ZEOLITE CEMENT IN MARTIAN VOLCANICLASTIC ROCKS.

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Introduction. There is a consensus that volcanic activity, action of water and wind, impact cratering, and cryogenic processes have shaped the surface of Mars [1-3]. Older pyroclastic deposits and impact comminuted volcanic material would be buried under newer volcanic material. If water is stored as permafrost near the surface, any heating by volcanism or impact, would melt a part of the permafrost and set up a convection-cell-like flow [4]. The flow will be most efficient in the volcaniclastic layers because of their higher porosity and permeability relative to volcanic rocks. Existence of liquid water and the flow, however, will be transient dependent upon the longevity of the heat source. If so, the temperature and the water-rock ratio in the circulation system will decrease with time from an initial high, favoring early dissolution of magmatic phases and subsequent precipitation of diagenetic phases. Such diagenesis will lithify buried volcaniclastic debris in Mars. On the basis of examples from Earth and on thermodynamic grounds, we argue that zeolite is the likely cement in Martian volcaniclastic rocks.

Earth. "Zeolites are ubiquitous constituents in the vugs and cavities of basalts" and are probably the most abundant cement in volcaniclastic rocks in the Earth [5]. Whereas the vug filling and veins of zeolites are likely to occur in Martian basalts, much larger amounts are expected in volcaniclastic sediments. Zeolitization of tuffs and other pyroclastic material, probably in alkaline playa lakes, has produced thick economic deposits [e.g., 6,7]. More ubiquitous, however, is the occurrence of diagenetic and very low-grade metamorphic zeolite in volcaniclastic rocks [8]. Hydrolysis of volcanic glass raises pH, activities of SiO_2, and activity ratios of $(Na^+ + K^+)^2/H^+$ or even that of Ca^+/H^+ sufficiently in the pore fluids of volcaniclastic material to precipitate zeolites [e.g., 9-11]. We conclude that it is normal and common on Earth for a sequence of volcaniclastic sediments to have zeolite as a secondary mineral. Absence of authigenic zeolites could indicate a low-pH and dry or nearly dry system unless other non-volcanogenic minerals such as calcite or dolomite are dissolved from intercalated sedimentary sequences providing a ready source for $CaCO_3$ cement.

Mars. A few have speculated on zeolite as one product of Martian pedogenic processes [12-14]. Extensive bedded zeolite deposition on Mars may also be likely, which may store a large amount of CO_2 and have a profound effect on evolution of the Martian atmosphere[15]. The activity of CO_2 in Martian diagenetic fluids would affect the cement that would bind Martian sediments.

A sub-permafrost aquifer beneath the melting isotherm at the base of the Martian cryosphere enables the cycling of water between the near-surface crust, atmosphere, and polar caps [16]. We assume that the chemical composition of the rocks in this groundwater aquifer is that calculated for the "soil-free rock" [17]. The composition closely approximates volcanic andesite (62% SiO_2) with a CIPW normative content of 37% plagioclase ($An_{39}Ab_{61}$) approximating the composition of andesine, 21% quartz, 18% diopside, 17% hypersthene, and 4% orthoclase.

Thermodynamic Considerations. We are investigating the relative stability of plagioclase with respect to zeolites in the postulated groundwater aquifer on Mars. We select the calcic zeolites heulandite and stilbite because they are common terrestrially and thermodynamic data are available [18]. A highly simplified chemical equilibrium between anorthite and heulandite can be written as follows:

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{silica}}{5H_4SiO_{4\,(aq)}} \leftrightarrow \underset{\text{heulandite}}{CaAl_2Si_7O_{18}\cdot 6H_2O} + \underset{\text{water}}{4H_2O_{(aq)}}$$

Stilbite differs from heulandite primarily in containing additional structural H_2O and both minerals exhibit extensive solid solution between calcium and sodium. Standard Gibbs free energies of formation at 25°C, 1 bar [18] for plagioclase and heulandite were compositionally corrected to approximate those of the normative plagioclase from the "soil-fee rock" [17] and a theoretical heulandite with the same Ca/Na atomic ratio (0.64). The value obtained for the Martian plagioclase (andesine) is $\Delta G^o_{form} = -3827.2$ kJ·mol^{-1} and for the heulandite, $\Delta G^o_{form} = -9708.7$ kJ·mol^{-1}. Free energies of formation for water and aqueous silica are -237.1 kJ·mol^{-1} and -1307.5 kJ·mol^{-1}, respectively. The calculated value of the equilibrium constant (K_{eq}) for the above reaction is $10^{51.25}$. If we assume that the water is low in dissolved solids (thermodynamic activity ≅ 1.00), then the activity of dissolved silica when equilibrium is attained between plagioclase and heulandite $= a_{H4SiO4} = (1/K_{eq})^{1/5} = 10^{-10.25}$.

The solubility of quartz in neutral waters at 25°C, 1 bar is approximately 10^{-4}m and that of amorphous silica is substantially greater, $10^{-2.8}$m [19]. The presumed Martian andesitic rocks and detritus are quartz normative and should contain quartz, and initially, after volcanism, may have contained amorphous silica. In either case, the dissolved silica in the Martian groundwater would likely contain much more dissolved silica than the plagioclase-heulandite equilibrium value of $10^{-10.25}$. Consequently, the excess dissolved silica in the groundwater would thermodynamically favor alteration of plagioclase to heulandite.

It should be noted that heulandite (and stilbite) are zeolites that contain more silica than the proposed feldspar source (i.e. dissolved silica is a reactant). In contrast, if similar calculations are made for the reaction of albite ($NaAlSi_3O_8$) to form the zeolite analcime ($NaAlSi_2O_6\cdot H_2O$), silica is a product of the reaction because analcime is undersaturated in silica (i.e. contains less than albite). However, the equilibrium constant in this case becomes large and the zeolite (analcime) is still favored over the feldspar (albite) under the expected aqueous conditions.

CONCLUSION: Although other potential (and more complex) reactions and assemblages have not been investigated and the kinetics of the above reactions on Mars are not known, the stability and ubiquity of zeolites as observed in terrestrial volcanic systems on Earth and as inferred on Mars, is reinforced by the thermodynamic calculations.

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