WIDESPREAD DIAGENESIS ON MARS AND IMPLICATIONS FOR CRUSTAL FLUIDS. R. E. Milliken,
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Introduction: Post-depositional modification of sediments and sedimentary rocks is commonplace on Earth during burial and crustal recycling. Though much of this may be linked to subsidence and plate tectonics, martian sediments and sedimentary rocks are also likely subject to post-depositional processes due to interaction with fluids in the near-surface and crust, possibly at elevated temperatures. Diagenetic processes that record information on the distribution of fluids and regions of possible increased geothermal gradient provide insight into ancient crustal properties, and in this context clay minerals are of particular interest.

Conversion of smectite to illite or chlorite during burial diagenesis is typical in terrestrial sedimentary basins [1], and this process is the integrated result of the availability of time, temperature, and fluids. The apparent antiquity of many martian clays (>3 Ga) suggests time is not a limiting factor, and given that even modest geothermal gradients on ancient Mars (e.g., 10°C/km) would yield acceptable temperature conditions at several kilometers depth, the primary control on the extent of illitization or chloritization on Mars is likely the availability of fluids. Indeed, the apparent persistence of smectites on Mars over billions of years has led to the speculation that water may have been limited for much of Mars' history [2], and previous studies have suggested many martian clays may have originated via crustal processes under a cold and arid climate rather than by surface weathering under warmer, wetter conditions [3].

Opaline silica is also known to change during prolonged exposure to fluids, either at the surface or through interaction with pore fluids during burial, and it will transform from opal-A to opal-CT or microcyrstalline quartz [4]. As with clay transformations, this process proceeds in the presence of water. Therefore, identification of specific silica compositions (e.g., opal-A versus chalcedony) has the potential to provide insight into water availability and longevity [2].

Were martian clays formed in near-surface environments, or are deep crustal formation environments implied? Is there evidence that martian clays have changed as a result of burial diagenesis? If so, what does this imply about crustal fluid circulation and geothermal gradients on early Mars? How confident are we in the types of clays that have been identified using orbital data? What is the variability in the forms of hydrated silica on Mars? Do these phases record evidence for prolonged interaction with surface waters?

These and other related questions are the motivation behind this study, which focuses on a detailed reappraisal of orbital spectra to assess the evidence for diagenetic processes on Mars as they relate to clay mineral and hydrated silica compositions. CRISM reflectance spectra are analyzed to determine the presence of possible mixed-layer clays and search for variations in the hydration state (and associated structural changes) in hydrated silica deposits. Current results indicate that mixed-layer clays may be widespread on Mars in a variety of geologic settings and that hydrated silica deposits are highly variable in hydration state, indicating possible variations in crystallinity. When integrated with recent *in situ* rover observations (e.g., [5]), these orbital data indicate diagenesis was widespread on Mars and that sediment interaction with pore fluids, either in near-surface or deep basinal settings, took place over prolonged periods.

Methods: CRISM reflectance spectra and spectral ratios (spectrum from a region of interest divided by spectrum of a nominally 'dusty' region) were processed and analyzed using techniques commonly employed by the CRISM team [e.g. 6,7]. Locations of interest were first identified by examining CRISM browse products [8] to indicate whether or not clays or silica may be present, and individual CRISM observations were then processed and studied in detail to extract reflectance spectra. Particular attention was given to craters of various sizes in order to assess possible variations in mineralogy with depth, both by looking at exposed crater walls as well as ejecta deposits. An ongoing and complementary project that focuses on the mineralogy of crater central peaks is discussed by [9].

CRISM reflectance spectra or spectral ratios were then compared to laboratory data for a variety of clay minerals and hydrated silica compositions. In addition to qualitative visual comparisons, parameters related to spectral properties at specific wavelengths (often associated with specific absorption bands) were constructed to highlight subtle changes in spectral properties related to important changes in mineralogy. Mixed-layer chlorite/smectite, for instance, is structurally distinct from smectite yet the spectral variations in the ~2-2.5 µm wavelength region can be subtle. Spectra of physical mixtures of smectite and chlorite were also acquired in the lab for comparison to specra of structurally interstratified chlorite/smectite clays.

Results: To date, analysis of CRISM images over 150 unique locations exhibiting evidence for clay minerals and direct comparison to laboratory spectra suggests many previously reported smectite deposits are instead consistent with mixed-layer chlorite/smectite. Though spectra for some locations, including Gale Crater, Mawrth Vallis, and portions of Nili Fossae, are consistent with smectitic clays, these occurences are not as common as mixed-layerclays or chlorite deposits (Fig. 1) [10]. Though possibly biased by the (currently) small numbers, the smectite deposits are commonly more consistent with Mg-bearing varieties (e.g., saponite), with occurences of Fe-rich varities (e.g., nontronite) being subordinate. Chlorite has been identi-
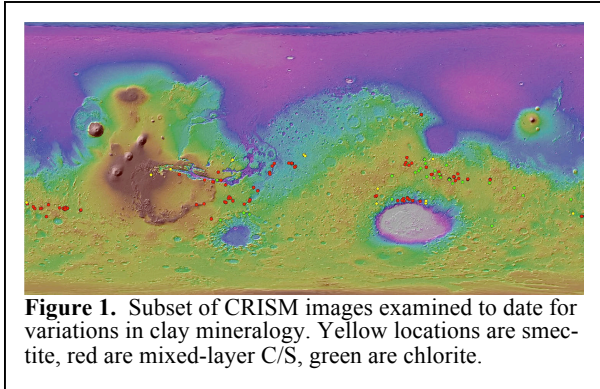
Figure 1. Subset of CRISM images examined to date for variations in clay mineralogy. Yellow locations are smectite, red are mixed-layer C/S, green are chlorite.

fied in a number of locations, but illite is rare by comparison.

Hydrated silica has been observed from orbit in a variety of settings on Mars, including the plains surrounding Valles Marineris [7], volcanic regions [11], and crater central peaks [9]. These deposits are identified by the presence of Si-OH vibrations near ~1.4 and ~2.21 µm as well as by H_2O features near ~1.4 and ~1.9 µm [7,12]. Though all are consistent with various examples of opaline silica or hydrated silica-rich glass, these martian deposits are variable in their hydration state (Fig. 2). This is most noticeable by variations in the strength/presence of the 1.9 µm absorption and the center wavelength position of the ~1.4 µm absorption, where the latter 'shifts' from ~1.41 to ~1.38 upon loss of H_2O [7]. Such variations in H_2O content may reflect variations in local relative humidity or P_{H_2O}, but they are also consistent with variations in the crystallinity of the hydrated silica deposits. As opal-A transitions to opal-CT or microcrystalline quartz (or chalcedony), for example, H_2O may be lost or available to fewer sites.

Discussion & Conclusions: Detailed study of hydrated mineral deposits on Mars indicates mixed-layered clays are more common than previously recognized. These phases, particularly when found in proximity to smectite or chlorite occurrences, indicate clay transformations and thus fluid-controlled diagenesis may have been widespread on ancient Mars. Though not without ambiguity from orbital data alone, these observations suggest prolonged water-sediment interactions, possibly in basinal settings or regions of enhanced crustal heat flow.

Interestingly, two locations that contain clays but lack clear evidence of chloritization or illitization are locations one might expect to favor such processes: Gale crater, where clays occur under several kilometers of overburden, and Mawrth Vallis, home to some of the oldest clay-bearing terrains on Mars. This may indicate decreased availability of post-depositional fluids in these locations or that the clays in these deposts are significantly younger than the depositional age of the strata in which they reside. *In situ* observations are required to further test these hypotheses.

Hydrated silica deposits on Mars also exhibit spectral variability that may be linked to differences in water content and thus crystal structure, possibly reflecting differences in 'maturity'. Current results do not indicate systematic trends between hydrated silica type and geologic setting, and silica deposits with distinct differences in hydration state may be in close proximity. Regardless, these observations also indicate that water-sediment interactions may have been prolonged in the near-surface during the Hesperian and possibly Amazonian, becoming more localized through geologic time.

Water-related diagenetic processes appear to have been important on Mars during the Noachian and Hesperian, and these processes do not appear to be confined to a few select locations. Instead, orbital observations suggest such processes were widespread on Mars and that water persisted in the near-surface and/or crust for long enough periods to transform clay minerals and opaline silica. However, not all clay or silica deposits exhibit evidence for these processes, and the lateral and vertical difference in locations between these distinct mineral assemblages provides important insight into the evolution of fluid pathways through time on Mars.
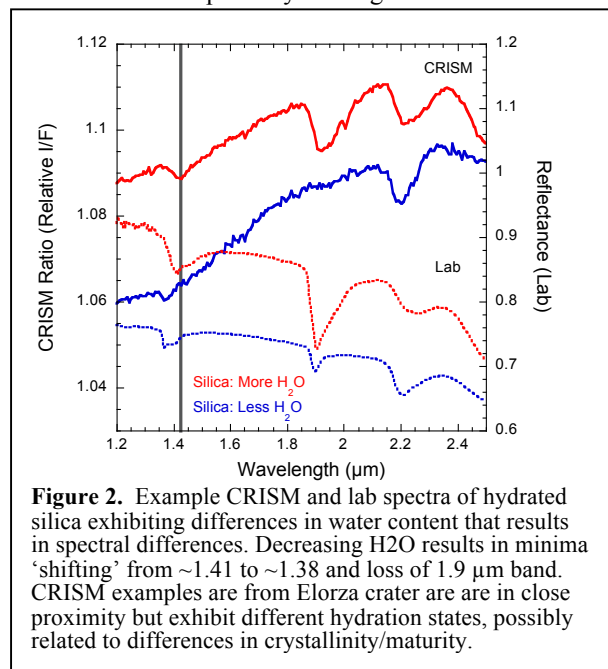
Figure 2. Example CRISM and lab spectra of hydrated silica exhibiting differences in water content that results in spectral differences. Decreasing H2O results in minima 'shifting' from ~1.41 to ~1.38 and loss of 1.9 µm band. CRISM examples are from Elorza crater are are in close proximity but exhibit different hydration states, possibly related to differences in crystallinity/maturity.

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