Project Report: Grinding Through the Ediacaran-Cambrian Transition

ROSE, C.V.[1], PRAVE, A.R.[1], BERGMANN, K.D.[2], CONDON, D.J.[3], KASEMANN, S.A.[4], MACDONALD, F.A.[5], HOFFMANN, K.-H.[6], TRINDADE, R.I.F.[7] & ZHU, M.[8]

[1] *School of Earth & Environmental Sciences, University of St Andrews, Fife KY16 9AL, UK*
(e-mail : ap13@st-andrews.ac.uk; cvr@st-andrews.ac.uk)
[2] *Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[3] *NERC Isotope Geosciences Laboratories, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK*
[4] *MARUM - Center for Marine Environmental Sciences and Faculty of Geosciences, University of Bremen, Germany*
[5] *Department of Earth Sciences, University of California Santa Barbara, CA 93106, USA*
[6] *Regional Geoscience Division, Geological Survey of Namibia, Windhoek, Namibia*
[7] *Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, 05508-900 São Paulo, Brazil*
[8] *Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences, Nanjing 210008, China*

Abstract: The Neoproterozoic Era (1000 - 541 Ma) was one of the most dramatic in Earth history: metazoans evolved, the supercontinent Rodinia formed and broke apart, the global carbon cycle underwent high-amplitude fluctuations, oxygen concentrations rose and climate experienced at least two episodes of worldwide glaciation. However, the discontinuous and fragmented nature of outcrop-based studies has hindered developing quantitative models of Earth system functioning during that Era. The *Geological Research through Integrated Neoproterozoic Drilling* (GRIND) project will begin to rectify this scientific shortcoming by obtaining 13 cores, each between 150 to 600 m in length, through the archetype successions that record the environmental and biogeochemical context during which animals evolved. The specific targets are the Ediacaran-Cambrian transition (ECT; c. 560-530 Ma) strata of west Brazil (Corumbá Group), south China (Doushantuo, Dengying and equivalent formations) and south Namibia (Nama Group). Our objective is to create a core network of correlative ECT strata that will enable the construction of a high resolution, temporally constrained geobiological, stratigraphic and geochemical database, as well as to provide a legacy archive for future research. The goal is to understand the drivers of the Neoproterozoic Earth system revolution: it began with simple eukaryotes that populated Earth during the preceding billion years of the Mesoproterozoic, underwent multiple Snowball Earth events and emerged with the oxygenated, diverse ecosystems of the Cambrian. The excellent outcrops of the Nama Group in Namibia are central to the success of the GRIND project, as is the invaluable expertise and support of the Geological Survey of Namibia. The stratigraphy of these rocks is well-documented and is an archetype of the late Ediacaran to early Cambrian. Furthermore, the presence of abundant ash beds offers excellent opportunities for obtaining high-precision U-Pb geochronology, making the Nama Group an ideal target for acquiring precise temporally constrained and detailed geobiological and geochemical data to meet our research goals.

Key words: Corumbá Group, Doushantuo Formation, Dengying Formation, Ediacaran, International Continental Scientific Drilling Program, Nama Group, Neoproterozoic

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Introduction

The Neoproterozoic Era (1000 - 541 Ma) began with simple eukaryotes that populated Earth during the preceding billion years of the Mesoproterozoic and ended with the oxygenated and diverse ecosystems of the Cambrian. In the interim, some of the most dramatic changes in Earth history occurred (Fig. 1): animals appeared from a world of bacteria and algae (Cohen & Macdonald, 2015) the supercontinent Rodinia formed and broke apart (Evans, 2013; Li *et al*. 2008), the carbon cycle underwent high-amplitude fluctuations (Halverson *et al*. 2005), oxygen concentrations are thought to have risen (Lyons *et al*. 2014) and climate experienced at least two episodes of prolonged worldwide glaciation (Rooney *et al*. 2015). However, the fragmented nature of outcrop-based studies and lack of exact age constraints on the timing and durations of those episodes hinders the development of quantitatively constrained models of Earth system functioning during that Era.

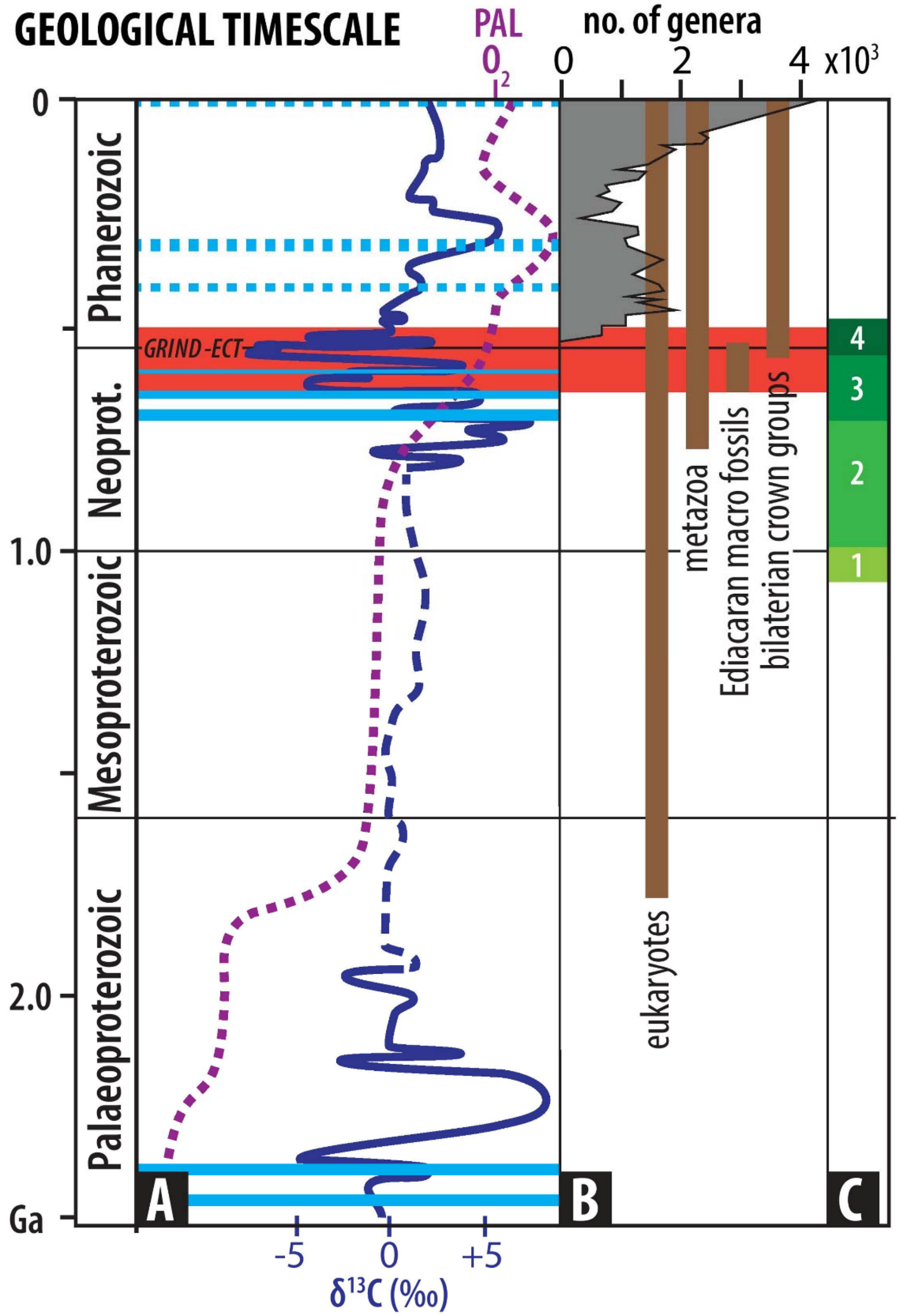

Figure 1. Selected secular trends revealing the distinctiveness of the Neoproterozoic. (A) C cycle and pO_2 (PAL - present atmospheric level). (B) Biospheric evolution. (C) Global tectonics: 1-Grenville orogeny; 2-Rodinia supercontinent; 3-Rodinia rift-to-drift phase; 4-Pan-African orogeny. Solid blue bands represent periods of global glaciations, dashed blue bands denote glaciations restricted to high-latitudes and the red band is the time interval to be targeted by GRIND-ECT.

The *Geological Research through Integrated Neoproterozoic Drilling* (GRIND) project (Condon *et al*. 2015) aims to address that shortcoming by creating a global core archive for the Neoproterozoic Era. Fresh, oriented cores will enable the construction of continuous high-resolution bio-, chemo- cyclo- and magnetostratigraphies integrated with geochemical and chronostratigraphic data. The project is an international, community-wide collaborative effort to understand better the nature and drivers of this pivotal time in Earth history and will be achieved via a series of coordinated drilling projects, undertaken sequentially, that target the key localities recording those Earth system transformations. The first phase of GRIND will focus on the Ediacaran-Cambrian transition (GRIND-ECT; Fig. 2, Time Slab C), with potential future phases targeting the remainder of the Neoproterozoic (Time Slabs A and B).

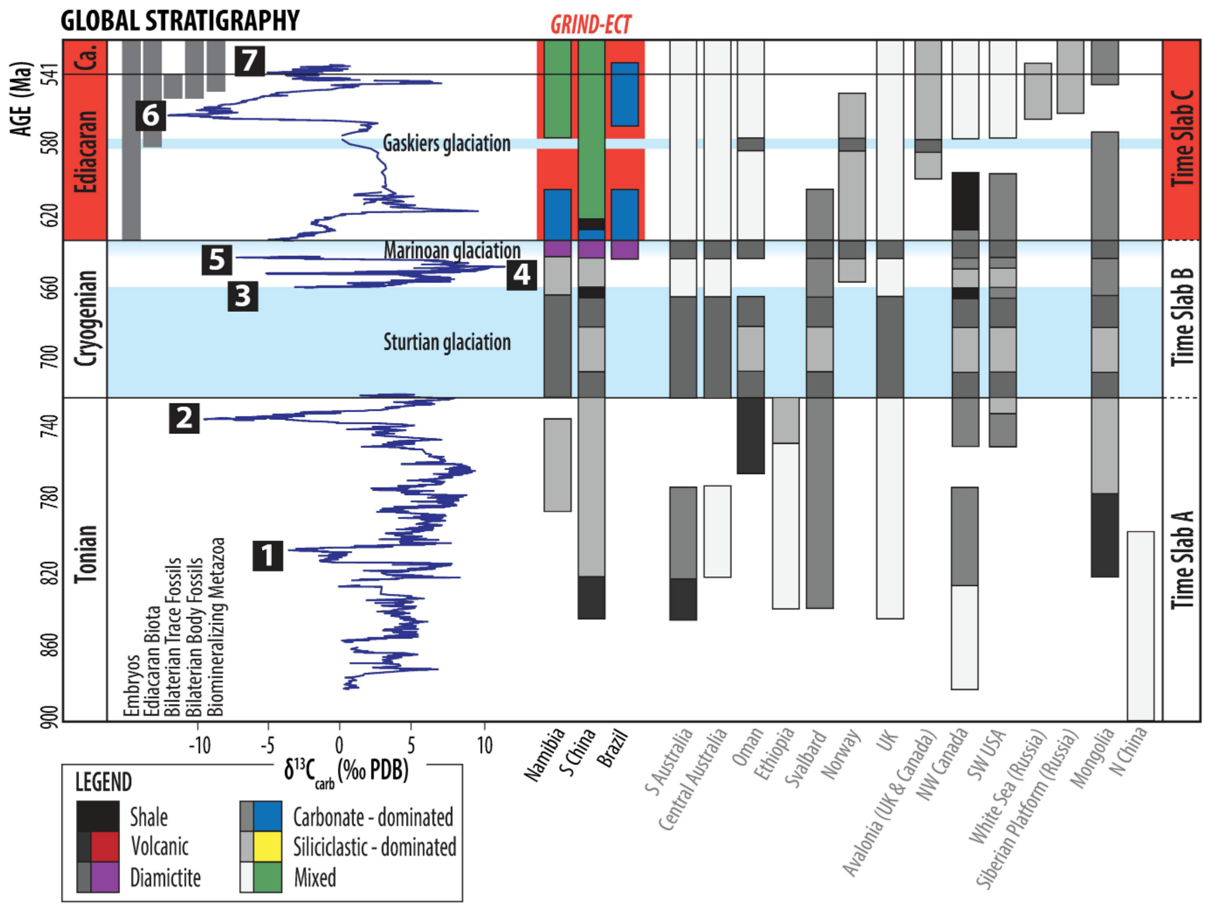

Figure 2. Neoproterozoic time slabs identified for drilling in the GRIND project and stratigraphy and major glacial periods for key successions worldwide. Red highlighted intervals denote the Time Slab C target of GRIND-ECT. Biospheric evolutionary trends are given to the left with a plot of the composite C-isotopic profile and excursions: 1-Bitter Springs; 2-Islay; 3-Keele Peak; 4-Taishir; 5-Trezona; 6-Shuram; 7-BASE. Ca - Cambrian. See text for references providing the sources of data.

Since Darwin's (1859) observation of the seemingly rapid appearance of fossils in Cambrian strata, resolving the causes and tempo of the 'Cambrian Explosion' remains one of science's great challenges (Erwin *et al*. 2011). GRIND-ECT will obtain sufficient temporal resolution and integration of geological, geochemical and biological data to address the following key questions:

- What were the timing and rates of the advent, expansion and extinction of Ediacaran biota?
- What were the environmental contexts and timing for changing skeletal mineralogy and diversification of biomineralising Metazoa?
- What was the pattern of oxygenation (globally and regionally) and how does it

relate to other geochemical patterns? Was there a Neoproterozoic oxygenation event?

- What were the timing, duration, genesis and implications for the global C cycle and the large amplitude C-isotope excursions in late Ediacaran to Cambrian strata?
- Is the Ediacaran-Cambrian boundary a synchronous worldwide biological event or a lengthy episode of biological innovation?

The ECT strata in west Brazil, south China and southern Namibia were chosen to answer these questions because their geological record from the Marinoan glacial to the early Cambrian is excellent, well understood and will guide drilling and supplement core data (Fig. 3). In addition, each country has expertise and infrastructure for drilling and coring. GRIND-ECT will be coordinated around three research foci (RF).

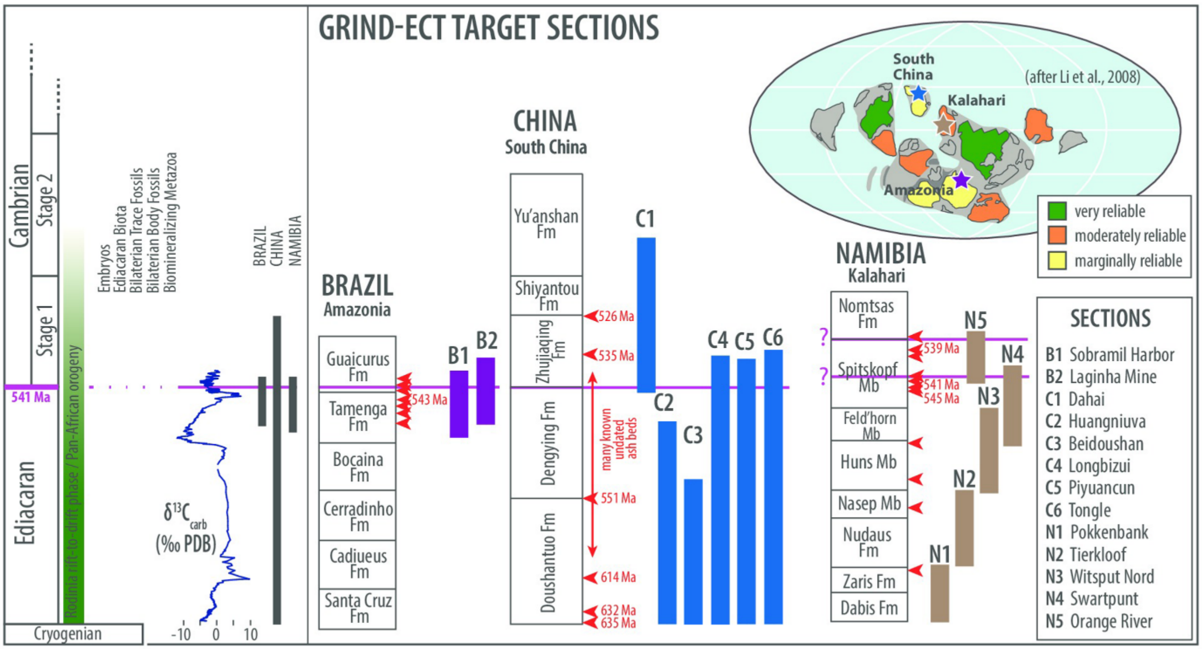

Figure 3. Schematic showing GRIND-ECT target sections in Brazil (B1-2), China (C1-6) and Namibia (N1-5), and their temporal relationship to key evolutionary, C-isotope and tectonic events. Red arrows represent ash beds. Inset map shows locations of drill sites (marked by stars) on a palaeocontinent reconstruction for the formation of Gondwana during the late Ediacaran. See text for references providing these data.

Research Focus 1: A highly resolved temporal framework

The goal of RF1 is to obtain precise dates on tuffs and organic-rich shales using U-Pb zircon CA-ID-TIMS and Re-Os geochronology and integrate those with palaeomagnetism and physical stratigraphy to construct age models for the ECT. ECT strata preserve the earliest known phosphatised Metazoa embryos, the first appearance datum of *Treptichnus pedum* and an increase in diversity of Metazoa, trace fossils and phytoplankton (Landing, 1994; Yin *et al.* 2007; Narbonne, 2005; Grotzinger *et al.* 1995; Cohen *et al.* 2009; Marshall, 2006). These evolutionary milestones are associated with C-isotope excursions (amplitudes of ≥8‰; e.g. Maloof *et al.* 2010; Smith *et al.* 2016; Zhu *et al.* 2017) and, although temporal coincidence is often assumed, their timing and duration remain to be constrained precisely. These data will underpin the work being done in RF2 and RF3.

Research Focus 2: Fossil record of early animal evolution

The goal of RF2 is to refine the patterns of biotic evolution of organic-walled and mineralised microfossils, metazoans and trace fossils and integrate those data with RF1 and RF3 to assess the links between and test hypotheses about biological evolution and environment. Documenting changes in morphology and skeletal mineralogy integrated with age data and geochemical and palaeoenvironmental data using the new cores, in conjunction with existing outcrop studies along with CT scanning to reveal ichnofossil assemblages, will yield ideas about the causes of increasing body size and ecological complexity vis-à-vis oxygen levels and biological innovation (e.g. Butterfield, 2017), such as structural defences against predation. Where appropriate, biomarkers will also provide insight into the late Ediacaran and early Cambrian communities (Love *et al.* 2009; Brocks *et al.* 2017) using drilling and sampling protocols established during Agouron-funded drilling to recover Archaean hydrocarbons (Brocks *et al.* 2008; Jarrett *et al.* 2013; Schinteie & Brocks, 2014; see French *et al.* 2015 for details).

Research Focus 3: Palaeoenvironmental conditions and the rise of oxygen

The goal of RF3 will be to determine palaeoenvironmental conditions using facies interpretations, geochemistry and elemental and stable isotope data integrated into the age model of RF1 and fossil record of RF2. This work will distinguish cause-and-effect relationships and basin-specific versus global-scale secular trends in geochemical and stable isotope patterns. Trace metal abundances, Fe speciation and a suite of traditional and non-traditional isotopes will be used to guide hypotheses on weathering and nutrient fluxes (e.g. Sr, Os, Li isotopes, P), ocean redox (e.g. Mo, δ^{238}U, Fe speciation) and biogeochemistry (e.g. δ^{34}S, δ^{15}N, δ^{98}Mo, δ^{13}C isotopes). Perturbations in C and S cycles and studies of redox-sensitive elemental ratios (e.g. Fe, U) have been used to link the advent of animals with a putative global rise in oxygen, the Neoproterozoic Oxygenation Event (Och & Shields-Zhou, 2012). Ediacaran oceans are postulated to have had spatially and temporally varying oxygenation, with ferruginous and anoxic deep waters and variably oxic surface waters but oxic everywhere by the end of the Ediacaran (Lyons *et al.* 2014). Other workers question this scenario (Butterfield 2009; Sperling *et al.* 2015). Hence, although temporal coincidence between the advent of skeletonisation and animals, and the inference for a rise in oxygen hints at causality, the precise role of oxygen in driving biological evolution remains uncertain. New core data will be compared to, and incorporated with, published geochemical and isotopic data from equivalent outcrop-based studies to create and test ideas linking changing ocean-atmosphere conditions and compositions to the evolution of animals.

Assessing diagenesis

The potential overprinting of original signals by diagenesis is a critical issue for assessing geochemical proxies that are used to yield information about ancient environmental conditions. Fresh cores are crucial because they recover rocks that have been minimally influenced by surface weathering. To identify samples in which geochemical and isotopic signals are preserved, screening protocols will be used that have been applied successfully to Neoproterozoic strata in many areas worldwide (e.g. Fantle & Higgins, 2014; Kasemann *et al.* 2005). Screening will first use basic observation (e.g. presence/absence of veins, recrystallisation textures, colour alteration), then petrography, SEM and cathodoluminescence imaging, followed by a battery of geochemical tests to assess for diagenetic overprints and to distinguish those from primary signals via patterns and trends in selected elements and their ratios (e.g. Al, Ba, Ca, Fe, Mg, Mn, P, S, Si, Sr) as well as stable isotope ratios and patterns (C, O, B, Ca, Mg).

In summary, RF1-3 will enable integration of new core data with published and in-progress outcrop-based studies worldwide. This approach will provide high-resolution sedimentological, geochemical, palaeobiological, palaeomagnetic, geochronological and cyclostratigraphic data to determine rates of change of biogeochemical processes, evolutionary tempos, and the spatio-temporal record of oxygenation across a spectrum of environmental settings.

Need for multi-craton, multi-site Neoproterozoic scientific drilling

Pristine cores recover complete intervals typically unattainable from outcrops that often have limited continuity of exposure and have been modified by weathering. Cores are crucial for evaluating diagenesis and for reducing uncertainty in proxy records, and the value of core networks has been demonstrated by the International Ocean Discovery Program (IODP). In contrast, few core archives exist for Neoproterozoic strata, exceptions being the South Oman Salt Basin and Australia's Centralian Basin which yielded benchmark works on biospheric evolution (Amthor *et al.* 2003; Bowring *et al.* 2007; Fike & Grotzinger, 2008; Fike *et al.* 2006; Pisarevsky *et al.* 2001; Walter *et al.* 2000). We expect a similar impact and value for the GRIND-ECT core network. Creating a worldwide, integrated network of cores through Neoproterozoic strata will yield unrivalled 3-D and 4-D stratigraphies for differentiating global from regional phenomena and for creating and testing hypotheses about, as well as advancing understanding of, the Neoproterozoic Era for scientific as well as natural resource perspectives. Previous experience with the International Continental Drilling Program (ICDP) FAR-DEEP (Melezhik *et al.* 2013) and NASA Agouron Deep Time drilling projects (Schröder *et al.* 2006) confirms that a continental scientific drilling programme would be decisive in delivering knowledge of the environmental and biogeochemical episodes that record how the Earth system transformed from simple eukaryotes through the ECT to the Cambrian Explosion. GRIND-ECT targets that important transition in Earth history: the advent of animals and the change to a well-oxygenated planet. Each of the three chosen localities has distinct, yet complementary records: fossiliferous organic-rich limestone and shale in west Brazil, microfossil-rich carbonate-dominated strata in south China, and macro- and trace fossil-rich carbonate-siliciclastic rocks in Namibia. Further, all sections have datable ash beds and organic-rich rocks for high-resolution U-Pb and Re-Os geochronology that will permit age models and correlations at high temporal resolutions to enable quantitative assessments of the mechanisms and rates-of-change leading to and culminating in the Cambrian Explosion.

Drilling and drill site selection

Despite the scientific importance of the ECT and years of detailed and meticulous mapping in the target locations, the fragmented nature of the outcrop, and its susceptibility to surface weathering, has hindered the development of quantitative models of Earth system functioning during that Era. These limitations will be overcome through the GRIND-ECT drilling programme. Existing detailed geological maps and outcrop-based datasets, structurally simple geology, industry-generated drilling data and in-country skill for drilling and coring provide a solid framework for identifying drill hole locations in west Brazil, south China and south Namibia. The strategy is to core correlative strata within and between nations to test models on the genesis, synchronicity versus diachronicity and global versus regional aspects of early animal evolution and its environmental context. Combined, the core archives will obtain a level of resolution that surpasses all current datasets and will offer rich opportunities for future research. Most cores will be between 150 – 400 m in length, with several approaching 600 m lengths; such shallow drilling depths combined with the well-understood geology of the drill sites maximise confidence that target strata will be recovered and structural problems avoided. Further, the existing and detailed knowledge from outcrop-based studies will help guide the drilling and supplement the core data. Drilling logistics are also straightforward: drill sites are in relative proximity to necessary infrastructure, roads and access to water, which will reduce costs and maintain a low drilling-operation-cost to post-drilling-research-cost ratio. The first phase of drilling will target the Nama Group in Southern Namibia.

Nama Group, Southern Namibia

Five cores, 200 – 450 m in length, will target the lower and middle Nama Group (Figs. 4 and 5; Table 1) with its diverse record of the ECT including the type *Nama assemblage* of Ediacaran rangeomorphs, erniettomorphs, calcified macrofossils and complex trace fossils (Wood & Curtis, 2014; Vickers-Rich *et al.* 2012; Penny *et al.* 2014). The Kuibis and Schwarzrand Subgroups are the drilling targets (the latter is dated between 547 ± 1 Ma and 540.61 ± 0.67 Ma; recalculated from Grotzinger *et al.* 1995) and consist of mixed carbonate-siliciclastic strata that define outer ramp through nearshore and fluvial-deltaic settings (Germs, 1983).

The stratigraphy of the Nama Group is well-documented and is an archetype of the late Ediacaran - early Cambrian (e.g. Grotzinger & Miller, 2008). Several C-isotope and redox-sensitive element ratio studies have been done on the Nama rocks, including those that archive the C-isotope excursions and fauna typical of the ECT. In addition, these rocks are central to models that postulate patchy ocean oxygenation and for ideas that the evolution of animals was driven by varying oxygenation of late Ediacaran oceans (e.g. Wood *et al.* 2015). Furthermore, the presence of abundant ash beds (e.g. Saylor *et al.* 2005) offers excellent opportunities for obtaining high-precision U-Pb geochronological data, making the Nama Group an ideal target for acquiring precise temporally constrained and detailed geobiological and geochemical data to meet the goals of Research Foci 1-3.

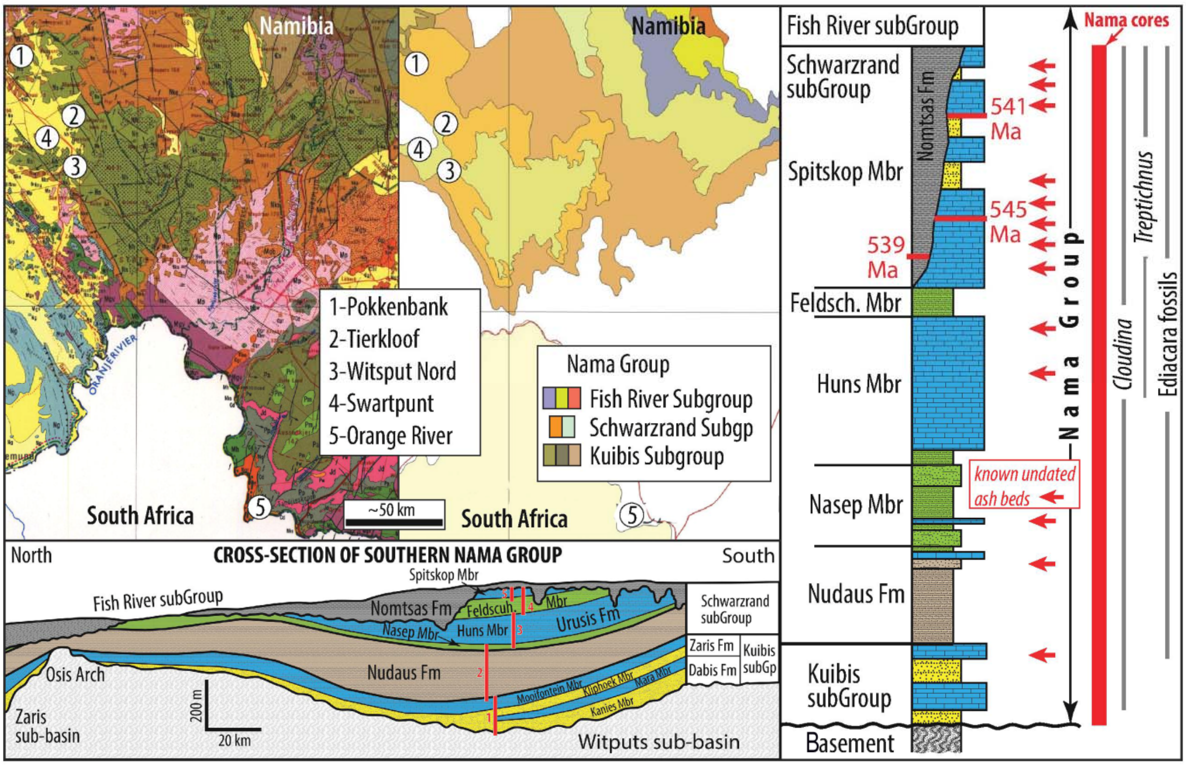

Figure 4. Geological map of southern Namibia (left) and Nama Group outcrop belt (right) showing drill site locations. Cross section of southern portion of Nama basin (Witputs sub-basin) shows the geological simplicity of the basin. Stratigraphic column shows positions of dated ash beds, including many known undated ash beds (red arrows). Red vertical bar indicates targeted coring interval, which captures the entire Ediacaran-Cambrian transition as recorded in the Kuibis and Schwarzrand Subgroups (Nama Group). Data obtained from references cited in text.

Site selection

Five sites were chosen in geologically well-understood areas near to roads and water sources thus mobilisation-demobilisation logistics are simple: Pokkenbank, Tierkloof, Witputs Nord, Swartpunt and Orange River (Figs. 4 and 5; Table 1). Exposure is excellent and the stratigraphy of the Nama rocks has been established by decades of detailed mapping. The rocks are flat-lying or dip at low-angles (<20°), there are few faults, none at the target sites, and most are sub-vertical and occur in clearly identifiable narrow zones (hundreds of metres in width); the frontal thrusts of the Gariep Orogen are to the west of the drilling sites and their subsurface projections are already known. Previous drilling confirms that the Nama rocks retain a layer-cake geology in the subsurface but those cores failed to capture the oldest stratigraphy that GRIND-ECT is targeting. Reconnaissance surveys of the sites corroborate the accuracy of the existing geological mapping, providing strong confidence that the stratigraphic intervals targeted for coring will be recovered.

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Table 1. Summary of core details for the south Namibia drilling sites.

drill site	location; elevation	target interval	core length	geology	access	water
Pokkenbank	27.160737S 16.545447E 1145 m	Dabis and Mooifontein Fms (Kuibis Subgroup)	c. 275 m	flat lying, mixed siliciclastic-carbonate sedimentary rocks	24.6 km along farm track off and NE of C13	water will be trucked in
Tierkloof	27.403949S 16.739627E 980 m	Nudaus Fm and Nasep Mbr (lwr Schwarzrand Subgp)	c. 300 m	flat lying, mixed siliciclastic-carbonate sedimentary rocks	6.4 km along farm track off and E of C13	access to nearby farm well
Witputs Nord	27.558859S 16.689447E 977 m	upper Nasep and Huns Mbrs (mid Schwarzrand Subgp)	c. 360 m	flat lying, mixed siliciclastic-carbonate sedimentary rocks	1 km along farm track off and N of C13	access to nearby farm well
Swartpunt	27.473417S 16.690464E 1011 m	Feldschuhhorn and Spitskop Mbrs (upr Schwarzrand Subgp)	c. 425 m	flat lying, mixed siliciclastic-carbonate-chert sedimentary rocks	6.8 km along farm track off and NW of C13	water will be trucked in
Orange River	28.685900S 17.494231E 243 m	top Spitskop Mbr (top Schwarzrand Subgp)	c. 200 m	flat lying, mixed siliciclastic-carbonate-chert sedimentary rocks	6.5 km along farm track off and W of C13	access to nearby farm well

Drilling

Günzel Drilling will do the drilling and coring, obtain permits, provide core boxes and temporary on-site core storage, multi-sensor logging equipment to enable initial characterisation of the cores, and core transportation. The Namibian Geological Survey will assist with all customs and shipping permits. *Günzel Drilling* has operated for almost two decades in Namibia and has ample experience in meeting the drilling and coring requirements of GRIND-ECT: core diameter of ≥56 mm, high drill core recovery, minimal or no contamination and low cost.

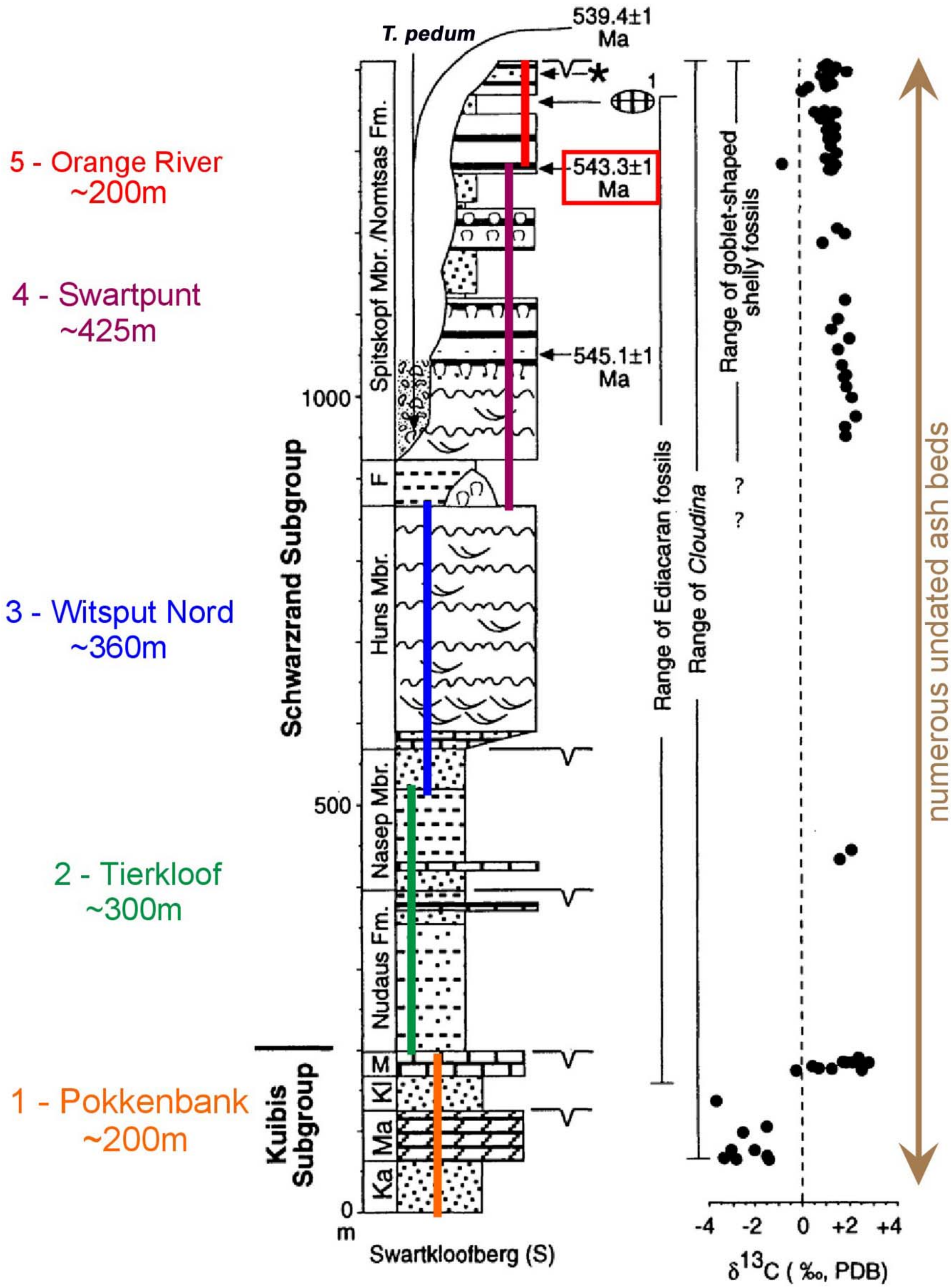

Figure 5. Schematic showing GRIND-ECT drilling target sections in Namibia and their stratigraphic context.

Core handling: characterisation, archiving and sampling

Drilling Information System data acquisition

Core data acquisition will use the ICDP Drilling Information System (DIS) for real-time capture of information at the drill site and for all subsequent data-gathering activities.

DIS will form a reference framework for use by all project scientists and the platform for integrating the varied data (lithological, palaeobiological, geochemical, geochronological, palaeomagnetic) to ensure that a consistent and uniform data management-integration-recording protocol is maintained and coordinated across GRIND-ECT.

Core archiving and repositories

The three-nation drilling programme will be undertaken sequentially: drilling will commence in Namibia in 2019, with subsequent drilling in Brazil and China. A total of c. 0.4, c. 2.6 and c. 1.5 km of core will be obtained for the Brazilian, Chinese and Namibian targets, respectively. Once on-site and initial core characterisation work is completed, cores will be transported to core repositories. One half of all cores will be retained in-country for research and educational training purposes and the other half will be shipped to the Federal Institute for Geosciences and Natural Resources (BGR) in Berlin-Spandau, Germany, for permanent archiving (Fig. 6). The BGR repository has technical staff and a suite of analytical equipment including multi-sensor and high-resolution XRF and CT scanners that will be available for use by project scientists. In Namibia, the core repository will be at the Ministry of Mines and Energy, Namibian Geological Survey, Windhoek. At each core repository, accessing the cores is free-of-charge. When the agreed GRIND-ECT moratorium restrictions end (three years from the drilling start date), the cores at both the in-country and BGR repositories will become freely available to the Earth Science community for study and educational training purposes. Importantly, having centralised, open access and easily accessible repositories will mark the first step towards meeting the goal of creating a global core archive for onshore continental scientific drilling that will match in scope and scale that of the IODP.

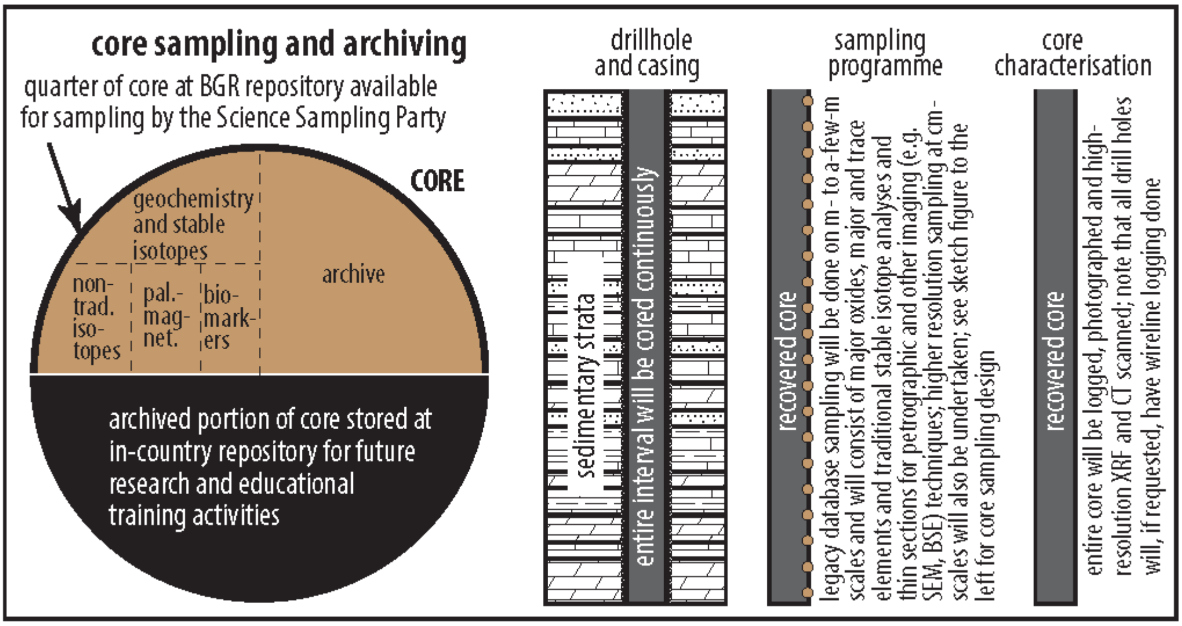

Figure 6. Core sampling and archiving design. Cores will be shipped to the BGR core repository in Berlin-Spandau, Germany, where cores will be slabbed in half. One half of the core will be for use by the Science Sampling Party and for archiving and future studies. The other half will be returned to the country of origin for research, educational training and capacity-building purposes. Prior to sampling, cores will be photographed and undergo high-resolution XRF and CT scanning. Samples will be for geochemical, isotopic, biomarker and palaeomagnetism analyses.

Science sampling party

Research will be via five Science Themes (Depositional Frameworks, Geobiology, Geochemistry, Geochronology, Palaeomagnetism), each with a designated Coordinator. Each Theme is designed to address the three Research Foci defined in

Section 1. It is estimated that within 3 months of the cores being transferred to repositories, the Science Sampling Party (SSP) will begin detailed core description and sampling; this will require several weeks (depending on the amount of core) to complete for each nations' cores. The SSP will consist of representatives from each Science Theme. A legacy dataset will be obtained at several m-scale sampling density in order to characterize the cores geochemically, to identify intervals of interest (isotope excursions, changes in faunal trends, extinctions, first occurrences) and to sample for thin-sections and imaging analyses (e.g. SEM, BSE). Sampling at higher-resolution, commonly at cm-scale spacing, will then be needed to characterise any high-frequency isotopic and biogeochemical patterns. In addition to standard geochemical analyses (major and trace oxides and elements), all samples will be analysed for $\delta^{13}C_{bulk}$, $\delta^{18}O_{bulk}$, $\delta^{13}C_{org}$, organic C/N, TOC and $CaCO_3$. Biogenic carbonate $\delta^{18}O$, $\delta^{13}C$ and Sr isotopes will also be measured on carbonate rocks. ICP-MS and automated mineral analysis calibration of core-scan XRF will be undertaken on selected samples. Sampling of ash beds for U-Pb geochronology and organic-rich intervals for Re-Os dating will be done jointly with the geochemistry sampling. Samples will initially be available for use by GRIND-ECT scientists. Once the GRIND-ECT moratorium ends, cores (both in-country and at the BGR) will be made available for study to any researcher worldwide.

Summary

The goal of GRIND-ECT is to deliver a worldwide network and archive of time-calibrated cores for open-access sharing and state-of-the-art research. This three-nation drilling programme will be undertaken sequentially: drilling will commence in Namibia in 2019, with subsequent drilling in Brazil and China. The identified drill sites will sample shallow-to-deeper marine rocks across shelf-to-basin transects. The work aims to 1) construct a highly resolved temporal framework that will lead to the development of age models for the ECT; 2) refine the patterns of biotic evolution of organic-walled and mineralised microfossils, metazoans and trace fossils, and identify the links between as well as test hypotheses about biological evolution and environmental change, and 3) determine the palaeoenvironmental and biogeochemical conditions that led to the rise of oxygen and distinguish cause-and-effect relationships and basin-specific versus global-scale secular trends in geochemical and stable isotope patterns.

All cores will be split into halves with one-half being archived in repositories within each of the target nations and used for research purposes by GRIND-ECT scientists and for education and training for national capacity building and outreach activities. The other half of all cores will be permanently archived in the Federal Institute for Geosciences and Natural Resources in Berlin-Spandau. The cores at all the repositories will be available for future research and education activities and will mark the first step towards creating an on-shore continental scientific drilling archive that will match in stature that of the IODP. Central to GRIND-ECT's success is the geology of the Nama Basin, which is known in exceptional detail owing to outstanding 3-D surface exposure, enabling the creation of a highly resolved age model integrated with the palaeontological record of Ediacaran early Cambrian biospheric evolution, oxygenation and biogeochemical cycling.

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