GLOBAL SURFACE PHOTOSYNTHETIC BIOSIGNATURES OF ANOXIC BIOSPHERES. M. N. Parenteau¹, W. B. Sparks², R. E. Blankenship³, T. A. Germer⁴, C. M. Telesco⁵, N. Y. Kiang⁶, E. Pallé⁷, L. Kolokolova⁸, F. T. Robb^{9,10}, V.S. Meadows¹¹; ¹Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035 (mary.n.parenteau@nasa.gov); ²Space Telescope Science Institute, Baltimore, MD 21218; ³Departments of Biology and Chemistry, Washington University in St. Louis, St. Louis, MO 63130; ⁴National Institute of Standards and Technology, Gaithersburg, MD 20899; ⁵Univ. of Florida, Gainesville, FL 32611; ⁶NASA Goddard Institute for Space Studies, New York, NY; ⁷Instituto de Astrofísica de Canarias (IAC), Vía Láctea s/n 38200, La Laguna, Spain ⁸Univ. of Maryland, College Park, MD, 20742; ⁹Institute of Marine and Environmental Technology, Baltimore, MD 21202; ¹⁰Univ. of Maryland School of Medicine, Baltimore, MD 21201; ¹¹Astronomy Department, University of Washington, Seattle, WA 98195.

Introduction: The study of potential exoplanet biosignatures -- the global impact of life on a planetary environment -- has been informed primarily by the modern Earth, with little vet explored beyond atmospheric O₂ from oxygenic photosynthesis and its accompanying planetary surface feature, the vegetation "red edge" reflectance. However, these biosignatures have only been present for less than half the Earth's history, and recent geochemical evidence suggests that atmospheric O₂ may have been at very low - likely undetectable - levels, until 0.8 Ga [1]. Given that our planet was inhabited for very long periods prior to the rise of oxygen, and that a similar period of anoxic life may occur on exoplanets, more studies are needed to characterize remotely detectable biosignatures associated with more evolutionarily ancient anoxygenic phototrophs.

Results: *Reflectance spectra*. Similar to the remotely detectable "red edge" of chlorophyll a – containing vegetation, we measured the reflectance spectra of pure cultures and environmental samples of purple sulfur, purple non-sulfur, heliobacteria, green sulfur, and green non-sulfur anoxygenic phototrophs. Our measurements revealed "NIR edge(s)" due to absorption of light by bacteriochlorophyll (Bchl) pigments.

We used the pure culture spectra to deconvolve complex spectra of environmental samples of microbial mats. We observed multiple NIR edges associated with multiple pigments in the mats. We initially expected only to detect the absorption of light by the pigments in the surface layer of the mat. Surprisingly, we detected cyanobacterial Chl a in the surface layer, as well as Bchl c and Bchl a in the anoxygenic underlayers. This suggests that it does not matter "who's on top," as we were able to observe pigments through all mat layers due to their different absorption maxima.

The presence of multiple pigments and thus multiple "NIR edges" could signify layered phototrophic communities and possibly strengthen support for the detection of a surface exoplanet biosignature. Additionally, these data characterize "ecosystem" signatures for microbial communities present in marine intertidal areas and continental lacustrine and hydrothermal settings. Future work aims to characterize anoxygenic ecosystem signatures in the open ocean (aerobic purple non-sulfur anoxygenic phototrophs).

We are also working towards understanding the "rules" that dictate the spectral features of anoxygenic phototrophs so that they can be predicted for exoplanets, and will assess their remote detectability as a function of environmental context across a range of spatial scales: (1) local field measurements of environmental samples, (2) regional on modern Earth (continents and oceans) using airborne sensors and Earth-observing satellites, and (3) planetary-scale in exoplanetary disk-averaged spectra under various atmospheres and cloud coverage levels.

Polarization spectra. The Bchls and Chls pigments are optically active molecules with several chiral centers. The phenomenon of chirality is a powerful biosignature: recent studies of universal biology describe it thus: "One of the very few universal features of biology is homochirality" [2]. Because of the optical activity of biological molecules, i.e., their influence on the polarization of light, and chirality, this biosignature can be remotely observed on planetary scales using circular polarization spectroscopy. Precision full Stokes spectropolarimetry is required. We measured the circular polarization spectra of the same samples analyzed for the reflectance work. The reflectance, transmission, and absorption spectra were obtained. We observed strong correlations between the absorption maxima of the pigments and features in the circular polarization reflectance spectra. We are currently reconciling our measurements on whole cells and complex communities with the long history of circular dichroism measurements made of isolated pigmentprotein complexes in biochemical studies.

Summary: In general, this work aims to inform the search for life on exoplanets at a similar stage of evolution or biogeochemical state as the pre-oxic Earth.

References: [1] Planavsky et al. (2014) *Science, 346,* 635–638. [2] Jafarpour et al. (2015) *Phys. Rev. Lett.* 115, 158101.

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