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RESEARCH COMMENTARIES

PLANETARY SCIENCE:

Deuteronomy?: A Puzzle of Deuterium and Oxygen on Mars[Yuk L. Yung and David M. Kass](#)

Mars is covered by ancient channels which strongly suggest the existence of a warmer past climate that supported liquid water near the surface ([1](#)). This is very different from the current cold and arid conditions. It is difficult to reconstruct this early, potentially life-sustaining, climate, or to determine how it evolved into the current extremely hostile climate. One of the few clues we have to the evolution of the martian climate is the isotopic signature left by the various processes that have modified the atmosphere over time. Two reports in this issue, one by Krasnopolsky *et al.* ([2](#)) on page [1576](#), the other by Farquhar *et al.* ([3](#)) on page [1580](#), add new data to the search for answers.

If we understand the fractionation caused by the various processes that may have affected the atmosphere and know the current isotopic values of the various reservoirs, it should be possible to reconstruct the early climate and its evolution to the present climate. One of the key issues in understanding the martian climate and how it changed is to understand the history and size of the water reservoirs.

It is quite clear that the current mean column-integrated 8.8 mm of H₂O in the martian atmosphere is much too little to have created the features seen on the surface. This amount of atmospheric water is controlled by planet-wide low surface temperatures. The summer polar cap temperatures and seasonal changes in the atmospheric water vapor imply that much more water is frozen at the poles and possibly in the regolith or interior of the planet ([1](#)). Another "reservoir" was pointed out in a classic paper by McElroy ([4](#)) in 1972. Using a combination of Mariner 9 observations of the corona of hydrogen atoms ([5](#)) and a model for the aeronomy of Mars, McElroy indicated that there is an escaping flux of hydrogen (1×10^8 to 2×10^8 atoms cm⁻² s⁻¹), which is

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matched by a corresponding escape of oxygen atoms at half the hydrogen rate, so that the net result is the loss of H₂O from Mars. Over geological time, the present escape rate implies a total loss of water equal to 280 mbar in the atmosphere, or 3 m of water uniformly spread over the martian surface. This is a lower limit because there was probably more water in the early atmosphere and the young sun may have driven a more active photochemical system. Inclusion of these considerations raises the amount of escaped water to ~80 m (6). Even the lower limit is at least five orders of magnitude more water than is in the current atmosphere. Owing to the low surface temperatures, the bulk of the current reservoir is in the polar caps or permafrost. A crucial question is, how big is the current reservoir?

	3 m lost (4)		80 m lost (6)	
	Global layer	Polar cap	Global layer	Polar cap
$F = 0.02$ (2)	0.5 m	400 km	13 m	1100 km
$F = 0.32$ (8)	0.2 m	200 km	5 m	700 km

Estimates of exchangeable water reservoir sizes. Amount of water remaining for different amounts lost, depending on the F factor used. The amounts are expressed as a global layer of water. For comparison, each amount is also expressed as a polar cap of a given diameter [calculated according to (13)]; for comparison Antarctica is about 4000 km in diameter, and the martian northern permanent cap is about 1200 km in diameter. All values were calculated with Rayleigh distillation (8).

Fortunately, there is a way to test the theory and, in the process, estimate how much water (or at least a lower limit) must remain on Mars. Most of the loss processes will result in an isotopic fractionation of the gases left behind (usually by preferentially removing the lighter element). In 1988 Owen *et al.* (7) discovered that martian water is enriched in deuterium. The deuterium/hydrogen (D/H) ratio deduced from this measurement is six times the terrestrial value. This provides a powerful constraint on the amount of water that has escaped and the amount that is remaining on the planet, as summarized in the table. However, the results are dependent on a model-derived fractionation factor, F . The F value based on the most complete model of photochemistry of Mars is 0.32, determined by eight kinetic processes defined and discussed in detail by Yung *et al.* (8).

The ingenious set of observations of Lyman- α emission from Mars made with the Hubble Space Telescope by Krasnopolsky *et al.* (2) detected deuterium in the upper atmosphere of Mars. The authors deduced a value of $F = 0.02$. This significantly increases the size of the remaining exchangeable water reservoirs, as shown in the table.

Although the water is the ultimate source of the atmospheric hydrogen, molecular hydrogen is the major carrier of hydrogen species to the upper atmosphere of Mars. Thus its D/H ratio is crucial in computing the F factor. The partitioning of D between

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HD and HDO (partially deuterated molecular hydrogen and water, respectively) in the atmosphere may be defined by $R = (\text{HD}/\text{H}_2)/(\text{HDO}/\text{H}_2\text{O})$. To reconcile their measurements with the photochemical model, the authors suggest that there may be a conceptual error in the current photochemical models of Mars. Instead of kinetic reactions, the D/H ratio of the hydrogen that escapes from Mars may be determined by thermodynamic equilibrium between HD and H₂O:



The value of R is 1.6 according to the kinetic theory of Yung *et al.* (8), but if determined by the above equilibrium (reaction 1), $R = 0.14$ for a temperature (T) of 200 K, typical of the temperature at the surface of Mars. The measurements of deuterium imply a value of $R = 0.09$, much closer to the thermodynamic than the kinetic value. However, the suggestion (2) that the rate constant for



is $k_2 \geq 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ strongly violates the laboratory value of $10^{-33} \text{ cm}^3 \text{ s}^{-1}$ (9). There are two possible solutions of this paradox. The first is that there is a hitherto unknown reaction that can reduce the value of R in the model of Yung *et al.* (8). The second is that there is a hitherto unknown catalyst on Mars that can raise the rate coefficient of reaction 2 by 10 orders of magnitude. In the experimental paper by Lécluse and Robert (9) the catalytic effects of charcoal, silica, phyllosilicates, and iron were found to be negligible. The resolution of this puzzle will be a major advance in our understanding of the evolution of the martian atmosphere.

According to McElroy (4) the escape rate of oxygen must be at least half that of hydrogen (oxygen from other sources, for example CO₂, will increase the rate significantly). Over the age of the planet this loss should leave a detectable signature in the enrichment of ¹⁷O and ¹⁸O relative to ¹⁶O (10). New observations of the anomalies in ¹⁷O and ¹⁸O the martian meteorite ALH84001 are reported by Farquhar *et al.* (3). The authors discovered that the oxygen isotopes in the carbonate are fractionated with respect to silicate minerals. The interpretation of measurements of oxygen isotopes is even more difficult than that of hydrogen (which has only two major reservoirs, H₂ and H₂O) because oxygen has many reservoirs (CO₂, H₂O, silicates, and other minerals). These carbonate measurements, along with the D/H fractionation in the SNC meteorites [(11), and see figure 1 of (3)], conflict with the previous simple explanation following from the theory outlined in (4, 10). Given the complexity of the oxygen isotopic system, however, it is premature to rule out this theory.

Farquhar *et al.* (3) favor a fractionation mechanism involving the exchange of an oxygen atom between ozone and CO₂, mediated by the metastable atom O(¹D) (12). Although a promising mechanism for producing mass-independent nonequilibrium fractionation, unlike atmospheric loss-driven fractionation, it requires the complementary isotopic component to be stored somewhere on the planet. There must be hitherto unidentified sinks for oxygen to store the other component of the process. Are these sinks in ferric oxides and hydroxides in the martian regolith today? We do not know the answer yet. If confirmed, this new theory opens up an exciting vista of the atmospheric chemistry of ancient Mars.

Returning to the title of this commentary, we should note that Moses cautioned the people to remain faithful to God in the midst of the pagan Canaanite culture they were

about to enter. We leave it to the reader to decide which culture (kinetics or thermodynamics; escape or exchange) is the pagan one. The reader may wonder why we need to learn about the history of the martian climate. The reason is that Mars can be viewed as a laboratory where drastic climate change experiments were carried out, and because it does not have plate tectonics, the records of the experiments (written in the language of isotopic fractionations) are preserved. Similar evidence on Earth has been continually destroyed by tectonics and reequilibration. Metaphorically, the tablets of Moses have been wiped clean by planetary processes. Deuteronomy (The Second Giving of the Law) may be found in the Temple of another planet.

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