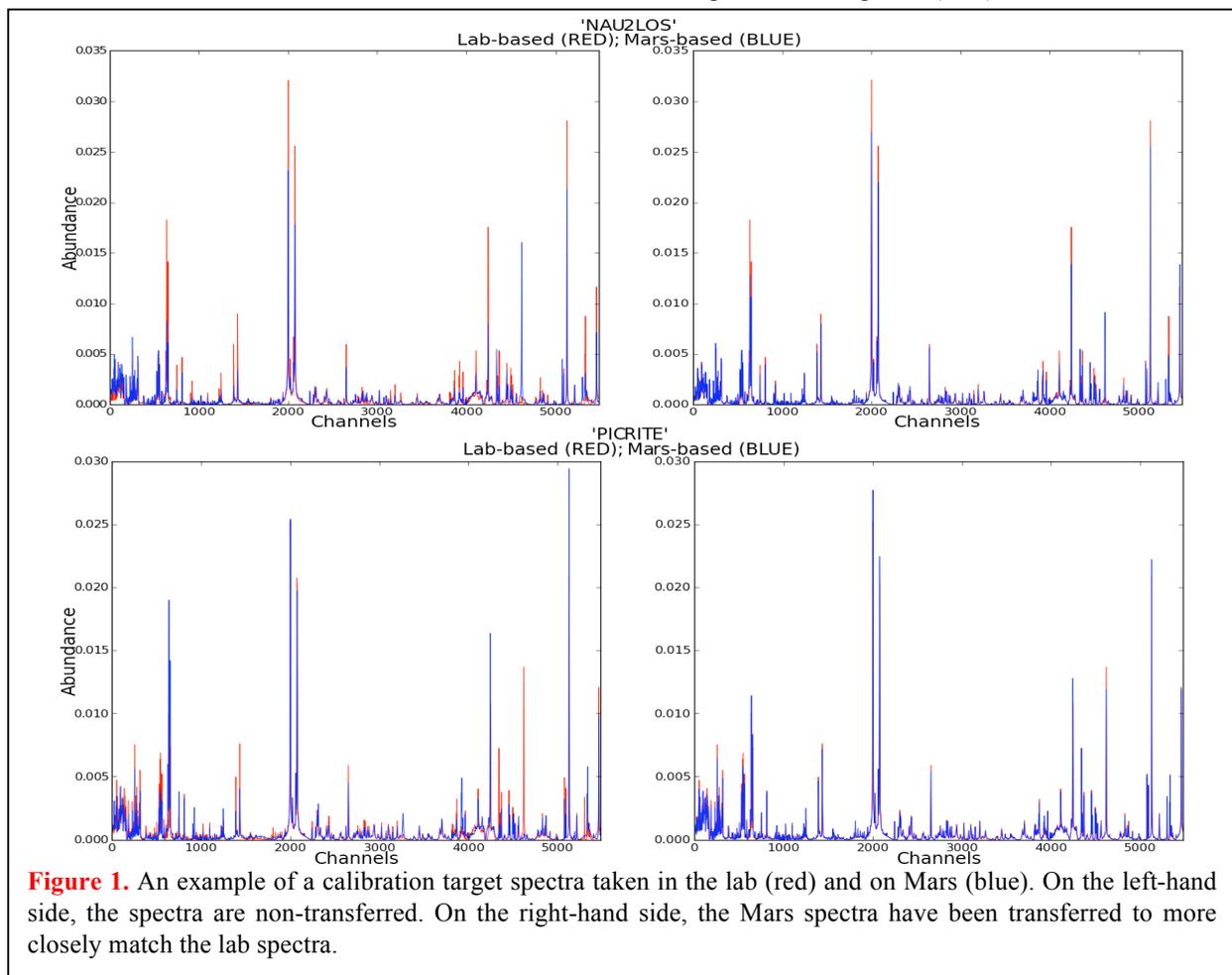


**CALIBRATION TRANSFER OF LIBS SPECTRA TO CORRECT FOR MARS-EARTH LAB DIFFERENCES.** T. Boucher<sup>1</sup>, M.D. Dyar<sup>2</sup>, C. Carey<sup>1</sup>, S. Giguere<sup>1</sup>, S. Mahadevan<sup>1</sup>, S. Clegg<sup>3</sup>, R. Anderson<sup>4</sup>, and R. Wiens<sup>3</sup>, <sup>1</sup>University of Massachusetts, 140 Governors Dr. Amherst, MA 01003, USA (boucher@cs.umass.edu), <sup>2</sup>Mount Holyoke College, 217 Kendade Hall, South Hadley, MA 01075, USA, <sup>3</sup>Los Alamos National Laboratory, Los Alamos, NM 87544, USA, <sup>4</sup>U.S. Geological Survey, Flagstaff, AZ 86001, USA.

**Introduction:** In all spectroscopic applications, there is a need to ensure that possible differences in instruments, environment, or experimental conditions are mitigated or negated. Calibration transfer (CT) is a technique for transferring a calibration curve from one instrument to another using a calculated transfer function, without the need to resample the calibration standards [1]. CT can also be used to transfer the calibration curve of an instrument from one set of environmental conditions to a differing set of conditions. CT provides an excellent solution to the task of reconciling data for inter- and intra-lab comparisons on Earth and in extraterrestrial applications.

In this work, CT is used to correct for environmen-

tal and instrument differences when predicting compositions of the laser-induced breakdown spectroscopy (LIBS) calibration targets created for the Mars rover *Curiosity*. Nine calibration targets of varying, known composition were mounted to *Curiosity*, with duplicates reserved for terrestrial labs [2]. Since arriving on Mars, the calibration targets have been lasered hundreds of times, and a comparison between the Mars-based and the lab-based spectra can be seen on the left-hand side of **Figure 1**. Although great care was taken in the lab to simulate the Martian atmosphere and the Chem-Cam instrument, the spectra of the same calibration targets are still noticeably different. In this work, we used partial least squares (PLS) to calculate a transfer



function between the calibration targets to align spectra from Mars and terrestrial laboratories.

**Data and Methods:** A subset of seven calibration targets located aboard *Curiosity* were used to formulate a CT function to relate Martian spectra recorded by ChemCam to lab-based spectra recorded under simulated Mars conditions using a similar LIBS instrument. To gauge the quality of the transfer function, a calibration curve, fit using lab-based spectra, was used to predict the composition of the Martian calibration targets, with and without the use of the transfer function. To fit the 10-component PLS calibration curve, 329 mineral samples recorded at Los Alamos National Laboratory under Mars-like conditions were used [3]. This calibration curve was fit to predict the weight % oxide of nine major elements (e.g., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>). All of the spectra used in the experiment were baseline removed and normalized according to Wiens et al. [4].

Leave-one-out cross validation (LOO-CV) was used to *quantitatively* measure the effectiveness of the transfer function. For each fold of cross validation, a transfer function  $T$  was calculated using all but one calibration target, and then the omitted target was transformed using  $T$  and predicted using the calibration curve.

The transfer function  $T$  was calculated using:

$$CalTargets_{Lab} = (CalTargets_{Mars} - \mu_{Mars}) \times T + \mu_{Lab}, \quad (1)$$

where  $CalTargets_{Lab}$  and  $CalTargets_{Mars}$  were the 6 training calibration targets recorded in the lab and on Mars respectively, and  $\mu_{Lab} = \text{mean}(CalTargets_{Lab})$  and similarly for  $\mu_{Mars}$ . To solve for  $T$  in equation 1, we used a standard PLS algorithm [5] with only one component, setting  $X = CalTargets_{Mars} - \mu_{Mars}$  and  $Y = CalTargets_{Lab} - \mu_{Lab}$ . By mean centering the data, the PLS algorithm yielded a zero bias, and so  $T$  was equal to the final PLS model weights. After calculating  $T$ , it was used to transfer the 7<sup>th</sup> testing calibration target (like in equation 1), and the lab calibration curve was used to predict the transformed target. For com-

**Table 1.** Element-wise root-mean-squared error of predicted samples from the leave-one-out cross validation of the seven calibration targets [2].

|                                | RMSEP<br>w/o CT | RMSEP<br>w/ CT | %<br>Difference |
|--------------------------------|-----------------|----------------|-----------------|
| SiO <sub>2</sub>               | 12.76           | 12.84          | -0.60           |
| TiO <sub>2</sub>               | 0.89            | 0.81           | 9.76            |
| Al <sub>2</sub> O <sub>3</sub> | 12.31           | 8.44           | 31.41           |
| FeO <sub>T</sub>               | 7.93            | 5.05           | 36.31           |
| MnO                            | 0.07            | 0.04           | 35.46           |
| MgO                            | 7.73            | 5.91           | 23.54           |
| CaO                            | 5.63            | 2.20           | 60.98           |
| Na <sub>2</sub> O              | 2.91            | 1.92           | 34.05           |
| K <sub>2</sub> O               | 0.70            | 0.36           | 48.04           |

parison, the non-transferred testing target was also predicted using the same curve. **Figure 1** shows a comparison between the Mars and the lab spectra with and without CT, providing compelling *qualitative* evidence of the effectiveness of CT for LIBS spectra.

**Results and Discussion:** The root-mean-squared error of prediction (RMSEP) expressed in weight % was first analyzed for each of the nine major elements predicted (**Table 1**). Using CT decreased the RMSEP of all elements predicted except SiO<sub>2</sub>, which had an insignificant increase in RMSEP. CT proved to be especially effective for CaO, Al<sub>2</sub>O<sub>3</sub>, and FeO<sub>T</sub>.

The effectiveness of CT was analyzed across the calibration targets individually in **Table 2**. The sample-wise performance was similar to the element-wise performance, where CT effectively lowered the RMSEP for six of the seven targets. The predictive performance for all calibration targets except shergottite was improved.

**Table 2.** Sample-wise root-mean-squared error of predicted samples from the leave-one-out cross validation of the seven calibration targets [2].

|             | RMSEP<br>w/o CT | RMSEP<br>w/ CT | %<br>Difference |
|-------------|-----------------|----------------|-----------------|
| KGAMEDS     | 8.207           | 6.582          | 19.807          |
| NAU2HIS     | 10.631          | 8.976          | 15.574          |
| NAU2LOS     | 7.008           | 4.343          | 38.022          |
| NAU2MEDS    | 8.461           | 7.279          | 13.972          |
| NORITE      | 5.875           | 3.202          | 45.492          |
| PICRITE     | 5.151           | 4.680          | 9.136           |
| SHERGOTTITE | 3.157           | 3.155          | 0.036           |

Thus, our results show that PLS-based CT successfully transfers Mars calibration target spectra to more closely resemble spectra of the same targets acquired with a different instrument at Los Alamos. Furthermore, CT improves the ability of the lab calibration curve to accurately predict elemental composition.

In the future, we plan to examine sparse transfer methods. In this experiment, the seven LOO-CV transfer functions were all dense  $5485 \times 5485$  matrices of 64 bit (double precision) floating-points, which totaled more than 1.6 GB. A sparse representation would reduce the storage and memory costs of using CT.

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