MARS VOLATILE EVOLUTION FROM SNC AND PLANETARY DATA ANALYSIS.
Bruce M. Jakosky, University of Colorado, Boulder, CO 80309-0392 (email jakosky@argyre.colorado.edu), and John H. Jones, Code SN-4, NASA/Johnson Space Center, Houston, TX 77058 (email jjones@snmail.jsc.nasa.gov).

Understanding the martian volatile system and its evolution with time is fundamental to understanding the history of the martian surface: The earliest geology is closely tied in with the extant climate and the nature and distribution of water at or near the surface. Subsequent history, including such effects as weathering of surface materials and evolution of the polar deposits, also closely connects to the behavior of volatiles. We examine the evidence pertaining to the evolution of the volatile inventory and its distribution in the martian system throughout time, based on in situ measurements from spacecraft, earthbased telescopic observations, and terrestrial analyses of the SNC meteorites. Our goals are to try to arrive at a self-consistent (and unique?) view of the system, and to describe measurements that could be made to resolve uncertainties and ambiguities.

The observations and their implications are as follows:

I. The standard view: All outgassed water is in the polar caps and atmosphere.

1) D/H in the martian atmosphere is about 5 times the terrestrial ratio. Given the preferential escape rate of H compared to D at the present, loss of about 90 % of the water in the atmosphere + exchangeable reservoirs must have occurred (Yung et al., 1988).

2) At the present escape rate, about 3 m of water would be lost over time. In this case, the present exchangeable reservoir would only contain around 0.3 m water.

3) Escape rates were higher in the past due to greater solar uv flux and solar wind velocities and intensities. Luhmann et al. (1992) suggest that 30 m of water might have escaped since 3.5 b.y. ago. This would require that any exchangeable reservoir contain about 3 m of water.

4) Volume of the north polar cap probably is equivalent to about 20 m globally. The paucity of craters requires that a layer about 1 km thick must have been deposited recently, equivalent to a global layer about 10 m thick. If this is predominantly water ice and represents the only exchangeable reservoir, then around 90 m of water must have escaped. However, the composition and water content of these deposits are uncertain (Jakosky et al., 1995), so these estimates are correspondingly uncertain.

5) Interpretation of the measured D/H ratio should take into account new, unfractionated water supplied to the atmosphere by catastrophic flooding or by outgassing of volcanic materials (Carr, 1990; Greeley and Schneid, 1991). If the water makes it into the atmosphere + polar cap system, then it would at least partially reset D/H to a lower value.

II. An alternative view: Some water is in the crust.

1) D/H in water in the crust (as represented by the SNC meteorites) is enriched by up to about 5 times terrestrial (Watson et al., 1994). As D/H can fractionate to such large values only by escape to space, the water in the crust must have interacted substantially with atmospheric water.

2) A plausible mechanism for exchanging water between the crust and atmosphere is via circulation in hydrothermal systems. The SNC meteorites show abundant mineralogical and petrological evidence for weathering and hydrothermal alteration (Wentworth and Gooding, 1994), and the inferred abundance of both crustal water and igneous activity on Mars suggests that hydrothermal systems have been present.

3) The spread in D/H values obtained in various minerals in the individual SNC meteorites suggests that there was mixing between a fractionated reservoir that has exchanged with the surface and an unfractionated reservoir that has not.

4) Carr (1987) suggests that the crust may contain several hundred meters of water, based on the amounts of water required in order to carve the outflow channels. As the integrated amount of escape to space and the exchangeable volume of water in the polar deposits are unknown, no unique information can be obtained regarding the sizes of the fractionated and unfractionated reservoirs. For example, if 50 m of water has been lost to space, then the remaining fractionated reservoir could be 5 m, and the remaining unfractionated reservoir could be a couple hundred meters. These abundances are sufficient to drive vigorous hydrothermal circulation.

5) Oxygen isotopes measured in water derived from the SNCs show disequilibrium with the igneous minerals (Karlsson et al., 1992). Movement off of the martian fractionation line can occur as a result of atmospheric escape of oxygen to space (Jakosky, 1993), again suggesting exchange of atmospheric water with the regolith.

III. Another alternative view: Early fractionation.

1) Carr (personal communication) suggests that D/H was enhanced by escape of hydrogen to space during accretion, towards the end of an early hydrodynamic outflow epoch. Such outflow is inferred to have occurred based on the observed Xe isotopic fractionation (see Pepin, 1991). In the most extreme case, all crustal water would have been fractionated early, and the similarity of the atmospheric and crustal values requires some interaction between the crust and atmosphere although the time for that interaction is not specified. The spread of D/H in crustal rocks would represent mixing between fractionated water and juvenile magmatic water from the mantle that had not undergone fractionation.

2) Although the greatest fractionation of D/H can occur during the waning stages of hydrodynamic outflow, substantial fractionation can occur also during the main phase of outflow if substantially larger amounts of hydrogen are lost. For well-developed hydrodynamic flow, the relative escape rates for H and D are very close (ratio of 0.8-0.9; see Zahnle et al., 1990). For 300 m of crustal water to have remained behind and been fractionated, for example, 1.5-3 km of water must have escaped.

3) However, escape subsequent to hydrodynamic outflow should have fractionated atmospheric water by some additional amount. If the SNC value was set during hydrodynamic outflow, we can examine the effects of subsequent additional escape and fractionation. It is unlikely, for example, that there has been more than an additional 20 % fractionation in D/H, based on the error bars shown by Watson et al. Fractionation by 20 % through geologic time would require that about 30 % of the available water in the system be lost (see Yung et al., 1988). Only in the case of a nearly constant water loss rate (3 m over time) can this be accommodated by the atmosphere + polar caps. If, for example, 30 m of water had been lost subsequent to hydrodynamic outflow (as suggested by Luhmann et al.), then the system must contain one hundred m water in order to buffer the additional isotopic fractionation. In such a case, exchange with water in the crust still is required throughout geologic time.

4) We believe that it is unlikely that the most recent catastrophic floods could have reset atmospheric D/H to its early value. The inferred polar deposition of 1 km in the last 10^8 yrs (Plaut et al., 1988) appears to require that the present atmospheric value also represents the value throughout the bulk of the polar deposits.

5) Finally, it is not clear whether a near-surface reservoir of water could be fractionated in D/H while deeper water has not been. Such would require that water be retained within the interior rather than having passed through the atmosphere during the escape epoch. We note that Xe in the SNCs appears to show a fractionated atmospheric reservoir and an unfractionated reservoir of mantle origin (Drake et al., 1994). Such a model also could be consistent with the range of D/H observed by Watson et al.

IV. Escape of volatiles other than hydrogen.

1) Loss of heavier atmophilic species can occur by photochemical processes and by pick-up-ion sputtering. Enrichment of $^{15}N/^{14}N$ relative to terrestrial requires that this has occurred.

2) Enrichment of $^{38}Ar/^{36}Ar$ argues for efficient removal of species by sputtering. Up to 90 % of the Ar may have been removed over time (Jakosky et al., 1994). Substantial loss of other species such as CO_2 would have occurred as well.

3) Lack of enrichment of O and C isotopes requires exchange with a non-atmospheric reservoir. The large uncertainty in the present enrichment of atmospheric isotopes precludes a unique evaluation of possible reservoirs and inventories.

V. Where do we go from here?

1) D/H is fundamental to our view of martian volatile evolution despite the currently ambiguity between early fractionation and continuing fractionation through time.

2) However, either case appears to require continuing exchange of water between the atmosphere and the deep crust.

3) Better measurements of present-day atmospheric isotope ratios can allow a unique determination of volatile escape and reservoir exchange. Of especial value are O and C for non-atmospheric reservoirs of climatically relevant species, Ar and Ne for pick-up-ion sputtering and atmospheric evolution through time, and D/H for resolving the water-evolution issue.