Early life and its implications for astrobiology – a case study from Bitter Springs Chert, Australia

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Abstract: Early life research faces additional challenges than those of the study of later life forms. Due to the dematerialization of the earliest rocks, valuable information about the early Earth is forever lost. Furthermore, early life was small and morphologically basic, effectuating abiotic pseudofossils to infiltrate the fossil record. A central theme is the close connection early life research share with astrobiology, manifested by the notion that early terrestrial life research should be conducted with as much vigilance as potential fossil findings from a remote planet. Both fields benefit from a broad-minded approach as the basic building blocks of life, previously thought to be present in all life forms, might have room for interchangability. Therefore, the biomarkers traditionally searched for might not reveal the full story of life. Petrography, XRF, SEM and FTIR was applied to rocks from Bitter Springs Formation, Australia, in hope to detect biogenic material. Hydrocarbons were detected in one of the samples through FTIR analysis, which is a strong indicator for biogenicity. Many structures were found that are most probably bacterial fossils and oncoid structures.

Keywords: Early life, astrobiology, exobiology, microorganisms, origin of life, Bitter Springs, Amadeus Basin, stromatolites, microfossil, SEM, XRF, FTIR

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Forskning kring tidigt liv och dess implikationer för astrobiologi - en fallstudie från Bitter Springs Chert, Australien

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Sammanfattning: Forskning kring tidigt liv möter svårigheter utöver de som forskning kring senare liv ställs inför. På grund av att de tidigaste bergarterna inte finns bevarade har viktig information om jordens tidiga förhållanden för evigt gått förlorad. Dessutom var de tidigaste livsformerna små och morfologiskt enkla, vilket betyder att abiotiska pseudofossil lätt kan infiltrera fossilarkivet. Ett centralt tema är den nära kopplingen mellan forskning kring tidigt liv och astrobiologi, delvis på grund av att tidigt liv på jorden måste undersökas med samma hårda krav som vi skulle ställa på potentiella fossil från andra planeter. Båda forskningsfälten gagnas av vidsynthet då det är möjligt att de byggstenar vi traditionellt sett kopplat till livsformer kan bytas ut mot andra ämnen. Det är därför möjligt att sökandet efter traditionella biomarkörer inte räcker till för att klarlägga livets fulla historia. Petrografiska undersökningar, XRF, SEM och FTIR applicerades på stuffer från Bitter Springs Formation, Australien, för att se ifall de innehöll biologiskt material. Kolväten hittades genom FTIR-analys, vilket är en stark bioindikator. Flera strukturer hittades som högst troligtvis är fossila bakterier och oncoider.

Nyckelord: Tidigt liv, astrobiologi, exobiologi, mikroorganismer, livets ursprung, Bitter Springs, Amadeus Basin, stromatoliter, mikrofossil, SEM, XRF, FTIR.

Ämnesinriktning: Berggrundsgeologi.

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1 Introduction

This paper comprises a review of the scientific field of early life research. It also explains how early life research on Earth can provide implications for astrobiology, and how both fields benefit from the merging we see today. The reader will gain insights about the various approaches of early life research, in which the natural sciences benefit from joining forces. Fossil findings enable us to see what early life forms looked like and biological studies are retracing genetic information back to the roots of the tree of life. Chemical evidence of past life comes in the form of isotopes and biomarkers. Technical advancements enable us to discover more about our distant ancestors, and new experiments are showing us that we still do not know the limits of life. A variety of sciences from geology, biology, chemistry, to astrobiology and even philosophy must intertwine when the answer to one of the most fundamental existential questions is sought: what is life?

Within the duration of this project a case study of how to search for traces of life in Precambrian rocks was conducted with material from the Bitter Springs Formation in Australia (~820 Ma). The Formation is known for its diverse Proterozoic microbiota, primarily preserved in carbonaceous chert nodules. A method was developed for how to search for early life using multiple techniques, and recommendations for analysis of Precambrian fossils will be given. Due to the morphologic simplicity of Precambrian fossils, pseudofossils can easily be mistaken for biogenic structures. Putative Precambrian fossils should therefore be investigated with multiple analyses before they can be judged as biogenic.

1.1 Aims and objectives

The aim of this study was to compile a review of the emergence of life and its earliest history, as well as of the current status of the scientific field of early life research. Proterozoic rocks, collected in Bitter Springs Formation, Australia, were analysed as a case study. The applied techniques were; thin section production, optical microscopy, X-ray fluorescence, scanning electron microscopy and Fourier transform infrared spectroscopy. Becoming proficient in these techniques was another aim. An additional objective was to understand how early life research is related to astrobiology.

2 Background

2.1 Origin of life

The question of how life is formed has been a central philosophical theme for thousands of years and the natural sciences, which initially developed as an extension of philosophy, subsequently adopted the question. "Spontaneous Generation" was the paradigm for the origin of life from the time of the ancient Greeks until the 19th century. The model states that life self-generates, usually from different kinds of decaying material. By observational proof it was determined that life emerged from life, through the passing of a special living force. The lack of this force, *vis vitalis*, in unliving things made the notion that abiogenic matter could transform into biogenic matter impossible (Chernyshenko, 2010). Spontaneous Generation was gradually rejected, as it could not be scientifically proven (Benton & Harper, 2009). Towards the *fin de siècle*, the question of the origin of life became a hot topic in the scientific community. In the beginning of the 20th century, Oparin and Haldane independently and simultaneously developed the biochemical model (Penny, 2005). It was suggested that in a strongly reducing atmosphere, as opposed an oxic one, organic molecules could be synthesized from inorganic chemicals if a sufficient amount of energy is added to the system (Chernyshenko, 2010). In the 1950's, they were proven right through the experiments of Miller and Urey. By simulating an analogous environment to the one in which the first life forms appeared, they sought to repeat the emergence of life. The early Earth was replicated in bottles with water that substituted for the ancient ocean, and various gases substituting for the ancient atmosphere. An electric discharge, substituting for lightning or UV radiation, would start the formation of the first biomolecules (Miller, 1953). The Miller-Urey experiments successfully showed that amino acids can form from inorganic molecules, given the right surroundings, and they mark the beginning of prebiotic chemistry as a field of science (Orgel, 2004). Modern theories are essentially variations and expansions of the Oparin-Haldane model.

2.1.1 Prebiotic chemistry

Prebiotic chemistry is concerned with the molecules that subsequently developed into life forms (Orgel, 2004). By present-time definition, all life is cellular. Since it has been deemed unlikely that all cellular features were developed simultaneously, several prebiotic structures must have appeared before the emergence of the first cell. We call these prebiotic since nothing prior to the first cell is defined as living. The first steps leading up to cell formation would be of a chemical nature, followed by a genetic mutation (Penny, 2005).

2.1.2 The RNA world hypothesis

All organisms have DNA and proteins in their cells, which are vital to survival and replication. DNA is filled with genetic information but cannot function outside the cell nucleus. Proteins catalyze metabolic reactions and are necessary to uphold life but lack genetic information and cannot replicate (Penny, 2005). Replications of nuclear acids are dependent on the processes of protein enzymes, but protein enzymes cannot be formed without nuclear acids, found in the DNA. This prebiotic quandary invoked a search for a third molecule, capable of conducting both of these functions. This molecule was likely to be an important step towards full-fledged biogenesis (Orgel, 2004). In 1968, Crick suggested that RNA could be the sought after molecule. The proposi-

tion that RNA under some circumstances was able to act as both information storage and an enzyme (Crick, 1968) was later proved and coined as the "RNA world hypothesis". The RNA world hypothesis is still valid and prebiotic research is mainly concerned with the episode prior to RNA formation (Orgel, 2004). As soon as replication started, evolution did too. Through advantageous mutation highly fitted genotypes could become increasingly abundant, and new functions and structures could develop (Knoll, 2003).

2.2 Geological history of the early Earth

2.2.1 Hadean (4.6-4 Ga)

The Earth was formed through the slow accretion of gases and dust 4.6 billion years ago. Due to frequent collisions with celestial bodies and intense volcanism, it was initially in a molten stage. After 0.5 billion years of accretion, the Earth had reached its approximate present size, and simultaneously the temperature on the planet started to drop. Zircons originating from the Hadean are indicative of a developing crust. The earliest zircon findings to date are from western Australia and U-Pb dated to an age of 4.2 billion years (Iisuka *et al*., 2006). Water vapour that was present in the atmosphere liquidized as a consequence of the decrease in temperature and formed the first oceans (Mix *et al*., 2006). The presence of water on the planet has also been established by studying the Hadean zircons (Harrison, 2009). Celestial impacts, a characteristic phenomenon of the Hadean, repeatedly vaporized those early oceans and sterilized the surface (Wacey, 2009). The impact frequency reached an intensity peak between 4.1 and 3.85 billion years ago, which is called the "Late Heavy Bombardment" (Mix *et al*., 2006). The present atmosphere is fundamentally different from the primordial, which consisted mainly of methane, ammonia, hydrogen and helium and was strongly reducing (Chernyshenko, 2010). The early crust vanished due to erosion and reworking, which means that the oldest rocks, the "Acasta Gneiss" from northwestern Canada, are found on the verge of the next Eon (Bowring & Williams, 1999). If there were plate tectonics movements at this time is a current controversy, with no conclusive evidence due to the vanished rock record (Harrison, 2009). The quest to unveil the mysteries of Hadean geology is being continued, but until more is known this period in the history of the Earth should be investigated as if a remote planet (Brasier *et al*., 2006).

2.2.2 Archean (4-2.5 Ga)

The Earth was during the early Archean still subject to the Late Heavy Bombardment, but subsequently the

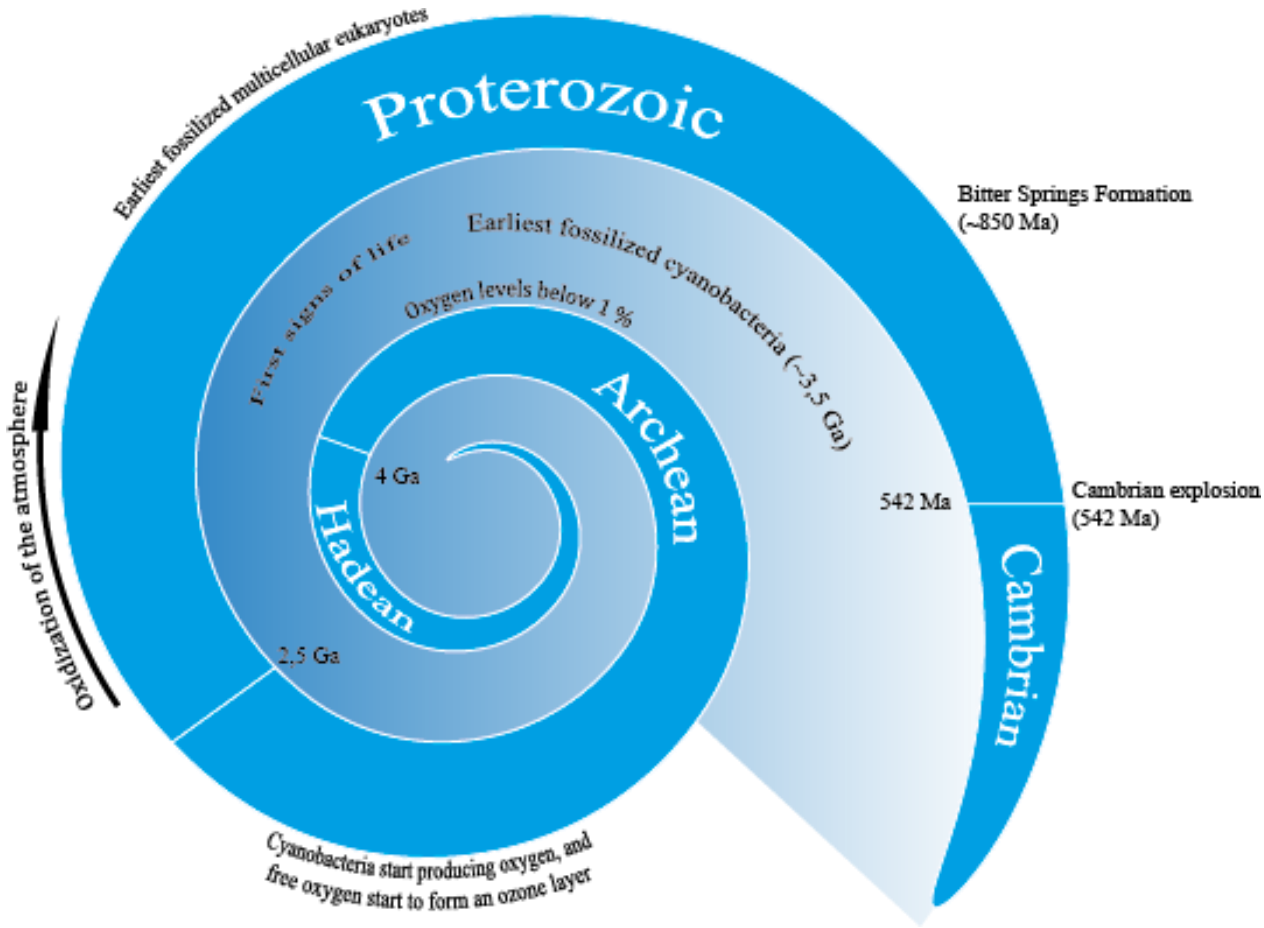

Fig. 1. A timeline of some important Precambrian events. Some events are not specified in exact ages, as they are continuously being revised.

planet grew more tranquil. Most Archean rocks have been subducted, recrystallized and eroded many times over, and metamorphic processes have heavily deformed the ones that still exist. Only a few localities have been spared, the best-preserved being the Pilbara Craton of western Australia and Barberton Greenstone Belt of South Africa and Swaziland. These formations have been dated to 3—3.5 billion years, and have only been altered into greenschist facies (Schopf *et al*., 2007). Archean body fossils are essentially limited to these locations, but chemical signals of biogenicity have been observed in other places. Even though the solar luminosity was 20 % lower during the Archean compared to its present level, the Earth was warm. If solar luminosity were to drop by a fifth today the global temperature would be below the freezing point, but geological records clearly reveal that the oceans were in liquid form during this time (Sagan & Mullen, 1972). In facrt, oxygen isotope analysis reveals that the Archean oceans may have been 55°C to 85°C (Knauth, 2003). These contradicting factors gave rise to the ”faint young sun paradox”, coined by the legendary astronomer Carl Sagan and George Mullen. High amounts of greenhouse gases, trapping solar energy within the Earthly aerospace, could be the reason why an Archean hydrosphere could have existed (Sagan & Mullen, 1972). In addition, the energy emitted from the centre of the Earth may have been higher (Wacey, 2009).

The Archean atmosphere was reducing, which means that the Earth did not have a protecting ozone layer at the time (Knoll, 2003). One of the most important indicators of an oxygen-depleted Archean Earth is grains of pyrite found in sedimentary material from ancient rivers. The pyrite is formed by the activity of sulphate-reducing bacteria and subsequent reactions with iron in the water. If oxygen were abundant in the water and the atmosphere, the pyrite would destabilize. Today pyrite is found in igneous rocks but not in river sediments that have undergone weathering, although in sediments older than 2.2 billion years they are found in plenitude (Knoll, 2003). Further evidence of an anoxic Archean world is derived from the abundance of methane-reducing bacteria, evidently thriving until approximately the same age. Since oxygen respiring organisms are more effective in breaking down organic molecules, they usually dominate in habitats belonging to their fundamental niche (Farquhar *et al.,* 2007).

2.2.3 Proterozoic (2500–542 Ma)

Isotopic evidence from the study of sulphur isotope ratios in sedimentary rocks suggests a transition from an anaerobic to aerobic atmosphere around 2.45 billion years ago (Farquhar *et al*., 2007). Geological evidence comes in the form of Banded Iron Formations, which becomes abundant approximately 2.4 billion years ago. Analyses of stratigraphic units underlying the formations indicate atmospheric oxygen to be lower than 1 % of its present level (Knoll, 2003). The transformation from a reducing to an oxic atmosphere ultimately calls for a permanent reduction in hydrogen atoms, which may have happened as hydrogen escaped into space according to research done by NASA. Methane produced by organisms might have reached the upper atmosphere, where the molecular bonds between hydrogen and carbon were broken by the intense UV radiation. Hydrogen is one of the few elements light enough to escape gravity, and its decrease facilitated the net increase of water oxidation (Knoll, 2003; Mix *et al.,* 2006). Oxygenic photosynthesis developed several hundred million years prior to the significant rise in atmospheric oxygen. Biomarkers indicate oxygenic photosynthesis 2.7 million years ago, but it could have developed significantly earlier (Catling & Claire, 2005). The time lag between oxygenic photosynthesis and the oxygenization could be explained by the lack of oxygen respiring organisms. Without them, the oxygen production is less efficient (Knoll, 2003). Proterozoic rocks are far more abundant and better preserved than Archean ones, and several localities with exceptional preservation have been discovered (Schopf *et al*., 2007).

2.3 Where did life start?

The climatic conditions on the Archean Earth were obviously very different from the present climate. UV radiation levels made superficial life improbable. It is believed that life firstly formed in water, and hydrothermal vents constitute a primary candidate environment. Commonly referred to as “black smokers”, these openings along mid-oceanic ridges are locations where heat and chemical compounds from within the Earth are being emitted. The depth of the oceans would have prevented UV radiation from reaching the sea floor and, in addition to this, chemicals necessary for building organic molecules were present (Mix *et al*., 2006). The black colour of the smoke is the result of high concentrations of iron sulphide being released from within the Earth, and the chimney-like structure comes from the rapid cooling when minerals make contact with the water (Wacey, 2009). The biotas around modern hydrothermal vents are several magnitudes higher than on the rest of the sea floor, but even though the vents are obviously capable of sustaining life, doubts have been raised as to weather the primordial biological structures could have formed there. The RNA structure is sensitive to high temperatures and can dissolve when exposed to heat. The water from the vents can reach 400°C and this is the reason why it has been argued that hydrothermal vents might not be the starting point of life, but rather an early habitat (Mix *et al.,* 2006). Alternative locations for the origin of life are “cold smokers”, which are similar environments but without extreme heat (Penny, 2005), or less proximal areas to hydrothermal vents (Mix *et al*., 2006).

The starting point of life on Earth will perhaps never be found, because life might not even have emerged on this planet. The panspermia theory suggests that the primordial biomolecules, or even microbes, came from carbonaceous meteorites called chondrites,

or comets (Cooper *et al.,* 2001). The panspermia theory has neither been rejected nor accepted. It does not contradict the chemical origin of life as the same mechanisms could have worked in an extraterrestrial environment as well. Mileikowsky *et al*. (2000) states that if microbes live or have lived on Mars it is in fact not only possible but also probable that some of them made it to Earth travelling on meteorites. By exposing living microbes to different kinds of environmental stress, it could be concluded that some microbes were indeed capable of surviving the trip to Earth. Likewise, pieces of Earth could have been ejected into space during the Late Heavy Bombardment, and microbes living inside them could have travelled from Earth to Mars. Therefore, if Mars is or ever were inhabited by organisms, they might have come from Earth (Mileikowsky *et al*., 2000).

2.4 The microbial world and the earliest life forms

Although the timing of the first life forms is heavily debated, scientists are approaching a consensus to a minimum of 3.5 billion years of biologic history on Earth (Benton & Harper, 2009; Schopf *et al*., 2007). Although the How's, Where's and When's of the origin of life are not yet conclusive, we do know that unicellular microbes were the first life forms on Earth and that they are still numerically dominating the biosphere. Microbes shape the Earth through their metabolism and emission of waste products. They affect the atmosphere, the soil and the water on this planet by recycling organic and inorganic elements. The most profound change they invoked was the oxygenization of the atmosphere, which made all multicellular life possible (Konhauser, 2007; Wacey, 2009). Microorganisms are those within the size range from the smallest known cell to the largest organisms that are not visible with the naked eye (Javaux & Benzerara, 2009). The oldest claims of life come from the Isua Greenstone Succession on Greenland, based on fractionations of carbon isotopes in graphite grains produced 3.8—3.6 billion years ago (Rosing, 1999). Living organisms prefer to use lighter isotopes rather than the heavier ones, causing an anomaly in the ratios of isotopes compared to abiogenic matter. If proven to be biogenic, they will be the oldest fossils found so far, but the sole use of carbon isotopes for concluding biogenicity is controversial and not generally accepted (Mix *et al*., 2006). Carbon isotope fractionations that are indistinguishable from biogenic ones have been produced in laboratories, which usurp carbon isotopes as a definite indicator of life (Wacey, 2009). If life has been under way for more than 3.8 billion years the absent rock record constitutes a problem (Horneck, 2000). Instead of searching for physical evidence, we will then have to use the information stored in our genes to find the final pieces. Stromatolite structures with a presumed age of 3.495 billion years have been found in the Dresser Formation, Warrawoona Group, western Australia. The fossils occur in beds of cherts interbedded by volcanic rocks. The difference in the stromatolite shapes implies that life had already started to diversify and was well under way at this point (Dunlop *et al*., 1978). Unfortunately, no biochemical signatures have been extracted from the presumed fossils. Stromatolite-like structures can be produced abiologically, which makes these structures somewhat questionable, but the characteristic conical shape distinguish them from any abiogenic structure observed to this date. In the same formation, sulphate isotopes consistent with signatures produced during bacterial metabolic sulphur reduction have been identified, as well as structures interpreted as bacteria (Wacey, 2009). These indications combined could be seen as conclusive evidence.

2.4.1 A single ancestor

All organisms we know of today originated from a single ancestor. Support in favour of this theory lies within the cell structure, which contains several features shared by all known life forms. All life contains DNA, and the amino acids in the proteins that build DNA are very similar, even between remotely different organisms. The fact that the same kinds of enzymes are used for metabolic processes and that all cells use lipids around the protoplasm constitute other evidence (Horneck, 2000). Which group of organisms that initially diverged from our last common ancestor, however, is still a mystery. Before the advent of molecular biology, phylogenetic relationships were essentially determined through morphology. This was a major problem in early life research, since the ancient life forms are morphologically similar. Despite recent technical advancements, the genetic code of the earliest ancestor has yet to be deciphered. Information about organismal descent is preserved in chromosomes, but with each generation the genetic blueprint becomes increasingly altered and vital information can be permanently lost. The phenomenon of lateral gene transfer constitutes another hinder when tracing our ancestral roots (Delsuc, 2005).

2.4.2 Lateral transfer of genes

We usually think of genes as passing from one generation to the next, but genealogy has revealed the first life forms to be genetic chimeras. Some genes have evidently been transferred between different groups of organisms after their evolutionary split, and not only once but repeatedly. This is blurring the base of the tree of life (Knoll, 2003). All genes present in the first life forms are potentially transferrable, but different kinds of genes have different tendencies to do so (Gribaldo & Brochier-Armanet, 2006). Informational genes (e.g. rRNA) do not transfer as easily as operational genes (e.g. metabolic genes), and if the right genes are found and studied there is hope for the problem to be resolved in the future (Jain *et al*., 1999).

2.4.3 Three domains

The root of the tree of life consists of three domains;

Bacteria and Archaea (functionally grouped as Prokaryota), and Eukarya. It was previously believed that Archaea was a side branch to Bacteria, but in the 1970's it was not only concluded that Archaea should be classified as a third domain; furthermore they are closer related to Eukarya than to Bacteria (Woese & Fox, 1977). Eukarya and Archaea share homologous ribosomal proteins and have a similar DNA replication apparatus, whereas Bacteria are differently constructed. Since Bacteria and Archaea are not each other's closest relatives, Prokarya is actually a polyphyletic taxonomical group. Even so, they share many morphological characteristics such as the absence of a cell nucleus, or organized cell functions (Gribaldo & Brochier-Armanet, 2006). The similar somatic organization makes the grouping of prokaryotes useful when describing their mode of life, but not their descent. Prokaryotes are the simplest of all cells as they only have the absolute vital structures; a membrane, cytoplasm and DNA (Chernyshenko, 2010). Prokaryotes do not have a cell nucleus with genetic information stored in chromosomes. Instead, prokaryotic genetic information lies free within their nucleoid. Prokaryotes reproduce asexually. Rapid regeneration and fast growing populations, as well as lesser adaptability to changing environments characterize this reproduction strategy. Asexual reproductions observed in modern prokaryotes are binary fission and budding, but fossil remains that would prove the usage of these methods are yet to be found (Wacey, 2009). The size of prokaryotes has remained fairly constant since the Proterozoic, and they have not increased significantly in complexity (Finlay & Esteban, 2009).

The eukaryotic cell is normally 10 to 100 times larger than the prokaryotic cell and is superficially and internally more complex. Unlike Prokaryota they comprise organelles, such as cell nuclei, mitochondria/chloroplasts, lysosomes, endoplasmic reticulum, cytoskeleton and kinetosomes (Chernyshenko, 2010). Prokaryotes lack a cytoskeleton, which restrains them from growing large. Eukaryotes, on the other hand, later developed into protozoans, animals, fungi and plants. Sterols are fatty acids composed of hydrocarbons, which are incorporated in the eukaryotic cell membrane. Since they are not present in any known prokaryote, the emergence of sterols in the rock record (2.7 billion years old) is seen as proof of eukaryotic presence. Like in the dubious case of carbon isotope ratios, sterols have also been questioned as valid proof of biogenicity, and more work is needed to understand the reliability of molecular fossils (Wacey, 2009; Marshall *et al*., 2009). In the beginning of the late Precambrian, cyanobacteria dominated the biosphere. In the middle of the late Precambrian, eukaryotes had diversified and algae and fungi were becoming increasingly abundant, but with the exception of the Ediacaran fauna, the biota in the Precambrian consisted solely of microorganisms (Schopf & Blacic, 1971). There is no consensus in the scientific society regarding which domain appeared first (Fig. 2), although many

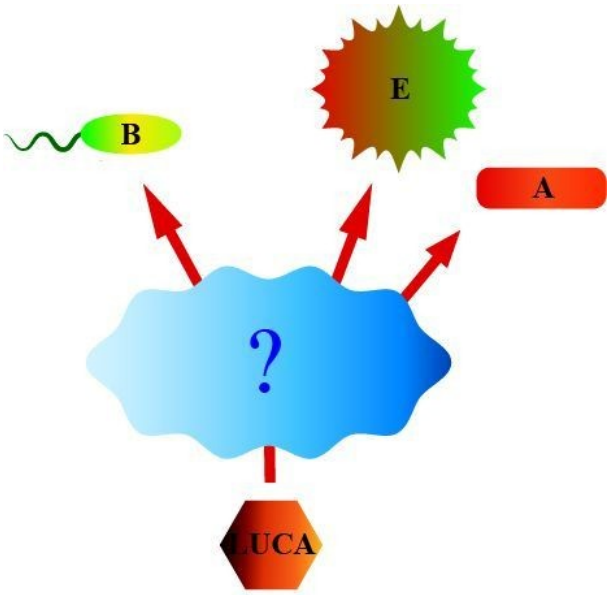

Fig. 1. A depiction of our vague understanding of the initial diversification of the three domains. From our Last Universal Common Ancestor, lateral gene transfer has blurred out phylogenetic information. Bacteria are more distantly related than Eukarya and Archaea are to each other, but how and when the initial splits of the domains occurred is still not a resolved matter.

believe that prokaryotes with their simplistic morphology and their early emergence in the fossil record would be the obvious predecessor (Vesteg *et al.*, 2006). Forterre and Philips (1999) suggest that prokaryotes instead diversified from the eukaryote lineage and later went through a process of simplification through gene loss. It is also possible that the domains split from another, later extinct, lineage (Gribaldo & Brochier-Armanet, 2006). Another theory states that eukaryotes evolved from a fusion between Bacteria and Archaea, which would in part explain their chimerical nature (Delsuc, 2005).

2.4.5 Microbe metabolism

Metabolism is the extraction, usage and storage of energy from nutrients by means of chemical reactions and is an absolute necessity for life (Chernyshenko, 2010). There are three primary metabolic groups. (1) Heterotrophy is the obtaining of energy and carbon by ingestion of organic molecules made by other organisms, either aerobically or anaerobically. Anaerobic heterotrophy is also called fermentation, and is a rather uncommon way to metabolise. (2) Photosynthesis is the usage of light and CO_2 to produce chemical energy, and (3) chemosynthesis is the harvesting of energy from inorganic chemical compounds (e.g. nitrate, sulphate and metallic oxides of manganese and iron).

Chemosynthesis is presently only conducted by prokaryotes and was most likely the metabolism first developed, and methanogens, which are chemosynthetic organisms that gather carbonic acid and hydrogen and emit methane and carbon acids as waste products, probably preceded others (Chernyshenko, 2010).

Sulphur respiring organisms also developed early, but they were initially very inefficient. They thrived in sulphur rich environments being the only life forms that could exist there. Lateral gene transfer later spread the metabolic preference to other groups, and they subsequently rose in efficiency (Knoll, 2003). By the end of the Archaean, heterotrophy as well as photosynthesis were also developed (Finlay & Esteban, 2009).

Cyanobacteria are the only branch of prokaryotes known to use oxygenic photosynthesis, but they were not the primordial photosynthetic organisms. Like their predecessors, the first cyanobacteria did not produce oxygen as a waste product. Chemical and body fossil findings support the presence of oxygen producing cyanobacteria 2.5—2.6 billion years ago, and many groups of anoxygenic photosynthetic bacteria surely existed before them (Olson & Blankenship, 2004). With the activity of oxygenic photosynthesis, the oxygen levels rose. Organisms being unable to tolerate oxygen either died or were forced to retreat further down in the water column and sediments, and so anaerobic organisms came to occupy the niche they have today. Oxyphilic organisms could consequentially claim vacant habitats. Chemosynthetic bacteria that use oxygen and hydrogen to create reactions and gain energy thrived in the new world, but the real winners were oxygen respiring organisms (Knoll, 2003). Oxygen respiration is much more efficient than other metabolisms, which is why aerobic organisms could increase in complexity (Finlay & Esteban, 2009). In the modern bacterial domain, heterotrophy is the dominating metabolic group. By ingesting organic material already developed by other organisms, they freeload from primary producers. The most extreme case of freeloading in the biological history might be the story of endosymbiosis, which will be discussed in the next section.

2.4.6 Endosymbiosis

The eukaryotic cell contains a number of organelles, which are subunits specialized in performing specific functions. Endosymbiosis is the process that provided the eukaryotic cell with mitochondria and chloroplasts, and is furthermore an example of how reality sometimes outshines imagination. The formerly mentioned heterotrophic free loading occurred as a eukaryotic cell ingested a bacteria without digesting it, which was possible as the bacteria managed to deactivate the digestive enzymes inside the eukaryote (Knoll, 2003). The bacteria became assimilated in the eukaryotic cell and started to work as an organelle. The theory of engulfing eukaryotes was not an immediate success when raised by Mereschkowski in 1905, but is the shared notion today (Chernyshenko, 2010). The ancestral mitochondrion was an aerobic bacterium. Mitochondria produce ATP and are sometimes referred to as "cellular power plants". They exist in almost all eukaryotes and are strikingly similar throughout the eukaryotic domain. The chloroplast organelle, which allows absorption of solar energy in plant and algal cells, is the result of the assimilation with a cyanobacterium (Chernyshenko, 2010). Mitochondria and chloroplasts in eukaryotes respond to antibiotic treatments in the same way as bacteria, and differently from the rest of the body. They also contain their own genetic information, which partially corresponds to bacterial DNA. Gene analysis has shown that chloroplasts share more genetic information with cyanobacteria than with plants and algae, which is the most important proof of endosymbiosis (Knoll, 2003). Through endosymbiosis, photosynthesis developed in many lineages of protists and algae separately. As previously mentioned, there are uncertainties regarding the sequential evolution of the domains. Bacteria might sound like the obvious predecessors because of the role they had in eukaryotic evolution, but eukaryotes might have existed devoid of organelles for a long time before the emergence of bacteria.

2.4.7 Cyanobacteria as a case study for evolutionary stasis

It can be argued that the oxygenization of the Earth was the most important event in the history of our planet. That would consequently make cyanobacteria, the primordial oxygen producers, the most important organisms that ever saw the light of day (Shi & Falkowski, 2008). Stromatolites are continuously found in the fossil record from 2.8 billion years ago onward. The earliest stromatolites are dated, based on different levels on scepticism, to 3.1—3.5 billion years old (Olson & Blankenship, 2004). Except for the earliest found cyanobacteria, which have no modern analogue due to fundamental differences to the Archean environment, ancient cyanobacteria are strikingly similar to modern forms. They are a highly diverse group of organisms, but their evolutionary differentiation does not seem to have changed much through geological time. Rather, their morphology seem to have changed more when becoming established in a new environment. It is probable that cyanobacteria diversified early into the approximate forms of their modern descendents (Knoll, 2003).

The general conception used to be that evolution was a gradual process, as Darwin originally described it. It is now generally accepted that evolution works through punctuated equilibrium, with short periods of change and longer periods of stasis. Scientists are asking themselves why these, and many other groups of early life forms, have virtually only exhibited stasis since their early diversification. Sewall Wright developed the adaptive landscape model in 1932, which is a metaphor explaining how evolution works. Each organism has its own personalized landscape to which it can adapt. Beneficial mutations in its genotype would bring it closer to a peak, whereas negative mutations would bring it closer to a valley. The genotype closest to the peak will have the highest fitness, and those situated further down survive and reproduce to a lesser extent. How the landscape looks depend largely on the environment in which the organism exist, and how

many functions it can perform (Wright, 1932). Bacteria perform few functions, which heightens the evolutionary pressure to develop a certain genotype that optimally performs that function. When their fitness in one particular environment is at its highest peak, they remain there, and when cyanobacteria invaded new habitats they quickly adapted to the local environmental conditions. This model fits well with what we see in the paleontological record (Knoll, 2003). In contrast to cyanobacteria, the late Proterozoic eukaryotes species did not exist for enormous time spans. Therefore, they are more useful when measuring relative age in the Proterozoic strata (Vidal & Moczydlowska-Vidal, 1997).

2.4.8 Increasing biological complexity

During the Archean and for most of the Proterozoic, only microbes existed. There is no universal method of measuring biological complexity, but the most commonly used is by the number of cell types. Most prokaryotes and many eukaryotes are unicellular (Hedges *et al*., 2004). Phagothropy, the ability to engulf food, was the most important innovation for increasing biological complexity in eukaryotes. Phagotrophy was a prerequisite for endosymbiosis, which led to the subsequent development of mitochondria and chloroplasts (Finlay & Esteban, 2009). The transition from the microbial world to the multicellular world of the Phanerozoicum was made possible due to the oxygenization of the Earth. Approximately 1.8 billion years ago, the first multicellular organisms appeared, and cells within the newly obtained multicellular body were assigned different functions. Multicellularity developed several times in different eukaryotic lineages (Chernyshenko, 2010). An atmosphere without oxygen limits the body size of an organism to less than 1 mm, but now larger life forms could develop (Finlay & Esteban, 2009). After the rise in oxygen levels, organisms with more than two cell types developed. Between 1.5 and 1 billion years ago, the maximum complexity rose from 10 to at least 50 (Hedges *et al*., 2004). 750 million years ago, intricate food webs had started to develop, where cyanobacteria and algae made up the nutritional base and protozoans were predators. Signs of protozoans eating other protozoans indicate multiple levels in the food chain (Knoll, 2003).

2.5 Life in extreme environments

Extremophiles are organisms living and thriving in the outer margins of the field of life, which refers to environments where the presence of life forms is not limited by physical or chemical parameters (Chernyshenko, 2010). Extreme environments are those categorized by humans to be extreme; to extremophiles, on the other hand, they are fully normal. Phylogenetic studies suggest that our last common ancestor was thermophilic (Rothschild & Mancinelli, 2001), meaning that it had an optimal growth rate in temperatures above 80 degrees (Gribaldo & Brochier-Armanet, 2006). This does not necessarily mean that the earliest life forms were thermophilic, but it becomes evident that “extremophile” is a subjective term (Rothschild & Mancinelli, 2001).

An increasing number of species being able to tolerate exposure to exceedingly high or low temperature, pH, pressure or oxygen levels, as well as extreme desiccation, salinity or radiation levels are continuously being found (Rothschild & Mancinelli, 2001). They are most common in Prokaryota, but have been found in lineages from all three domains (Gribaldo & Brochier-Armanet, 2006). The spectrum for surviving is broader than the spectrum for total functionality. The most sensitive function is reproduction, which only occur in environments to which the organism is well adapted. Extremely high temperatures lead to protein degradation. Low temperatures reduce the activity of enzymes, and with decreasing temperature metabolic activity might be totally blocked (Chernyshenko, 2010). The Archaean domain, in which we find the most exceptional extremophiles, is not well studied compared to the other microbial domains, and the field of life might be even larger than we think (Gribaldo & Brochier-Armanet, 2006). Carbon, energy and water is necessary in the reproduction of new organisms, but once produced, extremophiles can survive almost anywhere (Konhauser, 2007). Wherever there is a sufficient energy source and water, there seems to be life (National Research Council, 2007).

2.6 Fossilization and preservation

It was previously thought that only sedimentary rocks could preserve organic matter, but it is now known that both magmatic and metamorphic rocks have the capability to do so (Javaux & Benzerara, 2009). Precambrian microfossils have been found from the metamorphic grades of sub-greenschist to amphibolite facies, but confirming biogenicity and syngenesis is increasingly difficult with deformation and age (Igisu *et al*., 2006). Microfossils can be preserved either as lithifications through compression, or by permineralization. For obvious reasons, permineralization result in the most well preserved structures (Schopf *et al*., 2010). Laboratory experiments have given insights into the processes of fossilization, which, as a complement to the fossil record, facilitates recognition of true biogenic structures. Elevated temperatures catalyze fossilization, and results in similar fossils as those being produced in lower temperatures for a longer period of time. It has also been demonstrated that organic matter is preserved more often than previously imagined (Javaux & Benzerara, 2009).

Body fossils are the morphological remains of an organism. Under exceptional conditions soft parts may be preserved, but normally only the hard parts are. Early life forms lack hard parts, which makes preservation less likely (Konhauser, 2007). Cyanobacteria colonies excrete a substance called EPS (extra-cellular polymeric substances). The substance works as an adhesive to which particles from the sea column get stuck, which causes the wrinkled structures seen in the

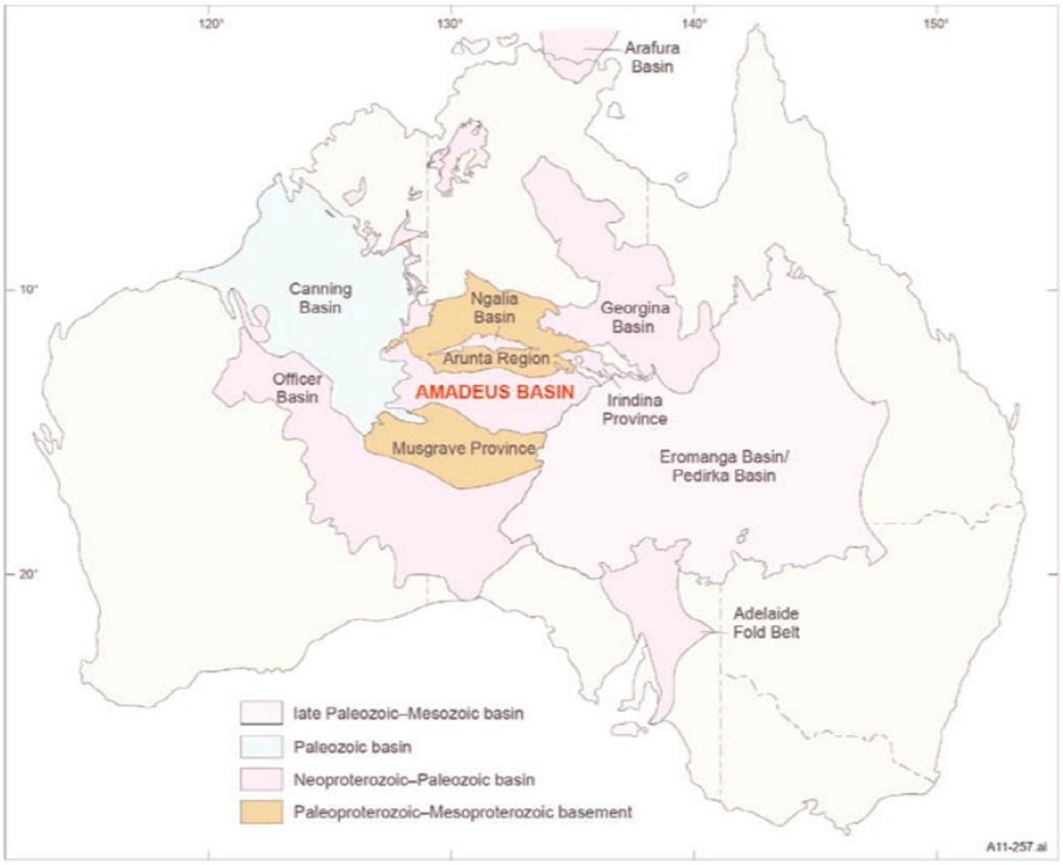

Fig. 3. Map of Australia. Amadeus Basin is marked in red. From Edgoose (2012).

fossil record. The EPS can form mineralised biofilms that persist even when all other traces of the organisms are gone, but microfossils have a better chance of preservation if they are covered by it. Cyanobacteria are also larger than most bacteria, which gives them a better chance of being at least partially preserved (Wacey, 2009). The calcium carbonates they produce aid them in establishing a post-mortem equilibrium with their surroundings, which also facilitates original mineral preservation. When preserved in other sediments (e.g. silica or pyrite), the risk of mineral replacement is higher (Javaux & Benzerara, 2009). Most Precambrian fossils with their original structure are preserved in silica. This is probably because of the small grain size of silica, which can form around even small structures. With other minerals, such as pyrite, the grain size is too large to form around the small microstructures (Konhauser, 2007). In carbonaceous matter, microfossils can be preserved as carbonaceous objects. Because of the sedimentation and the mechanical stress they are put under, they are often found flatted and deformed. Taphonomic degradation could actually be a good thing, as it shows that the cell wall was indeed flexible. If the sedimentation is rapid, they can be preserved in three dimensions, but a perfectly undeformed 3D structure might also be an indicator that one is dealing with an abiologic structure (Javaux & Benzerara, 2009).

Chemical fossils are the result of organismal metabolic activities, waste products and decay. They are also the most likely type of fossil to be preserved. The most common types of chemical fossils are light isotopes of carbon and sulphur. Since no element, as we know it, can replace carbon as the fundamental building block of life, it is generally concluded that early life was also carbon based. Therefore, it is also probable that early life caused carbon isotope fractionation (Wacey, 2009). Sulphur is one of the first elements used in metabolism (Shen *et al*., 2001). Isotope analysis of ancient sulphides, such as pyrite, can detect biogenic sulphate reduction and oxidation. The ratios of sulphur isotopes in rocks are therefore indicative of sulphur-metabolizing microbes. The lighter isotopes are more easily incorporated in the H_2S. The most common molecular fossils are hydrocarbons (e.g. sterols) from cell lipids, which can survive low-grade metamorphism. Fischer-Tropsch type reactions are abiogenic, but can produce isotope fractionations that fall within the range of biological activity. They can be created in the reaction between CO_2 and metals, or from the reduction of siderite. It is also possible for hydrothermal vents to produce light carbon isotope fractionations, and this poses a problem when analyzing putative fossils from those habitats (Wacey, 2009).

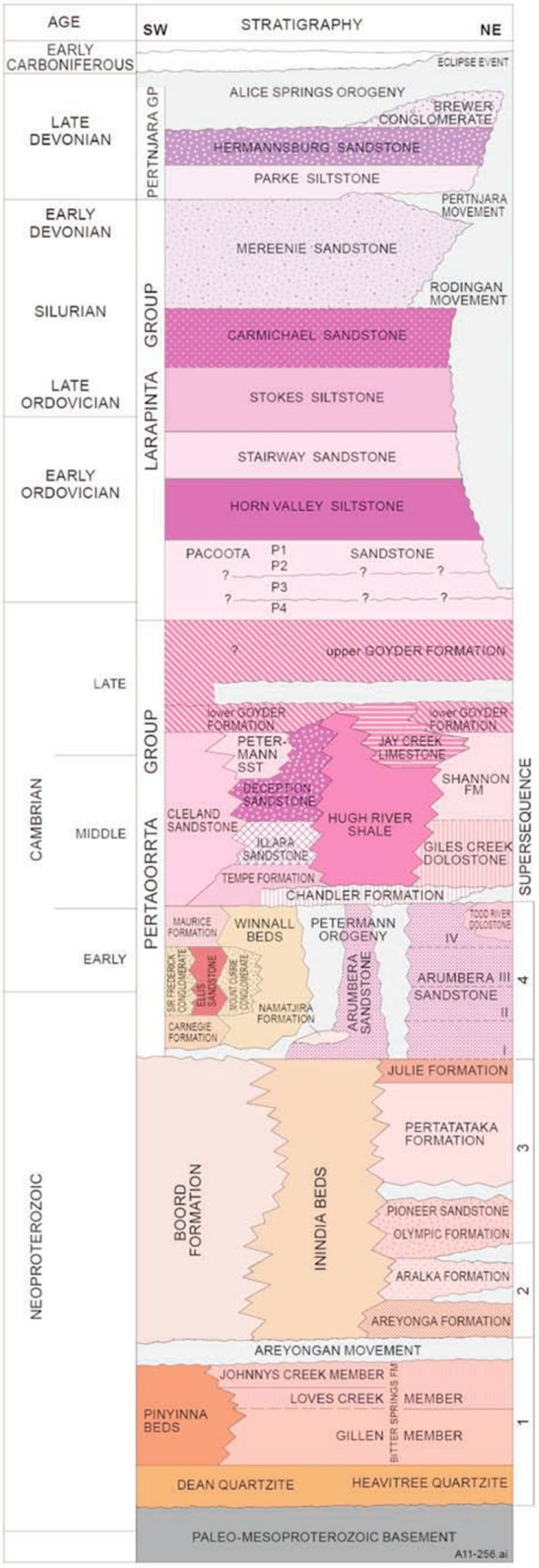

Fig. 4. Stratigraphy of Amadeus Basin, Australia. From Edgoose (2012).

3. Geological setting: Bitter Springs Formation, Australia

Bitter Springs Formation belongs to the basal part of the Amadeus Basin stratigraphy. The intercratonic sedimentary Amadeus Basin, which host up to 14 kilometres thick sedimentary successions, is situated in central Australia over an area of 170 000 km^2 (800 km E-W, 300 km N-S; Fig. 3). The depositional history of the Amadeus Basin began in the Neoproterozoic (around 850 Mya), and continued until Devonian (360 Mya). During the sedimentation of the Bitter Springs Formation, the Amadeus Basin was part of the Centralian Superbasin, which was created in the intercratonic extension during the breakup of Rodinia. The northern and southern boundaries of the Amadeus Basin were later set by two orogenic events; the Petermann Orogeny (580—540 Ma) and the Alice Springs Orogeny (450—300 Ma). The western and the eastern boundaries are defined by where they are overlaid by younger basins. The underlying layer is the Musgrave province basement, which is of Paleo-Mesoproterozoic age. The Amadeus Basin starts with the Heavitree and Dean quartzites, which are concurrent sedimentations in different parts of the basin. They are interpreted to be deposited in an high-energy, shallow shelf environment. Based on zircon dating, the quartzite depositions have a maximum age of 1050—1000 Ma (Edgoose, 2012).

The Bitter Springs Formation directly overlays the Heavitree and Dean quartzites. Bitter Springs Formation comprise three members; Gillen, Loves Creek and Johnny's Creek (Fig. 4). They are composed mainly of crystalline dolomitic limestone, limestone, dolostone, sandstone, red calcareous siltstone, halite, evaporites and chert. Stromatolites are common in Loves Creek and Johnny's Creek Member, which also includes a spilite layer that has been used to date the members to an approximate age of 820 Ma (Edgoose, 2012). Intertidal and fluvial depositions characterize the initial depositions, with a maximum water depth during the formation of Gillen Member. In Loves Creek Member the water shallows and the depositional environment shifts to lacustrine. Highly altered basalts can also be found here. Closer to the top of the formation, stromatolites, microfossils and acritarchs have been found (Walter *et al.*, 1995). Evaporites as a consequence of salt tectonics occur here, as the Bitter Springs Formation includes the earliest known major salt deposit (Blewett, 2012). The top of Bitter Springs Formation has been dated using the Stromatolite assemblage *Acaciella australica*, to older than 800 Ma (Edgoose, 2012).

3.1 Microfossil preservation

Bitter Springs is one of the most well preserved localities for Precambrian fossils. Cell division, cell walls and membranes, surface textures and cellular contents

are some of the things found in this locality (Schopf & Blacic, 1971). It has been exhaustively described by Schopf & Blacic (1971), who identified 38 genera of microfossils in the formation. Coccoid and filamentous cyanobacteria are found in abundance, as well as eukaryotic cells and acritarchs, and various eukaryotic thallophytes (e.g. fungus and algae). According to Schopf & Blacic (1971), many cyanobacteria taxon are similar to modern forms that dominate stromatolite formations today. Sedimentation in Bitter Springs was predominantly carbonaceous, making it an ideal growth environment for algae and stromatolites. For some reason, amorphous silica was precipitated which buried the biota and later permineralized them. The rapid precipitation prevented compression of the fossils and many have been preserved in an exceptional state (Schopf & Blacic, 1971). The waters in which they existed were saline and anoxic, which seems to have facilitated fossilization as it prevented bacterial sulphate reduction (Southgate, 1986).

4. Methods and material

In order to identify microfossils or organic traces in the rocks, a number of methods were used; Petrographic studies, X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). All of the experiments were conducted at the Geological Department at Lund University except for FTIR, which was carried out at MaxLab in Lund.

4.1 Material

The material used for this study comprises four rocks, collected in 2012, from Johnny's Creek Member, Bitter Springs Formation (Fig. 5).

4.1.2 Production of thin sections

From each sample one thin section was produced. The four samples and their corresponding thin section will be referred to as A to D. The rocks were cut in thin slices and glued to glass slides using epoxy adhesive. The rocks were then grinded to preferred thicknesses. In order to preserve potential microfossils in three dimensions and to prevent the mineral grains from becoming transparent, they were kept relatively thick (approximately 200-400 µm). Because of the differences in rock quality, the thin sections were grinded to varying thicknesses. The thin sections were later polished with diamond sandpaper until a smooth surface was attained. The thin sections were not covered by glass. Four thin sections (30 µm) from the same rocks were delivered by a professional thin section manufacturer. They were covered by glass, which prohibited further investigations for chemical composition, and were therefore only studied in optical microscopy.

4.1.3 Additional cuttings and HF maceration

Two additional rock slices from two rocks (A and D) each (4 in total) were cut to a thickness of approximately 0.5 cm and polished. Two sections were then polished with liquid diamond paste (1 µm) until superpolished surfaces were attained. Two sections were put in hydrofluoric acid for approximately one minute to attain etched surfaces in which siliciclastic material would be dissolved and biological material would become pronounced.

Fig. 5. Pictures from Johnny's Creek Member, where the rocks were collected.

4.1.4 Preparations for FTIR

Material from the rocks was removed using a drill with a diamond drillhead. The pulverized material was collected in clean glass jars. Ten samples were taken from different rocks. Both the diamond top and rocks were cleaned before each sampling using ethanol and dried with high-pressure air.

4.2 Petrography

Thin sections were searched for potential microfossils. Helpful guidelines were taken from an extensive publication on the microfossils of Bitter Springs (Schopf & Blacic, 1971), in order to pinpoint potential biological structures. Filamentous and coccoid bacteria, macro- and microscopic stromatolite structures, fungi and algae were among the described fossil types. Biogenicity criteria derived from Wacey (2009) was taken into consideration.

4.3 XRF

Investigation by X-Ray Fluorescence (using Niton XL 3t Goldd+ with software NDT) was done on fresh surfaces from the samples A-D in order to gain information regarding the general chemical characteristics of the rocks. Some tests were also run on the weathered surface of sample A. A system check of the equipment was preformed at the start of each testing day. Before the first, and later between every 10-15 readings, a sample with known chemical composition (standard 2709a) was tested to estimate accuracy and recognize potential drift. Sample A-D were analyzed and each sample was tested at selected spots (3mm in diameter) between 6 and 15 times depending on the size of the sample. Four identical tests were run for each selected spot, in total lasting 12 minutes per spot (three minutes per test). Based on those four readings, a mean was calculated for each spot. No anomalies were detected. The spots were chosen so that they would represent differential areas of the samples. The surface of sample A appeared weathered, and three tests were taken from the external surface (A13-15 in Appendix).

4.4 SEM

Thin section A, C and D, super polished slices of sample A and D and HF acid macerated sections of A and D were investigated by scanning electron microscopy (SEM, model Hitachi S-3400N with EDS analyser software INCA, developed by Oxford Instruments). The samples were beamed with 15 kV at a 10 mm working distance. Thin sections were cleaned with 95 % ethanol and handled with rubber gloves prior to insertion into the SEM. Since the studied samples could not be carbon coated, the SEM results were not precise. Using the high vacuum setting, voltage accumulates in the surfaces of the studied samples, and the results are therefore only semi-quantitative. With the low vacuum setting, the results are even more inaccurate but the imaging is better, which results in better aim when targeting specific structures. Although the results cannot be used for quantitative analysis, they reveal which elements are present and give indications of their relative concentrations. As suggested by Wacey (2009) it is important that the same structures found with SEM can be found with an optical microscope. With the high contrast and low colour resolution that characterizes SEM imaging, topographic differences can resemble morphologically simple fossils. The reported structures from SEM analysis are therefore only those that were found both with SEM and optical microscope, which was challenging due to the minute size of the putative fossils and the dissimilarity between SEM and microscope imaging.

4.5 FTIR

FTIR was conducted at MaxLab research facility in Lund using a Hyperion 3000 microscope, which is connected to a Bruker IFS66/v FTIR spectrometer. This enables visual aim of putative fossil structures before beaming them. The pulverized material was spread out using a clean pair of pliers on a calcium

Table 2 explains why various methods are being applied. Petrography is the best method for detecting fossils in thin sections. XRF provides quantitative information on the chemical content of samples, but does not detect light elements. SEM could not be used for quantitative results, as the studied material could not be carbon coated, but is good for detecting interesting structures through elemental mapping. FTIR is the only method applied that provide information on molecular bonds, which is why it can be used as verification tool for putative chemical or body fossils.

	Microscopic imaging	**Elemental Analysis**	**Molecular Analysis**	**Speciality**	**Weakness**
Petrography	+	-	-	Identifying fossil structures	No chemical information
XRF	-	+	-	Provides quantitative chemical content information	Does not detect light elements
SEM	+	+	-	Provides chemical information, imaging and elemental mapping	Produces semi-quantitative analysis results, as the samples cannot be carbon coated
FTIR	+	-	+	Detects molecular bonds	Demands substantial preparations

Fig. 6. Bruker IFS66/v FTIR spectrometer connected to a Hyperion 3000 microscope at MaxIV, Lund.

fluoride lens designed not to absorb any infrared light, and semi-dense spots were selected for testing. When the material was too dense, there was no signal, and when it was too thin, the spectrum fluctuated heavily. Some samples had to be tested numerous times to get an acceptable reading. The super polished sections of sample A and D were also tested using the backscatter setting, which reveals the chemical content on the surface but not further into the section. Before initiating the beaming, a background scanning was performed. Through the use of Opus Spectroscopy Software an absorption spectra was obtained. Each spectrum was produced from 128 scans, which were automatically calculated into a mean. As the samples were put in ambient air, a weak CO_2 signal (absorption at 2400 cm $^{-1}$) would always be detected (Benning *et al*., 2004), although it was later compensated for using the Opus Spectroscopy software. The absorption will create different signals depending on the structure of the molecule. Special features in the spectra can detect the presence of lipids, proteins, fatty acids, nucleic acids and polysaccharides. It is a non-intrusive method, even when studying samples for long periods of time. FTIR spectroscopy detects molecules with bonds between different elements (e.g. C-H and C=O), but it does not detect single elements or single element molecules. By identifying peaks in the spectrum, information about the molecular composition was derived. Each compound will peak at different values, which produces a spectra used for elemental analysis (Benning *et al.,* 2004).

5 Results

Data from XRF analysis is presented in Table 1. By calculating the mean from all test spots from each sample, the general chemical composition of each rock was acquired (for full data set, *cf*. Appendix). For this table, the three test spots made on the external surface of sample A were removed as the internal chemical composition was sought. Elements detected but not displayed, due to their minor addition to the composition, were; S, Ti, As, Sr, Zr, Mo and Ba. XRF does not detect elements lighter than Neon, which means that the amount of detected elements will not be total. Although the testing spots from each rock were chosen to represent differential areas, the fluctuations in chemical composition did not show any obvious deviations in accordance to the different characteristics of the test spots. In sample A and B the testing spots showed a diffuse anti-correlation between silica and calcium (*cf*. Appendix), although silica is the heavily dominating component. Sample C and D contain nearly no calcium, which means that the same relationship cannot be established for them. The analysis on the weathered surface of sample A showed a differentiating chemical composition; chlorine, potassium, aluminium and iron were higher and calcium and silica were lower than on the cut surface. Although no fully quantitative results could be drawn from SEM (high-vacuum) analysis, large amounts of oxygen were detected throughout the samples, which is an element that cannot be detected in XRF. Additional elements detected in low concentrations with SEM were: carbon, aluminium, calcium and magnesium.

Tab. 1. The table shows means that were calculated using data from XRF. All values are stated in ppm and percentages.

	A	B	C	D
Si	436202 (43.62%)	452544 (45.25%)	519783 (51.98%)	474331 (47.43%)
Ca	64638 (6.46%)	81766 (8.18%)	649 (0.06%)	1491 (0.15%)
Al	5806 (0.58%)	7621 (0.76%)	7216 (0.72%)	13502 (1.35%)
P	8225 (0.82%)	11184 (1.12%)	7789 (0.78%)	10156 (1.02%)
Fe	1367 (0.14%)	356 (0.04%)	108 (0.01%)	1238 (0.12%)
Cl	7294 (0.73%)	2999 (0.3%)	1262 (0.13%)	1289 (0.13%)
K	303 (0.03%)	313 (0.03%)	559 (0.06%)	1966 (0.2%)

A shared feature throughout the thin sections is the occurrence of darker spots, which are macroscopically displayed in sample A (Fig. 7). These spots range in colour from black to brownish red, and are highly distinguishable from the matrix. The spots are either aggregated in clusters, or dispersed over larger areas.

Sample A: The overall chemical composition detected through XRF was comprised of silica (43.62%) and calcium (6.46%). The matrix of the thin section is essentially homogenous in colour, but striations with a coloration ranging from red to yellow occur in a steep SW-NE direction on the left side of the sample, which seem to be continuously connected to the distinct layered structure on the exterior surface (Fig. 8). On the

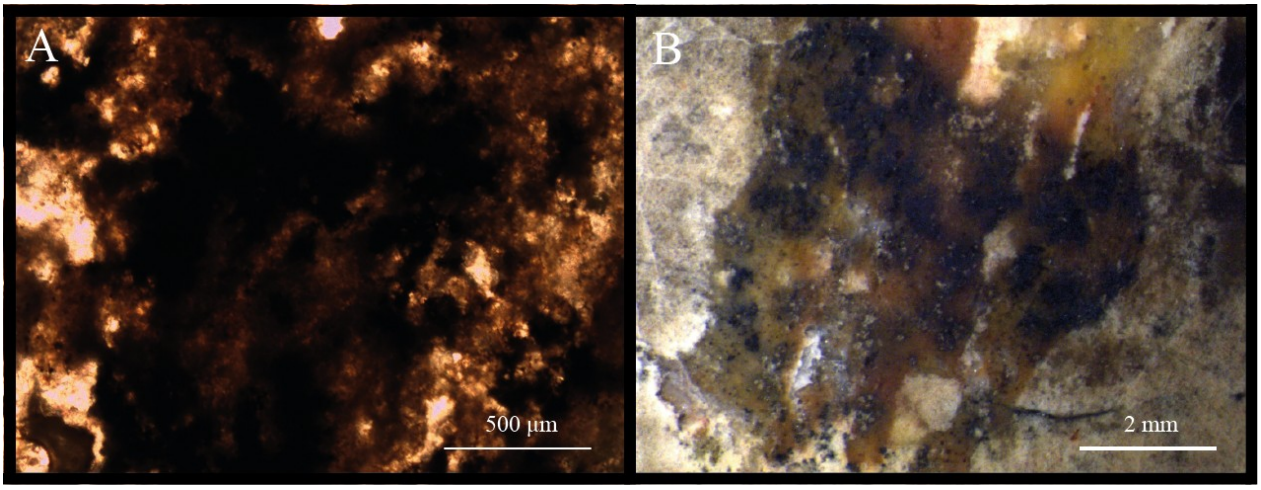

Fig. 7. Clusters of dark spots in the middle of sample A. **A.** From optical microscopy (thin section A). **B.** From stereomicroscopy (super polished sample A).

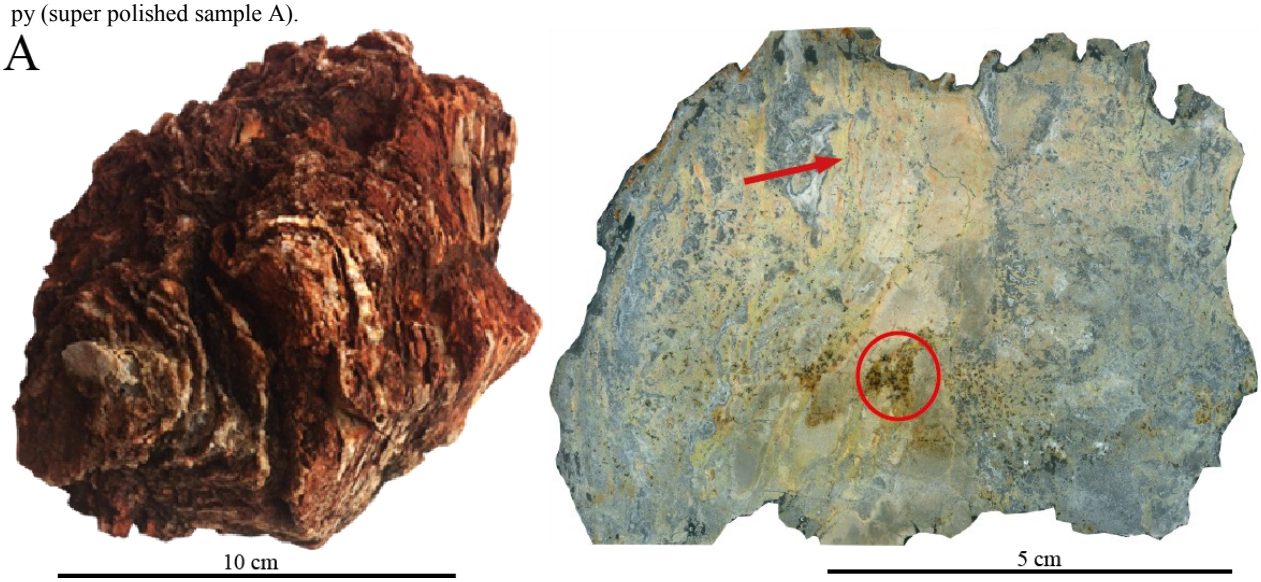

Fig. 8. Sample A to the left. Thin section produced from sample A to the right. The circle marks an area where dark spots are clustered. The arrow points towards red striations in the thin section..

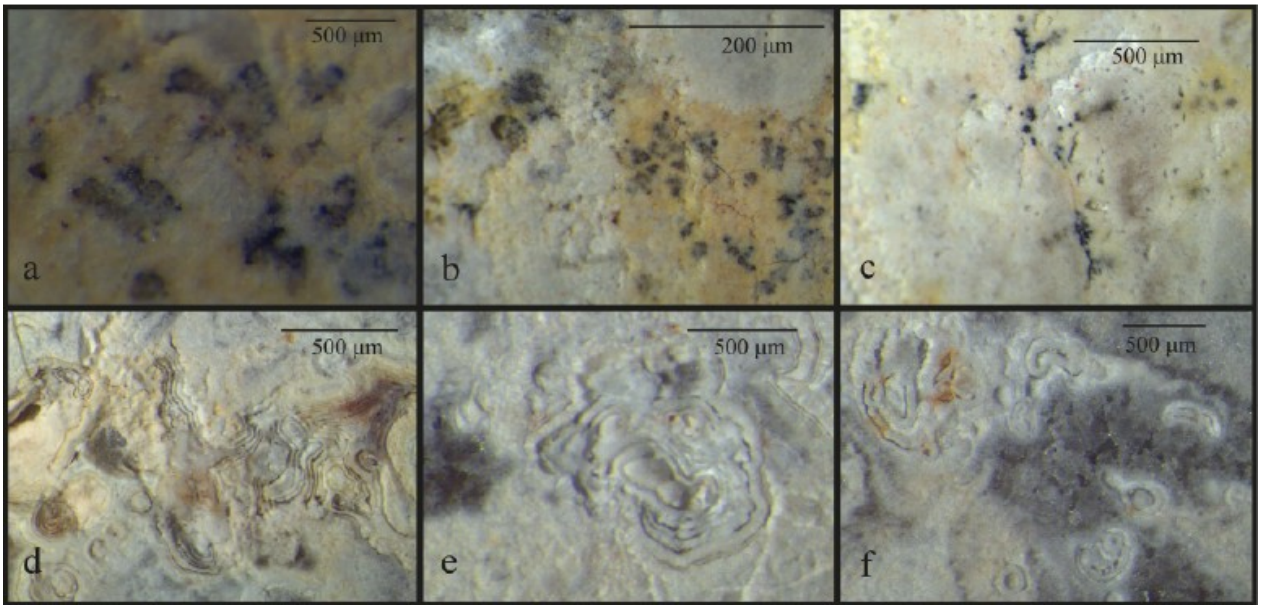

Fig. 9. HF macerated sections. **A-C**: From sample A. **D-F**: From sample D.

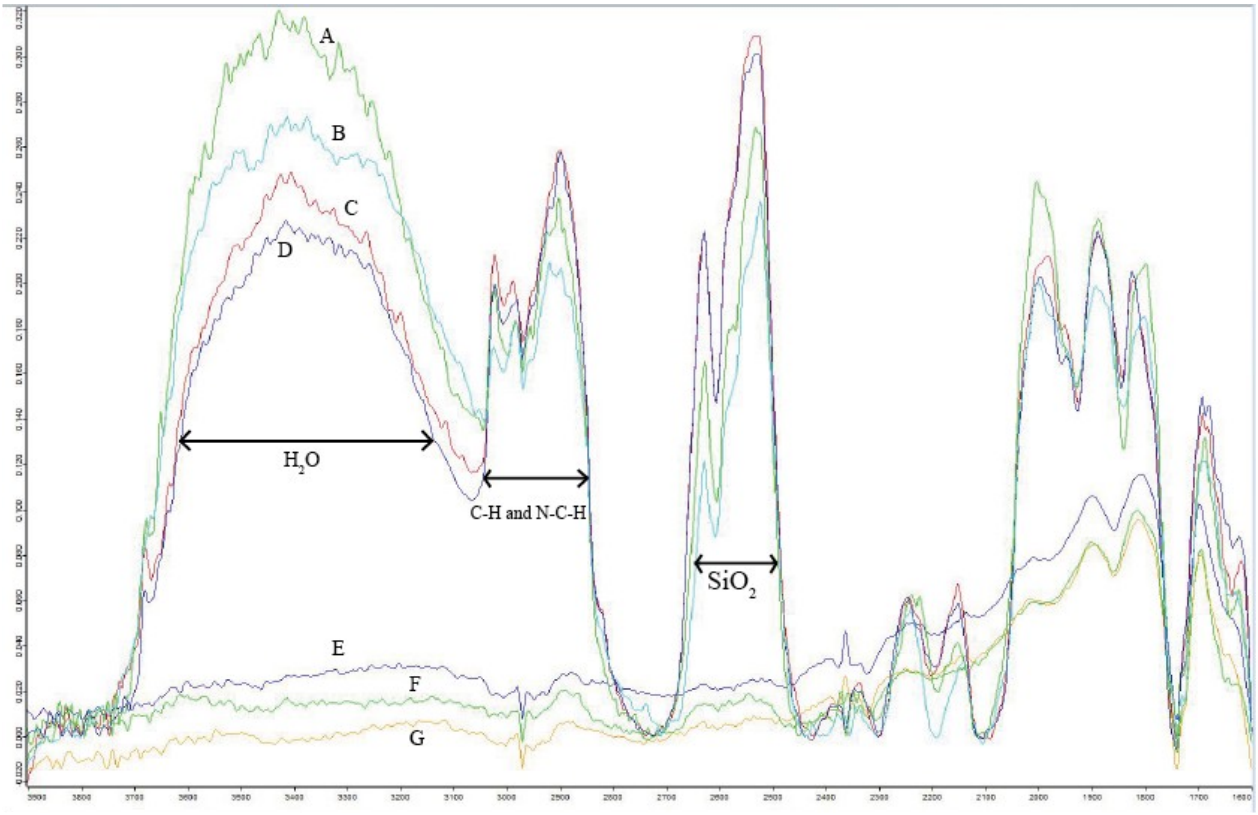

Fig. 10. FTIR spectra from sample A. Spectra A-D were derived when targetting exposed dark spots. The peak around 3030 cm^{-1} to 2830 cm^{-1} are within the area where hydrocarbons and hydrocarbons with nitrogen are absorbed. Spectra E-G was derived when targeting other areas on sample A.

right side of the sample, there are no apparent structures. Within these striations, which are occasionally sinuous, aggregations of dark spots are found in abundance. Two larger aggregations occurred, and in the rest of the striations the dark spots are more dispersed. Outside the striations, they are found in much less abundance. The area with aggregated black dots (Fig. 7) was tested with SEM (low-vacuum) and elevated carbon levels were detected compared to the surrounding matrix. In areas where carbon levels were higher, calcium, magnesium and faint signals of aluminium were also detected. In some spots, carbon levels were higher than calcium levels; in other spots they were approximately equal. In some spots, calcium levels were higher. When exposed to HF maceration, the dark spots appeared to be unaffected (Fig. 9). The HF macerated section had higher calcium levels than in the untreated sections, and fluorine was also detected. The super polished section from Sample A is similar to the thin section when studied in a stereomicroscope, although the red striations are more sinuous in this section and the colours are more lustrous. FTIR-spectra from superficially exposed dark spots showed peaks around 3030 cm^{-1} to 2830 cm^{-1} , which are areas where C-H and N-H-C are absorbed. Other areas in the section produced very different spectra, without peaks in the area for organic molecules (Fig. 10; Appendix). The pulverized material from sample A also showed faint peaks in the C-H area, but less pronounced.

Sample B: The overall chemical composition was

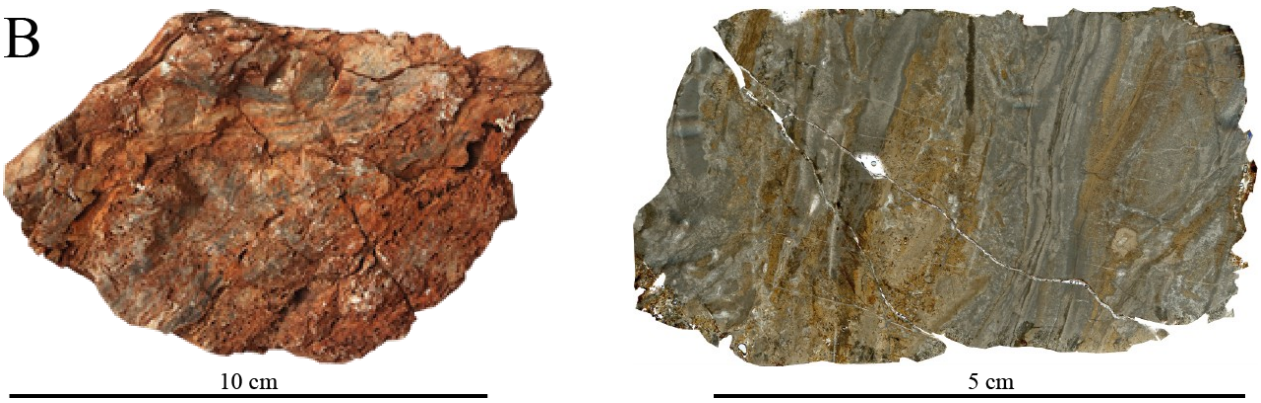

Fig. 11. Sample B to the left. Thin section from sample B to the right.

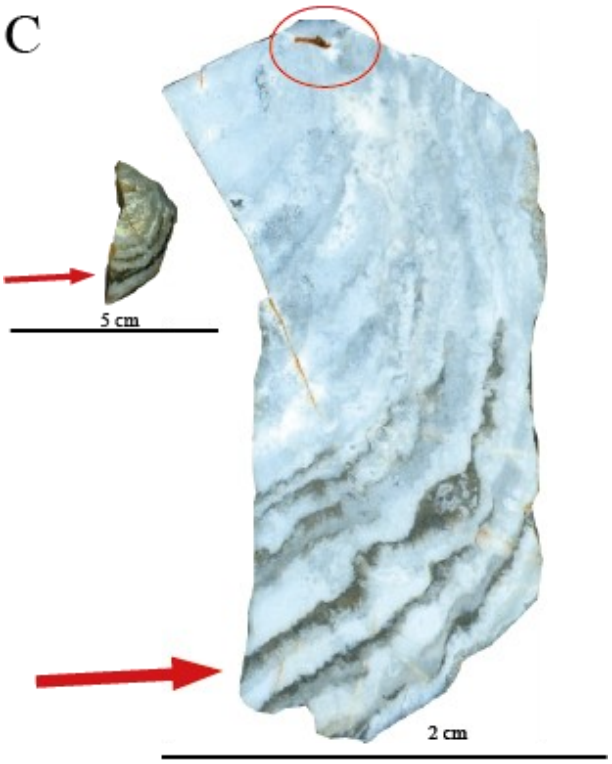

Fig. 12. Sample C to the right. Thin section from sample C to the left. The arrows point towards the layering discussed in the text. The circle marks the macroscopic structure discussed in the text.

very similar to sample A; silica (45.25%) and calcium (8.18%) was detected in XRF, and SEM analysis (high -vacuum) revealed substantial oxygen levels. The thin section is grey and has a relatively homogenous but layered morphology. The layering is more unison in colour than in the rest of the samples. Small dark spots are detected where the layers are darker (Fig. 11).

Sample C: XRF analysis showed an elevated amount of silica in the sample (51.98%) and low calcium levels (0.06%). The dark striations on the exterior surface go through the whole sample and when cut in half, they appear increasingly clear. The striations are aligned in a dome-like shape and are wavy with irregular arcs, which are directed at the same angle. Like in the previous thin sections, patches of black dots are present (Fig. 12). Structures were found that morphologically resemble cellular structures. The most distinguished structure is an irregular reddish-brown structure near, but not in contact with, one of the edges (Fig. 13). The structure was also investigated in SEM (low vacuum). Test points were taken from inside the structure and immediately outside. The structures displays high amounts of carbon, and significantly lower silica and oxygen levels compared to the external part of the structure. Tests run on the bottommost part of the structure (as seen from the picture) also resulted in faint potassium, magnesium and aluminium peaks.

Sample D: In chemical composition, sample D is similar to sample C (47.43% silica and 0.15% calcium), but with a slight elevation in aluminium (1.35%) compared to the other samples. This thin section displays a more complicated structure than the others (Fig. 14). Repeated patterns of lighter and darker brown layers are interrupted by some material of middle brown to reddish brown colour, with distinguishing layered dome-like structures. The dome-shaped structures occur in large portions of the thin-section, also as interruptions in the layered area. Some dome-like structures display smaller spherical structures in association to the layers (Fig. 15). The superpolished section derived from sample D reveal patches of transparent amorphous silica. With this transparency into the section, it is apparent that these dome-shaped structures are three-dimensional (Fig. 15c-d). There was no apparent effervescence when placing the section in HF acid, but there were substantial alterations

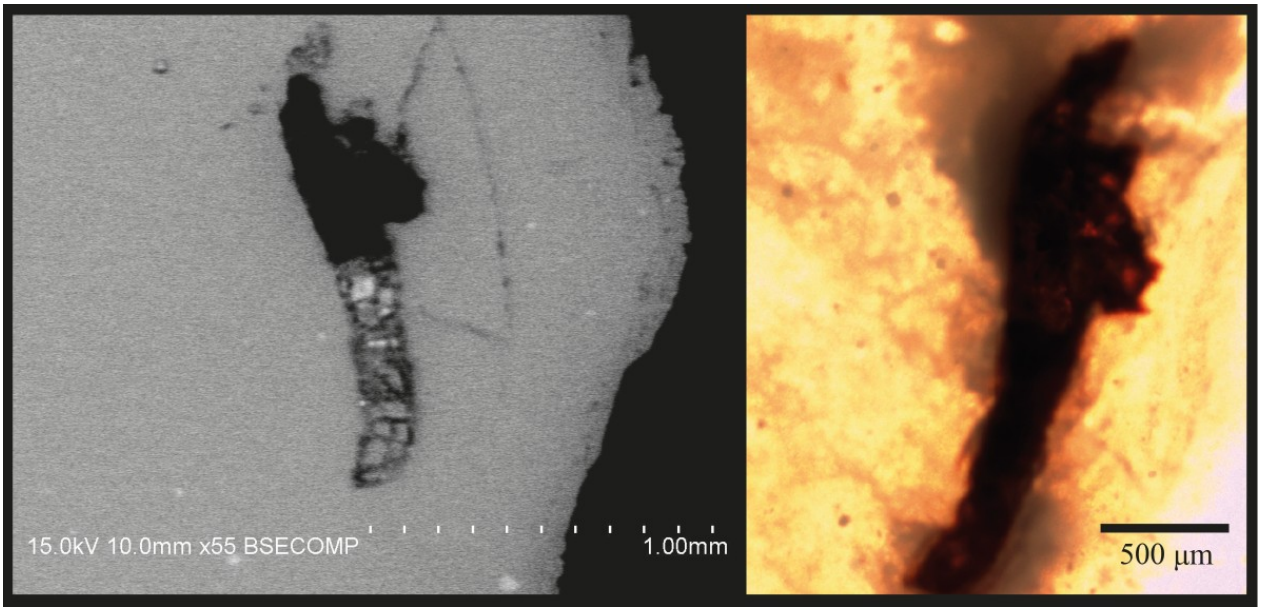

Fig. 13. Macroscopic structure from thin section C. SEM imaging to the left, optical microscope imaging to the right.

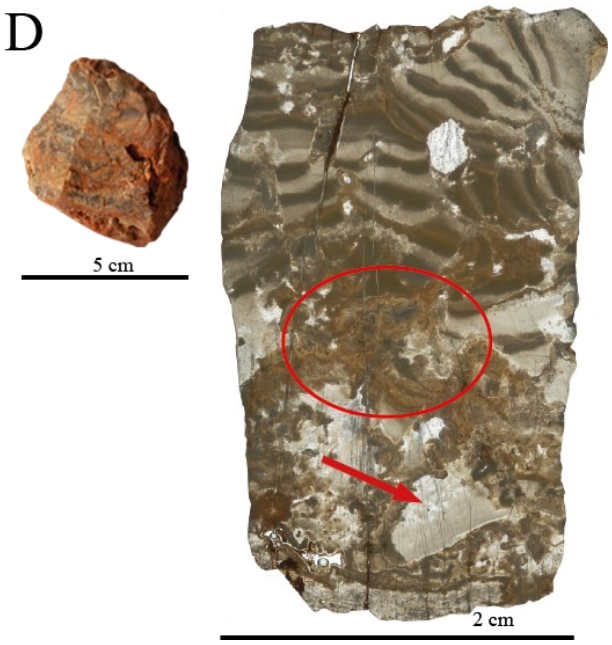

Fig. 14. Sample D to the right. Thin section D to the left. The circle marks an area where dome-like structures are in abundance. The arrow points towards an area of amorphous silica .

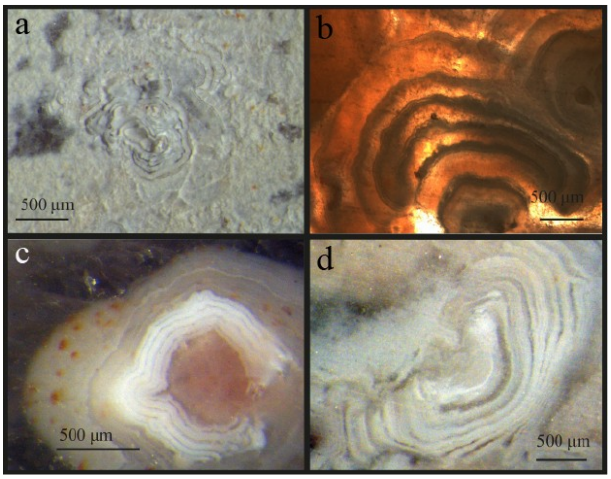

Fig. 15. Dome-like structures from sample D. **A**: HF macerated dome-like structure. The inhomogeneous maceration indicates different materials to occur inside the layers and between them. **B**: optical microscope picture of a dome-like structure: **C** and **D**: dome-like structures in super polished slices of sample D. The structures are continuing down into the rock.

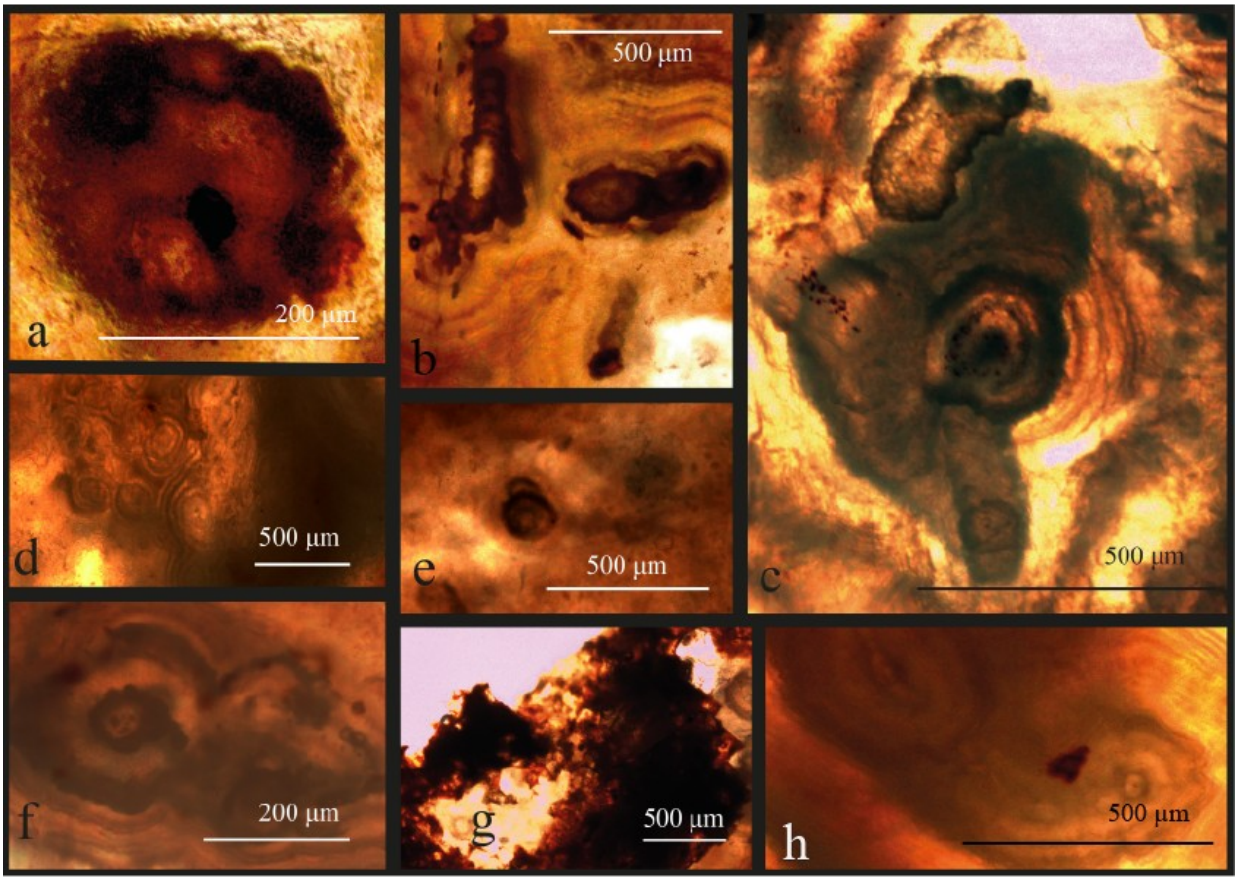

Fig. 16. Selected interesting areas from thin section D (all except **E**) and C when studied in optical microscope. **A**: Coccoid formations inside a reddish brown circular area. This structure holds similarities to cyanobacteria, which often aggregate in clusters and have been found in Bitter Springs Formation. **B**: Two unidentified objects in the upper part of the picture. The structure in the bottommost part displays potential coccoids in a pearl-band arrangement. The structure is obliquely aligned in relation to the surface, but the exposed area (lowest part) is reddish brown. **D**: These circular patterns occur repeatedly. **E**: Possible cell wall. **G**: Reddish brown material, possibly biogenic. **H**: Diffuse pearl-band structure.

on the section. The dome-like structures became conspicuously laminated, as the layers macerated inhomogenously (Fig. 15a). When analyzed in SEM (high-vacuum), fluctuating levels of carbon was found in thin section D (ranging from 0 to 15 %). The highest carbon level was detected when targeting a dome-like structure. No calcium peaks were detected in this thin section. Various structures were detected in optical microscope; especially interesting are Fig. 16a, b, c and h. The super polished section of sample D was studied in FTIR, but no organic signals were detected. The section only emitted silica signals (*cf.* Appendix).

6. Discussion

The Bitter Springs Formation is a late Proterozoic unit, and well known to host microfossils, chemical fossils and stromatolites. Furthermore, from previous environmental analyses it is clear that these rocks were not formed in a turbulent environment (Edgoose, 2012), which might result in formations similar to stromatolites. In the search for the earliest life forms in localities previously unknown to host traces of life, increased vigilance is strongly advised. The thin sections produced at the University proved far more useful than the ones attained from the thin section manufacturer. It became evident that each rock must be grinded to its own optimal thickness, in accordance to its specific features, and that a standardized thickness will not work for all rocks. The thin sections should continuously be checked in a microscope as they are being worked on, and in order to preserve three-dimensional fossils they should be kept relatively thick. To use the same sample for all investigations is highly recommended. XRF can be used if information regarding the mineral composition of the rock is being sought. In cases where the affiliation of a fossil to a specific site is being questioned this method would be very useful. It is also useful for understanding the fossilization process in a particular area. XRF analysis provides information on the chemical composition of the samples, but it does not detect biological building blocks such as carbon, nitrogen, hydrogen or oxygen. Although it does provide a reading of phosphorus, that element is within the "noise region" and is not a highly reliable source of information. The environmental interpretation of rocks from the Bitter Springs Formation as a result of silica precipitation in a shallow shelf environment fits well with the results from XRF analysis; domination of silica with a significant amount of calcium (primarily in sample A and B). The anti-correlation between calcium and silica might come from the fact that where the silica concentration is at its highest, there is basically not room for anything else. Although the calcium in sample A and B indicate limestone to be present, the samples did not effervescence when exposed to HF acid. Since the aluminium levels were extremely minute, feldspar could also be eliminated as a potential mineral. Due to the weathering, iron and aluminium levels were higher on the external surface of the rock, which is typical for weathered rocks as it has very low mobility and does not erode as easily as other elements. SEM is recommended for pinpointing interesting sites that can be further tested with FTIR. Although it does not distinguish between biogenic and abiogenic elements, SEM provides valuable insights regarding locations where further analyses should be conducted. FTIR is useful for ultimate determination if a structure is biogenic or not. By using the backscatter setting in FTIR, thick sections could also be analyzed. The results were not as precise as those produced by a penetrating beam on a thin section, but these kinds of sections are much more easily produced and three-dimensional microfossils can be kept intact. Thin sections used for this cannot be placed on glass, which makes these more challenging to produce. For the acceptance or rejection of fossils, the use of thicker sections was sufficient. FTIR has until recently mostly been used on larger fossils (e.g. acritarchs), but due to improvements in spatial resolution new possibilities in the analysis of smaller microfossils are opening up. The potential usage of FTIR spectroscopy for the detection of extraterrestrial life during future space missions is also being investigated (Marshall *et al*., 2006).

Sample A: Due to the fact that sample A externally resembles a stromatolite, more confidence can be added to the interpretation of the internal features, although it is not evidential. As the red striations are continuations of the layering on the exterior surface, the layers might have been somewhat separated, which allowed microbes to enter the rock, and during silicification it closed. It is also possible that the microbes lived on those layers before being permineralized. The right side of the sample seems to have been reworked, possibly dissolved and cemented back together. The homogenicity in the material indicates that it is made of the same material as the rest of the sample and is probably of the same age. As no quantitative data could be derived from the use of low vacuum SEM, only visual evidence and relative chemical compositions could be drawn from the analysis. From the analysis of the dark spots on sample A (Fig. 7), it can be concluded that they are more carbonaceous than the surrounding matrix but also that they comprise calcium, which indicates the presence of $CaCO_3$. This fits with the environmental model for Bitter Springs Formation, but it is also a characteristic of cyanobacteria. SEM cannot detect chemical bonds, meaning that it cannot be concluded from this type of analysis if it is biogenic or abiogenic, although due to its colour and morphology it is probably biogenic. Due to the fact that the dark spots appeared unaffected by HF further indicates biogenicity. The dark spots in the striations indicate that organic material was once present, but that it later degraded. The heightened fluorine levels in the HF macerated section were in all probability present as a consequence of the HF treatment. The calcium peak was also more pronounced, which might mean that some of the siliciclastic material dissolved and the calcium level rose in comparison. The dark

spots analyzed in FTIR resulted in peaks in areas associated with organic material, which is a strong indicator of biogenicity. The pulverized material from one of the clusters of dark spots also resulted in a faint peak in the C-H absorption area, which indicates a biogenic origin for them as well. The peak is within the same area as the peaks from microfossils from Bitter Springs Chert, studied in FTIR by Igisu *et al*. (2009).

Sample B: Apart from the dark spots occurring in all of the thin sections, no structures were detected that could be interpreted as biogenic.

Sample C: The clear striations indicate some sort of biogenically produced formation. Since dark spots are more abundant in the darker layers, and since the striations are wavy with irregular arcs directed at the same angle, it might be argued that this was produced by stromatolitic activity. The macroscopic structure on thin section C (Fig. 13) displays highly elevated carbon levels compared to the encompassing minerals and is probably biologic. The preservation comes across as fundamentally different from the rest of the rock, and might not be contemporary to the sedimentation. Even though there are no obvious cracks in relation to the structure, it is situated near the edge of the sample and might hade entered the rock at a different stage.

Sample D: The darker and lighter layers appear to be primordial compared to the chaotic dome-like structures, although their similar preservation mode indicates that they are close in age. The super polished section reveals the dome-like structures to be three-dimensional. In Fig. 15b, spherical structures (possible microbes) are found in association to the layering and the layers are brighter on the upper surface and darker on the lower. The shapes of the layers are following that of the nucleus. These features are characteristics of oncoids, according to Jones & Renaut (1997). Microbes in association with oncoid layers can grow by several magnitudes due to silicification, which could explain why they are easily detected. Oncoids are most commonly occurring in shallow sea environments, which correspond with the depositional environment for the sample. A flat base, such as in these structures, is a common morphological type for oncoids (Jones & Renaut, 1997). The elevation in carbon (detected in high-vacuum SEM) in one of these structures further indicates biogenicity. The HF macerated slices of sample D shows that the layers in the dome-like structures macerate in variable amounts, which could be due to an organic sheet covering the layers. The likelihood of a mineral zonation is small due to the fact that the maceration affected the layers of the structure so differently. Ooids are generally uniform in size, circularly symmetric and have a radial-concentric internal structure. The putative oncoid structures are more heterogeneous in size and morphology and are not radial-concentric. The structures are therefore probably not ooids. The structures do not contain aluminium, which means that bauxite can also be rejected as a potential cause for the structures. Furthermore, bauxite is generally more spherical than these. Several of the structures in Fig. 16 are similar to bacteria. The pearl band formations of spherical structures included in a larger sphere (Fig. 16a) are typical for cyanobacteria. The pearl band structure in Fig. 16b resembles coccoid bacteria, and the colour of the exposed sphere is reddish brown, indicating carbonaceous material. The spherical structure in Fig. 16c includes a bent filament formation with overlaying material of a reddish brown colour, which could be interpreted as a bacterial filament with degraded biogenic material. As none of the structures in Fig. 16 were tested by other methods they cannot be deemed as certainly biogenic, although there is a strong possibility that they are.

6.1 Contaminations and pseudofossils

Precambrian fossils are small, incompletely preserved and can be mimicked by abiologic processes. This makes the separation between fossils and pseudofossils hard to distinguish. In the identification of prokaryotic microbes from the Precambrian, more than morphologically focused palaeontology is needed. The combination of optical identification of morphology in concert with chemical analysis of individual fossils is a way to avoid mistakes (Schopf *et al*., 2002).

7. Conclusions

- The applied techniques were successful in detecting traces of life in the rocks from Bitter Springs Chert, Australia.
- FTIR is an excellent tool for investigating traces of early life.
- It is not necessary to produce thin sections for the detection of microfossils in FTIR, as long as they are superficially exposed.
- FTIR analyses on the superpolished sections gave better results than on the pulverized rock material, but both preparation methods suffice.
- Investigating thin sections, thicker superpolished sections and HF macerated sections in combination provides differentiating insights about the rock, and is recommended.
- Producing ones own thin sections are recommended, as there is not a standardized optimal thickness for petrographic studies of microfossils, and as a microfossil specialist best knows what structures are interesting.
- It is essential that potential fossils observed in SEM are also observed in a microscope, as abiologic structures easily mimic the simple morphology of Precambrian microfossils.
- A superpolished but relatively thick thin section is recommended for the usage of petrography, SEM and FTIR. The same section should optimally be used for all techniques.
- The FTIR analysis detected what is most probably biomolecules in the exposed dark spots in sample A. Therefore; these structures can be concluded as being chemical fossils.

- Since similar dark spots occur in all samples, these are probably also biogenically produced.
- The structures in Fig. 16 could not be analysed for chemical content, but due to their morphology (which is similar to authentic fossils found in Bitter Springs Chert) and colour (reddish brown to black) they are most probably biogenic.
- Based on morphology, the spherical structures associated to the layers, colour and the result from HF maceration, it is concluded that the dome-like structures are probably oncoids.

8. Implications for astrobiology

8.1 Definition of life

One might say that the philosophical question of the definition of life is unrelated to the biological counterpart. But "life" is a term that humans have created to make a distinction between what we see as living and what we do not. We cannot do objective science because we cannot observe the world in an objective way. Our senses prohibit objectivity, and truth and perception will always be intertwined (Chernyshenko, 2010). When studying objects at a molecular level, it is possible to establish definitions of "natural kinds" that we used to define by human conventions. For example we can now define water as 'H_2O' and nothing else, whereas we used to define it as almost anything that is fluent, colourless, odourless and tasteless. By human convention, we might define life as something being able to reproduce and metabolize, but by those means we are merely describing its observable and measurable properties and not the absolute definition. It is possible that in the future our understanding of biology will provide us with an absolute definition of life, provided that life is indeed something that can be defined. If prebiotic research reaches its objective in recreating the steps leading up to the first life forms, we will be a lot closer to a definition. Finding life on other planets will also provide insights about the shared features of living matter (Cleland & Chyba, 2002).

8.2 "Weird life"

It is becoming increasingly clear that early life research must also look for traces of "weird life", which are organisms that stray from the chemical composition and mode of life that we are familiar with. All life might not be dependent on water, and might not be consisting of the molecules we normally link to biogenic substances (National Research Council, 2007). Organisms are normally composed of carbon, oxygen, sulphur, phosphorus, hydrogen and nitrogen, with additional trace elements that may vary between species. It was previously an unquestioned notion that the six main elements could not be exchanged, but is now questioned as Wolfe-Simon *et al*. (2011) claimed to have found evidence of bacteria incorporating arsenic instead of phosphorus. The bacterium, GFAJ-1, was found in Mono Lake, California, which is a hypersaline and alkaline lake with high concentrations of arsenic (Wolfe-Simon *et al*., 2011). Arsenic and phosphorus is connected vertically in the periodic table and behave similarly. Because of their similarity, arsenic is toxic to most organisms because it can readily be incorporated in their bodies. In 2012, a group of researchers tried to replicate the experiments proving that the bacterium used arsenic in their genetic backbone, but failed to do so (Reaves *et al*., 2012). The matter is currently unresolved but regardless of the outcome, early life research should strive for broad-minded thinking, and embrace the possibility that biosignatures other than those we are presently seeing as evidence of biogenicity might not be the only ones (Wolfe-Simon *et al*., 2009). The study of extremophiles is essential in order to truly understand the limits, and the definition, of life.

8.3 Merging early life research and astrobiology

The chances of finding present extraterrestrial life are far less likely than that we would find fossilized traces of past life, which is one of the reasons why geology has a natural place within the field of astrobiology. Not only are geologists trained in recognizing fossilized remains, without knowing the geological context less strength could be given to prove their authenticity. The intertwining of early life research and astrobiology is apparent as it has been suggested that early earthly fossils must be analyzed with the same intensity as extraterrestrial fossils, since we know very little about the geological and environmental context of both (Brasier *et al*., 2006).

Any form of life that has been identified so far is our proximate or distant relative. That may be because life only emerged once; but it might also mean that the life forms we are able to detect, alive and in the fossil record, are those that are essentially similar to us. Our current understanding of life might be true only for our lineage. The molecules we associate with life might not be fixed and biosignatures found in the fossil record might have been overlooked. The same questions must be asked in astrobiology; do we even know what we are looking for? The compulsory incorporation of carbon or the usage of water might not be the case for all past life forms on Earth, and it may not be the case for extraterrestrial life forms (National Research Council, 2007). However, since the biomolecules we know of today are also the most abundant elements in the universe, chances are that they consist of at least some of these. It is important that a database of biosignatures will be constructed so that potential Martian biosignatures will not be overlooked, and that false biosignatures will not be given authenticity (Marshall *et al*., 2006). The fossilization process from extant extremophiles to extinct extremophiles found in the rock record, especially if we find arsenic based or other anomalous fossils, also needs to be further analy-

sed. Since Martian life will probably be found firstly in the rock record, it is essential that the fossilization process on Earth is well understood before drawing conclusions about the Martian counterpart.

8.4 Where should we look for life?

If a celestial body (e.g. planet, satellite or moon) can sustain life at a surface or subsurface-level, it is considered to be habitable. The inhabitability of multiplying celestial bodies is being revised as terrestrial life is being found in more extreme environments on Earth. Through the BioPan experiments increased knowledge regarding terrestrial organisms tolerance to life in space is also being derived, which might lead to more planets and moons being deemed as habitable (Demets *et al*., 2005). Water and availability of essential organic building blocks are the basal prerequisites for habitability. Mars constitute the focal point for extraterrestrial research, not because it is the only celestial body weened to contain life, but because it is the only planet within our present reach for on-site research. Europa, for example, which is one of the moons of Jupiter, has been shown to contain hydrogen and possibly large amounts of liquid water beneath the icy surface (Hand & Brown, 2013). The early Earth and Mars probably shared many physiological as well as chemical properties. It is known that Mars, like Earth, had liquid water and fluvial systems 3.5 billion years ago and may have been on the same level of planetary evolution. It is therefore not unlikely that both planets contained microbial life (Brasier & Wacey, 2012). Mars may still contain liquid water beneath the surface, which can be kept fluent due to radioactive decay (Mix *et al*., 2006) and the search for liquid water is the main focus for NASA's present research on Mars. Subsurface explorers and sample returns are future goals for NASA's exploration of Mars that will facilitate the search for extraterrestrial life (NASA, 2013). Especially interesting to investigate are the areas of exposed water ice near the southern pole on Mars (Titus *et al*., 2003). A subsurface biota is a possibility for Martian life, similar to hydrothermal or deep subsurface communities on Earth. UV radiation levels on Mars are very high, but so they were on the Archean Earth. High radiation is an agent of rapid mutation because it heightens the selective force on organisms for developing surviving strategies. Life on Earth developed multiple strategies for coping with the Archean radiation, and the same might be true for Mars. When the water disappeared, the Martian organisms might have developed an endolithic lifestyle where they would escape much of the radiation. If life on Mars exists today, it is probable that they would get their energy from chemotrophy just like the early microbes on Earth (Horneck, 2000). Europa, one of the moons of Jupiter, is another potential life holder, and Lake Vostok has been described as a good analogy for the environment on that moon (Rothschild & Mancinelli, 2001). Space missions in the near future will hopefully reveal that we are not alone in the universe — a notion that would fundamentally change how we gaze at the night sky.

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11. Appendix

11.1 XRF

Table A1. XRF data. Each sample was tested 6 to 15 times depending on the size of the sample. A13-15 are taken from the external surface of sample A, which can explain their differentiation from the rest of the sample. Some values were lower than detectable, and are left blank.

Reading No	Al	Al Error	Si	Si Error	P	P Error
Ax01	9424.51	1859.83	353881.56	2558.79	8227.83	513.56
Ax02	7717.81	1600.31	435421.86	3110.18	10133.10	592.24
Ax03	4349.79	1880.32	312487.19	2491.37	6406.92	509.74
Ax04	6034.12	1384.77	371175.67	2598.30	8708.79	482.41
Ax05	7367.62	1450.14	458981.90	2804.69	10197.11	562.92
Ax06	4850.61	1408.89	492297.44	2946.65	8760.06	589.90
Ax07	4702.52	1497.22	490853.49	2941.44	7994.59	598.82
Ax08	4236.06	1257.37	508395.05	2897.35	7232.40	554.70
Ax09	4654.22	1382.89	475513.83	2876.76	8107.73	562.31
Ax10	6736.48	1656.22	408328.99	2663.20	8886.23	520.78
Ax11	4231.48	1282.90	470206.46	2860.35	7429.12	536.14
Ax12	5362.86	1558.73	456876.66	2719.71	6621.67	544.30
Ax13	32806.71	2182.96	265243.85	2691.22	5119.17	449.55
Ax14	28427.89	1946.40	271552.90	2643.13	6762.62	454.93
Ax15	36208.42	2381.39	249508.20	2591.53	4026.91	426.69
Bx01	7750.14	1359.61	531352.85	2847.39	13648.00	613.75
Bx02	5546.22	1419.82	457229.92	2672.37	10548.98	552.90
Bx03	10681.17	1609.52	479855.46	2754.16	12933.31	599.56
Bx04	13032.21	1632.91	463034.35	2721.91	16441.62	611.93
Bx05	9129.07	1551.94	489988.66	2757.83	13272.90	608.74
Bx06	6398.19	1391.75	501825.32	2752.57	11494.47	584.11
Bx07	6120.79	1634.39	412202.64	2590.96	9038.20	537.90
Bx08	6367.35	1698.14	390232.00	2564.13	9005.00	532.43
Bx09	6914.44	1344.10	494825.08	2687.78	11393.19	562.83
Bx10	4268.09	2145.54	304896.28	2334.39	4063.61	412.48
Cx01	7215.60	1215.42	500447.04	2896.05	9685.35	545.43
Cx02	6197.21	1207.07	481691.76	3025.00	7627.38	535.11
Cx03	6667.08	1268.21	525285.07	2950.10	8868.82	569.91
Cx04	13217.02	1420.09	511766.26	2914.15	7435.88	534.93
Cx05	5296.89	1218.52	544812.66	2905.79	7218.89	553.11
Cx06	4699.55	1199.25	554697.71	2905.24	5899.93	547.79
Dx01	16514.38	1537.98	442573.85	3040.60	7851.98	524.37
Dx02	24115.55	1687.35	437896.74	2847.86	10921.23	524.19
Dx03	8361.14	1328.77	478013.07	3086.94	13387.77	634.22
Dx04	13697.97	1576.27	507785.46	3126.05	14844.67	654.04
Dx05	12122.97	1413.67	463110.59	3063.89	9314.96	552.69
Dx06	15117.20	1420.76	483185.26	2806.22	9378.83	519.81
Dx07	15671.08	1505.79	494759.64	2938.85	12253.26	578.99
Dx08	9030.24	1264.91	462429.70	3048.29	9420.76	537.41
Dx09	13947.25	1453.24	462928.25	3041.63	6956.68	526.69
Dx10	6438.71	1247.86	480246.52	3120.06	7229.19	546.38

Reading No	S	S Error	Cl	Cl Error	K	K Error	Ca	Ca Error
Ax01		141.13	7477.73	160.24		199.89	109978.02	1150.87
Ax02		131.78	6369.32	160.95	485.98	87.26	36979.65	677.47
Ax03		173.71	10057.33	194.48	269.17	139.78	165684.23	1573.17
Ax04		129.23	8716.64	167.23	232.93	86.95	70731.56	859.78
Ax05		120.77	4469.61	126.95	285.27	83.61	51837.01	744.61
Ax06		118.47	5275.92	141.23	197.16	77.07	36639.85	638.49
Ax07		131.95	6130.40	156.35	267.30	88.91	51183.43	789.18
Ax08		103.53	7895.01	162.65	268.72	60.83	15243.21	389.95
Ax09		127.36	7701.30	166.18	289.99	76.81	36506.46	623.15
Ax10		138.86	8975.89	175.69	232.89	119.19	79833.91	947.85
Ax11		116.55	7595.05	160.37	276.11	72.56	29961.23	558.38
Ax12	198.41	137.77	6859.83	159.13	532.94	112.05	91079.80	1067.10
Ax13		183.91	36437.46	450.14	8568.64	255.94	9165.69	338.70
Ax14	428.42	125.80	30405.55	385.29	8218.49	244.34	7893.56	309.42
Ax15		185.41	38258.65	457.87	9242.89	268.27	10215.58	362.28
Bx01		84.04	1267.30	74.25	220.83	54.79	13708.93	358.71
Bx02		117.27	970.16	75.20	258.99	89.94	76786.76	916.61
Bx03		115.96	800.52	75.19	233.63	89.38	65870.18	862.63
Bx04		109.90	1022.34	77.67	240.76	112.23	62649.63	816.47
Bx05		119.14	2043.44	94.57	273.81	84.72	58085.76	794.74
Bx06		101.60	1588.76	82.60	388.16	80.42	46059.27	679.43
Bx07	166.63	129.70	2048.66	99.77	409.36	116.29	131534.09	1318.50
Bx08		159.14	9149.51	182.97	535.24	124.13	140438.36	1393.31
Bx09		112.42	8203.57	159.60	271.04	70.82	33733.74	566.30
Bx10	224.14	135.55	2899.27	109.38	300.32	198.99	188793.87	1631.72
Cx01	99.70	73.46	988.11	63.46	543.07	60.37	795.35	86.04
Cx02	309.00	73.19	1588.77	79.02	823.34	75.91	784.62	93.21
Cx03	267.33	70.03	1269.50	72.81	787.29	71.88	664.48	84.17
Cx04	220.95	66.28	1863.96	81.74	1365.49	90.60	1082.25	104.07
Cx05	180.75	69.76	817.02	62.15	569.41	61.32	363.02	63.17
Cx06		94.16	1047.77	66.24	575.63	61.55	203.03	52.89
Dx01		111.22	1781.04	87.51	3258.34	146.30	1906.26	146.59
Dx02		98.70	1993.49	87.46	5304.65	177.80	2829.00	171.87
Dx03		88.02	1120.98	74.58	579.52	67.52	1222.13	115.47
Dx04		94.88	763.92	71.17	735.38	75.61	1434.74	127.31
Dx05		94.04	2109.52	92.14	2062.69	117.76	1560.62	129.90
Dx06		80.69	1673.85	77.08	1833.87	100.40	1751.46	126.18
Dx07		88.48	869.01	68.44	1727.94	102.44	776.84	92.90
Dx08		77.76	403.07	53.64	707.86	72.91	868.66	97.99
Dx09		100.49	1743.21	86.24	2543.17	129.76	1527.05	134.05
Dx10		87.13	437.18	60.34	906.48	82.39	1038.19	108.68

Reading No	Ti	Ti Error	Fe	Fe Error	As	As Error	Sr	Sr Error
Ax01		75.73	1887.76	117.18	14.84	9.16	8.67	1.41
Ax02	60.24	33.63	200.63	71.05		14.36	12.48	1.66
Ax03		111.92	5025.01	191.89	21.92	9.89	12.31	1.72
Ax04	62.77	52.46	1246.11	96.06	12.94	10.17	13.44	1.54
Ax05		64.53	2128.95	121.06	13.62	12.55	7.87	1.36
Ax06		55.03	1871.74	117.33	14.52	11.41	6.19	1.30
Ax07		66.50	1745.53	118.58	17.04	12.04	6.84	1.38
Ax08		48.87	160.31	62.10		11.09	3.74	1.10
Ax09		52.18	456.03	75.13		14.60	8.42	1.36
Ax10		62.82	875.19	88.51	12.70	10.49	11.59	1.51
Ax11		50.67	662.23	80.24	11.74	10.95	9.81	1.40
Ax12	188.91	51.94	146.17	65.84	13.27	11.03	11.65	1.59
Ax13	996.74	54.06	6172.81	198.00	16.92	12.15	3.12	1.18
Ax14	964.80	51.21	6178.57	191.48		15.14	3.61	1.17
Ax15	1625.44	66.12	15783.07	310.91	14.38	12.45	5.93	1.35
Bx01		44.94		80.28	14.81	11.57	5.94	1.18
Bx02	96.25	68.15		102.10	11.97	14.46	19.66	1.80
Bx03		66.26		99.08	11.45	12.17	18.41	1.79
Bx04		61.12		84.88	13.11	9.31	16.00	1.66
Bx05		61.71		84.53	12.00	10.04	19.58	1.81
Bx06	50.91	54.80	149.27	61.69		14.21	13.72	1.55
Bx07	217.26	56.29		105.49	12.91	12.00	36.05	2.47
Bx08	86.82	87.49		111.52	15.27	12.98	29.51	2.30
Bx09		48.10	562.01	73.00		10.16	10.34	1.36
Bx10	164.08	87.80		112.95		15.21	39.56	2.56
Cx01	193.99	25.14		74.75	10.92	10.60	2.99	1.02
Cx02	139.73	27.96	89.26	93.19		12.80	2.17	1.02
Cx03	118.78	27.08		92.79	11.04	11.13	3.84	1.07
Cx04	209.65	27.76	126.51	65.64		13.07	3.57	1.05
Cx05	99.72	25.86		75.44		10.97	2.09	1.00
Cx06	93.62	24.68		104.96	13.90	11.77	3.25	1.04
Dx01	507.71	39.50	1937.12	112.40	12.90	10.43	1.75	1.38
Dx02	877.47	45.25	3888.00	141.94		12.33	1.98	1.01
Dx03		42.76		107.43		15.95	1.97	1.26
Dx04	65.22	27.76	247.06	68.43	12.24	9.55	2.05	1.05
Dx05	226.56	31.74	891.48	87.38	13.19	10.21		1.50
Dx06	218.68	28.02	1284.55	89.34	10.44	11.05	2.24	1.13
Dx07	228.81	31.13	932.05	84.95		12.00	2.14	1.13
Dx08	105.03	24.39	366.54	70.88		12.72	2.17	1.39
Dx09	360.39	35.75	1314.71	97.34	13.28	10.64		1.50
Dx10	62.87	28.98	283.71	68.40		12.71	1.76	1.38

Reading No	Zr	Zr Error	Mo	Mo Error	Ba	Ba Error
Ax01			2.69		2.56	174.37	59.97
Ax02			2.48		2.74	122.03	62.08
Ax03		3.61	3.63		2.63	283.75	69.81
Ax04			2.72		2.13	123.31	55.64
Ax05			2.55		2.44	168.05	58.55
Ax06			3.01		2.39	134.94	66.28
Ax07		3.89	2.83		3.89	134.16	68.96
Ax08			1.83		2.48	134.98	54.32
Ax09			2.17		2.33	126.86	70.63
Ax10			2.95		2.52	111.03	64.85
Ax11			2.19		2.48	125.46	54.71
Ax12			2.81		2.43	155.61	62.14
Ax13		3.92	2.67		2.40	133.72	61.72
Ax14		16.47	2.46		3.09	118.44	89.61
Ax15		22.55	2.78	3.59	2.60	108.43	74.52
Bx01			1.80		2.02	104.52	52.08
Bx02			2.23		2.44	129.90	58.55
Bx03			2.55		2.77	113.33	58.61
Bx04			2.18		2.14	126.91	56.73
Bx05			2.47		2.25	141.74	58.53
Bx06			2.23		2.13	122.12	54.90
Bx07			2.54		2.51	161.44	63.87
Bx08			3.04		2.47	192.54	65.69
Bx09			2.39		2.19		83.89
Bx10			2.55		2.42	198.80	64.68
Cx01			1.57		1.86	108.62	51.52
Cx02			2.78		2.03	106.02	66.37
Cx03			1.70		1.96	121.18	51.88
Cx04			1.63		1.87	133.63	51.80
Cx05			2.56		2.18		89.89
Cx06			2.45		1.95	133.03	57.95
Dx01			1.91		2.14	112.36	76.31
Dx02			2.72		2.26	123.27	58.14
Dx03			2.14		2.13		96.13
Dx04			2.18		2.18	118.21	57.69
Dx05			1.86		2.12	113.17	55.17
Dx06			2.86		1.84	118.28	55.69
Dx07		3.14	1.94		2.00	103.22	52.59
Dx08			1.71		2.00	143.48	57.67
Dx09			1.83		2.36	104.79	54.68
Dx10			1.87		2.74	115.25	62.28

Standard	Mg	Al	Si	P	K	Ca
2709a	25143.4	65509.8	282142.4	1951.13	21529.35	18537.9
2709a	23191.92	68121.21	290445.5	2339.183	21604.62	18934.09
2709a	24657.76	68607.59	290918.3	2871.515	21613.65	18875.57
2709a	23404.29	67394.01	289883.2	2419.09	21681.79	18743.5
2709a	20622	65095.01	285191	1798.41	21571.59	18600.04
2709a	24073.77	69068.09	292511.9	2447.69	21718.6	18708.56
2709a	25229.94	69685.46	292566.8	2464.59	21692.94	19058.74
Mean value	23760.44	67640.17	289094.2	2327.37	21630.36	18779.77
Reference value	14600	73700	30300	688	21100	19100
Procentual deviation from standard	162.7	91.7	95.4	338.3	102.5	98.3

Standard	Ti	V	Cr	Mn	Fe	Cu
2709a	3426.26	137.87	224.45	470.53	35240.13	83.49
2709a	3514.22	164.05	232.06	467.26	35231.07	83.17
2709a	3486.11	129.54	217.49	446.93	35149.32	81.69
2709a	3476.55	159.5	218.63	443.53	34987.42	83.69
2709a	3395.69	162.25	220.99	460.91	35053.28	80.91
2709a	3446.09	191.11	210.64	445.77	35112.15	79.26
2709a	3494.28	129.58	225.44	462.32	35088.46	79.93
Mean value	3462.75	153.41	221.39	456.75	35123.12	81.74
Reference value	3360	110	130	529	33600	33.9
Procentual deviation from standard	103	139.5	170.3	86.3	104.5	241.1

Standard	Zn	As	Rb	Sr	Zr	Ba
2709a	72.25	31.73	45.87	211.05	138.72	862.43
2709a	74.3	30.25	45.39	211.95	147.01	847.16
2709a	72.56	31.05	45.62	210.80	135.54	834.48
2709a	74.785	29.09	45.52	210.35	145.24	830.44
2709a	71.74	30.9	45.1	210.39	160.56	844.59
2709a	73.25	32.65	45.7	209.2	152.33	838.65
2709a	72.68	28.67	45.13	212.81	149.11	821.66
Mean value	73.08	30.62	45.47	210.94	146.93	839.92
Reference value	103	10.5	99	239	195	979
Procentual deviation from standard	70.9	291.2	45.9	88.2	75.3	85.8

11.2 FTIR

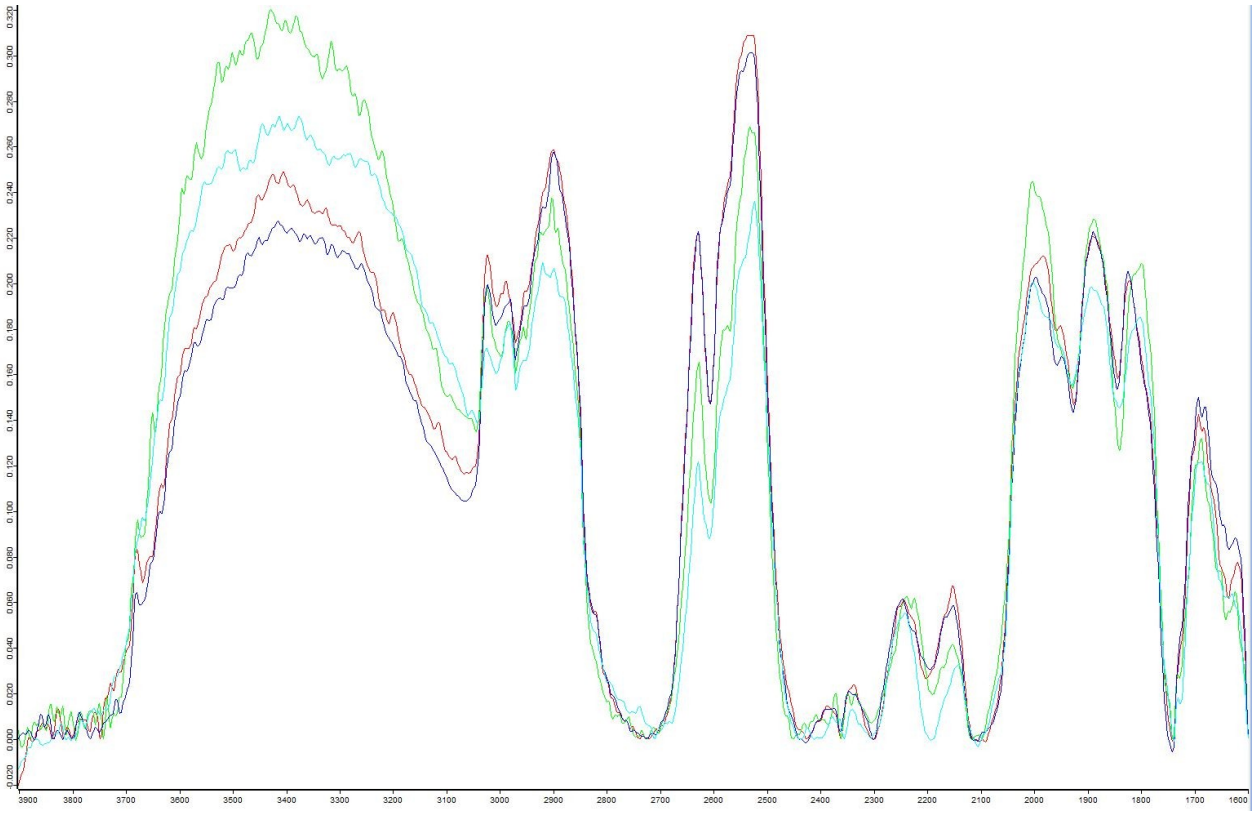

Fig. A1. The spectra derives from the targeting of exposed dark spots in the superpolished section of sample A.

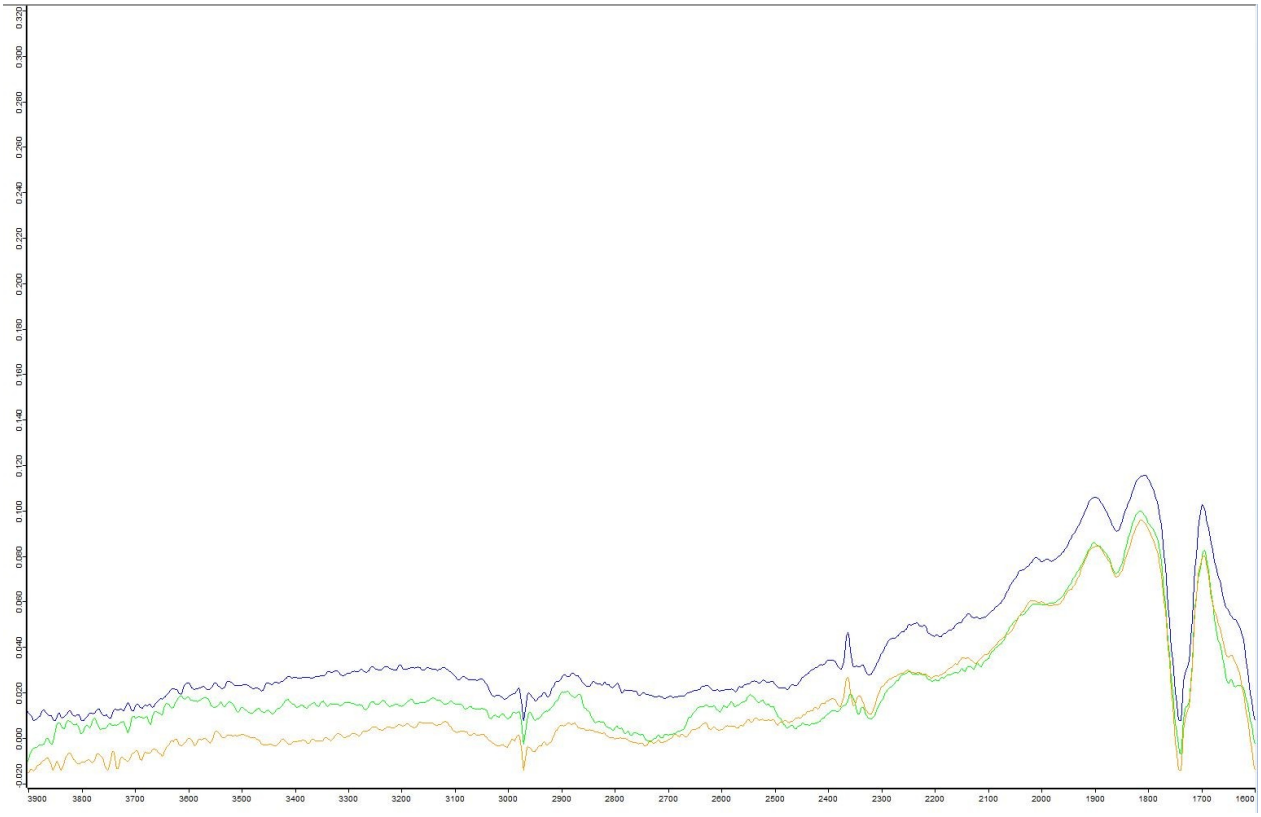

Fig.A2. The spectra derives from the targeting of other areas than exposed dark spots in the superpolished section of sample A.

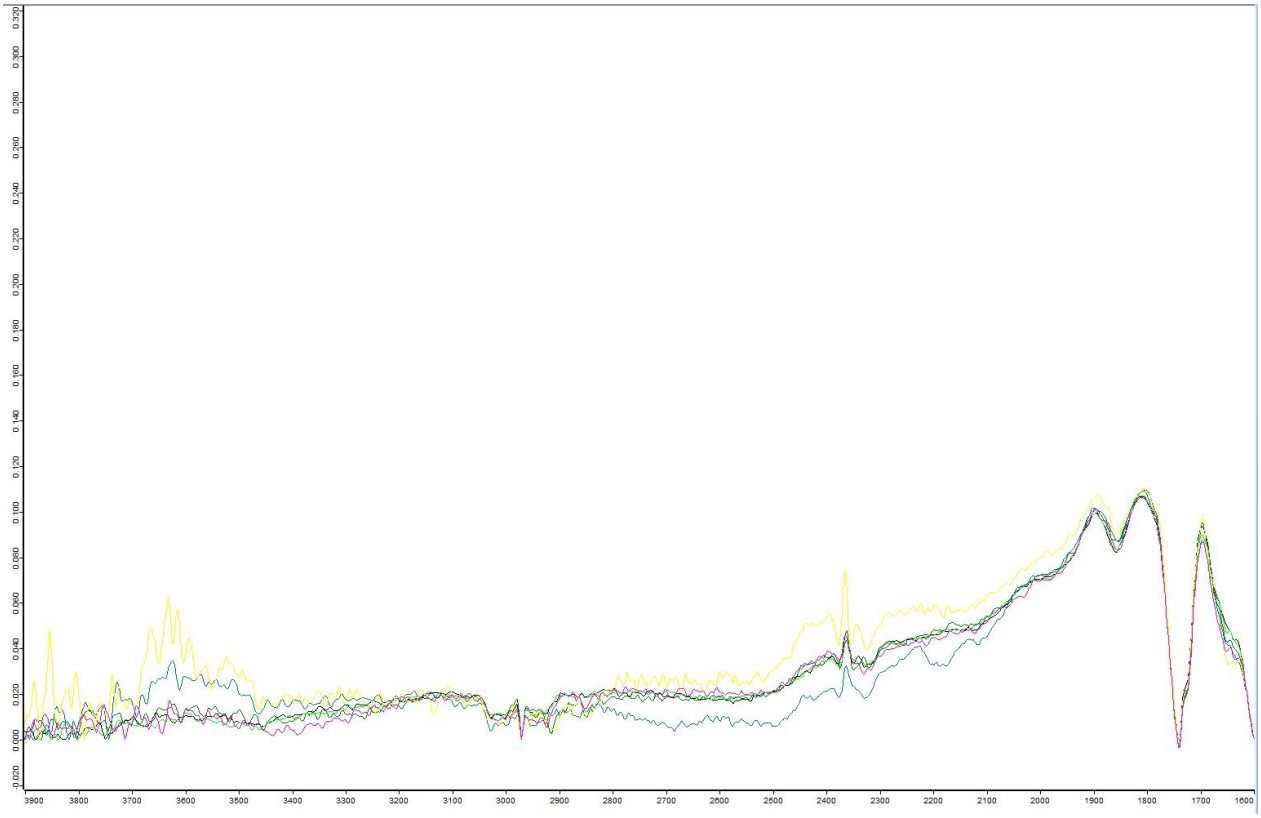

Fig.A3. The spectra derives from various testings on the superpolished section of sample D.

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