PHYSICAL AND MOLECULAR BIOSIGNATURE PRESERVATION IN HYDROUS FERRIC OXIDES: IMPLICATIONS FOR DETECTION ON MARS WITH MSL AND FUTURE MISSIONS.

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Introduction: An ideal biosignature preserves both physical and molecular evidence of the organism(s) of interest. Here, we document the detection of physical biosignatures (mineralized microbial filaments) co-occurring with molecular biosignatures (fatty acids detected as methyl esters [FAMEs]) in hydrous ferric oxides (HFO) ranging in age from modern to 1000's of years old from the Iron Mountain gossan, CA. Gossans, dominated by iron oxides, have been proposed as Martian environmental analogs [1]. Organic molecules can be thermodynamically unstable in the presence of iron oxides [2], but may be preserved in mineralogically diverse sediments [3,4].

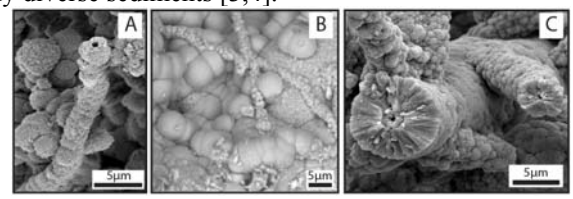

Figure 1. HFO-mineralized filaments in modern (A) and older (B, C) hydrous ferric oxides.

Methods: HFO samples were collected from the gossan in 2011 and a mine water effluent pipe in 2012.

Physical biosignatures (Fig. 1) were characterized by identifying mineral and microbial textures with scanning electron microscopy (SEM). We evaluated mineral filament biogenicity using published criteria [5,6], which include A) a mineral precipitating environment, B) structures observable as a part of the host rock, and C) biological morphology (e.g. cellular lumina, uniform diameters, and evidence of flexibility).

For molecular biosignatures, rock samples were broken open and sampled from their interior under organically clean conditions. Powdered rock samples were reacted with tetramethylammonium hydroxide (TMAH): MeOH (25%) and underwent thermochemolysis at 600°C to hydrolyze and methylate fatty acids. Subsequently, FAMEs were detected with gas chromatograph mass spectrometry (GCMS).

Results and Interpretations: HFO filaments all fit criteria A, B, and C. Based on fulfillment of the criteria, mineral filaments are interpreted as mineral-coated microbial filaments preserved as biosignatures.

FAMEs were detected in modern (SS, Table 1) and 100s-1000s of years old (PS) HFO. Fe-oxidizing bacterial isolates (ES) and environmental samples (IFS) were tested, with similar FAMEs detected. Terrestrially, FAMEs are microbial markers. These results demonstrate that FAME biomarkers are detectable with the thermochemolysis method in microbes, modern HFO, and older HFO, and indicate that FAMEs may be preserved over longer timescales than previously expected in HFO on Earth and possibly on Mars.

Table 1. FAMEs present in Fe(III)-dominated biologic and HFO samples. + = identified. - = not identified.

		n-C10:0	*n*-C12:0	*n*-C14:0	n-C15:0	*n*-C16:0	*n*-C16:1ω7	*n*-C17:0	*n*-C18:0	*cis*-C18:1ω9	*trans*-C18:2ω9
Bio-logic	ES1	+	+	+	+	+	+	+	+	+	-
	ES2	+	-	+	-	+	-	-	+	+	-
	IFS6	+	+	+	+	+	-	-	+	+	-
HFO	SS12	-	+	+	+	+	+	-	+	+	+
	SS6	-	+	+	+	+	+	+	+	-	-
	PS5G	+	+	+	-	+	-	-	+	+	-
	PS17	+	+	+	-	+	-	-	+	+	-

Conclusions: Mineral filament biosignatures provide insight into biosignature detection by instruments on MSL and future missions. Individual filaments are below the resolution of the MSL MAHLI instrument, but sinuous filaments forming mat-like textures are resolvable [5]. Future missions which utilize SEM-like imaging may be capable of detecting these features.

The MSL SAM instrument will use a similar thermochemolysis method. SAM-like analyses on a laboratory GCMS indicate SAM is capable of detecting FAMEs in HFO. Future missions that utilize alkaline thermochemolysis would be capable of detecting these biosignatures if they are sufficiently abundant.

Current and future surface missions have the ability to detect biosignatures similar to those described here. The dual identification of physical and molecular biosignatures would be a powerful way to instill confidence in martian biosignature detection. If present, these features could be preserved in HFO-bearing environments including Hematite Ridge on Mt. Sharp.

References: [1] Burns, R.G. (1987) *LPSC XVIII*, 141-142. [2] Sumner D.Y. (2004) *JGR* 109, E12007. [3] Parenteau M.N. et al. (2014) *Astrobiology* 14, 502-521. [4] Lalonde K. et al. (2012) *Nature* 483, 198-200. [5] Williams, A.J. et al. (2015) *Astrobiology* 15, 637-668. [6] Williams, A.J. et al. (2016) *Geomicrobio J*, accepted.