

**CHEMCAM PASSIVE SPECTROSCOPY OF ATMOSPHERIC O<sub>2</sub> AND H<sub>2</sub>O.** T. H. McConnochie<sup>1</sup>, M. D. Smith<sup>2</sup>, S. Bender<sup>3</sup>, M. J. Wolff<sup>4</sup>, J. R. Johnson<sup>5</sup>, M.T. Lemmon<sup>6</sup>, R. C. Wiens<sup>7</sup>, S. Maurice<sup>8</sup>, O. Gasnault<sup>8</sup>, D. Blaney<sup>9</sup>, L. P. DeFlores<sup>9</sup>, A.-M. Harri<sup>10</sup>, O. Kemppinen<sup>10</sup>, M. Genzer<sup>10</sup>, J. E. Moores<sup>11</sup>, M. H. Wong<sup>12, 13</sup>, M. G. Trainer<sup>2</sup>, F. J. Martín-Torres<sup>14</sup>, M.-P. Zorzano<sup>14</sup>, M. de la Torre Juarez<sup>9</sup>, <sup>1</sup>Department of Astronomy, University of Maryland, College Park, MD 20742 (tmconno@umd.edu), <sup>2</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, <sup>3</sup>Planetary Science Institute, Tucson, AZ 85719, <sup>4</sup>Space Science Institute, Boulder, CO 80301, <sup>5</sup>Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723 <sup>6</sup>Texas A&M University, College Station, TX 77843, <sup>7</sup>Los Alamos National Laboratory, Los Alamos, NM 87545, <sup>8</sup>Institut de Recherche en Astrophysique et Planetologie, Toulouse, France, <sup>9</sup>Jet Propulsion Laboratory, Pasadena, CA 91109 <sup>10</sup>Finnish Meteorological Institute, Helsinki, Finland, <sup>11</sup>Centre for Research in Earth and Space Science, York University, Toronto, Canada, <sup>12</sup>University of Michigan, Ann Arbor, MI 48109, <sup>13</sup>University of California, Berkeley, CA <sup>14</sup>Centro de Astrobiología, Madrid, Spain.

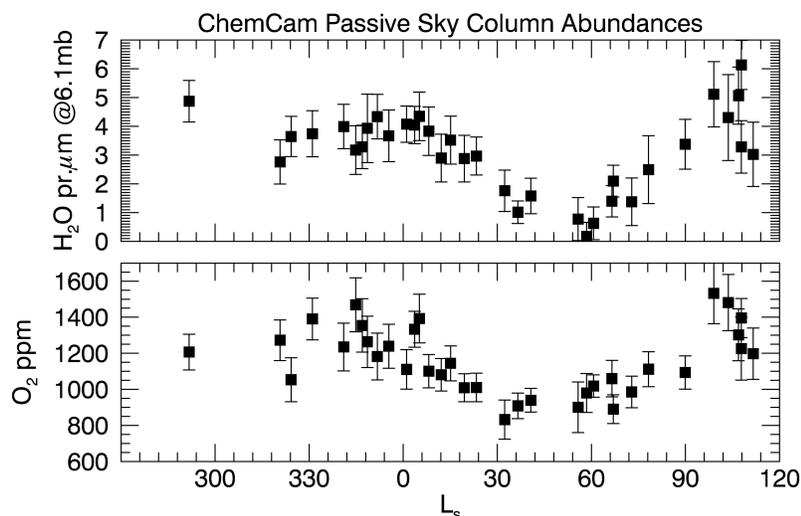
**Introduction:** Although the Mars Science Laboratory's (MSL) ChemCam spectrometer was designed primarily for laser-induced breakdown spectroscopy [1] it has also proven effective as a passive spectrometer [2]. Here we describe the use of ChemCam for passive-mode spectroscopy of the sky and present preliminary results for the column abundances of O<sub>2</sub> and H<sub>2</sub>O vapor.

Both O<sub>2</sub> and H<sub>2</sub>O are key players in the photochemical cycle of atmospheric CO<sub>2</sub>. O<sub>2</sub>, along with CO, is produced from the photolysis of CO<sub>2</sub>. Odd-hydrogen species catalyze the recycling of O<sub>2</sub> and CO back to CO<sub>2</sub>, and those odd-hydrogen species in turn are produced by photolysis of H<sub>2</sub>O [3,4]. The atmospheric component of the Martian water cycle is thus important not just for explaining the distribution of water on the planet but also for determining the abundance of O<sub>2</sub> and other CO<sub>2</sub> photolysis products.

Nair et al. [3] adopted an O<sub>2</sub> abundance of 1200 ± 200 ppm based on ground-based data from the 1970s and 1980s. More recent measurements by the Herschel spacecraft and MSL's own Sample Analysis at Mars (SAM) mass spectrometer have yielded values which are somewhat higher but nevertheless statistically equivalent (1450 ± 90 ppm for SAM [5], column-integrated 1400 ± 120 ppm for Herschel [6]). The ChemCam passive-mode column integrated abundances presented here are unprecedented in their frequency and precision and so can provide a stringent new test of photochemical models. They also complement ongoing but less frequent in-situ atmospheric sampling by SAM [7].

Water vapor column abundances on global scales have been routinely measured by Mars Global Surveyor [e.g. 8], Mars Express [9], and Mars Reconnaissance Orbiter [10,11]. The ChemCam passive measurements uniquely provide local-scale column abundances over MSL, helping to bridge the gap between the aforementioned orbital measurements and the local-scale near-surface in-situ humidity monitoring by MSL's Rover Environmental Monitoring Station (REMS) [12]. They also provide an opportunity for cross-validation with the REMS humidity measurements.

**Methods:** Each ChemCam passive sky measurement consists of spectra acquired at two different pointing elevation angles. The measurements were performed at local solar times of 11:35 on average, ranging from 10:10 to 13:45. The analysis begins by calculating the ratio of the sky spectra at the two pointing elevations to eliminate contributions from the solar spectrum and from any small variations in instrument response. We then make a small correction for the detector back-



**Figure 1:** Preliminary column abundance of water vapor (top) and column-average O<sub>2</sub> volume mixing ratio (bottom) determined from ChemCam passive sky spectra. 2σ errors bars are shown. The water vapor column is scaled by surface pressure, as is commonly done with orbital data, to yield a 6.1 mb surface pressure equivalent column. The data set averages for the data shown here are 1163 ppm for O<sub>2</sub> and 3.1 pr. μm for H<sub>2</sub>O.

ground, remove the continuum, and compare with a radiative transfer model to minimize the  $\chi^2$  difference between the model and data. In deriving  $\text{H}_2\text{O}$  and  $\text{O}_2$  abundances, we use only the 700 - 850 nm portion of the spectrum. We also derive the  $\text{CO}_2$  column abundance and compare it with the known mixing ratio [5] to check the accuracy of our retrievals.

The radiative transfer model, previously used by [10], is a discrete ordinates multiple-scattering calculation that incorporates gas absorption via the correlated-k approximation. Key inputs to this radiative transfer model include surface pressure measured by REMS [13] and atmospheric opacity measured by MSL's Mastcam [14]. Our current methodology assumes that deviations from uniform vertical mixing are negligible for all gas species.

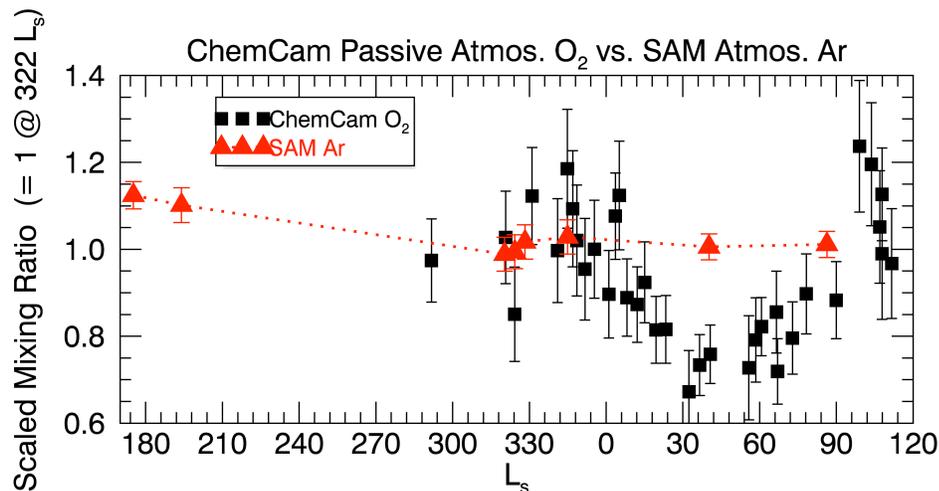
We do observe the retrieved  $\text{CO}_2$  abundance to deviate from the known value, although only rarely by more than 15%. We interpret these deviations to result from the aerosol properties and vertical distributions deviating from their assumed values, which leads to inaccurate vertical weighting functions. Since variation in aerosol properties over the 700 - 850 nm spectral range is minimal, the weighting function inaccuracies will perturb all abundances by the same factor given our assumption of uniform vertical mixing. For the results presented here we have therefore scaled our retrieved abundances by the ratio of retrieved  $\text{CO}_2$  abundance to the known value of 96%. Note that this correction reduces the scatter of nearby observations but has a no effect long-term trends and no effect on average abundances.

**Results:** Figure 1 shows a preliminary summary plot of all ChemCam passive sky measurements through MSL surface operations sol 590. The water vapor column abundances are effectively identical to

those obtained from MRO CRISM water vapor column measurements localized in the vicinity of Gale crater [11], with one significant exception. The exception is the substantial decrease in water vapor observed by ChemCam between  $L_s = 15^\circ$  and  $L_s = 90^\circ$ , which is not detected in the localized [11] CRISM data. A seasonal drop in  $\text{H}_2\text{O}$  in this period is however detected in the much less noisy zonally averaged CRISM data as well as in the MGS Thermal Emission Spectrometer data [10].

Figure 2 shows a comparison of SAM-measured atmospheric Ar (c.f. [7]) with the ChemCam  $\text{O}_2$  results. Since  $\text{O}_2$  is thought to have a photochemical lifetime of  $> 30$  years [4], its mixing ratio should vary seasonally in a manner identical to inert non-condensable gasses in the face of  $\text{CO}_2$  depletion and enhancement due to the  $\text{CO}_2$  cycle. Instead,  $\text{O}_2$  shows a  $\sim 30\%$  depletion in mixing ratio in the  $L_s \sim 40$  season (relative to  $L_s \sim 322$ ) despite a negligible decrease in Ar mixing ratio. This points towards the presence of a not-currently-understood phenomenon in the photochemistry and/or the vertical profile of  $\text{O}_2$ .

**References:** [1] Wiens R. C. et al. (2013) *Spectrochimica Acta Par B*, 32, 1–27. [2] Johnson J. R. et al. (2014) *Icarus*, in press. [3] Nair H. et al. (1994) *Icarus* 111, 124. [4] Clancy R. T. and Nair H. (1996) *JGR* 101, 12785. [5] Mahaffy et al. (2013) *Science*, 341, 263–266. [6] Hartogh P. et al. (2010) *A&A*, 521, L49. [7] Trainer M. G. et al. (2014) 8<sup>th</sup> International Conference on Mars. [8] Smith M. D. (2004) *Icarus*, 167, 148–165. [9] Maltagliati L. (2011) *Icarus*, 213, 480–495. [10] Smith M. D. et al. (2009) *JGR*, 114, E00D03. [11] Toigo A. D. et al. (2013) *JGR*, 118, 89. [12] Gomez-Elvira et al. (2012) *Space Science Reviews*, 2012, 583–640. [13] Harri A-M. (2014) *JGR*, 119, 82–92. [14] Lemmon M. T. et al. (2014) 8<sup>th</sup> International Conference on Mars.



**Figure 2:** Mixing ratio of SAM-measured Ar and ChemCam-measured  $\text{O}_2$  as a function of  $L_s$ . Both quantities are scaled to 1.0 at  $L_s = 322^\circ$ .  $2\sigma$  error bars are shown.