CARBON LIMITED SOILS OF ICELAND: ANALOGS FOR IDENTIFYING CARBON-MINERAL INTERACTIONS IN GALE CRATER, MARS SURFACE MATERIALS.

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Introduction: The Mars Science Laboratory's Curiosity rover mission to Gale Crater, Mars has a goal to search for organic carbon and corresponding evidence of ancient microbiology preserved in clay mineral-rich sedimentary deposits [1]. No clear correlation of clay mineral (smectite) abundances with the Sample Analysis at Mars (SAM) carbon detections (up to 2000 ppm C) [2] has been established, suggesting other phases may preserve organic C in martian sediments. Terrestrial volcanic glass soils can accumulate C due to the C-complexing abilities of poorly crystalline Al- and Fe-oxyhydroxides [3]. The X-ray amorphous component (20 to 73 wt. %) in Gale Crater materials [4,5] has received little consideration regarding organic C preservation in Gale Crater. The objectives of this work are to 1) Evaluate C content and level of soil development of basaltic glass-bearing Icelandic soils to determine the role that poorly crystalline phases have in complexing organic C in carbon limited soils and 2) Determine if evolved gas analysis (EGA) of well-characterized Mars analog basaltic materials from Iceland can be used to interpret SAM data to understand the nature of organic-C mineral/geochemical associations in Gale materials.

Materials and Methods: Three soils were sampled with increasing distance from the Vatnajökull glacier, Iceland to represent increasing soil parent material age (< 10Kyr to 2 Ma) and increasing C content. Site 1, site 2, and site 6 occurred 100 m, 18 km, and 90 km from the glacier, respectively. Soil pits were dug and sampled according to standard methods (e.g., soil color, structure, and texture (grain size)) to distinguish soil horizons for sampling. All soils were dried at 60°C and sieved to <2 mm. The <2mm and >2mm fractions were analyzed by Rigaku MiniFlex X-ray diffractometer (XRD) (CoKa) for mineralogy. Mineral phases and amorphous abundances were determined by Rietveld refinement with a corundum internal standard. Total chemistry (Si, Al, Fe, Mn, Ca, Mg, K, Na, Ti) was determined by lithium meta-borate fusion followed by ICP-OES solution analysis. Total C was determined by induction by furnace analysis while total organic C was determined by sample leaching with HCl followed by induction by furnace analysis. Poorly crystalline and carbon bound Al and Fe were estimated by oxalate and pyrophosphate extractions, respectively. Extracted solution Al and Fe were measured by ICP-OES. EGA of select samples was conducted on Labsys differential scanning calorimeter/thermal gravimeter connected to Pfeiffer Thermostar GSD-320. Soils were heated from 25 to 1000°C at 35°C/min under 10 sccm He and 30 mbar pressure, similar to operating conditions of the SAM instrument.

Results: The gravel parent material from all three sites consisted mostly of feldspar, pyroxene and minor olivine, which is comparable to Gale crater mineralogy [4,5]. The site 1 parent material, which was collected closest to the glacier, possessed an ~1.5 nm X-ray diffraction peak consistent with phyllosilicates that likely formed through subglacial volcanic processes. Secondary phases detected in site 1 soils included clinoptilolite, an X-ray amorphous phase, and the inherited phyllosilicate. Site 2 had no evidence of phyllosilicate in the soil or parent material while site 6, furthest from the glacier, had a minor 1.4 nm peak consistent with a pedogenic phyllosilicate. All soils possessed 30 to 50 wt.% amorphous phases (consistent with Mars abundances [4,5]). Chemical mass-balance analysis indicated no soil chemical gains or losses, relative to parent gravel, which was consistent with pedogenic formation of amorphous phases in all soils.

Total carbon levels (325-600 ppm C) (Fig. 1) were consistent among sites and similar to lower levels detected on Mars (160-2300 ppm C) [e.g., 2]. Inorganic C was prevalent closest to the glacier because organic C concentrations (100 ppm C; Site 1) were much lower than total C (600 ppm C) (Fig. 1). Organic C concentrations at sites 2 and 6 were similar to total C (Fig. 1) suggesting that organic C contributed a significant fraction of C to these soils. The soils collected at sites 2 and 6, further from the glacier, were more developed and had more time to accumulate organic C than site 1.

Carbon did not correlate with oxalate and pyrophosphate extractable Al and Fe (Fig. 2). This was attributed to low C concentrations relative to much higher abundance of poorly crystalline (oxalate extractable) Al and Fe in these soils (Fig. 2). The detection of pyrophosphate extractable Fe and Al was consistent with poorly-crystalline Fe- and Al-oxyhydroxides having a role in complexing C in these carbon limited soils.

The Iceland soils were similar to Mars materials because most CO_2 evolved below 600°C, which was
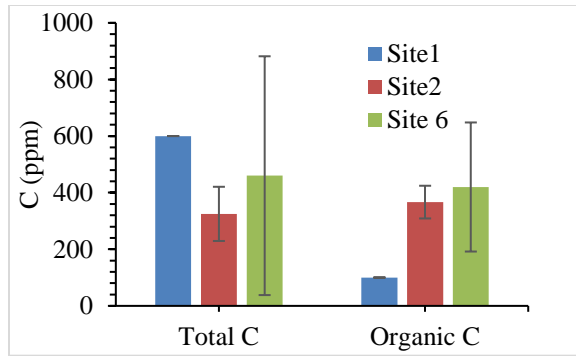
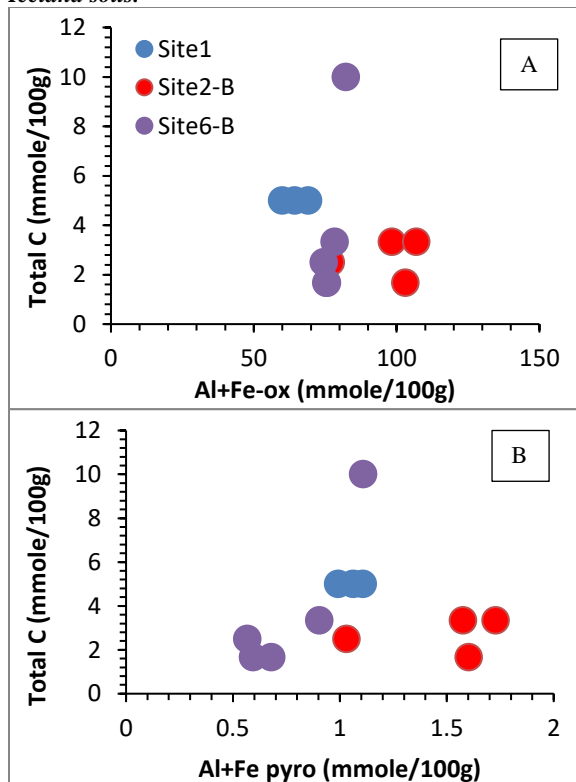*Figure 1. Total C and organic C detected in Mars analog Iceland soils.*

Figure 2. Total C versus a) oxalate and b) pyrophosphate extractable Al + Fe from Mars analog Iceland soils.

Figure 3. Evolved CO_2 versus temperature from Mars analog Iceland basaltic soils and Gale Crater loose-eolian materials. 1. Red line, 2. Green line.

consistent with the presence of oxidized organic C and Fe-carbonate (Fig. 3). Fe-carbonate appeared to contribute most of evolved CO_2 in the site 1 soil instead of organic C. The evolved CO_2 from site 2 and 6 soils was conversely, attributed to organic C, because total C and organic C values were similar (Fig. 1). CO_2 evolutions from Iceland soils suggest that evolved CO_2 from the Mars samples below line 1 (420°C) could be consistent with organic C whereas evolved CO_2 peaks near line 2 (500°C) could have contributions from carbonate (Fig. 3). The presence of organic C complexed by Fe and Al in the site 2 and 6 soils (Fig. 2b) suggested that organic C (carboxylates) [6]
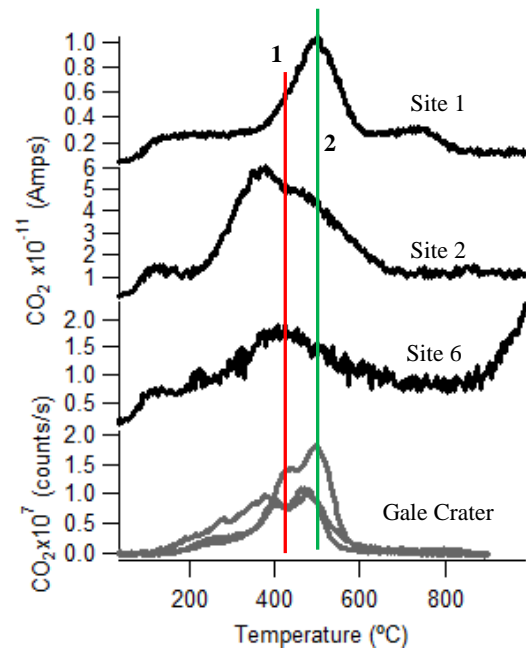
complexed by Fe and Al could contribute to evolved CO_2 detected below line 2 in the Iceland and Gale Crater materials (Fig. 3).

Icelandic basaltic soils and Gale Crater surface materials have similar amorphous and total C contents with comparable evolved CO_2 profiles. The presence of C bound to poorly crystalline Fe and Al in the Icelandic soils suggests similarly complexed C could be contributing to evolved CO_2 in Gale Crater materials. Future work will verify the presence of Fe/Al-carboxylate phases in the Icelandic soils through GC/MS analysis. While the biological origin of organics in Icelandic soils could differ from the origin of martian organics, the organic complexes (e.g., carboxylates) could be similar. [7] Evolved gas analysis of well characterized terrestrial analog soils can therefore be used to interpret SAM carbon detections and thus understand the nature of organic-C mineral/geochemical associations in Gale materials.

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