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MARTIAN WEATHERING PRODUCTS AS TRACERS OF CLIMATE CHANGE AND ATMOSPHERE/HYDROSPHERE EVOLUTION ON MARS.

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Introduction. Primary objectives for exploration of Mars include determination of (a) the distribution, abundance, and sources and sinks of volatile materials, and (b) the interaction of surface materials with the atmosphere [1]. Both objectives fall within the purview of planetary surface weathering studies [2] and require documented samples of weathered materials, including rock surfaces, soils, and sediments. Major issues to be addressed in selecting and studying Martian samples in this context are summarized in the following review.

1. What abundances of potential atmosphere- or ocean-forming elements are located in the regolith? *Reversible sinks* include physically condensed species (ground ice, frosts and adsorbed gases) that can recirculate under the influence of diurnal, seasonal, or climatic temperature cycles. In contrast, *irreversible sinks* (hydrated silicates, carbonates, oxides, etc.) are resistant to surface temperature cycles and will return volatiles to global circulation only under extreme duress (e.g., catastrophic meteoroid impacts or volcanic intrusions). First-order goals are to determine the abundance and distribution of ground ice and volatile-bearing secondary minerals as a measure of whether Mars' atmophile-element endowment was sufficient to have once supported a thicker, more Earth-like atmosphere and hydrosphere. Carbonates, for example, are theoretically crucial but unproven sinks for Martian CO_2 [3]. Efforts to detect Martian carbonates by Earth-based remote sensing have not been successful [4] although calcite has been found in at least one SNC meteorite (EETA79001) [5]. *Mars Observer* may be able to detect and map carbonates but direct laboratory study of soils and sediments is the only effective way to determine the times and modes of carbonate formation.

2. Do weathering products of various ages indicate systematic climate changes? In the absence of abundant biogenic fossils, Martian paleoclimates must be deduced from the mineralogical and stable-isotopic compositions of fossil weathering products in soils. Under current conditions on Mars, gas-solid weathering reactions should predominate and few genuine clay minerals should be forming [6, 7]. Some evidence suggests, though, that clay mineral(oid)s might be major components in Martian soils [8], indicating metastable preservation after formation in environments dominated by liquid-solid, water-based reactions. Critical issues are how and when liquid water became available to drive weathering, whether silt- and clay-sized materials contain true phyllosilicates or simply palagonite/allophane phases, and whether substantial quantities of zeolites were formed [9]. Ratios of D/H, $^{13}C/^{12}C$, and $^{18}O/^{16}O$ in secondary minerals should permit calibration of weathering temperatures, provided that isotopic compositions of other participating volatile reservoirs (ground ice, atmospheric water vapor and CO_2, etc.) can also be determined. Exchangeable ions in clay minerals and zeolites would reveal the chemistry of the solutions with which they were last equilibrated. In addition, gases occluded in the same phases might provide samples of the Martian atmosphere as it existed during various weathering epochs. Absence of nitrates and absence of significant $^{15}N/^{14}N$ fractionations by regolith phases must be confirmed as tests for models for atmospheric $^{15}N/^{14}N$ fractionation and their implications for loss of the early Martian atmosphere. Finally, analysis of cosmic-ray-produced particle tracks and nuclides in rock surfaces and layered regolith samples would permit inference of how atmospheric shielding (i.e., density) has changed over time [10]. To date climatic periods, ages of old soils and sediments might be obtained by the Sm-Nd chronometer (Rb-Sr might be too susceptible to disturbance by weathering) whereas younger samples might be dated by the U-Th disequilibrium and ^{36}Cl methods.

3. Did mechanisms and rates of chemical weathering change through time and did they fractionate surface compositions? Martian surface materials receive high doses of ultraviolet radiation [11] and, as either a consequence or coincidence, contain trace quantities of oxidants that react vigorously with water and simple organic compounds [12]. It has been speculated, though not established, that ultraviolet-catalyzed reactions have dominated chemical weathering on Mars [13], including formation of unusual peroxides or superoxides that would destroy Martian organic compounds. Clearly, though, UV-driven reactions can only be important in the outer few micrometers of the Martian surface so that it is imperative to understand whether different weathering processes operate at depth and how styles of weathering might have changed through time. Independent of UV influence, low-temperature weathering can drastically fractionate K from other lithophiles [14], producing misleading impressions of the ^{40}K contents (an index for internal heat generation) of the parental materials. *Mars Observer* will provide global maps of K abundance that can be correctly interpreted only if weathering effects are understood through sample studies.

4. What samples are needed? Paleoclimate studies must distinguish soils from sediments [2], requiring regolith drill-core samples that document the zonal structures and parent/daughter material relationships that are essential features of soils. Interpretation of duricrust genesis (cyclical vs. recent-only processes) must also rely on search for multiple duricrust layers in continuous cores. Process-oriented weathering studies will require chips (or short drill cores) of natural surfaces from large rocks of various types and ages so that contemporary rock weathering can be distinguished from pedogenic or fossil weathering recorded in the regolith. At the minimum, Noachian-, Hesperian-, and Amazonian-age units should be sampled to establish basic weathering and volatile-sink trends through time. In addition, atmospheric dust should be sampled to establish its possible traceability to known units or weathering epochs.

Stable-isotopic and trapped-gas studies of ground ice are essential complements to similar studies of soils. It is doubtful, though, that ground ice can be sampled within a few meters of the surface at any location outside the polar circles. Based on geomorphic evidence, ground ice is rare to absent within ± 30° latitude of the Martian equator but increases in abundance toward the poles [15]. According to model calculations, ground ice could survive on Mars for 10^9 y if covered by at least 10 m of ultrafine-grained and effectively non-porous soil [16]. For all geologically reasonable values of regolith particle-size and porosity, though, diffusion of water vapor from buried ice into the atmosphere should preclude survival of temperate-latitude ground ice over Martian geologic history at any depth shallower than 100 m [17]. Accordingly, acquisition of ground ice samples will probably require a mission to a polar site.

All samples must be protected from thermal degradation and from both pro- and retro-grade, mineral/volatile reactions. Important paleoclimate indicators are expected to be metastable mineral assemblages with stable-isotopic signatures that are susceptible to further atmospheric exchange reactions. An upper limit of 263° K for storage should preserve thermally labile compounds and ice but a design goal of 240° K should be implemented to control desorption and reactivity of atmospheric gases. **References:**

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