the problem of ray motion within such a resonator becomes identical to a classic problem in nonlinear dynamics: that of the motion of an elastic billiard ball on an oddly shaped billiard table. For most table shapes the motion is chaotic, which means that the trajectories of two balls (or rays) with almost identical initial conditions would diverge from one another exponentially. One can think of this as arising from the slightly different "kicks" each ray is given at the boundary, the effect of which is amplified by the nonlinear dependence of the angle of incidence on the previous angle of incidence. This is quite remarkable since it opens the door for chaotic studies with light rays.

This analogy has initiated experimental searches for chaotic effects in deformed quantum cascade lasers. These lasers (*4*) are nearly ideal two-dimensional optical billiards because light propagates in the plane of the semiconductor layers polarized perpendicularly to the layers.

Although the existence of chaotic billiard motion means that the trajectory of any one ray is in practice impossible to predict, it does not imply that the emission of light from such a resonance is unpredictable. The electromagnetic resonance is equivalent to an ensemble of such rays, and it is possible to predict where the rays are most likely to escape and in what directions. The escape process as described by Nöckel *et al.* (*3*) involves a diffusive "spiraling in" of the angle of incidence of the trapped rays until this angle falls below the critical angle for total internal reflection and escapes by refraction. This has a strong tendency to happen at or near the points of highest curvature on the boundary, leading to highly directional emission in the far-field. This approach was used to explain the highly anisotropic emission of laser light from deformed liquid droplets containing a lasing dye (*5*), a long-observed but poorly understood effect. A quantitative theory of the emission directionality for these materials with a relatively small index of refraction has been developed (*6*).

In contrast, the new lasers are based on the stable ray motion that survives when the resonator is substantially deformed: a "bow-tie" resonance (lower part of figure) develops as the remaining stable mode. However, the chaotic behavior in the rest of phase space (surrounding the bow-tie) plays an important role as it suppresses competing lasing resonances, which are still present from lower deformations. This is an important point: the chaotic resonances basically feed the stable orbit, and the gain is only limited by diffusion processes within the pump medium. In addition, this lasing principle opens new possibilities for injection control in lasers. By changing the lateral distribution of the injection current through special contact geometry the interplay between the chaotic region and the stable mode can be controlled and dynamic processes within the nonlinear medium can be studied.

A new parameter for laser design is thus introduced with this work: deformation of the resonator. In conventional lasers, the output power depends on the resonator length, whereas here the power increases exponentially with deformation. It is remarkable that the transition from whispering-gallery modes to bow-tie modes appears at certain deformations where simultaneously the spectral properties are also improved.

These new laser-resonators provide a system for fundamental studies of mode behavior at the boundary to chaos, thus creating a playground for mesoscopic physics in optical systems. The theoretical concepts do not directly relate to optical physics but to the field of quantum chaos. This field, which has been an active branch of theoretical physics for about two decades, seeks to understand the consequences of chaotic classical motion for the associated quantum dynamics. The same concepts apply to the wave equation for light in the short wavelength limit where ray optics apply: light rays exhibit chaotic motion. Quantum or "wave" chaos theory allows one to classify and understand the possible solutions of the wave equation, which are hard to find with numerical methods because of unsymmetrical boundary conditions.

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PLANETARY SCIENCE

Deuteronomy?: A Puzzle of Deuterium and Oxygen on Mars

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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 μm of H_2O 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 matched by a corresponding escape of oxygen atoms at half the hydrogen rate, so that the net result is the loss of H_2O 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

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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?

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).

	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*).

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 HD and HDO (partially deuterated molecular hydrogen and water, respectively) in the atmosphere may be defined by $R = (HD/H_2)/(HDO/H_2O)$. 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 H_2O:

$$HD + H_2O \leftrightarrow H_2 + HDO \qquad (1)$$

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

$$HD + H_2O \rightarrow H_2 + HDO \qquad (2)$$

is $k_2 \geq 10^{-23}$ cm^3 s^{-1} strongly violates the laboratory value of 10^{-33} cm^3 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 CO_2, will increase the rate significantly). Over the age of the planet this loss should leave a detectable signature in the enrichment of ^{17}O and ^{18}O relative to ^{16}O (10). New observations of the anomalies in ^{17}O and ^{18}O 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, H_2 and H_2O) because oxygen has many reservoirs (CO_2, H_2O, 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 CO_2, 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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