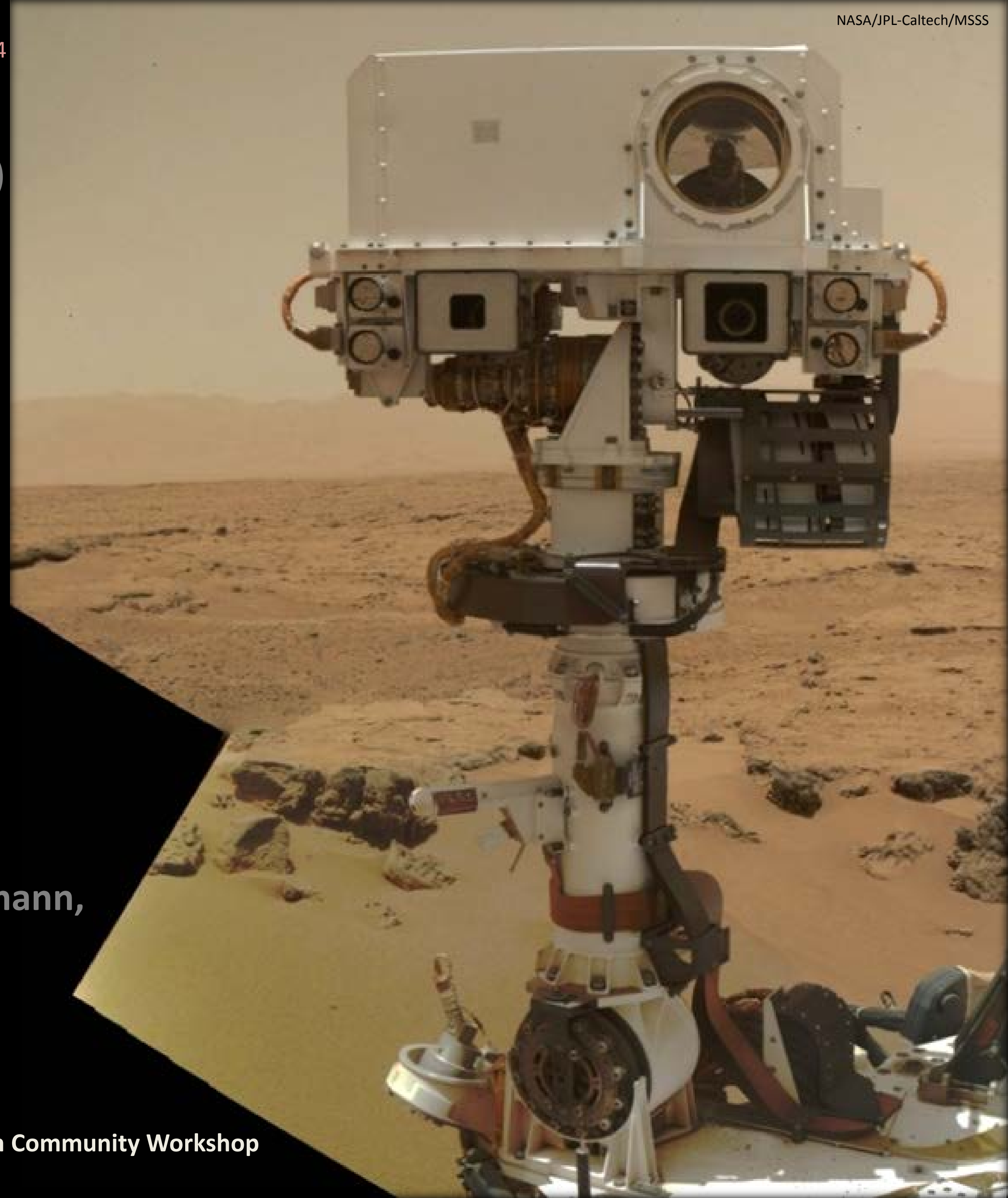
Lunar and Planetary Science Conference, March 16th, 2014

COMMUNITY USER WORKSHOP ON PLANETARY LIBS (CHEMCAM) DATA

LIBS data processing – Level 2



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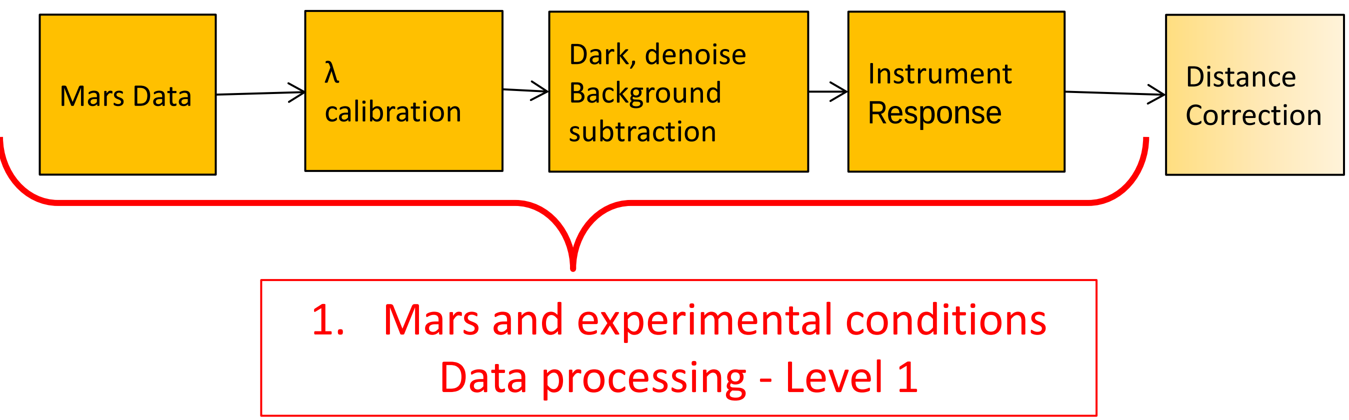
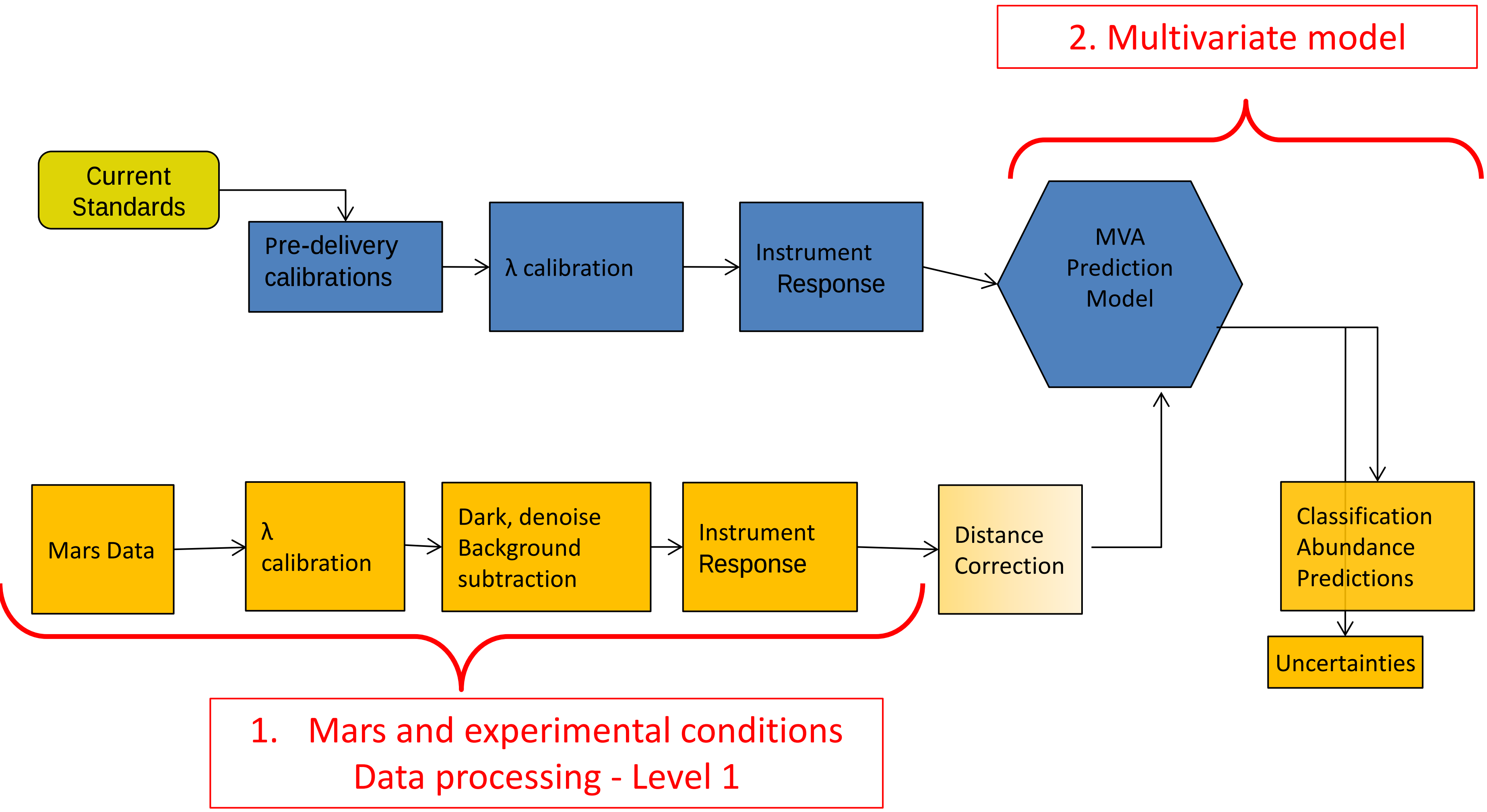
LIBS data processing – Level 2




2. Multivariate model
Current Standards
Pre-delivery calibrations
λ calibration
Instrument Response
MVA Prediction Model
Mars Data
λ calibration
Dark, denoise Background subtraction
Instrument Response
Distance Correction
Classification Abundance Predictions
Uncertainties
1. Mars and experimental conditions
Data processing - Level 1

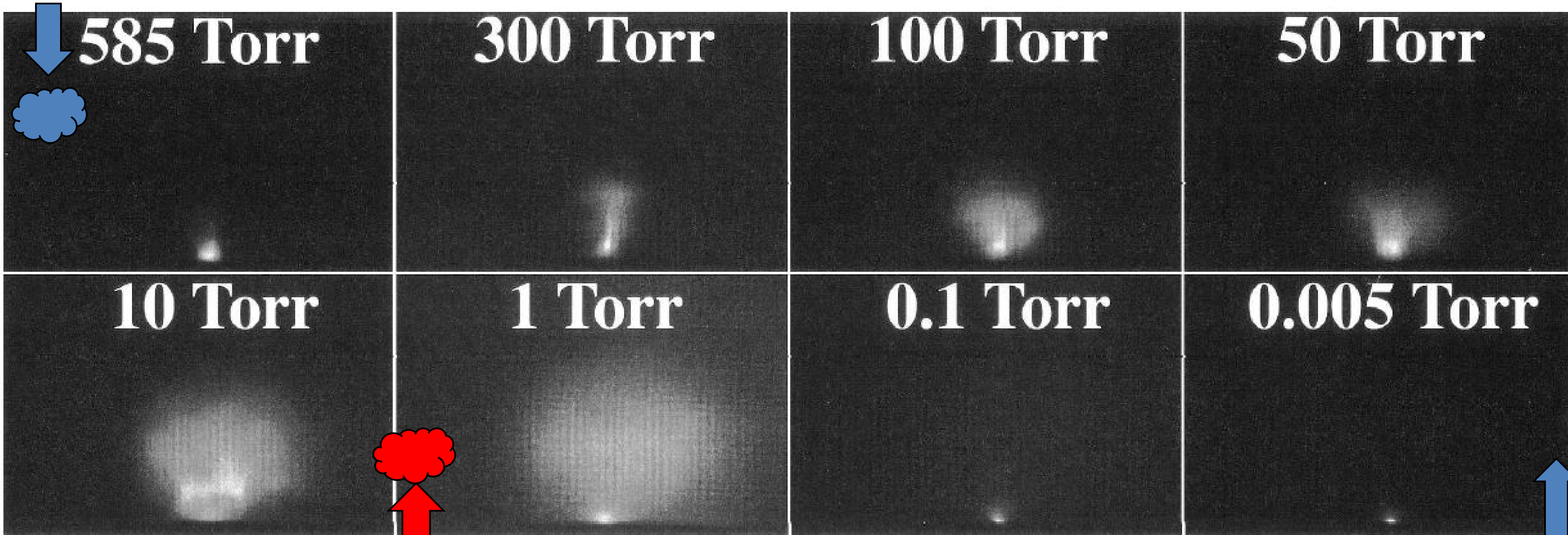
Mars conditions vs. experimental conditions

Environmental conditions on Mars almost constant (observations taken at ~ same time)

- Temperature variations can shift λ. Corrected automatically to better than 0.2 pix. MVA models errors increase <10% (Wiens et al. 2013)
- Pressure change (~40 Pa) has negligible effect on the plasma intensity and temperature.
- Note: calibration taken under Mars conditions

Evolution of LIBS plasma with pressure

Earth atmospheric pressure (760 Torr)



Mars atmospheric pressure (5-7 Torr)

Lunar surface pressure (10^{-8}-10^{-12} Torr)

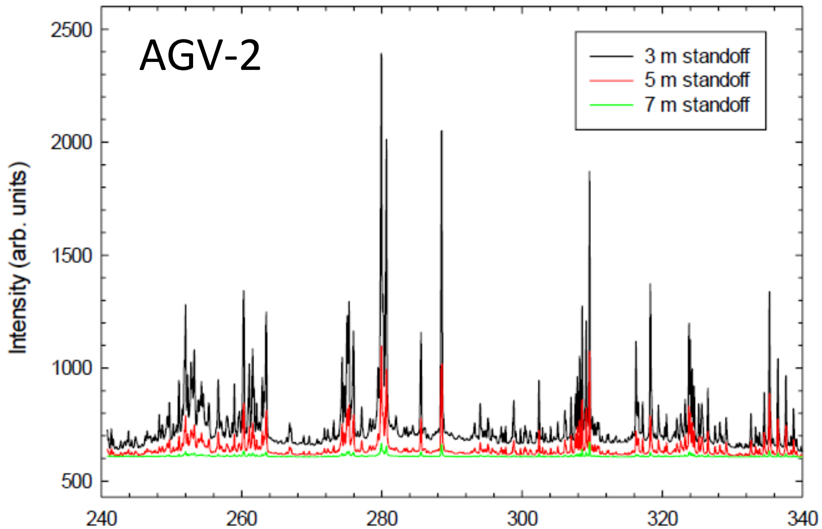
REMS Mars daytime variation 40 Pa ~ 0.3 Torr

Knight et al. 2000: Al I emission at 394.4 nm, Los Alamos soil; gated window between 50ns and 200ns.
See also: Clegg et al., 2007; Mezzacappa et al., LIBS 2010; Lasue et al., LPSC 2011

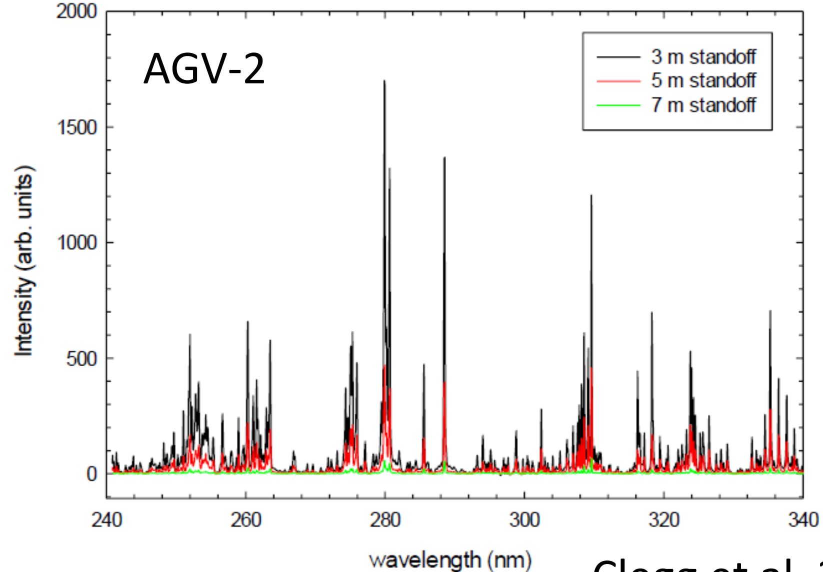
AGV-2 Calibration Spectra at 3, 5, and 7 m Standoff Distance

Distance correction

Raw Spectra

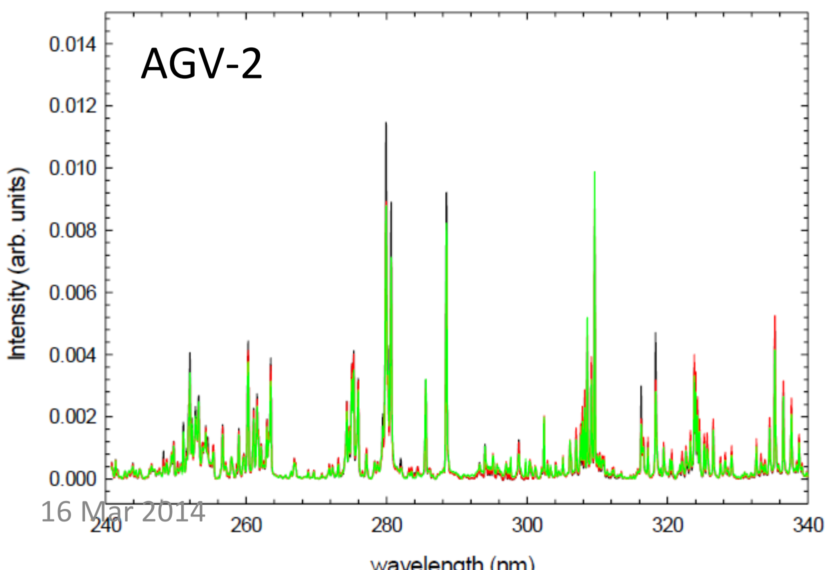


Continuum Removed



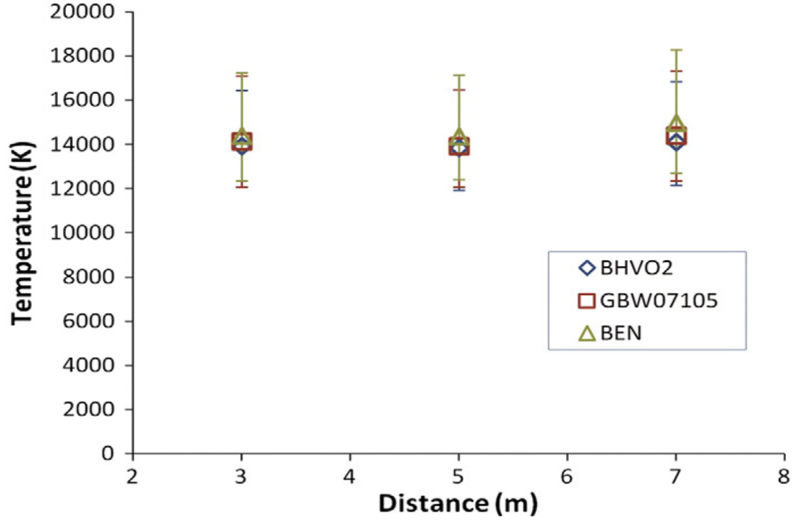
Clegg et al. 2013

Continuum Removed + Normalized



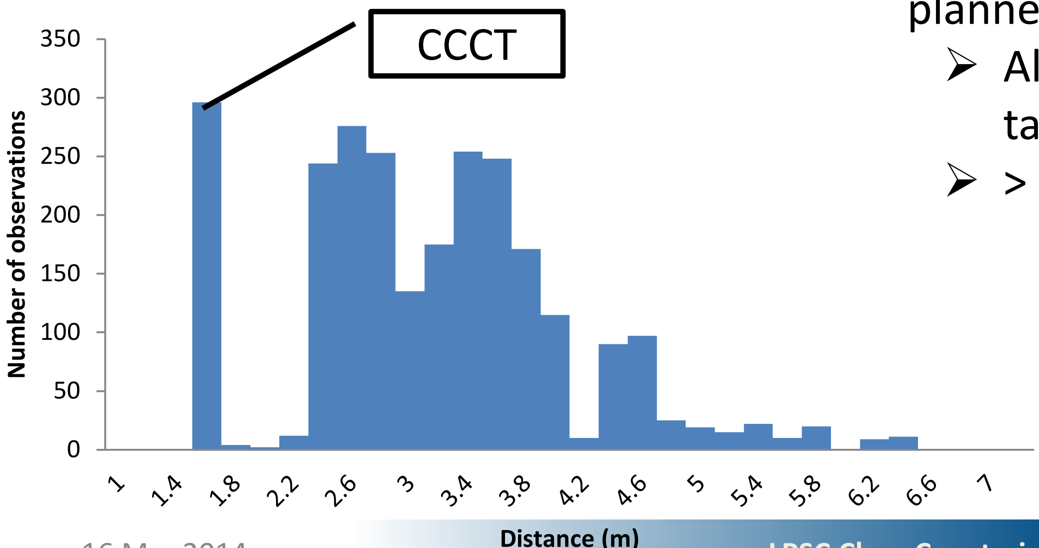
- Background subtraction, instrument response ($1/r^2$) and normalization correct to 1st order
- Improved distance correction in progress (Melikechi et al., 2014, Mezzacappa et al., 2014)

Distance correction



- Plasma temperature is independent of distance Wiens et al., 2013

Distance of observation



- ~75% of observations between 2m and 4m, but some out to 7m.
- Observations using the arm require strategic planning, but ChemCam observations can be planned tactically
    - Allows rapid response to interesting targets
    - > 100000 shots last December

Multivariate Analysis Quantification

- Chemical matrix effects complicate LIBS quantitative analysis
  - Univariate analysis tends to fail when the model and unknowns differ
  - Multivariate analysis developed to compensate (Clegg et al., 2008; Dyar et al., 2012)
- Partial Least Squares 2 (PLS2)
  - Regress multiple x observations (spectra) against *multiple* y variables (elemental compositions)
  - Problems:
    - Single set of calibration spectra are selected for all (major) elements.
    - Single number of principal components (PCs) used for all (major) elements.
- Partial Least Squares 1 (PLS1)
  - Regress multiple x observations (spectra) against *single* y variable (elemental composition)
  - Advantages:
    - Customizable: # of components, normalization, training set can be optimized separately for each element.
    - This makes it much easier to re-optimize in the future as new training spectra are introduced.

Quantitative elemental calibration

- 66 Geochemical Standards Calibration Database, Collected with the ChemCam Flight Model under Mars atmospheric conditions
- Partial Least Squares 1 (PLS1)
- Generate independent optimized models for all major element oxide: SiO_2, TiO_2, Al_2O_3, FeOT, MgO, CaO, Na_2O, K_2O
  - Adjustable parameters:
    - Training spectra

1. Number of components
2. Normalization
3. "Optimum" model defined as minimum leave-one-out cross validation RMSE

- Al_2O_3 and CaO are exceptions based on expected geochemical behavior

- Sample Identification (Cluster Analysis) (for the Level 3 and above)
  - Principal Components Analysis (PCA)
  - Soft Independent Modeling by Class Analogy (SIMCA)
  - Independent Components Analysis (ICA)

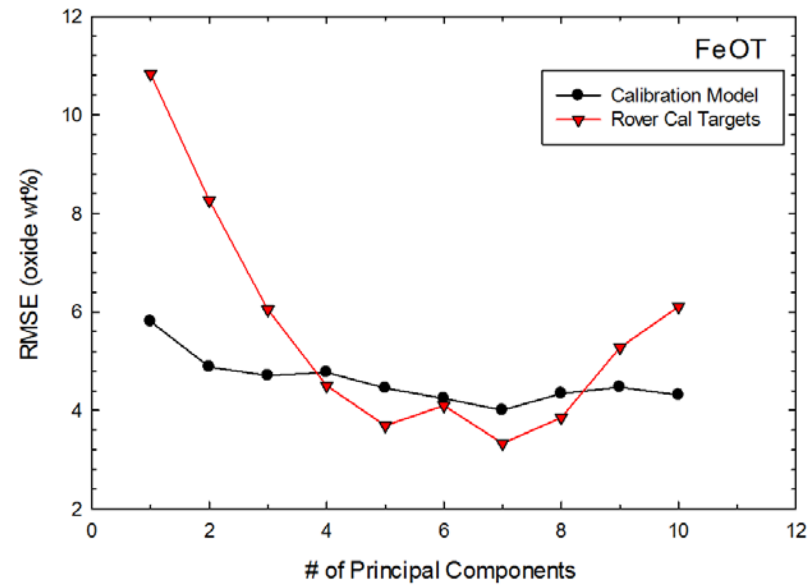
Quantitative elemental calibration

- Root Mean Square Error (RMSE)
  - RMSE is the standard chemometric method to estimate model accuracy
  - Derived from the laboratory calibration standards collected on FM prior to delivery
    - 66 Standards, 4 analyses per standard
  - Leave one standard out of the model.
    - Use the resulting model to calculate the composition of the standard left out of the model.
    - Calculate the error (E^2) in the concentration
      - E^2 = (accepted value – observed value)^2

$$RMSE = \left(\frac{\sum_{n\ standards} E_i^2}{n - 1} \right)^{0.5}$$

Quantitative elemental calibration

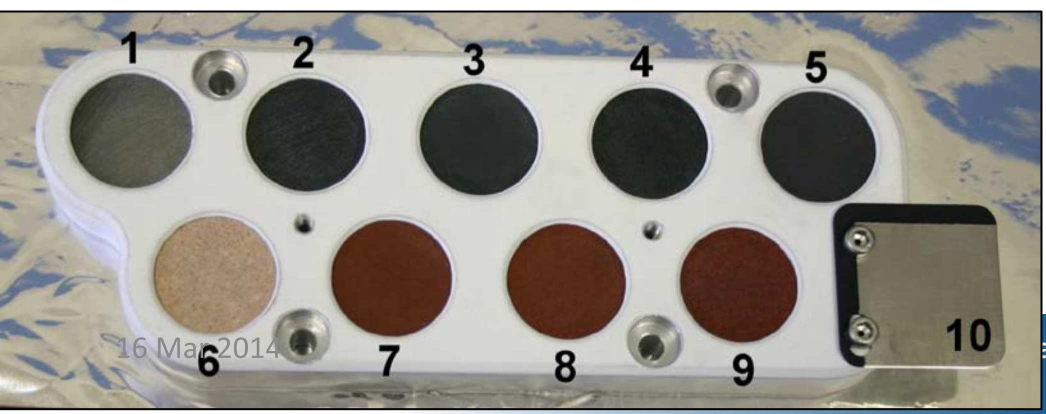
- Model Adjustable Parameters
  - Principal Components (PCs)
  - Normalize to Integrated Intensity
    - Normalize to sum of all pixels (6144) from all spectrometers
    - Normalize to sum of all pixels (3x2048) in each respective spectrometer (UV, VIS, VNIR).
  - Standards used in the model.
- Select Elemental Model with the Minimum Validation RMSE.



Calibration Targets on Rover

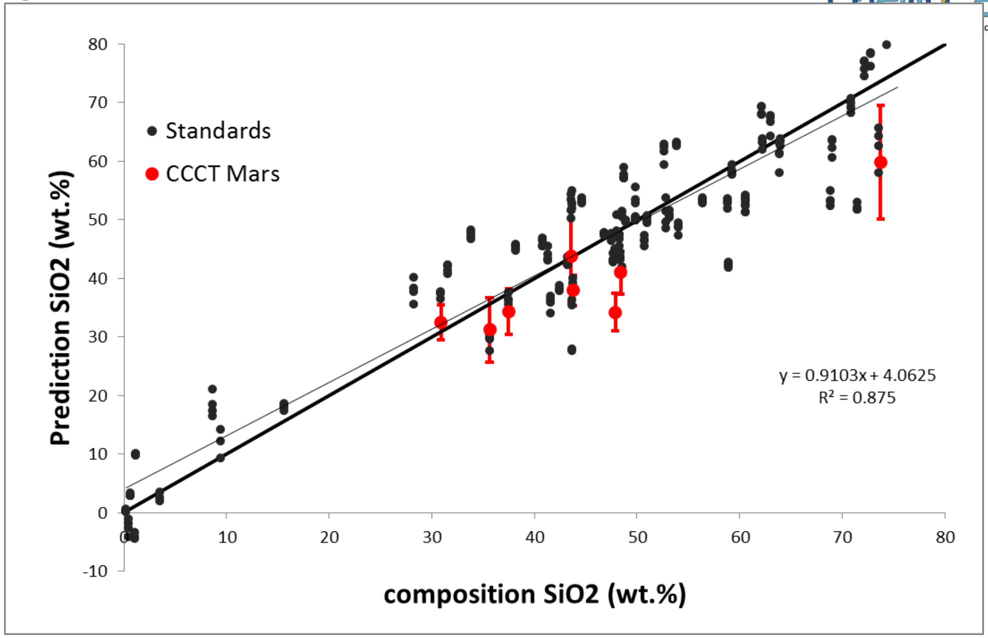
1. Macusanite volcanic glass
2. Norite synthetic glass
3. Picrite synthetic glass
4. Shergottite synthetic glass
5. Graphite
6. Kaolinite ceramic
7. Nontronite ceramic
8. Nontronite ceramic
9. Nontronite ceramic
10. Titanium plate (diagnostics)

References:
1-4: Fabre et al., 2011
6-9: Vaniman et al., 2012



Quantitative elemental calibration

Matrix effects and some experimental effects are taken into account in the multivariate training set.



	SiO2	TiO2	Al2O3	FeOT	MgO	CaO	Na2O	K2O	Total
TRAINING SET MIN.	0.2	0	0	0	0	0.1	0	0	
TRAINING SET 1ST QUARTILE	40.8	0.27	5	2.7	0.8	2.5	0.3	0.3	
TRAINING SET MEDIAN	48.6	0.68	13.1	6	2.2	7.1	2.4	0.8	
TRAINING SET 3RD QUARTILE	59.3	1.47	16.1	12.1	6.4	12.8	3.4	1.8	
TRAINING SET MAX.	75.4	5.9	38.8	36.2	49.2	54.9	5.9	6.4	
NORMALIZATION	3	1	1	1	1	3	1	3	
NUMBER OF COMPONENTS	8	10	4	7	8	8	10	4	
RMSEP	7.1	0.55	3.7	4	3	3.3	0.7	0.9	10.1

Quantitative elemental calibration

Table 4. Precisions obtained on synthetic glass Norite and Shergottite rover calibration targets. Exact compositions are given for reference.

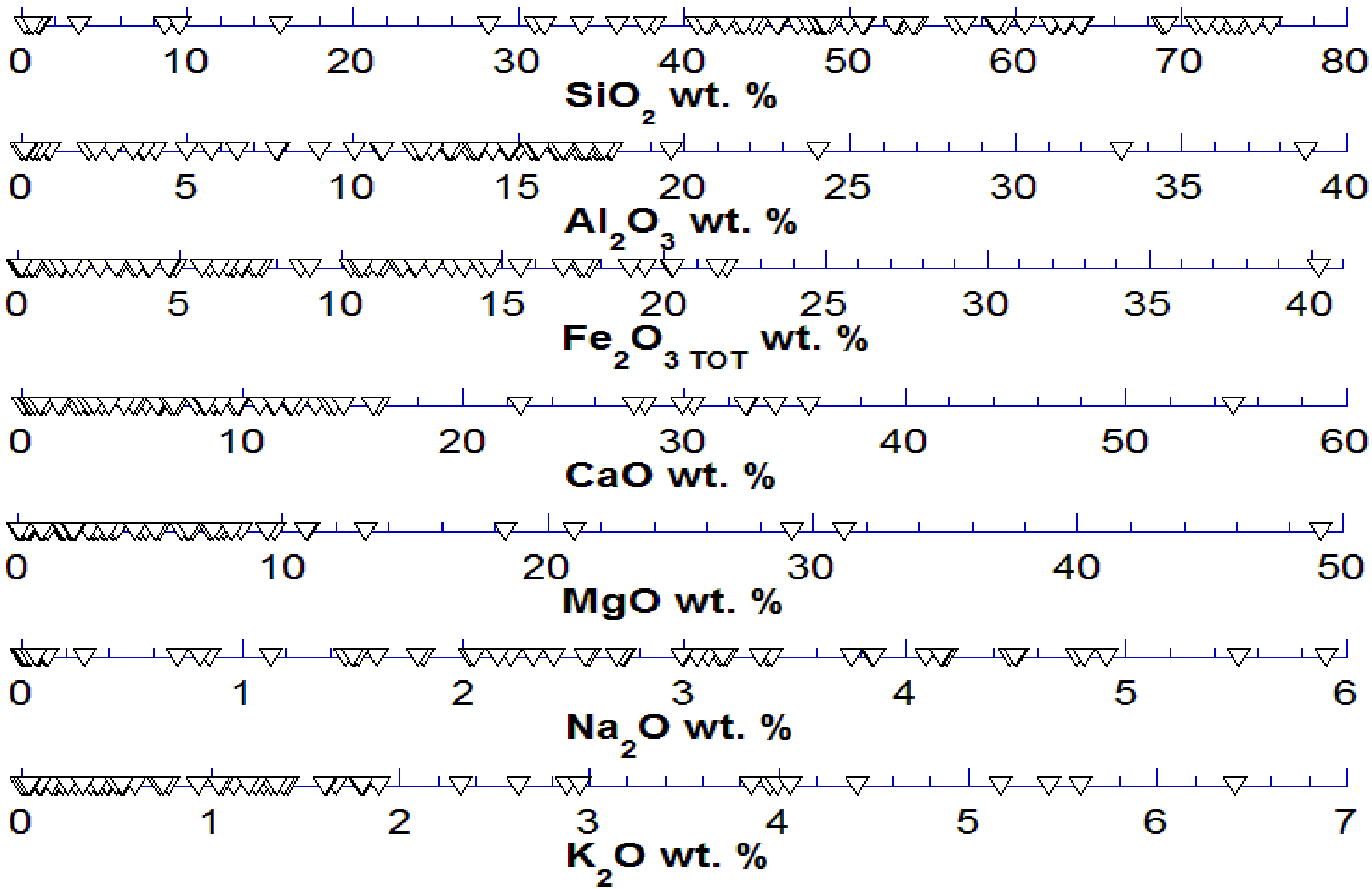
	n	SiO_2	TiO_2	Al_2O_3	FeOT	MgO	CaO	Na_2O	K_2O
Norite[a]		47.9	0.70	14.7	15.9	9.62	12.8	1.53	0.06
Std dev sol 352	9	0.34	0.05	0.12	0.24	0.12	0.32	0.11	-----
Std dev sol 357	9	0.68	0.04	0.21	0.27	0.13	0.50	0.12	-----
Shergottite[a]		48.4	0.43	10.8	17.6	6.39	14.3	1.57	0.11
Std dev sol 271	7	0.60	0.03	0.18	0.26	0.14	0.37	0.10	0.04
Std dev sol 352	9	0.62	0.04	0.14	0.23	0.15	0.30	0.09	0.04
Std dev sol 357	9	0.37	0.02	0.07	0.12	0.07	0.35	0.11	0.04
Mean std dev	5	0.43	0.05	0.13	0.27	0.09	0.30	0.11	0.04
Std dev, all Shergottite obs.	25	1.53	0.14	0.57	1.83	0.49	0.42	0.49	0.14

[a]Norite and Shergottite compositions are from Wiens et al. (2013).

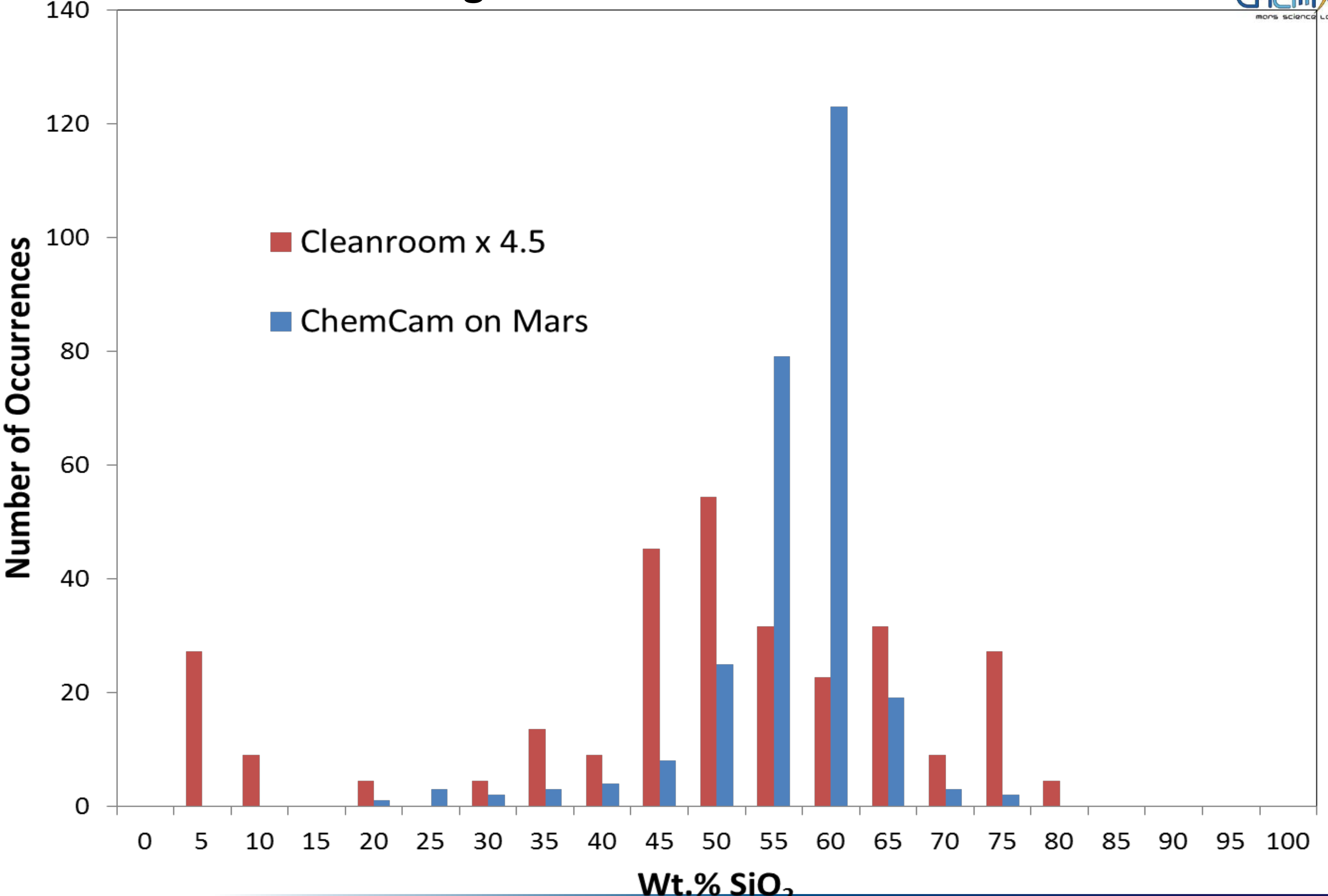
Blaney et al., submitted

Calibration database ranges

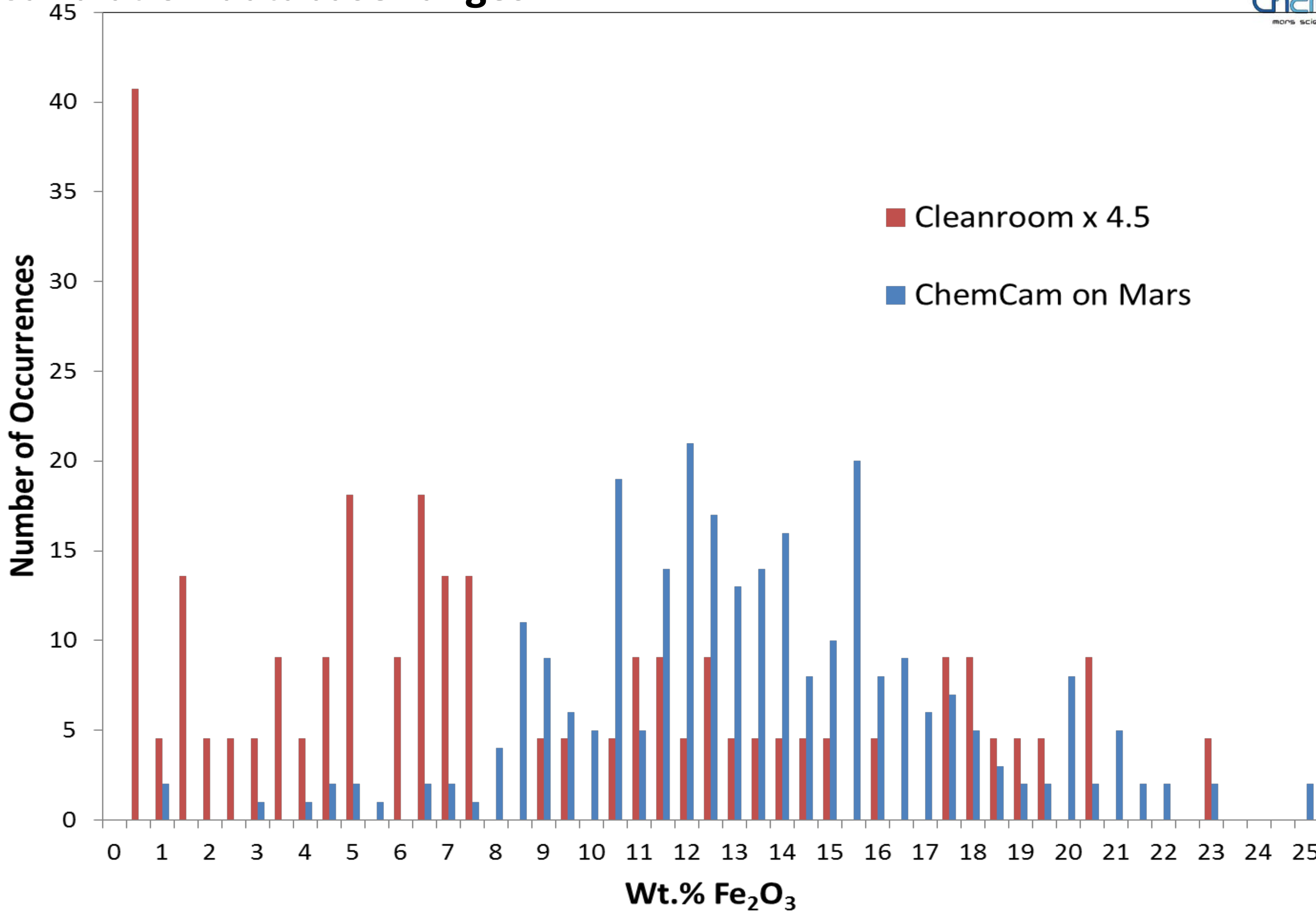
Wiens et al., 2013



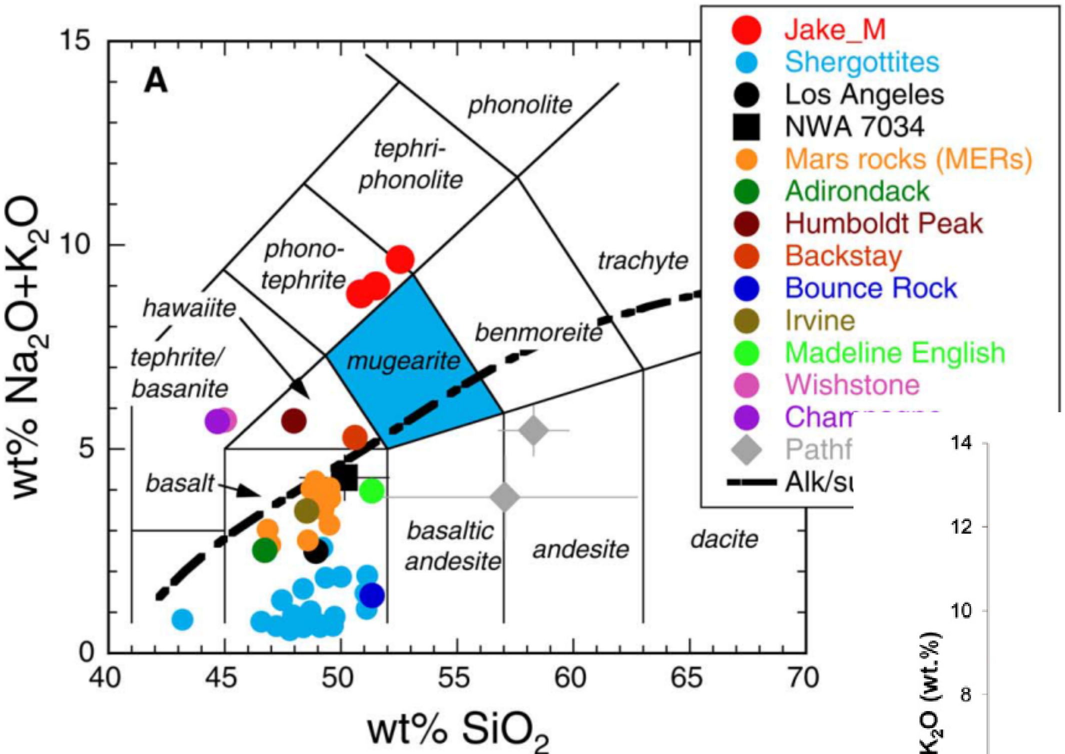
Calibration database ranges



Calibration database ranges



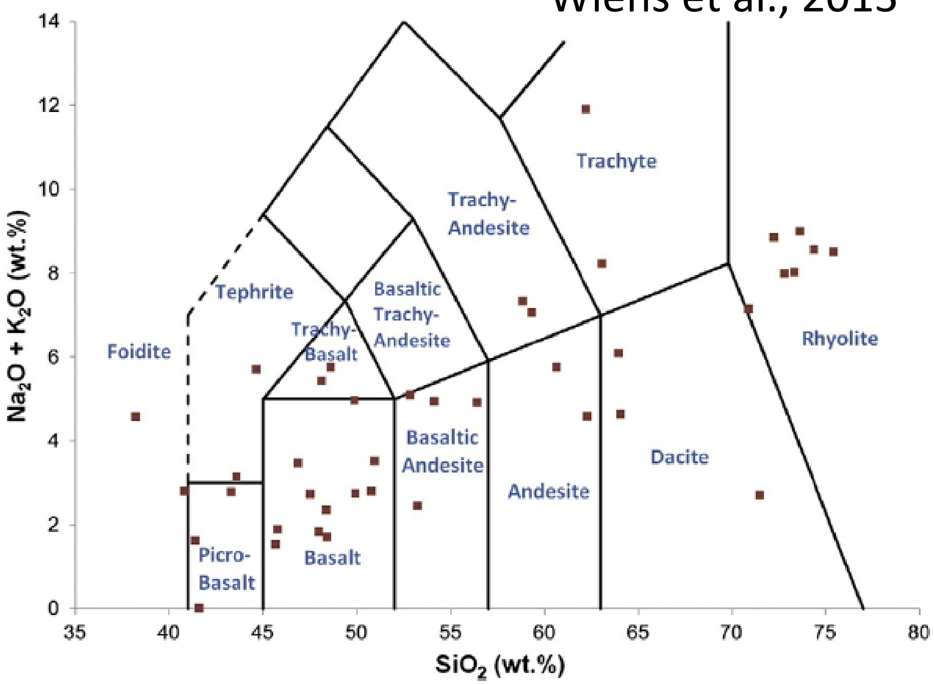
Calibration database ranges



Stolper et al., 2013

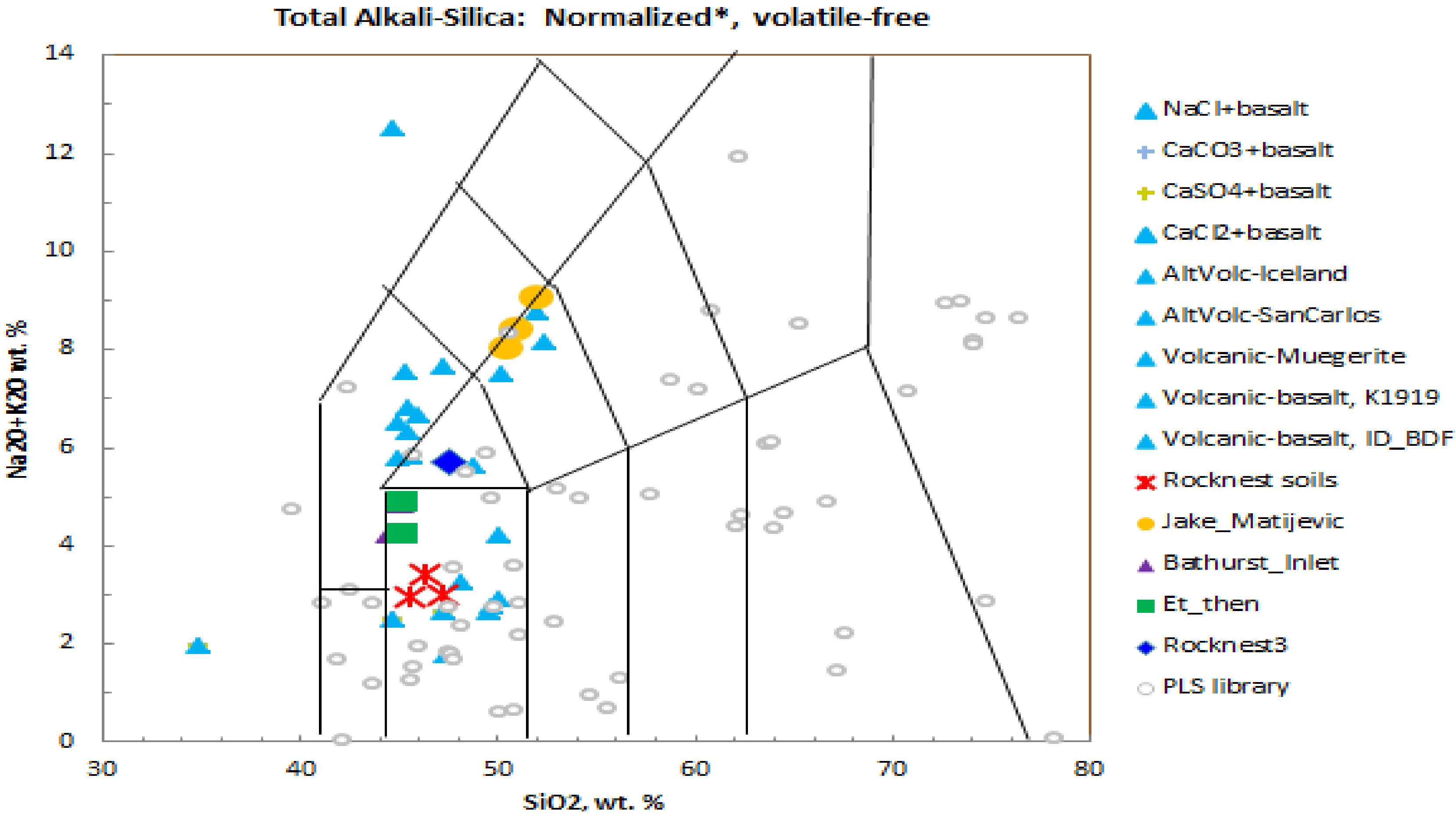
Jake M. region is not covered by current database.

Wiens et al., 2013



Calibration database ranges

Early results motivated us to add more standards to improve PLS models because compositions of some surprisingly alkali-rich Gale rocks fell toward the edges of the training set. This work is ongoing (Ehlmann et al., 2013)



Calibration database ranges

- Compositions in the cleanroom standards cover most of the range of predicted Mars compositions, but often with very few samples.
- Augmentation of training set should improve our predictions

Conclusions

- Environmental and Mars conditions
  - Distance and other effects are corrected for by our processing.
  - Prediction database taken with the flight model under Mars conditions (P, atmosphere)
- Multivariate analysis quantification
  - PLS1 errors assessed by RMSEP take into account the matrix and some experimental effects
  - Precision is better than accuracy
- Future work
  - Distance correction implementation
  - Database improvements

To be continued with more advanced processing

Thank you