

THE SEARCH FOR RARE EARTH ELEMENTS AND YTTRIUM (REY) IN CHEMCAM LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) DATA. A. M. Ollila¹, S. Clegg¹, A. Reyes-Newell¹, O. Forni², P.-Y. Meslin², N. Lanza¹, P. Gasda¹, B. Clark³, O. Gasnault², S. Maurice², R. Wiens¹. ¹Los Alamos National Laboratory, Los Alamos, NM, USA, amo@lanl.gov, ²IRAP, Toulouse, France, ³SSI, Boulder, CO, USA.

Introduction: Rare earth element and yttrium (REY) compositions provide critical information for understanding various geological processes. REY tend to concentrate in minerals such as phosphates and manganese oxides of marine origin. The ChemCam instrument uses Laser-Induced Breakdown Spectroscopy (LIBS) to analyze the chemistry of a material. With this technique, a laser is used to ablate a small volume of a sample. A plasma is formed and as the excited species in the plasma relax, light is given off at wavelengths characteristic of the elemental composition. When present at high concentrations, the ChemCam instrument on the martian rover Curiosity is able to detect REY.

Methods: Using the ChemCam laboratory unit at the Los Alamos National Laboratory, spectra were collected of La-Lu plus Sc and Y (and excluding Pm) as pure (99.9+%) oxides under martian conditions (7 Torr CO₂). Spectra were collected at 1.6 m using 11 mJ/pulse laser power except for Y, which was collected at 3 m with 14 mJ/pulse laser power. REY enriched materials were also analyzed including two rare earth ores (USZ-25-2006 and USZ-42-2006), two oceanic Mn nodules, two phosphate rocks (14-94 and SARM32), and three apatite crystals from Norway, an unknown locality, and Brazil. From information obtained from the certificate included with the REE ores, the dominant REE-bearing phase in USZ-25-2006 is apatite and in USZ-41-2006 is synchisite-bastnaesite (carbonate). Based on the lab spectra, the Norway apatite is likely a chlorapatite while the others are likely fluorapatites. Additionally, a variety of common geological materials with typical, generally low, concentrations of REY were analyzed for comparison. These include basalts, clays, sulfates, carbonates, and Mn-oxides of non-marine origin (57 total samples).

Full compositions including REY are available for the REE ores, ocean nodules, and most of the other geological materials but are not yet available for the phosphate rocks and apatites. USZ-25-2006 and USZ-42-2006 are dominated by Ce (29,000 ppm and 27,600 ppm, respectively), followed by La (~19,300 ppm and 21,100 ppm) with lesser (<10,000 ppm) amounts of the remaining REY. The Mn ocean nodules have lower concentrations of REY (<320 ppm) and are also dominated by Ce and La.

A limited suite of ChemCam data from Gale crater, Mars were also analyzed for REY features. The samples

selected include spectra that display either (1) a strong CaF molecular feature that may indicate the presence of apatite or fluorite [1], (2) high Mn concentrations, or (3) high concentrations of P, including those that are also enriched in Mn, Fe, and/or Mg [2]. These samples are Epworth point 5, Buit Lake point 2, Blackhead point 7, Beacon points 1 and 3, Harrison point 4, Caribou point 5, Stephen point 2 and 3, Khoabendus point 14, Canon Brook point 3, Blue Hill point 6 and 8, Glasnakille point 10, and aegis post 1754a.

Results: The pure oxide REY spectra are very rich in peaks with >100 peaks identified for each element. A list of the three most intense peaks is provided in Table 1. In the REE ores, six La peaks have been tentatively identified (La II 317.255/317.266, 338.188, 412.439, 433.496, 452.364, 462.117 nm) and two Ce peaks (Ce II 416.678 and 462.946 nm). Y has been identified in the Norwegian apatite and tentatively in the apatite of unknown origin. Y peaks are found at 281.787, 294.687, 321.761, 324.321, 417.871, and 437.616 nm. Several of these peaks are shown in Figure 1. No REY peaks were identified in the Mn nodules, phosphate rocks, or the

Element	Subset of the Intense Peaks, nm
La	(III) 317.266, (II) 395.022, (III) 265.229
Ce	305.701*, (III) 303.218, (III) 260.454
Pr	(III) 298.141, (III) 298.669, 396.586*
Nd	290.709**, 290.905**, 290.464**
Sm	330.730*, 443.504*, 428.133*
Eu	(II) 413.086, (II) 420.623, (II) 443.681
Gd	262.889*, (III) 290.558, 310.11*
Tb	329.376*, 322.036*, 328.562*
Dy	250.503**, 251.823**, 321.714*
Ho	389.184*, 251.189**, (II) 283.252
Er	(III) 276.005, (III) 250.935, (III) 279.336
Tm	(II) 307.397, (III) 249.019, (II) 313.217
Yb	266.703*, (II) 329.014, 275.112*
Lu	(III) 260.403, 305.844*, (III) 277.332
Sc	269.929*, 273.491*, 424.793*
Y	(III) 294.687, (III) 281.787, 437.615*

*Multiple possible transitions present in the NIST database

**Not in the NIST database

Table 1: List of the most intense REY peaks in pure oxide spectra. When possible, peak wavelengths are matched to those in the NIST database [2].

other geological materials. No REY peaks were identified in the martian dataset.

Conclusion and Future Work: Numerous REY peaks have been identified in laboratory ChemCam LIBS spectra of pure REY oxides. Ce, Y, and La have likely been identified in REE ores and apatite crystals; concentrations of La and Ce in the ores are high (>~20,000 ppm). REE chemistry will be obtained on the phosphates used in this study to determine if their chemistry is consistent with the LIBS spectra. No REY have been identified in the subset of martian data from Gale crater studied here. This is consistent with work on ChemCam detections of apatites on Mars by [4].

To determine more precise detection limits, additional samples using relevant geological matrices doped with REE should be made and analyzed.

References: [1] Forni O. et al. (2015) *GRL*, 42, 1020-1028. [2] Meslin P.-Y. et al. (2018) 49th LPSC #1447. [3] Atomic Spectra Database 78, version 5.7, doi: <https://dx.doi.org/10.18424/T4W30F>. [4] Forni O. et al. (2020), this conference.

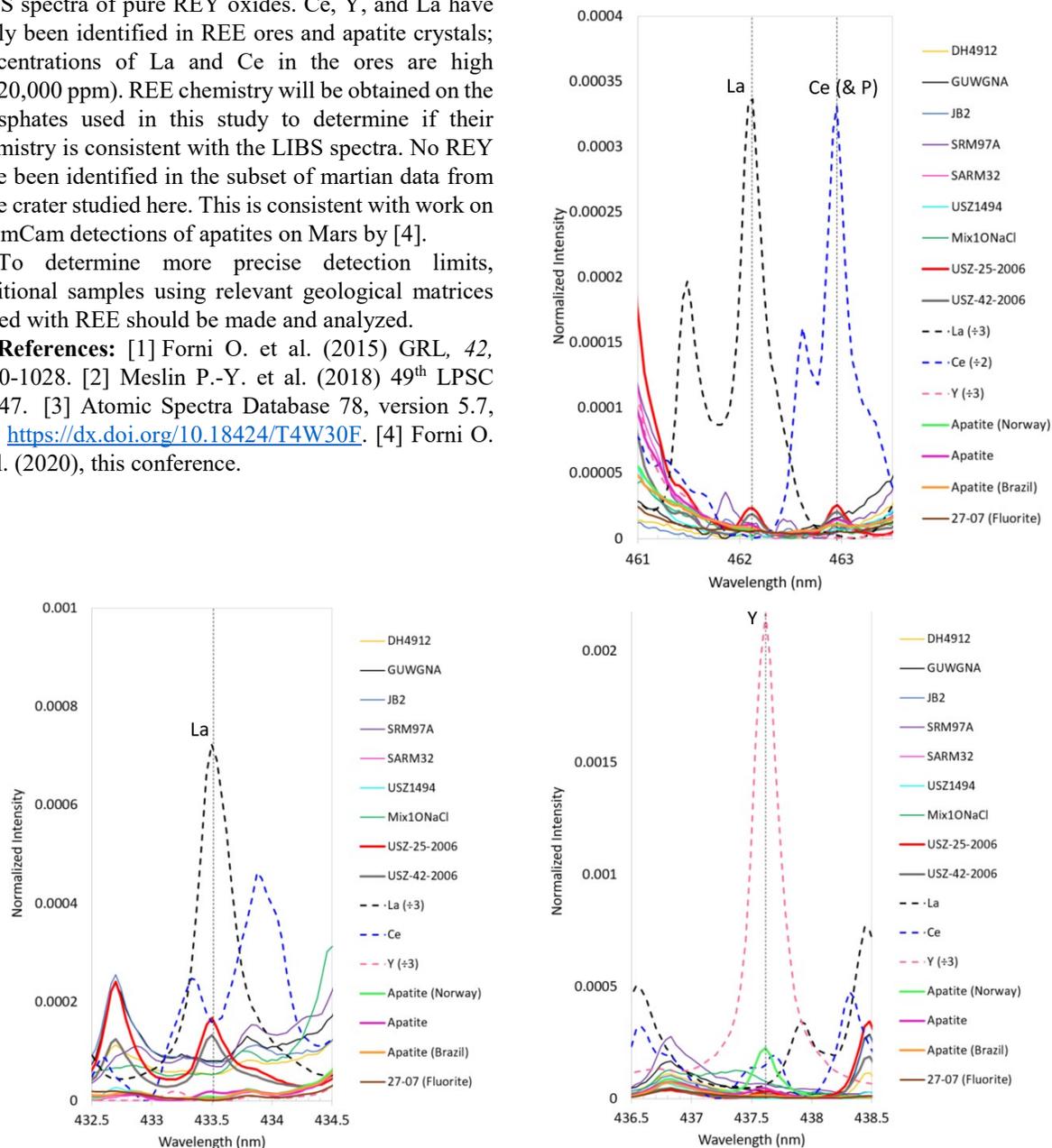


Figure 1: Top Right – Possible La and Ce peaks in the USZ REE ores. Lower Left – La peaks are present in the USZ REE ores and possibly the apatite of unknown origin. Lower Right – Y peak in the Norwegian apatite and possibly in the apatite of unknown origin and USZ-25-2006. The other spectra are geological materials used to provide points of comparison for the REE ores and apatite. They consist of an olivine (DH4912), granite (GUWGNNA), kaolinite (SRM97a), halite (Mix1ONaCl), and fluorite (27-07). Note the scaling of the REY oxide spectra change in each plot.