

# **Report for Wallara-1 core: Dissolved oxygen levels evidenced by biomarkers**

With two data files

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## **Abstract**

Organic-molecular dissolved-oxygen index (Pristane/Phytane ratio) above storm wave base, from Cryogenian and Ediacaran marine sedimentary rocks from the Wallara-1 core in Amadeus basin, Australia indicates oxic conditions in marine surface water in this area during those times.

## **Introduction**

The Neoproterozoic was a critical period that witnessed a fundamental change of life's evolutionary history. Fossil records indicate that primitive metazoa such as sessile and segmented fronds and bilaterians proliferated in the late Ediacaran, 580 to 550 Ma (Condon et al., 2005; Narbonne, 2005) and they formed the "Ediacaran biota". A compilation of the patterns of fossil and molecular diversification, comparative developmental data, and information on ecological feeding strategies indicate that the major animal clades diverged many tens of millions of years before their first appearance in the fossil record, demonstrating a macroevolutionary lag between the establishment of their developmental toolkits during the Cryogenian [(850 to 635 million years ago Ma)] and the later ecological success of metazoans during the Ediacaran (635 to 541 Ma) and Cambrian (541 to 488 Ma) periods (Erwin et al., 2011).

A causal link between oxygenation in the sea and the evolution of animals has been suggested in many papers (Shields et al., 1997; Payne et al., 2009, 2011; Narbonne 2010). An increase in the oxygen content of shallow-marine environments was

physiologically necessary for the emergence of large, highly energetic animals (Raff and Raff, 1970; Rhoads and Morse, 1971). These physiological requirements for oxygen predict that geochemical evidence for well-oxygenated marine waters should coincide with, or slightly antedate, fossil records of animals with high oxygen demand (Johnston et al., 2012).

Canfield et al. (2007; Newfoundland, deep sea) and Johnston et al. (2012; Eastern European Platform) showed that deep and shallow ocean oxygenation coincided with the appearance of Ediacaran biota based on the ratio of highly reactive iron to total iron. A similar geochemical formula was applied to fossil-bearing sections from South China and the Yukon (McFadden et al., 2008; Narbonne and Aitken, 1990), however the relationship between the fossil record and redox transitions in these basins is less clear.

## **Methods and materials**

We attempt to evaluate paleoredox condition during this critical period using pristane/phytane ratios. Pristane and phytane come from phytol, which is an important part of phytoplanktonic chlorophylls. Under relatively oxidizing conditions a significant proportion of phytol can be oxidized to phytenic acid, which may then undergo decarboxylation to pristane before finally being reduced to pristane (Killops and Killops, 2005). In contrast, under relatively anoxic conditions phytol is more likely to undergo reduction and dehydration to phytane, via dihydrophytol (phytanol) or phytene. The ratio of pristane:phytane may provide a measure of redox conditions during diagenesis, with values  $<1$  being typical of anoxic conditions and values  $>1$  suggesting oxic conditions (Didyk et al., 1978). Pristane in zooplankton and vitamin E and phytane from phytanyl ether lipids in archaeobacteria may influence pristane/phytane ratios (Goossens et al., 1984). Zooplankton and vitamin E have a much smaller volume than phytoplankton. Phytane and biphytane are derived from ether lipids of archaea (Rosa and Gambacorta, 1988), whereas biphytane was not detected from all samples studied. After the Silurian or Devonian, soil erosion may cause higher pristane/phytane ratio because of the intrusion of pristane and phytane originated from land plants. This is not the case for the Ediacaran and Cambrian because of the lack of land vegetation. Based on these three reasons, pristane/phytane ratio can be used to estimate redox condition of

the seawater at sediment surface.

We detected dissolved oxygen levels (DOL) based on the pristine/phytane ratio from marine facies sequences of Cryogenian-Ediacaran age at Wallara-1 core in Amadeus basin. These facies are composed of the Bitter Springs Formation (Carbonates and dolomitic siltstone), Areyonga Formation (dyamictite; Sturtian Glaciation), Aralka Formation (dark gray shale), Olympic Formation (dyamictite; Marinoan Glaciation), cap dolomite, Partatataka (dark gray or reddish brown shale) and Arumbera Sandstone (reddish brown siltstone). Age of the Bitter Springs Formation is assigned to Tonian (Swanson-Hysell et al., 2012), the others to late Cryogenian to Ediacaran (Fig. 1).

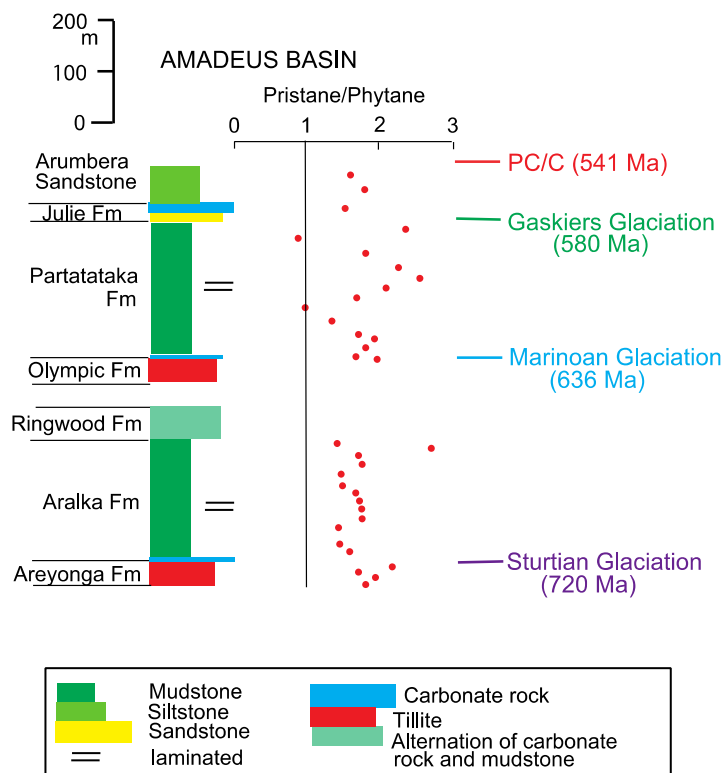
Hand-sized specimens were powdered for each sample after removal of apparent surface contaminants. All samples were Soxhlet-extracted with dichloromethane/methanol (7:1, v/v) for 48 h. We chromatographically separated out the major compounds using silica gel column chromatography (Oba et al., 2009). Identification of the hydrocarbons was performed using an Agilent 6893 gas chromatograph interfaced to an Agilent 5973 mass selective detector (MSD).

### **Residues or processed material**

Residues after the analysis are powder.

### **Results**

Values for the pristane/phytane ratio are 1.1 to 2.1 in the Bitter Springs Formation, 1.7 to 2.2 in the Areyonga Formation, 1.4 to 1.8 except for one sample 2.7 in the Aralka Formation, 1.8 and 2.5 in the Olympic Formation, 2.1 to 2.4 in cap dolomite, 1.3 to 2.6 except for two low values (0.9, 1.0) in the Partatataka Formation, 1.6 and 1.8 in the Arumbera Sandstone (Fig. 1, attached Table 1). We also show other biomarker data from the Olympic Formation, cap dolomite, and the lowermost part of the Partatataka Formation (Table 2 attached).



**Fig. 1.** Pristane/phytane ratios in upper Cryogenian-Ediacaran age at Wallara-1 core in Amadeus Basin, central Australia.

## Discussion

Paleowater depths of the sampled cores were estimated based on sedimentary structures and lithology. Paleowater depths of all formations of the Wallara-1 core are above storm wave base (SWB; approximately 0 to 100 m water depth), corresponding to surface water. The high ( $> 1$ ) pristane/phytane values in the Tonian and the Sturtian glaciation to the latest Ediacaran indicate oxic conditions in the surface water.

These data plus the other pristane/phytane values from Australia and South China in surface water and intermediate water show more informative results on dissolved oxygen changes in the sea.

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