

RAMAN/LIBS STUDY OF ORGANOMETALLIC COMPOUNDS IN HIGH RICH ACIDIC-FERRUM MINERALS. APPLICATIONS FOR THE STUDY AND SEARCH OF LIFE IN MISSIONS TO EUROPE AND ENCELADUS. P. Such, P. Sobron, E. Lallai, M. Daly.

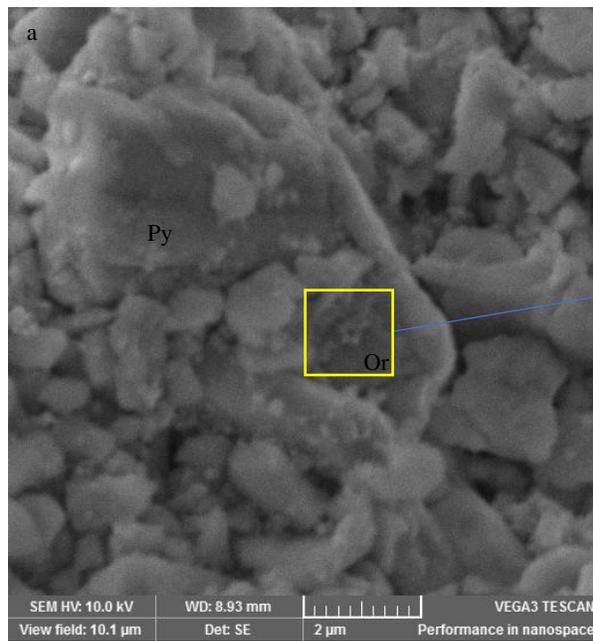
1-Center for Research in Earth and Space Science, Petrie Science and Engineering Building, York University - Toronto, Canada. Corresponding author: suchpam@yorku.ca. 2-Impossible Sensing, 3407 S Jefferson Ave, St. Louis, MO 63118.

Introduction: Recently studies on meteorites shows evidence of extraterrestrial arrival of cyanide complex crucial for the develop of life on earth [1]. This organometallic complex can develop in acidic rich materials that have suffer meteorization and the enrichment of ferrum forming cyanides-amino acids compounds that can be also found on earth close to geysers related to volcanic activity. Recently studies in CM meteorites samples (M52364 Murchison and M58168 NWA 4838) in an Atomic Force Microscope and SEM microscope have shown evidence of amino acids molecules found in the surface of pyrite minerals in matrix, evidence of the organic compounds presented associated to ferrum in meteorites (figure 1a and 1b). Acidic environments like the ones existing along Europe active eruptive fractures or in Enceladus geysers plumes can be adequate places of study in order to search for this compounds. Europe have shown compositions evidence of magnesium sulphates (potentially epsomite) on Europa's trailing side; salty oceans containing sodium, potassium and magnesium chlorides bombarded from behind by sulfur being emitted by its neighbor Io to form sulfates (the sulfur being whacked into the trailing hemisphere of Europa by the rotation of the magnetosphere). Most of the sodium and potassium are sputtered (i.e., knocked off the surface) to create a thin atmosphere, leaving behind the magnesium sulfates as the product of radiolysis occurring on the ocean brines [2]. During Cassini mission flyby 5 through Enceladus plumes have reported a plume composition dominated by a mixture of CO₂, CO, NH₃, CH₄, H₂CO and a host of organic species, reminiscent of the volatile composition of a comet [3]. Both moons evidence similar chemical compositions that can be found in mineralogy associated with geysers cones and geysers deposits in volcanic environments that were proven to contain these organometallic compounds associated with cyanide and ferrum, like the *cacodyls* discovery by Bunsen when studying geyser environments in 1899. During a surface exploration mission, laser Raman and laser-induced breakdown spectroscopy (LIBS) techniques are uniquely suited tools for detailed mineralogy and geochemistry investigations on icy planetary bodies. In addition to working in contact mode (in situ), the major advantage of stand-off Raman and LIBS is the ability to conduct rapid analyses of targets at distances, ranging from <1 to tens of meters. This capability allows identify potentially interesting samples to be examined

in further detail by additional in-situ payload instruments. The Life Analysis, Capture, and Retention on an Orbiting Saturn Spacecraft (LACROSS) is a Raman instrument concept designed to minimize sample alteration and maximize signal-to-noise for analysis of plume ices in Ocean Worlds. Developed by Impossible Sensing under NASA SBIR [4] it demonstrated plasmonic technology enabling ultra-sensitive (ppb), spatially resolved (pseudo-imaging) surface-enhanced Raman spectroscopy (SERS). The excellent SERS performance of LACROSS plasmonic aerogel in a real-world application [IN19] demonstrates (i) high accessibility of the plasmonic hotspot to adsorbed geothermal fluid and (ii) unique ability to exploit the aerogel 3D architecture. The advantages of combining both techniques for the analysis of a given sample are evident: LIBS can reveal the relative concentration of major (and often trace) elements present in a bulk sample, whereas Raman yields information on the individual mineral species and their chemical and structural nature. Thus combining the data from both tools enables definitive mineral phase identification with precise chemical characterization of most major and minor and some trace mineral species. In the context of planetary surface exploration, a combined instrument can provide a rapid mineralogical/chemical evaluation of the target that will be useful for the determination of organometallic compounds that can be present in acidic icy environments near the plume deposits.

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References: [1] Smith K.E, House C.H, Arevalo R. D., Dworking J. P. & Callahan M. P. Organometallic compounds as carriers of extraterrestrial cyanide in primitive meteorites. *Nature Communications* 10, Article number: 2777 (2019). [2] <https://www.planetary.org/blogs/guest-blogs/2013/0305-brown-sea-salt.html>. [3] Waite, J. & Magee, Brian & Brockwell, T. & Zolotov, Mikhail & Teolis, Ben & Lewis, W.. (2011). Enceladus Plume Composition. *LPI Contrib.* 1774. 61-. [4] Sobron P. (2019) New method for airborne particle capture and analysis. NASA New Technology Report NSSC18P2096.



M58168_matrix 3348

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	776	3.28	4.83	9.71	0.83	25.12
Oxygen	8	7858	22.11	32.52	49.03	3.23	14.63
Sodium	11	0	0.00	0.00	0.00	0.00	3.87
Magnesium	12	4359	3.89	5.72	5.68	0.24	6.20
Aluminium	13	327	0.29	0.42	0.38	0.05	17.12
Silicon	14	10965	11.96	17.60	15.12	0.54	4.49
Sulfur	16	294	0.33	0.49	0.37	0.05	15.28
Potassium	19	0	0.00	0.00	0.00	0.00	1.30
Calcium	20	3412	13.01	19.14	11.52	0.54	4.13
Chromium	24	93	0.71	1.04	0.48	0.11	15.78
Iron	26	727	11.87	17.46	7.54	0.80	6.76
Silver	47	99	0.53	0.78	0.17	0.09	16.30
Iridium	77	0	0.00	0.00	0.00	0.00	1.85
Platinum	78	0	0.00	0.00	0.00	0.00	1.78
Gold	79	0	0.00	0.00	0.00	0.00	1.72
Sum		67.98		100.00	100.00		

b

Figure 1a. Detail of organometallic molecule in face of pyrite mineral in Murchison meteorite SEM image (center in Or detail). **1b.** SEM analysis data of the area of the molecule.