

HIGH-RESOLUTION SPECTROSCOPY OF MARS: RECENT RESULTS AND IMPLICATIONS FOR ATMOSPHERIC EVOLUTION. V. A. Krasnopolsky, *Catholic University of America and NASA Goddard Space Flight Center, Greenbelt MD 20771, USA (vkras@lepvx3.gsfc.nasa.gov)*, T. C. Owen, *Institute for Astronomy, University of Hawaii, Honolulu HI 96822, USA*, J. P. Maillard, *Institute d'Astrophysique de Paris, 75014 Paris, France*.

Introduction. It is believed that Earth, Venus, and Mars were formed by the same rocky and icy planetesimals, which resembled meteorites and comets in their composition, respectively. These planets are thus expected to have initially had the same chemical and isotope composition. Scaling the mass of the terrestrial ocean by the planetary mass ratio, the expected initial H₂O abundance on Mars is a layer of about 1 km thick. Scaling the abundance of CO₂ on Venus, the expected initial CO₂ abundance on Mars is 15 bars. Evidently, significant parts of the initial H₂O and CO₂ abundances have been lost. Intense meteorite impact erosion and hydrodynamic escape of hydrogen (which could drag to escape more heavy species) were dominant loss processes in the first 0.8 Byr. Later, atmospheric sputtering by O⁺ ions resulted in the dissociation of CO₂ and massive losses of O, C, and H. Formation of carbonates also reduced CO₂ to its present abundance which currently exists in the atmosphere, on the polar caps, and is absorbed by regolith. Water loss is currently due to thermal escape of H and nonthermal escape of O, both formed by photodissociation of H₂O.

All loss processes resulted in fractionation of the H, O, and C isotopes. Therefore, the current isotope ratios in H₂O and CO₂ are clues to the history of volatiles on Mars. There are three tools to study H₂O and CO₂ isotopes in the martian atmosphere: (i) mass spectrometry from landing probes, (ii) analyses of Mars' gases trapped in the SNC meteorites which were ejected from Mars, and (iii) high-resolution spectroscopy of the H₂O and CO₂ bands. Method (i) is the best but is the most expensive. Mass spectrometers to be used should be designed for high-precision isotope measurements. Method (ii) makes it possible to reach an uncertainty $\sim 0.1\%$. However, the obtained results are affected by some uncontrolled interactions: isotope fractionations of (1) trapped gases and (2) those released in pyrolysis, (3) contribution of the impactor, isotope exchanges (4) in the terrestrial environment and (5) with the host rock during pyrolysis. Therefore, the spectroscopic data are of great interest, though their formal accuracy is lower.

High-resolution spectroscopy is also a tool to study the current atmosphere of Mars by mapping of some photochemically important species and searching for some minor constituents and their variations.

D/H Ratio. This is one of the basic values for Mars' evolution. HDO on Mars was first detected by Owen et al. (1988) using the Fourier Transform Spectrometer (FTS) at the Canada-France-Hawaii Telescope (CFHT). The observed spectrum at 3.7 μm had a resolving power $R = \nu/\delta\nu = 9 \times 10^4$ and a signal-to-noise ratio $S/N = 200$. Later, a similar observation was made using the FTS at the Kitt Peak National Observatory (KPNO), with $R = 2.7 \times 10^5$ and $S/N = 60$ (Krasnopolsky

et al. 1997). Both results are very similar, and

$$\frac{D}{H} = (5.5 \pm 2) \times \text{SMOW}$$

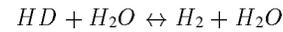
Here SMOW is the isotope ratio in the Standard Mean Ocean Water which has $D/H = 1.56 \times 10^{-4}$. (This means that $\text{HDO}/\text{H}_2\text{O} = 3.12 \times 10^{-4}$ in SMOW.)

Further progress in this problem is the recent detection of atomic deuterium in Mars' atmosphere (Krasnopolsky et al. 1998). The Goddard High-Resolution Spectrograph (GHRS) at the Hubble Space Telescope (HST) had a resolving power of 1.6×10^4 with an aperture of 1.74 arcsec (10^5 for 0.22 arcsec), and both martian and telluric, both deuterium and hydrogen Lyman- α emissions were observed and resolved.

A coupled photochemical and radiative transfer code reproduces the observed intensity of the martian deuterium line (23 ± 6 rayleighs at the limb) at the HD mixing ratio of 6 ± 2 parts per billion (ppb). Then $\text{HD}/\text{H}_2 = (1.5 \pm 0.6) \times 10^{-4}$, and enrichment

$$\epsilon = \frac{\text{HD}/\text{H}_2}{\text{HDO}/\text{H}_2\text{O}} = 0.09 \pm 0.04$$

This value is much smaller than $\epsilon = 1.6$ predicted by a photochemical model by Yung et al. (1988). This is due to a conceptual error in the model: instead of chemical kinetics, the enrichment is determined by thermochemical equilibrium



which results in $\epsilon = 0.14 \pm 0.06$ at $T = 200 \pm 20$ K and agrees with the measured value. Thermochemical equilibrium is established because of the very long lifetime of H₂ on Mars, 1200 years. However, some aspects of this equilibrium are not clear (Yung and Kass 1998).

Another improvement in the theory of hydrogen isotope fractionation on Mars is nonthermal escape. Previously ignored, it appears to be a dominant loss process for D, H₂, and HD. Charge transfer with the solar wind protons, electron impact ionization and photoionization above the ionopause result in sweeping out the ions, which are formed in these processes, by the solar wind. The calculated escape fluxes Φ_H and Φ_D result in a fractionation factor

$$F = 2 \frac{\Phi_D/\Phi_H}{\text{HDO}/\text{H}_2\text{O}} = 0.02$$

which is much smaller than the previous value $F = 0.32$ from the model of Yung et al. (1988).

The known D/H ratio and fractionation factor make it possible to apply a simple three-reservoir model to water on Mars. The bulk reservoir has the terrestrial D/H ratio, the second reservoir is in isotope equilibrium with the third reservoir which includes water in the atmosphere and in the seasonal

polar caps. (This water sublimates completely and therefore has the atmospheric D/H ratio.) Reservoir 2 gets water from reservoir 1 and loses it to reservoir 3. Thermodynamic equilibrium between reservoirs 2 and 3 requires

$$(D/H)_{ice} \approx 7 \times SMOW$$

in reservoir 2. This model results in a relationship between the total loss of water H_2O_{lost} and reservoir 2 (exchangeable with the atmosphere, H_2O_{exch}):

$$\frac{H_2O_{lost}}{H_2O_{exch}} \approx 6$$

If reservoir 2 is the north polar cap (which is equal to a planetwide H_2O layer 9 m thick, Zuber et al. 1998), then the lost water is 54 m. This value is between the estimates of Jakosky et al. (1994) and Kass and Yung (1995), 30 and 80 m, respectively. The lower limit to reservoir 2 may be obtained assuming a constant H_2O escape rate at the current level of $1.2 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Then $H_2O_{lost} = 5 \text{ m}$ and $H_2O_{exch} \approx 1 \text{ m}$. The latter exceeds the variations in the polar cap mass during the obliquity cycle of 10^5 years by an order of magnitude and therefore does not look small. (This estimate is based on the summertime loss of 0.1-0.8 mm/yr from the perennial north polar cap (Haberle and Jakosky 1990) and assuming the annual budget as 10% of this value.) Stuempner et al. (1998) prove that the recently discovered evidences in favor of magnetic field on early Mars (Acuna et al. 1998) could significantly reduce sputtering of volatiles to space.

Studies of D/H in the SNC meteorites show a variety of values reaching $D/H = 3.2 \text{ SMOW}$ (Leshin et al. 1996). This variety is due to the different age of the meteorites, different degree of exchange with the atmospheric water, and possible contaminations of terrestrial water.

Oxygen and Carbon Isotope Ratios. These ratios are determined by the present water amount, the regolith-atmosphere-cap reservoir of CO_2 , the carbonate abundance, the initial abundance of CO_2 , and losses of H_2O and CO_2 by escape processes.

Mass spectrometric measurements from the Viking landing probes resulted in the O and C isotope ratios which copied the terrestrial values within $\pm 5\%$ (McElroy et al. 1977). High-quality spectroscopic data on the oxygen isotopes in water vapor were obtained a decade ago using the FTS at the Kuiper Airborne Observatory. However, only a preliminary analysis of those data has been made, and the published values (Bjoraker et al. 1989) need a substantial revision (Bjoraker, personal communication).

High-resolution spectroscopy at $3.7 \mu\text{m}$ gave $^{18}\text{O}/^{17}\text{O} = (0.93 \pm 0.04) \times \text{SMOW}$ (Krasnopolsky et al. 1996). ($^{18}\text{O}/^{17}\text{O} = 5.38$ in SMOW.) Among the observed 200 lines of the 628 and 627 CO_2 isotopes, sixty lines with closely equivalent widths were chosen. A code was developed which divided the atmosphere into 30 layers and the Voigt profile of each line in each layer into 60 intervals. However, the observed $^{18}\text{O}/^{17}\text{O}$ ratio was a by-product of the observation of HDO, and $3.7 \mu\text{m}$ is not the optimal spectral region to study the isotope ratios in CO_2 .

Therefore, we planned two sessions of high-resolution observations of the CO_2 and H_2O isotopes using the FTS at the CFHT. One session was in January-February 1999, and the results were imperfect due to bad weather. We will repeat the observations in September 1999.

The current escape of H_2O (which is a balanced escape of 2H and O) is much stronger than the current escape of CO_2 (which is a balanced escape of C and 2O; some oxygen may also be lost in surface oxidation). Therefore, oxygen is delivered to the atmosphere as H_2O . Photochemical exchange between H_2O and CO_2 tends to establish almost equal oxygen isotope ratios in both species. Thermodynamic equilibrium of the isotopes tends to enrich CO_2 in heavy oxygen. It is not clear which of these processes dominates, and both species are subjects to our study. Martian H_2^{18}O and H_2^{16}O lines are seen in the spectrum. However, the signal-to-noise ratio should be improved using a longer exposure to obtain the isotope ratio with a low uncertainty.

Helium and Argon. Helium was detected on Mars by observing its line at 584 \AA with the Extreme Ultraviolet Explorer (Krasnopolsky et al. 1994). The line is excited by resonant scattering of the solar photons at 584 \AA by helium atoms, and the measured intensity of 57 ± 15 Rayleighs corresponds to the helium mixing ratio of 4 ± 2 ppm (Krasnopolsky and Gladstone 1996).

The main escape process for helium on Mars is electron impact ionization above the ionopause and sweeping out of the ions by the solar wind. Photoionization and photoelectron impact ionization also contribute to this process. Escape due to collisions with hot oxygen atoms and charge exchange of He^+ with neutral species between the exobase and the ionopause result in 25% of the total loss which is equal to $7 \times 10^{23} \text{ s}^{-1}$ for $\text{He} = 4$ ppm. Sputtering and charge exchange with solar-wind protons and α -particles are negligible (Krasnopolsky et al. 1993; Krasnopolsky and Gladstone 1996). The calculated escape rate results in a lifetime of He on Mars of 5×10^4 years. This means that the helium abundance reflects the current conditions in the atmosphere. The obtained escape rate agrees with that measured from the Phobos orbiter, $(1.2 \pm 0.6) \times 10^{24} \text{ s}^{-1}$ at solar maximum (Barabash et al. 1995). (There is some confusion in the comparison of the EUVE and Phobos data in Barabash et al. (1995); this comparison has been done properly in Krasnopolsky and Gladstone 1996.)

Helium on the terrestrial planets results from radioactive decay of uranium and thorium in their interiors and outgassing to the atmospheres. This outgassing is similar to that of ^{40}Ar which is formed by decay of potassium. With the known abundance of ^{40}Ar in the atmosphere (6×10^{39} atoms), the helium escape rate ($2.3 \times 10^{40} \text{ Byr}^{-1}$), and the K/U ratio (4500, measured by the γ -spectrometer from the Phobos orbiter (Surkov et al. 1990)), it is possible to solve equations for decay of K, U, and Th and outgassing of ^{40}Ar and He. This model (Krasnopolsky and Gladstone 1996) involves a loss of all atmospheric argon by intense impact erosion in the first 0.8 Byr and later sputtering of argon. However, this model strongly requires that the helium outgassing rate should be smaller than its current loss rate by a factor of 2-4. This implies that the dif-

ference may be covered by the solar-wind α -particles which deposit helium to the atmosphere. Later Brecht (1997) calculated the efficiency of 30% for this deposit which is much higher than an estimate of Krasnopolsky et al. (1994) based on some early papers. The flow of α -particles in the solar wind is known, and their influx to Mars' atmosphere is equal to $\approx 5 \times 10^{23} \text{ s}^{-1}$, that is, close to the helium escape rate. Therefore, solar-wind α -particles is a source of helium on Mars which is comparable or even exceeding the outgassing of helium from the interior.

The model shows that the current outgassing coefficient on Mars is smaller by an order of magnitude than that on Earth. Outgassing occurs mostly via volcanism, and this agrees with other geological evidences of a low volcanism on Mars. The model also gives relative (g/g) abundances of K and U in Mars' interior (0.6 and 1.7 of the Earth's values, respectively). According to the model, loss of argon by impact erosion and sputtering was substantial and constituted 75% of the current atmospheric abundance. (Magnetic field on early Mars may reduce this estimate.)

Species Variations and Mapping. Since the discovery of water vapor on Mars, it has been a subject for mapping with high-resolution spectroscopy. Long-term observations using the band at $0.82 \mu\text{m}$ were made by E. S. Barker (Jakosky and Barker 1984) and later by Rizk et al. (1991) and Sprague et al. (1996). DiSanti and Mumma (1995) used the band at $1.13 \mu\text{m}$ for this purpose.

Observations with the low-resolution spectrograph from the Phobos orbiter (Rosenqvist et al. 1992) favored high variability of CO on Mars. Theory does not support this effect, and high-resolution spectroscopy in the infrared and microwave regions (Lellouch et al. 1991, Encrenaz et al. 1991, Billebaud et al. 1992, 1998) precludes variations exceeding a factor of 2. However, the smallest location studied were of 0.4 Mars' radius, that is, much larger than those observed with the Phobos. Hunten (1993) suggested an explanation of the CO variations as an instrument artifact. According to Krasnopolsky (1993), some variations are possible at the polar caps due to intense sublimation/condensation of CO_2 , and the 11-year solar cycle variations of CO are expected at 35%.

Espenak et al. (1991) detected ozone at different locations (including low latitudes) on Mars using infrared heterodyne spectroscopy at $9.6 \mu\text{m}$. They achieved a resolving power of 10^6 . Ozone was also observed by Clancy et al. (1996) using ultraviolet spectroscopy with the HST.

According to the recent theory of seasonal variations at the low and middle latitudes on Mars (Clancy and Nair 1996), the total ozone abundance (which is retrieved from the above observations) varies only by 20%, while ozone at 20-40 km varies by an order of magnitude. Therefore, Krasnopolsky (1997) revived the old discovery of the O_2 dayglow at $1.27 \mu\text{m}$ (Noxon et al. 1976, Traub et al. 1979) and suggested the use of the O_2 dayglow and its rotational temperature for mapping of high-altitude ozone on Mars. (This dayglow is excited in photolysis of ozone and is quenched by CO_2 below 20 km.) This concept for photochemical mapping also includes H_2O and CO. Currently the best instrument for this mapping is the

CSHELL at the IRTF which is a long-slit spectrograph with a resolving power of 4×10^4 . First applications by Krasnopolsky to the IRTF observing time were not supported. Then, under his suggestion, DiSanti and Mumma used a part of their observing time for this idea. Recently Krasnopolsky conducted independent observation of the O_2 dayglow.

Search for Minor Constituents. Upper limits of 3 ppb to HCl and H_2CO (Krasnopolsky et al. 1997) were obtained from the KPNO spectrum at $3.7 \mu\text{m}$. They preclude any role of these species in Mars' photochemistry. A search for H_2O_2 at $8 \mu\text{m}$ resulted in an upper limit of 30 ppb (Krasnopolsky et al. 1997) which is close to the values predicted by the models.

The KPNO spectrum at $3.7 \mu\text{m}$ favored a possible presence of methane at a level of 70 ± 50 ppm, that is, below the 2σ -detection limit. Methane is unstable on Mars and may be related to a biosphere. Due to the importance of the problem, we made in January 1999 an observation of the CH_4 band at $3.3 \mu\text{m}$ using the FTS at the CFHT to check this result. The analysis is in progress.

Photochemical models predict a large H_2 mixing ratio of 7-50 ppm on Mars. However, H_2 escaped detection despite the numerous spacecraft that visited Mars. The best method for spectroscopic detection of H_2 is observations of the PI (6-v") lines of the H_2 Lyman band system. These lines are excited by the solar Lyman- β and will be observed using the Far Ultraviolet Spectroscopic Explorer (Krasnopolsky and Feldman 1998).

References

- Acuna, M. H., et al., *Science* 279, 1676, 1998.
- Barabash, S., E. Kallio, R. Lundin, H. Koskinen, *J. Geophys. Res.* 100, 21307, 1995.
- Bjoraker, G. L., M. J. Mumma, H. P. Larson, *Bul. Am. Astr. Soc.* 21, 991, 1989.
- Billebaud, F., J. P. Maillard, E. Lellouch, T. Encrenaz, *Astron. Astrophys.* 261, 647, 1992.
- Billebaud, F., J. Rosenqvist, E. Lellouch, J. P. Maillard, T. Encrenaz, F. Hourdin, *Astron. Astrophys.* 333, 1092, 1998.
- Brecht, S. H., *J. Geophys. Res.* 1102, 11287, 1997.
- Clancy, R. T., H. Nair, *J. Geophys. Res.* 101, 12785, 1996.
- Clancy, R. T., et al., *J. Geophys. Res.* 101, 12777, 1996.
- DiSanti, M. A., M. J. Mumma, *LPI Tech. Rep.* 95-04, p. 11, 1995.
- Encrenaz, T., et al., *Ann. Geophys.* 9, 797, 1991.
- Espenak, F., M. J. Mumma, T. Kostiuik, D. Zipoy, *Icarus* 92, 252, 1991.
- Hunten, D. M., *Icarus* 101, 42, 1993.
- Jakosky, B. M., E. S. Barker, *Icarus* 57, 322, 1984.
- Jakosky, B. M., R. M. Haberle, *J. Geophys. Res.* 95, 1359, 1990.
- Jakosky, B., R. O. Pepin, R. E. Johnson, J. L. Fox, *Icarus* 111, 271, 1994.
- Kass, D. M., Y. L. Yung, *Science* 268, 697, 1995.
- Krasnopolsky, V. A., *Icarus* 101, 33, 1993.
- Krasnopolsky, V. A., *J. Geophys. Res.* 102, 13313, 1997.
- Krasnopolsky, V. A., P. D. Feldman, *Proposal to FUSE #90*, 1998.

MARS' SPECTROSCOPY: V. A. Krasnopolsky et al.

- Krasnopolsky, V. A., G. R. Gladstone, *J. Geophys. Res.* 101, 15765, 1996.
- Krasnopolsky, V. A., S. Chakrabarti, G. R. Gladstone, *J. Geophys. Res.* 98, 15061, 1993.
- Krasnopolsky, V. A., S. Bowyer, S. Chakrabarti, G. R. Gladstone, J. S. McDonald, *Icarus* 109, 337, 1994.
- Krasnopolsky, V. A., M. J. Mumma, G. L. Bjoraker, D. E. Jennings, *Icarus* 124, 553, 1996.
- Krasnopolsky, V. A., G. L. Bjoraker, M. J. Mumma, D. E. Jennings, *J. Geophys. Res.* 102, 6525, 1997.
- Krasnopolsky, V. A., M. J. Mumma, G. R. Gladstone, *Science* 280, 1576, 1998.
- Lellouch, E., G. Paubert, T. Encrenaz, *Planet. Space Sci.* 39, 219, 1991.
- Leshin, L. A., S. Epstein, E. M. Stolper, *Geochim. Cosmochim. Acta* 60, 2635, 1996.
- McElroy, M. B., T. Y. Kong, Y. L. Yung, *J. Geophys. Res.* 82, 4379, 1977.
- Noxon, J. F., W. A. Traub, N. P. Carleton, P. Connse, *Astrophys. J.* 207, 1976.
- Owen, T., J. P. Maillard, C. de Bergh, B. L. Lutz, *Science* 240, 1767, 1988.
- Rizk, B., et al., *Icarus* 90, 205, 1991.
- Sprague, A. L., D. M. Hunten, R. E. Hill, B. Rizk, W. K. Wells, *J. Geophys. Res.* 101, 23229, 1996.
- Stuempner, W., H. Lammer, S. J. Bauer, *Ann. Geophys.* 16 (suppl. 111), C1002, 1998.
- Surkov, Yu. A., et al., *Pisma Astron. Zh.* 6, 355, 1990.
- Traub, W. A., N. P. Carleton, P. Connes, J. F. Noxon, *Astrophys. J.* 229, 846, 1979.
- Yung, Y. L., D. M. Kass, *Science* 280, 1545, 1998.
- Yung, Y. L., J. S. Wen, J. P. Pinto, M. Allen, K. K. Pierce, S. Paulson, *Icarus* 76, 146, 1988.
- Zuber, M. T., et al., *Science* 282, 2053, 1998.