ORIGIN OF ACID FLUIDS ON MARS: IMPACTS vs. VOLCANISM. M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404. E-mail: zolotov@asu.edu

Introduction: Martian surface materials demonstrate signs of weathering at low-pH aqueous conditions. The detections of ferric sulfates in Meridiani Planum and Gusev crater indicate acid conditions at the time of the deposition [1-4]. Preferential low-pH dissolution of olivine and pyroxene in basaltic materials could be responsible for faint pyroxene features in the near-IR [5] and thermal-IR [6] spectra of northern low-albedo regions (see details in [7-9]), low concentrations of Fe and Mg in surface layers of basalts in Gusev crater [10], as well as the presence of plagioclase in jarosite-bearing bedrocks at Meridiani Planum [11]. A likely presence of secondary amorphous silica in northern low-albedo regions [12-14], in layered Meridiani bedrocks [15], and several rock classes at the Columbia Hills in Gusev crater [11] may also indicate low-pH environments and a lack of complete neutralization of solutions in many locations [7-9,16,17]. Finally, correlations between P, S and Cl and elevated P contents in some rocks and soils reveal aqueous transport of phosphorus at low pH [4,18].

Volcanic degassing [e.g., 19] and aqueous oxidation of sulfides [e.g., 20,21] have been invoked to explain formation of martian acid solutions and aerosols. Here, I discuss relative roles of volcanism and impacts in origin and fate of low-pH fluids on Mars.

Role of oxygen in the formation of acids: Molecular oxygen and other strong oxidants (O_3, H_2O_2) could have played a major role in the formation of strong acids on Mars. Strong oxidants are needed to form sulfuric acid from degassed SO_2 [19] and H_2S. O_2 is a key reactant in aqueous oxidation of Fe sulfides that also leads to the formation of H_2SO_4 [e.g., 20-22]. Without oxidants, aqueous oxidation of Fe^{2+} does not lead to the production of protons. Involvement of O_2 into H^+-generating oxidation of SO_2, H_2S, Fe sulfides, and Fe^{2+} makes acid weathering a near-surface phenomenon.

A limited role of volcanism: The effect of volcanism on generation of acid solutions is mostly attributed to degassing of SO_2, H_2S, and HCl. However, likely consumption of photochemically-produced atmospheric oxidants (O_2, O_3, H_2O_2 [23]) in reactions with reduced volcanic gases (H_2S, CO, H_2, and S_2 [24]) would limit the generation of sulfuric acid through oxidation of SO_2 and H_2S. Without photosynthesis, active volcanic degassing could have limited amounts of strong oxidants on early Earth [25] and Mars [26]. Without atmospheric oxidants, only moderate acid solutions could form because of a limited abundance of volcanic HCl [24,27], a mild dissociation of H_2S in solutions, and weaker dissociation of sulfurous acid (H_2SO_3, forms through hydrolysis of SO_2) compared to sulfuric acid. Acid generation through formation of Fe sulfides from dissolved H_2S (e.g., $2H_2S + Fe^{2+} \rightarrow 2H^+ + H_2 + FeS_2$) is limited by the supply of Fe^{2+} through dissolution of ferrous silicates. Likewise, formation of low-pH fluids would have been limited in the anoxic martian subsurface. An alkaline nature of martian subsurface solutions [28], high concentrations of cations in brines, and low water/rock ratios would have favored rapid neutralization of weak volcanic acids. Finally, volcanic eruptions could not have led to acid raining owing to cold and dry climate throughout history [29].

Impacts as a major source of oxidants and acids: Effects of large impacts on acid weathering could have been greater than the effects of volcanism. On Earth, the role of impacts in generating acid aerosols and rains has been realized in the context of Chicxulub crater at the Cretaceous-Tertiary boundary [30-32]. These studies show that the Chicxulub impact into sulfate-bearing sediments released several orders of magnitude more sulfur gases compared to a volcanic eruption. On Mars, elevated abundances of sulfates in the regolith imply similar effects. Impact generation of SO_2 and/or SO_3 though decomposition of sulfates [30, 33, 34], as well as other oxidized gases (O_2, O_3, NO, NO_2 [e.g., 35,36]) provided reactants to form strong acids in cooling impact plumes. Oxidation of sulfides in target and projectile contributed to the release of S-bearing gases. Note that mass independent fractionation of S isotopes observed in martian meteorites [37] does not exclude impact degassing and recycling of sulfur. On the surface, aqueous interaction of strong oxidants with Fe^{2+} and pyrite caused oxidation of S and Fe and produced H^+. In addition, atmospheric oxidants, which would not be abundant during periods of volcanic activity, would react with impact-generated H_2S, SO_2, and NO to form SO_3, NO_2, and NO_3, as well as oxidize Fe^{2+} in surface solutions. In H_2O-bearing impact environments, hydrogen halides could form through decomposition of soil halides (NaCl, $MgCl_2$, etc.) and chlorapatite.

Dissolution of SO_3, SO_2, H_2S, NO_2, NO_3, and HCl in water droplets formed through condensation in an impact plume would have led to an array of acids. Although sulfuric and hydrochloric acids were probably most abundant, cometary impacts caused formation of nitrous and nitric acids [35]. Raining from impact clouds, which is expected in the present climate [38], generated acid solutions on the surface.

Plentiful impact-generated fines and glasses would be primarily altered by acid rains and aerosols, consistent with an altered nature of martian dust and air-blown particles. Acid rainfalls also affected upper surface layers and locally penetrated to deeper horizons. Acid rains could have been responsible for the vertical migration of Si and Fe^{3+} suggested for excavated soils in Gusev crater [39,40]. The elevated abundance of Si and Fe^{3+} observed at depth of ~10 cm [40] may reflect dissolution of surface minerals in low-pH solutions followed by precipitation of silica and Fe^{3+} hydroxide in the subsurface. The lack of evidence for carbonates, smectites, and zeolites in Gusev soils indicates short-term acid attacks [cf. 8,9]. Acid precipitation from impact plumes may also account for the high abundance of amorphous or semi-crystalline material and lack of detection of crystalline phyllosilicates, carbonates, and zeolites in heavily altered rocks at Columbia Hills [11]. This reveals a low-temperature acidic alteration that occurred over a limited time scale. The diverse and patchy nature of aqueous processes in Columbia Hills [4] could be related to mixing from impact event(s), implying transient involvement of solutions.

An interaction of heavily altered salt-rich deposits (as in Meridiani Planum, [3]) with acid rainwater could have not led to rapid neutralization, but increased the amount of salts in deposits. Impact-generated acid rainfalls over proposed impact surge deposits at Meridiani Planum [41] does not contradict with arguments for low-pH aqueous conditions [e.g., 3] and agrees with an addition of S and Cl to basalts [cf. 42]. A formation of several Fe^{3+} phases in layered bedrocks [1,15] could have been driven by impact-generated oxidants. A possibility exists that the deposition of surge deposits and low-pH processes were related to single impact.

A large degree of rock alteration and/or elevated secondary silica content in northern low-albedo regions [12-14] could be related to impact degassing of more abundant ground ice, sulfate, and other hydrated salt deposits as compared to equatorial and southern highlands. Finally, a correlation of P with S and Cl observed in MER landing sites could be explained by multiple acid rainfalls that delivered S and Cl and favored P mobility [18].

Chemical and physical weathering by impact-generated acid fluids: A high impact rate in Noachian implies an efficient acid weathering followed by surface erosion, aqueous transport, and deposition of salts and suspended particles in temporal water reservoirs. In fact, [38] show that impact-generated rainfalls could have been responsible for the high erosion rate in Noachian time [43] and the formation of valley networks. No warm and wet climate is needed for impact-induced exogenic processes. It follows that a majority of aqueous oxidation, formation of secondary silica, and Mg-Fe-Ca sulfates could have occurred in the earliest period of geological history.

With or without a warm/wet climate, frequent large impacts in Early Noachian caused stronger rainfalls and longer duration of weathering episodes compared to subsequent epochs. Warm/wet climate would have reduced the impact of acid weathering because of dilution of acids in persistent and neutralized surface water reservoirs. The longer duration of weathering episodes favored partial and/or local neutralization in temporal reservoirs. A presence of nontronite in Meridiani Planum [15] may reflect partial neutralization that facilitated the growth of Fe^{3+} oxide concretions [21]. At Columbia Hills, an existence of poorly crystalline [11] kaolinite-type aluminosilicates in some Clovis class rocks indicates mildly acidic conditions [44] (pH > ~3.5 [8,9]), which may imply some neutralization of initial acid solutions.

In other locations, more advanced neutralization could have occurred. An evaporitic formation of carbonates in the ALH85001 martian meteorite [45] about 3.9-4.0 Ga ago implies non-acidic pH. The only local occurrence of smectite deposits [46] in Noachian-age regions indicates spatially limited neutralization. Using terrestrial analogues, the formation of observed layered clay deposits could have occurred through surface weathering followed by aqueous transport in suspension and accumulation in water reservoirs. A massive nature of Noachian clay deposits and low permeability could have prevented their weathering by subsequent acid attacks. To conclude, acid weathering on early Mars probably played a larger role compared to subsequent epochs, though achieved larger degrees of neutralization because of longer existence of surface solutions and their temporal accumulation in surface reservoirs, where clays deposited.

Conclusion: Volcanic eruptions and impacts could have been responsible for multiple short-term episodes of acid weathering as a dry and cold climate prevailed over Mars history. Impact generation of oxidants (O_2, O_3, SO_3, NO_2) caused formation of strong acids and incremental Fe^{2+} oxidation, the processes that are not efficient during O_2-deficient periods of volcanic degassing. Signs of acid weathering at MER landings sites and northern low-albedo regions could be related to impact processes. Although impact-generated acid rainfalls could have caused intense weathering and erosion in Noachian time, dilution of acids and a prolonged existence of surface solutions favored local neutralization, and formation, transport, and deposition of clays. Although the intensity of impact-induced acid weathering declined in time, low-pH aqueous processes could have been important during the Hesperian epoch, when volcanism reached its highest levels in history and large impacts still occurred.

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