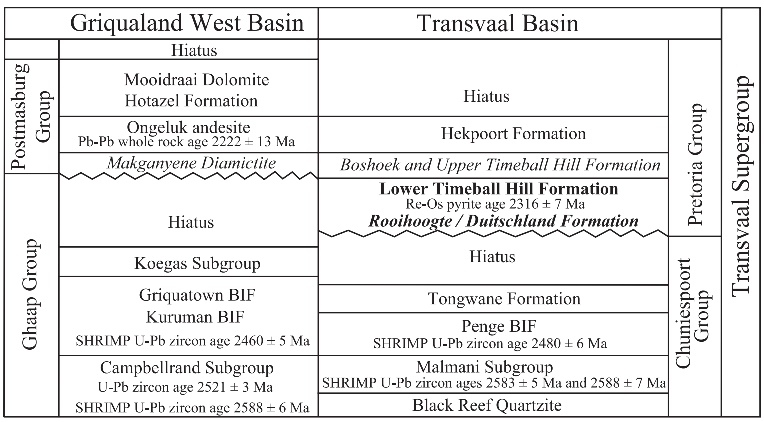

Fig. 2. Stratigraphy of the Transvaal Supergroup as exposed in the Griqualand West and Transvaal structural basins (modified from Bekker et al. [1]). Dated units are shown in bold; units containing glacial diamictites are shown in italics. The age of the Kuruman iron formation is from Pickard et al. [51]; Re–Os age for the Rooihoogte-Lower Timeball Hill formations is from this paper; see Bekker et al. [1] for references to other ages. BIF=banded iron formation; SHRIMP=sensitive high-resolution ion micro-probe.

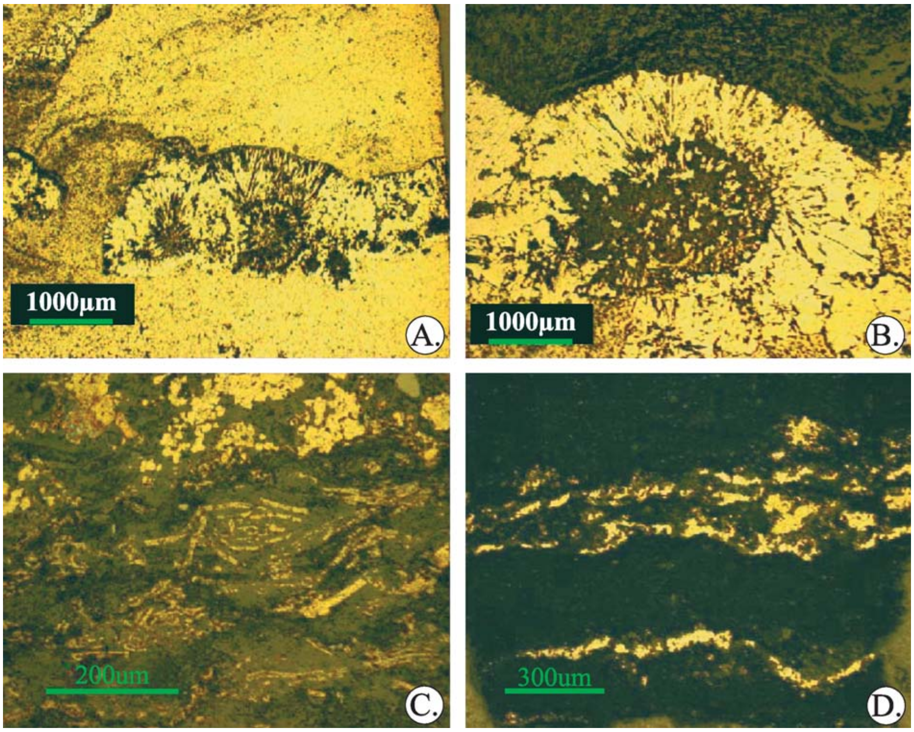

Fig. 3. Photomicrographs illustrating early diagenetic origin of pyrite: (A) spheroids overgrown by fibrous pyrite in pyrite matrix; (B) laminae consisting of clay minerals, organic matter, and silt-sized quartz grains bend around pyrite spheroid indicating pyrite growth before compaction; (C) microbial mat rip-ups mineralized by pyrite; (D) wavy and crinkly mineralized microbial mat structures in organic-rich shale.

mineralized by pyrite form wavy–crinkly laminae and are similar to those in shales of the Mesoproterozoic Belt Group, Montana and in many Phanerozoic units [40]. Parallel laminations are defined by variable crystal size and by variations in the concentration of clay, silt-sized quartz grains, and organic matter. Small amounts of sphalerite, chalcopyrite, and galena occur with the pyrite, and small pyrite grains contain Se, Pb, and rarely, As. These textural and mineralogic characteristics, the association of the pyrite with organic-rich shales, and the δ^{34}S values ranging from −29.6‰ to −25.6‰ V-CDT suggest an early diagenetic origin by bacterial reduction from seawater sulfate for all or nearly all of the pyrite [2].

3. Sampling, analysis, and results

Samples were selected from a 3-m section of drill core (EBA-2, drilled by Gold Fields; Fig. 1) in highly carbonaceous shales spanning the boundary between the Rooihoogte and Timeball Hill formations (Fig. 2). Precise positions are given in Table 1. Sulfide separates were obtained by drilling with a 1-mm diamond drill bit to assure good spatial resolution. Equilibration of 200–500 mg sulfide aliquots with ^{185}Re and ^{190}Os spikes was achieved by Carius-tube digestion [41]. Os was recovered by distilling directly from the Carius tube (procedure modified from Brauns [42], trapping Os in HBr and purifying by microdistillation [43]. Re was recovered by anion exchange [44]. Isotopic analyses were carried out by negative thermal ionization mass spectrometry using Pt filaments (results in Table 1).

Pyrite separates from three drill core samples yield a 7-point isochron with an age of 2315.8±4.3 Ma and an initial ^{187}Os/^{188}Os ratio of 0.1121±0.0012 (Fig. 4). With one exception, each analysis was made on a unique mineral separate from a different part of the drill core. Runs LL-1 and LL-7 for Timeball Hill sample EBA-2/30 represent two separate dissolutions of the same mineral separate. The isochron age,

Table 1
Re–Os isotopic data for Rooihoogte and Timeball Hill pyrites

AIRIE run #	Sample	Depth in core (m)	Re (ppb)	Os (ppb)	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$
Timeball Hill Formation						
LL-1	EBA-2/30	1333.0–1333.1	16.61 (8)	0.678 (3)	296 (3)	11.7 (1)
LL-7			17.21 (3)	0.725 (4)	278 (2)	11.1 (1)
LL-59			18.23 (1)	0.727 (1)	317 (1)	12.56 (4)
Rooihoogte Formation						
LL-8	EBA-2/67	1335.48–1335.68	31.85 (3)	8.13 (1)	20.84 (4)	0.931 (2)
LL-61			40.20 (2)	30.82 (5)	6.47 (1)	0.3668 (9)
LL-9	EBA-2/55-2	1335.65–1335.85	51.17 (3)	6.28 (1)	49.02 (9)	2.043 (5)
LL-62			40.27 (2)	8.088 (8)	27.28 (3)	1.185 (2)

Numbers in parentheses are 2σ absolute errors for the last digit reported. All data are blank corrected; blanks are: for LL-1, 7, 8 and 9, Re=2.60±0.01 pg, Os=5.1±1.0 pg, $^{187}Os/^{188}Os$=0.190±0.002; for LL-59, Re=1.73±0.03 pg, Os=9.52±0.07 pg, $^{187}Os/^{188}Os$=0.263±0.006; and for LL-61 and 62, Re=6.00±0.05 pg, Os=3.91±0.01 pg, $^{187}Os/^{188}Os$=0.187±0.001.

statistical uncertainty, and initial $^{187}Os/^{188}Os$ ratio are consistent with those acquired for four samples from the Rooihoogte Formation alone (see inset in Fig. 4). The low statistical uncertainty for the age understates the true error, as it does not include the 0.31% uncertainty for the ^{187}Re decay constant [45]. This uncertainty should be included and the age reported as 2316±7 Ma. At 2316 Ma, the $^{187}Os/^{188}Os$ ratio for average chondrite was 0.1112 (calculated from values in Shirey and Walker [46]), within error of the isochron initial $^{187}Os/^{188}Os$ ratio. Thus, Os with an approximately chondritic isotopic composition prevailed in the Transvaal Basin at the time of Rooihoogte-Timeball Hill deposition.

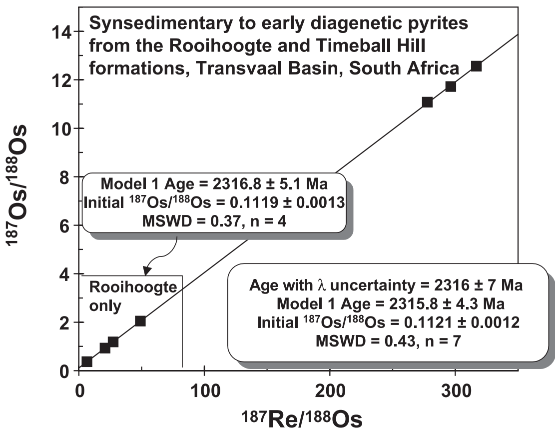

Fig. 4. Isochron for six pyrite separates (with one replicate) from three drill core samples. Error bars (not shown) are smaller than symbols. Regression based on Isoplot/Ex [52], using the decay constant of Smoliar et al. [45]. Statistical uncertainty underestimates true error. The age reported should be 2316±7 Ma, which includes the 0.31% uncertainty in λ, the ^{187}Re decay constant.

4. Discussion

4.1. Implications of initial $^{187}Os/^{188}Os$ ratio

Given the possible controls on the Os isotopic composition of Paleoproterozoic oceans, we entertain four potential explanations for the chondritic initial $^{187}Os/^{188}Os$ ratio recorded by the Paleoproterozoic Rooihoogte-Timeball Hill pyrites. First, by chance, we may have sampled a time interval corresponding with a major impact, so that seawater Os was temporarily swamped by extraterrestrial input. This requires fortuitous timing, however, and no independent evidence exists for an impact event at this time.

Second, unusual magmatic/hydrothermal conditions or restricted basin architecture can cause local predominance of magmatic/hydrothermal input of Os to seawater. There are two arguments against this interpretation, however. Stratigraphic evidence points to a deltaic system, open to the ocean, rather than a restricted basin. Also, strongly negative sulfur isotope ratios in the same samples [2] argue against a restricted basin or any setting in which a hydrothermal flux of H_2S could overwhelm seawater sulfate as the major source of sulfur for the pyrite.

Third, because Re and Os are mobilized in hydrologic systems only under oxidizing conditions, anoxic atmospheric conditions could have restricted their entry into the hydrologic cycle, thus severely limiting the delivery of dissolved continental Os to the oceans. The pyrite samples analyzed in this study, however, lack evidence for MIF of sulfur isotopes and have highly negative δ^{34}S values indicating seawater sulfate concentrations consistent with initiation of the oxidative part of the sulfur cycle [2]. In addition, the upper part of the Timeball Hill Formation includes shallow-water ironstone consisting of hematitic pisolites and oölites, implying that the level of atmospheric oxygen was high enough to oxidize Fe in deltaic and fluvial settings. However, atmospheric oxygen might have been sufficiently limited during the early stage of the rise of atmospheric oxygen that the amount of dissolved Os provided by the riverine flux was not sufficient to overwhelm the hydrothermal/magmatic flux.

Alternatively, if the atmospheric oxygen level was high enough for oxidative weathering of exposed Archean crust and sediments during Rooihoogte-Timeball Hill time, a fourth explanation is required. The low ^{187}Os/^{188}Os ratio for Rooihoogte-Timeball Hill pyrites may reflect a much lower concentration of Re and Os in Archean than in more recent continental rocks. Yang and Holland [47] report low Re concentrations in Archean carbonaceous shales and attribute them to anoxic weathering. Similarly, anoxic conditions in the Archean should result in low seawater Os concentrations, and correspondingly low Os concentrations in Archean marine shales. The combination of low Os concentrations in rocks undergoing weathering and immobility of Os under anoxic weathering conditions must have greatly limited the riverine flux of Os from the continents to the oceans during the Archean. The most prolific ^{187}Os contributor in the Phanerozoic, oxidative weathering of black shales [18] was largely unproductive in the Archean. Thus, Os in Archean seawater was dominated by magmatic/hydrothermal sources.

If this is the case, we suggest that there was a time lag between increasing atmospheric O_2 and a measurable response in the Os cycle. If the rise of atmospheric O_2 in the Paleoproterozoic initiated oxidative weathering, it would cause increased transport of dissolved Os from the crust to the oceans. Initially, however, the available Os in crustal rocks would be limited because exposed Archean black shales had low Os concentrations. This delayed response is supported by limited of correlation between organic carbon and Re in 2.0–2.1 Ga shales compared to the strong correlation seen in ca. 1.6 Ga and younger shales [47]. Hence, magmatic/hydrothermal sources of Os may have continued to dominate for some time in the absence of Os-rich continental sources. The ^{187}Os/^{188}Os ratio of seawater might have increased only gradually as the riverine input of dissolved Os increased and younger marine shales were uplifted and exposed to oxidative weathering.

4.2. Implications of the age

The 2316±7 Ma age for the Rooihoogte-Timeball Hill synsedimentary to early diagenetic pyrites provides a new age constraint for the carbon isotope excursions in carbonates of the correlative Duitschland Formation. It also provides a minimum age for the initiation of the Paleoproterozoic glacial epoch, bracketing the first and second glacial events between 2.45 and 2.32 Ga. The last glacial event of the Paleoproterozoic glacial epoch recorded by glacial diamictite in the upper Timeball Hill Formation is now bracketed between 2.32 and 2.22 Ga.

In addition, the age has significant paleoenvironmental and tectonic implications. The Boshoek Formation, sitting above the diamictite of the Timeball Hill Formation, is overlain by the Hekpoort Formation (Fig. 2). A 2222±13 Ma Pb–Pb whole rock isochron age for the Ongeluk andesite, correlated with the Hekpoort Formation, was recently confirmed by SHRIMP and TIMS ages for zircons from this unit (N.J. Beukes, personal communication). It is highly unlikely that less than 1 km of siliciclastic sediment comprising the Timeball Hill and Boshoek formations required 100 Ma to accumulate in a deltaic setting with a high sedimentation rate. We therefore propose a major, yet unrecognized hiatus either within or above these units. The hiatus may have occurred at the base of the Boshoek Formation where conglomerate and mature quartzites sit on the glacial diamictite of the upper Timeball Hill Formation. Alternatively, it may be at the base of the subaerial Hekpoort Formation, above transgressive black shales of the Boshoek Formation [32]. This interpretation is consistent with the Huronian record in Ontario, where three glacial diamictites are overlain by a 3-km-thick passive margin succession containing mature quartzites that are likely broadly correlative with those of the

Boshoek Formation. The entire Huronian package was folded and subsequently intruded by the 2219.4±3.5 Ma Nipissing diabase [48], implying that significant time elapsed between the last glacial event and the 2.22 Ga magmatic event.

If indeed there is a major hiatus between the Timeball Hill diamictite and the Hekpoort Formation, it would imply a significant time break between the Makganyene diamictite and the overlying section in the Postmasburg Group, Griqualand West Basin (Fig. 2). Specifically, this hiatus implies that (1) paleomagnetic data for the Ongeluk andesite cannot be used to infer low-latitude Paleoproterozoic glaciation [34], (2) Mn- and Fe-deposits of the Hotazel Formation cannot be attributed to ocean oxidation in the aftermath of the Paleoproterozoic Snowball Earth [49], and (3) carbon isotope data of the Mooidraai Dolomite cannot be used to constrain the carbon isotope composition of the post-glacial ocean [35].

The 2.32 Ga age also implies a long hiatus between the Rooihoogte/Duitschland Formation and the underlying ca. 2.48 Ga Penge Iron Formation and locally preserved Tongwane Formation, which were folded, uplifted and eroded before the Duitschland and Rooihoogte formations were deposited. Thus, the compressional event is now constrained between 2.48 and 2.32 Ga. This deformation may correlate with the compressional event in Western Australia that led to deposition of the Turee Creek Group sediments in a compressive back-arc basin and to deformation of the underlying iron formations [50]. Similarly, it may be contemporaneous with 2.48–2.42 Ga extension and mantle plume magmatism within the Kenorland supercontinent.

5. Summary and conclusions

In summary, our isochron age of 2316±7 Ma for synsedimentary–early diagenetic pyrite from the Rooihoogte-Timeball Hill formations demonstrates the utility of the Re–Os system for dating carbonaceous shales, even for Paleoproterozoic and perhaps older units. Conclusions are:

(1) Seawater at 2.32 Ga had a chondritic initial $^{187}Os/^{188}Os$, requiring predominantly primitive magmatic/hydrothermal input of Os.

(2) The rise of atmospheric oxygen started before 2.32 Ga, but the atmospheric oxygen level probably remained too low to introduce a sufficient riverine flux of dissolved Os by oxidative weathering to overwhelm the hydrothermal/magmatic flux of Os. Alternatively, the low initial Os isotopic ratio might reflect low concentrations of Re and Os in the Archean crust and sediments.

(3) A significant deformation event in South Africa is bracketed between 2.48 and 2.32 Ga.

(4) The first two Paleoproterozoic glacial events occurred between 2.45 and 2.32 Ga, and the third occurred between 2.32 and 2.22 Ga.

(5) Paleomagnetic data for the Ongeluk andesite, Mn-and Fe-deposits of the Hotazel Formation, and carbon isotope data for the Mooidraai Dolomite may have no bearing on Paleoproterozoic Snowball Earth since they are most likely separated by a major hiatus from the underlying Makganyene glacial diamictite.

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