MINIMUM TIMES TO FORM CLAY IN MARTIAN SURFACE AND NEAR-SURFACE ENVIRONMENTS.

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Introduction: Clay minerals are the most common alteration products of water-rock-gas interactions on Earth. Because these hydrous alteration minerals are thermodynamically stable over a wide range of P-T-x conditions [1], significant amounts of clay may have also formed in Martian environments where liquid water or water vapor was present. It has been speculated that liquid water or vapor may have persisted for weeks to thousands of years in diverse surface and near-surface Martian environments, ranging from an ocean and channelized surface flows, to the potentially higher temperature environments associated with volcanic or impact-induced hydrothermal systems [2]. If true, then a significant fraction of the surface of early Mars experienced water-rock-gas interactions that could have resulted in the formation of extensive clay deposits. Clay deposits are inferred to exist on Mars, based on orbital measurements of spectra at or near the detection limits of the instrument [3]. The duration of aqueous alteration on Mars can be estimated by evaluating the time required to form secondary alteration products. In this work, we estimate the minimum time required to produce detectable amounts of clay by aqueous alteration of volcanic glasses under different sets of idealized Martian surface and near-surface conditions.

Model: Although several types of solid phases observed in martian meteorites or inferred to exist on the surface of Mars may react with water to form clays, our model assumes that hypothetical Martian clay deposits formed exclusively after the dissolution of volcanic glasses, and that the rate of clay formation was equivalent to the rate of glass dissolution. This approach is conservative, because mineralic phases generally dissolve about an order of magnitude slower than amorphous phases (i.e. glasses) of the same composition, and explicit reactions describing the formation of clay after glass dissolution may require the contribution of additional dissolved species, such as $Al(OH)_4^-$, not considered in our model. To further minimize the time required to produce detectable amounts of clay, our calculations assume a spectral detection limit of 5 volume percent clay, although the actual limit may be significantly higher with current orbital data [3].

We used a standard rate law to describe glass dissolution rates on Mars, $R(g/day) = k*As* a(H^+)^x *(Q/K - 1)$, where k is the rate coefficient, As is the specific reactive surface area, $a(H^+)^x$ is the hydrogen activity term, and the affinity term, $(Q/K - 1)$, is a description of the extent of solution disequilibrium. Assigning the affinity term a value of -1, which assumes that Martian solution compositions were significantly undersaturated with respect to glass, maximized estimated reaction rates. Glass dissolution rates were then calculated for different Martian conditions by considering various physical and chemical dependencies of the effective rate constant (i.e. $k*As*a(H^+)^x$). All rate coefficients (k) used in our model were calculated using methods and data resulting from the experimental dissolution of volcanic glasses [4].

Minimum clay formation times on Mars were estimated for temperatures ranging from 5-100°C. Alteration temperatures in some environments on the surface of Mars, such as putative ocean or outflow channels, may have maintained zero or subzero temperatures. More work is needed, however, to extrapolate rate law parameters downward from 5°C. We used an alteration temperature of 100°C to represent possible near-surface hydrothermal activities associated with Martian calderas and craters. Although temperatures in these Martian environments may have been significantly higher, our results effectively highlight the significance of the temperature dependence of reaction rates on early Martian alteration scenarios.

We evaluated the effects of variable glass composition, pH, and reactive surface area on estimated clay formation times. To bound the compositional dependence of the rate coefficient, we assume that the SiO_2 content of Martian glasses ranges between 47.9 and 66.2 wt.%; consistent with the composition of the Martian meteorite QUE 94201 [5] and a residual melt composition formed by crystallization of the calculated parent liquid of the Martian meteorite Chassigny [6]. Values of pH were adjusted from 2-10 to consider the wide range of solution compositions permitted by previous scenarios of early Martian alteration [7,8,9]. Reactive surface areas were characterized by approximating Martian alteration environments as loosely consolidated conglomerations of individual grains with diameters of 1 micron, 100 microns and 1 centimeter. Estimation of clay formation rates in less permeable hydrothermal environments is underway.

Results: Results of the low SiO_2 calculations are plotted below. All else being equal, alteration of the low SiO_2 glass is ~ 5 times faster than that of the high SiO_2 glass. Hence, our calculations suggest that clay deposits would have formed significantly faster in basaltic,

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rather than andesitic, terranes on Mars. The effect of pH on estimated clay formation times is significant, but smaller than the other factors we considered. Estimated clay formation rates are most rapid under extreme acidic and alkaline conditions, reflecting trends in glass dissolution experiments. Assumptions about alteration temperature and grain size have the largest effect on estimated clay formation times. The strong inverse correlation shown in our plot between reaction rate and assumed grain size illustrates the extreme susceptibility of anhydrous Martian dust to hydration reactions. Even in very cold environments where reactions are sluggish, detectable amounts of clay could form from the alteration of dust-sized particles of high SiO_2 glass in less than half a year, or in just a few weeks from the alteration of low SiO_2 dust. Reaction rates also increase very rapidly with temperature. Even at the modestly high temperature of 100^oC, suggesting that detectable amounts of clay should have formed in and around Martian hydrothermal systems on time scales perhaps as short as a few hours to a few years. Even in the relatively cool hydrothermal system, such as the 100^oC system considered here, reaction rates should be sufficiently high to generate detectable amounts of clay on time scales perhaps as short as a few hours to a few years.

Conclusions: Our calculations suggest that significant amounts of clay can be expected to have formed around hydrothermal systems, are very likely to have formed in association with a long-standing ocean, and may or may not have formed within ephemeral river channels. The approach developed in this work to estimate clay formation times can be extended to provide a more comprehensive analysis of the duration of aqueous alteration on Mars.

References: [1] Chernosky *et al.* (1991) in MSA reviews in Mineralogy vol. 19; 295, edited by S. W. Bailey, Blacksburg, VA [2] Carr (1996) Water on Mars. Oxford Univ. Press, New York. [3] Banfield (2002) J. Geophys. Res. 107, 9-1. [4] Tompson *et al.* (1999) UCRL-ID-132300, Lawrence Livermore Natl. Lab., Livermore, CA. [5] Lodders (1998) Meteor. Planet. Sci. 33, A183. [6] Minitti and Rutherford (2000) Geochim. Cosmochim. Acta 64, 2535. [7] Banin et al. (1997) J. Geophys. Res. 102, 13, 341. [8] Griffith and Shock (1995) Nature 377, 406. [9] Schaefer (1993) Geochim. Cosmochim. Acta 57, 4619.

Clay formation times after low SiO2 (47.9 wt. %) glass alteration