MARTIAN ACIDIC ENVIRONMENTS THROUGH TIME: OPPORTUNITIES FOR LIFE.

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Introduction.

It has been proposed that a CO_2 dominated atmosphere in early Mars would rendered mildly acidic oceans [1] by releasing free protons in the sequence $H_2O + CO_2(g) \leftrightarrow H_2CO_3 \leftrightarrow H+ + HCO_3^-$. The presence of soluble iron in its waters contributed even more to oceanic acidification: hydrolysis of ferrous ion generates free protons by the equilibrium $Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+$, and the acidification is much more effective if the iron is in the form of ferric ion, a product of iron photooxidation: $Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$. Moreover, jarosite minerals, as well as evaporite deposits containing magnesium sulphate salts, a typical sublimation residue, have been detected by the MER Opportunity in the sediments deposited at Meridiani Planum, a near-equatorial region of Mars. The amount of salts detected, up to 40% [2], leads us to expect that sulphate levels in ancient martian oceans were at least at the same order of magnitude as those derived from weathered ultramafic rocks on Earth. Following the Opportunity results, however, we can assume a Fe^{3+}–enriched solution in equilibrium with jarosite at least locally and/or temporarily, so potentially displaying sulphate levels up to 13.5 mM [1].

The acidic Noachian oceans.

For the Noachian oceans, aqueous thermodynamic calculations [1] considering such a solution enriched in iron hydroxides and sulphate result in a pH between 5.3 and 6.2 for the siderite–Fe^{2+} equilibrium; and if the ferrous iron was photolytically oxidized to ferric, the final pH was between 1.9 and 2.1 for the siderite–Fe^{3+} equilibrium. The subsequent evolution of the acidic environment over time results in Fe^{3+}–sulphatic species dominating the chemistry of the oceans.

Hesperian-Amazonian transient acidic wet environments.

Also under modern environmental conditions on Mars, jarosite has been formed in transient supercold episodic acidic brines at Meridiani. Jarosite metastability in Meridiani indicates that mostly arid environments have prevailed after jarosite precipitation, as jarosite becomes unstable and fastly decomposes to ferric oxyhydroxides in the presence of liquid water [3]. But, was Meridiani jarosite formed in ancient times, with no subsequent aqueous alteration during perhaps billions of years, or was it formed in a more recent period of water stability? Several factors illustrate that considerig Meridiani jarosite as an ancient mineral assemblage may pose severe problems.

If jarosite formed millions or billions of years ago, not only chemical but also physical environmental parameters at Meridiani must have been kept strictly constant during the entire time for jarosite to remain stable. And this scenario does not correspond with our current knowledge about Mars. Very recent weathering processes of surface materials in Mars includes: (1) significant changes in the near-surface water reservoirs, and atmosphere composition and pressure, due to large excursions in planetary obliquity [4] and/or continuing extensive volcanism [5,6]; (2) planet-wide [6,7] and specifically equatorial [5] glacier activity; (3) wind eroding rocks, transporting dust particles, forming wind streaks and blanketing the soil [8], as reported for Meridiani [9]; and (4) small-diameter and fresh craters, with impact-related crushed layers mantling previous deposits, suggesting local exposure ages of the surface as recent as 1 My, as dated for Meridiani [10]. These processes affected jarosite assemblages over time, contributing to the formation of the sulphur-enriched soil described by the MER Opportunity [2,9].

Along with the mineralogy, the local geomorphology tells the story of recent aqueous chemical weathering in Meridiani: some images taken by Opportunity show channeled features shaped by almost contemporary liquid water (Fig. 1). The presence of unweathered basalt in the same location indicates that liquid water was present only transiently in Meridiani at the time when jarosite was formed [3,9].

Thus, the only valid conclusion after the analysis of Meridiani mineralogy is that jarosite was formed in a very recent, virtually contemporary, transient wet environment. This interpretation has profound implications on the ongoing debate about the actual age of the water-related geology at Meridiani [2,9]. It is possible that the mineralogy revealed by Opportunity reflects supercold recent times of local episodic acidic brines. As episodic aqueous processes also occurred at Meridiani several billions of years ago [2], shallow surface water may have been flowing recurrently on Meridiani (and even on other martian locations) during a major portion of Mars history (Hesperian and Amazonian times [11]). As noted above, the occurrence of hemispheric oceans, also probably acidic [1], may represent a localized stage in the distant martian past [11].

Opportunities for life.

A well-characterized terrestrial analogue to the acidic martian environments are the headwaters of the Tinto River system (in the southwest of Spain), an extreme acidic environment controlled by iron geomicrobiology which produces ferric iron-enriched sediments dominated by sulfate and oxihydroxide parageneses, resulting in goethite, hematite and jarosite, analogous to the minerals found in Meridiani [2,12]. In the living Tinto River system, the values of pH, redox potential, and Fe^{3+} and sulphate concentration remain constant under variable climate regimes. Life is highly diverse in the Tinto system [13,14], allowing to suggest comparable acidic aquatic habitats hosting a putative biosphere on Mars. In fact, if biological inhabitation of Mars is considered plausible, moderate acidic environments represent the closest terrestrial analogue for a biogenic environment, similar to that where life originated on the Hadean-Early Archaean Earth [15,16].

In contrast to the ideas by Summer [17], suggesting that the composition of the sedimentary rocks in Meridiani points that organic compounds are unlikely to be preserved within them, in the Tinto River system, the remobilization of iron and its subsequent precipitation as ferric minerals preserves biological remains sometimes in remarkable detail, suggesting an analogue record in the rock exposures derived from the acidic martian environments.

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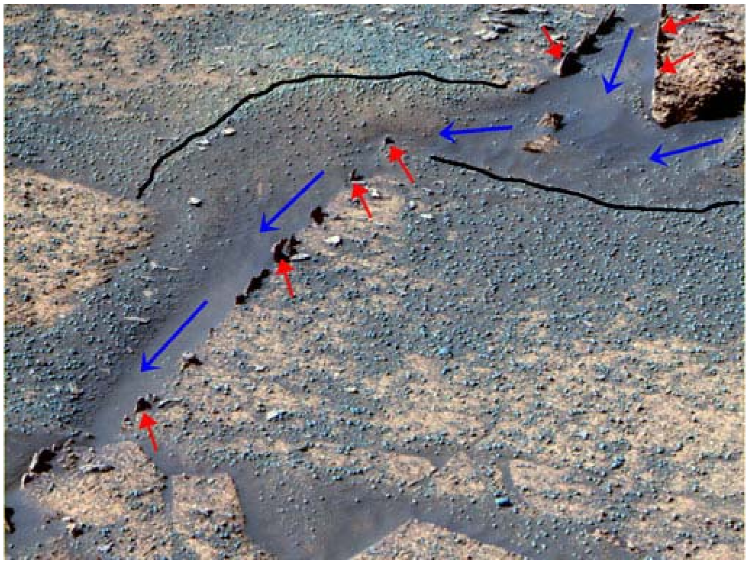

Figure 1: Opportunity picture 16-JF-02-crop-B170R1_th544, obtained inside Endurance crater [18]. The channeled feature has been formed by water flowing through fractures, as indicated by the blue arrows, and shows no obvious evidence of subsequent eolian, fluvial, frost/defrost, or any other alteration processes. Black lines remark the maximum water level. Red arrows indicate the location of centimeter-size pointy features aggregated by the water flowing, which delicacy unambiguously suggests a very recent epoch of formation. Image courtesy NASA/JPL/Cornell.