Calibration Reference Materials for New XRF Instruments and Impact of Sulfur on Reported Si and Al Measurements in IMPROVE

Ann M. Dillner, Warren H. White, Hege Indresand

UC Davis

IMPROVE Steering Committee Meeting, 2011

Calibration Reference Materials

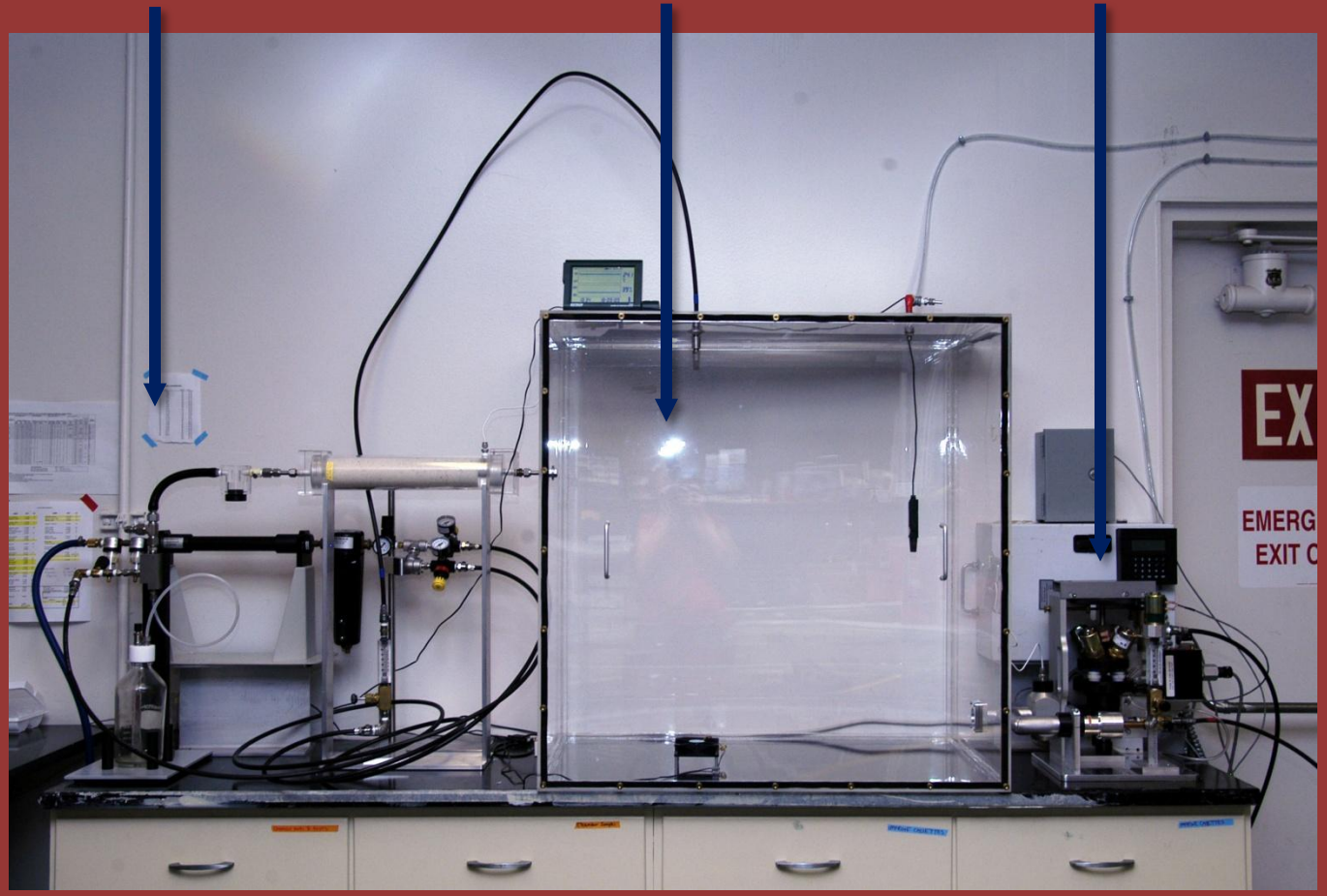
- Collected pure, anhydrous particles onto teflon filters using IMPROVE sampler to mimic ambient samples
  - Ammonium sulfate for S
  - NaCl for both Na and Cl
  - IMPROVE range of masses
- Pre and post weighed 3 times
- Three sets of filters for each compound
  - Reference Materials (RMs) used in calibration
  - Backup set of RMs
  - IC analysis

Aerosol Generation and Sampling System

Generation System

Mixing Chamber

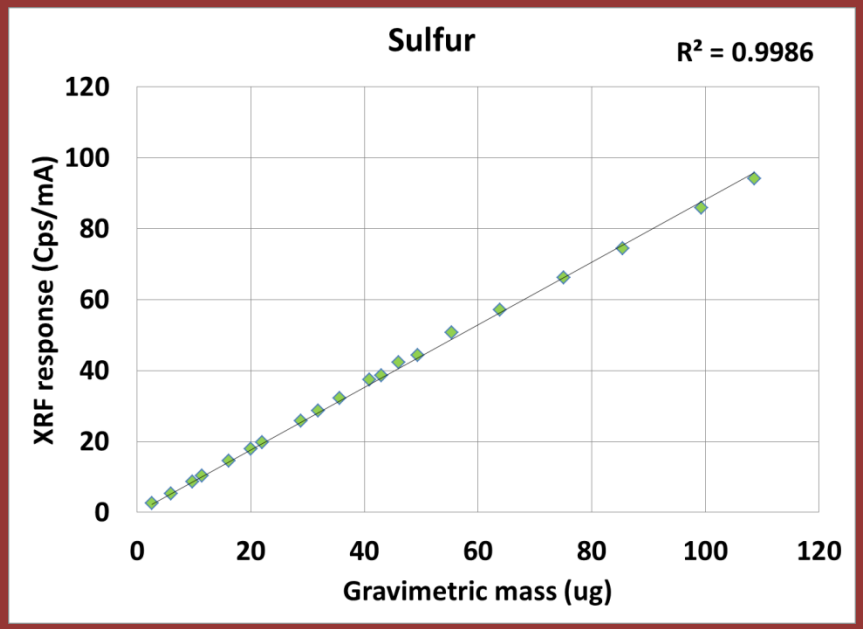
IMPROVE $PM_{2.5}$ Sampler

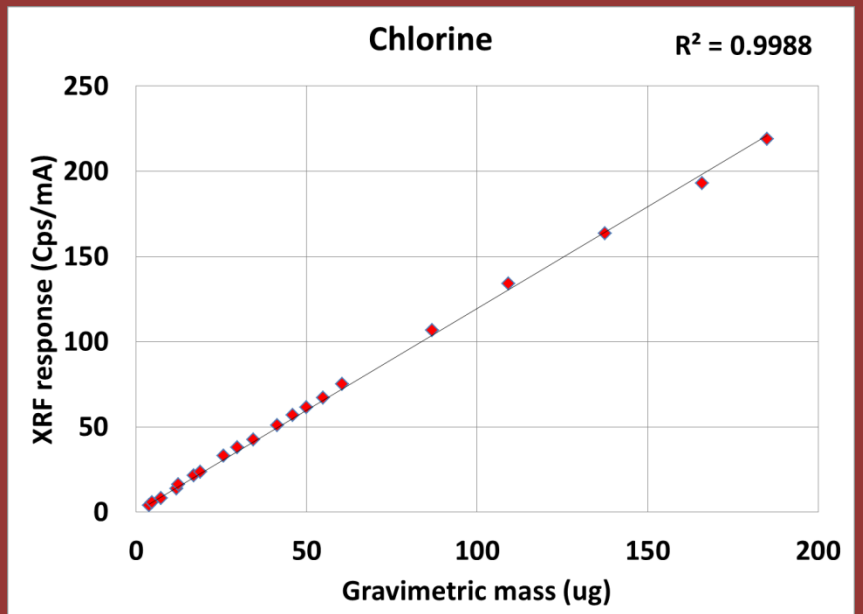


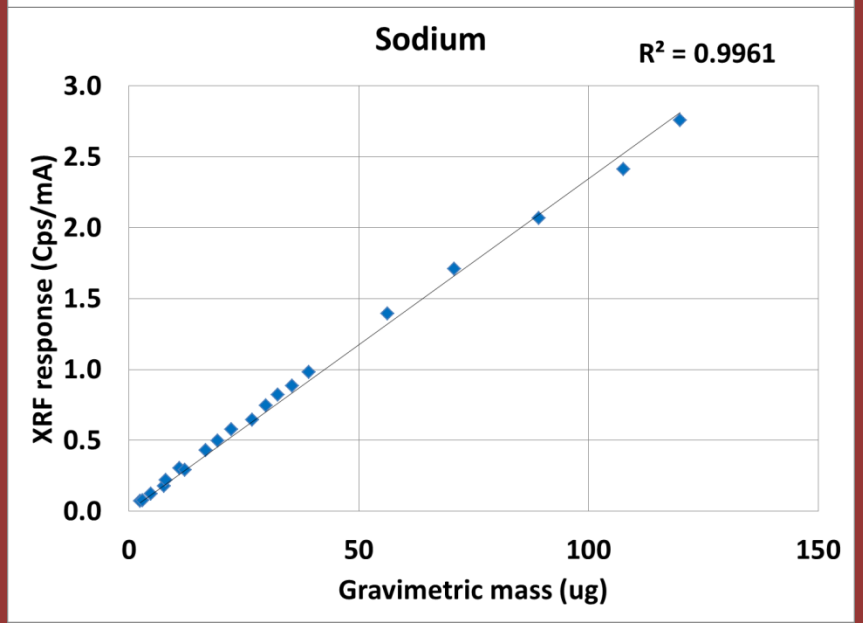
Evaluate for contamination

- Compare RMs to laboratory and pure water blanks
  - XRF - elements
  - IC - ions
  - FTIR – organics and water
  - No contamination found
- IC data
  - Confirmed stoichiometry of ammonium sulfate and sodium chloride
  - Confirmed mass loadings of ions

Calibration Curves







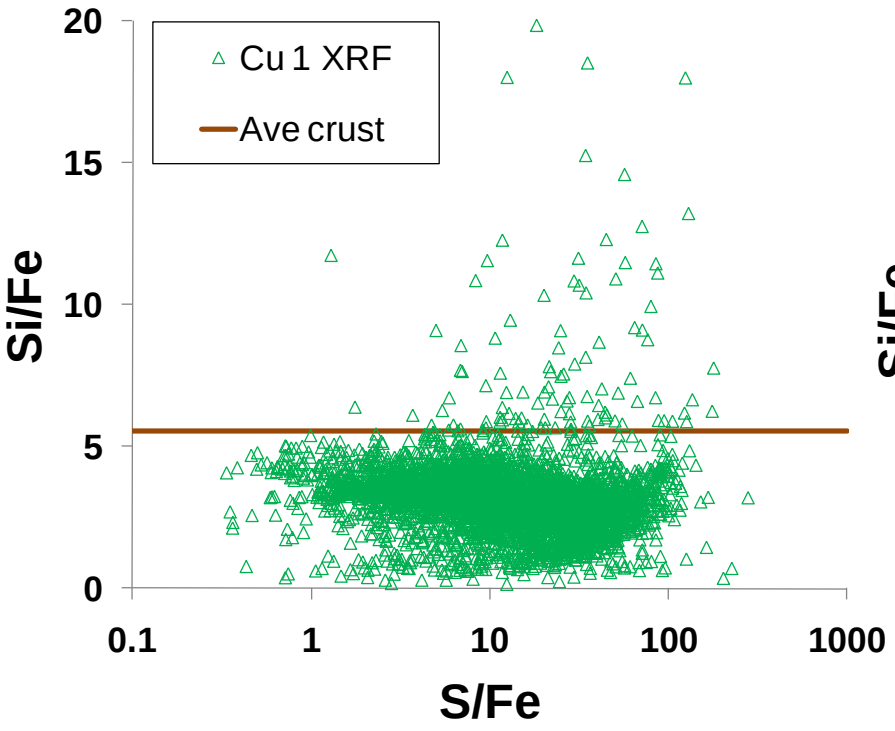
Application of RMs for calibration

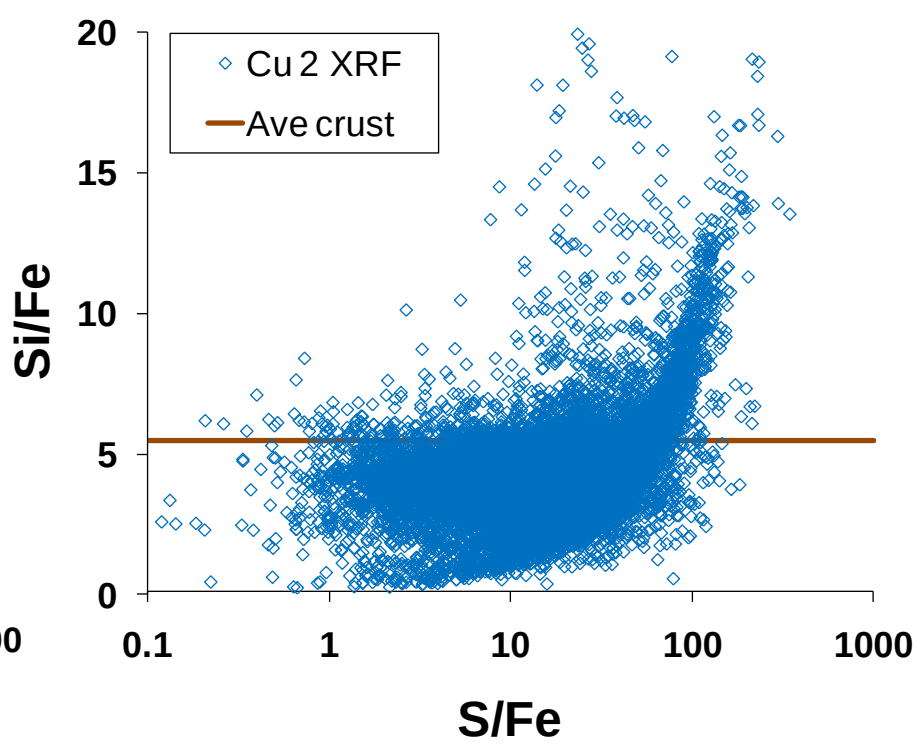
- Uncertainty in calibration factor with RMS
  - Sulfur 1.4% at 99th%ile confidence interval (CI)
  - Chlorine 1.6% at 99th%ile CI
  - Sodium 2.8% at 99th%ile CI
- Uncertainty in commercial standards
  - All elements 5%
- Don’t need area - data reported as mass per filter
  - Commercial standards in mass/area
- Additional standards - begin in next few months
  - New Ultra-micro-balance allows lower masses

Si and Al at rural IMPROVE sites

- Si and Al are important soil components
  - Data advisory #10 - errors in Si when S/Si is high
  - Data advisory #11 - Al above MDL reported as ND
- At rural sites, Fe, as well as Si and Al is
  - Primarily from soil
  - Si/Fe and Al/Fe constant for each soil type
- Sulfur
  - anthropogenic (ammonium sulfate)
  - S/Fe is ratio of sulfur to soil in the sample

Si/Fe as a function of S/Fe for two similar IMPROVE Cu-XRF systems



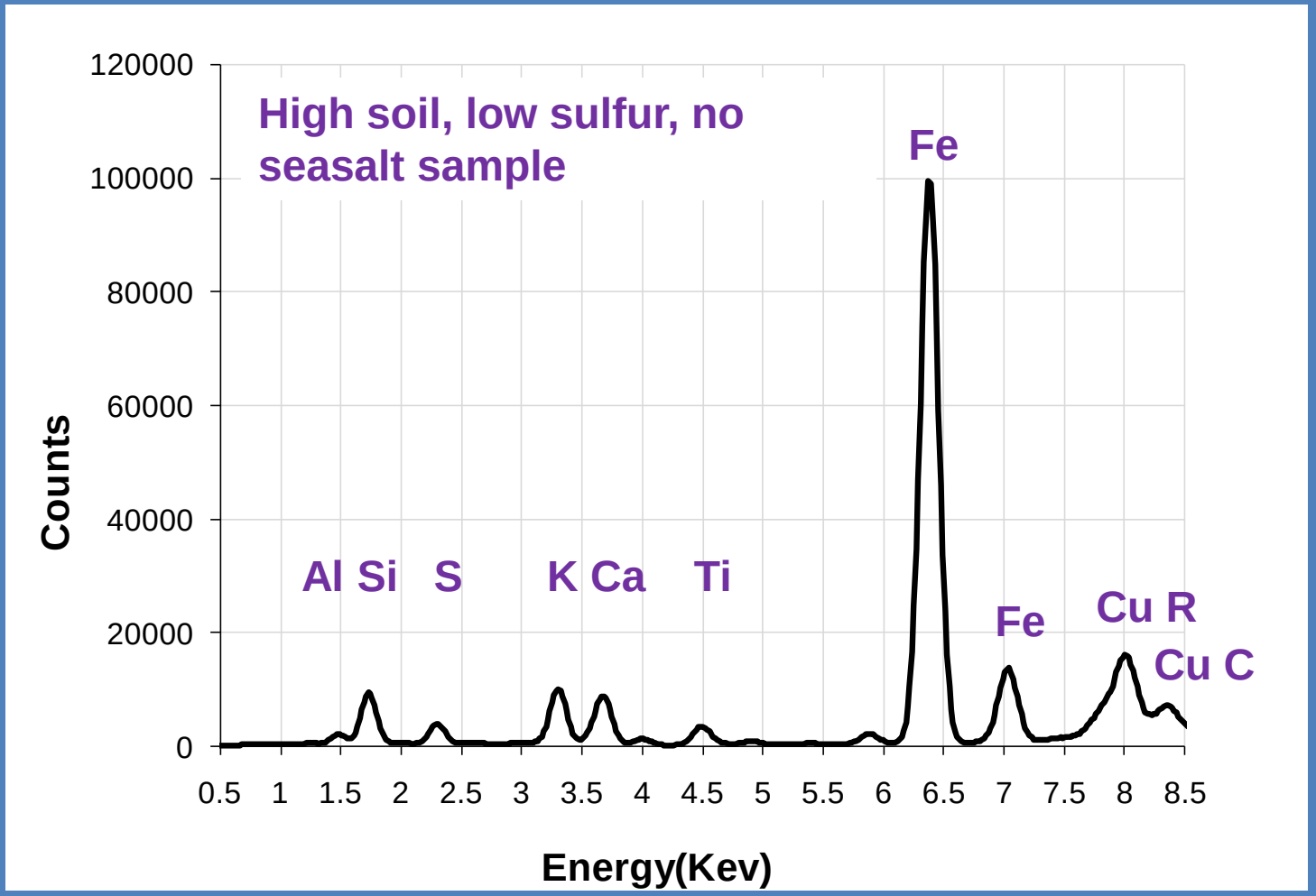


2008 data from all sites excluding eight sites considered predominantly urban (BIRM1, DOUG1, MEAD1, PHOE1, PHOE5, FRES1, SAWE1, SAGU1). The average Si/Fe ratios in earth crust is shown as a reference (Mason and Moore, 1982). Data from 2005-2010 behaves similarly.

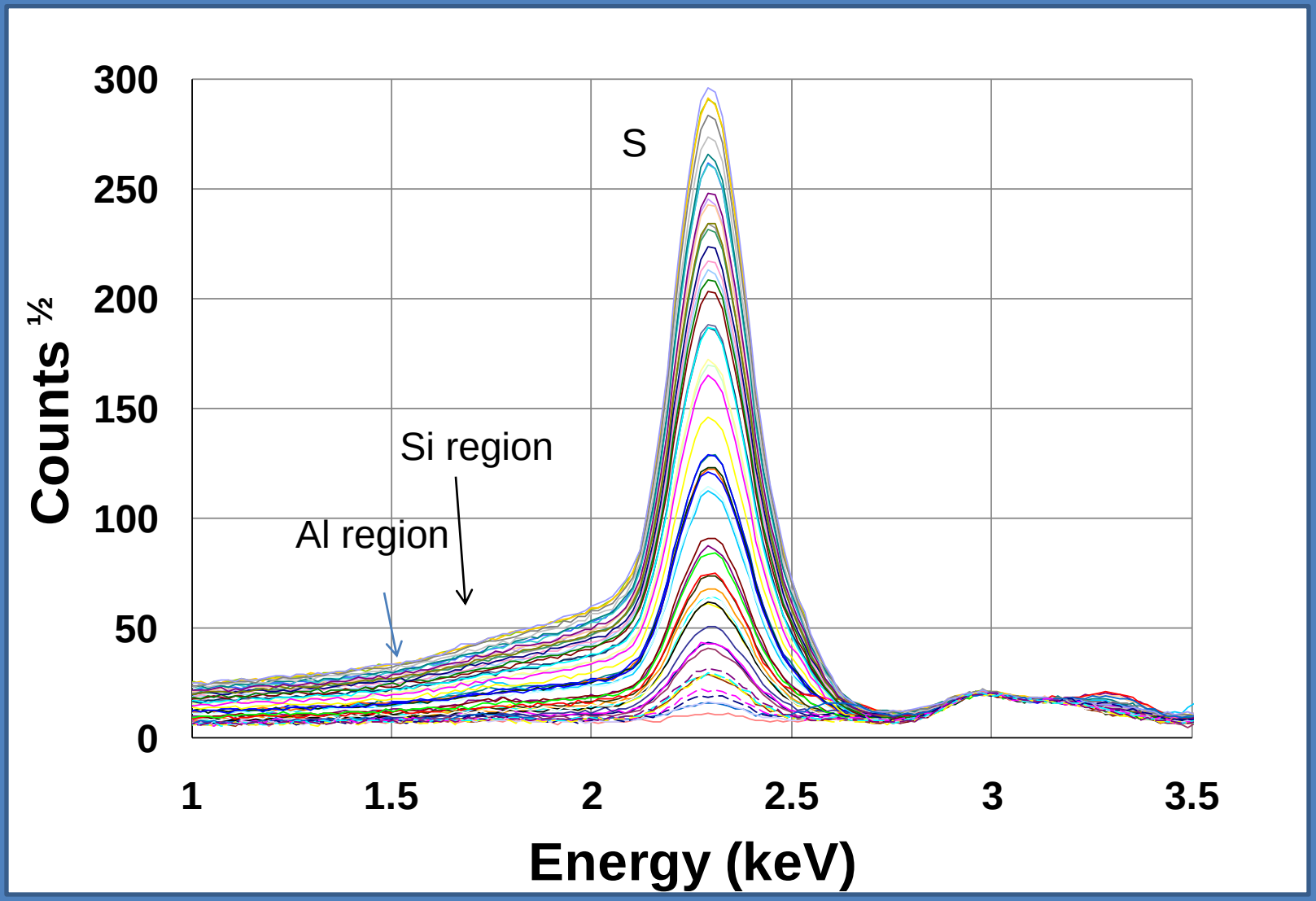
Si and Al measurements in IMPROVE

- Si and Al are light elements
  - low energy
  - small peaks
- Light elements are difficult to measure
  - low energy subject to attenuation or “matrix effects” by particles in the sample
    - Expect an under-reporting of mass unless properly matrix corrected
  - Small peaks can be modified by tail on the more intense sulfur peak, i.e., “spectral interference”

IMPROVE
Cu-anode XRF system spectrum



Spectra of pure ammonium sulfate within IMPROVE range



Objectives

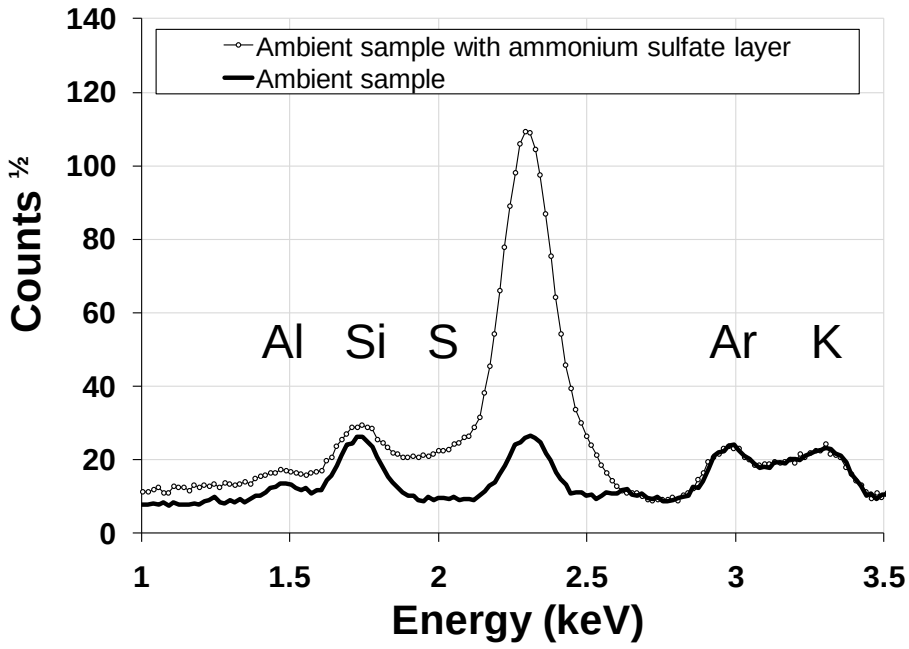
- Determine the conditions under which S impacts reported Si and Al in IMPROVE
- Determine the extent of the impact of S on Si and Al measurements
- Compare to an XRF instrument that does not have a low-energy tail on sulfur

Methods

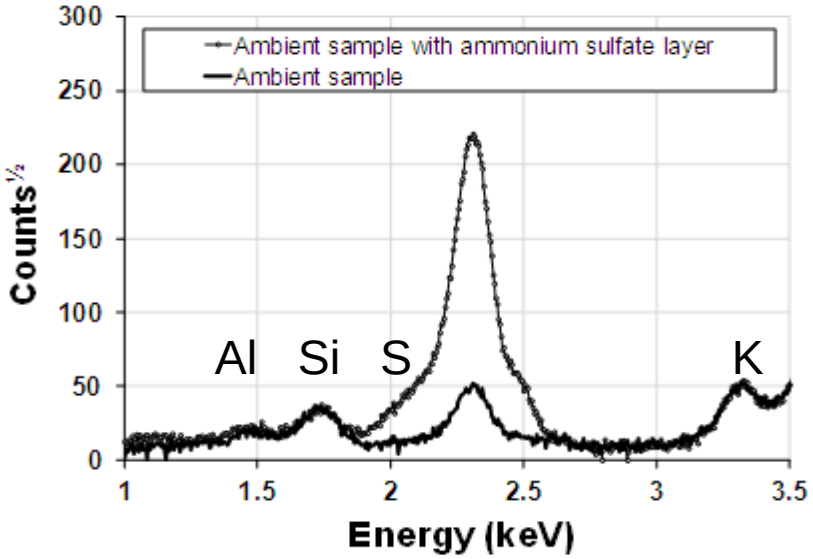
- Collect ambient samples:
  - Low sulfur
  - Si and Al concentrations vary over IMPROVE range
- Add pure, dry ammonium sulfate to produce S/Fe ratios observed in the network
- Analyze samples before and after addition of S
  - IMPROVE XRF instrument – Cu2
    - Matrix corrected using IMPROVE methodology
  - DRI's PANanalytical Epsilon 5 (about 60% of samples)
    - Not matrix corrected

Ambient samples without and with layer of sulfate

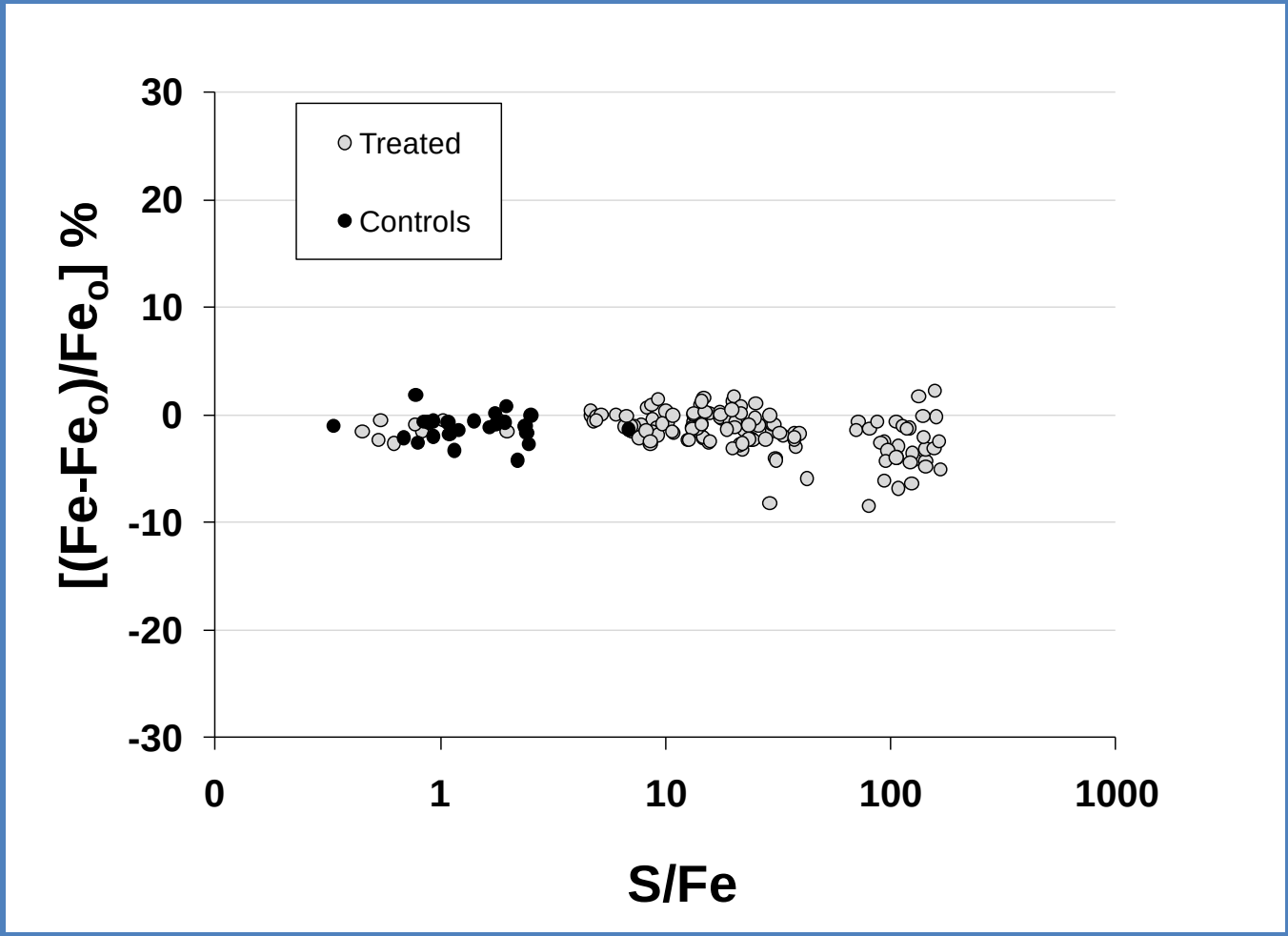
IMPROVE Cu2 XRF system



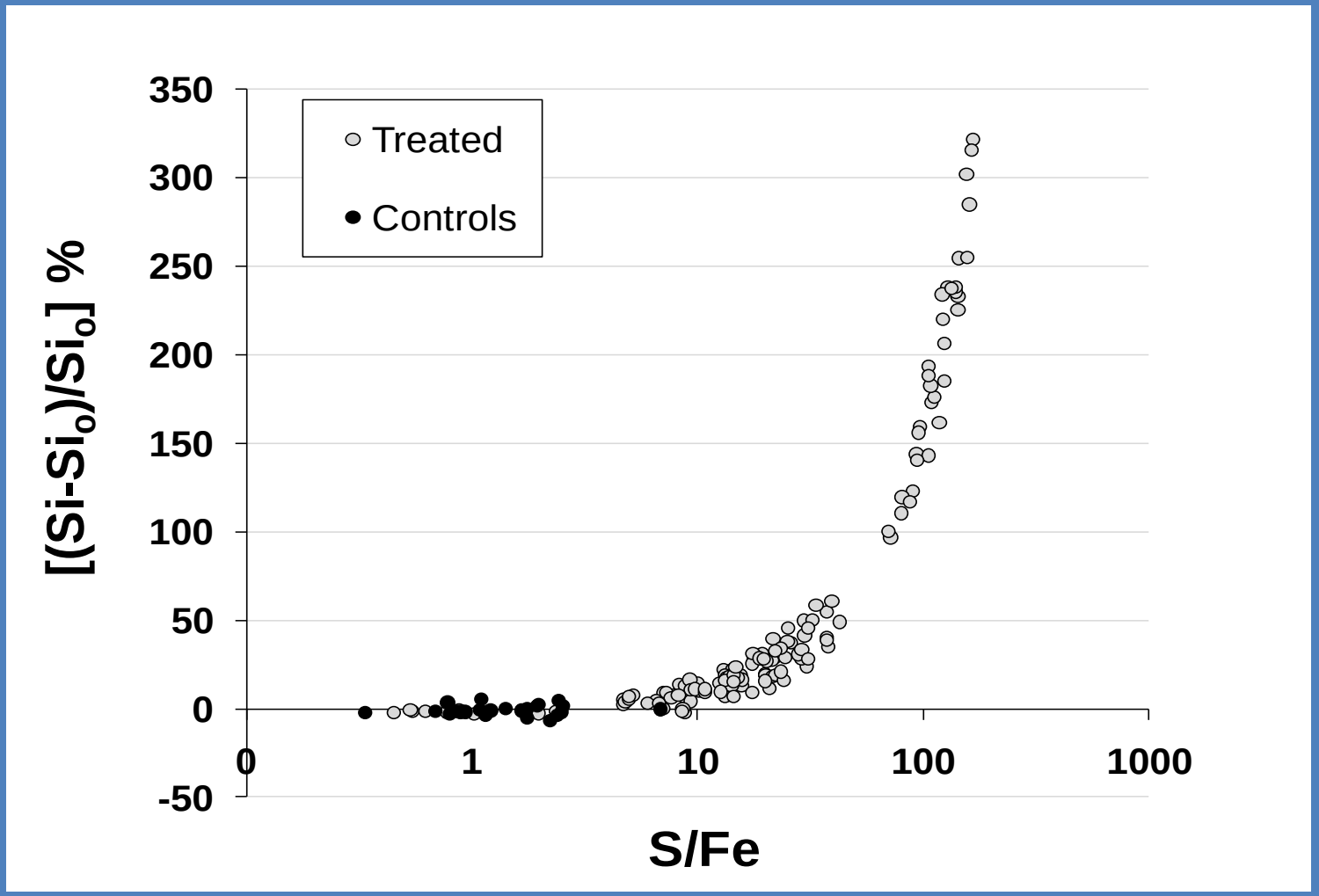
DRI PANalytical XRF



Fe is not impacted by S in IMPROVE (and DRI)

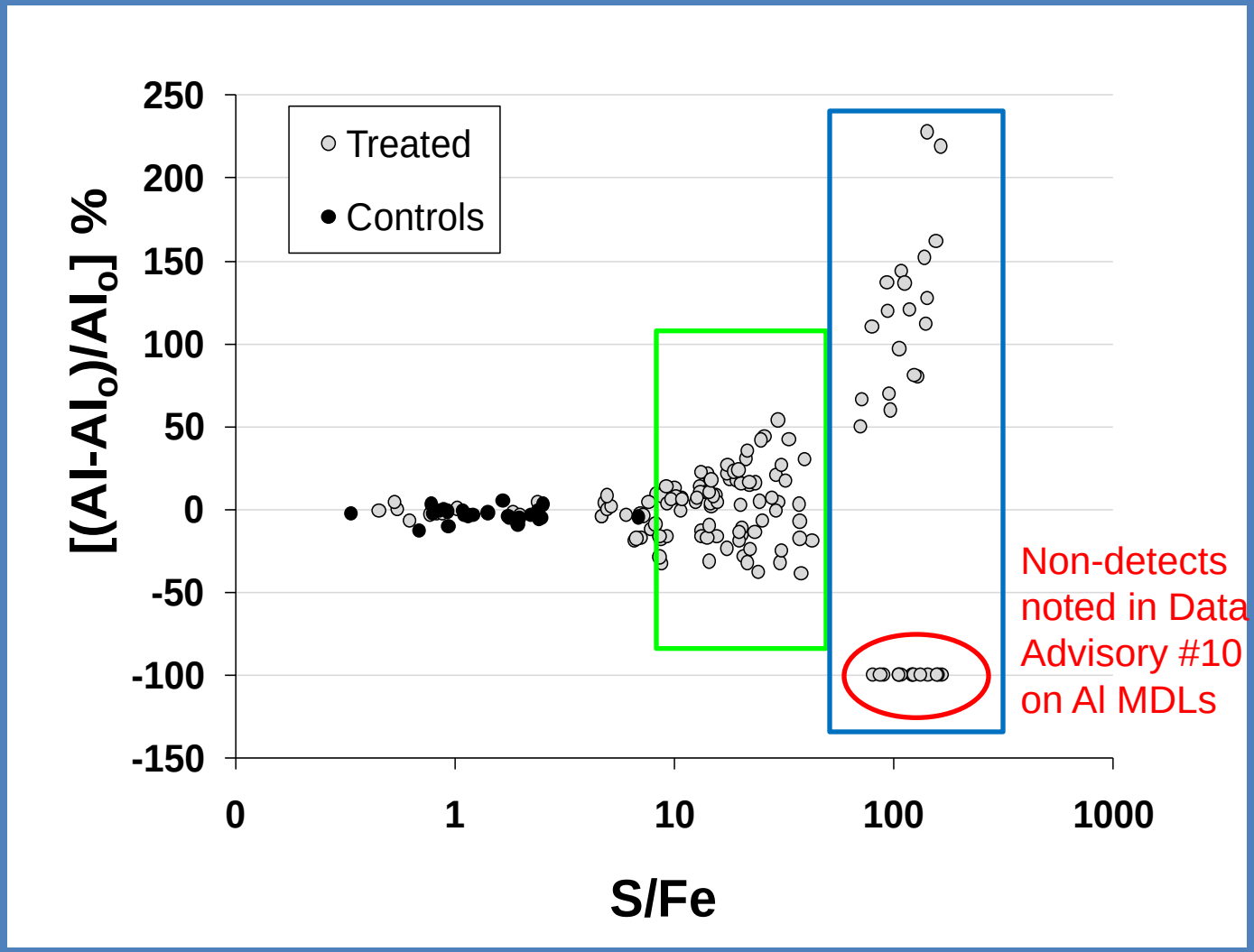


Si increases with increasing S/Fe in IMPROVE



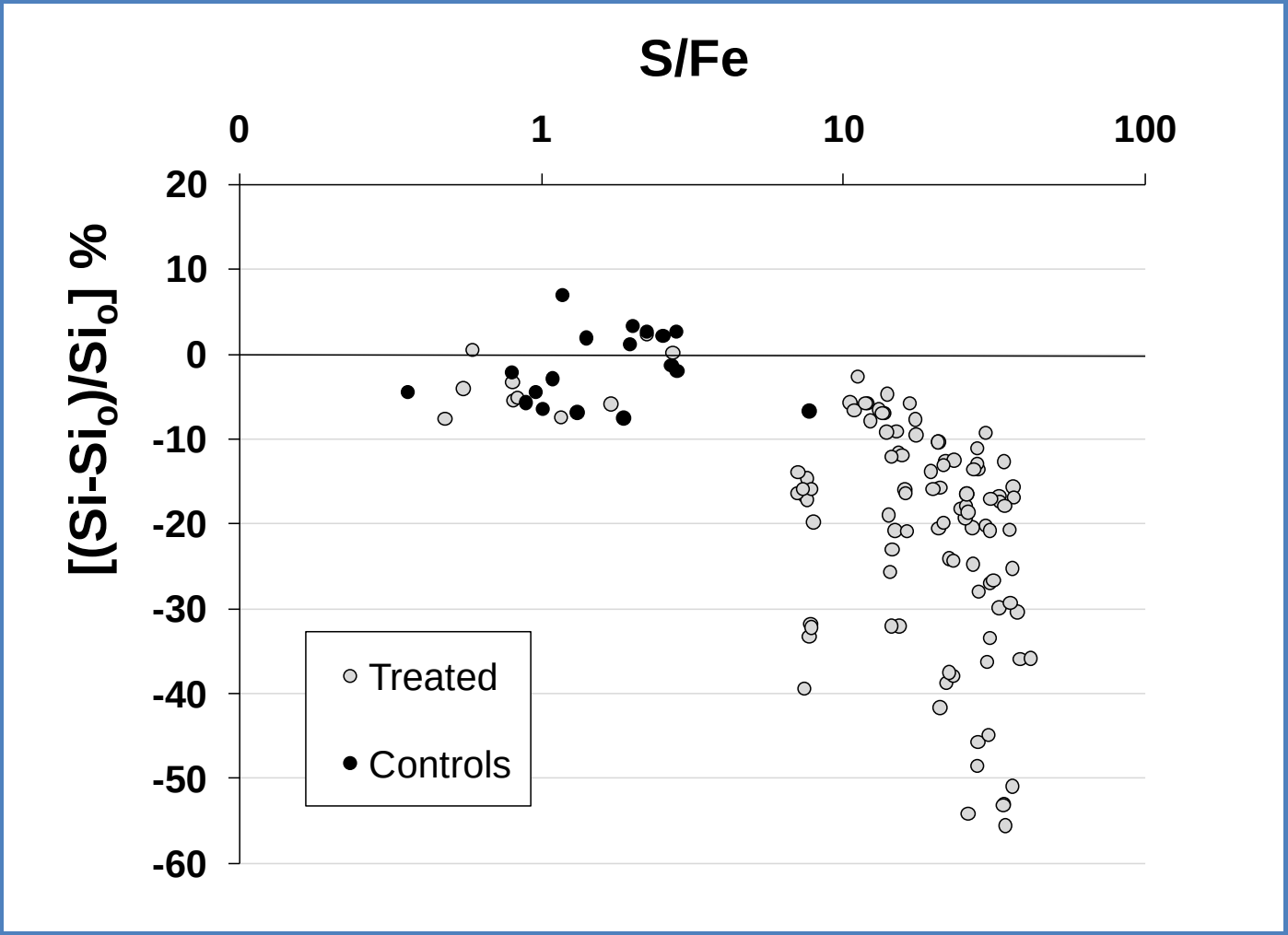
Not a function of Si mass

Al impacted by increasing S/Fe in IMPROVE

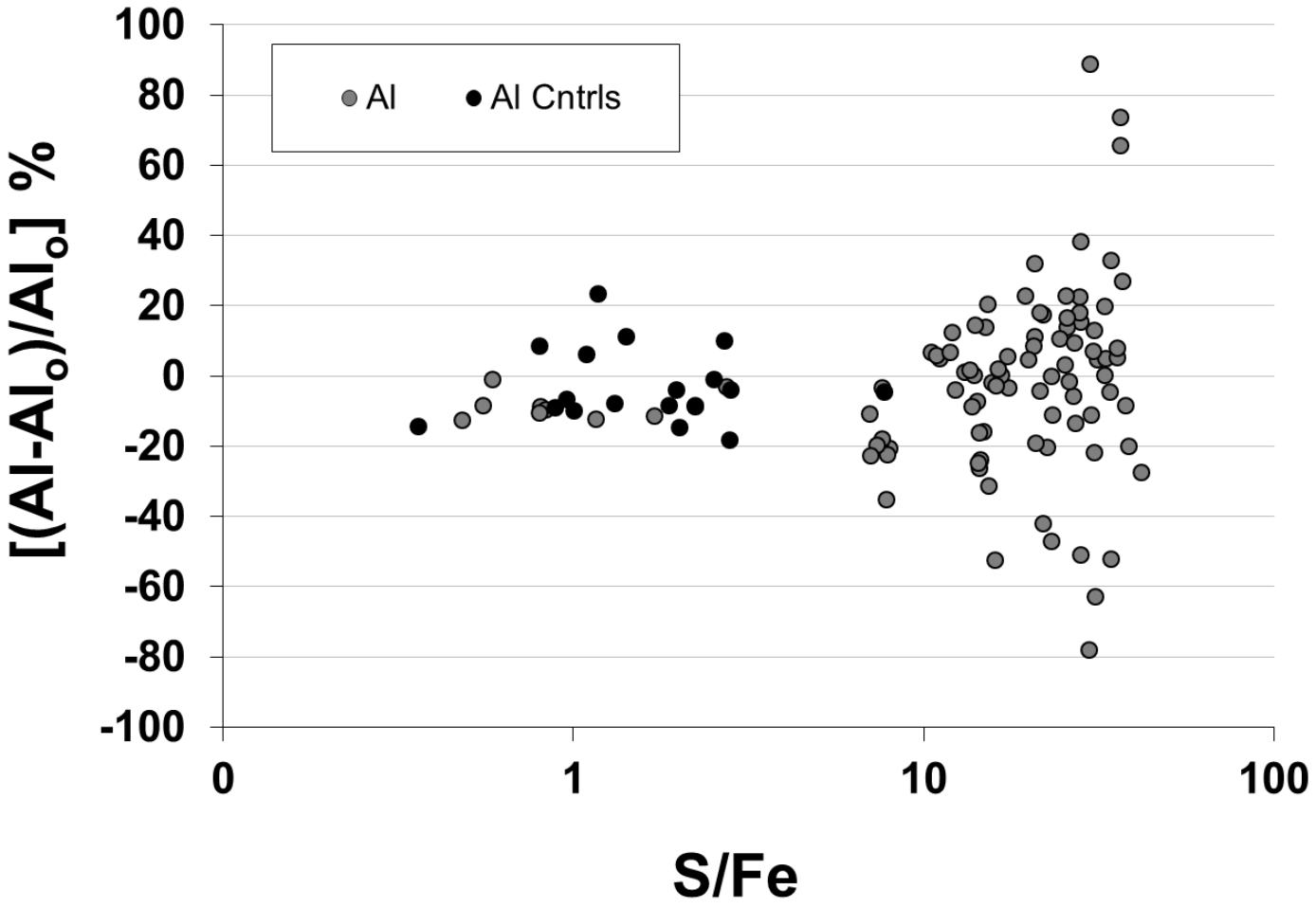


Not a function of Al mass

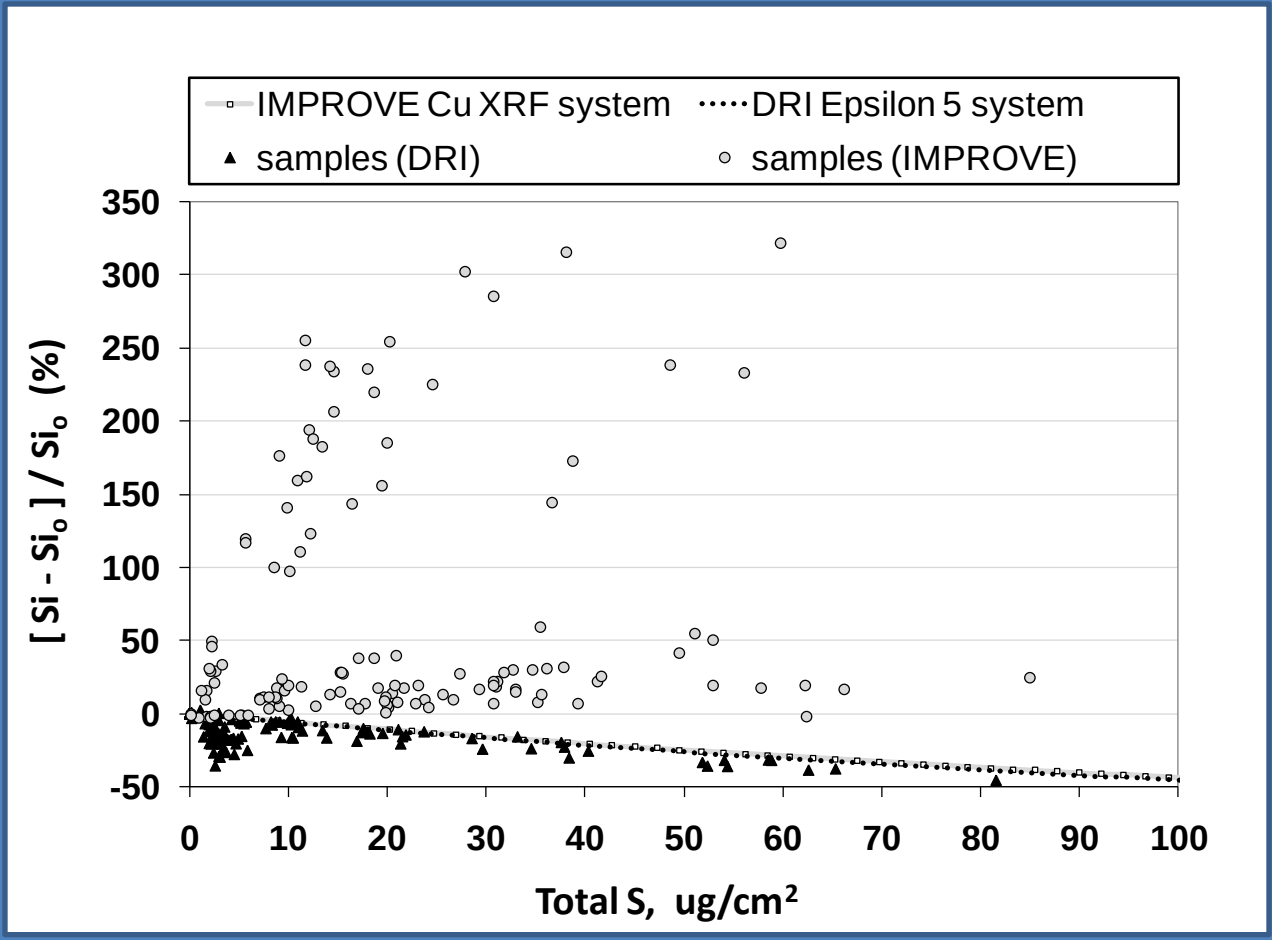
Si decreases with increasing S in DRI PANalytical Ep 5



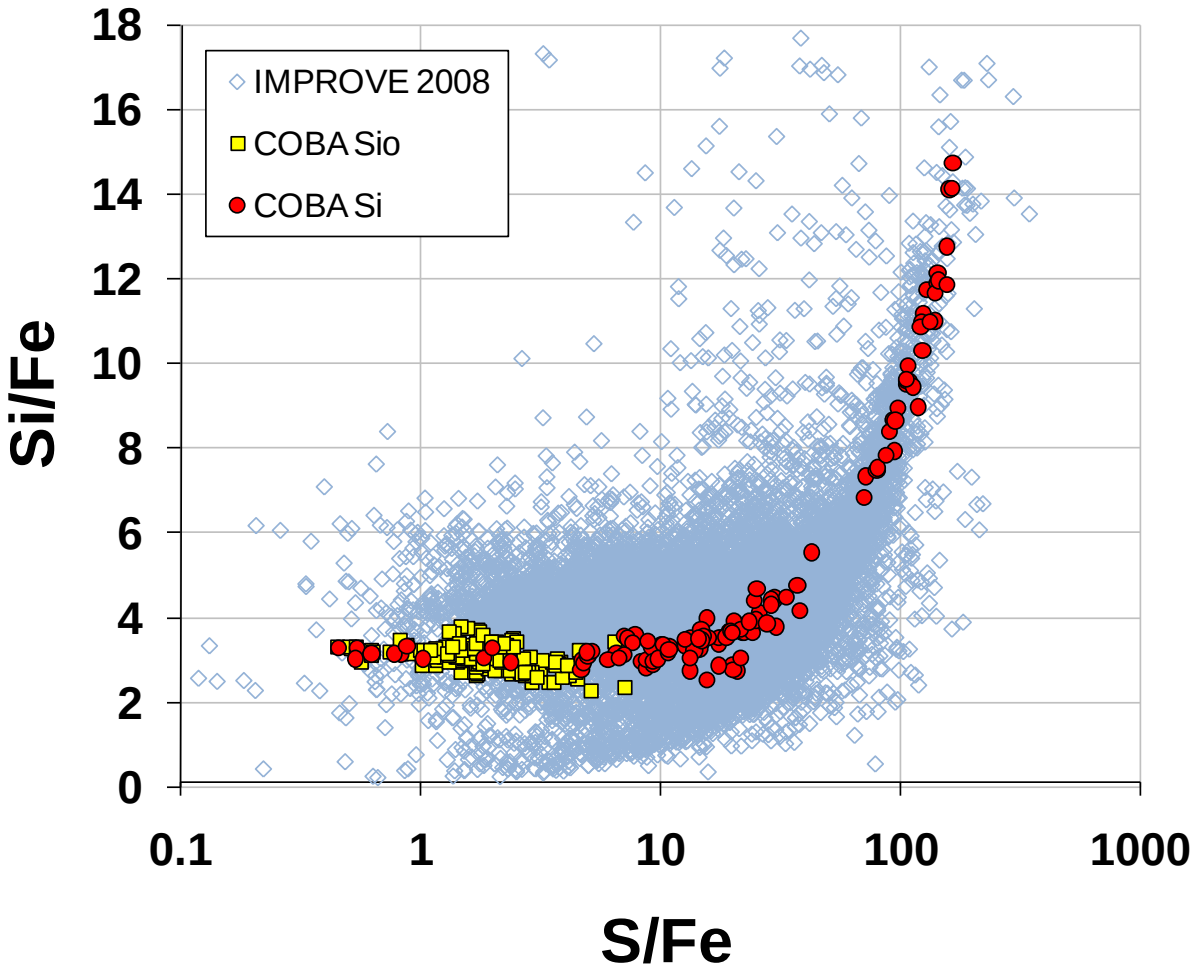
DRI's Al behaves similarly to IMPROVE's for S/Fe<75



Modeled attenuation of Si by S



Ambient samples with and without added sulfate and 2008 IMPROVE data



Recommendations for using IMPROVE data obtained from Cu2*

- Samples with S/Fe < 10 is unaffected by S
  - Accounts for 38% of Cu2 IMPROVE data in 2008
- Samples with S/Fe > 75 and Si/Fe > 6 (6% of Cu2 data),
  - Si concentrations are likely over reported by ≥2
  - Al concentrations either over reported by >50% or erroneously reported as below MDL
  - Use data with extreme caution
- Samples with 10 < S/Fe < 75 (56% of data),
  - Si mass over reported by up to 60%
  - Al data may have errors up to ±50%
  - Use data with care

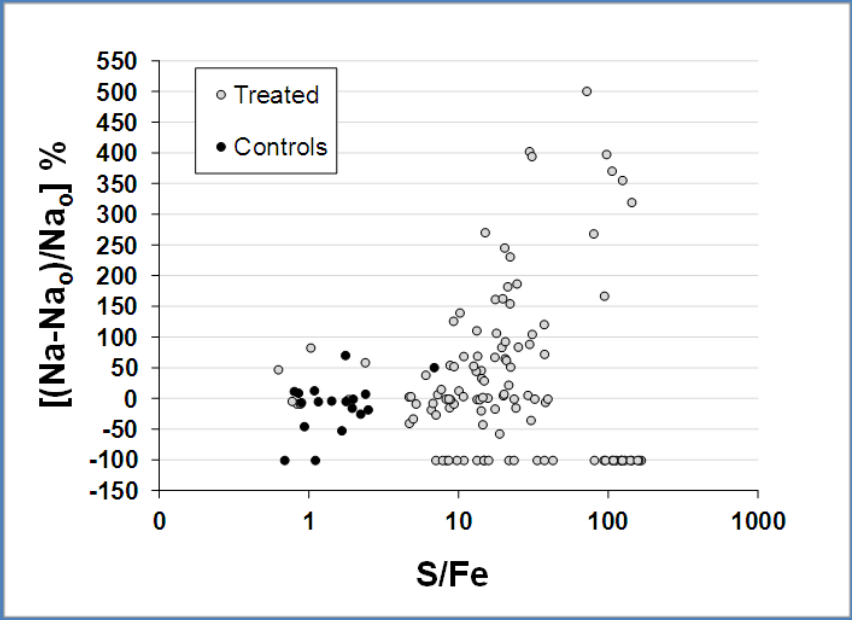
*October and December, 2005
Jan, April, June, Aug, Oct, 2006
Jan, Feb, July, Sept, Oct, 2007
All except Feb, April, June, 2008
All of 2009 and 2010

Conclusions

- Some IMPROVE Si data over-reported and some Al is mis-reported when sulfur is high relative to soil and should be used with care
- Matrix correction for Si and Al generally accentuate this error by ~10%
- Error caused by the low energy tail on the sulfur peak which is a function of the type of detector used
- Errors in non-matrix corrected DRI data are partially explained by attenuation (matrix effects) of light elements
  - This result not directly applicable to IMPROVE's new DRI instruments because we operate them differently.

Na and Mg – difficult to measure especially in presence of high S/Fe

Sodium



Magnesium

