An anoxic atmosphere on early, volcanically active Mars and its implications for life. S. F. Sholes[1], M. L. Smith[1], M. W. Claire[2], K. J. Zahnle[3], D. C. Catling[1], [1]Univ. of Washington, Dept. Earth & Space Sciences / Astrobiology Program, Seattle WA, USA (sfsholes@uw.edu). [2]Univ. of St. Andrews, Dept. Earth & Environmental Studies, St. Andrews, Scotland. [3]Space Sciences, NASA Ames Research Center, Moffett Field, CA, USA.

Introduction: Mars' modern atmosphere is oxidizing and dominated by the photochemistry of CO_2 and H_2O. Early Mars, however, experienced widespread volcanism [1], which would have injected gases into the atmosphere such as H_2, CO and SO_2 that react rapidly with oxidants. Here, we investigate the effects of volcanic outgassing on the bulk chemistry and redox state of the early martian atmosphere. We find that early Mars could easily have had an anoxic, reducing atmosphere under typical estimates of past amounts of volcanism. Such an atmosphere is much more conducive to prebiotic chemistry than an oxidizing one.

Photochemical Model: We use a modified version of a published 1-D photochemical code [2]. To simulate possible volcanic gas compositions, we varied magmatic oxygen fugacity (fO_2), water content (wt% H_2O), and pressure of degassing, based on parameter-space established by Gaillard et al. [3].

The mixing ratios of CO_2 and H_2O were fixed in the model [2] and we considered how varying fluxes of volcanic SO_2, CO, H_2, H_2S, and S_2 would have affected Mars' atmospheric chemistry. Volcanic emissions are simulated by fixing an upward flux for each species that correspond to volcanic crustal production fluxes ranging 10^{-4} to 2 km^3 yr^{-1}. The model calculated steady-state atmospheric chemistry.

Results: Results suggest that the martian atmosphere was anoxic even at modest levels of volcanic crustal production, ~10^{-2} to 10^{-1} km^3 yr^{-1} (Fig. 1). Over the past 3.8 Gyr, the average crustal production rate has been estimated as ~0.17 km^3 yr^{-1} [4]. Other estimates suggest the martian volcanic magma flux was ~0 to 5 km^3 yr^{-1} during the same period [5-7]. Consequently, our calculations suggest that Mars may have experienced long periods of anoxia when volcanic outgassing was sustained.

In the model, at low levels of volcanism (<10^{-3} km^3 yr^{-1} crustal production rates, Fig. 1), the atmosphere is similar to the modern one. As the volcanic emission rate is increased, O_2 falls while CO and H_2 rise. Finally, the atmosphere reaches full anoxia (>0.03 km^3 yr^{-1}, Fig. 1) with negligible O_2 where CO and H_2 dominate, while carbonyl sulfide (OCS) rises to a ppm level.

The bulk composition of Mars is more enriched in S than the Earth [3], and so S plays a far greater role in volcanism. The simulated atmospheres are characterized by the formation of large amounts of sulfate aerosols. In highly reducing atmospheres,

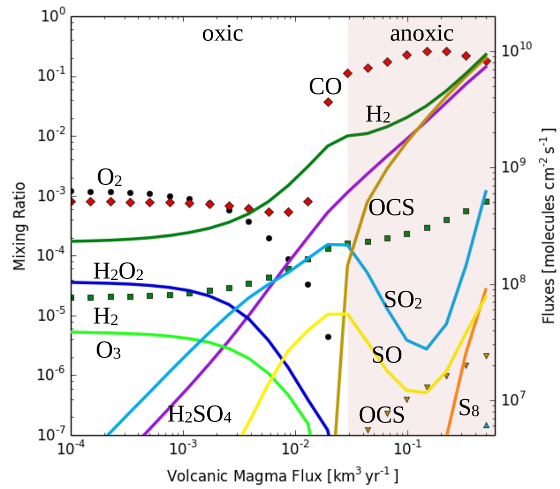

Fig. 1: Atmospheric response to increasing levels of volcanic degassing for a fO_2 of $10^{-8.5}$ (FMQ), 0.4 wt% H_2O buffer at 0.01 bar. Symbols represent mixing ratios (mapped to left axis) and solid lines represent depositional flux and H_2 escape (mapped to right axis). Shaded area shows anoxic atmospheres.

elemental polysulfur (S_8) aerosols also form. We find that magmatic buffers where S was more stable in the melt would have required more volcanic activity to reach anoxia. Such buffers are typically drier and, counter-intuitively, have lower fO_2. If less S had been outgassed, fewer sulfate aerosols (H_2SO_4) would have been produced, which consumes less oxygen.

Discussion: Extensive periods of an anoxic and reducing atmosphere early in Mars' history (in the early Noachian and periodically through to the mid-Amazonian) could be conducive to an origin of life on Mars. Reducing atmospheres enable prebiotic chemistry, such as atmospheric amino acid synthesis, which has been discussed in the context of possible reducing atmospheres on early Earth [8].

High levels of CO persist for all simulated mantle buffers. (We assumed a cold dry Mars and thus no major sinks for CO). The CO contributes to the anoxia, and potentially could have provided a substrate for methanogenic metabolism.

References: [1] Robbins et al. (2011), *Icarus* 211, 1179-1203. [2] Zahnle et al. (2008), *JGRP*, 113, E11004. [3] Gaillard et al. (2013), *SSR* 174, 251-300. [4] Greeley and Schneid (1991), *Science* 254, 996-998. [5] Xiao et al. (2012), *EPSL* 323–324, 9-18. [6] Schubert et al. (1992), in *Mars*. [7] Breuer and Spohn (2006), *PSS* 54, 153-169. [8] Kasting (1993), *Science* 259, 920-926.