EXPLORING RELATIONSHIPS BETWEEN MAJOR ELEMENT CATIONS AND ORGANIC PRESERVATION IN SILICA. K.R. Moore[1], D.T. Flannery[2], M. Tuite[1], J.D. Tarnas[1], T. Bosak[3], and K. H. Williford[1], [1]NASA Jet Propulsion Laboratory, California Institute of Technology, [2]Queensland University of Technology School of Earth and Atmospheric Sciences, [3]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology.

Introduction: Ancient biosignatures are key to understanding the emergence and evolution of life in different environments and possibly on different planets. Microbes thrived on Earth from at least the early Archean (~3.5 billion years ago) to the present, but fossil evidence of these microbes is commonly difficult to identify and interpret. This is because the soft, labile organic material in microscopic organisms that existed before the Phanerozoic Eon is less easily preserved compared to shells and bones made by the more recent organisms. Early diagenetic chert preserves numerous exceptional examples of microbial body fossils and organic matter during the Proterozoic[1] and some (though fewer) examples are known from the Archean[2,3]. These biosignatures and the minerals and processes that preserved them provide an important window into the early biosphere on Earth and may aid in the identification and interpretation of potential biosignatures in Jezero crater.

Here we present new insights into organic matter preservation by early diagenetic chert in shallow marine environments and reveal that the organic matter is commonly associated with calcium-, magnesium-, and aluminum-rich phases. These results shed light on the interactions between the biosphere and geosphere on the Archean and Proterozoic Earth and suggest that interactions among organic matter and major element cations in seawater may have promoted the preservation of organic matter by chert. Based on these results, we suggest that the association of these elements with hydrated silica can aid in the identification of any potentially similar biosignatures in the hydrated silica deposits in Jezero crater. If such biosignatures exist, these results will also help us to interpret how organisms may have interacted with the martian environment in the past.

Methods: Petrographic thin sections and freshly fractured rock surfaces of two samples of the ~1.8 Ga Duck Creek Formation, one sample of the ~2.4 Ga Turee Creek Formation, and one thin section of the ~1.6 Ga Balbirini Dolomite were analyzed by scanning electron microscopy (SEM) equipped with an Oxford Instruments X-Max^N 150 mm^2 silicon drift detector energy dispersive spectroscopy system (EDS) at the Jet Propulsion Laboratory (JPL). Uncoated samples were affixed to SEM stubs with carbon tape and analyzed under variable pressure mode at 30 Pa, 15 keV accelerating voltage, working distance of 10 mm. Chemical maps were generated at magnification of 1.5kx with 6 frames and 2048 x 1536 pixel resolution. Spot analyses were collected at the same magnification and spectra and maps were processed using Oxford Instruments AZtec software.

Results: Carbon rich domains were present in all four samples analyzed, either in the form of laterally continuous laminae (Balbirini Dolomite) or isolated domains distributed heterogeneously throughout the chert matrix (Turee Creek and Duck Creek Formations). We interpret these domains as organic material based on the high intensity carbon peaks in EDS spectra from these regions and their dark appearance and fluffy texture in petrographic thin sections and SEM images. The relative intensities of the carbon peaks in EDS spectra compared to calcium and magnesium was inconsistent with spectra of carbonate minerals, further supporting an organic interpretation.

The organic domains and laminae were preserved in the chert facies of all three formations. However, the chemical composition of these domains and the surrounding minerals was different from the chert that did not contain organic matter. EDS spectra from organic-free regions of chert showed high intensity silicon and oxygen peaks, as would be expected from microcrystalline SiO_2. In contrast, EDS maps of organic rich regions revealed that a combination of calcium, magnesium, and aluminum were consistently associated with the organic matter (Figure 1). BSE images highlighted the presence of a variety of nanoscopic crystals and spheres embedded within the organic matter and EDS spot analyses demonstrated that the relative abundances of aluminum, magnesium, and calcium varied among different organic regions and between different domains and different samples. Out of 46 organic regions analyzed across the four samples, all contained calcium, magnesium, and aluminum and none contained organic matter associated with silicon and oxygen alone.

Discussion: The preferential association of organic matter with calcium, magnesium, and aluminum in chert from the Duck Creek Formation, Turee Creek Formation, and Balbirini Dolomite suggests that these elements may have played a role in the preservation of organic matter by chert. Microbial fossilization experiments have recently shown that modern cyanobacteria analogous to the oldest diagnostic cyanobacterial fossils can mediate the precipitation of amorphous silica in seawater that is undersaturated with respect to silica[4]. Cyanobacteria do this by using magnesium cations in solution as a bridge between negatively charged organic surfaces and negatively charged silicic acid[5].

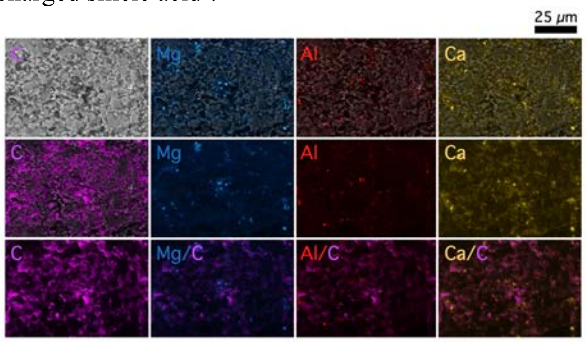

Figure 1: SEM image and EDS chemical maps or an organic rich region of the Duck Creek Formation showing the spatial distribution of Mg, Al, and Ca compared to organic carbon throughout the chert matrix.

Microbial mats in Qatar[6,7] and other environments[8,9,10] have also been found to bind magnesium as well as calcium and aluminum within the biofilms and facilitate the precipitation of amorphous phases, carbonate minerals, and authigenic clays. It is possible that a similar microbially-mediated mechanism preserved biosignatures in Proterozoic marine environments using any combination of calcium, magnesium, and aluminum to promote mineral precipitation.

The results presented here reveal a potential biological contribution to the precipitation of chert in Proterozoic marine environments and suggest that interactions among organic surfaces and ions in solution may have facilitated biosignature preservation. If these interactions did indeed facilitate the precipitation of chert and preservation of biosignatures, these results additionally provide a novel approach to search for and identify biosignatures in hydrated silica on Earth and on Mars. We propose that chert or hydrated silica whose chemical and mineralogical composition indicate an association with calcium-, magnesium-, and/or aluminum-rich phases have a higher likelihood of containing organic matter. In fact, these spectral signatures may themselves be indications of microbially-mediated mineral precipitation and therefore biosignatures in their own right.

These biologically-mediated processes likely required silica concentrations greater than 70 ppm[3] and elevated salinity, conditions that may have been met in shallow marine and evaporitic environments in the past. The water chemistry of the lake that filled Jezero crater remains unknown, but such conditions may have also been met in regions around the shoreline, an environment that may have been captured in the marginal deposits of the crater. NASA's Perseverance rover will investigate the chemistry and mineralogy of these and other deposits in the crater, possibly including hydrated silica deposits[11]. Using the Planetary Instrument for X-ray Lithochemistry (PIXL)[12], the rover would be able to map at a fine-scale the distribution of calcium, magnesium, and aluminum with a spot size of ~100 µm in silica-rich deposits and assess their potential to host biosignatures based on our analyses of Proterozoic chert-hosted organics. Using the Scanning Habitable Environments with Raman & Luminescence for Organics and Chemicals (SHERLOC) instrument[13], we could map any spatial associations of organic matter with these calcium-, magnesium-, and aluminum-rich regions to further assess their biosignature potential.

Future work will seek to identify calcium-, magnesium-, and aluminum-bearing mineral phases associated with organic matter in Proterozoic cherts and investigate additional chert-hosted biosignatures to further our understanding of biosignature preservation and aid in the identification and interpretation of biosignatures preserved by hydrated silica.

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