

DEUTERIUM TO HYDROGEN RATIOS IN SOLID AND ATMOSPHERIC SAMPLES FROM THE SAM EXPERIMENT IN GALE CRATER. P.R. Mahaffy¹, C.R. Webster², A. Brunner^{1,3}, S.K. Atreya⁴, A. McAdam¹, J. Stern¹, S. Kashyap¹ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771 (Paul.R.Mahaffy@nasa.gov), ²Jet Propulsion Laboratory, Pasadena, CA 91109, ³CRESST, U. Maryland, College Park, MD 20740, ⁴U. Michigan, Ann Arbor, MI 48109.

Introduction: Fundamental to the study of the habitability of early Mars is the question of the persistence of surface water and the atmospheric conditions necessary to sustain surface liquids for extended periods of time. Current and planned measurements from orbit with the Mars Express and MAVEN missions explore processes of atmospheric escape such as sputtering, solar wind interaction, thermal escape, and dissociative recombination. Extrapolation of the current rate of atmospheric loss back in time may provide insight into surface conditions on early Mars when lakes such as those suggested by MSL's investigations in Gale crater were present.

A number of isotope ratios of light elements in the present martian atmosphere (¹³C/¹²C, ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, ³⁸Ar/³⁶Ar, and D/H) [e.g. 1,2,3] have been measured by the Sample Analysis at Mars (SAM) instrument of the Mars Science Laboratory (MSL). All demonstrate enrichment in the heavy element relative to expected values if there had been no atmospheric loss to space over martian history. These in situ measurements build on and refine previous Viking [4], remote sensing [e.g. 5, 6] meteorite [e.g. 7,8,9] measurements.

D/H is one of the most promising candidates, to date, for identification of the isotopic composition of volatiles captured in rocks from the ancient atmosphere and ancient fluids. Water is the most abundant volatile thermally released from the Yellowknife Bay phyllosilicates discovered by the SAM and CheMin experiments of MSL and its D/H is measured by both the Tunable Laser Spectrometer (TLS) and the Quadrupole Mass Spectrometer (QMS) of the SAM suite.

Methods: SAM samples gases with its QMS as they are evolved from 1 or more ~50 milligram portions of powdered sample delivered to a quartz cup and heated in a helium stream from a selected starting temperature to ~900 °C. At any point in this evolved gas analysis (EGA) heating sequence the stream of gas may be directed for a period of time to a previously evacuated TLS. C, O, and H isotopes of CO₂ and H₂O are analyzed with the TLS with supporting measurements from the QMS, which samples continuously over the entire EGA sequence. Isotope ratios for D/H in water are obtained with the TLS by scanning with a near infrared (NIR) laser over the wave number range of 3594.4 cm⁻¹ to 3593.2 cm⁻¹, where multiple HD¹⁶O and H₂¹⁶O absorption lines are present. The QMS analysis utilizes primarily the m/z 19 and 20 signals where primary contributions come from HD¹⁶O⁺ and H₂¹⁸O⁺ respectively. The TLS ¹⁸O/¹⁶O ratio is used to predict

the intensity of the QMS m/z 18 peak from H₂¹⁶O⁺ which is often saturated. Corrections for contributions from other isotopologues such as H₂¹⁷O⁺, HD¹⁶O⁺, H¹⁸O⁺, and ⁴⁰Ar⁺⁺ are implemented and corrections are applied for instrument backgrounds. Most of the hydrogen released during the EGA sequence is contained in H₂O with a smaller fraction in H₂ and these gases are the most abundant hydrogen containing molecules.

Results: At the time of the submission of this abstract, a single atmospheric measurement of D/H in water had been implemented. However, more than a dozen solid sample portions were analyzed. The D/H ratio in the low temperature water evolved from these samples is similar to the atmospheric value and to the average atmospheric D/H inferred from ground based spectroscopy. The Yellowknife Bay mudstones in contrast to the windblown sand and dust samples that were the first solid SAM samples analyzed show a high temperature water peak that is associated with dehydroxylation of clays. A special experiment designed among other things to more clearly separate this high temperature component from the low temperature evolved water was successful and gave a D/H ratio intermediate between that of the atmosphere and that of the terrestrial oceans (SMOW).

Discussion: The high temperature water in the Yellowknife Bay mudstones may represent the isotopic composition of the water that transformed the basaltic material washed down from the crater rim into the Yellowknife Bay mudstones. We conclude that early escape processes such as hydrodynamic escape [e.g. 10,11] must have substantially fractionated hydrogen prior to the formation of the Yellowknife Bay mudstones. Subsequent fractionation provided the values recorded in the current atmosphere and the low temperature water evolved from materials analyzed by SAM.

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