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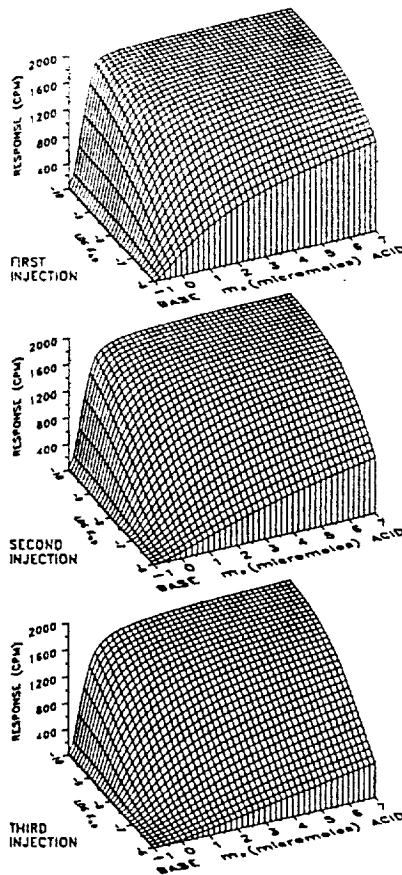
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THE pH OF MARS. R. C. Plumb^{1,2}, J. L. Bishop², and J. O. Edwards², ¹Worcester Polytechnic Institute, Worcester MA 01609, USA, ²Brown University, Providence RI 02912, USA.

The Viking Labeled Release (LR) experiments provided data that can be used to determine the acid-base characteristics of the regolith. Constraints on the acid-base properties and redox potentials of the martian surface material would provide additional information for determining what reactions are possible and defining formation conditions for the regolith. A number of chemical models [1] and simulation experiments [2-8] attempted to explain the LR results. A recent chemical model suggests that nitrates are present, as well as a carbonate with a solubility similar to that of calcite [9].

During the LR experiments after the oxidation process was complete (~5 days) the magnitude of the LR signal was controlled by the distribution of ¹⁴CO₂(g) between the gas phase and the moist solids in the LR cell. That distribution was controlled by chemical



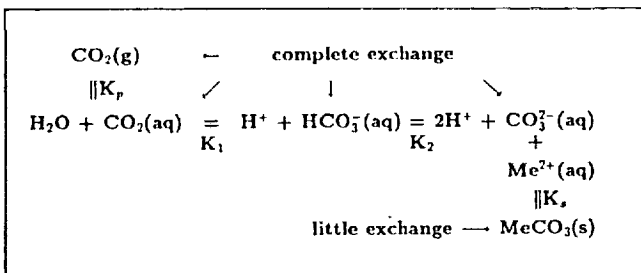
The LR responses produced by the oxidation of 2.8×10^{-6} moles of labeled carbon in nutrient (one carbon of one nutrient component in one aliquot) as a function of:

- 1) the number of aliquots of nutrient injected into system,
- 2) K_w of the most soluble carbonate present, and
- 3) the amount, m_i , of soluble acid or base in the sample.

all for $P_0 = 2$ mbar and $I_m = 2 \times 10^{-2}$.

The decrease in response on successive injections results from shifts in chemical equilibria which depend upon K_w , m_i , P_0 , the amount of the liquid phase, and on the ionic strength, I_m .

Fig. 2.



(1) mass balance

$$P_0 V/RT + K_1 M[\text{H}^+]^2 / K_1 K_2 K_p P = PV/RT + K_p P M + K_1 K_p P M / [\text{H}^+] + K_1 K_2 K_p P M / [\text{H}^+]^2$$

(2) charge balance

$$[\text{H}^+] + 2K_1[\text{H}^+]^2 / K_1 K_2 K_p P + F_{OA}[\text{H}^+] / (K_{OA} + [\text{H}^+]) \cdot m_o / M = K_1 K_p P / [\text{H}^+] + 2K_1 K_2 K_p P / [\text{H}^+]^2 + K_w[\text{H}^+] + K_{AA} F_{AA} / (K_{AA} + [\text{H}^+])$$

P_0	≡	initial pressure of CO_2
M	≡	mass solvent
P	≡	equilibrium pressure of CO_2
F_{OA}	≡	concentration of organic acids (formate, glycolate and lactate) in nutrient
K_{OA}	≡	average dissociation constant of organic acids
F_{AA}	≡	concentration of amino acids (alanine and glycine) in nutrient
K_{AA}	≡	average dissociation constant of amino acids
m_o	≡	moles of soluble acid ($m_o > 0$) or soluble base ($m_o < 0$) in regolith sample

Fig. 1. Chemical and isotopic exchange equilibria in labeled release experiment.

equilibria that are sensitive to acid-base conditions. Levin and Straat [10] demonstrated that the second injection reabsorption occurs as a result of a shift in chemical equilibria involving $\text{CO}_2(\text{g})$, water, and soil. Calculations devised to determine the pH of Mars must include (1) the amount of soluble acid species or base species present in the LR regolith sample and (2) the solubility product of the carbonate with the limiting solubility [11].

Results and Discussion: The equilibria for CO_2 in a heterogeneous system are shown in Fig. 1. This equilibrium system as represented is completely general. Several metal carbonates may be present. $\text{MeCO}_3(\text{s})$ refers to the particular metal carbonate that is the most soluble of those that do not dissolve completely. Less soluble carbonates, if present, do not enter into the equilibria; more soluble carbonates dissolve completely and are not present as solids in the system after wetting. The limiting case of no metal carbonates present corresponds to a vanishingly small K_s , i.e., a K_s that does not enter into the equilibria.

Exchange of ¹⁴CO₂ among the soluble species and $\text{CO}_2(\text{g})$ occurs rapidly, but the $\text{MeCO}_3(\text{s})$ does not enter into the exchange pool, except for the surface layer, which is a negligibly small quantity.

It was observed in the Viking studies that successive injections of nutrient decreased the magnitude of the response. This is what

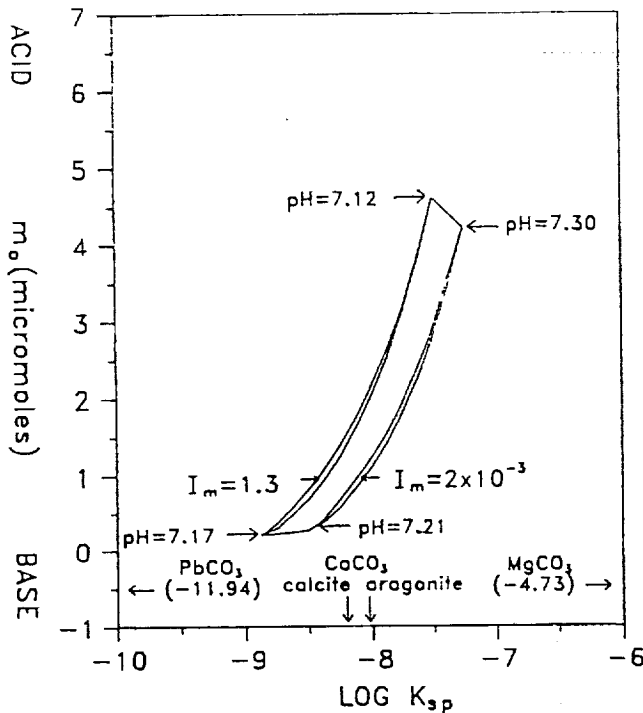


Fig. 3. The zone of compositions that would produce the 21.5–22.5% LR reabsorption upon both the second and third injections. The ionic strength of wet martian regolith is unknown; a range of 2×10^{-3} to 1.3 has been assumed. The pressure of atmospheric CO_2 trapped in the cells after loading, thermal equilibration and venting is estimated to have been 2 mbar. The pHs are the values that would be observed if 0.5 mL samples of regolith were sealed in 10 mL volumes with martian atmosphere at 6 mbar and wet with 0.5 mL of deionized H_2O at 25°C.

one would expect from consideration of the equilibria involved. Qualitatively, the addition of more liquid into the system would have two effects. First, the amount of $\text{CO}_2(\text{aq})$ would increase because the amount of liquid phase increases, causing a decrease in the amount of labeled $\text{CO}_2(\text{g})$. Second, and more important, more $\text{MeCO}_3(\text{s})$ dissolves, increasing the exchange pool and causing the fraction of the $^{14}\text{CO}_2(\text{g})$ in the gas phase to decrease.

The equilibria and the decreased responses on successive injections are described quantitatively by the (1) mass balance and (2) charge balance equations. Allowance has been made for ionic strength using assumed limits and for activity coefficients at various ionic strengths as calculated using the Davies equation. Thermodynamic equilibrium constants have been adjusted to 283 K. The effects of K_s and of the amount m_0 of soluble acid or base present in the sample are shown in Fig. 2.

There is a narrow zone of composition that will produce the observed reabsorption effect for a particular injection. The similar magnitudes of successive injection reabsorption limits the zone of acceptable compositions still further. The zones for two extreme ionic strengths are shown in Fig. 3. Since the ionic strength is unknown, compositions between these zones must also be considered as possible.

Conclusions: This theoretical analysis has been confirmed experimentally by quantitative simulations of the reabsorption effects [9]. The kinetics of the LR oxidation reaction provide additional evidence that $\text{CaCO}_3(\text{s})$ must be present.

This analysis shows that CaCO_3 (either as calcite or aragonite) has the correct K_{sp} to have produced the Viking LR successive injection reabsorption effects. Thus CaCO_3 or another MeCO_3 with very similar solubility characteristics must have been present on Mars. A small amount of soluble acid, but no more than 4 μmol per sample, could also have been present. We conclude that the pH of the regolith is 7.2 ± 0.1 . This is the value that would be observed if 0.5 mL sample of regolith were sealed in a 10-mL volume with a martian atmosphere at 6 mbar and wetted with 0.5 mL of deionized H_2O at 25°C. The variation in pH values is very small, which is a consequence of carbonate buffering.

Acknowledgments: This model was devised and the calculations were carried out by R. Plumb before his death. Bishop and Edwards have abstracted his work and submitted it in his memory in light of his deep interest in the chemistry of Mars. The work by Plumb on the chemistry of Mars was supported by NASA.

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536 91 ABS ON.
THE MINERALOGIC EVOLUTION OF THE MARTIAN SURFACE THROUGH TIME: IMPLICATIONS FROM CHEMICAL REACTION PATH MODELING STUDIES.

G. S. Plumlee¹, W. I. Ridley¹, J. D. De Braal², and M. H. Reed²,
¹Mail Stop 973, U.S. Geological Survey, Denver Federal Center, Denver CO 80225, USA, ²Department of Geological Sciences, University of Oregon, Eugene OR 97403, USA.

This report summarizes results to date of the MSATT-sponsored project, "Chemical Reaction Path Modeling at the Martian Surface Through Time." We have used chemical reaction path calculations to model the minerals that might have formed at or near the martian surface (1) as a result of volcano- or meteorite impact-driven hydrothermal systems [1]; (2) as a result of weathering at the martian surface during an early warm wet climate [2,3]; and (3) as a result of near-zero [4] or sub-zero °C brine-regolith reactions in the current cold climate.

Fundamentals of Chemical Reaction Path Modeling: Computer-driven chemical reaction-path modeling [5] quantitatively predicts the changes in water chemistry, amounts of minerals precipitated or dissolved, and amounts of gases formed as the result of specified geochemical processes such water-rock reactions, fluid mixing, or fluid boiling. The modeling is based upon equilibrium chemical thermodynamics, and takes into account both chemical reactions (through equilibrium constants) and mass balance relations between all solid, aqueous, and gaseous phases in a specified