New hydrogen-isotope measurements refine the picture of water on Mars

Atmospheric maps and *in situ* spectrometry of clay minerals constrain climate models and the prevalence of water in the planet's ancient past.

The upper atmosphere of Mars, like that of Earth, is slowly leaking into space. Hydrogen, the lightest element, suffers the fastest loss, and carbon dioxide now makes up all but 4% of Mars's tenuous atmosphere. Near-UV sunlight dissociates water vapor into constituent hydrogen and oxygen atoms that eventually diffuse into the upper atmosphere and, after subsequent chemical reactions and interactions with the solar wind, can escape the planet's weak gravity.

Because deuterium is twice as massive as hydrogen, it is less likely to escape, and over geologic time the atmosphere's D/H ratio has steadily risen. The ratio was first measured more than a quarter century ago from Doppler-shifted molecular absorption lines of heavy and light water, HDO and H_2O, recorded atop Mauna Kea in Hawaii. Blue- and redshifted lines distinguish Mars's water vapor from Earth's as the planets approach each other and recede every couple of Earth years. The highly enriched ratio that was observed—roughly six times the D/H of Earth's oceans, the Vienna Standard Mean Ocean Water (VSMOW)—is evidence that at least 80% of Mars's surface water has been lost.

Using data from a survey that ran from March 2008 through January 2014, NASA's Geronimo Villanueva, Michael Mumma, and their colleagues have now created the first spatially and temporally resolved maps of D/H on Mars.[1] The researchers adopted the same remote spectroscopic approach as in the earlier work: They used powerful telescopes to collect sunlight reflected from Mars's face. But instead of measuring only a hemispherically averaged value, the team stepped the rectangular entrance slit of an IR spectrometer eastward across the face of the planet and sampled dozens of spectra spaced along the North–South length of the slit for a few minutes at each position.

The resulting maps, each captured during a two-hour time window and with a resolution of 500 km, span a quarter of the Martian seasons—from late winter to late spring. That's an especially interesting time of year when the north polar ice cap sublimes and replenishes the northern hemisphere with water vapor. Figure 1 shows part of the cycle. Although the measured polar D/H ratio punctuates the record of water's historical evolution on the planet, the local variations in D/H, between 1 and 10 VSMOW, can reveal the richness and subtleties of its present climate.

Atmospheric anomalies

The water cycle is partly driven by temperature differences, which can reach as much as 100 K, across the planet. The vapor pressures of light and heavy water differ, so their ratio is a sensitive probe of the local temperatures, water-saturation levels, aerosol and dust-particle concentrations, and the transport of air masses. The IR spectra pick up only abundances of water vapor. So the preferential condensation of HDO could explain the strong D/H depletion seen, for example, in clouds over Elysium Mons and the mountainous Tharsis Montes region and in air approaching the cold south pole. Higher D/H ratios appear at low-altitude basins, such as Utopia Planitia.

"These maps will be a fantastic tool against which to judge how well our global climate models capture the behavior of the atmosphere," says Franck Montmessin, a CNRS researcher not affiliated with the work. Predictions don't entirely agree with the results.[2] Indeed, although isotope fractionation could ex-

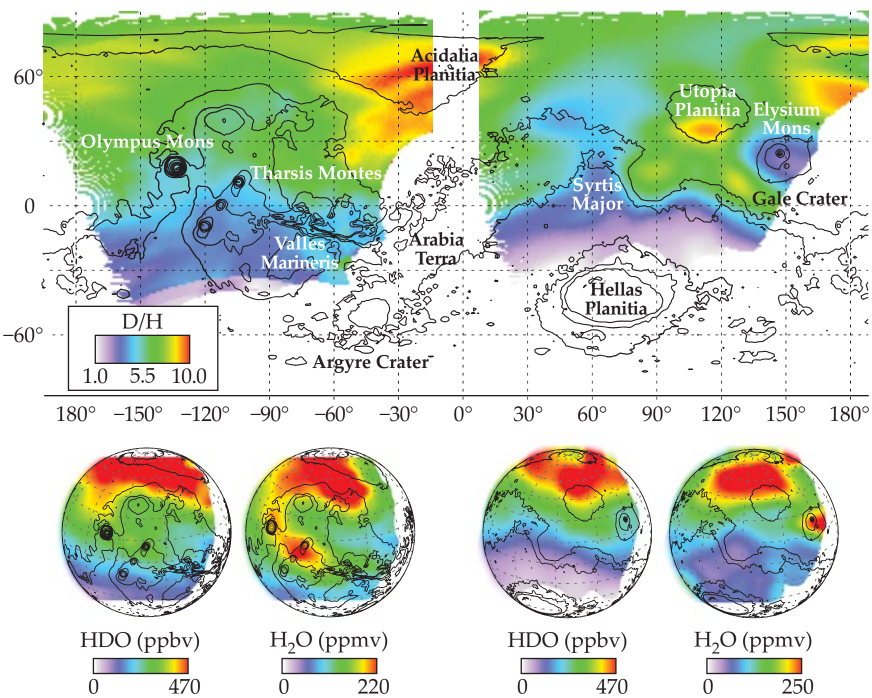

Figure 1. Mars in springtime, captured through the IR spectrometers aboard the Very Large Telescope in Chile and the Keck Observatory in Hawaii in January 2014. At top, the measured isotopic ratio of deuterium to hydrogen in the Martian atmosphere is normalized by that of Earth's ocean water, $(D/H)_{Mars}/(D/H)_{Earth}$. The rich structure of local peaks and dips may be due to heavy water's greater likelihood to condense or to planetary dynamics not yet understood. At bottom, the abundances of light and heavy water are plotted, in parts per million or parts per billion by volume, for the eastern and western hemispheres. Gaps (white) in the measurements occur because of Mars's orientation to Earth on different nights and from a scarcity of water vapor. (Adapted from ref. 1.)

Figure 2. Yellowknife Bay, photographed by the Mars rover *Curiosity* on 9 December 2013 inside Gale Crater. With its telltale geologic formations, sedimentary rocks, and clay minerals, the crater is thought to be an ancient lake bed. To derive a D/H value for the atmosphere about 3.2 billion years ago, *Curiosity* analyzed clay samples named John Klein and Cumberland with its spectrometers. The foothills of Mount Sharp, the rover's eventual destination, are visible in the distance on the left. (Courtesy of NASA/JPL-Caltech/MSSS.)

plain much of the D/H variability found where clouds, frost, and ground fog form, fractionation doesn't account for all of it.

Villanueva speculates that the maps may even locate new, otherwise hidden plumes of water. Proof already exists of shallow-buried ice at latitudes where models predict it should not be stable, and methane spikes found by NASA's *Curiosity* rover suggest venting from a subsurface reservoir of volatile molecules.

Armed with the new maps, the researchers were able to disentangle local climatic features from global averages. The process involved excluding all but those regions in which HDO and H_2O circulate in their fully vaporized phase. Near-equatorial and low-latitude regions were fair game, for example, when ground ice and surface frost had completely sublimed, but not cloud-covered areas or the poles, where most of the ice remains locked up all year. The team's representative value for the planet's bulk atmosphere, about 7 VSMOW, modestly refines the typically used hemispherically averaged D/H values of 5–6 VSMOW from decades earlier. Sublimation models[2] suggest the polar ice should be even more enriched—to about 8 VSMOW.

Back in time

Like Earth, Mars undergoes orbital oscillations that affect its climate. But without a large moon to stabilize it, the tilt of Mars's axis can swing wildly—from as little as 10° to more than 40°—over a few million years. During periods of highest obliquity, ice at the poles experiences greater warming from the Sun and is likely to vaporize entirely, only to refreeze during the next swing to lower obliquity. (See the article by Bruce Jakosky and Michael Mellon, Physics Today, April 2004, page 71.) Consequently, all near-surface and polar ice on Mars should repeatedly interact with the atmosphere and thus share a common D/H ratio.

Unfortunately, no one knows the full extent of the current water inventory on Mars. Ground-penetrating radars and neutron spectrometers on orbiting spacecraft provide estimates of the polar ice deposits and the amount of water in permafrost and other near-surface reservoirs at high latitudes.[3] (See Physics Today, August 2002, page 16.) Estimates of subsurface reservoirs are largely unknown. The shallow range probed by the orbiters may represent just the tip of a vast mantle of underground ice.

Knowledge of present and past D/H ratios and the amount of water that participated in atmospheric cycling constrains estimates of past water volumes. Ancient meteorites preserve a record of Mars's primordial D/H ratio of less than 1.28 VSMOW. Today, the polar deposits alone hold the equivalent of a planet-wide layer of water 21 m deep. Comparing the historical D/H ratio to the poles' modern-day enriched value, Villanueva and colleagues infer that the planet must have had a global-equivalent layer of at least 140 m in its early history.[1] Current models of hydrogen loss suggest that's a hard lower bound. During the "Noachian" period of Mars's history (prior to 3.8 billion years ago), both volcanism and asteroid impacts delivered new water to the surface, which could have rejuvenated the atmosphere's D/H.

Networks of rivers and streams, sedimentary rock deposits, and patterns that resemble ancient shorelines are all visible on Mars's surface. The inferred water could have pooled from such networks into an ocean that covered 20% of the planet in the northern plains. The idea is not new: In 1991 University of Arizona planetary geologist Robert Strom coined the region's name: Oceanus Borealis.[4]

From remote to local

The *Curiosity* rover has lived in Gale Crater, pictured in figure 2, since landing there in 2012. Pervading the landscape are mudstones that contain the clay mineral smectite, which forms only in the presence of liquid water. According to NASA's Paul Mahaffy, part of the *Curiosity* team, the inclined sedimentary strata discovered as the rover traveled toward the crater's central mound suggest the prevalence of flowing water in the region for an extended period of time—perhaps millions of years.

Earlier this year Mahaffy and colleagues reported *in situ* D/H measurements from two ancient clay samples designated John Klein and Cumberland.[5] *Curiosity* drilled holes into the rocks, heated a pinch of the extracted powder, and used a mass spectrometer and tunable laser spectrometer to analyze it. The powder was heated stepwise—first only to about 500 °C, hot enough to outgas weakly adsorbed water, whose analysis found a somewhat less than 6 VSMOW D/H enrichment that matches the new map's modern value at Gale Crater.

Continued heating to 900 °C released tightly bound hydroxyl groups that had been locked in the lattice structure for about 3.2 billion years. That water had a D/H imprint of 3 VSMOW, nearly half that of the present Martian atmosphere but substantially higher than expected so early in Mars's history. The value implies that Mars lost an enormous amount of its water inventory in the Noachian period—Villanueva suspects as much as half—and the remaining history consisted of long, slow desiccation.

Using a reasonable fractionation estimate and comparing the mudstone's D/H value with that of later meteorites, Mahaffy argues that at least twice the amount of water in Mars's poles has been lost since the formation of the clay. Over the next several months, *Curiosity* will be filling in the gaps in Martian water history as the rover continues its way upward on the foothills of Mount Sharp and samples ever younger layers of rock.

A different tack

The *Mars Atmosphere and Volatile Evolution* mission (*MAVEN*), a NASA-run program directed by University of Colorado's Bruce Jakosky and now in full swing, is directly probing the planet's upper atmosphere and its interactions with the Sun and solar wind. The hope is to understand the interactions well enough to run them backward in time and simulate Mars's early climate. As part of that project, one instrument aboard the *MAVEN* orbiter is measuring D/H at the top of the atmosphere.

Even before *MAVEN*'s first results are in, other projects have complicated the picture. The escape of atomic H from the Martian atmosphere isn't a steady, uniform process. According to *Hubble Space Telescope* images of hydrogen in Mars's corona and measurements by the *Mars Express* spacecraft of the atoms' geographical distribution there, the escape rate varies by up to an order of magnitude as a function of season. No current model predicts so large a change in flux.[6]

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Superresolution microscopy reveals chromosomes' smallest structure

It's long been thought that at size scales of tens of nanometers, our genetic material is packaged in a neat, orderly way. New observations show that's not the case.

To fit in a cell nucleus, a strand of DNA must be folded to a size orders of magnitude smaller than its stretched length. In the first step of that compaction, the DNA winds around 10-nm protein clusters to form units called nucleosomes; the whole DNA–protein complex is known as chromatin. Cell biology textbooks typically illustrate chromatin's structure as in figure 1a: with the nucleosomes evenly spaced along the DNA strand, like pearls on a string, and then arranged into a regular, compact 30-nm fiber.

The evidence for that tidy picture is spotty—and, some have recently argued, wrong. But the traditional tools for probing cells have trouble with structures tens of nanometers large: Conventional optical microscopy doesn't have the resolution, and electron microscopy and x-ray techniques lack the chemical specificity to distinguish the nucleosome proteins from other molecules.

Now Melike Lakadamyali, Maria Pia Cosma, and their colleagues at the Institute of Photonic Sciences (ICFO) and the Center for Genomic Regulation (CRG), both in Barcelona, Spain, are using superresolution microscopy to get a closer look at the structure of chromatin.[1] What they've found so far argues against the textbook view: Rather than being evenly spaced, nucleosomes are grouped into clusters, which the researchers call "clutches," as shown in figure 1b. Furthermore, the average number of nucleosomes per clutch differs between stem cells and ordinary, or somatic, cells. Though they don't yet know whether the clutch size is a cause or a consequence of the cell type, the researchers hope their work will lead to new insight into how stem cells differ-

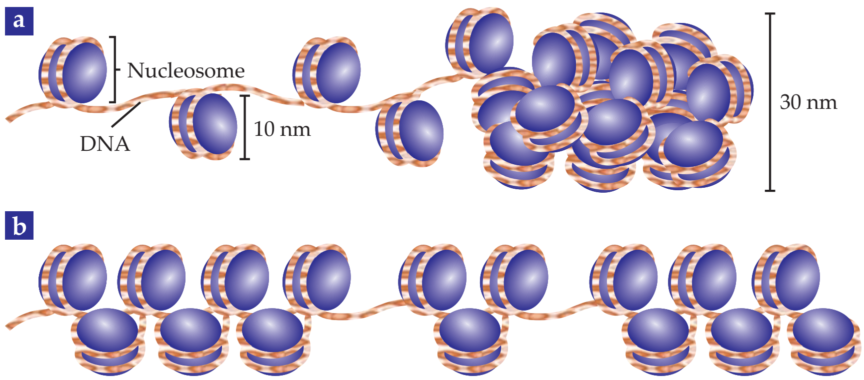

Figure 1. Chromatin, the DNA–protein complex that makes up chromosomes, contains 10-nm units called nucleosomes. **(a)** Textbooks show the nucleosomes evenly spaced on the DNA strand, and then regularly packed into a 30-nm fiber. **(b)** New results show that, in fact, the nucleosomes are heterogeneously grouped into clusters, or "clutches."