

**UPDATED EFFECTS OF BULK COMPOSITION ON PREDICTION ACCURACY OF TRACE AND MINOR ELEMENTS USING AN OLYMPUS PORTABLE XRF.** Cai R. Ytsma<sup>1</sup>, M. Darby Dyar<sup>1</sup>, A. S. Plumley<sup>1</sup>, Jane C. Watts<sup>2</sup>, and Josephine King<sup>2</sup>. <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075 (ytsma22c@mtholyoke.edu), <sup>2</sup>Harvey Mudd College, 301 Platt Blvd., Claremont, CA 91711.

**Introduction:** X-ray fluorescence (XRF) is a common method for quantifying the atomic composition of a sample surface and has been used extensively for elemental analyses of planetary surfaces. Technological advances have enabled development of portable X-ray fluorescence (pXRF) instruments convenient for laboratory and field work. These pXRF instruments make it possible to analyze samples in situ with novel ease.

Although previous research has shown that pXRF results are highly reproducible (precise), the accuracy of instrument predictions in geological samples is inconsistent among elements and can be very poor [1,2]. These variations may be due to element-specific interactions with the bulk composition of the material (matrix), which widely varies for geochemical standards.

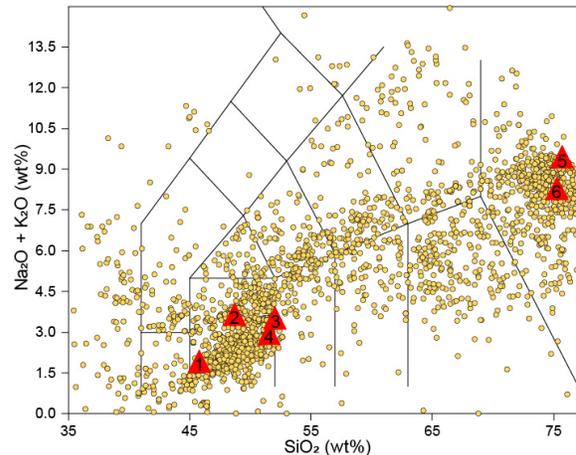
This project explores matrix effects on pXRF trace and minor element quantification with multivariate analysis. Accuracies resulting from models that use many diverse standards are compared against models built using identical matrices. It tests the assumption that calibrations using similar rock types will yield more accurate results than those using dissimilar ones.

**Samples and Spectral Acquisition:** This study analyzed 2,218 naturally occurring geological standards and 467 doped standards. For the latter, powders of seven different rock standards were individually doped with 21 trace elements. Standard matrices included three basalts ('Hawaii', 'Idaho', and 'Holyoke'), one granite ('Maine'), one rhyolite ('Mexico'), sea sand, and a 50:50 mixture of diopside and forsteritic olivine ('Ultramafic'). Compositions of the matrices are well within the range of the natural standards (Figure 1).

Dopants included 21 trace elements in concentrations ranging from 10 ppm to 10 wt%: Ba, Ce, Co, Cr, Cs, Cu, Ga, La, Mn, Mo, Nb, Ni, Pb, Rb, Sc, Se, Sn, Sr, Y, Zn, and Zr [3]. Doped standards with trace element concentrations higher than those in naturally occurring rocks were removed from the suite of calibration standards. The limits for removing those outliers were defined as  $1.5 \times$  the mean of all natural standards plus the inner quartile range, per element.

All samples were crushed to  $\ll 10 \mu\text{m}$  and pelletized at 5 tons of pressure. Spectra were acquired on an Olympus Innov-X DELTA Premium pXRF using 2-beam Geochem mode with a 120 s dwell time, resulting in 5,370 total spectra (one spectrum per standard per beam).

**Data Analysis:** To determine the impact of matrix matching, models were created using a) all standards, designated as 'All'; b) all doped standards, 'All Doped', and c) matrix-specific doped standards.



**Figure 1.** Total Alkali Silica diagram [4] of all 2,685 MHC standards (yellow dots), including six matrices (red triangles) investigated in this study: 1. Ultramafic; 2. Idaho; 3. Holyoke; 4. Hawaii; 5. Mexico; 6. Maine. Sea sand (97.70% SiO<sub>2</sub>) not shown.

The least absolute shrinkage and selection operator (lasso) performed multivariate regression on the calibration standards' full spectral range to create one quantitative model per dataset. Model accuracies were assessed using root-mean-squared errors (RMSEs) of cross-validation (CV) with # folds =  $\sqrt{n}$  standards).

**Results and Discussion:** Accuracies of the best models between the two beams are reported as ppm (Figure 2) and as percentages of the standards' average concentrations (Figure 3) for each element and dataset.

There is generally no clear advantage to using spectra of matrix-matched standards to predict unknowns with assumed similar compositions. There are a few elements where specific matrices give advantageous results but there is no generalizable result among elements studied. For example, the most accurate Ba models are for Maine and Ultramafic, though those are dissimilar compositionally with very different Si. Mn shows the largest spread in absolute values of RMSE-CV as a function of rock type, but again the highest error is for the Idaho basalt matrix and the lowest error for Mexico rhyolite, with others arrayed in between. Overlaps from other lines likely affected some of these element predictions more than others.

Of the matrix-specific models, trace element predictions using the sea sand and Mexico datasets were consistently poor (Figure 3). Both of these matrices are low in transition metals and high in Si, a relatively low-Z element. They may have less Rayleigh scattering and

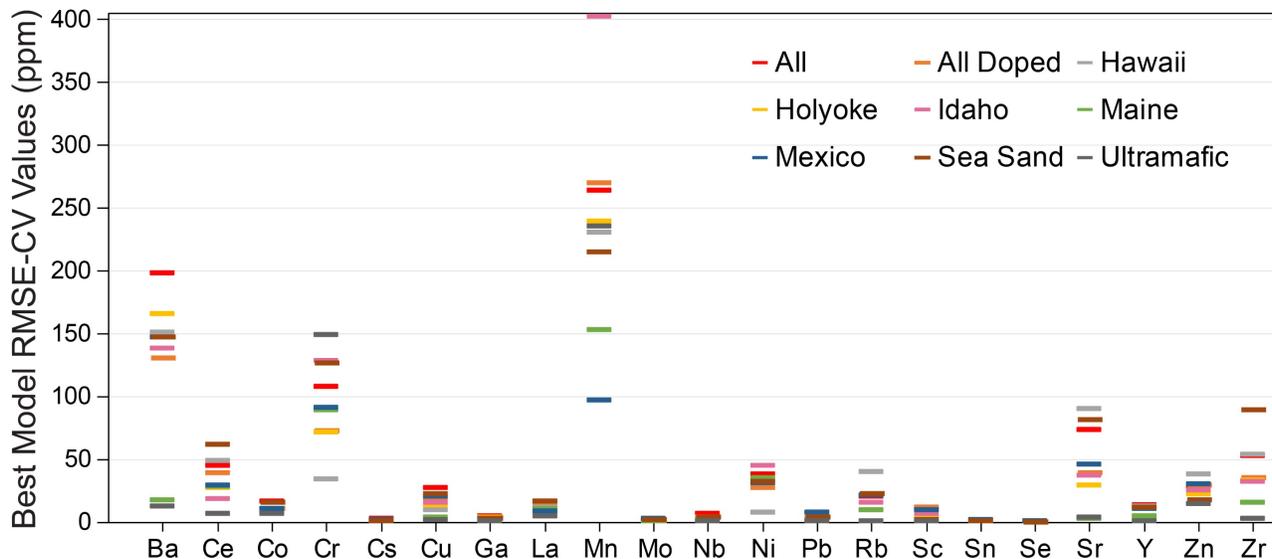


Figure 2. Comparison of model accuracies for all natural and doped samples, all doped samples, and individual rock matrices.

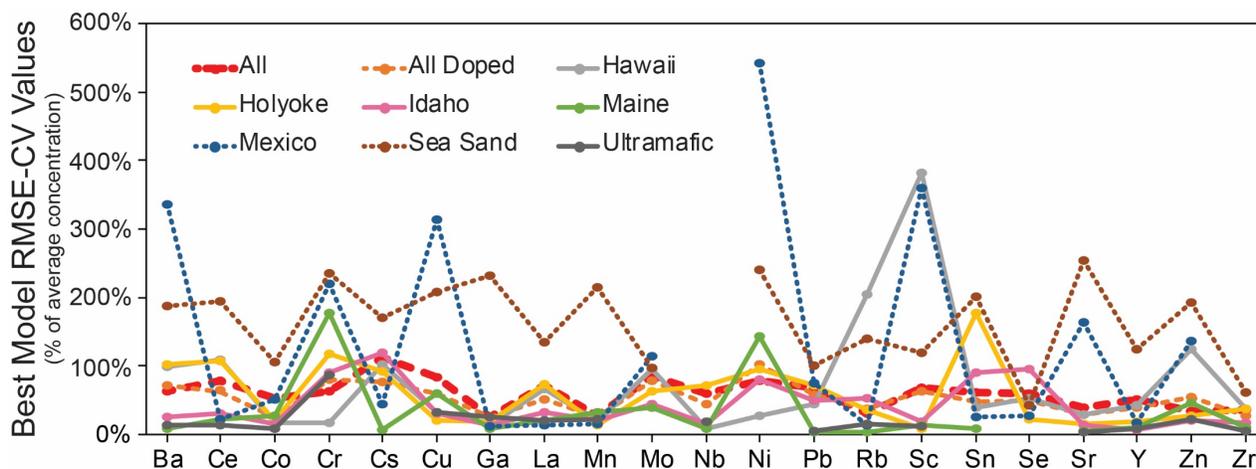


Figure 3. Comparison of model accuracies for all natural and doped samples (red dashes), all doped samples (orange dashes), and individual rock matrices (dotted for Mexico and sea sand, solid for other matrices).

therefore less secondary fluorescence of trace elements that would enhance emission signals. At the other extreme, the highest transition metal matrix, Ultramafic, created models with the best quantification accuracies. The presence of more high-Z elements may enhance trace element fluorescence and make their detection easier. However, none of the major oxide elements has an atomic number high enough to excite a majority of the trace elements studied here.

Differences among matrix-specific model inaccuracies may also be related to differences in the size of the standard suites. The average number of calibration standards among elements was 1,689 within ‘All’ standards and 57 within the matrix-specific datasets. Errors could be inflated for smaller datasets due to selection of folds in each regression. For example, the line of best fit may be more altered when five samples are removed from a suite of 25 standards than when 45 samples are taken from a suite of 2,000.

**Summary:** Differences among matrix-specific model performances illustrate that pXRF trace element quantification accuracies *are* affected by the bulk compositions of the standards used for modeling. The observed differences are not systematically a function of any specific variable, and so these data and this concept deserve further study. Future work should consider using a broader range of matrices to elucidate better more general trends with changing composition.

**Acknowledgments:** Supported by NASA grants to the Massachusetts Space Grant Consortium, NNX15AC82G, and RIS<sup>4</sup>E (NNA14AB04A). We thank Goddard SFC for the loan of the pXRF.

**References:** [1] Brand N.W. & Brand C.J. (2014) *Geochem. Expl. Env. Anal.* 14, 125-138. [2] Hall G.E.M. et al. (2014) *Geochem. Expl. Env. Anal.* 14, 99-123. [3] Dyar M.D. et al. (2019) *LPSC L*, Abstr. #1396. [4] Le Bas M.J. et al. (1986) *J. Petrol.*, 27, 745-750.