

MARTIAN SUBSURFACE WATERS: ALKALINE AND REDUCED THROUGHOUT HISTORY.

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Introduction: Throughout the history of Mars, aqueous solutions should have existed at some depths below the surface. On early Mars, high geothermal gradients and intensive volcanic activity would have favored near-surface existence of aqueous solutions and sapping of ground water (e.g., [1]). During later epochs, solutions could have been stable deep below the surface, usually below ice-bearing rocks, and only episodically released on the surface, as at present. Valley networks and especially outflow channels demonstrate the effects of released waters on surface morphology. Release of subsurface waters should also have affected surface chemistry and mineralogy via processes of water-atmosphere interaction, dissolution of surface minerals, exchange of elements between solutions and minerals, and mineral deposition. Despite the importance for surface chemistry and mineralogy, the composition of deep martian subsurface waters is not known.

Here we argue that in contrast to surface and near-surface aqueous solutions, which could have been episodic, oxidized, and acidic; deep subsurface waters are likely to have been alkaline, reduced, and may have contained dissolved H_2 , CH_4 and organic species of abiotic and/or biotic origin.

Surface solutions: acidic, oxidizing, but episodic:

Acid volcanic aerosols and near-surface aqueous oxidation of sulfides could have caused "acid weathering" [e.g., 2, 3] of near-surface martian rocks and may account for the formation of jarosite and other sulfates, and the deficiency of carbonates. Despite its potential influence on surface mineralogy, the impact of acid weathering could be very shallow. First, the amounts of SO_2 , H_2S , and HCl in volcanic gases are limited by their solubilities in magmas. Only a minor fraction of volcanic rocks can be weathered by volcanic acids (aerosols, gases, or solutions) because of mass balance constraints. Second, rapid interactions of acidic solutions with minerals should result in neutralization. Third, acid lakes on Earth are only found in calderas in active volcanoes [4] or in locations sourced by acid springs [5] and they are not likely to be a widespread phenomenon on Mars. Fourth, the formation of acidic conditions near the surface is limited by low concentrations of O_2 (needed to oxidize S^{2-} and Fe^{2+}), by the deficiency of massive sulfide deposits, as well as by a deficit of near-surface aqueous solutions throughout history. Fifth, there are no obvious signs of acidic weathering in Martian meteorites.

Table 1. Typical compositions (mg/liter) of spring water associated with weathering of ultramafic rocks [8].

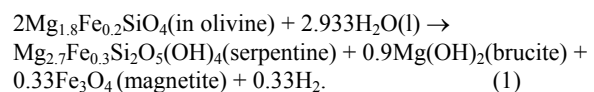
	Mg ²⁺ -HCO ₃ ⁻ type	Ca ²⁺ -OH ⁻ type
pH	~9	~12
T°C	22°	10°-15°
Ca ²⁺	3.3	50
Mg ²⁺	103	0.4
Na ⁺	7.6	~30
Cl ⁻	5.0	~30
HCO ₃ ⁻	493	0
CO ₃ ²⁻	23.26	0
OH ⁻	0.12	57.0

Finally, volcanic activity and weathering of massive sulfides occur locally on Earth and the same should be true on Mars. Therefore, acidic conditions were probably limited in space and time and "acid weathering" was probably a local near-surface phenomenon.

Subsurface waters: alkaline and reduced. Water-rock reactions, rather than interactions with atmospheric gases, determine the composition of deep subsurface solutions. The presence of olivine in the martian soil [6, 7] and the high abundance of mafic and ultramafic rocks on Mars inferred from remote sensing data and the compositions of martian meteorites imply that subsurface weathering on Mars probably resembles that on Earth. On Earth, low-temperature aqueous alteration of olivine-bearing rocks leads to dissolution of olivine and pyroxenes and formation of alkaline solutions that are often rich either in Mg^{2+} (at early stages of alteration) or Ca^{2+} , and also have elevated concentrations of Na^+ and Cl^- [8-10], as illustrated in Table 1. Subsurface weathering of basalts also leads to moderately alkaline solutions [11, 12].

Aqueous alteration of terrestrial mafic, and especially ultramafic, rocks demonstrates strong correlations between solution chemistry and secondary mineralogy. Thermodynamic models are highly applicable to chemistry of aqueous solutions formed through alteration of ultramafic rocks, as shown by application of reaction path modeling [10, 13]. Our reaction path calculations, aimed at modeling weathering of olivine-bearing rocks on Mars demonstrate the formation of alkaline solutions and reveal a sharp difference in the oxidation state of solutions and in secondary mineralogy between subsurface alteration (closed system) and atmospherically influenced near-surface weathering (open system), as shown in Table 2. Note that magnetite is among the alteration products in the closed system, but that goethite is present in the open system results. This is consistent with the presence of H_2 in the closed system fluid, and O_2 in the open system fluid composition. Note also that bicarbonate, CO_2 , and various carbonate complexes are present in the open system results, but that graphite dominates the speciation of carbon in the closed system. The appearance of graphite in the calculations suggests that metastable organic compounds may also be reaction products. In fact, a variety of organic solutes appear in the results if the formation of graphite is suppressed (c.f. [14]), consistent with detection of CH_4 and other hydrocarbons in serpentinites [9, 15, 16].

The results in Table 2 demonstrate that $Fe^{(II)}$ in olivine can be oxidized even if O_2 is not involved. In fact, water plays a major role in oxidation of ferrous silicates, as exemplified by oxidation of ferrous iron in olivine



Reaction (1) and similar pathways are observed during terrestrial alteration of ultramafic/mafic rocks and in model experiments [e.g., 17]. The limited involvement of dissolved

Table 2. Dominant composition of aqueous solutions (mol/kg H₂O), secondary mineralogy (moles), and gases (mole ratios) that represent initial stages of aqueous alteration of olivine below the martian surface (closed system) and near the surface (open system) at 0°C and 1 bar.

Closed system		Open system	
Antigorite	2.9E-04	Antigorite	2.9E-04
Graphite	1.0E-06	Calcite	2.8E-04
Greenalite	4.0E-05	Talc	3.9E-05
Magnetite	1.8E-03	Goethite	5.4E-03
Olivine	9.9E-01	Olivine	9.9E-01
H ₂ ,gas	9.9E-01	HCO ₃ ⁻	1.4E-04
H ₂ O,gas	5.0E-03	Ca ²⁺	1.1E-04
OH ⁻	1.2E-03	CO ₃ ²⁻	3.6E-05
H ₂ ,aq	9.7E-04	OH ⁻	1.2E-05
Ca ²⁺	6.0E-04	HSiO ₃ ⁻	9.0E-06
CaOH ⁺	4.2E-06	SiO ₂ (aq)	5.4E-06
HSiO ₃ ⁻	3.7E-06	CaCO ₃ ,aq	5.3E-06
HF ₂ O ⁻	2.4E-06	Mg ²⁺	4.6E-06
SiO ₂ ,aq	2.3E-08	CaHCO ₃ ⁺	1.9E-07
CaHSiO ₃ ⁺	2.0E-08	MgCO ₃ ,aq	1.3E-07
FeOH ⁺	4.7E-09	CO ₂ ,aq	4.9E-08
FeO,aq	3.3E-09	O ₂ ,aq	2.2E-08
pH	12.0	pH	10.0

Both cases model the reaction of 1 kg of liquid water with 1 mole of olivine, (Mg_{0.7}Fe_{0.27}Ca_{0.03})₂SiO₄ (158.6 g) but only 1% of olivine was allowed to 'react'. Note that H₂-rich gas is present when olivine reacts in the closed system. In the closed system, the C content is 1 ppm (in graphite). Formation of CH₄ was suppressed. In the open system, *p*O₂ is 10⁻⁵ bar and *p*CO₂ is 6.5 mbar. For both systems, olivine molar amounts represent non-reacted portion of the mineral.

O₂ in oxidation of Fe^(II) is supported by detection of H₂ in spring waters, seeps, and fluid inclusions produced during serpentinization [9, 16, 18]. In addition, oxidation of Fe^(II) with O₂ would decrease the pH, which is inconsistent with the alkaline pH of terrestrial springs in serpentinites, and points to oxidation by H₂O (see reaction 1).

Our calculations also demonstrate highly reduced conditions during early alteration of olivine and formation of a gas phase rich in H₂ (Table 2). Reduced environments during early stages of alteration of peridotites can even lead to formation of native metals [19, 20]. In fact, the detection of native metals in Chassigny [21] may indicate extremely reduced conditions of alteration. On Mars, low *p*O₂ in the atmosphere (10⁻⁵ bar) and a high Fe content in rocks imply minimal participation of O₂ in subsurface oxidation [22]. The limited aqueous alteration observed in martian meteorites [23] also indicates a short time for aqueous interactions and/or a deficiency of H₂O.

In contrast to O₂, atmospheric CO₂ can affect solution chemistry and secondary mineralogy during subsurface weathering. In fact, conversion of dissolved CO₂ into the carbonate ion (CO₃²⁻) in alkaline solutions may cause intense consumption of CO₂ from the atmosphere. The conversion of

CO₂ to CO₃²⁻ is responsible for precipitation of carbonates through weathering (serpentinization, palagonitization) of ultramafic/mafic rocks [8, 10, 13, 24]. Recently, this process has been employed to explain stable isotopic composition of carbonates in the ALH84001 martian meteorite, which is a pyroxenite [25].

Martian subsurface waters are likely to contain sulfate that, however, should not react with H₂ and organic compounds owing to inhibition of low-temperature redox reactions. Disequilibria between sulfates, H₂ and organic compounds create a potential for biologic sulfate reduction, as it happens in terrestrial serpentinites [20]. Likewise, disequilibria between CO₃²⁻ (or HCO₃⁻) and H₂ create a potential for biological methanogenesis, which in fact, may account for a greenhouse effect on early Mars and for the presence of 10 ppb of CH₄ [26] in the preset martian atmosphere.

Concluding remarks: Considerations of terrestrial analogs and test calculations of water-olivine interactions allow us to hypothesize that martian subsurface solutions were alkaline and reduced, and that they contained dissolved H₂ and organic compounds, as well as sulfates and chlorides. Release of these waters onto the martian surface would result in neutralization (or possibly, acidification) and oxidation of solutions through interaction with atmospheric CO₂ and O₂, surface materials, and mineral deposition. In addition to "acid weathering", these processes should have affected martian surface mineralogy and could be responsible for formation of ferrous sulfates [c.f. 27] and carbonates [25].

Weathering of ultramafic rocks results in a restricted and predictable set of weathering products that should be present in the martian subsurface. These minerals may only be present in small isolated surface areas and may escape detection by orbiting spacecraft.

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