

# **Areas of the World as Candidates to Apply Biomarkers to Study the Precambrian-Cambrian Boundary**

*Amy Kelly*

## **Abstract**

Many theories exist on the radiation of life that occurred at the Precambrian-Cambrian boundary, but there is by no means a consensus on what initiated it. It is important to understand this event because this was the beginning of the diversification of animal life, some of which evolved into all of the species of animals we have today and also so that we can understand other dramatic events in Earth history like the P/T boundary. Large amounts of data exist around the world on the strata, fossils, trace fossils, and isotopic signatures of carbonates in the strata that can be found around the Precambrian-Cambrian boundary. There has been some success in correlating this data, but not enough is known on the specific environmental changes of the time and its interaction with animal evolution. The goal of this project is to identify and study areas of the world that may be candidates to apply biomarkers to study the Cambrian explosion. We would like to study strata just below, at, and just above the Precambrian-Cambrian boundary in several areas around the world. Also, we would like to take a look at biomarkers in these locations. There is an unlimited potential of knowledge in these molecular fossils which have not been used in many of these locations yet and which will be very useful in answering questions about the origins of the abrupt changes in life across the Precambrian-Cambrian boundary and determining the primary cause.

## **Introduction**

*The Cambrian explosion.* The Cambrian explosion was a radiation of life, especially among the animal clade, that occurred around 540 Ma. The actual cause is still unclear although there are many theories. Many contest that an increase in dioxygen levels was a driving force.<sup>1,2,3</sup> Other theories invoke environmental perturbation as the push. These include tectonic factors, changes in ocean chemistry and changes in biogeochemical cycling.<sup>2</sup> If there was an extinction event right before the boundary, permissive ecology can also be used to explain the phenomenon. Permissive ecology is a concept of Knoll's that "these intervals of rapid environmental change caused temporary breakdowns of the established ecosystems with their harsh competition for resources and thereby permitted the new experiments in life that ultimately led to our modern world."<sup>4</sup> There are also many evolutionary innovations that can be used to explain the event, such as sex, multicellularity, the acquisition of plastids, and the advent of predators. At the same time of the boundary was the finding of the first mineralized skeletons.<sup>5</sup> Some of these have holes, telling of predation. It is possible that the skeletons arose as a response to predators, which also induced a variety of other changes, leading to the radiation.<sup>5</sup> Most likely however, all of these evolutionary innovations originated several hundred million years before the diversification, and thus were probably not a primary influence in the diversification.<sup>2</sup> Another evolutionary invention that possibly coincided with the boundary was the development of fecal pellets. These would have increased the flux of

organic matter to the ocean floor, oxygenating the surface waters, allowing an explosion of life.<sup>6</sup> The boundary also coincided with a time of enhanced tectonic activity along plate boundaries, which led to changes in ocean circulation and nutrient levels, transgressions, and the formation of shallow seas. If not the main cause, these conditions must have contributed to the diversification of life at that time.<sup>7</sup> Close to the boundary is a strong, short-lived negative carbon isotopic excursion in carbonates. This type of  $\delta^{13}\text{C}$  shift can be due to rapid decreases in organic productivity, and/or increased oxidation of organic carbon.<sup>8</sup> It is suggestive of a mass extinction because all other similar isotopic events are known to be widespread extinctions.<sup>1</sup> The last appearances of the early carbonate-shelled animals *Cloudina* and *Namacalathus* correlate with this excursion, further supporting the mass extinction hypothesis.<sup>9,10</sup> Others have found an overlap in Ediacaran and shelly fossils, conventionally considered to be of Cambrian age, and consider the evolutionary events to be continuous. This leads to the notion that the usually large gap seen in the fossil record may be more of a preservational feature than evidence of a mass extinction.<sup>11</sup> Indeed, some argue that the entire concept of a rapid increase in diversity at this time is merely a preservational artifact. Molecular clock studies, however, support the idea that it is a real event.<sup>12</sup> At the same time the animals radiated, acritarchs had a burst of diversification. Acritarchs are eukaryotic microfossils.<sup>2</sup> Since these are such different organisms from animals, the main branch of the tree of life that diversified, this suggests that the boundary was felt amongst all forms of life and therefore that ecology must have played some role.<sup>13</sup> Understanding these events is very important and fundamental to our understanding of the origins of complex forms of life. Stephen Jay Gould feels that the early Cambrian fossils “far surpass dinosaurs in their potential for instruction about life’s history” and “are the world’s most important animal fossils.”<sup>14</sup>

*Biomarkers.* Biomarkers are molecular fossils, derived from biochemicals, mainly lipids. Figure 1 shows two examples of diagenetic transformations of precursor lipids derived from an organism into the form we find in rocks today. With time, most of the functional groups are lost and racemization of chiral centers occurs.

**(Figure removed due to copyright restrictions.)**

Figure 1. Diagenesis to hopanes and steranes from Peters, Walters and Moldowan, 2005.<sup>15</sup>

Biomarkers are of importance because they can be preserved in times when no morphological remains can be and exist even when the precursor organisms have no hard parts. They can also be diagnostic of marine vs. land species, the thermal maturity of rocks, some specific taxa or biosynthetic pathways, and age. There are however, conditions that are mandatory for their preservation. The rock sample has to have low thermal alteration, and organic compounds are best preserved under anoxic conditions. Also, there cannot be any contamination from younger migrating oils, and there can be no human or modern contamination such as from any oil used during drilling. It is also best if the rock has high organic content. For our specific purposes, it is necessary for the geologic cross-section to go back to at least 550 Ma. Based on a preliminary survey of the literature, it appears that there are a few areas of the world that meet the qualifications

listed above in terms of preservation and finding molecular fossils that are potentially useful sources of information.

Biomarkers can contribute to our understanding of the causes of the Precambrian-Cambrian radiation of life. The carbon skeleton itself may be diagnostic of particular taxa and that taxa may be diagnostic for a particular environment such as saline, lacustrine, oxic, anoxic, etc. For example, Botryococcane is from *Botryococcus* which is diagnostic for lacustrine settings.<sup>16</sup> The taxa may also be diagnostic for a particular geologic age. For example, 24-norcholestane seems to be derived from diatoms, so the ratios of 24- to 27-norcholestanes can be used as an age parameter, most accurately when used on post-Jurassic rocks.<sup>17</sup> In fact, the presence of a specific skeleton may move back the currently accepted age range for certain events. The skeleton may be diagnostic of a particular biosynthetic pathway because the molecule may be the product of a specific physiology or it may require certain chemicals or other factors such as light, dioxygen, reduced sulfur, anoxia, etc. The presence of isorenieratane indicates the presence of green sulfur bacteria which require sulfide and therefore indicates euxinic conditions in the photic zone.<sup>16</sup> The isotopic signature of the biomarker is also valuable. It may be diagnostic of a particular biosynthetic pathway and can be used to separate marine biomarkers from non-marine biomarkers. For example, extreme depletion of <sup>13</sup>C, especially in isoprenoids, indicates the presence of methanotrophic archaea and the oxidation of biogenic methane.<sup>18</sup>

*Value of biomarkers.* Most of the biomarkers described above and most of the ones I plan to look for, which will be described later, correspond to bacteria or algae. Though the Cambrian explosion is mainly associated with the animal clade, these biomarkers are still very telling as to why the radiation occurred. It is necessary to look for environmental conditions and changes. These influence all life, not just the animals, and therefore the information bacteria provide can be correlated well with animals of the same age.

There are many questions that can be answered using a biomarker approach. They can be used to examine climate conditions at the Precambrian-Cambrian boundary and if they were the same around the world. Also we can answer if similar fauna existed and diversified at the same time throughout the world.

### **Hypotheses and Objectives**

*Hypothesis 1. The radiation of life was a result of the interactions of biodiversity with climate change and how they reinforced each other.* There was some environmental change which allowed the evolution of animals to progress, and these new innovations of animals then produced more climatic change. This cycle repeated itself, allowing a sudden radiation of life. The most likely initial environmental trigger was the increase in atmospheric oxygen. Once it reached a certain level, animals could increase in size, leading to numerous effects on the environment.<sup>1</sup>

*Hypothesis 2.* There was a lag in animal developments in certain areas of the world and some areas were more heavily affected by climate or tectonic change. It is unlikely that all areas of the world had all of the exact same environmental influences simultaneously. Our records may not have precise enough resolution to support this argument, but it is definitely something to look for when we find distinctive biomarkers in strata that we can date well.

*Purpose.* This study is of importance for several reasons. First, the late Neoproterozoic into the Cambrian is a fundamental time in the history of the Earth that needs to be fully explained. It can then help us understand the evolution of diverse multicellular life and of biosynthetic pathways through time. We need to study multiple areas of the world because that is the only way to draw a complete picture of the global events during this time period. It is also best if this work is done by one group so that comparisons between areas of the world can be made directly, without the worry of interlab errors due to differing methodologies or practices. The analysis of biomarkers will greatly aid in our understanding, giving us information that has not been available to us before. Biomarkers can provide more specifics than the data that has been gathered so far on the biological and isotopic signatures of the time. We can study individual taxa and determine the types of conditions in which they lived. This will make it much easier to see how the climate and fauna changed through time and determine the most important driving force of the radiation of life at the Precambrian-Cambrian boundary.

*Objectives.* The objectives are to identify the locations or combination of world-wide strata that are best fit to the needs described above, to use biomarkers to test hypotheses on the origin of the Cambrian explosion and to develop a more comprehensive story using the isotopic, trace fossil, body fossil, and new biomarker data.

### **Proposed Research**

*General.* A number of areas of the world seem promising for this research, including basins and strata in Australia, China, Siberia, Namibia, Oman, and Canada. We would like to study each of these areas by taking three samples from the strata just below, three at, and three just above the boundary in these areas. For China, Namibia and Oman there is one specific locality of interest. In Australia, the Centralian Superbasin and Flinders Ranges offer many possibilities for places to sample. In Siberia, there are three localities of interest, the Anabar, the northeast and the southeast. In Canada there are two, the Mackenzie Mountains and Newfoundland.

*Comparisons.* In Figure 2 is shown the paleogeographic relationship of the continents and sites of interest at the time of the latest Proterozoic. Paleolatitude is an important characteristic of these areas and needs to be kept in mind when comparing and contrasting data compiled. Due to this parameter, Newfoundland and Namibia are more likely to have biomarkers in common than Oman and China. Other information such as depositional setting and lithology are compared in Figure 3. It will be important to keep all of this information in mind in order to properly compare strata. Oil deposited in an arid evaporative basin cannot be directly compared with deep sea sediment. Once we

compare areas of similar depositional setting, lithology and paleolatitude, we can begin to make valuable correlations and comparisons.

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Figure 2. Paleogeographic relationship of the world in the Late Proterozoic from McKerrow et al 1992.<sup>19</sup>

Area and Strata	Age	Boundary	Lithology	Depositional setting	TOC	Thermal maturity	Paleolatitude	Fossils	$\delta^{13}\text{C}$ Isotopic signature	Biomarkers
<b>Australia</b>							15 N			
<i>Centralian Superbasin</i>										
Officer Basin: Ungoolya Group	Ediacaran		sandy shales, minor carbonate and turbidites	deep water, marine	~ 0.4 %			acritarchs	~+5, falls, rises to +3	high concentrations of acyclic isoprenoids, strong C <sub>29</sub> sterane preference, abundant diasteranes, 24-n-propylcholestanes predominate
Ouldburra Fm.	early Cambrian		carbonates, evaporites	restricted shallow marine carbonate environment	~ 0.3 %					high abundance of monomethyl alkanes with mid-chain branching, low concentration of C <sub>29</sub> steranes, 24-isopropylcholestane predominates, has 2a-methylhopanes
Amadeus Basin: Pertatataka Fm.	Ediacaran		shales, minor turbidite sandstone	foreland-basin, marine outer shelf	~ 0.3 %			stromatolites, acritarchs		24-n-propylcholestane is predominate, only slight C <sub>27</sub> or C <sub>29</sub> preference, methyl branched alkanes
Julie Fm.	latest Proterozoic		dolomite	marine				stromatolites	~+5	
Arumbera Sandstone		within	sandstone, minor siltstone, shale and carbonate	foreland-basin				Ediacaran fauna, diverse trace fossils, small shelly fossils above		
<i>Flinders Ranges</i>										
Wilpena Group, Rawnsley Quartzite	terminal Proterozoic	at top	sandstone	shore-face and tidal sand flat facies		Present		Ediacara, acritarchs		
Uratanna Fm.	early Cambrian	at bottom	sandstone and siltstone	shore face, progradation of delta				trace fossils ( <i>Treptichus pedium</i> and <i>Phycodes cirinatus</i> ) and anthropod-type trace fossils		
<b>China</b>							25 N			
<i>Yangtze Platform</i>										
Dengying Fm.	565 to 544 Ma	within	dolomite	peritidal	high			Ediacaran body fossils, Cambrian shelly fossils, <i>Cloudina</i> , microplants, tube worms, macroscopic algae, <i>Vendotaenia</i> sp.	rapid negative shift at boundary	
<b>Siberia</b>							15 S			
<i>Anabar</i>										

Staraya Rechka Fm.	Vendian		carbonate and siliciclastic	shallow marine					consistently negative	
Manykai Fm.	early Cambrian	at bottom	shale, mudstone, grainstone	shallow marine, flooding surface				small shelly fossils		
<i>Southeast</i>										
Yudomia Fm.	late Vendian	near very top	dolomitic carbonates	shallow water				stromatolites, acritarchs, trace fossils, shelly fauna	high +3.4 then drops at very top	
Pestrotsvet Fm.	lower Cambrian		limestone and dolomite	transgression	negligable			small shelly fossils, archaeocythans	sharp drop at very base	
<i>Northeast</i>										
Turkut Fm.	latest Proterozoic	at very top	dolostone and minor limestone, then dolomitic grainstone	shallowing from basinal to shallow ramp environment	0.07-3.49 mg C/ g			stromatolites, ichnofossils, small shelly fossils	~ 0, negative shift at top	
Kessyusa Fm.	early Cambrian		mixed siliciclastic, carbonate and volcanic facies	outer shoreface of a siliciclastic shelf, maximum flooding of shelf or initial highstand progradation	0.2-0.62 mg C/ g			small shelly fossils, acritarchs, calcified microbes, ichnofossils ( <i>Phycodes</i> sp.)		
<b>Oman</b>							5 S			
<i>Huqf Supergroup</i>										
Ara Group	548 - 540 Ma	within	evaporite, carbonate/ dolomite	shallow water with severe basin restriction, arid, part anoxic	up to 6%	diagenesis up to 120 °C, unmetamorphosed		stromatolites, microfossils, fossil cyanobacteria, thrombolite reefs with <i>Cloudina</i> and <i>Namacalathus</i> body fossils and calcified alga	slightly positive values with a large short-lived negative excursion near boundary	many mid-chain branched monomethyl alkanes, Pr/ Ph < 1, predominance of C <sub>29</sub> steranes
<b>Namibia</b>							45 S			
<i>Nama Group</i>										
Schwarzrand Subgroup	late Precambrian		limestones and terrigenous sediments	tide- and delta-influenced shore-face environments	ave. 0.34 mg C/ g			acritarchs, <i>Vendotaenia</i> , <i>Cloudina</i> , impressions and molds of Ediacarn-grade animals, icnotaxa ( <i>Phycodes pedum</i> )	moderately heavy	
Fish River Subgroup	Cambrian		sandstone with minor silty shales	fluvatile		Relatively immature			~ 1	
<b>Canada</b>										
<i>Mackenzie Mts</i>										
Ingta Fm.		within	interbedded shale and sandstone with minor limestone	shallow shelf		Moderately deformed, low metamorphism		stromatolites, trace fossils ( <i>Planolites</i> sp., <i>Phycodes pedum</i> ), acritarchs, shelly fossils	negative excursion just under boundary	
<i>Newfoundland</i>							45 S			

Chapel Island Fm.		within	sandstone, siltstones, minor limestones	shallow marine				ichnofossils ( <i>Phycodes pedum</i> ), simple arthropod traces, small shelly fossils, soft-bodied megafossils, impressions of vendotaenid algae, organic-walled microfossils		
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Figure 3. Full comparison of relevant strata.

*World Correlation.* All of the data gathered across the globe can be correlated together. In many sections around the world, the boundary is marked by a rapid increase in trace fossil diversity above the Ediacaran-type fossils and below the trilobites.<sup>20</sup> Many times, simple trace fossils occur below this and the more complex icnofossil *Phycodes pedum* occurs just above. At several localities the first appearance of small shelly fossils also closely approximates the boundary. In Figure 4 some of the formations of Figure 3 are divided into groups by their isotopic signatures and biostratigraphic properties. Many formations cannot be directly dated accurately, so analysis like that shown in Figure 4 can be invaluable when trying to date and compare these areas. This is one way we can correlate different sections from around the world to learn more about this period of time.

**(Figure removed due to copyright restrictions.)**

Figure 4. World stratigraphic correlation by isotopic signature and faunal distribution from Narbonne et al 1994.<sup>21</sup>

In Namibia, there are certain strata where zircons are found which can be very accurately dated. Using these dates and by correlating the isotopic signatures of Namibia to other areas of the world, these other areas can be approximately dated. Also, by compiling isotopic information from so many different strata from around the world like in Figure 5, we can complete the whole Late Proterozoic to Cambrian story. It is extremely rare for any one stratigraphic location to have remained complete and unmetamorphosed in the past 550 Ma. By putting them all together, we can substitute in certain pieces that are missing due to unconformities or are unreliable due to metamorphism and create a reliable, full data set from which to make and support hypotheses. These types of valuable correlations can be made using isotopic correlations like that shown in Figure 5, and using biostratigraphy as shown in Figure 6.

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Figure 5. Stratigraphic information and isotopic correlations of areas around the world from Saylor et al 1998.<sup>22</sup>

**(Figure removed due to copyright restrictions.)**

Figure 6.  
Biostratigraphic  
correlations across  
the world from  
Narbonne et al  
1987.<sup>23</sup>

Though all of this information is currently available, no theories can be concretely supported or denied. Some biomarker research has been done, but only in a few areas, and of those less than a handful were thorough.<sup>24</sup> With this study and the advanced techniques we have today, we can collect comprehensive biomarker data and fill in more of the story of the evolution of life to help explain the enigma that is the Cambrian explosion.

*Australia.* In Australia, one important area is the Centralian Superbasin, the locality of which is shown in Figure 7. It has well-preserved organic matter of terminal Proterozoic to Mid Cambrian age.<sup>25</sup> The preservation of and access to organic matter is good for the eastern Officer and Amadeus Basins. The strata discussed are all deposited in differing marine settings. In the Officer Basin, the Ungoolya Group is Ediacaran in age with sandy shales, minor carbonate and some turbidites. The Ouldburra Formation, also in the Officer Basin, is early Cambrian in age and composed of carbonates and evaporites. The stratigraphic column of the eastern Officer Basin is shown in Figure 7. A stratigraphic section of the NE Amadeus Basin with some biostratigraphic information is shown as well. In the Amadeus Basin is the Pertatataka Formation which is circa Ediacaran in age and composed of black, grey and red shales with minor sandstone beds. Stromatolites occur at the base. It also has a diverse acritarch assemblage, some of which are process-bearing.<sup>26</sup> In both the Pertatataka and the Ungoolya Group (formerly the Rodda Beds) of the Officer Basin are assemblages of very large sphaeromorph and acanthomorph acritarchs.<sup>27</sup> Above the Pertatataka Fm. are the Julie Formation and then the Arumbera Sandstone.<sup>28</sup> The Arumbera has Ediacaran fauna in its lower strata, an abundance of diverse trace fossils in the higher strata and underlies a carbonate unit with small, shelly fossils. It consists of sandstone with minor siltstone, shale and carbonate and is thought to straddle the boundary. The Julie Formation is a dolomite that contains stromatolites. It has high  $\delta^{13}\text{C}$  values, close to those of the lower carbonate of the Rodda Beds, around +5 per mil.<sup>27</sup> Higher in the Rodda Beds it falls, and then rises again to around +3 in the very top limestone. There have even been  $\delta^{13}\text{C}$  analyses done on specific hydrocarbons.<sup>25</sup>

Some biomarker research has already been done on the Centralian Superbasin by Logan et al.<sup>25</sup> They came across some interesting results that can be expanded to general Precambria-Cambrian boundary information. They found that high abundances of monomethyl alkanes with mid-chain branching are typical of marine sediments and oils of early Cambrian age and older. Cyanobacteria are known to contain a lot of isoalkanes, and so this data may suggest direct input of cyanobacterial hydrocarbons. They also found that for the  $\text{C}_{30}$  desmethylsteranes, the 24-*n*-propylcholestanes predominated in siliciclastic sediments.



**(Figure removed due to copyright restrictions.)**

Figure 7. From left to right: location of the Centralian Superbasin from Logan et al 1997, stratigraphic column of the eastern Officer Basin from Haddad et al 2001,<sup>29</sup> & stratigraphic section of the NE Amadeus Basin from Zang and Walter 1989.<sup>28</sup>

Another important area of Australia is the Flinders Ranges. The location and its stratigraphic information are shown in Figure 8. The area has excellent exposure in semi-arid terrain and is easy to access. It also has expanded stratigraphic thickness. There is a three km thick terminal Proterozoic Wilpena Group. The top is the base of the Cambrian. It has clear palaeontological, sedimentological and carbon isotopic context.<sup>30</sup> One can find Ediacara in the Wilpena Group, also possibly acritarchs. The Uratanna Formation marks the beginning of the Cambrian. It disconformably overlies the Rawnsley Quartzite and is mainly found in the northern Flinders Ranges. Elsewhere, the Parachilna Formation lies above the Rawnsley Quartzite.<sup>31</sup> The Uratanna Formation contains trace fossils such as *Treptichus pedum* and *Phycodes cirinatus*. It also has arthropod-type trace fossils, *Rusophycus* cf. *Avalonensis*.

**(Figure removed due to copyright restrictions.)**

Figure 8. Location and stratigraphic column of the Flinders Ranges from Droser et al 1999.

*China.* In China, the Dengying Formation is potentially ideal for our purposes. The formation is spread across the Yangtze Platform and spans from 565 to 544 Ma. It is a dolomite sequence with microplants, tube worms and macroscopic algae, Ediacaran body fossils and Cambrian shelly fossils including *Cloudina*.<sup>32</sup> It is dominated by white to light grey dolomite.<sup>8</sup> The Cambrian strata are composed of grey fossiliferous limestone with some interbedded black shales, which likely contain ample amounts of biomarkers. It shows a large and rapid negative shift in  $\delta^{13}\text{C}$  at the Precambrian-Cambrian boundary. The isotopic and stratigraphic information are shown in Figure 9. The rocks in these strata have relatively high concentrations of organic carbon. The Dengying is divided into four members, the Hamajing, Shibabtan, Baimatuo and Tianzhushan Members. There are small shelly fossils in the topmost section, the Tianzhushan.<sup>33</sup> The pennatulid *Paracharnia dengyingensis* and the macroscopic algal remains of *Vendotaenia* sp. appears in the Shibabtan Member, which is particularly organic-rich.

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Figure 9. Isotopic and stratigraphic information for the Dengying Formation from Lambert et al 1987.

*Siberia.* In Siberia there are three areas of potential importance, the Anabar, the northeast and the southeast. In general, negative values of  $\delta^{13}\text{C}$  characterize the late Proterozoic in Siberia and become more positive toward the boundary level, eventually becoming positive.<sup>34</sup> In the late Precambrian there is an increase to around +4 per mil on the Siberian platform followed by a drop to low values. The boundary may be close to these minima.<sup>35</sup>

The Anabar region includes the terminal Proterozoic through the Tommotian. It is made of shallow marine carbonates with subordinate siliciclastic lithologies.<sup>36</sup> Of importance are the Staraya Rechka Formation and the Manykai Formation. There is an unconformity between the two, and the bottom of the Manykai Formation marks the beginning of the Cambrian. The  $\delta^{13}\text{C}$  values in the Staraya Rechka Formation are consistently negative. The lower Manykai contains small shelly fossils.<sup>37</sup> The stratigraphic and isotopic information are shown in Figure 10.

**(Figure removed due to copyright restrictions.)**

Figure 10. Stratigraphic and isotopic information for the Anabar Region of Siberia from Knoll, A. H.; Kaufman, A. J.; Semikhatov, M. A.; Grotzinger, J. P. 1995.

The formations in southeast Siberia that encompass the late Proterozoic to early Cambrian are the Yudomia, Pestrotsvet and Tumuldur Formations. The Yudoma Fm. is of late Vendian age and comprised of dolomitic carbonates with stromatolites, a few acritarchs and rare trace fossils.<sup>38</sup> Shelly fauna are found in the top 1 m. The Precambrian-Cambrian boundary is found in the uppermost part of the Yudoma Formation.<sup>35</sup> There is a slight disconformity that marks the base of the Pestrotsvet Fm., a limestone and dolomite layer of the lower Cambrian with negligible organic matter. Many species of small shelly fossils and archaeocyathans appear at the base of the Tommotian in the Pestrotsvet.<sup>36</sup> There is a sharp drop in  $\delta^{13}\text{C}$  values around the base of the Pestrotsvet / top of the Yudoma Formation. A high value of +3.4 per mil occurs around 15 m below the boundary and then the values drop sharply.<sup>39</sup> The isotopic data are shown in Figure 11.

**(Figure removed due to copyright restrictions.)**

Figure 11. Isotopic data for two areas in southeast Siberia from Brasier et al 1990.<sup>40</sup>

In northeast Siberia, the boundary at the top of the Turkut Fm. is the Precambrian-Cambrian boundary. The Turkut Fm. is made of dolostones and minor limestones, overlain by dolomitic grainstone and stromatolite bioherms.<sup>39</sup> Ichnofossils are rare. Small shelly fossils occur at the top of the formation and are more diverse in the base of the Kessyusa Fm. above. The top of the stromatolitic unit has dolostones with pores filled with bitumen. It lies between underlying hydrocarbon source rocks and overlying reservoir-sealing shales. The TOC content is 0.07-3.49 mg C/ g. The  $\delta^{13}\text{C}$  values

through most of the Turkut Fm. stay near zero until there is a negative shift at the top. The Kessyusa Fm. is bound on both sides by erosional surfaces.<sup>41</sup> It is composed of mixed siliciclastic, carbonate and volcanic facies and contains shelly fossils, acritarchs, calcified microbes and ichnofossils such as *Phycodes* sp. The density of trace fossils increases from the base to the top of the formation. The TOC content is 0.2-0.62 mg C/g. The isotopic and stratigraphic information are shown in Figure 12.

**(Figure removed due to copyright restrictions.)**

Figure 12. Stratigraphic and isotopic data for northeast Siberia from Knoll, A. H.; Grotzinger, J. P.; Kaufman, A. J.; Kolosov, P. 1995.

*Oman.* The area of interest in Oman is the Ara Group of the Huqf Supergroup. The Huqf Supergroup is about 560-540 Ma.<sup>42</sup> One problem is that the Ara Group is subsurface and would require coring. The Ara Group is divided into at least six carbonate to evaporite sequences. It is a 548-540 Ma thick evaporite unit with interbedded dolomite layers that is dated very precisely. Organic content in basinal shales can reach up to 6 % TOC.<sup>43</sup> It contains rich hydrocarbon source rocks.<sup>44</sup> The oils derive from algal and bacterial organic matter that was deposited in partly anoxic waters that had some connection to the open ocean. Diagenetic and thermal alteration did occur but never above 120 °C, so the Group is considered to be unmetamorphosed.<sup>42</sup> It contains thrombolite reefs with *Cloudina*, *Namacalathus* body fossils, and the calcified alga *Angulocellularia* spp. The *Cloudina* and *Namacalathus* are abundant in the A1-A3 carbonate units. The rocks contain well-preserved microfossils. Some cores contain an abundant variety of hard-walled micro-organisms that are indicative of the Neoproterozoic. There are abundant kerigenous organic matter, stromatolites, microbial framestones, some fossil cyanobacteria and other microfossils. It also has cyanobacterial remains and early shelly fossils. These support the idea that the boundary is close to the top of the Ara Group. The boundary is at the top of the Huqf Supergroup, in the Ara Group. In the same area as the boundary is found the last appearance of *Cloudina* and *Namacalathus* and a large short-lived negative excursion in the carbon isotopes.<sup>10</sup> The Huqf has a similar shaped  $\delta^{13}\text{C}$  trace to the rest of the world. From a few strata beneath the Ara up (refer to Figure 13), the Khufai Fm has  $\delta^{13}\text{C}$  values that are relatively constant at around +4 per mil PDB.<sup>42</sup> At the top there is a sharp drop to between -8 and -11 per mil. These values remain low in the Shuram, increasing to -4 to -5 per mil near the top. They continue to increase into the Buah reaching around 0 per mil. The Ara generally has slightly positive values. The A1 shows an increase to about 2 – 3 per mil which is then constant through the A5 except for the A4 where there is an abrupt decrease to around -5 per mil. Values increase to about -2 per mil through the rest of A4. A thin ash bed in the A4 unit is considered the boundary here and is dated to be 542 Ma. The geographic, stratigraphic and isotopic information are shown in Figure 13 and includes the cycles of the Ara Group just discussed. The Huqf oil is characterized by large contents of mid-chain branched monomethyl alkanes.<sup>45</sup> This may be evidence for direct input of cyanobacterial hydrocarbons.<sup>25</sup> They also have pristane/ phytane ratios less than 1, which indicates anoxic deposition.<sup>46</sup> Stable carbon isotopic analyses have been made of the *n*-alkanes and monomethyl alkanes.<sup>45</sup> The mid-chain methyl alkanes were slightly

depleted in comparison to the average value of the *n*-alkanes, but no apparent conclusions were drawn.<sup>45</sup> It is important to note, however, that there was enough material for these measurements to be made.

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Figure 13. Geographic, stratigraphic and isotopic information for Oman from Amthor et al 2003.

*Namibia.* Another region is the Nama Group of Namibia, which is part of the Damara Supergroup. The Nama Group is divided, bottom to top, into the Kuibis, Schwarzrand and Fish River subgroups. The group decreases in maturity from the Kuibis to the Fish River subgroup. The Schwarzrand is comprised of thick limestones and terrigenous sediments, while the Fish River is sandstone with minor silty shales. The grey to black shales of the Kuibis and Schwarzrand subgroups contain an assemblage of organic-walled microfossils, including acritarchs and fragments of the macrofossil *Vendotaenia*.<sup>47</sup> Abundant *Cloudina* is also present. In the Nama Group are foliose shells that may be metaphytes and calcified shells of *Namacalathus hermanastes* that are associated with stromatolitic biostromes and thrombolitic carbonates.<sup>48</sup> Found in the Kuibis and Schwarzrand subgroups are casts, molds and impressions of Ediacaran-grade animals.<sup>47</sup> Also in the lower Nama Group are many ichnotaxa. The Nama Group has the complex trace fossil *Treptichnus*.<sup>49</sup> The upper Schwarzrand contains the trace fossils *Phycodes pedum* and *Diplichnites*, possibly indicative of a Cambrian age.<sup>47</sup> The Fish River subgroup has *Phycodes pedum* and other Cambrian trace fossils.<sup>50</sup> Most of this compiled biostratigraphic information is shown in Figure 14. The TOC in the Nama varies from 0.01 to 0.98 mg C/ g, with an average value of around 0.34 mg C/ g. There was thermal alteration in the Nama Group corresponding to around 170-200 °C. In this range, metagenesis occurs, and biomarkers are severely diminished in concentration.<sup>51</sup> The microfossils are often poorly preserved.<sup>47</sup> In order to see them you need to obtain drill cores because of the surficial weathering. The Fish River subgroup is relatively immature though.<sup>52</sup> It is suggested that the lower Nama Group is late Precambrian in age and the Fish River Subgroup is of Cambrian age, but the exact boundary is not known. In the Nama Group, the  $\delta^{13}\text{C}$  values of the carbonates rise from -4 to +5 per mil in a short stratigraphic interval in the upper Kuibis.<sup>20</sup> The top of the Kuibis is isotopically heavy, the Schwarzrand is moderately heavy until the Fish River where it is around 1 per mil at the Precambrian-Cambrian unconformity.<sup>20,22</sup> These trends are very similar to other areas of the world. There is also usually a sharp negative excursion just below the boundary which is inferred to be contained within the unconformity here.

**(Figure removed due to copyright restrictions.)**

Figure 14. Biostratigraphic information for the Nama Group from Jensen et al 2000.

*Canada.* The last area is Canada, including the Ingta Fm. of the Mackenzie Mountains and the Chapel Island Fm. of Newfoundland. The Ingta Fm. consists mainly of interbedded shale and sandstone with subordinate limestone units, mainly siliciclastic rock.<sup>53</sup> At the top of the formation are two units of carbonate rocks, the upper of which is a stromatolite biostrome complex with preserved algal stromatolites. The formation also

has abundant, well-preserved trace fossils like *Planolites* sp. and *Cochlichnus serpens*. A negative  $\delta^{13}\text{C}$  excursion is seen in the Ingta Fm., just under the boundary, which is found in this formation and was determined faunally.<sup>21</sup> The strata are only moderately deformed. Acritarchs are present with spiny processes, implying low metamorphism. The lower two-thirds of the formation contain abundant small, simple burrows like *Helminthoidichnites* and *Planolites*. In the upper third, *Phycodes pedum* can be found, indicating Cambrian sediments. The upper formation also contains shelly fossils. The stratigraphic and isotopic data are shown in Figure 15.

**(Figure removed due to copyright restrictions.)**

Figure 15. Stratigraphic and isotopic data of the Mackenzie Mountains in Canada from Corsetti and Hagadorn 2000.<sup>54</sup>

The Burin Peninsula in Newfoundland has a very thick succession of strata through the transition.<sup>23</sup> It is also readily accessible. Part of the Chapel Island Fm., including the boundary, is exposed here, at Fortune Head. The stratigraphic section is shown in Figure 16. The boundary here has the ichnofossil *Phycodes pedum*, simple arthropod traces, and small shelly fossils (*Sabellidites cambriensis*) above it and *Harlaniella podolica* below it. More recently, *Treptichnus (Phycodes) pedum* has also been found a few meters below the boundary which is currently the GSSP.<sup>55</sup> Other biostratigraphic guides found above and below the boundary here are soft-bodied megafossils, carbonaceous impressions of vendotaenid algae, and organic-walled microfossils. The formation is divided into five members. The boundary appears near the base of the second member. Member two is composed of siltstone and sandstone beds with minor amounts of shales.

**(Figure removed due to copyright restrictions.)**

Figure 16. Stratigraphic section from the southern Burin Peninsula. CIF is the Chapel Island Formation, RF above it is the Random Formation.<sup>56</sup>

*Key Biomarkers.* I will be using biomarkers to study the areas described in detail above. For this age period, there is a strong  $\text{C}_{29}$  sterane preference in the sediments and oils of Oman, Siberia, and Australia.<sup>25</sup> This and other patterns found from previous research will be important to remember in analyzing data to make sure they were not contaminated. If a certain stratum is entirely different from all known data, it is likely that the stratum has been compromised by younger oils and should be analyzed with caution. My methods of analysis will be according to the Standard Operating Procedures of the MIT Geobiology laboratories.<sup>57</sup> For the best results, only rocks with TOC > 1 wt. % and atomic H/C > 1 will be analyzed.<sup>58</sup> This is so I have enough material to trust my results and to make sure that they are not too thermally mature to be of use. Rock-Eval pyrolysis will be used as a quick screening of thermal maturity, with a lower bound of 200 mg HC/ g TOC.<sup>58</sup>

I will look for certain biomarkers and study specific ratios. They are all compiled in Figure 17. Of great interest are the molecules that are diagnostic for certain taxa.

Some cyanobacteria make 2-methylbacteriohopanepolyols and therefore 2-methylhopanoids may be used as biomarkers for cyanobacteria.<sup>59</sup> These tell us not only that cyanobacteria were present in these systems, but that oxygenic photosynthesis was taking place. The presence of steranes, especially cholestane and its 28- to 30-carbon analogs suggest the presence of eukaryotes.<sup>60</sup> The presence of 3 $\beta$ -methylhopanes is suggestive of methanotropic bacteria.<sup>46</sup> Isorenieratane is indicative of anaerobic green sulfur bacteria, meaning there was photic zone anoxia. Aryl carotenoids would mean it was euxinic in the photic zone.<sup>16</sup> I will look for  $\beta$ -carotane because it is suggestive of the presence of halophilic bacteria in arid, lacustrine settings.<sup>46</sup> I will also study the *n*-alkanes. If *n*C<sub>15</sub>, *n*C<sub>17</sub> and *n*C<sub>19</sub> are abundant, this means that algae was a biological player at this time. If I find a lot of *n*C<sub>23</sub>-*n*C<sub>31</sub> (odd) then there was an abundance of non-marine algae. I will also look for C<sub>30</sub> 4-desmethylsteranes since they are very diagnostic of marine organic matter. Studying various hopanes will be important as they are formed mainly from bacteria. As an age parameter, I will also look at the C<sub>28</sub>/C<sub>29</sub> steranes. This analysis is best applied to marine source rocks, which will be valid for most of my samples, as seen in Figure 3. In Precambrian to Cambrian time the ratio should be low because the C<sub>28</sub> steranes rise may be associated with the diversification of phytoplankton assemblages through time.<sup>61</sup> If I find the ratio is greater than 0.5, then the rock may have been contaminated or may not be of the expected age. Another useful molecule is C<sub>30</sub> 24-isopropylcholestanes since they are very common for this time period.<sup>62</sup> The presence of 24-*n*-propylcholestanes indicates a marine source, and the ratio of isopropyl to *n*-propyl varies with age. I expect a high ratio of isopropyl to *n*-propyl since the isopropyl isomer seems to be related to sponge input and sponges were one of the first metazoans to diverge and had a much lower abundance through the Phanerozoic. Also of importance is the 24-nordiacholestane ratio. The 24-nordiacholestane is a C<sub>26</sub> sterane. The ratio is of the isomers 24/(24+27) and roughly follows diatom evolution and should therefore be very low for our samples.<sup>17</sup> I will look at the C<sub>30</sub> hopane/moretane ratios. The hopane ratio will increase with maturity.<sup>63</sup> To check maturity, I will analyze the sterane 20S/(20S + 20R) values. If they are at or near 0.55, they are relatively mature.<sup>15</sup> As already mentioned earlier, it will be important to first compare biomarkers and their ratios between strata with like environmental setting, age and thermal maturity to properly relate all of this data into accurate information.

*Value of biomarkers.* As described in the introduction, most of these biomarkers correspond to bacteria or algae. Though the Cambrian explosion is mainly associated with the animal clade, these biomarkers are still very telling as to why the radiation occurred. It is necessary to look for environmental conditions and changes. These influence all life, not just the animals, and therefore the information bacteria provide can be correlated well with animals of the same age.

Biomarker	Organism/Maturity	Environmental Setting	Expectation
2-methylhopanoids	cyanobacteria	oxygenic photosynthesis	
Steranes (esp. cholestane and its 28- to 30-carbon analogs)	eukaryotes		
3 $\beta$ -methylhopanes	methanotropic bacteria		
Isorenieratane	green sulfur bacteria	photic zone anoxia	
Aryl carotenoids	euxinic in the photic zone		
$\beta$ -carotane	halophilic bacteria	arid, lacustrine	
<i>n</i> -alkanes: <i>n</i> C <sub>15</sub> , <i>n</i> C <sub>17</sub> and <i>n</i> C <sub>19</sub>	algae		
<i>n</i> C <sub>23</sub> - <i>n</i> C <sub>31</sub> (odd)	non-marine algae		
C <sub>28</sub> /C <sub>29</sub> sterane ratios			low
C <sub>30</sub> 4-desmethylsteranes	marine organic matter		
C <sub>30</sub> 24-isopropylcholestanes	ratio of isopropyl to <i>n</i> -propyl varies with age	marine source	present, high ratio of isopropyl to <i>n</i> -propyl
24-nordiacholestane ratio	diatom evolution		very low
Hopanes	bacteria		
C <sub>30</sub> hopane/moretane ratios	hopane ratio will increase with maturity		
Sterane 20S/(20S + 20R)	at or near 0.55, they are relatively mature		

Figure 17. Table of key biomarkers and the information they provide.

*Possible outcomes.* If I find that the diversification was greatly offset in certain areas of the world it would suggest that the rise of oxygen was not the major source since it should be relatively constant in concentration across the globe, at least within a few thousand years. It will be important to compare the environmental conditions across the different areas. If they were the same around the world at this time, then environmental conditions were obviously a key factor, but if they were drastically different, then maybe the exact conditions were not the primary factor for diversification. If they all changed drastically at this time though, even if it was not the same conditions everywhere, then the hypothesis that the changes in the climate at the time due to tectonics and other factors would be supported. It will also be interesting to see if there were pulses in radiation or if radiation in one area triggered diversification in another area. It will be very important to date the strata as accurately as possible to see if as life started to diversify in one area, it caused ecological changes allowing other areas to diversify. Or, if on a geological timescale the radiation was relatively synchronous, if the initial radiation then enhanced further diversification globally.

*Expectations.* I expect that the biomarkers will give a different climatic story at some of the locations, that some of the locations will show radiation of life slightly before the rest, and that once life began to evolve it changed the climate further, reinforcing its radiation. One interpretation would then be that something triggered the radiation, hopefully in this study we will find what it was, and that this diversification altered the environment in some way such as increasing the oxygen content of the Earth, and paved the way for exponential radiation among many clades of life.

## Summary

The areas best suited to solve this question will be found with this research, and the ones that seem the most likely are in Australia, China, Siberia, Oman, Namibia, and

Canada. After this work is done, there will be a complete set of information with which to support or discount old theories and to develop new ones about the radiation of life into the Cambrian. Through the use of biomarkers, we will have a greater understanding of the taxa alive at this time and of the global climatic conditions and how they changed over the boundary period. If there are certain areas that prove to be quite interesting we will of course return for a more detailed stratigraphic section to study. Also, it would be very valuable in the future to further look at areas of high organic content by taking a look at isotopic measurements. These are quite useful since they are usually conserved well through time and can also give specific information as to the sources of a certain stratum or even the specific source of a desired biomarker like pristane or phytane or a suite of *n*-alkanes. These are also quite valuable since they can usually be properly compared across all environmental conditions. The main focus on this research will be to find which areas will be best for follow-up research like isotopic studies and to begin unraveling the story with the presence and ratios of biomarkers. The impact of this work will be vast across many fronts including geology and paleontology. I cannot yet say what questions may remain, but I expect much debate to continue.



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