HIDDEN TEXTURES IN A MARINE CARBONATE REVEALED BY DEEP UV SPECTROSCOPY. G. Wanger[1,3], V.J. Orphan[2], R. Bhartia[1], [1]Dept of Earth Sciences, University of Southern California, Los Angeles, CA (gwanger@jpl.nasa.gov), [2]Division of Geological and Planetary Sciences, Caltech, Pasadena, CA, [3]Jet Propulsion Laboratory - Planetary Science, Pasadena, CA.

Cold water methane seeps are found across the world's ocean floors. These seeps are the base for a consortium of well-studied microbes [1][2]. Through these microbial activities carbonate deposits ranging from cm scale to hundreds of m^2 are sometimes found. One curious morphotype of these deposits are 'doughnut' shaped formations 10's of cm in diameter. The formation of marine carbonates is likely mediated by microbial activity and indeed active microbes have been observed within these carbonates [3]. Sectioning thorough one such 'doughnut' (See Fig) revealed an ~3 cm structure. Here we reveal mm to cm-scale, cryptic biosignatures using Deep-UV spectroscopic techniques hidden therein.

Mapping and characterizing carbon bearing materials is fraught with challenges. Commonly used analytical techniques such as EDS, XRF, etc. can map the presence of carbon but offer little about the form which that carbon takes. DUV spectroscopy (e.g. Raman and fluorescence) are burgeoning techniques uniquely capable of rapidly mapping and characterizing carbon in many forms. Organic molecules, especially those with aromatics exhibit strong fluorescence upon DUV excitation allowing for picogram detection limits. When and if minerals fluoresce, the typical emissions are longer than 400 nm. This high organic fluorescence signal and the fact that most minerals do not fluoresce in the UV facilitates rapid mapping guiding more detailed downstream analyses.

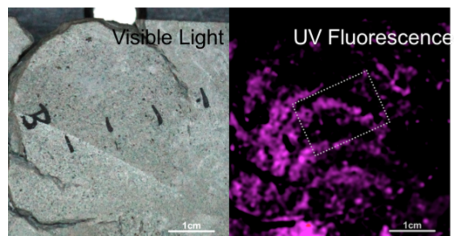
DUV-Raman capitalizes on the largely fluorescence free region below 270 nm to both provide chemical identity to many carbon bearing compounds and some mineralogy. Resonant enhancement of key molecular vibrations e.g. CN, CH, NHx, C=O, C=C, and NOx, and OH are particularly valuable in biomarker detection.

The path from macro to micro analyses for this marine carbonate was guided by a section of the NAI-Life Underground Spectral Pipeline which includes other techniques such as XRF, EDS, SIMS, IR, etc. Each technique listed builds upon the strengths of the others to give a true multi-dimensional understanding of biosignatures both extant and ancient.

The marine carbonate section was scanned with a DUV fluorescence mapping instrument (i.e. MOSAIC). The MOSAIC's lower spatial resolution allows for rapid mapping (i.e. s-min) of lager areas [4] and its low spectral resolution gives some insights to the types of organics present but it's use is to direct downstream analyses.

Further inspection of the carbonate with DUV Raman instrument (i.e. MOBIUS) showed that the organic molecules within the brighter fluorescence regions correspond to small shifts in the carbonate peak (~1080-1090 cm^{-1}) from a dolomite to a more calcite-like mineral matrix. These regions also show variability in the 'maturity' of the carbon based on the shape of the graphitic peak at ~1590 cm^{-1}.

Electron microscopy of the of the carbonate show micron scale variations in elemental distribution (e.g. Si, Mg) correlated with the banding pattern observed with MOSAIC. However, these elements or minerals they form are not typically fluorescent in the UV.



Future Direction: The DUV data from the marine carbonate highlight the strengths of these multi-modal analytical techniques to reveal complex, cryptic putative biosignatures. Spectroscopy using visible or infrared wavelengths is a well vetted science now bolstered by advances in DUV spectroscopy [4][5]. Organic molecules (e.g. bio- and abiological), specifically those with aromatic rings exhibit strong fluorescence allowing for sub-ppb detection facilitating rapid precise mapping of trace organics. The existence of fluorescence free spectral region facilitates Raman spectroscopy adding the capability of further organic characterization. The power of these instruments to and characterize organics and minerals is demonstrated on terrestrial samples such as the marine carbonates. Now this ability will be put to the test on Mars with SHERLOC, a DUV Raman/fluorescence system set to fly on the Mars 2020 mission.

References: [1] Naehr T. H. et al. (2007) *DSR Part II, 54(11-13):* 1268–1291. [2] Case D. H., et al. (2015) *MBio, 6(6):e01348-15*. [3] Marlow et al. (2015), Geobiology 13:303-307 [4] Bhartia R. et al. (2010) *AEM,* 76(21)7231. [5] Bhartia R. (2010) *LPS,* Abstract #2674.

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