Mars Analog Tunable Laser Spectroscopy at a Site of Active Serpentinization

Steve Vance[1] [1]Jet Propulsion Laboratory, Caltech, MS 183-401, 4800 Oak Grove Dr., Pasadena, CA 91024 (svance@jpl.nasa.gov)

The Tunable Laser Spectrometer (TLS) is one of three instruments (QMS, GC, TLS) that comprise the Sample Acquisition Mission (SAM) on NASAs 2011 Mars Science Laboratory (MSL). TLS has unprecedented capability for measuring methane, water and carbon dioxide abundances in the martian atmosphere and in gas evolved from heated soil samples. In addition, TLS will measure the $^{12}C/^{13}C$ isotope ratios in both CH_4 and CO_2 and the $^{16}O/^{17}O/^{18}O$ isotope ratios in CO_2. Comparison among atmospheric and soil isotope ratios promises insight into the role of water in Mars's interior, and potentially life-sustaining fluid-rock interactions. We discuss measurements of isotope compositions from spring samples collected at The Cedars, a site of active serpentinization and possibly an analog for the Nili Fossae, using tunable laser spectroscopy with instrumentation similar to TLS. Comparable measurements can be made by TLS when MSL reaches its destination.

Serpentinization on Earth and Mars

Hydration of olivine and pyroxene minerals (serpentinization) at moderate temperatures [100 to 300 oC 1] generates heat, hydrogen and other materials relevant to supporting and possibly originating life. On Earth, serpentinization-driven hydrothermal systems and hot springs have been identified in multiple locations, notably at Lost City [2] and along the Pacific coast of North America [3]. We are investigating fluid and gas compositions at The Cedars in Northern California in order to understand the systems biogeochemistry and, by extension, that of similar systems. The carbonate mineralogy and abundance of methane at the Cedars bears comparison with the Nili Fossae region of Mars, where hydrated magnesium carbonate [4] and significant exhalations of methane [5] were recently identified.

The Cedars: a site of active serpentinization

The Cedars, at Cazadero, CA in Sonoma county, is among the first serpentinizing sites to be identified [6]. The system is dominated by ultramafic materials. The springs are highly alkaline (pH 11), precipitating carbonate [as hydromagnesite and carbonatite 3] where fluids emerge from underground. Where spring water mixes with the atmosphere, stong redox gradients form, from which microbial communities generate methane most probably from acetotrophy (Morrill et al., submitted). The hydrology of the Cedars can yield insight into the systems depth and the volume of material being serpentinized. Reaction temperatures and underground residence times of waters at the Cedars affect the isotopic character of the spring water. We describe measurements of isotopic composition of waters at the Cedars. Samples of spring water and gas bubbles were collected during the Summers of 2007 and 2008 for isotopic analysis. Sample were collected from the Barnes Spring Complex (BSC), Mineral Springs Complex (MSC) and CS1. Oxygen and hydrogen isotopes indicate the alkaline BSC and MSC springs (samples CS1, NS1 and BS7) are enriched in deuterium and/or ^{16}O relative to meteoritic water. The former may be attributed to a process that removes hydrogen from meteoric water, consistent with high methane concentrations (5-15%) observed from gas bubbles. The latter is consistent with fractionation of heavy oxygen into carbonates [7].

Isotope Spectrometry

The Tunable Laser Spectrometer (TLS) instrument aboard the Mars Science Laboratory (MSL) uses two thermoelectrically-cooled solid-state tunable lasers, one centered at 2.78 and the other at 3.27 μm (and developed at JPL), to quickly and directly measure absolute and isotopic compositions in CO_2, CH_4 and H_2O to unprecedented precision (0.2 ppm, 0.5 ppb, 0.2 ppm, respectively; Webster and Mahaffy, poster P51A-1391). By comparison, isotope mass spectrometers, though well established, require chemical conversion of CH_4 and H_2O to other molecules before analysis of isotopic content. This is more labor intensive and does not lend itself to portability. We use spectral windows comparable to those employed by TLS to examine samples from the Cedars, in preparation for an in situ field campaign that will track methane and water isotopic compositions of targeted springs through their seasonal cycle.

Second harmonic detection (in which the laser is modulated at one frequency with synchronous detection at twice that frequency) permits identification of small-signal features. The field device will employ a commercial laser capable of probing H_2O, HDO, $H_2^{18}O$, and $H_2^{17}O$ in a single scan, as well as a JPL-built laser to measure $^{12}CH_3D$ and $^{13}CH_4$.

For comparison with laser spectrometer results, H and O isotope compositions of water from the Cedars were measured using chromium reduction and CO_2 exchange mass spectrometer systems following phosphoric acid treatment. The samples show strong fractionation from meteoric water [8]. The direction of fractionation is complementary to H and O isotopic measurements in serpentine and carbonate [7] from the Cedars. Methanogenesis by bacteria (Morill et al. GCA, submitted) also explain the observed fluid fractionation. In situ monitoring of water and methane isotopic compositions will allow us to distinguish between them.

References

[1] D. E. Allen and W. E. Seyfried. Serpentinization and heat generation: Constraints from Lost City and Rainbow hydrothermal systems. *Geochimica et Cosmochimica Acta*, 68(6):1347–1354, 2004.

[2] D. S. Kelley, J. A. Karson, G. L. Fruh-Green, D. R. Yoerger, T. M. Shank, D. A. Butterfield, J. M. Hayes, M. O. Schrenk, E. J. Olson, G. Proskurowski, M. Jakuba, A. Bradley, B. Larson, K. Ludwig, D. Glickson, K. Buckman, A. S. Bradley, W. J. Brazelton, K. Roe, M. J. Elend, A. Delacour, S. M. Bernasconi, M. D. Lilley, J. A. Baross, R. T. Summons, and S. P. Sylva. A serpentinite-hosted ecosystem: The Lost City hydrothermal field. *Science*, 307 (5714):1428–1434, 2005.

[3] D.B. Wenner and HP Taylor. D/H and O 18/O 16 studies of serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta*, 38(8):1255–1286, 1974.

[4] B.L. Ehlmann, J.F. Mustard, S.L. Murchie, F. Poulet, J.L. Bishop, A.J. Brown, W.M. Calvin, R.N. Clark, D.J.D. Marais, R.E. Milliken, et al. Orbital Identification of Carbonate-Bearing Rocks on Mars. *Science*, 322(5909): 1828, 2008.

[5] SK Atreya, G. Delory, T. Encrenaz, W. Farrell, V. Formisano, P. Mahaffy, M. Mumma, and N. Renno. Martian methane: Faster destruction, bigger source. 2008.

[6] I. Barnes, VC LaMarche, and G. Himmelberg. Geochemical Evidence of Present-Day Serpentinization. *Science*, 156(3776):830–832, 1967.

[7] JR O'Neil and I. Barnes. C13 and O18 compositions in some fresh-water carbonates associated with ultramafic rocks and serpentinites: western United States. *Geochim. Cosmochim. Acta*, 35:687–697, 1971.

[8] H. Craig. Isotopic Variations in Meteoric Waters. *Science*, 133(3465):1702, 1961.