A COLD WET MARS: A TESTABLE HYPOTHESIS FOR ANCIENT MARS OCEAN FREEZING POINT DEPRESSION VIA LOW MOLECULAR WEIGHT ORGANICS. M. D. Fries[1] and A. Steele[2]. [1]NASA Astromaterials Acquisition and Curation Office, JSC, Houston, TX 77058 [2]Carnegie Institution for Science, Washington DC. Email: marc.d.fries@nasa.gov

Introduction: Mars exhibits widespread evidence of surface water in the distant past, but global modeling has had difficulty producing climatological conditions conducive to a wet surface. The hypothesis discussed here examines a different way of approaching the problem rather than focusing on climate, instead an examination of the nature of the surface liquid itself. Previous work has largely assumed that martian surface water was a brine analogous to terrestrial ocean water, but recent discoveries suggest that significant amounts of light organic compounds may have been present via abiogenic native production of light organics on Mars [1]. Light organics such as methanol and formaldehyde have an approximate order-of-magnitude greater freezing point depression than brine, potentially lowering the freezing point of martian surface fluids sufficiently to remain liquid even if the mean surface temperature is below zero Centigrade. As Mars evolved and the surface transitioned to the strongly oxidized conditions seen today, the light organics would have oxidized to carbon dioxide and may be a constituent of the atmosphere today. Considerable work must be done to constrain the freezing points of Mars-relevant organic/water and organic/salt/water mixtures, but this investigation might explain the presence of surface fluid on a cold early Mars – a cold, wet Mars as opposed to a warm, wet Mars. Additionally, this approach may work in conjunction with climatological modeling to better describe early conditions conducive which adequately explain observations. This hypothesis can be tested by examination of ancient fluid inclusions (either *in situ* or via Mars Sample Return) such as those commonly found in halite, preserving samples of ancient martian surface fluid.

Discussion: Previous work on the subject of ancient martian surface water has focused on the competing possibilities of a dry, cold Mars or a warm, wet Mars. Considerable attention has been paid to atmospheric composition, and variations therein which could potentially have produced a warm, wet Mars in the distant past [e.g. 2-5]. This work focuses on the possibility that variation of the surface liquid composition could explain or help to explain the presence of liquid water on early Mars. Even if it does not fully account for liquid water, expanding the temperature range for liquid fluid on Mars results in a concordant expansion in the range of atmospheric compositions and pressures that may have been present.

Light Organics Freezing Point Depression: Recent work on martian meteorites has revealed evidence of mechanisms conducive to the in situ production of LOs via electrochemical, serpentinization, and carbonate replacement mechanisms [1, 6]. Fundamentally, these processes reduce dissolved CO_2 in subsurface brines to produce a range of compounds. These compounds span a redox range extending from fully reduced carbonaceous solids and PAHs, to methane and larger derivatives (ethane, propane, butane, etc.) to moderately reduced species such as methanol, formaldehyde, and larger derivatives thereof. There is a considerable range of parameters that need to be examined to quantify the freezing point depression produced for Mars-relevant light organics as well as addition of dissolved salts. Since the actual composition of early martian light organics is at present unknown, we must examine simple cases for the time being. Examining the simple case of a methanol/water mixture, methanol fractions of 0.05, 0.15, and 0.25% (w/w) produce freezing point depressions of -3.1, -10.5, and -20.3°C respectively. The volume of light organics present on early Mars is currently unknown, and this obviously is a significant consideration. It is reasonable to expect that future research will place reliable limits on light organics concentration on early Mars.

Fate of Light Organics: The light organics central to this hypothesis are no longer observed on Mars, at least in their original form. As Mars' surface evolved from its early wetter state to today, the surface oxidized considerably as seen in present-day concentration of oxidized iron, perchlorates, and other species. Light organics would also have been subject to oxidation, losing hydrogen to form CO_2. If the early martian oceans contained enough light organics to depress the freezing point sufficient to remain liquid, would the amount of CO_2 produced during oxidative loss be within limits of the current-day atmosphere? As a first-pass estimate, we can take the amount of methanol present at several concentrations for estimates of early martian ocean volumes from literature and convert that methanol to CO_2 to estimate volumes of CO_2 produced. Carr and Head (2003) [4] and DiAchille and Hynek (2010) [7] estimate Mars' early oceans at 2.3e7 km^3 and 1.24e8 km^3 in volume, respectively. For the ocean in [4], a methanol/water fraction of 0.05, 0.15, and 0.25 would produce 0.39, 1.16, and 1.93 bar of CO_2 if oxidized to entirety. For the more voluminous oceans in

[7], methanol/water fractions of 0.05, 0.15, and 0.25 would produce 2.08, 6.23, and 10.39 bar of CO_2. Note that these are simple calculations assuming invariant volume and could use refinement but are sufficient for this first-pass examination. Results from the MAVEN mission indicate that Mars has lost at least 0.8 bar of CO_2 over its lifetime with some variation due to past escape rates [8]. Therefore, concentrations of light organics in Mars' early oceans are probably constrained to a practical limit of ~0.25 methanol/water for the oceans described in [4] and ~0.05 for the oceans in [7]. Note that the allowable range of light organic concentration depends heavily on the volume of Mars' early oceans, with the entire range of concentrations for the oceans in [4] amounting to lower values than the starting value (0.05 methanol/water) in [7]. For the oceans in [4], freezing point depression of up to ~-20°C is within reason, while for the oceans in [7] a lower depression is expected. Note that this is a simple model that can be refined in future work.

Evolution: Temporal factors should also be considered in future testing of this hypothesis. A brine ocean may have frozen quickly after formation, but the evolution of light organics occurred on a timescale that is not currently quantified. The mechanism of light organic production is reduction of subsurface brines by serpentinization, carbonate replacement, and/or electrochemical reaction at oxide mineral surfaces [1]. The evolution of light organics would occur from the subsurface and diffuse upward, on time scales that require further investigation. The possibility exists that light organics accumulated under frozen oceans, generating liquid as the organic concentration increased. The results may include an ice cap with a relatively concentrated organic/water liquid mix underneath, or perhaps melting of permafrost in other regions to produce surface eruptions of liquid.

A Testable Hypothesis: Although other mechanisms for testing this hypothesis likely exist, one scientifically robust approach would be analysis of ancient samples of martian surface water. This is a possibility, as ancient halite has been reported in both a martian meteorite [9] and from orbital data. Halite has proven to preserve fluid samples on million-year timespans on Earth, and some meteorites have preserved samples of water which date to over 4 Ga old [10]. Samples of fluid-bearing halite should be considered a high science priority [11].

Implications: The presence of light organics in early martian oceans might explain, in full or in part, the current discrepancy between observed evidence of ancient liquid water and difficulties in modeling an ancient Mars atmosphere capable of sustaining liquid surface water. Even if it does not provide a standalone explanation, incorporating the potential for sub-zero liquids on Mars will expand the range of atmospheric compositions and pressures allowable. Also, the scenario of relatively light organics-rich oceans has interesting implications for the study of potential life on Mars, and for the study of origin of life on terrestrial worlds. The early martian – and perhaps terrestrial – oceans become chemically more comparable to "primordial soup", and somewhat closer in composition to Titan's present-day oceans than a simple brine.

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