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CHEMICAL FROST WEATHERING OF OLIVINE: EXPERIMENTAL STUDY AND IMPLICATIONS; S.L. Harris, R.L. Huguenin, Geology/Geography, University of Massachusetts, Amherst, MA 01003.

It has been proposed that chemical frost weathering of silicates may occur in the contemporary Mars surface environment (1,2) Exposure of olivine and other mafic silicates to H_2O at frost temperatures was proposed to result in the incorporation of H^+ into the crystal, converting oxide ions to hydroxide ions. Incorporation of electrons (derived from OH^- in the frost), at positive defects (e.g. Fe^{3+} substituted for Fe^{2+}) was proposed to restore charge balance and convert OH^- to H_2O_2. Production of H_2O_2 was observed experimentally (2,3).

A new experiment has been performed to test the proposal that H^+ reacts with O^{2-} to form OH^- during the frost weathering of olivine. The olivine used is the same as that in (2) and has composition Fo_{86}. The olivine was placed in an atmosphere and temperature controlled chamber. The sample chamber pressure was maintained at $\approx$ 760 torr N_2, except during initial frost formation and desorption. Frost was formed on the olivine by cooling the sample below -10^o C with a flow of H_2O saturated N_2 gas into the sample chamber. Frost desorption was accomplished by cycling the temperature below 0^o C with a cold trap in the system and the vacuum pump running. Reflectance spectra of the olivine samples were taken before, during, and after frost formation. Band positions were extracted from spectra using the Bands Data Analysis System described by (4).

The penetration of H^+ into the crystal structure during weathering should be observable from spectra. The H^+ should react with O^{2-} in the crystal to produce structural hydroxyl. The structural hydroxyl absorption bands would occur at wavenumber positions that are close to those of absorbed H_2O and surface hydroxyl ions, thus they would not be uniquely indicative of structural hydroxyl found by penetration of H^+ into the lattice. With the H^+ that has been proposed to migrate to cation vacancies (3), a more diagnostic spectral signature is a shift in the Fe^{2+} absorption band positions arising from a change in the crystal field splitting parameter Dq. Dq is defined as Dq $\approx Q/R^5$ where Q is the charge on the ligands and R is the metal-ligand interatomic distance (5). Since Dq is proportional to Q, a change in Q from 2 (O^{2-}) to 1 (OH^-) should produce a decrease in Dq.

Huguenin (3) found that approximately 9 x 10^{19} H^+ were incorporated into a 1 gm sample after exposure to frost. The number of $Mg^{2+} + Fe^{2+}$ cations in a 1 gm sample of olivine is approximately 4.8 x 10^{21}. If the H^+ were incorporated at or adjacent to the cation sites, then there would be a predicted 1.9 % decrease in Dq.

Absorption bands in the olivine spectra are due to electronic transitions and charge transfers by the d shell electrons in Fe^{2+}. The wavelength position of the band centers depend on the charge of the ligands and on the dimensions and symmetry of the Fe^{2+} site. In a perfect octahedral site the five d-shell orbitals are split into a triply degenerate, t_{2g}, set and a doubly degenerate, e_g, set due to the presence of the surrounding six O^{2-} ligands. The $d_{x^2-y^2}$ and d_{z^2} orbitals, which point directly to coordinating ligands, are raised in energy to the e_g set. The d_{xy}, d_{xz} and d_{yz} orbitals lie between the ligands and are lowered in energy to the t_{2g} set. Fe^{2+} has six d electrons, five of which have parallel spin directions in the ground state. The sixth electron occupies the lowest energy level with its spin in the opposite direction. Absorption occurs when the sixth electron is moved from the ground state energy level to one of the higher energy levels. The energy separation between the t_{2g} and e_g orbitals is termed the crystal field splitting and, it is denoted by Dq or $\triangle o$ (5,6).

The crystal structure of olivine contains 2 six-coordinated sites; a centrosymmetric M(1) site and a non-centrosymmetric M(2) site. There is no site preference so that Mg^{2+} and Fe^{2+} are randomly distributed between the sites (6,7). Thus, there are contributions from Fe^{2+} in both M(1) and M(2) sites in absorption spectra. Burns (6,7) has assigned the absorption bands occurring around 11,700 and 9,000 cm^{-1} to the M(1) site and the absorption band at $\approx$ 9540 cm^{-1} to the M(2) site.

The experimental results showed an average decrease of $400cm^{-1}$ in the olivine M(2) site band position upon frost weathering. Shifts in M(1) site band position were not apparent, although a small shift may have escaped detection. Burns (6) gives a Dq value of $8330cm^{-1}$ for Fe^{2+} in the M(2) site of an Fo_{88} olivine. The observed shift in the M(2) site band position would correspond to a shift in Dq of $\approx$ 4.8 %. This is somewhat larger than the predicted shift, but it generally supports the proposed model.

The observed shift in band position has two implications. First, it supports the proposed frost weathering model and its occurrence on Mars. It was predicted that 10^0 - 10^3 meters of H_2O may have been lost to weathering over the planets history, and the results here support that prediction. Second, it suggests that frost-weathered olivine may have absorption band positions that are lower in energy than the

$$\frac{Fe^{2+}}{Fe^{2+} + Mg^{2+}}$$

ratio would predict. This would have significant impact on interpretation of the Fe^{2+} content of olivines on Mars from their absorption band positions.

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