No evidence of extraterrestrial noble metal and helium anomalies at Marinoan glacial termination

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ABSTRACT

High concentrations of extraterrestrial iridium have been reported in terminal Sturtian and Marinoan glacial marine sediments and used to argue for long (likely 3-12 Myr) durations of these Cryogenian glaciations. Reanalysis of the Marinoan sedimentary rocks used in the original

study, supplemented by sedimentary rocks from additional terminal Marinoan sections, however, do not confirm the initial report. New platinum group element concentrations, and $^{187}\text{Os}/^{188}\text{Os}$ and $^3\text{He}/^4\text{He}$ signatures are consistent with crustal origin and minimal extraterrestrial contributions. The discrepancy is likely caused by different sample masses used in the two studies, with this study being based on much larger samples that better capture the stochastic distribution of extraterrestrial particles in marine sediments. Strong enrichment of redox-sensitive elements, particularly rhenium, up-section in the basal postglacial cap carbonates, may indicate a return to more fully oxygenated seawater in the aftermath of the Marinoan snowball earth. Sections dominated by hydrogenous osmium indicate increasing submarine hydrothermal sources and/or continental inputs that are increasingly dominated by young mantle-derived rocks after deglaciation. Sedimentation rate estimates for the basal cap carbonates yield surprisingly fast rates of a few centimeters per thousand years. This study highlights the importance of using sedimentary rock samples that represent sufficiently large area-time products to properly sample extraterrestrial particles representatively, and demonstrates the value of using multiple tracers of extraterrestrial matter.

1. Introduction

The most extreme and prolonged ice ages of the past two billion years were the Sturtian (717 to 660 Ma) and Marinoan (~645 to 635 Ma) panglacial epochs of the Cryogenian period (Gradstein et al. 2012), when ice sheets flowed into the ocean close to the paleomagnetic equator (Harland, 1964; Embleton and Williams, 1986; Schmidt et al., 1991; Sohl et al., 1999; Evans, 2000, 2003; Macdonald et al., 2010; Evans and Raub, 2011). High orbital obliquity (Williams, 1975) and albedo instability associated with large ice caps (Kirschvink, 1992) are among the proposed explanations for Cryogenian glaciations. High orbital obliquity causes the Hadley cells

46 to reverse direction (i.e., equatorial downwelling), shifting the arid zones to the equator. This
47 prediction is not borne out by persistent subtropical paleomagnetic latitudes for evaporite
48 deposits over the past two billion years (Evans, 2006), assuming that obliquity cannot flip
49 between low and high values (Laskar et al., 1993). Moreover, mid-latitude sea-ice margins are
50 unstable under high obliquity (Ferreira et al., 2014). A stable atmospheric inversion in the winter
51 hemisphere creates a surface layer of calm air, which paralyzes wind-driven ocean mixing at the
52 sea-ice margin and thereby reduces the ocean heat capacity, facilitating winter sea-ice advance.
53 These considerations limit the apparent climatic scenarios that are consistent with tropical ice
54 sheets on the continents to three possibilities (Rodehacke et al., 2013): (1) ‘Snowball’, in which
55 the sea-ice margins meet at the equator and thicken to form dynamic sea glaciers (Warren et al.,
56 2002; Goodman and Pierrehumbert, 2003; Li and Pierrehumbert, 2011; Abbot et al., 2013), with
57 “some warm tropical ‘puddles’ in the sea of ice, shifting slightly from north to south with the
58 seasons” (Kirschvink, 1992); (2) ‘Jormungand’, in which the sea-ice margins stabilize between
59 12 and 24 degrees of latitude because of broadening of the ablative zone of dark sea ice when it
60 intersects the downward limb of the Hadley cells (Abbot et al., 2011; Voigt and Abbot, 2012);
61 and (3) ‘Waterbelt’, in which the sea-ice margins stabilize between 20 and 30 degrees of latitude
62 because of intensified ocean mixing at the sea-ice margin as the width of open water narrows
63 (Rose, 2015). In the Snowball state, extraterrestrial (ET) matter should be trapped by the sea
64 glacier and advected to the ablation zone, where it accumulates at or near the ice surface until
65 terminal deglaciation (Abbot and Pierrehumbert, 2010; Li and Pierrehumbert, 2011). In the
66 Jormungand and Waterbelt states, in contrast, ET matter should be advected to the sea-ice
67 margins, where it is continuously flushed into the ocean in the zone of most intense ocean
68 mixing (Rose, 2015).

The report of significant iridium (Ir) anomalies – allegedly of extraterrestrial origin – coinciding with Sturtian and Marinoan glacial terminations created the prospect of using the accumulation rate of ET matter as a chronometer for glacial durations (Bodiselitsch et al., 2005). Extraterrestrial matter is enriched in Ir ~10,000-fold compared to average eolian dust, upper continental (Kurat et al., 1994; Peucker-Ehrenbrink and Jahn, 2001) and oceanic (Peucker-Ehrenbrink et al., 2003, 2012) crusts. Iridium therefore serves as one of the most sensitive refractory tracers for the presence of ET matter in sediments. Concentrations of up to 1.9 ng/g Ir, similar in magnitude to many K-Pg boundaries (Cretaceous-Paleogene, e.g., Alvarez et al., 1980; Schulte et al., 2010), have been reported just above the base of the postglacial (cap) carbonates that overlie the youngest Sturtian (~660 Ma) and Marinoan (~635 Ma) glacial sediments of the Lufilian Arc in central Africa (Bodiselitsch et al., 2005). The Ir anomalies are apparently not associated with anomalies of elements enriched in the continental crust (e.g., Al, Fe, Th, Cs). Rather, they are coupled with unusual concentrations of other noble metals, specifically gold. This geochemical evidence has been used to argue for an ET pedigree of the Ir (Bodiselitsch et al., 2005).

Following the approach used by Alvarez et al. (1980) for determining sediment accumulation rates across the K-Pg boundary, based on a constant flux of small ET matter to Earth, Bodiselitsch et al. (2005) suggested that ET matter had accumulated on the Marinoan ice sheets and sea glaciers for at least 3, more likely 12 million years (Myr), depending on the assumed flux of ET matter to Earth (Love and Brownlee, 1993; Schmitz et al., 1997). The data and model assumptions permit an even longer duration of 41 ± 20 Myr. The ET material supposedly was stored for prolonged periods in the thick sea glaciers and ice sheets and quickly delivered to marine sediments during deglaciation. As both types of ice are in a dynamic state in a snowball

earth (Pierrehumbert et al., 2011), the global ice residence time is much less than the duration of the snowball epoch. However, unlike the Jormungand or Waterbelt climate states, in a snowball earth, ET material entrained in sea glaciers remained in the ice and accumulated over time in the equatorial ice ablation zone (Abbot and Pierrehumbert, 2010), because the meteoric fraction of the sea glacier only sublimates, while only the marine (freeze-on) ice undergoes basal melting (Li and Pierrehumbert, 2011). Some leakage of ET material stored in all meteoric ice sheets will occur through basal melting and drainage of meltwater into the ocean at ice grounding lines. However, in a snowball earth climate state the global ice volume is dominated by sea glaciers that entrain ET material, not by ice sheets.

In this study we use the coherent geochemical properties of platinum group elements (PGE: palladium, iridium, osmium, platinum), in conjunction with rhenium-osmium isotope systematics, to test the presence and origin of the purported extraterrestrial Ir anomalies in a number of Cryogenian glacial terminations, including some of the same samples analyzed by Bodiselitsch et al. (2005). In contrast to the Bodiselitsch et al. (2005) study, we sampled critical intervals continuously and homogenized “strips” of sedimentary rock to obtain continuous geochemical records. In searches for geochemical anomalies, this approach ensures that no major anomalies – if present – will be missed. As long as extraterrestrial contributions in sedimentary rocks can be quantified, a global inventory can be calculated by integrating over many sites with variable ET accumulation rates. Such an approach, akin to estimates of global PGE inventories across the K-Pg boundary (Tredoux et al., 1989; Goderis et al., 2013), could be used to estimate the flux of ET matter deposited across the glacial-postglacial transition.

In addition to the PGE, we tested the use of helium (He) isotopes and concentrations as an additional tracer for the presence of ET matter in the sediments studied. The large contrast in

isotope ratios and concentrations of He in ET matter and Earth's crust makes He an even more sensitive tracer for the presence of ET matter in sediments than Os isotopes and PGE abundance pattern. Moreover, in a study of Ordovician limestones in south central Sweden, Patterson et al. (1998) have shown that some extraterrestrial He can survive protracted storage in sedimentary rocks as old as – and possibly older than – 480 Myr, despite its inherent volatility.

2. Samples and Sampling Procedures

Sections of sedimentary rocks spanning the Marinoan glacial-postglacial transition from a variety of depositional environments along the shelf-slope transition of the Otavi platform, Namibia (Hoffman et al., 1998, 2007; Hoffman and Halverson, 2008; Hoffman, 2011), were cut with a portable, petrol-powered, air-cooled Stihl TS 400 Cutquik circular saw equipped with a new diamond saw blade (Fig. 1a-c). In this area of central and northern Namibia, the glacial Ghaub Formation underlies the postglacial Maieberg cap carbonates. A total of five sedimentary sections were sampled from a variety of outcrops of the diamictite-cap dolomite transition. The results from two such sections are reported here (section P6538 [for map and section see Fig. 12 of Hoffman, 2005], 1 km North of Fransfontein, East of the road: 20°11.970' S, 015°00.987' E, 1150 m above mean sea level [m.a.s.l.]; and Hoanib River valley: 19°19.116' S, 013°59.481' E, 895 m.a.s.l.)

Figure 1 (a) Pre-glacial Ombaatjie Formation (bottom), Ghaub (Marinoan) glacial diamictite (above), boundary clay (center) to post-glacial cap carbonate (top) transition on the Otavi platform in NW Namibia, section 081105.04 – before cutting, with approximate position of the section (black rectangle); (b) during cutting; (c) after chiseling of the section from the cut trench.

Two parallel cuts about 5 cm apart and about 14 cm deep were made across the transitions (Fig. 1b,c). The sections were marked, photographed, then extracted with chisel and hammer, photographed again and bagged for transport to the laboratory (Fig 1a-c). There, strips of ~3 cm width and 5-10 cm length were cut from these sections with a diamond saw blade. The outsides of the strips were washed, cleaned with Al_2O_3 powder in a sandblaster to remove impurities from the sawing, and then cleaned with pressurized air to remove Al_2O_3 beads. The strips were then broken with a hammer between plastic bags, crushed in a jaw crusher equipped with tungsten carbide plates, and pulverized in an Al-ceramic barrel in a shatter box. The equipment was cleaned with silica powder between samples to avoid cross contamination, and preconditioned with a small amount of sample material that was subsequently discarded.

Additional samples from NW Canada (transition from Stelfox diamictite into the overlying Ravensthorpe cap dolomite, Mackenzie Mountains, including continuous samples of the bottom 1 meter of the cap dolostone) and South China (transition from Nantuo diamictite into overlying Doushantuo cap dolostone, Huajipo section, Yangtze Gorges area, Hubei Province, Fig. 2) were obtained from the Harvard University collection and processed for analysis as described above.

Figure 2 Nantuo tillite to basal Ediacaran cap dolostone (lower Doushantuo Formation) transition at the Huajipo section, Yangtze Gorges area, Hubei, South China, with osmium concentrations and $^{187}\text{Os}/^{188}\text{Os}$ values superimposed. Approximate sample locations are indicated by the white stars. Red line marks the boundary clay. Green line marks a 635 ± 0.5 Myr old volcanic ash (Condon et al., 2005). Person near bottom for scale. (Photo: PF Hoffman)

The samples from the Mackenzie Mountains include the continuous one meter interval of basal Ravensthorpe cap dolomite from the Gayna River section ($64^{\circ}49'\text{N}$, $130^{\circ}28'\text{W}$, 1855 m.a.s.l.; for map, schematic stratigraphy and field photo see Figs. 1 and 4b in Macdonald et al., 2013) that was complemented by a sample of the 2-12 cm thick underlying clay layer and several

discrete samples of the underlying Stelfox diamictite that were taken from the Cranswick Lake section (65°06'N, 132°27'W, 1606 m.a.s.l.) and the Stone Knife River section (64°41'N, 129°53'W, 1596 m.a.s.l.) Sampling of the Ravensthorpe cap dolomite at the Gayna River section was extended up to 4.3 meters above the base of the cap dolomite by discrete, non-continuous sampling. The total (not decompacted) thickness of the strata above the Ravensthorpe formation at the time of Cretaceous thrusting was 5.5 km (Gordey et al., 2010), and the strata was likely thickened to ~8 km as a result of thrusting and before erosion. Assuming a geotherm of 25°C km⁻¹ yields prolonged temperatures of ~150°C before thrusting, and transient heating to <210°C after thrusting is possible based on thermal maturation data for upper Devonian hydrocarbon-bearing units near the top of the pre-thrust section (MacNaughton et al., 2008). Such prolonged heating could have affected the integrity of the primary He budget of these rocks.

Marinoan syndeglacial cap dolostones like the Keilberg Member in NW Namibia, Ravensthorpe Formation in NW Canada and basal Doushantuo Formation in South China form the transgressive tracts of exceptional depositional sequences associated with global ice-sheet meltdown at the end-Cryogenian glacial termination (Kennedy, 1996; James et al., 2001; Hoffman and Schrag, 2002; Shields, 2005; Hoffman et al., 2007; Bao et al., 2008). The glacioeustatic component of the large-scale marine transgression was global and geologically rapid (kyrs) because of positive feedbacks in the climate system (e.g., ice-albedo feedback, ice-elevation feedback, GHG-temperature feedback, isostasy-outgassing feedback) and because most Marinoan ice sheets were tropically located (Li et al., 2013). Marinoan cap dolostones have $\delta^{13}\text{C}_{\text{carb}}$ profiles and an assortment of unusual sedimentary features that easily distinguish them from older Cryogenian (Sturtian) postglacial cap carbonates (Kennedy et al., 1998; Hoffman et al., 2011). The Marinoan cap dolostones in Namibia, NW Canada, South China and elsewhere

are easily recognizable and a product of global change, implying global synchronicity, which led to the placement of the GSSP for the Ediacaran Period at its base (Knoll et al., 2006). The validity of this stratigraphic assignment has been borne out by radiometric geochronology. U-Pb zircon ID-TIMS dates of 635.2 ± 0.5 and 635.5 ± 0.8 Ma have been obtained from tuffs within Marinoan cap dolostones in South China and Tasmania, respectively (Condon et al., 2005; Calver et al., 2013), and tuffs in terminal Marinoan glacial deposits have been dated by the same method at 635.5 ± 0.5 Ma in Namibia (Hoffmann et al., 2004). In NW Canada, a Re-Os isochron age of 632.3 ± 5.9 Ma has been obtained from organic-rich black shale directly overlying the Ravensthorpe cap dolostone (Rooney et al., 2015).

3. Experimental

3.1. $^{187}\text{Os}/^{188}\text{Os}$ and PGE concentrations

For PGE and $^{187}\text{Os}/^{188}\text{Os}$ analyses ~10 gram of sample powder was spiked with a mixed-PGE tracer solution enriched in ^{99}Ru , ^{105}Pd , ^{190}Os , ^{191}Ir , and ^{198}Pt and processed according to procedures described in detail in Ravizza and Pyle (1997) and Hassler et al. (2000). Osmium isotopes were analyzed by distilling (sparging) volatile Os into a Thermo Fisher Neptune inductively-coupled plasma mass spectrometer (ICPMS) equipped with multiple ion counters, using data acquisition and data reduction routines described in detail in Sen and Peucker-Ehrenbrink (2014). Concentrations of PGE were determined on a Thermo Finnigan Element2 ICPMS using the sparging solutions left after $^{187}\text{Os}/^{188}\text{Os}$ analyses (Hassler et al., 2000). Whenever possible (Ru, Pd, Os, Pt), PGE concentrations were determined using at least two isotope ratios that ideally yield concentrations that agree within analytical error. In cases when the difference in concentration calculated by two isotope ratios is larger ($\geq 19\%$), we chose to

report the lower concentration, as this minimizes the potential of concentrations being affected by unrecognized interferences. The analytical methods for PGE concentrations and $^{187}\text{Os}/^{188}\text{Os}$ values have been carefully evaluated with international reference materials and in-house standards (see Peucker-Ehrenbrink et al., 2003).

3.2. Rhenium and Molybdenum concentrations

Rhenium concentrations in all and molybdenum (Mo) concentrations in the Ravensthorat sections were determined by isotope dilution (^{185}Re , ^{98}Mo) on ~100 mg aliquots of the same sample powder after digestion in hot mineral acids, ion exchange chromatography and Element2 ICPMS data acquisition using methods described in detail in Miller et al. (2011). We emphasize that Os and Re-Mo concentration data were generated using different splits of the same powder. This procedure is not ideal for Re-Os isochron analyses, as nugget effects contribute to variability in PGE concentrations. We therefore do not attempt to use Re-Os isochron relationships to determine ages of any of the samples analyzed in this study. Results are summarized in supplemental data table 1 (Table S1).

3.3. $^3\text{He}/^4\text{He}$ and He concentrations

Three contrasting samples from the Ravensthorat sections – a cap carbonate, a boundary clay, and the matrix of a glacial diamictite – were prepared for He isotope analyses by manually crushing and pulverizing pieces of rock in a stainless steel mortar and pestle that had been cleaned first with acetone and then with isopropanol. Manual crushing avoids heating the sample powder that is associated with mechanical grinding in planetary disc mills and thus minimizes loss of helium during sample preparation. 8.25 grams of a cap dolomite sample (PI 0.05) were decarbonated in an isopropanol-cleaned Erlenmeyer flask with a mixture of 30 ml ultra-clean (Millipore, $\geq 18.2 \text{ M}\Omega$) water and up to 30 ml ~1.8 N acetic acid. The large sample

volume is needed to maximize the area-time product in order to minimize bias against larger ET particles (Farley et al., 1997) in carbonate sediments of poorly constrained accumulation rates (Hoffman and Schrag, 2002; Hoffman et al., 2007; Font et al., 2010). Dilute acetic acid is an effective means for dissolving carbonate without affecting extraterrestrial He (Marcantonio et al., 1999). The acetic acid was added stepwise to the water over several days, aided by repeated 15-minute intervals of ultra-sonication. Finally, 2/3 of the supernatant was decanted and 6 ml of ~1.8 N acetic acid was added to test for additional degassing of CO₂ during ultra-sonication. After the reaction stopped, the solution was filtered through a pre-cleaned 0.45 µm silver filter, placing this filter into a filter holder of a vacuum filtration device. The Erlenmeyer flask was washed three times with 18.2 MΩ Millipore water followed by three washes with isopropanol. The sample was then air-dried in the vacuum pump for one hour before the Ag-filter was placed onto an isopropanol-washed thick Al-foil and wrapped tightly to avoid material escaping from the foil package. Two additional samples, ~0.85 g of a boundary clay (P5B -0.05) and ~1.5 grams of the fine-grained matrix of a glacial diamictite (P5B -0.30) were treated in a very similar manner. The only difference was that the samples were first suspended in 5 ml 18.2 MΩ Millipore water and 2.5 ml of ~1.8 N acetic acid was added stepwise, followed by repeated ultra-sonication. No degassing of CO₂ was observed during the treatment of these two clay-rich samples.

The tightly wrapped Al-foil packages were loaded into the ultra-high-vacuum sample extraction line of a helium isotope mass spectrometer. Once outgassing was reduced to an acceptable level, samples were dropped into a double vacuum resistance furnace and heated to 1600°C. The volatiles were introduced into a noble gas extraction line optimized for purification of He. Ion beam intensities of ³He and ⁴He were analyzed in a 90 degree sector mass

spectrometer dedicated to helium, locally referred to as MS2 (Kurz et al., 2004). Total procedural blanks for ^3He and ^4He did not exceed 0.5% and 1%, respectively, of the lowest concentrations measured in the samples (cap dolostone P1-0.05) and typically were about 4 orders of magnitude smaller. We consider these contributions negligible. Results are summarized in supplemental data table 1 (Table S1).

3.4 Major and Trace Element concentrations

Major and trace element concentration of the Ravensthoat sections samples (Mackenzie Mountains, NW Territories, Canada) were determined in the SARM lab at the CRPG-CNRS at the University of Nancy, France. Major and some trace element concentrations were measured by ICP-AES on LiBO_2 fusions and complemented with additional trace element analyses by ICPMS. International reference materials were used to control data quality. The data and relevant metadata for all samples, analytical uncertainties and an international reference standard (USGS-SDO-1) are summarized in supplemental data table 1 (Table S1).

4. Results

4.1. Ravensthoat Sections

The carbonate-rich nature of most of this section is clearly visible in the high Ca and Mg concentrations and significantly elevated Mn concentrations relative to the continental crustal average (Fig. 3a,b). In order to evaluate trends in element concentrations across the section, we use an approach that first subtracts a local detrital component from the bulk and then normalizes the residual element concentrations to upper continental crustal (UCC) concentrations (McLennan, 2001).

Figure 3 (a) Zirconium-normalized element enrichment/depletion relative to upper continental crust (McLennan, 2001) in cap carbonates from the Ravensthorpe sections, Mackenzie Mountains, NW Canada. Elements are ordered from left to right in decreasing order of compatibility in the continental crust. Elements with notable anomalies are highlighted in red. Legends mark height (in m) of cap carbonate samples above the boundary clay. (b) Same as (a), but with an expanded scale.

If $[X]_i$ is the concentration of element X in sample i, and $[X]_{ref}$ is the concentration of the same element in the sample from the section that is most influenced by detrital matter, the residual concentration of element X in sample i, $[X]_{ir}$, normalized to UCC is calculated as:

$$[X]_{ir} = \{([X]_i - ([X]_{ref} [Zr]_i / [Zr]_{ref})) / [X]_{UCC}\}$$

Normalization to zirconium (Zr) can be replaced by normalizations to other “immobile” elements such as Al or Th (Hodson, 2002), but the choice of internal normalizing element has little effect

on the observed abundance pattern. We subtract a local detrital component because the sample that is most strongly influenced by detrital matter in this section, the boundary shale, has slightly higher Zr concentrations (225 $\mu\text{g/g}$) than average UCC (190 $\mu\text{g/g}$, McLennan, 2001). This ensures that residual concentrations, i.e. bulk minus the detrital component, are positive.

Uranium, strontium and phosphorus show minor enrichments in the non-detrital fraction relative to UCC, whereas Re and Os exhibit both enrichments and depletions depending on the position within the section and the choice of normalizing element (Fig. 3b). The section is characterized by a prominent spike in concentrations of PGE at the boundary between the cap dolostone and the underlying diamictites, with Ir concentrations exceeding 100 pg/g at the boundary (Figs. 3b, 4a,c). Concentration differences between the two lithologic units range from almost two orders of magnitude in the case of Os and Re (Fig. 4b), to more than an order of magnitude for Ir (Fig. 4a,c), to about one order of magnitude in the case of Pt and Pd (Fig. 4c). The shapes of CI-chondrite normalized concentration pattern show little variation despite more than an order of magnitude variation in absolute concentrations (Fig. 4c).

Figure 4 (a) Iridium concentrations (left) and Ir/Al weight ratios (right) in the diamictite to cap carbonate transition in the Ravensthorpe sections, Mackenzie Mountains, NW Canada. Note that only the first meter above the boundary clay has been sampled continuously. (b) Osmium and Re concentrations (left) $^{187}\text{Re}/^{188}\text{Os}$ (center) and present-day (gray line and white squares) as well as initial (black line and squares) $^{187}\text{Os}/^{188}\text{Os}$ in the diamictite to cap carbonate transition in the same section. (c) CI-normalized PGE concentrations in diamictite (gray lines), boundary clay (red line) and cap carbonate (blue lines) in the same section. Also shown are the distance of

311 cap carbonate samples above the boundary clay (in m), and concentration of pure CI-chondrite
312 matter in sediments (in parts per million, ppm). UCC composition is shown as gray field
313 (Peucker-Ehrenbrink and Jahn, 2001, and references therein).

314 All samples are enriched in Os relative to Ir, and many, but not all, samples are also
315 characterized by enrichments in Re (Fig. 4c). While concentrations of PGE do not change
316 significantly above 0.5 m from the boundary shale, Re concentrations increase up-section by
317 almost an order of magnitude (Fig. 4c). Correspondingly, $^{187}\text{Re}/^{188}\text{Os}$ vary by more than one
318 order of magnitude from the boundary shale to the top of the section (Fig. 4b). Ingrowth-
319 corrected $^{187}\text{Os}/^{188}\text{Os}$ values vary little across the lithologic transitions, but tend to become less
320 radiogenic (~ 0.6 to ~ 0.25) in the overlying cap dolostone away from the boundary (Fig. 4b).
321 Interestingly, concentrations of some redox-sensitive elements (U, Re) in the calculated detrital-
322 free sediment fraction systematically increase from the base of the cap dolostone to the top of the
323 section (Figs. 3a,b, 4b). Helium isotope ratios and concentrations in the three samples analyzed
324 (Fig. 5) are typical of UCC (Marcantonio et al., 1998).

Figure 5 ^3He concentrations and $^3\text{He}/^4\text{He}$ for three samples (diamictite, boundary clay, cap carbonate) from the Ravensthorpe sections, plotted with marine sediments (small black dots), magnetic particles extracted from marine sediments (open diamonds), IDPs (open triangles; Nier et al., 1990; Nier and Schlutter, 1992), bulk lunar fines (large gray circle, Geiss et al., 1970) and 480 Myr old limestone from Kinnekulle, Sweden (large gray-rimmed circles, Patterson et al., 1998). Mixing lines between bulk lunar fines (ET) and UCC are strongly curved concave up with increasingly positive slope.

4.2. Section 080705.01

The geochemical structure of this section is slightly more complex than that of the Ravensthorpe sections. The lithologic boundary at ~100 cm depth is characterized by a ~10-fold spike in Pd concentrations to more than 3 ng/g, somewhat broader and less well pronounced concentration peaks in Pt (increase by a factor of ~3 to almost 0.8 ng/g) and Ir (increase by a

factor of 2-3 to ~15 pg/g), and little change in Os concentrations (Fig. 6a). Variations in $^{187}\text{Re}/^{188}\text{Os}$ with depth, particularly in the lower portion of the section that includes the diamictites, are a reflection of the bimodal composition of the diamictite with more clay-rich and more carbonate-rich enclaves (Fig. 6b). $^{187}\text{Re}/^{188}\text{Os}$ values are low near the Pd and Pt concentration anomalies at 100 cm depth. While there is a slight and rather broad minimum in $^{187}\text{Os}/^{188}\text{Os}$ (~0.65) at that depth, the fine structure across that boundary reveals an ingrowth-corrected increase from ~0.6 to a value of ~0.85 at 100 cm depth. $^{187}\text{Re}/^{188}\text{Os}$ and age-corrected $^{187}\text{Os}/^{188}\text{Os}$ increase up section from ~100 cm depth, with $^{187}\text{Os}/^{188}\text{Os}$ values reaching ~0.9 (Fig. 6b) and Re concentrations increasing by about an order of magnitude (supplemental data table 1). Horizons enriched in Mo (100 cm, 220 cm) do not correspond to those enriched in Re (10-15 cm), indicating complex enrichments of redox-sensitive elements in this section. The CI-chondrite normalized PGE concentrations have fractionated pattern with low Os and Ir concentrations and an order of magnitude higher Pt, Pd and Re concentrations (Fig. 6b). The enrichment of Os relative to Ir, if present, is much less pronounced than in the Ravensthoat sections.

Figure 6 (a) Osmium, Ir, Pt, and Pd concentrations in section 080705.01 (P6538, near Fransfontein, NW Namibia). (b) $^{187}\text{Re}/^{188}\text{Os}$, $^{187}\text{Os}/^{188}\text{Os}$ (white: present-day, black: initial; black arrow indicates negative initial ratio), and CI-normalized PGE concentration patterns (solid lines: cap carbonates, stippled lines: diamictites. There is no discernable boundary clay in the same section. Gray field shows UCC composition (Peucker-Ehrenbrink and Jahn, 2001, and references therein).

4.3. Section 081105.04

This section transitions at ~80 cm depth from the underlying Ghaub diamictite into the overlying cap dolostone. The boundary is marked by ~10-fold increases in Pd (up to 2.3 ng/g), Pt (up to 1.6 ng/g), Os (up to 0.8 ng/g) and Ir (up to 0.12 ng/g) concentrations (Fig. 7a). Rhenium concentrations decrease across the boundary, but increase 10-fold in the 20 cm overlying the lithologic contact (Fig. 7b and supplemental data table 1). Correspondingly, $^{187}\text{Re}/^{188}\text{Os}$ value decrease by almost two orders of magnitude at the boundary relative to the

diamictites, recovering within ~20 cm of the boundary to values ~30-50 (Fig. 7b). Age-corrected $^{187}\text{Os}/^{188}\text{Os}$ values increase by ~0.2 units to ~1 at the boundary, decrease to ~0.7 within the overlying 20 cm of cap dolostone and continue to decrease up-section to values of 0.3-0.5.

Figure 7 (a) Osmium, Ir, Pt, and Pd concentrations in section 081105.04 (NW Namibia, 19°19.116'S, 013°59.481'E). (b) $^{187}\text{Re}/^{188}\text{Os}$, $^{187}\text{Os}/^{188}\text{Os}$ (white: present-day, black: initial), and CI-normalized PGE concentration patterns in the same section (UCC composition is indicated as gray field, Peucker-Ehrenbrink and Jahn, 2001, and references therein). Black arrow indicates negative initial ratio. Bold solid black line in CI-normalized PGE concentration pattern indicates

boundary clay sample. Thin solid black lines indicate cap carbonate samples, whereas stippled black lines indicate diamictite samples.

CI-normalized PGE concentrations again show a step-like, fractionated abundance pattern with low Ir concentrations and supra-chondritic Os/Ir (Fig. 7b). As in the two other sections, the abundance pattern of the most PGE-rich sample is very similar in shape to those of the other samples and does not become more akin to undifferentiated ET matter (Fig. 7b).

4.4. Replicate Analyses of the Kambishi Core:

As observed in the three sections described above, Ir concentrations in four samples from the original core that Bodiselitsch et al. (2005) investigated do not exceed 0.05 ng/g (K-61=44 pg/g; MJ-6=19 pg/g; MJ-18=35 pg/g; MJ-21=42 pg/g) and are thus far lower than the originally reported values (K-61=1881±85 pg/g; MJ-6=14±7 pg/g; MJ-18=420±40 pg/g; MJ-21=111±21 pg/g; Bodiselitsch et al., 2005). Sample K-61 for which Bodiselitsch et al. (2005) report 1881 pg/g was analyzed twice. The first isotope dilution analyses on 1.01 g sample powder did not yield quantifiable results because the sample was overspiked, indicative of very low Os concentrations in the sample. A replicate, properly spiked isotope dilution analysis on 1.7 g sample material yielded a concentration of 44 pg/g Os. Osmium concentrations in these four previously analyzed samples do not exceed 0.1 ng/g, whereas Pt concentrations reach 1.8 ng/g (MJ-21). Iridium concentrations are even lower, and neither Ir concentrations nor Ir/Al (Fig. 8) yield the anomalies reported by Bodiselitsch et al. (2005). The CI-chondrite normalized PGE abundance pattern show a step-like pattern with low Os and Ir and elevated Pt concentrations. Measured $^{187}\text{Os}/^{188}\text{Os}$ are ~ 2, and are not age corrected due to lack of Re data.

Figure 8 Reanalysis of splits of the Kipushi KH1150PVSSW core (Marinoan section) across the diamictite/cap carbonate transition. Original data from Bodiselitsch et al. (2005) are shown in red (Ir) and green (Ir/Al) lines that connect data points (small squares). Note that Bodiselitsch et al. (2005) did not sample continuously. New data show Ir concentrations (red stars) and Ir/Al data (green stars) for splits of the same samples. Top buff-colored strata: dolomitic shale of the Middle Kundelungu Group, pink: Calcaire Rose, blue: Diamictite, Petit Conglomerat, bottom buff-colored strata: dolomitic shale of the Upper Nguba Group. Left panel shows the full section (0-130 meters), middle panel shows details between 40 and 75 meters, right panel shows details of the glacial-postglacial transition (53-57 meters).

4.5. Nantuo Tillite and Doushantuo Cap Dolostone, Huajipo Section, Hubei, South China

Four samples taken across the tillite-basal cap dolostone transition show a drop in Os concentrations from ~25 pg/g in the tillite to concentrations of ~2-4 pg/g in the overlying basal Doushantuo cap dolostone (sample C1-2). The boundary clay contains 38 pg/g Os. Measured

(not age corrected) $^{187}\text{Os}/^{188}\text{Os}$ values decrease from ~0.92 in the tillite to ~0.86 in the boundary clay and in the lowermost portion of the basal cap dolostone (Fig. 2). $^{187}\text{Os}/^{188}\text{Os}$ values increase to ~0.98 two meters above the contact in the cap limestone (sample C3).

5. Discussion

5.1. PGE Anomalies and their Origin:

This study was intended to investigate whether the reported Ir enrichments at Cryogenian glacial terminations are extraterrestrial in origin and can be used to constrain the duration of ice sheets and sea glaciers during the Marinoan glaciation (Bodiselitsch et al., 2005). Alternatively, the data may provide insights into the accretion rates of ET matter, provided sedimentation rates can be constrained independently with geochronological methods. While we found concentration anomalies of PGE at the transitions from glacial diamictites to overlying cap carbonates, we found little evidence for extraterrestrial contributions to these anomalies. Instead, multiple lines of evidence point to terrestrial sources of PGE enrichments. While we cannot exclude the possibility that differentiated ET material contributed significantly to the observed anomalies, such sources currently constitute a small fraction of ET matter accreted on Earth. Such a source is also contrary to the arguments advanced by Bodiselitsch et al. (2005) who assumed chondritic composition in their calculations of the duration of the glaciations. Most importantly, reanalysis of splits of the core material analyzed by Bodiselitsch et al. (2005) did not yield the reported enrichments in Ir. A potential explanation for this discrepancy could be related to the masses of sediments used for the analyses. Bodiselitsch et al. (2005) used ~0.1 gram of sample material for Instrumental Neutron Activation Analysis (INAA; Bodiselitsch, 2004). The analytical data reported here were done on several grams of material. It is

conceivable that the fortuitous inclusion of small, rare ET particles, possibly only a single particle, in the INAA analyses caused the high Ir and Au concentrations reported by Bodiselitsch et al. (2005). For the sample with the highest concentration reported by Bodiselitsch et al. (2005) a single CI-chondritic particle with 500 ng/g Ir, a density of 3 g/cm³ and a diameter of ~285 µm can cause the observed Ir concentrations of 1.8 ng/g if only 0.1 g of sediment was analyzed. The chance of having such rare particles affect concentrations is much reduced if significantly larger sample volumes are analyzed. For instance, including a single such particle in the 2-4 g of sediment used in this study only causes Ir concentrations of 0.095 to 0.14 ng/g, similar to values observed by us. This nugget effect is the reason that area-time products of $\geq 2 \text{ m}^2 \text{ yr}^{-1}$ are needed to obtain reproducible PGE analyses of sediments affected by accumulation of ET matter with a present-day near-Earth particle size distribution (see Peucker-Ehrenbrink and Ravizza, 2000; Peucker-Ehrenbrink, 2001). It is thus possible that the small sample masses used by Bodiselitsch et al. (2005) were not appropriate for the geological application, and that the implications of that study are not statistically significant. The fact that Bodiselitsch et al. (2005) detected concentration anomalies near glacial-postglacial transitions could simply reflect the fact that these transitions were more densely sampled, thereby increasing the likelihood of occasionally encountering rare ET particles in the small sample volumes. The fact that the authors detected concentration anomalies in the diamictites as well as the cap carbonates supports this interpretation. We note that other scenarios for the discrepancies in the analytical results such as contamination during sampling or sample preparation cannot be excluded. It is also possible that anomalous concentrations of ET matter do exist at the transition between glacial and postglacial sediments and that our sampling efforts simply missed those anomalous layers. However, we consider it more likely that the PGE concentration anomalies we observe

are equivalent to those found by Bodiselitsch et al. (2005), but are of terrestrial rather than extraterrestrial origin. A lack of evidence for ET signatures in postglacial deposits from NW Namibia was also noted by Gyollai et al. (2014), though the methods used for detecting Ir by INAA were less sensitive than those used by Bodiselitsch et al. (2005), and similar small sample sizes (~0.15 g) were used.

5.2. Sedimentation Rates

The steady flux of ET matter to marine sediments has been used successfully to reconstruct sample-specific sedimentation rates. The three approaches that are based on the most highly enriched elements/isotopes in extraterrestrial vs. terrestrial material are 1) ^3He (e.g. Marcantonio et al., 1996, 1998; Higgins et al., 2002; Farley et al., 1997), 2) Os isotopes (e.g. Esser and Turekian, 1993; Pegram and Turekian, 1999; Peucker-Ehrenbrink, 1996), 3) iridium (e.g. Alvarez et al., 1980; Dalai and Ravizza, 2006, 2010), or combinations of them. However, these calculations require preservation of the original geochemical signal that, in the case of the volatile tracer such as He, is not likely. Reconstructions of sedimentation rates that are based on Os isotopes in bulk sediments require an independent reconstruction of the $^{187}\text{Os}/^{188}\text{Os}$ of contemporaneous seawater, a parameter that is not constrained for the period of the Neoproterozoic investigated here. Partitioning the sedimentary Os isotope budget into an ET component (Meisel et al., 1996; Kurat et al., 1994) and a detrital component with fixed $^{187}\text{Os}/^{188}\text{Os}$ values for the end-members is likely not appropriate during times of drastically changing environmental conditions in land-proximal environments.

We take a different approach that is based on using an element associated with the detrital fraction (Zr, Th, or Ti) to estimate the fraction of bulk Ir ($[\text{Ir}]_b$) that is associated with the detrital

component for which we assume UCC composition. We further assume that this fraction has an Ir concentration ($[\text{Ir}]_{\text{UCC}}$) of 22 pg/g and an Os/Ir of ~1 (Peucker-Ehrenbrink and Jahn, 2001).

$$[\text{Ir}]_{\text{ET}} = [\text{Ir}]_{\text{b}} - [\text{Ir}]_{\text{UCC}} [\text{Zr}]_{\text{b}} / [\text{Zr}]_{\text{UCC}}$$

The choice of crustal indicator element does not change the results significantly. We also assume that the remainder of the Ir is of extraterrestrial origin with an Os/Ir of ~1 (Kurat et al., 1994).

$$[\text{Ir}]_{\text{ET}} = [\text{Os}]_{\text{ET}}$$

The remainder of the Os budget, corrected for radiogenic ingrowth since deposition, is assumed to be of hydrogenous origin, thus explaining observed Os/Ir values >1 in the bulk samples (Figs 4c, 7b). This calculation implies that the samples contain no hydrogenous Ir. As a result, sedimentation rates calculated here are minimum estimates. We further assume ingrowth-corrected (635 Ma) $^{187}\text{Os}/^{188}\text{Os}$ values of the UCC and ET end-members of 1.0 (Peucker-Ehrenbrink & Jahn, 2001) and 0.12 (Meisel et al., 1996), respectively. This allows us not only to calculate the $^{187}\text{Os}/^{188}\text{Os}$ of the hydrogenous component, i.e. contemporaneous seawater, but also to estimate the duration of sedimentation (T_{sed} , in kyr) for the depth interval (Δ_{sed} , in cm) each sample encompasses, if we assume that the mass accumulation rate (MAR) of ET osmium to Earth 635 Ma was similar to today ($\sim 1.2 \text{ pg Os g}^{-1} \text{ cm}^{-1} \text{ kyr}^{-1}$, Love and Brownlee, 1993; Peucker-Ehrenbrink, 1996).

$$\text{IC}_{\text{sw}} = (\text{IC}_{\text{b}} [\text{Os}]_{\text{b}} - \text{IC}_{\text{ET}} [\text{Os}]_{\text{ET}} - \text{IC}_{\text{UCC}} [\text{Os}]_{\text{UCC}}) / ([\text{Os}]_{\text{b}} - [\text{Ir}]_{\text{b}})$$

$$T_{\text{sed}} = \Delta_{\text{sed}} / ([\text{Os}]_{\text{ET}} / \text{MAR}_{\text{Os ET}})$$

The results of this 3-component mixing model are shown in Figure 9a-c. We caution that in dynamic land-proximal depositional settings the $^{187}\text{Os}/^{188}\text{Os}$ as well as Os and Ir concentrations

of the detrital component, may vary in time and space much more than in pelagic environments traditionally used to apply tracers of ET matter to constrain sedimentation rates. Despite these caveats, it is instructive to push the interpretation of the geochemical data for the most data-rich sections (Mackenzie Mountains, Canada) to the limit.

Figure 9 (a) Estimated sedimentation rates, (b) seawater ¹⁸⁷Os/¹⁸⁸Os at time of deposition, and (c) uranium (white bars) and rhenium (black bars) enrichment factors relative to average UCC (McLennan, 2001; Peucker-Ehrenbrink and Jahn, 2001). See text for details on the three-component mixing model.

We find variable ¹⁸⁷Os/¹⁸⁸Os of postglacial seawater (0.2 to 0.75) for the first 0.25 Myr of cap carbonate deposition (Fig. 9b). Calculated sedimentation rates are between 1.4 to 3.9 cm/kyr with somewhat faster accumulation in the lower 25 cm of the cap carbonates compared to the overlying 4 meters (Fig. 9a). This model assumes present-day accumulation rates of ET matter evenly distributed on Earth (Love and Brownlee, 1993; Peucker-Ehrenbrink, 1996). Faster sedimentation rates would result if some of the non-detrital Ir were seawater-derived (hydrogenous) rather than extraterrestrial in origin. The minimum sedimentation rates estimated

from our model are similar to results for slope deposits derived from stable isotope box models (3 cm/kyr) of Kasemann et al. (2014). In contrast, our estimates are much lower than estimates based on sedimentological features and results from climate models (380-1900 cm/kyr). In order to accommodate such fast sedimentation rates, almost all of the non-detrital Ir in the sediments must be hydrogenous rather than extraterrestrial in origin. While we have no tracer for the fraction of Ir that is hydrogenous in origin, using Zr-, Th-, and Ti-normalized Co concentrations to partition bulk Co concentrations into a local detrital (26 $\mu\text{g/g}$ Co vs. 17 $\mu\text{g/g}$ in UCC; McLennan, 2001) and hydrogenous component (Halbach et al., 1983) reveals that 22-57% (Zr-normalized), 0-39% (Th-normalized) or 25-56% (Ti-normalized) of the bulk Co inventories in the cap dolostones are likely of non-detrital origin, suggesting that a significant fraction of the non-detrital Ir is not associated with ET material, but rather hydrogenous in origin. Faster sedimentation rates than the minimum estimates given above are therefore permissible, and our model loses its ability to quantify sedimentation rates as the fraction of hydrogenous Ir in the samples increases.

5.3. Postglacial Environmental Conditions:

The data for all sections reveal systematic trends in the normalized concentrations of redox-sensitive elements, particularly Re and – in the Ravensthorpe sections – U, as well as trends in initial $^{187}\text{Os}/^{188}\text{Os}$ values in the lowermost cap carbonate sections (Fig. 9b). In the Ravensthorpe sections, enrichment factors above expected crustal Re concentrations increase from ~2 to ~30 from the base to the top of the section (Fig. 9c). In contrast, enrichment factors for U only increase from ~4 to ~10 over the same depth interval. In analogy to modern marine sediments deposited under reducing (sub-oxic to sulfidic) condition, Re is the most strongly enriched redox-sensitive element (Morford and Emerson, 1999). The presence of large marine sinks for

redox-sensitive elements during glaciations, possibly in a synglacial sulfidic ocean (Hurtgen et al., 2006), may have caused a decrease of concentrations of dissolved redox-sensitive metals in glacial seawater. However, low biological productivity under thick ice cover may have left deepwater depleted in organic substrate for microbial sulfate reduction, thereby creating an Fe-rich anoxic but not sulfidic deepwater (c.f. Mikucki et al., 2009) with low Re concentrations. Steadily increasing concentrations of redox-sensitive elements in post-glacial seawater may therefore reflect the return to more fully oxygenated seawater. However, it is also possible that the increase in enrichment factors up-section reflects a trend towards more reducing sediments, possibly caused by enhanced deposition, or preservation, of organic matter (Kunzmann et al., 2013), or by upwelling of reducing deepwater (Hurtgen et al., 2006). However, rapid deglaciation would have created a thick, low-density meltwater lid – the “Glacial Lake Harland” of Hoffman (2011) – overlying a cold snowball brine, thereby limiting interaction with the deep ocean. As sedimentary structures and textures in the cap carbonates indicate that the transgressive cap dolostone was deposited in the ocean mixed layer, cap dolostones formed in this meltwater lid and do not represent ‘marine’ deposits (Shields, 2005; Hoffman, 2011). Whether or how the observed geochemical trends, identified in several sections from different paleogeographic regions, are connected to ocean-wide trends in the evolution of dissolved oxygen, and deposition or preservation of organic carbon (Hurtgen et al., 2006; Sahoo et al., 2012) therefore remains speculative.

The sections dominated by hydrogenous Os (i.e., highest Os/Ir values, Figs 4c, 7b) show decreasing initial $^{187}\text{Os}/^{188}\text{Os}$ values above the PGE concentration anomalies (Figs. 4b, 7b). Initial $^{187}\text{Os}/^{188}\text{Os}$ consistently reach ~0.3, indicative of either a more dominant submarine hydrothermal flux or continental inputs dominated by weathering of young mantle-derived rocks.

The results from these sections could be interpreted as reflecting the isotopic evolution of local seawater under post-glacial conditions. The fact that the sections that are dominated by hydrogenous Os - including the Ravensthorpe sections that allows us to correct for detrital and extraterrestrial contributions - show similar trends could be interpreted as reflected in the inferred global evolution of the low-salinity lid immediately following the Marinoan glaciation.

In contrast, the section with Os/Ir values near unity (Fig. 6b) shows no significant temporal change in initial $^{187}\text{Os}/^{188}\text{Os}$ values above the PGE concentration anomaly (Fig. 6b). Initial $^{187}\text{Os}/^{188}\text{Os}$ values of 0.7 to 0.9 are somewhat less radiogenic than contemporaneous average UCC inputs ($^{187}\text{Os}/^{188}\text{Os}$ of ~ 1.0), assuming that that UCC reservoir has since evolved with an average $^{187}\text{Re}/^{188}\text{Os}$ of ~ 35 to present-day values of ~ 1.4 (Peucker-Ehrenbrink and Jahn, 2001). The slightly less radiogenic composition of the crustal end-member may reflect the nature of the local detrital inputs. However, the local detrital sources do not need to be reflected in the inferred isotope composition of post-glacial seawater, if the residence time of Os in the post-glacial ocean is sufficiently long to reflect a globally integrated weathering signal, similar to the modern marine Os isotope system.

6. Conclusion

The new data reported here show that PGE concentration anomalies in boundary shales or the lowermost cap carbonates are terrestrial in origin. Replicate analyses of large samples originally analyzed by Bodiselitsch et al. (2005) do not confirm the high Ir concentrations initially reported, but instead show consistently low Ir concentrations, upper crustal PGE concentration pattern and non-chondritic initial $^{187}\text{Os}/^{188}\text{Os}$. We suspect that undersampling of the ET particle population by using inadequately small sample masses in the original study led to discrepancy between that

data and our new data. This conclusion is supported by the helium data, which yielded continental crust isotopic compositions.

Concentrations of redox-sensitive elements (Re, U) increase up-section in the lowermost cap carbonates and could be related to increasing marine inventories of these elements after the glaciation, or more poorly oxygenated sediments as the productivity of the post-glacial ocean rebounds. These increases in concentrations are accompanied by variable initial $^{187}\text{Os}/^{188}\text{Os}$ values, each section recording different temporal evolutions from the PGE concentration anomaly to the top of the section. However, geochemical data for the sections that are dominated by hydrogenous Os reveal either an increasingly (up-section) dominant submarine hydrothermal contribution or a continental crust flux that is increasingly dominated by weathering of young mantle-derived lithologies, such as basaltic rocks, following deglaciation. Minimum sedimentation rates for the bottom four meters of cap carbonate deposition in the Mackenzie Mountains (Ravensthorpe sections) are estimated to have decreased from a maximum of 4 to a minimum of 2 cm per thousand years from bottom to the top of the sampled section, implying deposition of the bottom ~4 meters of the cap carbonates in less, possibly much less, than 0.24 Myr. These estimates, however, are predicated on the assumption that ET matter deposited during the formation of the sediments investigated here had been accumulating spatially and temporally evenly on the seafloor.

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Graphical Abstract

Colored lines: data from Bodiseltisch et al., 2005. Colored stars: this study, reanalysis of the original samples that showed the largest geochemical anomalies.