

PRESERVATION OF MICROBIAL METABOLISM IN IMPACT GENERATED LITHOLOGIES: IMPLICATIONS FOR MARS. H. M. Sapers¹, A. Pontefract², G. R. Osinski³, L. G. Whyte⁴, ¹Centre for Planetary Science and Exploration, University of Western Ontario and Department of Natural Resource Sciences, McGill University (haley.sapers@mcgill.ca), ²Centre for Planetary Science and Exploration, University of Western Ontario (apontefr@uwo.ca), ³Centre for Planetary Science and Exploration, University of Western Ontario (gosinski@uwo.ca), ⁴Department of Natural Resource Sciences, McGill University (lyle.whyte@mcgill.ca).

Introduction: Post-impact hydrothermal systems are one of the most favourable environments in which to search for evidence of life beyond Earth. Considering the ubiquity of impact events in the Solar System, investigating the potential of such environments to preserve evidence of life has significant implications for habitability on other terrestrial planets such as Mars. Here we report preliminary data from a interdisciplinary study assessing the potential of impact generated lithologies to both host and preserve evidence of microbial life.

Biological Benefits of Impact Events: The catastrophic biological effects of meteorite impact events are well established. However, meteorite impact events also create unique microbial niches¹ that may have been significant habitats on early Earth² and are important astrobiological targets on other rocky bodies such as Mars³. Impact generated lithologies represent understudied microbial substrates both for microbial colonization as well for the potential to preserve evidence of biological activity.

Following an impact event is a phase of thermal biology, characterized by extensive hydrothermal activity capable of hosting microbial communities with diverse metabolisms^{4,5}. Transition metals, such as Fe, play a significant role in microbial metabolism. Autotrophic microorganism exploit redox disequilibrium gaining energy required for growth through cascades of oxidation-reduction reactions^{6,7}. Post-impact hydrothermal systems and associated mineral deposits are characterized by extensive redox disequilibria making them attractive systems for microbial colonization^{4,5}. Iron- and sulfur-based metabolisms are of particular interest as they have been proposed as one of the earliest metabolic pathways on Earth⁸, and conspicuous patterns of iron oxidation states constitute an important biosignature both on early Earth and potentially on Mars considering the importance of Fe in microbial metabolism and the abundance of Fe on Earth and in the Solar System.

Gale Crater, Mars: The Curiosity rover is currently investigating the potential habitability of Gale crater, a 154 km diameter Noachian impact crater on Mars⁹. The sediments within the crater have been interpreted to have been deposited in a lacustrine environment¹⁰ It is plausible that Gale crater hosted an ear-

ly impact-induced hydrothermal system and crater lake^{11,12}. The lowest exposed stratigraphic unit studied to date, the Sheepbed mudstone, contains a out of equilibrium mineral assemblages including both sulfide and sulfate minerals and both ferric and ferrous iron minerals in addition to mixed-valence iron minerals in addition to an amorphous component^{10,13,14}. Although many interpretations exist for the complex geological context and deposition of the Sheepbed mudstone, its chemical and mineralogical make-up including the amorphous material are consistent with reworked impact materials including impact glass. Grotzinger *et al.*¹⁰ have interpreted Gale crater as a potentially habitable environment able to support chemoautotrophic metabolism such as microbial iron reduction.

Biosignatures in impact glass: Recently, microtubules interpreted as microbial trace fossils, were described in meteorite impact glass from the Ries impact structure, Germany¹⁵. Using synchrotron based X-ray spectromicroscopy, distinct patterns of reduced iron surrounding the tubule features in the Ries glasses were spatially correlated with the presence of organic carbon¹⁶. These tubule features have been interpreted to form similarly to microbial etching of submarine basaltic glass through local dissolution as microorganisms extract bio-essential elements from the glass¹⁷. This produces distinct patterns of reduced and oxidized Fe around the tubular features consistent with biological processing. We suggest the Fe speciation patterns surrounding the tubules represent the preservation of these metabolic reactions in the rock record.

Our work aims to empirically tie a specific biological process to an observed trace fossil by performing a series of *in vivo* and *ex vivo* experiments forcing microbial iron reduction on impact-generated substrates in order to reproduce the patterns observed in the Ries glasses. Characterizing experimentally microbially induced chemical changes to impact substrates will provide a biological standard with which to compare putative biological patterns of Fe and S reduction. Establishing Fe and S speciation biosignatures in impactite generated substrates has implications for studying the extent of early life on Earth as well as for the recognition of biological processes beyond Earth.

Experimental Summary: To assess impact lithologies as viable substrates for lithoautotrophic

growth, thermophilic iron (*Carboxydotherrnus ferrireducens*) and sulfate (*Thermodesulfobacterium commune*) reducers isolated from hydrothermal systems will be anaerobically cultured in minimal media on various impact substrates. Substrates will be chosen to compare impact-shocked substrates with unshocked equivalents to test the hypothesis that the impact process creates substrates with an increased potential to host lithoautotrophs due to increased bioavailability of essential elements. Impact glass from the Ries impact structure, representative of the substrates hosting the tubular trace fossils, will be compared with crystalline granite from the inner ring of the structure. Variably shocked basalts (low, medium, and high shock) from Lonar crater, India, are selected as Mars analog substrates and will be compared with Cretaceous basaltic glass from the Troodos Ophiolite, Cyprus, and unshocked Lonar basalt.

An innovative, interdisciplinary approach has been established to characterize the geochemical changes induced by active microbial metabolism and to assess the potential for microbial Fe and S reduction to be recorded in impact materials. Detailed scanning electron microscopy will assess microbial attachment and colonization of impactite surfaces. Energy dispersive X-ray spectroscopy mapping will allow for correlation between colonization and chemistry. Synchrotron near edge x-ray absorption fine structure (NEXAFS) spectroscopy combined with scanning transmission X-ray microscopy (STXM) is a powerful tool to assess biogenicity. Using the methodology established to characterize Fe speciation patterns in the Ries impact glasses, we will use NEXAFS spectroscopy to investigate experimentally controlled microbially induced geochemical changes in impactite substrates. The high spectral resolution of NEXAFS spectroscopy combined with the high spatial resolution of STXM can be used to speciate transition metals providing a spatially correlated map of oxido-reduction patterns and organically bonded carbon on a sub-micrometer scale.

Biosignatures: Interpreting *in situ* enigmatic features such as body or trace fossils, isotopic or molecular signatures, chemical disequilibria, or conspicuous mineralization as indicators of biological activity is a notoriously difficult task. Several studies have attempted to summarize biogenicity criteria to produce a systematic framework in which to assess enigmatic features, or to propose classification schemes for the organization of biologically ambiguous features. However, many of these features remain a source of contention in the literature. The goal of characterizing biosignatures is not only to identify attributes as uniquely produced by biological processes, but also to recognize these attributes as unambiguous indicators of life. Un-

derstanding and recognizing the biogeochemical processes that result in biosignatures in terrestrial analogs of potentially habitable environments on Mars will provide valuable information for future life detection missions

References: [1] Cockell, C. S., Lee, P., Osinski, G., Horneck, G. & Broady, P. (2002) *MAPS* 37, 1287-1298. [2] Westall, F. & Folk, R. L. (2003) *Precambrian Res.* 126, 313-330. [3] Cockell, C. S. (2004) *Adv Space Res* 33, 1231-1235. [4] Cockell, C. S. & Lee, P. (2002) *Biol Rev Camb Philos Soc* 77, 279-310 [5] Naumov, M. V. (2005) *Geofluids* 5, 165-184 [6] Gadd, G. M. (2010) in *Microbiology* Vol. 156 609-643 [7] Nealson, K. H. (1997) *Annu Rev Earth Pl Sci* 25, 403-434. [8] Weber, K. A., Achenbach, L. A. & Coates, J. D. (2006) *Nature Rev Microbiol* 4, 752-764 [9] Grotzinger, J. P. et al. (2012) *Space Sci Rev*, 170, 5-56. [10] Grotzinger, J. P. et al. (2013) *Science* [11] Cabrol, N. A., et al. (1999) *Icarus*, 139, 235-245. [12] Schwenzer, S. P., et al. (2012) *PSS*, 70, 84-95. [13] Ming, D. W., et al. (2013) *Science* [14] Vaniman, D. T., et al. (2013) *Science* [15] Sapers, H. M., Osinski, G. R., Banerjee, N. R. & Preston, L. J. *Geology* (in press). [16] Sapers, H. M., Osinski, G. R. & Banerjee, N. R. *EPSL* (in prep). [17] Staudigel, H., et al. (2008) *Earth Sci Rev* 89, 156-196.