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Chemical Weathering on Mars

Thermodynamic Stabilities of Primary Minerals (and Their Alteration Products) from Mafic Igneous Rocks

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Chemical weathering on Mars is examined theoretically from the standpoint of heterogeneous equilibrium between solid mineral phases and gaseous O_2, H_2O, and CO_2 in the Martian atmosphere. Thermochemical calculations are performed in order to identify important gas–solid decomposition reactions involving the major mineral constituents of mafic igneous rocks. Where unavailable in the thermochemical literature, Gibbs free energy and enthalpy of formation are estimated for certain minerals and details of these estimation procedures are given. Partial pressure stability diagrams are presented to show pertinent mineral reaction boundaries at 298 and at 240°K. In the present Martian environment, the thermodynamically stable products of gas–solid weathering of individual minerals at 240°K should be Fe_2O_3, as hematite or maghemite (from fayalite, magnetite, and Fe-bearing pyroxenes), quartz (from all silicates), calcite (from Ca-bearing pyroxenes and plagioclase), magnesite (from forsterite and Mg-bearing pyroxenes), corundum (from all Al-bearing silicates), Ca-beidellite (from anorthite), and szomolnokite, $FeSO_4$ or $FeSO_4 \cdot H_2O$ (from iron sulfides). Albite, microcline, and apatite should be stable with respect to gas–solid decomposition, suggesting that gas–solid weathering products on Mars may be depleted in Na, K, and P (and, possibly, Cl and F). Certain montmorillonite-type clay minerals are thermodynamically favorable intermediate gas–solid decomposition products of Al-bearing pyroxenes and may be metastable intermediate products of special mineral surface reaction mechanisms. However, the predicted high thermodynamic susceptibility of these clay minerals to subsequent gas–solid decomposition implies that they should ultimately decompose in the present Martian surface environment. Kaolinite is apparently the only clay mineral which should be thermodynamically stable over all ranges of temperature and water vapor abundance in the present environment at the Martian surface. Considering thermodynamic criteria, including possible gas–solid decomposition reactions, it is doubtful that significant amounts of goethite and clay minerals can be currently forming on Mars by mechanisms known to operate on Earth. If major amounts of goethite and clay minerals occur on Mars, they probably owe their existence to formation in an environment characterized by the presence of liquid water or by mechanism possibly unique to Mars. In any case, any goethite or montmorillonite-type clay mineral on Mars must ultimately decompose.

I. INTRODUCTION

Now that the Viking missions to Mars have provided the first quantitative data on the bulk chemical composition of Martian surface materials (Clark *et al.*, 1976) the question of mineral stability at the surface of Mars deserves renewed study. O'Connor (1968) reviewed the thermodynamic stabilities of selected minerals and their hydrate forms on Mars but did not consider the larger question of their derivation from primary rock-forming minerals. The present report expands this thermodynamic approach to include major rock-

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forming silicates and incorporates the current best information on the characteristics of the Martian environment as determined by the Viking 1 and 2 spacecraft.

Chemical weathering on Earth occurs almost exclusively in the presence of liquid water (Reiche, 1945; Krauskopf, 1967; Loughnan, 1969; Carroll, 1970). In addition to its role as a chemical reactant, liquid water facilitates reactions between solid minerals and other chemical species, notably the atmospheric gases O_2 and CO_2 and various aqueous ions. As a medium for the transportation of dissolved chemical species, liquid water is responsible for the leaching processes which commonly alter the bulk compositions of igneous rocks by significant amounts during chemical weathering.

Although channels of apparently fluvial origin exist on Mars (Hartmann, 1974; Weihaupt, 1974; Sharp and Malin, 1975) and water is known to exist in both the vapor form (Farmer *et al.*, 1976a,b) and solid form (Kieffer *et al.*, 1976), no liquid water has yet been identified on Mars. Transient ground fogs (Farmer *et al.*, 1976a) probably consist of ice crystals. It may be concluded that, in the present Martian environment, chemical weathering must occur predominantly, if not totally, without the aid of liquid water.

Because of the abundance of water on Earth, liquid–solid reactions have understandably received the greatest amount of attention in studies of chemical weathering (e.g. Correns, 1963; Loughnan, 1969). In planetary environments where water (especially liquid water) is scarce, however, reactions between atmospheric gases and solid minerals may control the rates and products of chemical weathering. Unfortunately, very little is known about the thermodynamics and kinetics of gas–solid weathering reactions (Wayman, 1963), although experiments important to the investigation of gas–solid weathering on Mars have been reported by Huguenin (1973a,b, 1974).

This report examines chemical weathering on Mars from the standpoint of thermodynamic equilibrium between primary rock-forming minerals and the atmospheric gases O_2, H_2O, and CO_2. The primary minerals which are considered are those common to mafic igneous rocks since such rocks have been tentatively identified on Mars by Earth-based spectral reflectance studies (Adams and McCord, 1969) and appear to be abundant at both Viking landing sites (Mutch *et al.*, 1976a,b). Furthermore, the bulk chemical composition of the surface fines at both Viking landing sites is consistent with an ultramafic or mafic igneous parentage (Baird *et al.*, 1976).

While this paper emphasizes the equilibrium thermodynamics of gas–solid reactions in its evaluation of possible weathering processes on Mars, the importance of kinetics and reaction mechanisms in controlling these processes is also discussed within the limits of currently available data. Where it is appropriate, the possible influence of liquid water on Martian weathering processes is also considered.

II. THERMOCHEMICAL CALCULATIONS

In the absence of liquid[1] water, chemical weathering on Mars is assumed to occur strictly by gas–solid reactions of the type

$$aS_1 + bG_1 + cG_2 + \cdots \rightleftharpoons kS_2 + 1S_3 + \cdots + xG_n + yG_{n+1} + \cdots, \quad (1)$$

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[1] Throughout this paper, "liquid" water is distinguished from "adsorbed" water vapor on the basis of the Kelvin equation (Adamson, 1967). For a partial pressure of water vapor, P', at temperature T, where the equilibrium vapor pressure at saturation is P_0, the nucleation of liquid water droplets requires that $(P'/P_0) > 1$. However, this condition should rarely if ever prevail at the surface of Mars (Anderson *et al.*, 1967). Water vapor adsorbed on silicate mineral surfaces should probably always be less than 1.5 molecular layers in thickness (Anderson *et al.*, 1967) and, hence, should definitely be less active (in the thermochemical sense) than true "liquid" water.

in which a single solid mineral, S_1, reacts with atmospheric gases, $G_1, G_2, \ldots$, to form solid decomposition products, $S_2, S_3, \ldots$, and residual gases, $G_n, G_{n+1}, \ldots$. Taking the activities of the solid phases to be unity (Lewis and Randall, 1961) the equilibrium constant for reaction (1) is

$$K = K_\gamma K_P = \left[\frac{(\gamma_{G_n})^x(\gamma_{G_{n+1}})^y\cdots}{(\gamma_{G_1})^b(\gamma_{G_2})^c\cdots}\right] \times \left[\frac{(P_{G_n})^x(P_{G_{n+1}})^y\cdots}{(P_{G_1})^b(P_{G_2})^c\cdots}\right], \quad (2)$$

where P is the partial pressure of each gaseous component and γ is its activity coefficient. At low total pressures, such as for the ambient atmospheres of both Earth and Mars, $\gamma \rightarrow 1$ such that $K_\gamma \rightarrow 1$ to give

$$K = K_P = \frac{(P_{G_n})^x(P_{G_{n+1}})^y\cdots}{(P_{G_1})^b(P_{G_2})^c\cdots}. \quad (3)$$

If the Gibbs free energy change, ΔG, can be calculated for reaction (1) at temperature T, then K is found (Lewis and Randall, 1961) as

$$K = \exp(-\Delta G/RT), \quad (4)$$

where R is the gas constant. By combining (3) and (4), sets of $P_{G_1}, P_{G_2}, P_{G_n}, P_{G_{n+1}}, \ldots$, can be found for which S_1 is in equilibrium with $S_2, S_3, \ldots$. These values can then be used to define the boundary for reaction (1) in a partial pressure stability diagram (Garrels and Christ, 1965, pp. 144–171).

The main difficulty involved in the application of (4) is the calculation of ΔG for the reaction, since the required values of the Gibbs free energy of formation, ΔG_f°, are not known for many minerals of interest. In this study, values of ΔG_f° were taken from published compilations when possible but, in cases where no value of ΔG_f° was available, a reasonable value was estimated by proportional scaling to the values of analogous compounds (Lewis and Randall, 1961). Values of ΔG_f° for clay minerals were calculated by the method of Nriagu (1975). In the Appendix the thermochemical data used in this paper are tabulated and the pertinent estimation methods are described. In most cases, the uncertainties in the estimated values should produce only minor shifts in the positions of reaction boundaries in the resultant stability diagrams. As will be seen, these uncertainties do not seriously affect the general conclusions to be drawn from the diagrams.

Since average Martian surface temperatures are significantly lower than those on Earth, mineral stabilities at these low temperatures are of special interest. The calculation of K in (4) for temperatures other than 298°K, however, requires knowledge of the variation of ΔG with T for the reaction. Specifically, the temperature-dependent heat capacity, $C_P(T)$, is required for each participant in reaction (1) so that the corresponding enthalpy change, ΔH, can be found by integration over the temperature range of interest:

$$\Delta H_{T_1,T_2} = \int_{T_1}^{T_2} C_P(T)dT. \quad (5)$$

Unfortunately, values of $C_P(T)$ are not known for most minerals. However, from the limited data which are available it can be shown that the variation of ΔH with T should be comparatively small over the temperature range of interest in this paper. For example, Weast (1975, p. B-235) gives $C_P(T)$ for microcline as

$$C_P(T) = 0.988 + 0.166T - 0.263T^{-5}, \quad (6)$$

where T is the temperature in degrees Celsius (°C). Combining (5) and (6) and integrating from $T_1 = -33$°C $(=240$°K$)$ to $T_2 = 25$°C $(=298$°K$)$ yields $\Delta H_{T_1,T_2} = 0.0188$ kcal/kg, or, 0.00523 kcal/fw. Since $\Delta H_{298}^\circ = -946.26$ kcal/fw for microcline (Robie and Waldbaum, 1968), ΔH changes by less than 0.0005% over the range of 240 to 298°K. Similar calculations for kaolinite, a possible decomposition product of microcline, give $\Delta H_{T_1,T_2}$

$= -0.000235$ kcal/fw, or, a variation in ΔH of less than 0.00002% over the range 240 to 298°K.

Therefore, it can be assumed that, over the temperature range of interest in this paper, ΔH is approximately constant for each reactant and product and that the enthalpy of reaction, ΔH_{rxn}, should also be approximately constant. Accordingly, variation of the equilibrium constant, K, with temperature can be approximated by the integrated form of the Clausius–Clapeyron equation (Lewis and Randall, 1961)

$$\ln (K_2/K_1) = (\Delta H_{rxn}/R)(T_1^{-1} - T_2^{-1}). \quad (7)$$

O'Connor (1968) treated the variation of K with T by extrapolating to $T < 298$°K using empirical equations intended for use at $T > 298$°K. In the present study, however, K_1 was calculated for each reaction at the standard temperature of $T_1 = 298$°K and then extrapolated to a lower temperature, T_2, by use of (7). This approach is simpler but, in the absence of complete $C_P(T)$ data, is probably no less accurate than O'Connor's (1968) method.

The stability diagrams presented in the following sections include reaction boundaries for 298, 240, and, in some cases, for 273°K. The 298°K boundaries are given for reference while the 240°K boundaries should be more representative of the environment at the surface of Mars. The seasonal average Martian surface temperatures are predicted (Kieffer, 1976) to be approximately 215°K at the Viking 1 landing site and approximately 170–220°K at the Viking 2 landing site. Maximum seasonal temperatures may reach 270°K at both sites (Kieffer, 1976) and 305°K at the equator (Best, 1971). The selection of 240°K as a typical Martian temperature represents a compromise between the actual temperature extremes and the inaccuracies involved in extrapolating thermochemical quantities to lower temperatures.

Because discussion of the following stability diagrams will continually involve environmental comparison of the Earth and Mars, some pertinent environmental quantities which influence chemical weathering have been compiled in Table I. These quantities have been calculated using the best information on the Martian atmosphere which is currently available, namely, direct measurements by the Viking 1 and 2 spacecraft. Noteworthy entries in Table I include the partial pressures of O_2, H_2O, and CO_2 in the atmospheres of Mars and Earth. As seen in the next section, the greater abundance of CO_2 and the lesser abundance of H_2O vapor on Mars should have an especially important effect on mineral stabilities at the Martian surface.

III. WEATHERING OF INDIVIDUAL MINERALS

The major mineral constituents of terrestrial mafic and ultramafic igneous rocks are olivine, orthopyroxene, clinopyroxene, and plagioclase (Carmichael *et al.*, 1974). While their chemical compositions may differ, these same minerals are also major constituents of extraterrestrial rocks, including stony meteorites and lunar rocks (Taylor, 1975). Therefore, this section considers possible gas–solid weathering reactions involving representative minerals from each of these major groups. Since the possible formation of iron oxides, sulfates, phosphates, and halides on Mars is also of interest, the weathering reactions of magnetite, troilite/pyrrhotite, apatite, and volcanic glass are also investigated even though these phases are generally present in mafic rocks in minor to accessory amounts only.

The approach taken here is to examine first the thermodynamics of selected gas–solid weathering reactions in order to construct mineral stability diagrams appropriate for Martian surface conditions. Finally, an attempt is made to resolve these results with available information on reaction mechanisms and kinetics so that likely *intermediate* chemical weathering products

TABLE I

IMPORTANT ENVIRONMENTAL QUANTITIES RELATED TO CHEMICAL WEATHERING ON EARTH AND MARS[a]

Quantity	Earth	Mars
Log P_{O_2} of atmosphere	−0.68	−5.0
Log [O_2] in liquid water equilibrated with atmosphere at 273°K	−3.35	−7.7
Log P_{CO_2} of atmosphere	−3.48	−2.2
Log [CO_2] in liquid water equilibrated with atmosphere at 273°K	−4.60	−3.3
Log P_{H_2O} of atmosphere	−1.81 (relative humidity of 50% at 298°K)	−2.22 (probable maximum limit = vapor pressure of ice at 273°K) −5.5 (observed maximum = 80 precipitable μm) −7.4 (1 precipitable μm)

[a] Entries for Earth were calculated from data given by Weast (1975), assuming a total pressure of 1 atm. Entries for Mars were calculated for an atmospheric composition of 95% CO_2 and 0.15% O_2 (Nier *et al.*, 1976; Owen and Biemann, 1976) at a total pressure of 6.50 mb (=0.00642 atm). Partial pressures of water vapor in the Martian atmosphere were calculated from the data of Farmer *et al.* (1976b). Partial pressures (P) are in atmospheres, while molarity is indicated with brackets.

can be identified along with the *ultimate* weathering products predicted on purely thermodynamic grounds.

A. THERMODYNAMIC STABILITIES AND GAS–SOLID REACTIONS

1. *Olivine*

The common alteration products of olivine on Earth are iddingsite and Mg-phyllosilicates, including serpentine, chlorite, and talc (Deer *et al.*, 1966). Iddingsite is a mechanical mixture of geothite or hematite with one or more Mg-phyllosilicates which usually cannot be identified because of their exceedingly fine grain size (Sun, 1957; Brown and Stephen, 1959). Thus, the weathering of olivine can be treated using Fe- and Mg-oxides, -hydroxides, and -phyllosilicates as the assumed possible products of decomposition. In the following discussions, talc will be used to represent the Mg-phyllosilicate component of the weathering products.

Forsterite. The important reactions involved in the gas–solid weathering of forsterite are compiled in Table II and summarized as mineral stability fields in Fig. 1. While talc should be a stable weathering product from forsterite on Earth, it should not be stable in the much drier,[2] CO_2-rich environment of Mars. On Mars, talc should decompose into magnesite + quartz, the two stable products of the direct reaction of forsterite with CO_2.

Fayalite. Pertinent results are summarized in Table II and in Figs. 2, 3, and 4. In the absence of O_2, minnesotaite (Fe-analog of talc) should coexist with siderite as a stable decomposition product of fayalite in moist environments (Fig. 2). However, fayalite, minnesotaite, and siderite are oxidizable so that hematite + quartz should result from their gas–solid decomposition (Figs. 3, 4). The gas–solid decomposition of minnesotaite may proceed very slowly, though, as suggested by its abund-

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[2] In this paper, "dry" and "moist" (and related terms) imply only relative abundances of water vapor, not the presence of liquid water.

TABLE II

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES IN THE SYSTEMS Mg_2SiO_4–H_2O–CO_2 AND Fe_2SiO_4–O_2–H_2O–CO_2[a]

Reaction	Log K (298°K)	Log K (240°K)
(2-1) $Mg_2SiO_4 + 2\ CO_2 \rightleftharpoons 2\ MgCO_3 + SiO_2$	12.0	19.3
(2-2) $4\ Mg_2SiO_4 + 5\ CO_2 + H_2O \rightleftharpoons Mg_3Si_4O_{10}(OH)_2 + 5\ MgCO_3$	44.9	69.0
(2-3) $4\ Mg_2SiO_4 + 6\ H_2O \rightleftharpoons Mg_3Si_4O_{10}(OH)_2 + 5\ Mg(OH)_2$	19.2	35.6
(2-4) $Mg(OH)_2 + CO_2 \rightleftharpoons MgCO_3 + H_2O$	5.15	6.68
(2-5) $Mg_3Si_4O_{10}(OH)_2 + 3\ CO_2 \rightleftharpoons 3\ MgCO_3 + 4\ SiO_2 + H_2O$	3.15	8.33
(2-6) $24\ Fe_2SiO_4 + 5\ O_2 + 6\ H_2O \rightleftharpoons 6\ Fe_3Si_4O_{10}(OH)_2 + 10\ Fe_3O_4$	457	583
(2-7) $4\ Fe_3Si_4O_{10}(OH)_2 + 3\ O_2 \rightleftharpoons 6\ Fe_2O_3 + 16\ SiO_2 + 4\ H_2O$	198	254
(2-8) $4\ Fe_3O_4 + O_2 \rightleftharpoons 6\ Fe_2O_3$	68.8	89.0
(2-9) $4\ Fe_3O_4 + O_2 + 6\ H_2O \rightleftharpoons 12\ FeO(OH)$	72.5	106
(2-10) $4\ Fe_3Si_4O_{10}(OH)_2 + 3\ O_2 + 2\ H_2O \rightleftharpoons 12\ FeO(OH) + 16\ SiO_2$	201	270
(2-11) $Fe_2O_3 + H_2O \rightleftharpoons 2\ FeO(OH)$	0.61	2.80
(2-12) $Fe_2SiO_4 + 2\ CO_2 \rightleftharpoons 2\ FeCO_3 + SiO_2$	6.24	11.8
(2-13) $3\ Fe_2SiO_4 + O_2 \rightleftharpoons 2\ Fe_3O_4 + 3\ SiO_2$	81.4	104
(2-14) $6\ FeCO_3 + O_2 \rightleftharpoons 2\ Fe_3O_4 + 6\ CO_2$	62.6	68.3
(2-15) $4\ FeCO_3 + O_2 \rightleftharpoons 2\ Fe_2O_3 + 4\ CO_2$	64.7	75.2
(2-16) $4\ Fe_2SiO_4 + 5\ CO_2 + H_2O \rightleftharpoons Fe_3Si_4O_{10}(OH)_2 + 5\ FeCO_3$	24.0	40.3
(2-17) $Fe_3Si_4O_{10}(OH)_2 + 3\ CO_2 \rightleftharpoons 3\ FeCO_3 + 4\ SiO_2 + H_2O$	0.88	6.98

[a] All reactants and products are solids except for O_2, H_2O and CO_2, which are gases.

ance in Mesabi iron ore deposits on Earth (Gruner, 1944). Therefore, minnesotaite, if formed in a relatively moist environment, might be a metastable product of gas–solid weathering of fayalite on Mars but should ultimately oxidize to hematite + quartz.

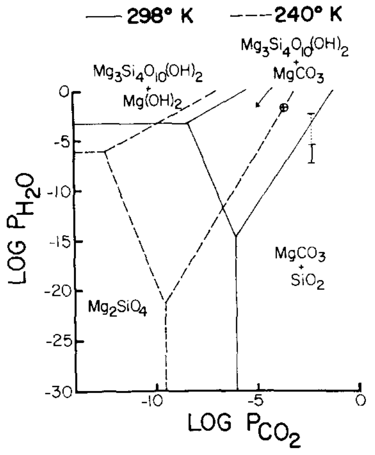

FIG. 1. Stability fields of forsterite and its decomposition products in equilibrium with gaseous H_2O and CO_2. (O_2 does not influence these stability fields.) The reference point for Earth (circle with cross) is for a relative humidity of 50% at 298°K. The observed range of water vapor abundance in the Martian atmosphere (bars joined by solid line) and its probable maximum limit, the vapor pressure of ice at 273°K (bar at top of dotted line), are shown. Units of P are atmospheres.

It is important to note that hematite, rather than goethite, is the stable sink for Fe^{3+} since the water vapor abundance in the Martian atmosphere should be too low to stabilize goethite (Fig. 3). While goethite on Earth should similarly dehydrate to form hematite, it will be seen later (Section IIIB) that goethite on Earth owes its metastable existence to an origin involving liquid water and to dehydration reactions which are commonly inhibited by kinetic effects. The point here is that goethite should *not* form from olivine on Mars if the reactions depicted in Fig. 3 control its chemical weathering.

In summary, the equilibration of olivine with the present Martian atmosphere should yield magnesite + hematite + quartz. If, however, gas–solid decomposition proceeds through various reaction intermediates the premature arrest of these reactions could yield different metastable mineral assemblages which might include siderite and Fe- and Mg-phyllosilicates.

2. Pyroxene

The weathering products of pyroxenes on Earth are similar to those of olivine (Deer *et al.*, 1966). An important difference is that montmorillonite clay minerals are also major chemical weathering products of Fe- and Mg-bearing aluminous pyroxenes (Ross and Hendricks, 1945).

Diopside. The pertinent gas–solid weathering reactions for diopside are summarized in Table III and Fig. 5. Talc and calcite should coexist as stable decomposition products of diopside on Earth but, on Mars, should be replaced by calcite + magnesite + quartz. It is apparent from Fig. 5 that diopside, by reaction with CO_2, can decompose into either dolomite + quartz, or into calcite + magnesite + quartz. The former reaction is favored thermodynamically [see reactions (3-1) and (3-2) in Table III], although its complementary reaction, the derivation of dolomite from talc [reaction (3-4) in Table III], requires the participation of solid calcite as a reactant. This gas–solid–solid reaction should be kinetically less favorable than the simple gas–solid decomposition of talc into magnesite + quartz [reaction (3-5) in Table III]. Accordingly, the most stable gas–solid decomposition products of diopside on Mars should be dolomite + quartz if a direct reaction pathway is followed, but may be magnesite + calcite + quartz if the decomposition of diopside involves talc as a reaction intermediate.

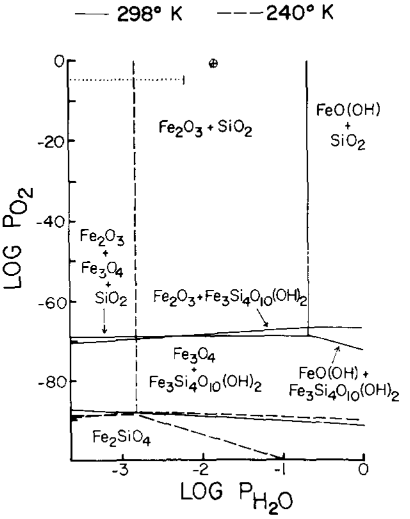

FIG. 3. Stability fields of fayalite and its decomposition products in equilibrium with gaseous O_2 and H_2O where CO_2 is absent. The probable maximum limit of Martian atmospheric water vapor abundance (bar at end of dotted line) is the vapor pressure of ice at 273°K. Other symbol same as in Fig. 1.

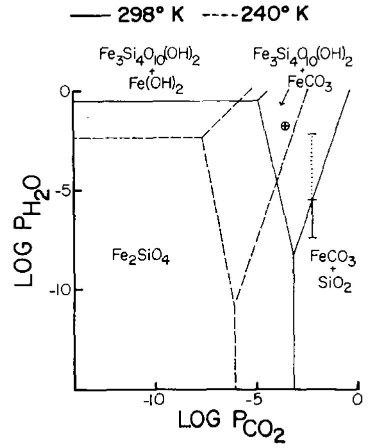

FIG. 2. Stability fields of fayalite and its decomposition products in equilibrium with gaseous H_2O and CO_2 where O_2 is absent. Symbols are same as in Fig. 1.

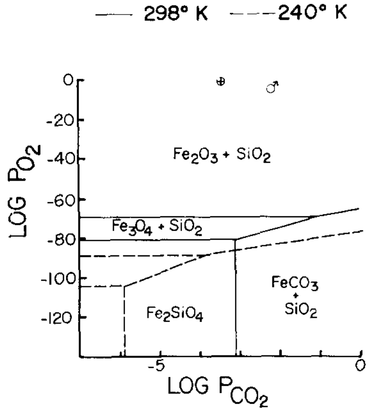

FIG. 4. Stability fields of fayalite and its decomposition products in equilibrium with gaseous O_2 and CO_2 where H_2O is absent. Reference points are shown for Earth (circle with cross) and Mars (circle with arrow).

TABLE III

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES IN THE SYSTEMS $CaMgSi_2O_6$-H_2O-CO_2 AND $CaFeSi_2O_6$-O_2-H_2O-CO_2[a]

Reaction	Log K (298°K)	Log K (240°K)
(3-1) $CaMgSi_2O_6 + 2\ CO_2 \rightleftharpoons CaMg(CO_3)_2 + 2\ SiO_2$	10.1	16.7
(3-2) $CaMgSi_2O_6 + 2\ CO_2 \rightleftharpoons CaCO_3 + MgCO_3 + 2\ SiO_2$	8.07	14.2
(3-3) $CaMgSi_2O_6 + 3\ CO_2 + H_2O \rightleftharpoons Mg_3Si_4O_{10}(OH)_2 + 3\ CaCO_3 + 2\ SiO_2$	21.1	34.2
(3-4) $Mg_3Si_4O_{10}(OH)_2 + 3\ CO_2 + 3\ CaCO_3 \rightleftharpoons 3\ CaMg(CO_3)_2 + 4\ SiO_2 + H_2O$	9.61	16.4
(3-5) $Mg_3Si_4O_{10}(OH)_2 + 3\ CO_2 \rightleftharpoons 3\ MgCO_3 + 4\ SiO_2 + H_2O$	3.15	8.33
(3-6) $4\ CaFeSi_2O_6 + O_2 \rightleftharpoons 2\ Fe_2O_3 + 4\ CaSiO_3 + 4\ SiO_2$	60.3	77.5
(3-7) $4\ CaFeSi_2O_6 + O_2 + 2\ H_2O \rightleftharpoons 4\ FeO(OH) + 4\ CaSiO_3 + 4\ SiO_2$	61.5	83.1
(3-8) $Fe_2O_3 + 2\ H_2O \rightleftharpoons 2\ FeO(OH)$	0.61	2.80
(3-9) $CaFeSi_2O_6 + 2\ CO_2 \rightleftharpoons CaCO_3 + FeCO_3 + 2\ SiO_2$	6.22	11.7
(3-10) $6\ CaFeSi_2O_6 + O_2 + 6\ CO_2 \rightleftharpoons 2\ Fe_3O_4 + 6\ CaCO_3 + 12\ SiO_2$	99.9	138
(3-11) $6\ FeCO_3 + O_2 \rightleftharpoons 2\ Fe_3O_4 + 6\ CO_2$	62.6	68.3
(3-12) $4\ FeCO_3 + O_2 \rightleftharpoons 2\ Fe_2O_3 + 4\ CO_2$	64.7	75.2
(3-13) $4\ Fe_3O_4 + O_2 \rightleftharpoons 6\ Fe_2O_3$	68.8	89.0
(3-14) $4\ CaFeSi_2O_6 + O_2 + 4\ CO_2 \rightleftharpoons 2\ Fe_2O_3 + 4\ CaCO_3 + 8\ SiO_2$	89.6	122
(3-15) $3\ CaFeSi_2O_6 + 3\ CO_2 + H_2O \rightleftharpoons Fe_3Si_4O_{10}(OH)_2 + 3\ CaCO_3 + 2\ SiO_2$	13.8	23.1
(3-16) $Fe_3Si_4O_{10}(OH)_2 + 3\ CO_2 \rightleftharpoons 3\ FeCO_3 + 4\ SiO_2 + H_2O$	0.88	6.98
(3-17) $CaSiO_3 + CO_2 \rightleftharpoons CaCO_3 + SiO_2$	7.31	11.1

[a] All reactants and products are solids except for O_2, H_2O and CO_2, which are gases.

Hedenbergite. The important gas–solid reactions involved in the weathering of hedenbergite are summarized in Table III and Figs. 6, 7, and 8. As with fayalite, minnesotaite may be a metastable decomposition product of hedenbergite (Fig. 6) which, upon equilibration with atmospheric O_2, should decay into hematite + quartz (Fig. 8). Again, as with fayalite, hematite, rather than goethite, should be the stable sink for oxidized iron (Fig. 7). Wollastonite may be a metastable sink for calcium (Figs. 7 and 8) if its decomposition into calcite + quartz is inhibited.

Augite. The composition of augite from igneous rocks varies considerably but the composition assumed for this study, $(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$, is a reasonable estimate for augite commonly found in terrestrial gabbros and basalts (Deer *et al.*, 1966). By designating all iron as Fe^{2+}, this composition is also generally applicable to augite in lunar basalts (Taylor, 1975). The pertinent reactions involving augite are summarized in Table IV and in Figs. 9 and 10.

In the Martian environment, the stable gas–solid decomposition products of augite should be hematite + calcite + magnesite + quartz + corundum (Fig. 9A). Even though sufficient Al and Si are available for their production, clay minerals are *not* the most stable gas–solid decomposition products of augite (Fig. 9B). While the production of clay minerals by gas–solid weathering of augite is thermodynamically favorable (Table IV and Fig. 9B), these clay-forming reactions are not among those which are most sensitive to P_{H_2O} and P_{CO_2}. The most pressure-sensitive reactions in the augite–O_2–H_2O–CO_2 system [reactions (4-1) through (4-4) in Table IV] define

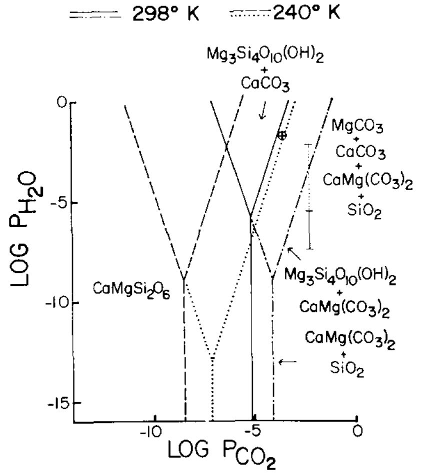

FIG. 5. Stability fields of diopside and its decomposition products in equilibrium with gaseous H_2O and CO_2. (O_2 does not influence these stability fields.) Note that talc decomposes to magnesite + quartz by reaction with CO_2 and to dolomite + quartz by reaction with calcite and CO_2. Symbols are same as in Fig. 1.

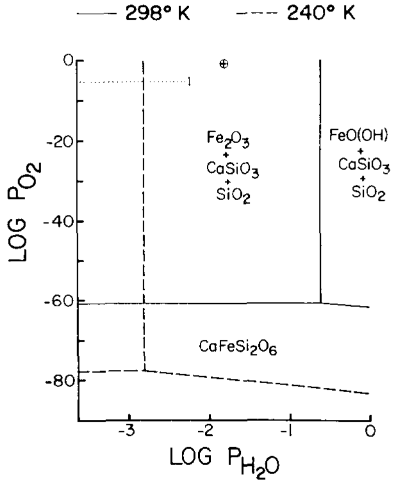

FIG. 7. Stability fields of hedenbergite and its decomposition products in equilibrium with gaseous O_2 and H_2O where CO_2 is absent. Symbols are same as in Fig. 3.

reaction boundaries in Fig. 9 which lie at decisively lower values of P_{H_2O} and P_{CO_2} than the comparable reaction boundaries for the production of clay minerals. For example, Fig. 9B shows that augite would be required to pass metastably across the talc reaction boundary in order to form clay minerals. Furthermore, it can be shown (Section IV) that most clay minerals can be, at best, only metastable phases in the present Martian environment.

Figure 10 shows the stability fields of augite and its weathering products for the case where liquid water is present. Comparison of Fig. 10 with Fig. 9 shows that

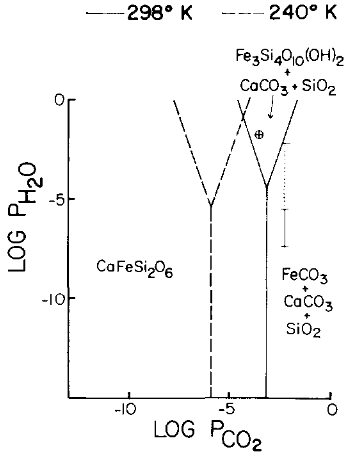

FIG. 6. Stability fields of hedenbergite and its decomposition products in equilibrium with gaseous H_2O and CO_2 where O_2 is absent. Symbols same as in Fig. 1.

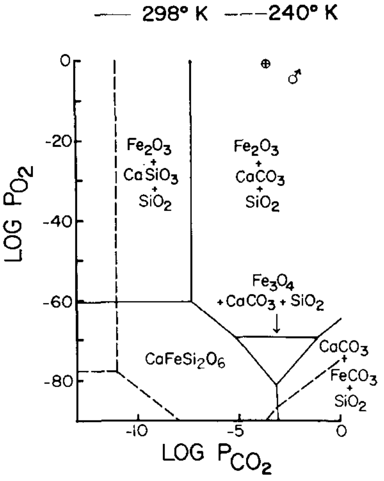

FIG. 8. Stability fields of hedenbergite and its decomposition products in equilibrium with gaseous O_2 and CO_2 where H_2O is absent. Symbols are same as in Fig. 4.

TABLE IV

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES IN THE SYSTEMS AUGITE–O_2–H_2O–CO_2 AND SUBCALCIC FERROAUGITE–O_2–H_2O–CO_2 [a]

Reaction	Log *K* (298°K)	Log *K* (240°K)
(4-1) augite $+ 0.1251\ O_2 + 0.2667\ H_2O + 0.0668\ CO_2$ $\rightleftharpoons 0.2667\ Mg_3Si_4O_{10}(OH)_2 + 0.25\ Fe_2O_3 + 0.7332\ CaSiO_3$ $+ 0.1\ Al_2O_3 + 0.0668\ CaCO_3$	8.42	11.5
(4-2) augite $+ 0.125\ O_2 + 0.8\ CO_2$ $\rightleftharpoons 0.8\ CaSiO_3 + 0.8\ MgCO_3 + 0.25\ Fe_2O_3 + SiO_2$ $+ 0.1\ Al_2O_3$	8.79	13.0
(4-3) $Mg_3Si_4O_{10}(OH)_2 + 3\ CO_2 \rightleftharpoons 3\ MgCO_3 + 4\ SiO_2 + H_2O$	3.15	8.33
(4-4) $CaSiO_3 + CO_2 \rightleftharpoons CaCO_3 + SiO_2$	7.31	11.1
(4-5) augite $+ 0.1249\ O_2 + 0.304\ H_2O + 0.0468\ CO_2$ $\rightleftharpoons 0.2667$ saponite $+ 0.0373$ Ca-B $+ 0.25\ Fe_2O_3$ $+ 0.703\ CaSiO_3 + 0.0468\ CaCO_3$	6.9	9.6
(4-6) augite $+ 0.1251\ O_2 + 0.2667\ H_2O$ $\rightleftharpoons 0.2667$ saponite $+ 0.25\ Fe_2O_3 + 0.756\ CaSiO_3$ $+ 0.056\ Al_2O_3 + 0.0652\ SiO_2$	6.4	8.8
(4-7) augite $+ 0.1251\ O_2 + 0.3204\ H_2O + 0.923\ CO_2$ $\rightleftharpoons 0.25$ nontronite $+ 0.0704$ montmorillonite $+ 0.6009\ CaSiO_3$ $+ 0.1462\ CaCO_3 + 0.7768\ MgCO_3$	8.64	13.1
(4-8) augite $+ 0.123\ O_2 + 0.49\ H_2O + 0.799\ CO_2$ $\rightleftharpoons 0.25$ nontronite $+ 0.24$ saponite $+ 0.08\ MgCO_3$ $+ 0.1462\ CaCO_3 + 0.0192\ Al_2O_3$	10.1	14.9
(4-9) subcalcic ferroaugite $+ 0.25\ O_2 + 0.4\ CO_2 + 0.2333\ H_2O$ $\rightleftharpoons 0.2333\ Mg_3Si_4O_{10}(OH)_2 + 0.5\ Fe_2O_3 + 0.4\ CaCO_3$ $+ 0.8668\ SiO_2 + 0.1\ Al_2O_3$	19.2	25.8
(4-10) subcalcic ferroaugite $+ 0.25\ O_2 + 1.1\ CO_2$ $\rightleftharpoons 0.4\ CaCO_3 + 0.7\ MgCO_3 + 0.5\ Fe_2O_3 + 1.8\ SiO_2$ $+ 0.1\ Al_2O_3$	19.9	27.8
(4-11) subcalcic ferroaugite $+ 0.2502\ O_2$ $+ 0.4905\ H_2O + 1.0191\ CO_2$ $\rightleftharpoons 0.4905$ nontronite $+ 0.0095\ Fe_2O_3 + 0.7\ MgCO_3$ $+ 0.3191\ CaCO_3 + 0.01907\ Al_2O_3$	16.4	26.6
(4-12) subcalcic ferroaugite $+ 0.2502\ O_2$ $+ 0.4905\ H_2O + 0.3191\ CO_2$ $\rightleftharpoons 0.2572$ nontronite $+ 0.2333$ saponite $+ 0.3191\ CaCO_3$ $+ 0.2428\ Fe_2O_3 + 0.01907\ Al_2O_3$	15.7	21.3
(4-13) subcalcic ferroaugite $+ 0.25\ O_2$ $+ 0.233\ H_2O + 0.3615\ CO_2$ $\rightleftharpoons 0.2333$ saponite $+ 0.3615\ CaCO_3 + 0.5\ Fe_2O_3$ $+ 0.06151\ Al_2O_3 + 0.9438\ SiO_2$	17.4	23.6
(4-14) subcalcic ferroaugite $+ 0.25\ O_2$ $+ 0.4695\ H_2O + 0.361\ CO_2$ $\rightleftharpoons 0.2333\ Mg_3Si_4O_{10}(OH)_2 + 0.2362$ nontronite $+ 0.06103\ Al_2O_3 + 0.2638\ Fe_2O_3 + 0.361\ CaCO_3$	17.5	23.8

[a] All reactants and products are solids except for O_2, H_2O, and CO_2, which are gases. Abbreviations: Augite = $(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$; subcalcic ferroaugite = $(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$; saponite = $Ca_{0.165}Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$; Ca-B = Ca-beidellite = $Ca_{0.165}Al_{2.17}(Al_{0.33}Si_{3.17})O_{10}(OH)_2$; nontronite = $Ca_{0.165}Fe_2^{3+}(Al_{0.33}Si_{3.67})O_{10}(OH)_2$; montmorillonite = $Ca_{0.165}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$.

the presence of liquid water changes the respective stability fields to a considerable extent and that talc becomes stable in the presence of liquid water. It should be emphasized that the liquid water postulated here is assumed to contain dissolved atmo-

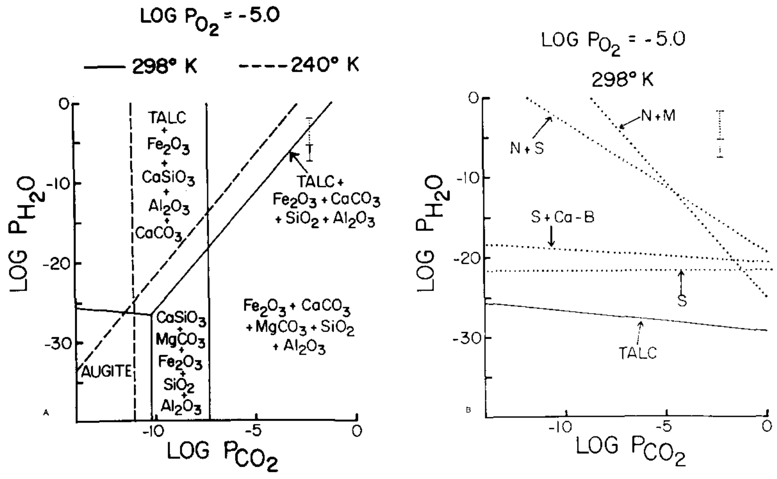

Fig. 9. (A) Stability fields of augite (composition given in Table IV) and its decomposition products in equilibrium with gaseous H_2O and CO_2 at the partial pressure of O_2 in the Martian atmosphere. (B) Reaction boundaries for the production of selected phyllosilicates by gas-solid weathering of augite. (Subsequent decomposition of the phyllosilicates has been neglected.) Symbols are same as in Fig. 1. Abbreviations: S = saponite, Ca-B = Ca-beidellite, N = nontronite, M = montmorillonite.

spheric gases at their equilibrium concentrations which, on both Earth and Mars, would make the water distinctly acidic. Such acidic water should accelerate the processes of chemical weathering but should also prevent the precipitation of minerals which require alkaline solutions for their formation. It should also be pointed out

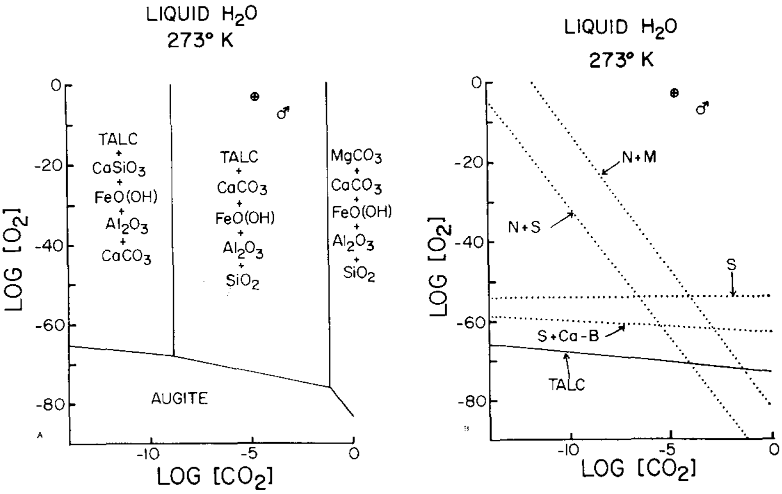

Fig. 10. (A) Stability fields of augite (composition given in Table IV) and its decomposition products in equilibrium with liquid water containing dissolved O_2 and CO_2. (B) Reaction boundaries for the production of selected phyllosilicates by weathering of augite in the presence of liquid water containing dissolved O_2 and CO_2. (Subsequent decomposition of the phyllosilicates has been neglected.) Reference points are shown for gas-saturated aqueous solutions on Earth (circle with cross) and Mars (circle with arrow). Dissolved gas concentrations are in molarity.

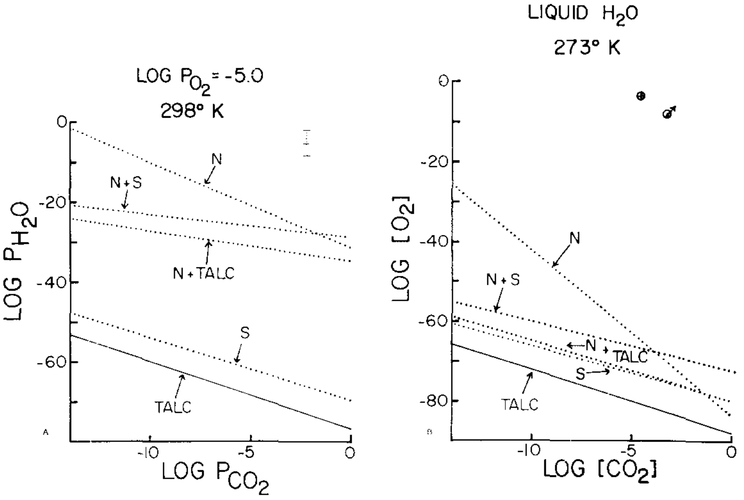

FIG. 11. (A) Reaction boundaries for the production of selected phyllosilicates by gas-solid weathering of subcalcic ferroaugite (composition given in Table IV). (Subsequent decomposition of the phyllosilicates has been neglected.) Symbols are same as in Fig. 1. Abbreviations: S = saponite, N = nontronite. (B) Reaction boundaries for the production of selected phyllosilicates by the weathering of subcalcic ferroaugite in the presence of liquid water containing dissolved O_2 and CO_2. Symbols are same as in Fig. 10B.

that while talc should be the stable phyllosilicate derived from augite, the formation of nontronite + saponite, and nontronite + montmorillonite, is also more favorable in the presence of liquid water. In fact, nontronite + saponite, and nontronite + montmorillonite, should be the clay minerals which most closely approach stability as weathering products of augite when liquid water is present (Fig. 10B).

Although talc should be a stable weathering product of augite in contact with liquid water (Fig. 10A), it should not be stable when equilibrated with the Martian atmosphere (Fig. 9A). Thus, talc may exist metastably on Mars if formed originally in liquid water but should decompose into magnesite + quartz upon equilibration with the present Martian environment. It can be shown (Section IV) that clay minerals of the montmorillonite group should behave similarly.

Subcalcic ferroaugite. The composition assumed for subcalcic ferroaugite, $(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$, should be representative of the range of compositions exhibited by late-formed clinopyroxenes in some mafic to intermediate volcanic rocks (Deer *et al.*, 1966). The pertinent gas–solid weathering reactions for subcalcic ferroaugite are listed in Table IV but, because of their demonstrable similarity to those of augite, the graphical display of the stability fields of subcalcic ferroaugite and its decomposition products is omitted. However, the reaction boundaries for the production of selected phyllosilicates from subcalcic ferroaugite are shown in Fig. 11.

As with augite, the stable gas–solid decomposition products of subcalcic ferroaugite on Mars should be calcite + magnesite + hematite + quartz + corundum. Even though Fe is more abundant in the primary mineral experiencing degradation, Fe-rich clay minerals are *not* the thermodynamically most favorable products of gas–solid weathering. However, comparison of Fig. 11 with Figs. 9 and 10 does show that reactions which form Fe-rich clay minerals (nontronite) become more competitive with the talc-forming reactions as the Fe content of the primary pyroxene mineral increases. As with augite, saponite should be the clay mineral which most closely approaches stability as a decomposition product of subcalcic ferroaugite (Fig. 11A) although nontronite may become highly competitive as a weathering product when liquid water is present (Fig. 11B).

In summary, the equilibration of pyroxenes with the present Martian atmosphere should yield an assemblage of calcite + magnesite + hematite + quartz + corundum, the relative proportions of these phases being determined by the composition of the pyroxenes. As discussed for diopside, either dolomite or calcite + magnesite may be the dominant carbonates, depending on the reaction pathway which is followed during weathering. Phyllosilicates should form from pyroxenes only when liquid water participates in the weathering reactions. When liquid water is present, aluminous pyroxenes may yield talc, saponite, nontronite, and montmorillonite (in approximately that order of thermodynamic preference) as the major phyllosilicate products of chemical weathering.

3. *Plagioclase*

The alteration products of plagioclase on Earth are dominated by clay minerals (Heinrich, 1965). In the following discussions, the chemically simplest clay derivatives, namely Ca-beidellite and Na-beidellite, will be assumed.

Anorthite. Important reactions involved in the gas–solid decomposition of anorthite are summarized in Table V and Fig. 12. On Earth, the stable phases derived from the gas–solid weathering of anorthite should be Ca-beidellite + calcite + corundum while, on Mars, the lower abundance of water vapor and the higher partial pressure of CO_2 should favor the formation of calcite + quartz + corundum. With decreasing

TABLE V

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES IN THE SYSTEMS $CaAl_2Si_2O_8$–O_2–H_2O–CO_2 AND $NaAlSi_3O_8$–O_2–H_2O–CO_2[a]

Reaction	Log *K* (298°K)	Log *K* (240°K)
(5-1) $CaAl_2Si_2O_8 + 2\ H_2O + CO_2 \rightleftharpoons Al_2Si_2O_5(OH)_4 + CaCO_3$	9.96	18.7
(5-2) $CaAl_2Si_2O_8 + 0.6309\ H_2O + 0.8959\ CO_2$ $\rightleftharpoons 0.6309$ Ca-B $+ 0.8959\ CaCO_3 + 0.05365\ Al_2O_3$ $+ 0.001625\ O_2$	7.91	13.2
(5-3) $CaAl_2Si_2O_8 + CO_2 \rightleftharpoons CaCO_3 + 2\ SiO_2 + Al_2O_3$	5.42	9.13
(5-4) Ca-B $+ 2\ H_2O + 0.165\ CO_2$ $\rightleftharpoons 1.5\ Al_2Si_2O_5(OH)_4 + 0.165\ CaCO_3 + 0.17\ SiO_2$	2.8	7.5
(5-5) Ca-B $+ 0.165\ CO_2 + 0.0025\ O_2$ $\rightleftharpoons 0.165\ CaCO_3 + 3.17\ SiO_2 + 1.5\ Al_2O_3 + H_2O$	−4.0	−6.4
(5-6) $2\ NaAlSi_3O_8 + 2\ H_2O + CO_2$ $\rightleftharpoons Al_2Si_2O_5(OH)_4 + Na_2CO_3 + 4\ SiO_2$	2.16	9.54
(5-7) $NaAlSi_3O_8 + 0.3333\ H_2O + 0.445\ CO_2$ $\rightleftharpoons 0.3333$ Na-B $+ 0.445\ Na_2CO_2 + 1.9434\ SiO_2 + 0.00095\ O_2$	0.5	2.6
(5-8) $2\ NaAlSi_3O_8 + CO_2 \rightleftharpoons Na_2CO_3 + 6\ SiO_2 + Al_2O_3$	−2.4	0
(5-9) Na-B $+ 0.165\ CO_2 + 2\ H_2O + 0.0025\ O_2$ $\rightleftharpoons 1.5\ Al_2Si_2O_5(OH)_4 + 0.165\ Na_2CO_3 + 0.17\ SiO_2$	1.6	6.3
(5-10) Na-B $+ 0.165\ CO_2 + 0.0025\ O_2$ $\rightleftharpoons 0.165\ Na_2CO_3 + 3.17\ SiO_2 + 1.5\ Al_2O_3 + H_2O$	−5.2	−7.9

[a] All reactants and products are solids except for O_2, H_2O, and CO_2, which are gases. Abbreviations: Ca-B = Ca-beidellite = $Ca_{0.165}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$; Na-B = Na-beidellite = $Na_{0.33}Al_{2.17} \times (Al_{0.83}Si_{3.17})O_{10}(OH)_2$.

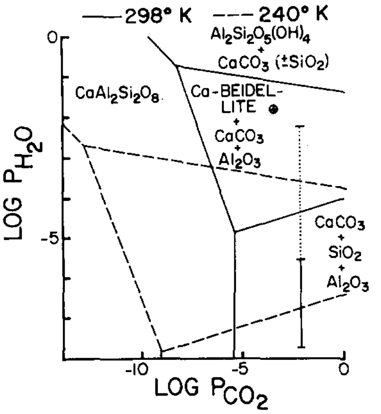

FIG. 12. Stability fields of anorthite and its decomposition products in equilibrium with gaseous H_2O and CO_2. (O_2 has negligible influence on these stability fields.) Formula for Ca–beidellite is given in Table V. Symbols are same as in Fig. 1.

temperature, however, Ca-beidellite should become more resistant to decomposition so that, at 240°K, Ca-beidellite should be stable on Mars, except in the driest environments (Fig. 12).

By methods used in previous sections, it can be shown that Ca-beidellite should be a stable weathering product of anorthite in liquid water at 273°K. Once removed from the aqueous environment, though, Ca-beidellite should decompose unless the temperature was drastically reduced to the range which currently characterizes the Martian surface. The survival of metastable Ca-beidellite on Mars would depend on both the temperature of its environment and the rate of its decomposition so that Ca-beidellite may be a stable phase in Martian regions having favorably low temperatures and favorably high water vapor abundances.

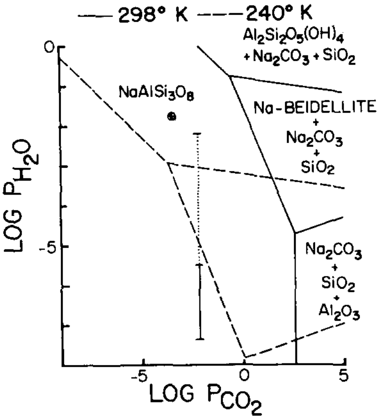

FIG. 13. Stability fields of albite and its decomposition products in equilibrium with gaseous H_2O and CO_2. (O_2 has negligible influence on these stability fields.) Formula for Na-beidellite is given in Table V. Symbols are same as in Fig. 1.

Albite. The pertinent reactions involving albite are given in Table V and Fig. 13. The most notable feature of Fig. 13 is that albite should be stable with respect to gas–solid weathering on both Earth and Mars. With decreasing temperature, Na-beidellite should become stable, but only within a very restricted range of water vapor abundance. Consequently, Na-beidellite probably should not be an important mineral among Martian weathering products. Under present conditions, albite can be considered stable on Mars.

Using reactions of the type given in Table V, it can be shown that K-feldspar should behave in essentially the same manner as albite. Specifically, K-feldspar should not decompose by gas–solid weathering on Mars but should persist as a stable phase in the absence of liquid water. K-Beidellite can only exist metastably and if formed originally by the intervention of liquid water.

The differences between the gas–solid weathering behavior of plagioclase and alkali feldspars may be important on Mars. The stability fields in Figs. 12 and 13 indicate that resistance to gas–solid decomposition should increase with increasing concentration of Na (or K) in the feldspar. As a result, the albite content of plagioclase in Martian parent rocks should determine the susceptibility of the plagioclase to weathering. Anorthite-rich plagioclase should weather easily while anorthite-poor plagioclase may not weather at all without the intervention of liquid water. In the

TABLE VI

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES IN THE SYSTEM $FeS-O_2-H_2O-CO_2$[a]

Reaction	Log K (298°K)	Log K (240°K)
(6-1) $FeS + 2\ O_2 \rightleftharpoons FeSO_4$	127	162
(6-2) $FeS + 2\ O_2 + H_2O \rightleftharpoons FeSO_4 \cdot H_2O$	131	169
(6-3) $FeSO_4 + H_2O \rightleftharpoons FeSO_4 \cdot H_2O$	3.3	6.6
(6-4) $FeS + 2\ O_2 + 7\ H_2O \rightleftharpoons FeSO_4 \cdot 7\ H_2O$	141	192
(6-5) $FeSO_4 \cdot H_2O + 6\ H_2O \rightleftharpoons FeSO_4 \cdot 7\ H_2O$	10.3	23.8
(6-6) $3\ FeS + 2\ O_2 \rightleftharpoons Fe_3O_4 + 3\ S$	125	160
(6-7) $4\ FeS + 3\ O_2 \rightleftharpoons 2\ Fe_2O_3 + 4\ S$	189	242

[a] All reactants and products are solids except for O_2, H_2O, and CO_2, which are gases.

extreme case, anorthite-rich plagioclase crystals would weather preferentially, thereby depleting the Martian weathering products in Na (and probably K). Depending on the prevailing conditions of temperature and water vapor abundance, the resultant assemblage could be Ca-beidellite + calcite + corundum or calcite + quartz + corundum. In either case, a separate residue of Na-rich (and comparatively K-rich) plagioclase might be formed.

4. Magnetite

On Earth, magnetite commonly alters to hematite and goethite (Heinrich, 1965). These and other important reactions involving magnetite have been given in Tables II and III and in Figs. 3, 4, and 8. These results confirm that magnetite should be readily oxidized to hematite on both Earth and Mars. Magnetite can exist metastably on Mars only as a reaction intermediate enroute to equilibration (Figs. 3, 4, and 8) or as a primary igneous mineral which has been kinetically inhibited in its weathering reactions. In either case, the stable gas-solid decomposition product of magnetite should be hematite rather than goethite (e.g. Fig. 3).

The metastable occurrence of magnetite at the Martian surface would be an important indication that thermodynamic equilibration of the weathering products has not been achieved (see also Section IVC).

5. Troilite and Pyrrhotite

The common sink for sulfur in crystalline mafic igneous rocks is pyrrhotite, $Fe_{1-x}S$ (Deer *et al.*, 1966). For the investigation of gas-solid weathering reactions, however, it is more convenient to use troilite, FeS, as the representative primary sulfide mineral. Accordingly, Table VI and Fig. 14 have been compiled for FeS rather than $Fe_{1-x}S$. The analogous reactions for pyrrhotite should be very similar except that native sulfur, S, should also be a decomposition product.[3] For example, reaction (6-1) in Table VI would, for pyrrhotite, be

$$Fe_{1-x}S + 2(1-x)O_2 \rightleftharpoons (1-x)FeSO_4 + xS. \quad (8)$$

Thus, analogous gas-solid decomposition reactions should exist for both troilite and pyrrhotite, but with elemental sulfur as an additional reaction product from pyrrhotite.

Figure 14 shows that the oxidation of iron(II) sulfide to iron(II) sulfate should occur spontaneously by gas-solid reaction on both Earth and Mars. An important

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[3] Complete oxidation of excess S^{2-} to SO_4^{2-} is thermodynamically favorable on Mars but would create a charge imbalance in the absence of available cations. Therefore, native S can only be a metastable reaction product [e.g., reaction (8)] and is used only to satisfy constraints of gas-solid reactions.

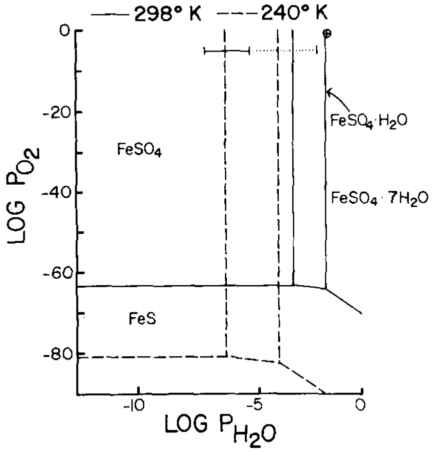

FIG. 14. Stability fields of troilite and its decomposition products in equilibrium with gaseous O_2 and H_2O. (CO_2 does not influence these stability fields.) The stability fields of pyrrhotite, $Fe_{1-x}S$, and its decomposition products should be similar to those for troilite but with native sulfur, S, as an additional gas–solid weathering product. Symbols are same as in Fig. 1.

competitive reaction, the oxidation of FeS to Fe_2O_3 [reaction (6-7) in Table VI], possesses a reaction boundary which lies only slightly higher than that for the FeS/$FeSO_4$ reaction in Fig. 14. If liquid water intervened, the FeS/Fe_2O_3 reaction would undoubtedly predominate since the soluble sulfide and sulfate ions could be removed by solution. In strict gas–solid weathering, however, the FeS/$FeSO_4$ reaction should prevail since the simultaneous hydration of $FeSO_4$ to $FeSO_4 \cdot H_2O$ [reaction (6-2) in Table VI] should produce a reaction boundary which lies below that of the FeS/Fe_2O_3 reaction in terms of required P_{O_2} and P_{H_2O}. Accordingly, the FeS/Fe_2O_3 reaction should compete most effectively in the Martian environments where liquid water is available to remove sulfide and sulfate ions from reaction sites.

In summary, the gas–solid weathering of iron sulfide on Mars should produce $FeSO_4$ ($\pm$S) in drier regions and $FeSO_4 \cdot H_2O$ ($\pm$S) in those regions where water vapor is most abundant. If liquid water later intervened, the dissolved sulfate would free Fe^{2+} which should be readily oxidized to Fe^{3+} and precipitated, ultimately, as FeO(OH) or Fe_2O_3. The sulfate ion would then be free to precipitate with other available cations.

6. *Apatite*

Apatite serves as the major sink for P and, to a lesser extent, as the sink for Cl and F in crystalline mafic rocks (Deer *et al.*, 1966). Thus, the decomposition of apatite should be the major source of P, Cl, and F during chemical weathering of mafic rocks. Since none of the components of apatite are oxidizable in geologic environments, hydration and carbonation reactions must control the weathering of apatite. Taking hydroxylapatite as an example, a representative gas–solid decomposition reaction might be

$$Ca_5(PO_4)_3OH + CO_2 \rightleftharpoons Ca_3(PO_4)_2 + CaHPO_4 + CaCO_3, \quad (9)$$

where all reactants and products are solids except for CO_2, which is a gas. At 298°K, the equilibrium constant for reaction (9) is calculated to be $\log K = -1181$, implying that hydroxylapatite should be very stable with respect to decomposition by gas–solid reaction with CO_2. With the participation of water vapor, an alternative reaction would be

$$Ca_5(PO_4)_3OH + H_2O + 2CO_2 \rightleftharpoons 3CaHPO_4 + 2CaCO_3, \quad (10)$$

for which $\log K = -1188$ at 298°K. Thus, hydroxylapatite (and, presumably, chlorapatite and fluorapatite) should be stable in the present Martian environment. Even the presence of liquid water should not significantly improve the favorability of reactions (9) and (10) at low temperatures unless the apatite is first dissolved.

Under natural conditions, the extraction of apatite from rocks should proceed by simple solution if liquid water is available and, as shown above, the reaction of apatite to form other compounds should not occur unless the apatite is first taken into solution.

It may be concluded that apatite should be stable on Mars unless in contact with liquid water.

7. *Glass*

Residual glass is ordinarily a minor component of extrusive mafic igneous rocks and a major component of pyroclastic volcanic rocks (Carmichael *et al.*, 1974). Thus, the chemical weathering of the possible glass fraction of Martian rocks deserves some consideration.

In the case of basalt, fractional crystallization typically produces residual glasses which are enriched in Si, Al, Na, K, and Fe relative to the crystalline fraction (Bowen, 1928; Carmichael *et al.*, 1974). These residual volcanic glasses are also enriched in S, Cl, and F (Ross, 1964). Sideromelane (basaltic glass) in contact with liquid water characteristically alters by hydration to palagonite (Moore, 1966; Hay and Iijima, 1968). However, the thermodynamic properties of sideromelane and palagonite are not sufficiently well known to permit quantitative evaluation of the pertinent reactions by the methods employed in preceding sections.

It must suffice to say that gas–solid weathering of basaltic glass on Mars might contribute Si, Al, Na, K, Fe, Cl, and F to the weathering products. The resultant mineral assemblage cannot be easily predicted although results from previous sections would suggest that oxides, carbonates, and sulfates (±chlorides and fluorides) might predominate.

B. RATES AND MECHANISMS OF GAS–SOLID REACTIONS

The preceding discussions have addressed the question of chemical weathering on Mars strictly in terms of thermodynamic equilibrium and, consequently, have predicted the *ultimate* products of chemical weathering on Mars. In this section, other important factors related to reaction kinetics and the formation of metastable intermediate weathering products are briefly discussed. These factors are treated in the two general categories of (1) gas–solid reaction rates, and (2) mineral surface structural effects. Neither category is discussed in a comprehensive fashion since each embraces subject material which is far beyond the scope of this paper. The following discussions are only intended to enumerate certain factors which may modify the conclusions reached in Section IIIA on purely thermodynamic grounds.

1. *Relative Rates of Gas–Solid Reactions*

It is intuitively obvious that reactions involving solids should be slow when temperatures are low and liquid media are absent. If strict gas–solid reactions are assumed, the question of reaction rate reduces to that of whether one gas–solid reaction is faster or slower than another.

For gas–solid oxidation reactions occurring at 100–350°K, Anderson and Gallagher (1961) report an empirical rate law of

$$q = (2.3/p) \log (kp + \log t) + mt^{1/2}, \quad (11)$$

where q is the amount of solid which reacts in time t and k, p, and m are constants. As described by (11), the initial stage of reaction (small values of t) obeys a logarithmic rate law while later stages (large values of t) involve diffusion of the reactant gas into the bulk solid at a rate proportional to $t^{1/2}$.

Diffusion of gas through a solid can be described by Fick's law (Le Claire, 1976) as

$$J_N = -D \operatorname{grad} N, \quad (12)$$

where J_N is the flux of gas molecules, N, through the solid and D is the diffusivity of gas N in the solid. Diffusivity varies with temperature, T, as

$$D = D_0 \exp(-E/k_B T), \quad (13)$$

where E is the activation energy of diffusion and k_B is Boltzmann's constant. Therefore, $D \ll D_0$ at the low temperatures which characterize the present Martian environment. Since D_0 increases as the molecular diameter of the gas decreases (Crank and Park, 1968, pp. 50–54) but also varies inversely with molecular dipole moment, these two effects may tend to balance each other such that D_0 is approximately the same for H_2O, O_2, and CO_2 diffusing through the same mineral.

For bulk diffusion of a gas into a solid mineral grain, (12) shows that J_N should be driven by grad N, which, in turn, should be determined by the concentration of the gas at the surface of the mineral. These surface concentrations can be approximated at low pressures by the Langmuir adsorption theory (Adamson, 1967) as

$$\Theta_i = (b_iP_i)/(1 + \sum_j b_jP_j), \qquad (14)$$

where Θ_i is the fraction of the total mineral grain surface which is covered by gas i having an adsorption coefficient of b_i and a partial pressure of P_i. Therefore, J_i should increase as Θ_i increases. In the Martian atmosphere, $P_{CO_2} \gg P_{O_2} > P_{H_2O}$ (Table I). However, chemisorption effects (Adamson, 1967; De Vienne, 1967) and relative boiling points of the atmospheric gases (Weast, 1975) indicate that $b_{H_2O} \gg b_{CO_2} > b_{O_2}$. Thus, it may be suspected that at the low temperatures characteristic of the Martian surface, H_2O should be the gas which is preferentially adsorbed on mineral surfaces. In fact, Fanale and Cannon (1971, 1974) have observed experimentally that $H_2O > CO_2$ in adsorption affinity on pulverized basalt.

From the preceding qualitative considerations it may be concluded that the relative rates of gas–solid weathering reactions, if controlled by adsorption effects, should be approximately hydration > carbonation ≥ oxidation in the present Martian environment. If diffusion of gas into the solid controls reaction rates, the relative order may be oxidation ≥ hydration > carbonation.

2. Structural Control by Mineral Surfaces

When liquid media are absent, familiar solution effects cannot be invoked to explain structural rearrangements during the chemical weathering of a mineral crystal. Instead, the energetically most favorable and convenient crystal structure rearrangements should predominate when more than one gas–solid reaction pathway is possible.

While the surface chemistry of minerals has yet to be adequately investigated, some attention has been given to surface effects involved in the weathering of magnetite (Mackay, 1961; Gazzarini and Lanzavecchia, 1969) and feldspars (DeVore, 1959; Garrels and Howard, 1959; Fripiat, 1964). Feldspar surfaces resemble the tetrahedral layers of phyllosilicates and tend to nucleate phyllosilicate decomposition products during alteration (DeVore, 1959). This observation agrees with the previous conclusion (Section IIIA) that Ca-beidellite should be a thermodynamically favorable gas–solid decomposition product of anorthite.

Similar surface structural effects apparently control, in part, the alteration of pyroxenes and amphiboles since topotaxial overgrowths of nontronite on hedenbergite (Eggleton, 1975) and montmorillonite on hornblende (Cole and Lanucki, 1976) are known to occur. The formation of these clay minerals presumably involves condensed films of liquid water on the surfaces of the primary mafic minerals. If relatively thick layers of adsorbed water vapor can perform the same function, then clay minerals may be more important products of gas–solid weathering of mafic inosilicates than thermodynamic considerations alone (Section IIIA) would predict. However, adsorbed water vapor on Mars may typically be less than about 1.5 molecular layers thick (Anderson *et al.*, 1967). In any case, subsequent decomposition of the clays into oxides and carbonates (Section IV) must also be considered.

Alteration surfaces formed on weathered minerals commonly act as barriers to further weathering. For example, goethite which, on thermodynamic grounds, should be expected to totally dehydrate in dry environments (Fig. 3) is a common metastable phase on Earth when protected by dehydration rinds of hematite. Metastable goethite is abundant on Earth because its decomposition is kinetically inhibited, a fact which in no way negates the thermodynamic requirement that liquid water be available for its formation (Section IIIA).

It may be concluded that specific reaction mechanisms may, in some cases, favor the formation of weathering products which are unstable in the thermodynamic sense. Such metastable phases, if present on Mars, might be artifacts of known processes which operated in paleo-environments or unknown processes which operate in the present environment but, regardless of origin, must *ultimately* equilibrate with the present environment. Therefore, uncertainties in rates and mechanisms of weathering reactions should have no impact on the conclusions reached previously (Section IIIA) on *stable* Martian weathering products.

IV. SUMMARY OF ALTERATION PRODUCT STABILITIES

A. General Considerations

Chemical weathering on Mars should be governed by (i) the primary rock-forming minerals (and their relative abundances) which are available for weathering, (ii) the environment of weathering (including temperature, atmospheric composition, and the availability of water), and (iii) the reaction pathways which are followed. For a given assemblage of primary minerals, the stable phases produced by their decomposition will depend critically on the presence or absence of liquid water.

For the weathering of mafic igneous rock-forming minerals on Mars, the results of Section III have been summarized in Tables VII and VIII. As can be seen, the stable products of weathering are significantly different for the case of gas–solid weathering (Table VII) as opposed to the case of weathering in the presence of liquid water (Table VIII). In the former case, the stable phases are dominated by oxides and carbonates while, in the latter case, phyllosilicates are important phases among the weathering products.

It must be emphasized that the approach taken in this study was to examine the weathering reactions involving individual primary minerals. Admittedly, the possible stable weathering products should vary more widely when two primary minerals (e.g., pyroxene and plagioclase) are allowed to interact during weathering. However, for the case of gas–solid weathering, the most probable process in the present Martian environment, the absence of an aqueous medium should prevent effective chemical communication between two separate solid phases. Consequently, interactive gas–solid–solid reactions should not be important on Mars.

It also must be reiterated that thermodynamic equilibrium was assumed for all reactions examined in this study. However, many of the reactions listed in Tables II through VI (and IX) are not truly reversible without the aid of a liquid solvent/catalyst such as water. Kinetic inhibition of reactions by thermal, physical phase, or other constraints might produce metastable intermediate phases of importance, as discussed below.

B. Clay Minerals and Other Phyllosilicates

The presence of phyllosilicates (viz., montmorillonite) in high-altitude Martian

TABLE VII

STABLE DECOMPOSITION PRODUCTS OF SELECTED MINERALS WHICH HAVE REACHED THERMODYNAMIC EQUILIBRIUM WITH THE PRESENT MARTIAN ENVIRONMENT BY GAS–SOLID REACTIONS AT 240°K[a]

Primary rock-forming mineral	Stoichiometric proportions of weathering products at 240°K
Forsterite, Mg_2SiO_4	$2\ MgCO_3 + SiO_2$
Fayalite, Fe_2SiO_4	$Fe_2O_3 + SiO_2$
Diopside, $CaMgSi_2O_6$	$CaCO_3 + MgCO_3 + 2\ SiO_2$
Hedenbergite, $CaFeSi_2O_6$	$0.5\ Fe_2O_3 + CaCO_3 + 2\ SiO_2$
Augite, $(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$	$0.125\ Fe_2O_3 + 0.8\ CaCO_3 + 0.8\ MgCO_3 + 1.8\ SiO_2 + 0.1\ Al_2O_3$
Subcalcic ferroaugite, $(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$	$0.5\ Fe_2O_3 + 0.2\ CaCO_3 + 0.35\ MgCO_3 + 1.8\ SiO_2 + 0.1\ Al_2O_3$
Anorthite, $CaAl_2Si_2O_8$	$0.6309\ Ca_{0.165}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2 + 0.8959\ CaCO_3 + 0.05365\ Al_2O_3$
Albite, $NaAlSi_3O_8$	Stable (no reaction)
Microcline, $KAlSi_3O_8$	Stable (no reaction)
Magnetite, Fe_3O_4	$1.5\ Fe_2O_3$
Troilite, FeS	$FeSO_4$ (or, $FeSO_4 \cdot H_2O$)
Pyrrhotite, $Fe_{1-x}S$	$(1 - x)\ FeSO_4 + xS$ (or, $(1 - x) \times FeSO_4 \cdot H_2O + x\ S$)
Apatite, $Ca_5(PO_4)_3OH$	Stable (no reaction)

[a] Note that dolomite may replace calcite + magnesite as the most stable carbonate phase, depending on the reaction pathway which is followed (see Section IIIA).

atmospheric dust was suggested by Mariner 9 remote infrared spectral sensing (Hunt *et al.*, 1973). More importantly, the first quantitative chemical analyses of Martian surface materials obtained from the Viking lander spacecraft (Clark *et al.*, 1976) can apparently be explained by a mixture of nontronite + saponite + montmorillonite with minor amounts of other minerals added (Baird *et al.*, 1976).

While Huguenin (1974) has argued that clay minerals should be by-products of the ultraviolet radiation-catalyzed oxidation of Fe-bearing silicates on Mars, the results presented here have indicated that clay minerals should not be major products of gas–solid weathering in the present Martian environment. Assuming thermodynamic equilibrium, the stable products of gas–solid weathering of mafic igneous rocks should be dominated by oxides and carbonates (Table VII). Clay minerals should be major products only when liquid water is present (Table VIII).

The formation of montmorillonite-type clay minerals on Earth occurs in alkaline aqueous solutions (Ross and Hendricks, 1945; Krauskopf, 1967; Loughnan, 1969) and frequently on mafic minerals where surface reactions are dominant and the supply of liquid water is limited (Keller, 1964). Thermodynamic considerations (Section IIIA) apparently require similar conditions for the formation of montmorillonite-type minerals on Mars.

Geologically, alkaline solutions are formed by the hydrolysis of silicates (sometimes carbonates) which are left in contact with liquid water for extended periods of time (Krauskopf, 1967; Loughnan, 1969). For these conditions to occur on Mars would require either a surface environment which is significantly different from that which currently exists or a subsurface environment in which liquid water is a stable phase for geologically significant periods of time. Liquid water, possibly having its triple point lowered by dissolved salts (Malin, 1974), may be a transient phase in certain portions of the Martian regolith (Farmer, 1976). However, such water might be distinctly acidic as the result of the hydrolysis of dissolved atmospheric CO_2 (Table I). Acidic water should readily transform montmorillonite-type clays into kaolinite + oxides + carbonates (Keller, 1964). Adsorbed atmospheric water vapor should form layers on silicate surfaces which are no more than about 1.5 molecular layers thick (Anderson *et al.*, 1967). Therefore, the source of water which would behave, at least thermodynamically, as "liquid" remains an enigma.

It is of interest to inquire, however, as to whether clay minerals could exist stably at all on Mars. Table IX and Fig. 15 summarize the probable stabilities of various phyllosilicates in an atmosphere containing gaseous O_2, H_2O, and CO_2. It is readily apparent that the abundance of water vapor plays an essential role in stabilizing most clay minerals on Earth. On Mars, where the average water vapor abundance is three or four orders of magnitude less than on Earth, only kaolinite should be stable on Mars at 298°K (Fig. 15a).

It should be noted that the formulas assumed for the various clay minerals (those suggested by Ross and Hendricks, 1945; Table IX) allow only for structurally bonded water and not interlayer water. Interlayer water is a characteristic feature of clay minerals on Earth and probably contributes to their stability but, on Mars,

TABLE VIII

STABLE DECOMPOSITION PRODUCTS OF SELECTED MINERALS WHICH HAVE REACHED THERMODYNAMIC EQUILIBRIUM WITH LIQUID WATER CONTAINING DISSOLVED O_2 AND CO_2 AT 273°K[a]

Primary rock-forming mineral	Stoichiometric proportions of weathering products at 273°K
Forsterite, Mg_2SiO_4	$0.25\ Mg_3Si_4O_{10}(OH)_2 + 1.25\ MgCO_3$
Fayalite, Fe_2SiO_4	$2\ FeO(OH) + SiO_2$
Diopside, $CaMgSi_2O_6$	$0.3333\ Mg_3Si_4O_{10}(OH)_2 + CaCO_3 + 0.6668\ SiO_2$
Hedenbergite, $CaFeSi_2O_6$	$FeO(OH) + CaCO_3 + 2\ SiO_2$
Augite, $(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$	$0.2667\ Mg_3Si_4O_{10}(OH)_2 + 0.5\ FeO(OH) + 0.8\ CaCO_3 + 0.7332\ SiO_2 + 0.1\ Al_2O_3$
Subcalcic ferroaugite, $(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$	$0.1167\ Mg_3Si_4O_{10}(OH)_2 + FeO(OH) + 0.4\ CaCO_3 + 1.3332\ SiO_2 + 0.1\ Al_2O_3$
Anorthite, $CaAl_2Si_2O_8$	$0.6309\ Ca_{0.165}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2 + 0.8959\ CaCO_3 + 0.5365\ Al_2O_3$
Albite, $NaAlSi_3O_8$	$0.3333\ Na_{0.33}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2 + 0.445\ Na_2CO_3 + 1.9434\ SiO_2$
Microcline, $KAlSi_3O_8$	$0.3333\ K_{0.33}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2 + 0.445\ K_2CO_3 + 1.9434\ SiO_2$
Magnetite, Fe_3O_4	$3\ FeO(OH)$
Troilite, FeS	$FeO(OH) + S$
Pyrrhotite, $Fe_{1-x}S$	$(1 - x)\ FeO(OH) + S$
Apatite, $Ca_5(PO_4)_3OH$	$Ca_3(PO_4)_2$ (by dehydration following dissolution) $3\ CaHPO_4 + 2\ CaCO_3$ (by reaction with H_2O and CO_2)

[a] Note that silicate minerals are presumed to react directly with O_2, CO_2, and H_2O, rather than to hydrolyze first, thereby forming alkaline solutions.

TABLE IX

IMPORTANT CHEMICAL REACTIONS AT LOW TEMPERATURES AND PRESSURES INVOLVING THE DECOMPOSITION OF PHYLLOSILICATES IN AN ATMOSPHERE CONTAINING GASEOUS O_2, H_2O, AND CO_2[a]

Reaction	Log K (298°K)	Log K (240°K)
(9-1) montmorillonite + 0.165 CO_2 $\rightleftharpoons$ 0.11 talc + 0.165 $CaCO_3$ + 0.835 Al_2O_3 + 3.56 SiO_2 + 0.89 H_2O	−2.8	−4.6
(9-2) montmorillonite + 0.165 CO_2 + 0.67 H_2O $\rightleftharpoons$ 0.835 kaolinite + 0.165 $CaCO_3$ + 0.33 $MgCO_3$ + 2.33 SiO_2	1.3	4.2
(9-3) montmorillonite + 0.165 CO_2 + 0.78 H_2O $\rightleftharpoons$ 0.835 kaolinite + 0.11 talc + 0.165 $CaCO_3$ + 1.89 SiO_2	0.95	3.32
(9-4) montmorillonite + 0.4031 CO_2 $\rightleftharpoons$ 0.5567 Ca-B + 0.33 $MgCO_3$ + 2.235 SiO_2 + 0.07314 $CaCO_3$ + 0.4433 H_2O + 0.00154 O_2	0.28	0.42
(9-5) montmorillonite + 0.495 CO_2 $\rightleftharpoons$ 0.165 $CaCO_3$ + 0.835 Al_2O_3 + 0.33 $MgCO_3$ + 4 SiO_2 + H_2O	−2.5	−3.7
(9-6) saponite + 0.4125 CO_2 $\rightleftharpoons$ 0.9175 talc + 0.2475 $MgCO_3$ + 0.165 $CaCO_3$ + 0.165 Al_2O_3 + 0.0825 H_2O	7.54	10.0
(9-7) saponite + 3.165 CO_2 $\rightleftharpoons$ 3 $MgCO_3$ + 0.165 $CaCO_3$ + 3.67 SiO_2 + 0.165 Al_2O_3 + H_2O	10.4	17.6
(9-8) Ca-B + 0.165 CO_2 + 2 H_2O + 0.0025 O_2 $\rightleftharpoons$ 1.5 kaolinite + 0.165 $CaCO_3$ + 0.17 SiO_2	2.8	7.5
(9-9) Ca-B + 0.165 CO_2 + 0.0025 O_2 $\rightleftharpoons$ 0.165 $CaCO_3$ + 3.17 SiO_2 + 1.5 Al_2O_3 + H_2O	−4.0	−6.4
(9-10) Na-B + 0.165 CO_2 + 2 H_2O + 0.0025 O_2 $\rightleftharpoons$ 1.5 kaolinite + 0.165 Na_2CO_3 + 0.17 SiO_2	1.6	6.3
(9-11) Na-B + 0.165 CO_2 + 0.0025 O_2 $\rightleftharpoons$ 0.165 Na_2CO_3 + 3.17 SiO_2 + 1.5 Al_2O_3 + H_2O	−5.2	−7.9
(9-12) nontronite + 0.165 CO_2 $\rightleftharpoons$ Fe_2O_3 + 0.165 $CaCO_3$ + 3.67 SiO_2 + 0.165 Al_2O_3 + H_2O	7.1	9.6
(9-13) talc + 3 CO_2 $\rightleftharpoons$ 3 $MgCO_3$ + 4 SiO_2 + H_2O	3.15	8.33
(9-14) kaolinite + CO_2 $\rightleftharpoons$ no reaction	—	—

[a] All other reactants and products are solids. Abbreviations: montmorillonite = $Ca_{0.165}(Al_{1.67}Mg_{0.33}) \times Si_4O_{10}(OH)_2$; saponite = $Ca_{0.165}Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$; Ca-B = Ca-beidellite = $Ca_{0.165}Al_{2.17} \times (Al_{0.83}Si_{3.17})O_{10}(OH)_2$; Na-B = Na-beidellite = $Na_{0.33}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$; nontronite = $Ca_{0.165} \times Fe_2^{3+}(Al_{0.33}Si_{3.67})O_{10}(OH)_2$; kaolinite = $Al_2Si_2O_5(OH)_4$; talc = $Mg_3Si_4O_{10}(OH)_2$.

might be immobilized or removed by freezing (Anderson *et al.*, 1967) or pumped away by the thin, dry atmosphere. These considerations and the intrinsic variations in interlayer water contents of clay minerals (Ross and Hendricks, 1945) justify neglecting interlayer water from the thermodynamic stability calculations.

Nontronite and saponite are noteworthy in that they are apparently two of the least-stable clay minerals. Saponite should readily decompose into talc [reaction (9-6), Table IX] while nontronite should decompose into oxides and carbonates [reaction (9-12), Table IX]. Because these reactions are favored at high partial pressures of CO_2, and adsorbed CO_2 is known to effectively penetrate montmorillonite-type structures (Fripiat *et al.*, 1974), saponite and nontronite should be highly susceptible to gas–solid decomposition on Mars. Other predicted decomposition reactions (Table

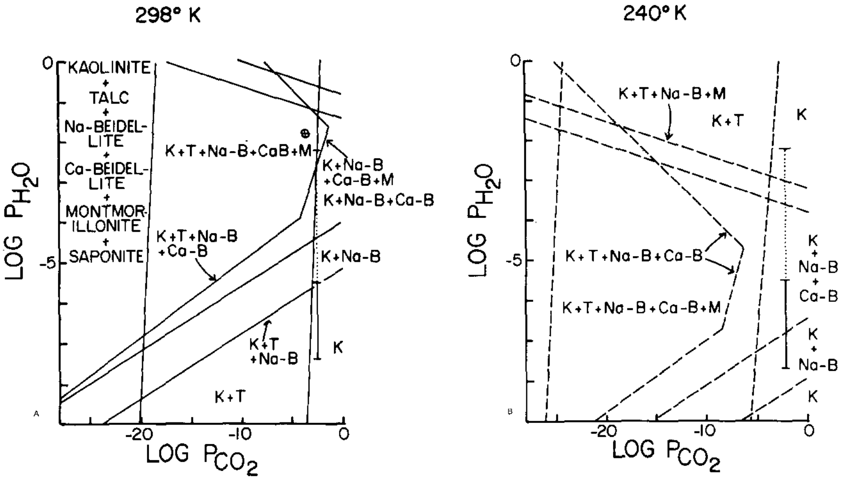

Fig. 15. (A) Stability fields of selected phyllosilicates in equilibrium with gaseous H_2O and CO_2 at 298°K. (O_2 does not appreciably influence these stability fields.) (B) Same stability fields as in (A) but at 240°K. Nontronite should not be stable in any of the fields shown here. Symbols are same as in Fig. 1. Abbreviations: K = kaolinite, T = talc, M = montmorillonite, Na-B = Na-beidellite, Ca-B = Ca-beidellite.

IX) may have similar importance on Mars since it is known that, on Earth, montmorillonite group minerals commonly weather to simpler clay minerals, especially kaolinite (Coleman, 1962; Altschuler *et al.*, 1963; Keller, 1964). The metastable existence of various montmorillonite-type minerals on Earth can be attributed to the greater abundance of H_2O and lesser abundance of CO_2 in the terrestrial environment relative to that of Mars. On Earth, the preferential adsorption of H_2O in the interlayer sites of clay structures (Barshad, 1960) inhibits the adsorption of CO_2 (Aylmore *et al.*, 1970) and, thereby, apparently prevents decomposition by reactions of the type given in Table IX. This blocking mechanism should be less effective on Mars in view of the much lower abundance of water vapor in the Martian atmosphere.

An important feature of Fig. 15B is that the stability fields of the various phyllosilicates expand with decreasing temperature. Specifically, kaolinite, Na-beidellite (and, by analogy, K-beidellite), and Ca-beidellite should be stable on Mars at 240°K, while only kaolinite should be stable at 298°K. As temperatures decrease further, more phyllosilicates should become stable.

The preceding considerations suggest that very few phyllosilicates should be thermodynamically stable on the surface of Mars. Clay minerals (or other possible intermediate weathering products) cannot be assumed stable on Mars on the basis of terrestrial analogy alone but must ultimately conform with thermodynamic constraints which seem to require their eventual decomposition. If major amounts of clay minerals currently exist on Mars, they can be metastable phases only and probably owe their existence to formation in an environment containing a greater abundance of water than is currently found at the surface. Highly specific reaction mechanisms of the type proposed by Huguenin (1973a,b, 1974) might favor the production of clays as *intermediate* weathering products but would not prevent their ultimate decomposition into simpler minerals.

C. OXIDES AND HYDROXIDES

One of the most important questions about Martian weathering regards the stability of goethite. Results presented here have shown that hematite, rather than goethite, should be the thermodynamically stable sink for Fe(III). Goethite should prevail only when the partial pressure of water vapor is $\geq 10^{-0.6}$ atm (see, for example, Fig. 3) or when liquid water is present (see, for example, Fig. 10A). These results agree with the experimental observations of Pollack *et al.* (1970a,b) which indicate that goethite should exist at the surface of Mars only if its dehydration to hematite is kinetically inhibited. In any case, it is not likely that significant amounts of goethite can be currently forming on the Martian surface.

Other oxides which should be stable at the Martian surface are given in Table VII. Magnetite is conspicuously absent from this list since it should readily oxidize to hematite (Section III) under present conditions. However, Hargraves *et al.* (1976a,b) report that surface fines at the Viking 1 and 2 landing sites contain 3–7% (by weight) of a strongly magnetic material. If this mineral is magnetite then nonequilibration of the Martian weathering products is implied. If the mineral is maghemite (γ-Fe_2O_3) which has not inverted to hematite (α-Fe_2O_3) because of kinetic inhibitions (Mackay, 1961), then thermodynamic equilibration of the bulk weathering products may be approximately complete. The resolution of this dilemma is of great importance to the evaluation of mineralogical models for Martian surface materials.

D. CARBONATES

As seen previously, and as summarized in Tables VII and VIII, $CaCO_3$ and $MgCO_3$ should be stable weathering products from all Ca- and Mg-bearing primary minerals on Mars. As discussed in Section III, direct gas–solid decomposition of pyroxenes should favor $CaMg(CO_3)_2$, rather than $CaCO_3 + MgCO_3$, as the stable carbonate product. Since these two alternative cases cannot be distinguished by chemical measurements alone, they can be considered equivalent in the absence of additional mineralogical information.

Na_2CO_3 and K_2CO_3, from the decomposition of alkali feldspars, should not be important phases on Mars unless liquid water was available for their formation.

$FeCO_3$ may form from Fe-bearing primary minerals but, upon equilibration with the Martian atmosphere, should decompose into Fe_2O_3. The presence of $FeCO_3$ among Martian weathering products would indicate a nonequilibrium mineral assemblage.

E. SULFATES

Assuming iron sulfide (FeS or $Fe_{1-x}S$) to be the primary sulfur-bearing mineral, strict gas–solid weathering on Mars should yield szomolnokite, $FeSO_4$ or $FeSO_4 \cdot H_2O$, as the stable decomposition product. As discussed in Section III, however, the oxidation of the primary sulfide to $Fe_2O_3 + S$ should compete effectively with the sulfate-forming reaction. An interesting feature of Martian weathering products might result if these two reactions occurred in complementary fashion.

If the primary iron sulfide was first oxidized to $FeSO_4$ and then dissolved by liquid water, the Fe^{2+} ion should be readily oxidized to Fe^{3+}, which, upon evaporation of the water, would form $Fe_2(SO_4)_3$ and Fe_2O_3 or FeO(OH). The iron oxide byproduct would be required by stoichiometry. If, however, other dissolved cations were present in the water which dissolved the initial $FeSO_4$, the products of evaporation might be iron oxide and one or more new sulfate compounds. The most likely candidates would be sulfates of calcium or magnesium since dissolved $CaCO_3$ and $MgCO_3$ should provide ample sources of Ca^{2+} and Mg^{2+}.

The solubility products of $CaCO_3$ and $MgCO_3$ at 285–290°K (Weast, 1975) are 9.9×10^{-9} and 2.6×10^{-5}, respectively.

Thus, liquid water equilibrated with these two phases should contain 9.9×10^{-5} mole Ca^{2+}/liter ($= 9.9 \times 10^{-5}\,M$ Ca^{2+}) and $5.1 \times 10^{-3}\,M$ Mg^{2+}. Using data from Weast (1975), the solubility products of $CaSO_4$ and $MgSO_4$ are calculated to be 2.4×10^{-4} and 4.7, respectively. Thus, if the postulated liquid water is saturated with both $CaCO_3$ and $MgCO_3$, the concentrations of sulfate ion required for precipitation are $2.4\,M$ $[= (2.4 \times 10^{-4})/(9.9 \times 10^{-5})]$ for $CaSO_4$ and $920\,M$ $[= (4.7)/(5.1 \times 10^{-3})]$ for $MgSO_4$. For the case of liquid water saturated with $CaMg(CO_3)_2$ (solubility product $= 3.7 \times 10^{-11}$), the corresponding sulfate ion concentrations required for precipitation are $0.14\,M$ for $CaSO_4$ and $2800\,M$ for $MgSO_4$. In either case, $CaSO_4$ should be the first to precipitate, followed by $MgSO_4$ only in the presence of excess sulfate ion and at the very last stages of evaporation of the liquid water.

Although gypsum, $CaSO_4 \cdot 2H_2O$, might form during the precipitation sequence outlined above, it should decompose into anhydrite, $CaSO_4$, upon equilibration with the Martian atmosphere, as illustrated in Fig. 16. Dehydration should be complete since the stabilization of bassanite, $CaSO_4 \cdot \frac{1}{2}H_2O$,

$$CaSO_4 + \tfrac{1}{2}H_2O \rightleftharpoons CaSO_4 \cdot \tfrac{1}{2}H_2O, \qquad \log K = -0.57 \text{ at } 298°K, \qquad (15)$$

requires the presence of liquid water or a water vapor pressure greater than 10 atm. The existence of either gypsum or bassanite on Mars (as metastable phases) would probably imply an origin involving liquid water.

If the preceding scheme is applicable to Mars, then the upward migration of any Martian groundwater containing dissolved sulfates should progressively enrich the surface in total sulfur, possibly as $CaSO_4$ or $MgSO_4$. From solubility considerations, the migration of $MgSO_4$ toward the surface should be favored over that of $CaSO_4$, implying that the cementing agent in Martian duricrust (Clark *et al.*, 1976; Baird *et al.*, 1976) could be $MgSO_4$.

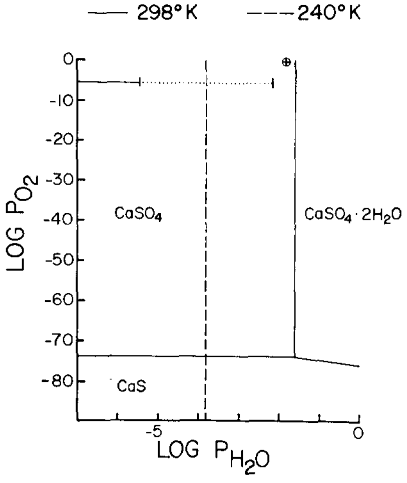

FIG. 16. Stability fields of oldhamite and its decomposition products in equilibrium with gaseous O_2 and H_2O. (CO_2 does not influence these stability fields.) Symbols are same as in Fig. 1.

F. HALIDES

If it is assumed that halide-bearing apatite is the only source of halides among the primary rock-forming minerals on Mars, then no chlorides should be among the products of gas–solid weathering since it has been shown (Section III) that apatite should be stable with respect to decomposition in the absence of liquid water. Accordingly, the existence of halide salts among the present Martian weathering products would imply an origin involving either the condensation of volcanic gases or the intervention of liquid water, or both.

V. CONCLUSIONS

This paper has applied chemical thermodynamic reasoning to the question of chemical weathering on Mars in an attempt to define limits to the mineral assemblages which can be expected among Martian weathering products. Important differences in weathering reactions based on the pres-

TABLE X

Values of ΔH°_{298} and ΔG°_{298} Used in Thermochemical Calculations[a]

Mineral name	Chemical formula	$-\Delta H^\circ_{298}$	$-\Delta G^\circ_{298}$	Source
Oxides				
Corundum	Al_2O_3	400.40	378.08	(1)
α-Quartz	SiO_2	217.65	204.65	(1)
Magnetite	Fe_3O_4	267.40	243.09	(1)
Hematite	Fe_2O_3	197.30	177.73	(1)
	O_2 (gas)	0	0	(1)
	H_2O (gas)	57.80	54.64	(1)
	H_2O (liquid)	68.32	56.69	(1)
	CO_2 (gas)	94.05	94.26	(1)
Hydroxides				
Goethite	$FeO(OH)$	133.75	116.6	(1), (5)
	$Fe(OH)_2$ (aq)	—	118.5	(3)
	$Fe(OH)_3$ (aq)	—	166.5	(3)
Brucite	$Mg(OH)_2$	221.20	199.46	(1)
	$Mg(OH)_2$ (aq)	—	202.12	(3)
	$Ca(OH)_2$ (aq)	—	214.22	(3)
	$NaOH$ (aq)	—	102.6	(3)
	$Al(OH)_3$ (aq)	—	274.2	(3)
	$Si(OH)_4$ (aq)	—	318.6	(3)
Carbonates				
Calcite	$CaCO_3$	288.59	269.91	(1)
Magnesite	$MgCO_3$	266.08	246.11	(1)
Dolomite	$CaMg(CO_3)_2$	557.61	518.73	(1)
Siderite	$FeCO_3$	177.81	161.03	(1)
	Na_2CO_3	270.3	250.4	(2)
Sulfides				
Troilite	FeS	24.13	24.22	(1)
Oldhamite	CaS	115.3	114.1	(2)
Sulfates and phosphates				
Anhydrite	$CaSO_4$	342.42	315.56	(2)
Bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$	376.47	343.02	(2)
Gypsum	$CaSO_4 \cdot 2H_2O$	483.06	429.19	(2)
	$FeSO_4$	220.5	198.3	(4)
Szomolnokite	$FeSO_4 \cdot H_2O$	296.8	257.5	(6)
Melanterite	$FeSO_4 \cdot 7H_2O$	719.98	599.44	(6)
Hydroxylapatite	$Ca_5(PO_4)_3OH$	3215.00	3123.50	(1)
Whitlockite	$Ca_3(PO_4)_2$	986.20	932.78	(1)
	$CaHPO_4$	435.2	401.5	(2)
Orthosilicates				
Forsterite	Mg_2SiO_4	520.37	491.94	(1)
Fayalite	Fe_2SiO_4	353.54	329.67	(1)
Ca-olivine	Ca_2SiO_4	553.97	526.07	(1)

TABLE X—*Continued*

Mineral name	Chemical formula	$-\Delta H^\circ_{298}$	$-\Delta G^\circ_{298}$	Source
Inosilicates				
Ca, Al-pyroxene	$CaAl_2SiO_6$	786.98	745.13	(1)
Diopside	$CaMgSi_2O_6$	767.39	725.78	(1)
Hedenbergite	$CaFeSi_2O_6$	682.59	643.23	(*)
Subcalcic ferroaugite	$(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$	684.26	644.42	(*)
Augite	$(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$	733.49	692.61	(*)
Wollastonite	$CaSiO_3$	390.64	370.31	(1)
Tektosilicates				
Anorthite	$CaAl_2Si_2O_8$	1009.30	955.63	(1)
High-albite	$NaAlSi_3O_8$	934.51	882.69	(1)
Phyllosilicates				
Kaolinite	$Al_2Si_2O_5(OH)_4$	979.46	902.87	(1)
Talc	$Mg_3Si_4O_{10}(OH)_2$	1415.21	1324.49	(1)
Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$	1145.2	1072.3	(*)
Saponite	$Ca_{0.165}Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$	1430.1	1338.4	(*)
Ca-beidellite	$Ca_{0.165}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$	1394.3	1304.9	(*)
Na-beidellite	$Na_{0.33}Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$	1392.7	1303.4	(*)
Montmorillonite	$Ca_{0.165}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$	1358.5	1271.4	(*)
Nontronite	$Ca_{0.165}Fe_2^{3+}(Al_{0.33}Si_{3.67})O_{10}(OH)_2$	1138.1	1065.1	(*)

[a] Estimated values (marked by *) are discussed in the text. Sources of data are (1) Robie and Waldbaum (1968), (2) Weast (1975), (3) Nriagu (1975), (4) Bent (1965), (5) Krauskopf (1967), and (6) Karapet'yants and Karapet'yants (1970). Units ase kilocalories/formula weight.

ence or absence of liquid water have been emphasized. Thermodynamic criteria of the type presented here are necessary for the full evaluation of the importance of various reaction mechanisms which have been proposed for weathering processes at the Martian surface.

For gas–solid weathering of mafic igneous rocks at the Martian surface it may be concluded that, upon attainment of thermodynamic equilibrium,

(a) oxides and carbonates should dominate the mineral assemblage of weathering products;

(b) hematite, rather than goethite, should be the stable mineral form of Fe(III);

(c) $FeSO_4$ or $FeSO_4 \cdot H_2O$ could be the stable weathering product of iron sulfides in the absence of liquid water [Fe_2O_3 or $FeO(OH) + S$ or, ultimately, SO_4^{2-}, should form when liquid water controls weathering];

(d) kaolinite is apparently the only clay mineral which should be thermodynamically stable over all ranges of temperature and water vapor abundance at the Martian surface (other clay minerals may exist metastably if formed in comparatively moist environments);

(e) halide salts should exist at the Martian surface only if formed by the direct condensation of volcanic gases or the weathering of halide-bearing apatite in liquid water; and

(f) the presence or absence of magnetite (and, to a lesser extent, siderite) in Martian surface fines may serve as an important indicator of the degree to which Martian weathering products have achieved thermodynamic equilibrium with the present environment.

These results are not presented as decisive answers to the many questions regarding the mineralogy of Martian surface materials. Instead, it is hoped merely that they will stimulate further detailed studies, both theoretical and experimental, of Martian weathering processes.

APPENDIX: THERMOCHEMICAL DATA FOR MINERALS

Table X lists the values of ΔH°_{298} and ΔG°_{298} for the participant phases in the chemical reactions examined in this study. The sources of these data are given in the last column.

For several minerals of interest in this study, sufficient thermochemical data were not available in the literature so that estimates of these properties were required. For montmorillonite, saponite, beidellite, and nontronite, the method of Nriagu (1975) was used to obtain ΔG°_{298}. This method gives results for kaolinite and Aberdeen montmorillonite which agree to within 0.5% with those obtained independently for the same minerals. For each montmorillonite-type mineral, ΔH°_{298} was obtained by multiplying the appropriate value of ΔG°_{298} by 1.0685, the value of $\Delta H^\circ_{298}/\Delta G^\circ_{298}$ for both talc and muscovite as reported by Pobie and Waldbaum (1968).

For other minerals, the methods used in estimating thermochemical properties involve proportional scaling using known values for analogous compounds. This general approach is similar to techniques described by Lewis and Randall (1961, pp. 515–531) and is given below in more detail for each mineral so treated.

Hedenbergite, $CaFeSi_2O_6$. From a stoichiometric standpoint, hedenbergite can be considered to form as 0.5 Ca_2SiO_4 + 0.5 Fe_2SiO_4 + SiO_2 = $CaFeSi_2O_6$. Accordingly, ΔH and ΔG were obtained by linear combination, in the same proportions, of the appropriate values for Ca-olivine, fayalite, and α-quartz. The same procedure applied to diopside, $CaMgSi_2O_6$, gave values of ΔH and ΔG which were 1.63801 and 1.66450% lower, respectively, than the values given for diopside by Robie and Waldbaum (1968). Assuming the same directional error in the values for hedenbergite, ΔH and ΔG for hedenbergite were multiplied by 1.06653 and 1.01693, respectively, to correct this error. The resultant values exhibited a ratio of $\Delta H/\Delta G = 1.061$, which agrees well with 1.057 for diopside.

Augite, $(Ca_{0.40}Mg_{0.40}Fe_{0.25})_2(Si_{0.90}Al_{0.10})_2O_6$. The same procedure used for hedenbergite was applied to augite as the linear combination 0.10 $CaAl_2SiO_6$ + 0.35 Ca_2SiO_4 + 0.40 Mg_2SiO_4 + 0.25 Fe_2SiO_4 + 0.70 SiO_2. The final results gave $\Delta H/\Delta G = 1.059$, which agrees very well with 1.057 (Robie and Waldbaum, 1968) for diopside.

Subcalcic ferroaugite, $(Ca_{0.20}Mg_{0.35}Fe_{0.50})_2(Si_{0.90}Al_{0.10})_2O_6$. The procedure used for hedenbergite was applied to subcalcic ferroaugite as the linear combination 0.10 $CaAl_2SiO_6$ + 0.15 Ca_2SiO_4 + 0.35 Mg_2SiO_4 + 0.50 Fe_2SiO_4 + 0.70 SiO_2. The final results gave $\Delta H/\Delta G = 1.062$, which agrees well with 1.057 (Robie and Waldbaum, 1968) for diopside.

Minnesotaite, $Fe_3Si_4O_{10}(OH)_2$. The method of Nriagu (1975) was applied to talc, $Mg_3Si_4O_{10}(OH)_2$, and gave a value of ΔG which was 0.5051% lower than that given for talc by Robie and Waldbaum (1968). Accordingly, the value of ΔG obtained for minnesotaite by the Nriagu (1975) method was multiplied by the correction factor 1.00508, which was derived from the talc results. To estimate ΔH for minnesotaite, the corrected value of ΔG was multiplied by 1.06849, the ratio of $\Delta H/\Delta G$ for talc as given by Robie and Waldbaum (1968).

The uncertainties in these estimated values are probably similar in magnitude to those of the published values which were used in their computation. These uncertainties should cause only minor shifts in the possible positions of the reaction boundaries in the log–log partial pressure diagrams given as Figs. 1–16. The uncertainty in the position of a particular reaction boundary should probably be no greater than 10–30% of the given position and should not affect the major conclusions of this study.

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