Chlorophyll-f: Earth's Unseen Production and Habitability Under Red Light

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Introduction:

Chlorophyll-f

Chlorophyll-f (chl *f*) was first discovered in 2010 being utilized by the cyanobacteria, *Halomicronema Hongdechloris,* living within the stromatolites of Hamelin pool, Shark Bay, Western Australia [1]. Laboratory-based studies have been able to characterize the absorbance of chl *f in vivo* and *in vitro* (naturally occurring as a combination of chl *a* + *f*) [2, 3]. *In vitro* absorption has a Soret band at 406 nm and a red absorption band of 707 nm, redefining what was thought to be the long wavelength limit for oxygenic photosynthesis held by chlorophyll *d* at 696 nm [4]. Notably, the absorbance efficiency *in vivo* can be extended to 740 nm [2].

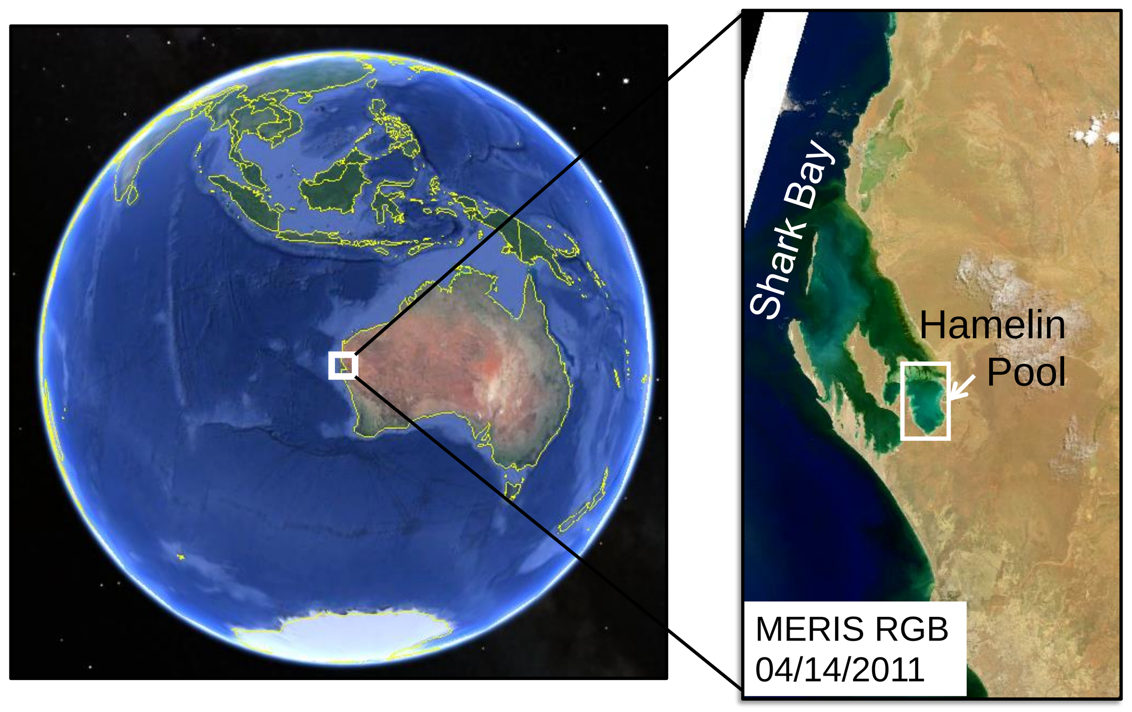
Earth's Primary Productivity

Although many more primary producers have since been found to use chl *f* [5,6], these studies have been limited to laboratory-based analyses. Remote sensing techniques offer the ability to monitor global primary production with great temporal and spatial resolution for considerably less than field measurements would cost. With no simple *in situ* technique for measuring chl *f*, remote sensing may provide an opportunity to better understand these red-shifted chlorophylls in our environment in both space and time. Based on the absorption characteristics of chl *f*, MERIS data has been chosen (having a band nearest the red absorbance maxima of chl *f* at 709 nm) to asses the potential of remotely detecting chl *f.*

Astrobiological Significance

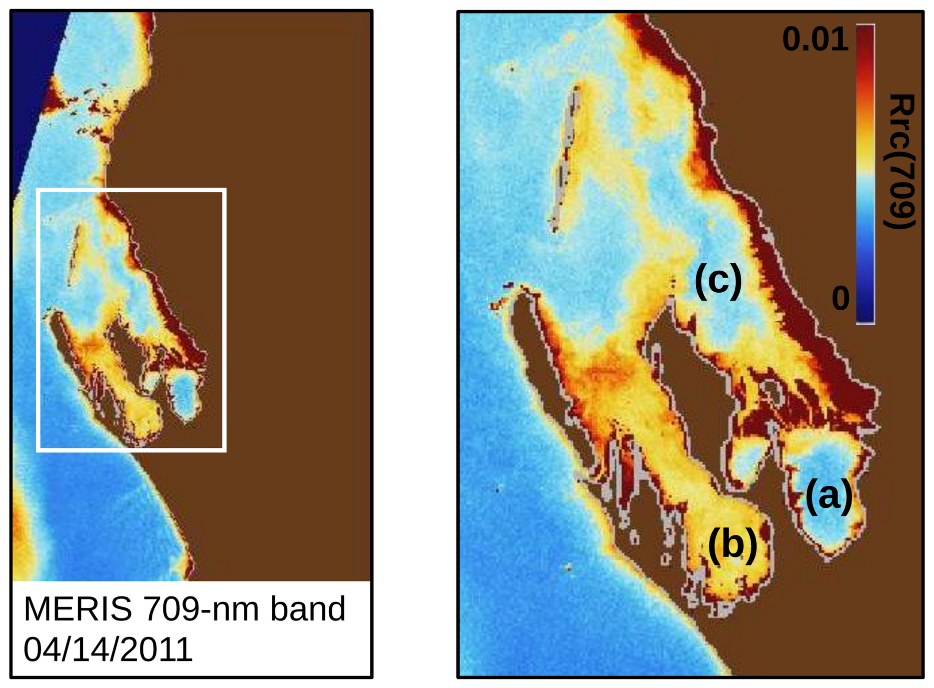
Much of oxygenic photosynthesis on Earth occurs via utilization of chl *a*, which absorbs wavelengths of light optimally suited for our sun's wavelength emission. But what about the wavelengths emitted by red dwarfs? Through utilizing red-shifted chlorophylls, such as chl *f*, planets and moons orbiting red dwarfs may be able to receive the necessary solar energy to drive photosynthesis. Because red dwarfs make up such a large percentage of the universe's observable stars understanding the surface reflectance of a planet utilizing red-shifted chlorophylls as a primary photopigment is likely to be a critical step in observing biosignatures of extrasolar life. The first step is to document an Earth-based reflectance signature.

Study Site: Hamelin Pool, Western Australia



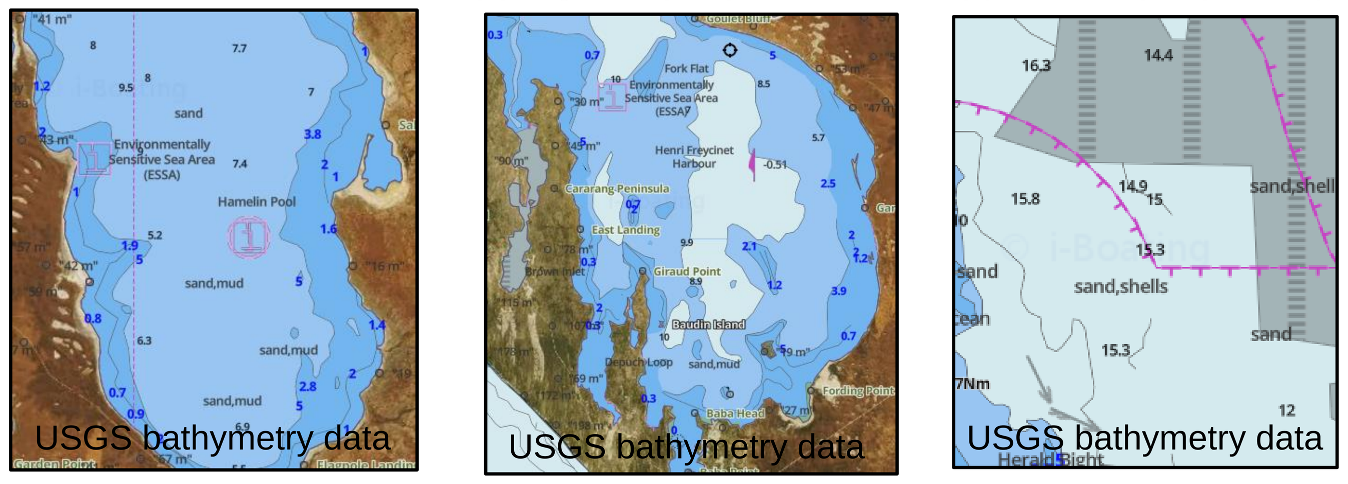
Initial Questions

1. Is there a lower relative reflectance at 709 nm in Hamelin Pool?



Hamelin Pool (a) has a lower relative reflectance (higher absorption) at 709-nm compared to nearby regions. Areas of highest reflectance coincide with seagrass-dominated bottom type and/or extremely shallow banks.

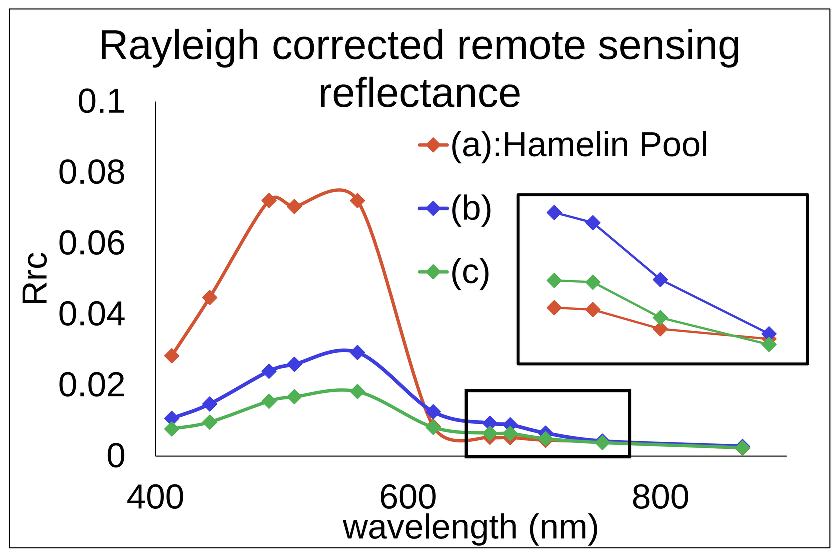
2. Can this be explained by bathymetry?



In comparison to local areas (e.g., regions (b) & (c)), Hamelin Pool has abnormally low Rrc(709) for a shallow average bottom depth. For example, region (b) is on average shallow, yet still deeper than Hamelin Pool and has higher overall Rrc(709) than Hamelin Pool.

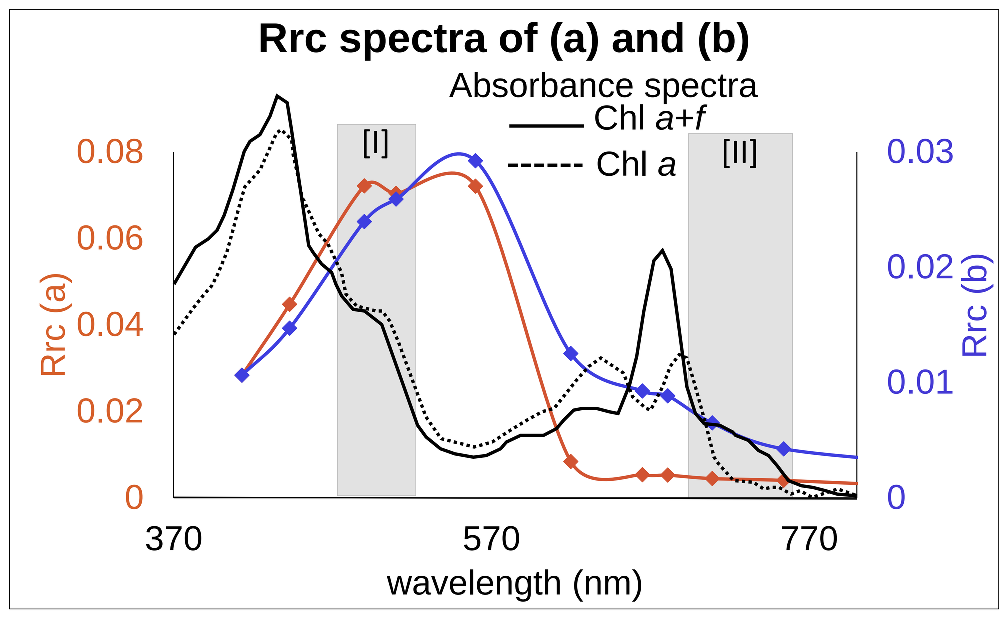
Initial Questions (cont'd)

3. Are there major differences in spectral shape between these regions?



Hamelin Pool (a) has significantly higher reflectance in all bands below 620 nm in comparison to other regions in Shark Bay. Additionally, (a) shows the smallest slope in the red and NIR wavelengths (665-nm to 754-nm).

4. How do these characteristics compare to the absorption of chl *f* containing bacteria?



Absorption spectra adapted from Chen and Blankenship (2011)

In region [I] there is a trough in reflectance due to the absorption of chlorophyll, however whether this is due to chl *a* or chl *a* + *f* can not be discerned from this feature alone.

Region [II] shows the effect of chl *f*, by which absorption is extended to 750 nm compared to the absorption of chl *a* alone, which is near zero at wavelengths greater than 700-nm. It is this characteristic that may allow for the detection of chl *f*, particularly in shallow water regions.

Future Work

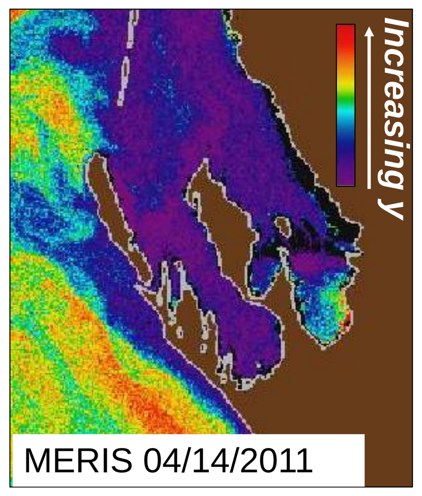
In situ

In order to validate any algorithm, collecting *in situ* samples is necessary. Although this study is focused on the region of Shark Bay, it is clear that chl *f* is utilized in other similar niche environments. Once the accuracy of a chl *f* algorithm can be assessed in Shark Bay, this study may be extended to multiple regions.

Remote Sensing

Although MERIS data was chosen for the preliminary study based on having daily repeat cycles and a band nearest that of chl *f*'s red absorption maxima, it is not presently collecting data. Optimally, hyperspectral data should be collected to fine-tune a chl *f* remote sensing quantification method including same-day *in situ* [chl *f*] measurements.

Preliminary Image Analysis

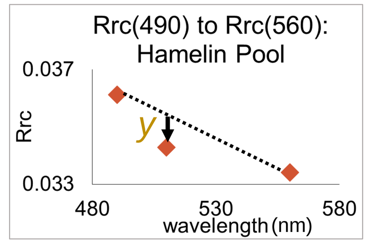


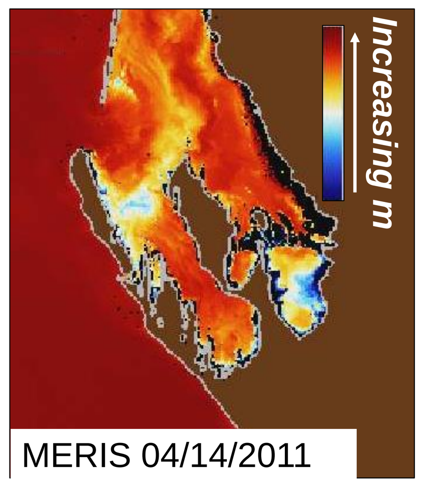
This false color image was created using the following equation to describe the trough in region [I], adapted from the phycocyanin index of Qi et al. (2014) [7].

$$y = Rrc'(510) - Rrc(510)$$

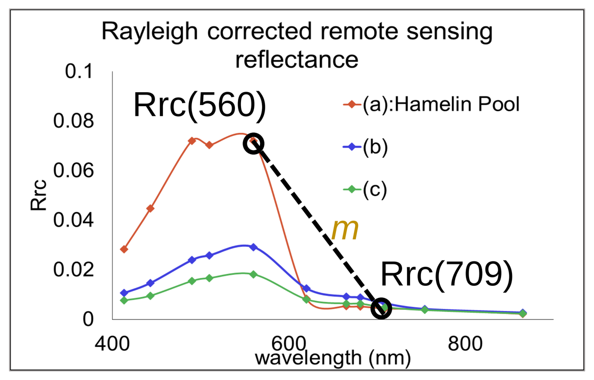
where,

$$Rrc'(510) = Rrc(490) + \frac{510 - 490}{560 - 490} * [Rrc(560) - Rrc(490)]$$

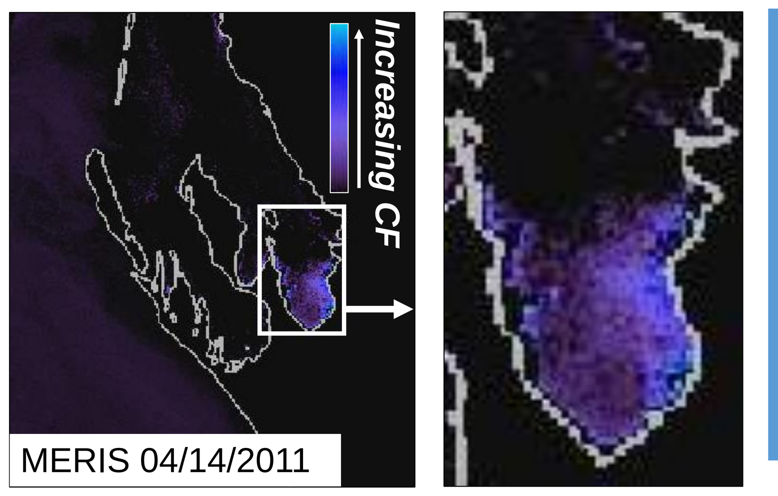




This false color image was created to describe the sharp slope formed from Rrc(560) to Rrc(709), *m*.



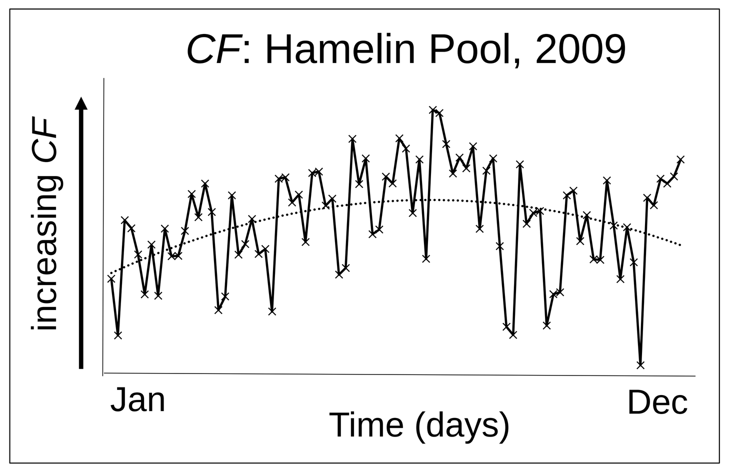
$$m = \frac{Rrc(709) - Rrc(560)}{709 - 560}$$

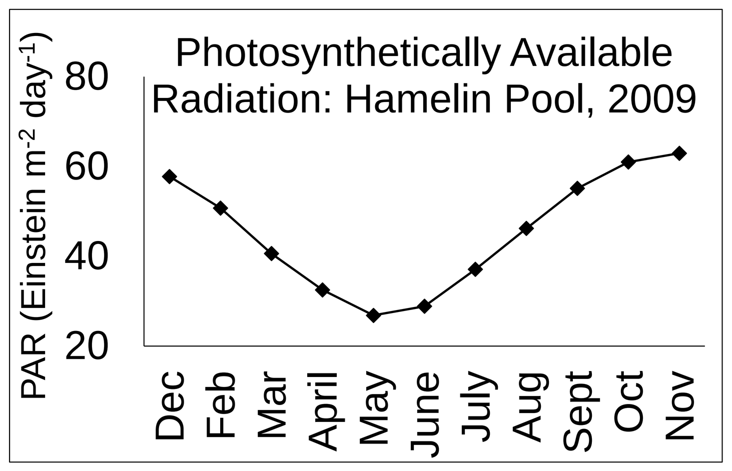


This false color image shows the first remote approximation of chl *f* distribution and was created as the multiplication of the above two images ($CF = -y * m$). high CF locations agree well with known stromatolite distribution in Shark Bay.

Preliminary Temporal Variability

It has been well established that the ratio of chl *a:f* in chl *f*-containing bacteria varies dependent on the availability of white to red light [1,3]. As such, it may be expected that during months of low angle sun light (e.g., low PAR), chl *f* increases. Possibly in order for the bacteria to harvest this additional energy in the longer wavelengths, which are less effected by atmospheric absorption. Our preliminary results agree with this hypothesis, showing higher *CF* during days of low average monthly PAR.





Acknowledgements and References

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[1] Chen M, Schliep M, Willows RD, Cai Z, Neilan BA, Scheer H. 2010. A Red-Shifted Chlorophyll. *Nature* 329(5997): 1318-1319. [2] Chen M, Blankenship R E. 2011. Expanding the solar spectrum used by photosynthesis. *TrendsPlantSci*. 16:427–31. [3] Chen M, Schliep M, Willows R, Cai Z-L, Neilan BA, et al. 2010. A red-shifted chlorophyll. *Science.* 329:1318–19. [4] Li Y, Cai Z, Chen M. 2013. Spectroscopic Properties of Chlorophyll *f. The Journal of Physical Chemistry* DOI:dx.doi.org/10.1021/jp402413d. [5] Akutsu S, Fujinuma D, Watanabe T, Ohnishi-Kameyama M, Ono H, Ohkubo S, Miyashita H, Kabayashi M. 2011. Physicochemical Properties of Chlorophylls in Oxygenic Photosynthesis — Succession of Co-Factors from Anoxygenic to Oxygenic Photosynthesis. *Photomed. Photobiol.* 33: 35-40. [6] Akutsu S, Fujinuma D, Furukawa H, Watanabe T, Ohnishi-Kameyama M, et al. 2011. Pigment analysis of a chlorophyll *f*–containing cyanobacterium strain KC1 isolated from Lake Biwa. *Photomed. Photobiol.* 33:35–40. [7] Qi L, Hu C, Duan H, Cannizzaro J, Ma R. 2014. A novel MERIS algorithm to derive cyanobacterial phycocyanin pigment concentrations in a eutrophic lake: Theoretical basis and practical considerations. *Remote Sensing of Environment* 154:298-317.