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ZEOLITES ON MARS: POSSIBLE ENVIRONMENTAL INDICATORS IN SOILS AND SEDIMENTS;

D. W. Ming and J. L. Gooding, NASA Johnson Space Center, Mail Code SN, Houston, Texas 77058.

Weathering products should serve as indicators of weathering environments and may provide the best evidence for the nature of climate change on Mars. No direct mineralogical measurements of Martian regolith were performed by the Viking missions, but the biology and X-ray fluorescence experiments provided some information on the physiochemical properties of Martian regolith. Most post-Viking studies of candidate weathering products have emphasized phyllosilicates (e.g., smectites) and Fe-oxides; zeolites are potentially important, but overlooked, candidate Martian minerals [1].

Zeolites would be important on Mars for three reasons. First, they are major sinks of atmospheric gases and, per unit mass, are stronger and more efficient sorbents than are phyllosilicates. Second, they can be virtually unique sorbents and shelters for organic compounds and possible catalysts for organic-based reactions. Finally, their exchangeable ions are good indicators of the chemical properties of solutions with which they have communicated. Accordingly, the search for information on past compositions of the Martian atmosphere and hydrosphere should find zeolites to be rich repositories.

Zeolites in Terrestrial Soils: There are two primary sources of zeolites in terrestrial soil. Zeolites can crystallize in situ during soil formation (i.e., pedogenic) or they can be inherited from the parent rock or from some other distant source (i.e., lithogenic). Zeolite occurrences in soils can be classified as follows: (1) pedogenic zeolites in saline, alkaline soils of non-volcanic origin; (2) pedogenic zeolites in saline, alkaline soils of volcanic origin; (3) lithogenic zeolites in soils from residual volcanic parent materials; (4) lithogenic zeolites in soils from eolian additions or fluvial deposition; and (5) zeolites in other soil environments. Most natural zeolites in weathering environments occur in arid climates.

There are over 40 naturally occurring zeolites and over several hundred synthetic zeolites with no natural counterparts. Clinoptilolite appears to be the most abundant zeolite found in soils, however, analcime, chabazite, heulandite, mordenite, phillipsite, natrolite, gismodine, stilbite, and laumontite have all been reported. Several of the more common zeolites found in soils are listed in Table 1.

Formation of Zeolites: The formation of analcime, phillipsite, and chabazite (low Si/Al atomic ratios; see Table 1) in soils usually requires alkaline pH solutions (sometimes >9) coming into contact with an aluminosilicate source (e.g., basaltic glass). High pH conditions favor the dissolution of the aluminosilicate (generally volcanogenic) source material which supplies Si and Al along with alkali and alkaline earth cations (e.g., Ca^{2+}, Na^+, K^+, and Mg^{2+}) into soil solution. Pedogenic zeolites (e.g., analcime and phillipsite) will form in situ once the soil solution becomes saturated with respect to the zeolite during evaporation of soil

TABLE 1. Representative unit-cell formula and selected chemical properties of zeolites commonly found in terrestrial soils.

ZEOLITE	REPRESENTATIVE UNIT-CELL FORMULA	Si/Al ATOMIC RATIO	pH STABILITY LIMIT[1]
Analcime	$Na_{16}\{Al_{16}Si_{32}O_{96}\}\cdot 16H_2O$	1.8-2.8	~5
Chabazite	$(Na_2,Ca)_6\{Al_{12}Si_{24}O_{72}\}\cdot 40H_2O$	1.4-3.0	~4
Clinoptilolite	$(Na_2,K_2,Ca)_3\{Al_6Si_{30}O_{72}\}\cdot 24H_2O$	4.3-5.3	<2
Mordenite	$Na_8\{Al_8Si_{40}O_{96}\}\cdot 24H_2O$	4.2-5.5	<2
Phillipsite	$(Na,K,Ca_{\frac{1}{2}})_5\{Al_5Si_{11}O_{32}\}\cdot 20H_2O$	1.3-2.9	~4

[1] minimum pH below which structural degradation occurs.

solutions near the surface. Analcime and phillipsite (zeolite ZK-19) have been synthesized from synthetic basaltic glass using various salt solutions under mild hydrothermal conditions (temperatures < 160°C) in the laboratory (Ming, unpublished data).

The Si-rich zeolites (e.g., clinoptilolite and mordenite) commonly form by the alteration of Si-rich tuffaceous sediments (e.g., rhyolitic glass) in open hydrologic systems. Ground waters percolating through volcanic sediments become enriched with Si, Al, and alkali and alkaline earth cations. Once the solubility of clinoptilolite or mordenite is exceeded, the zeolite precipitates in areas where volcanic glass has dissolved [2]. In most terrestrial weathering environments (i.e., soils), clinoptilolite and mordenite have remained as residual mineral phases during weathering of zeolite-rich, volcanic parent materials. Clinoptilolite and mordenite, as well as other zeolites, may be removed from erosional surfaces by wind and water and transported considerable distances before being deposited at the soil surface [3,4].

Zeolite Formation on Mars: Most of the Martian weathering products are thought to have altered from mafic and ultramafic rocks [5-7]. Hence, it would appear the Si-poor zeolites (e.g., analcime, phillipsite, and chabazite) would be favored to form over Si-rich zeolites (e.g., clinoptilolite). Rocks with less aluminum, though, such as the putative Martian parents of shergottite meteorites, might actually favor clinoptilolite or other zeolites that form at higher Si/Al ratios. Also, Antarctic analog studies of potential Martian weathering processes suggests the formation of chabazite. Berkley and Drake [8] found chabazite in Dry Valley Drilling Program cores as a hydrothermal alteration product of basalts; whereas, Gibson et al. [9] have reported in situ formation of chabazite in the active saline, alkaline zone of a Dry Valley soil. Zeolite-like phases are also suspected as weathering products in Antarctic meteorites [10].

The in situ formation of clinoptilolite or mordenite in terrestrial soils is virtually unknown. In fact, to the best knowledge of the authors, only one occurrence of in situ clinoptilolite formation has been reported in a weathered sodic soil of Canada [11].

If zeolites do exist on the surface of Mars, they probably formed in an ancient Martian weathering environment or have been removed from an erosional surface by eolian processes and deposited on the surface In the present Martian weathering environment, zeolites may exist as metastable phases. The high atmospheric CO_2 and high concentration of sulfur found in the eolian sediments analyzed during the Viking Mission [12] suggest that those surface materials formed in an acid sulfate weathering environment. Most zeolites are unstable in acid environments [3] with the exception of the highly siliceous zeolites (e.g., clinoptilolite and mordenite). Hence, clinoptilolite and mordenite may have a better chance of surviving compared to the Si-poor zeolites in the present Martian environment.

Sampling on Mars: Zeolites should be sought on Mars in pyroclastic deposits, altered impact rocks, and in soils. In addition, the low densities and large aspect ratios expected for zeolite crystals would favor their extended suspension in the Martian atmosphere so that atmospheric dust should also be collected.

Martian zeolite samples must be carefully preserved to prevent degradation and loss of information that they should contain. Zeolite-bearing samples should be kept sufficiently cold to minimize both gaseous and fluid exchange reactions between zeolites and Martian atmophile elements that might modify their usefulness as fossil weathering products.

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