science for a changing world

PROGRESS TOWARD U.S. NATIONAL MAPS OF SOIL MINERALOGY BY QUANTITATIVE X-RAY DIFFRACTION

William F. Cannon, Federico Solano, Tiffani Westphal, John Jackson

U.S. Geological Survey, Reston, Virginia 20192

OUTLINE

The present survey

What is quantitative x-ray diffraction?

How good is it?

What good is it?

SAMPLE SITES OF THE SOIL GEOCHEMICAL LANDSCAPES PROJECT

We are doing mineral analyses of A-horizon and subsoil at each site

60% complete in August 2011

METHOD

Use <2 mm size fraction

Samples are micronized for 3 minutes

Internal standard (10% ZnO) added to each sample

Dry powder in back-loading sample mounts for random orientation

Use CuKα x-radiation

THE X-RAY DIFFRACTION TECHNIQUE

In use for about a century

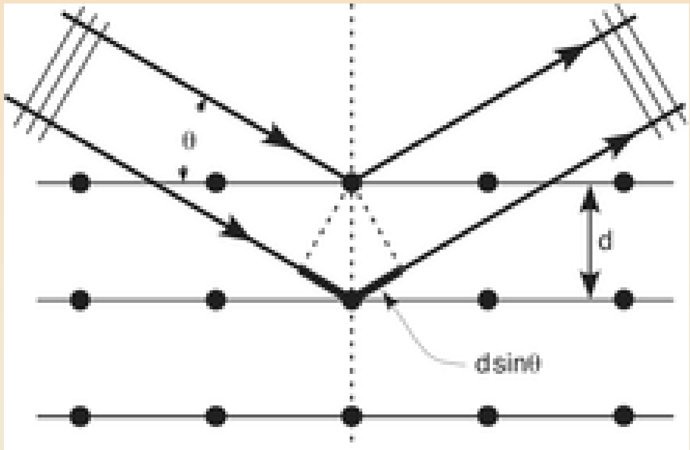
Early use was to determine crystal structure of compounds, including many minerals

But, once structures were determined for many minerals, it has become a technique for mineral identification (qualitative).

In recent decades quantitative analysis of complex mixtures of minerals has become feasible.

Basics of X-ray Diffraction

Measures interatomic spacing using constructive interference of an x-ray beam



The Bragg Equation

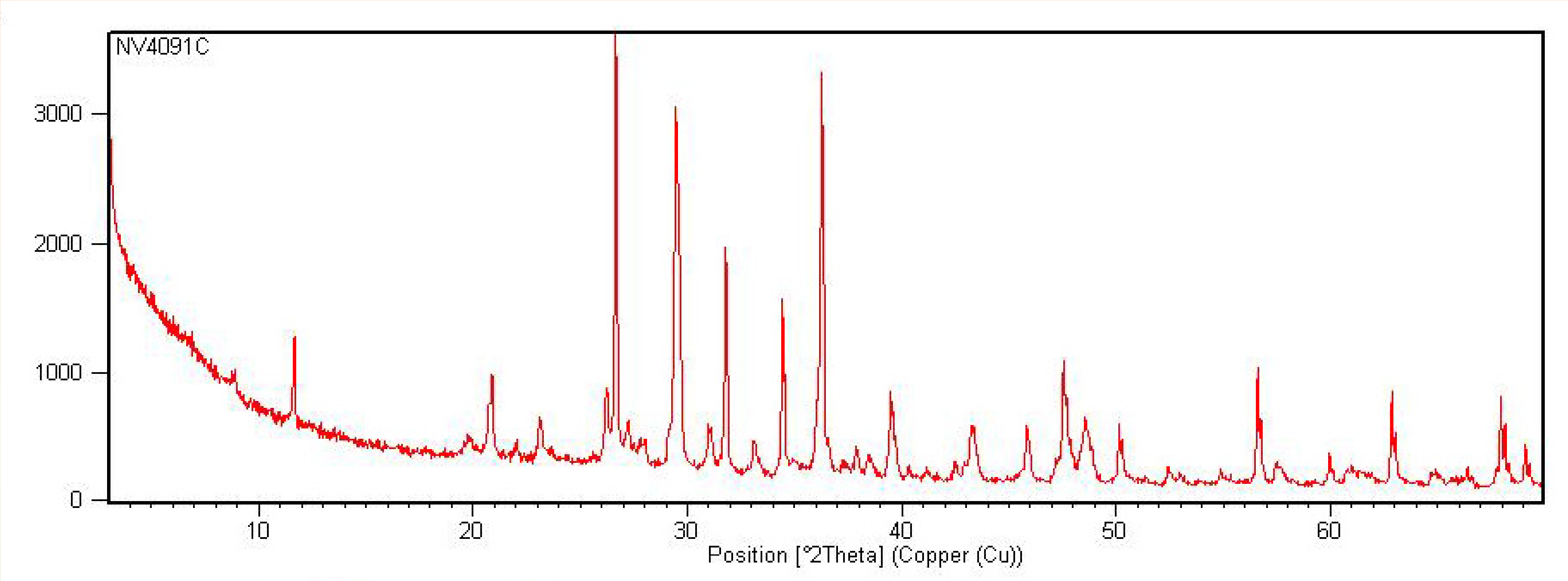
$$n\lambda = 2d\ \sin\Theta$$

1915 Nobel Prize in Physics

There is a unique combination of x-ray wave-length, angle of incidence, and interatomic spacing at which x-rays emerge from a crystal still in phase.

So, by using x-rays of known wavelength and measuring the angle of incidence, the interatomic spacing can be calculated

A TYPICAL DIFFRACTOGRAM OF SOIL



Sample contains nine identifiable minerals plus ZnO standard

QUANTITATIVE X-RAY DIFFRATION MINERALOGY

Rietveld Refinement Calculations

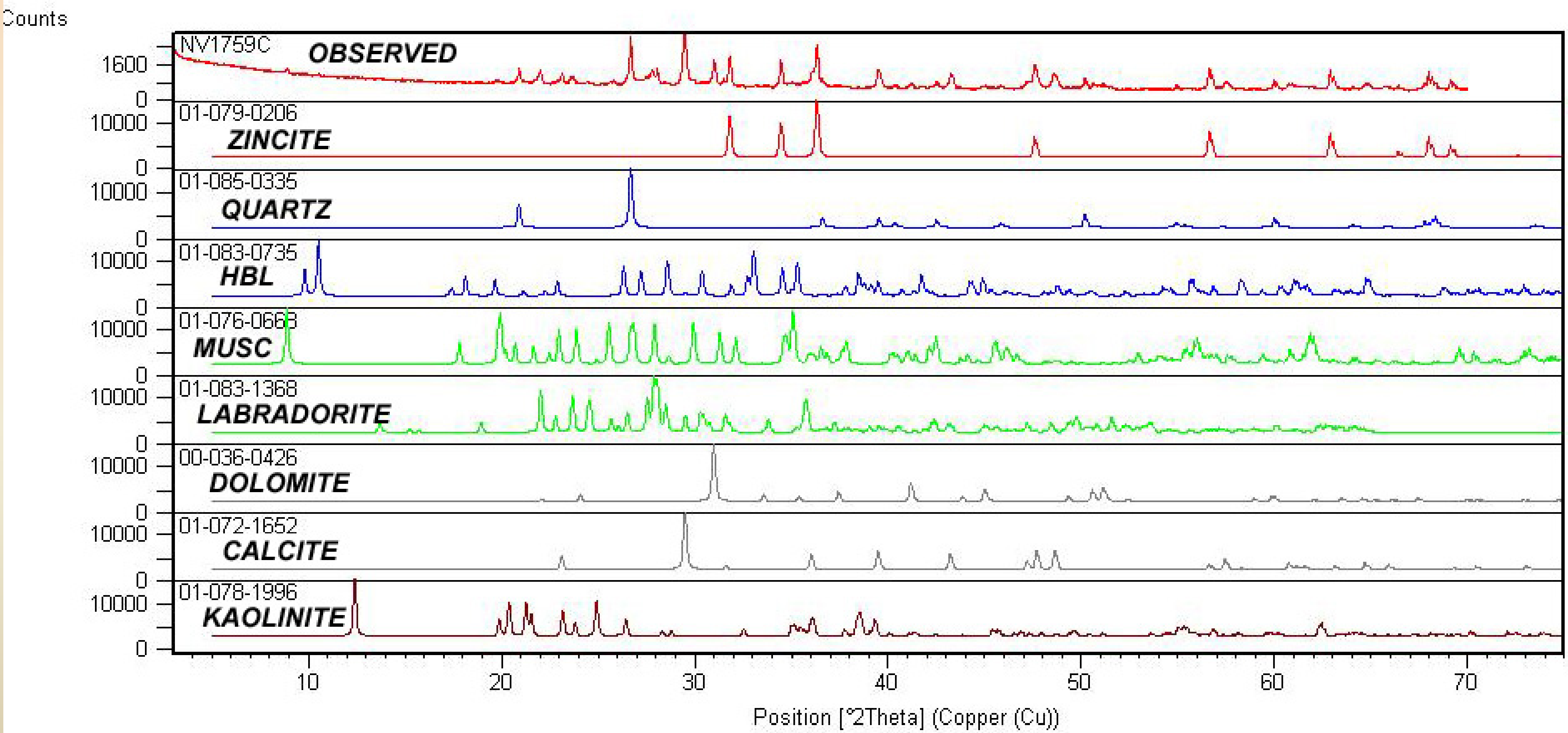
Developed by Hugo Rietveld, a Dutch physicist, in the late 1960's.

Deconstructs complex diffraction pattern into patterns of individual component minerals.

Simultaneously adjusts the percentage of each mineral to achieve the best least squares fit to observed pattern.

Also adjusts for other variables such as preferred orientation and peak shape.

A diffractogram of soil (top) and diffractograms of eight component minerals



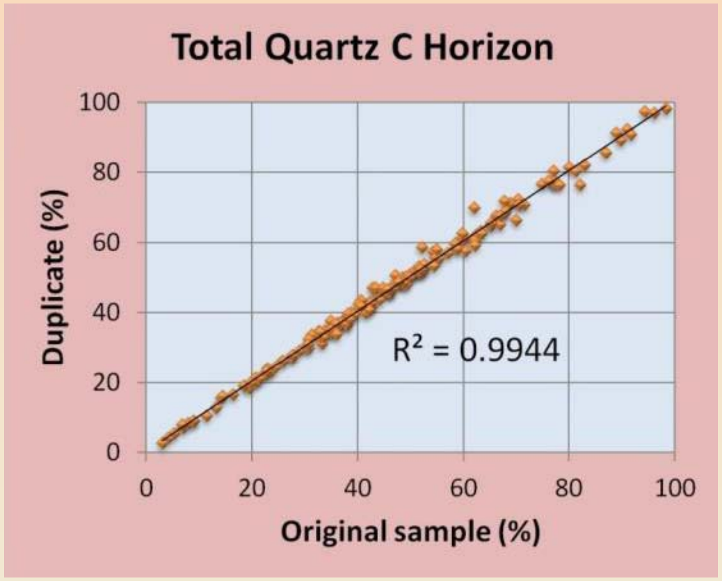
HOW GOOD IS THIS TECHNIQUE?

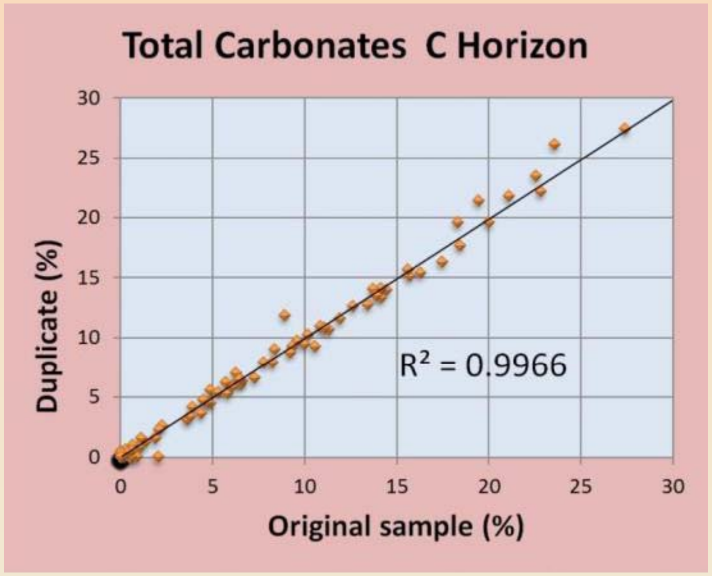
The method is fraught with potential errors, largely because of overlaps of diffraction peaks of minerals in complex mixtures such as soils.

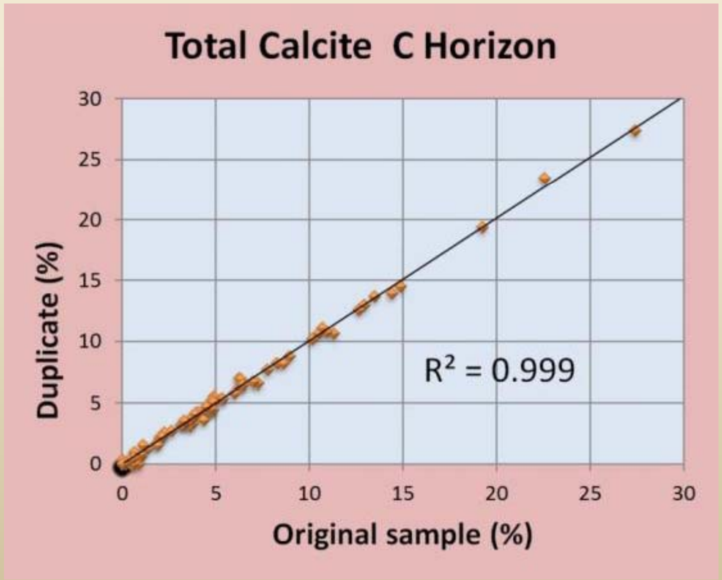
Rigorous QA/QC is necessary to qualify data as to the degree of reproducibility and accuracy.

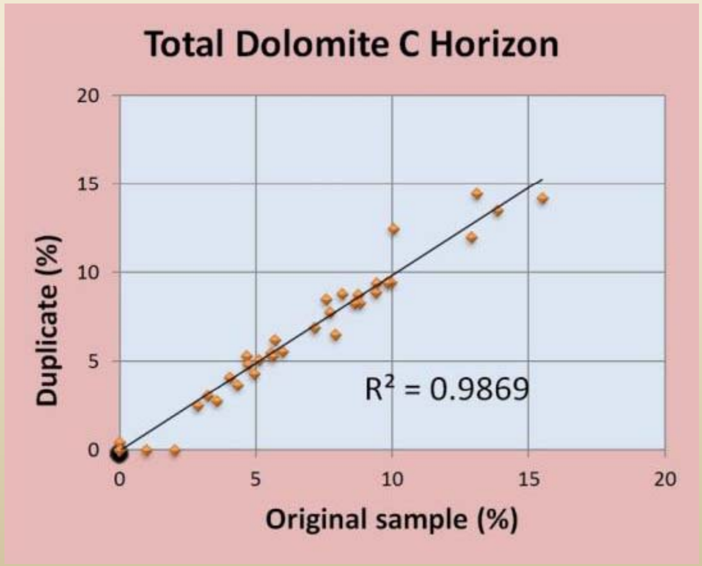
We run duplicate samples and standards at a rate of 1 each per 20 unknowns.

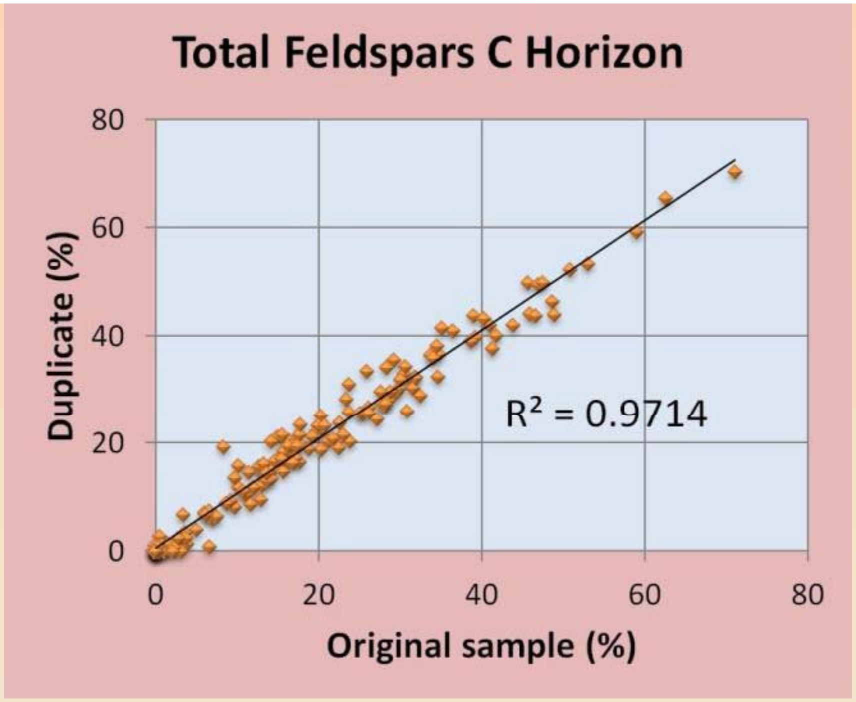
DUPLICATE ANALYSES

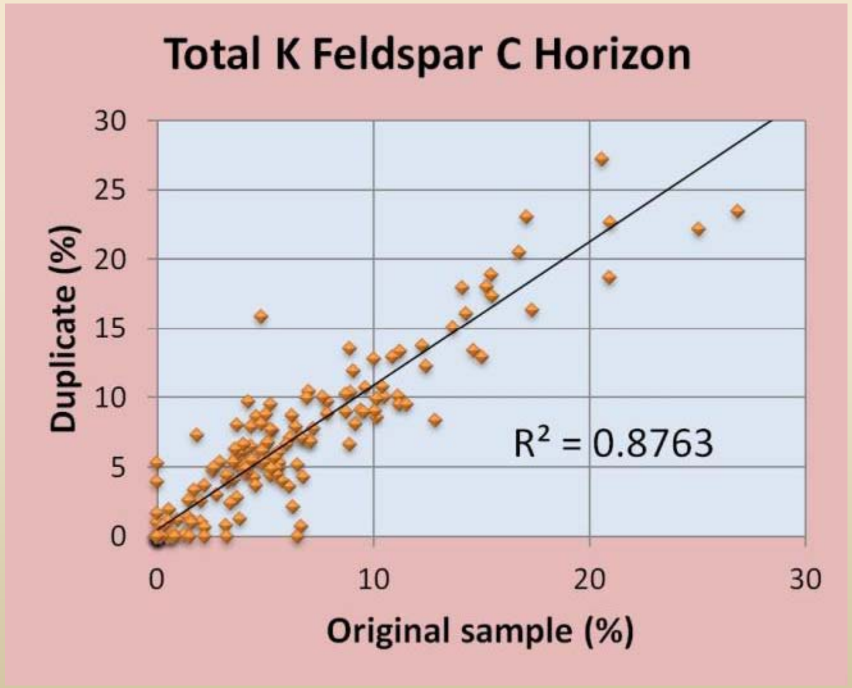


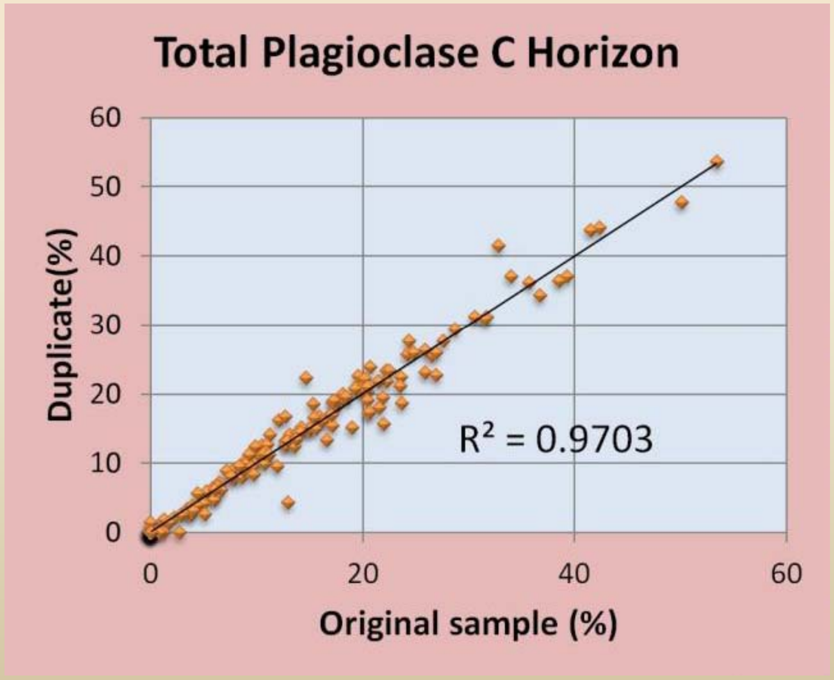







Total Feldspars C Horizon
Duplicate (%)
Original sample (%)
$R^2 = 0.9714$
0
20
40
60
80


Total K Feldspar C Horizon
Duplicate (%)
Original sample (%)
$R^2 = 0.8763$
0
5
10
15
20
25
30


Total Plagioclase C Horizon
Duplicate(%)
Original sample (%)
$R^2 = 0.9703$
0
10
20
30
40
50
60

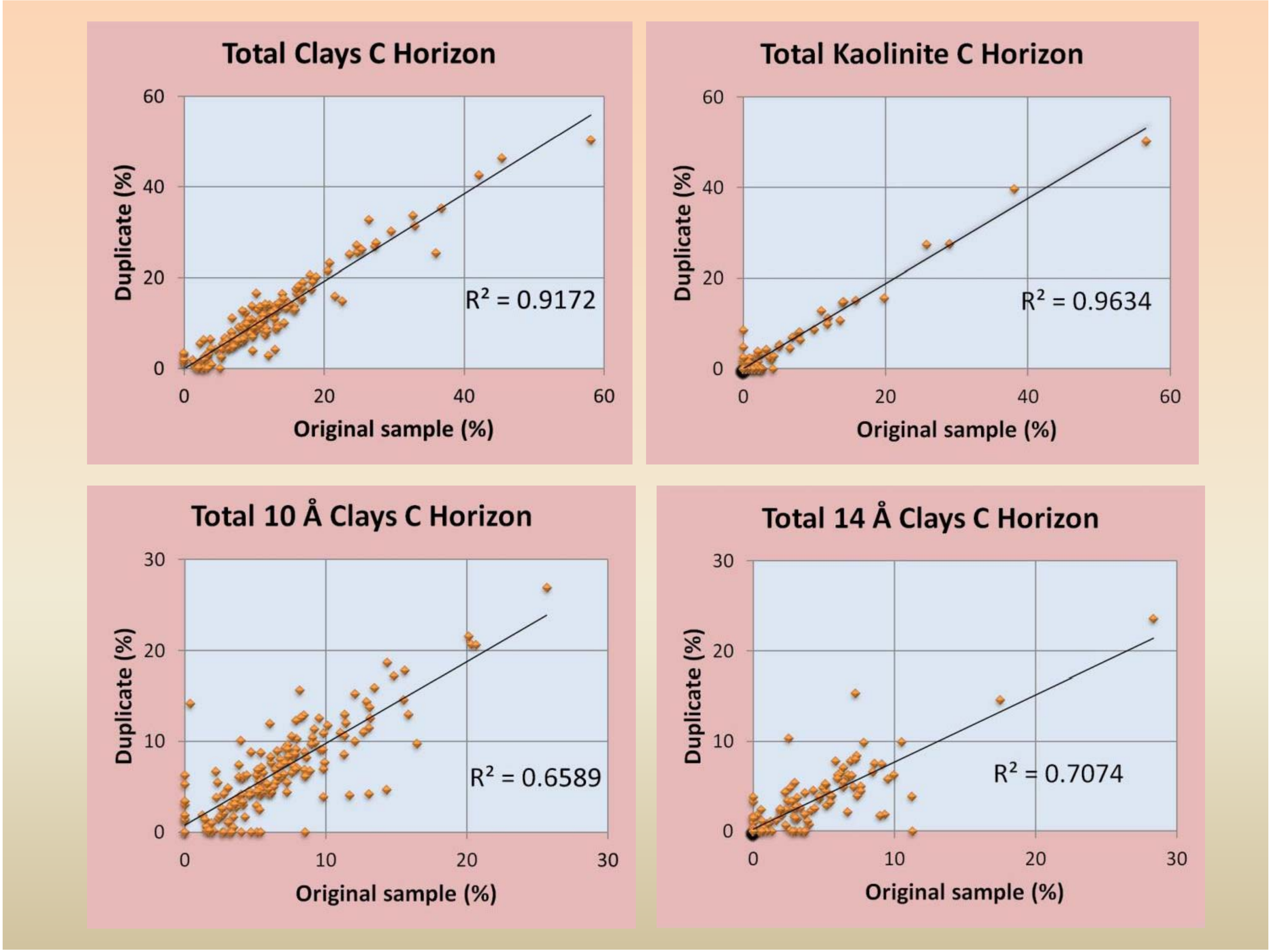
ISSUES WITH CLAYS AND MICA

Our analytical method, using randomly oriented dry powder mounts, is far from optimal to derive specific information about complex mixtures of clays typical of many soils.

Although more accurate characterization of clays can be done using a variety of other techniques, they are not practical to apply to 10,000 samples, at least at this stage of our study.

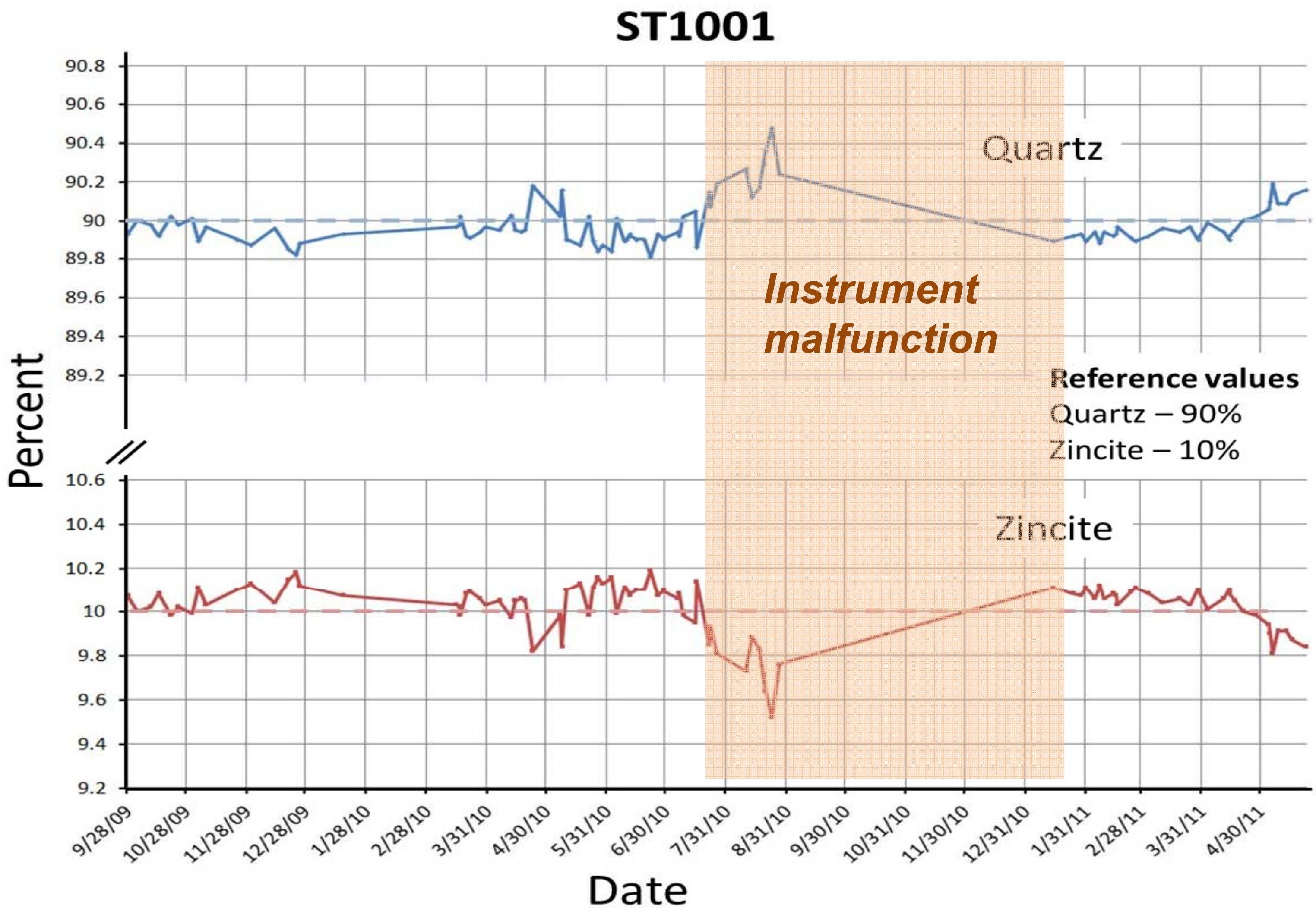
In addition, Rietveld calculations require information on the crystal structure of minerals, which is not available for some expandable and mixed layer clay minerals.

So, we have characterized clays and micas into three broad categories based on the d-spacing of the basal layering: 1) 14-15 angstrom clays, 2) 10 angstrom clays, and 3) 7 angstrom clays.


Total Clays C Horizon
Duplicate (%)
Original sample (%)
R² = 0.9172
Total Kaolinite C Horizon
Duplicate (%)
Original sample (%)
R² = 0.9634
Total 10 Å Clays C Horizon
Duplicate (%)
Original sample (%)
R² = 0.6589
Total 14 Å Clays C Horizon
Duplicate (%)
Original sample (%)
R² = 0.7074

STANDARDS

Our simplest standard consists of 90% quartz and 10% zincite



WHAT GOOD IS MINERALOGICAL DATA?

VALUE IN ITS OWN RIGHT

Carbonate content determines ability to neutralize acidic conditions.

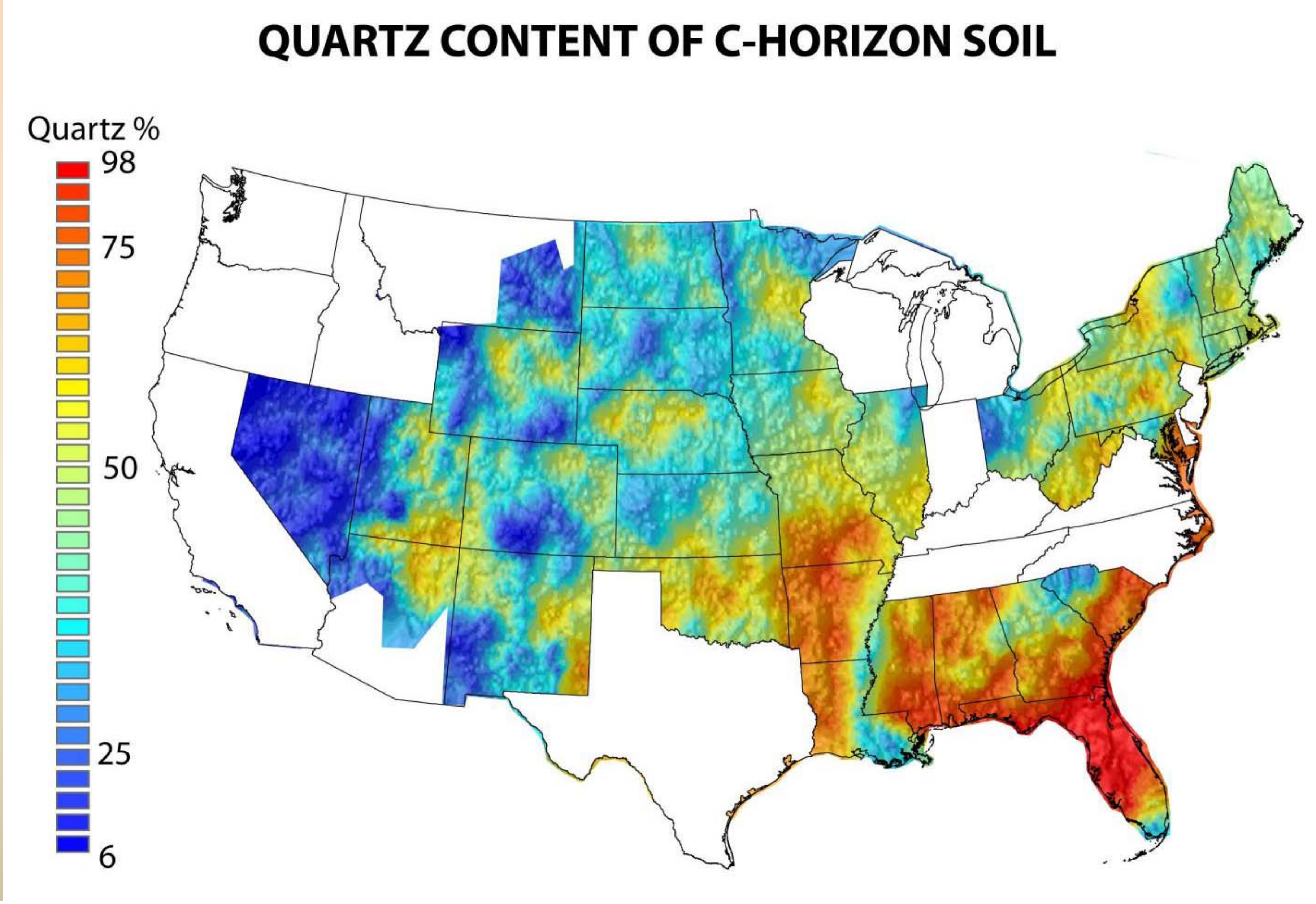
Clay content controls many interactions with trace elements and other compounds

VALUABLE AS AN AID IN INTERPRETING GEOCHEMICAL PATTERNS

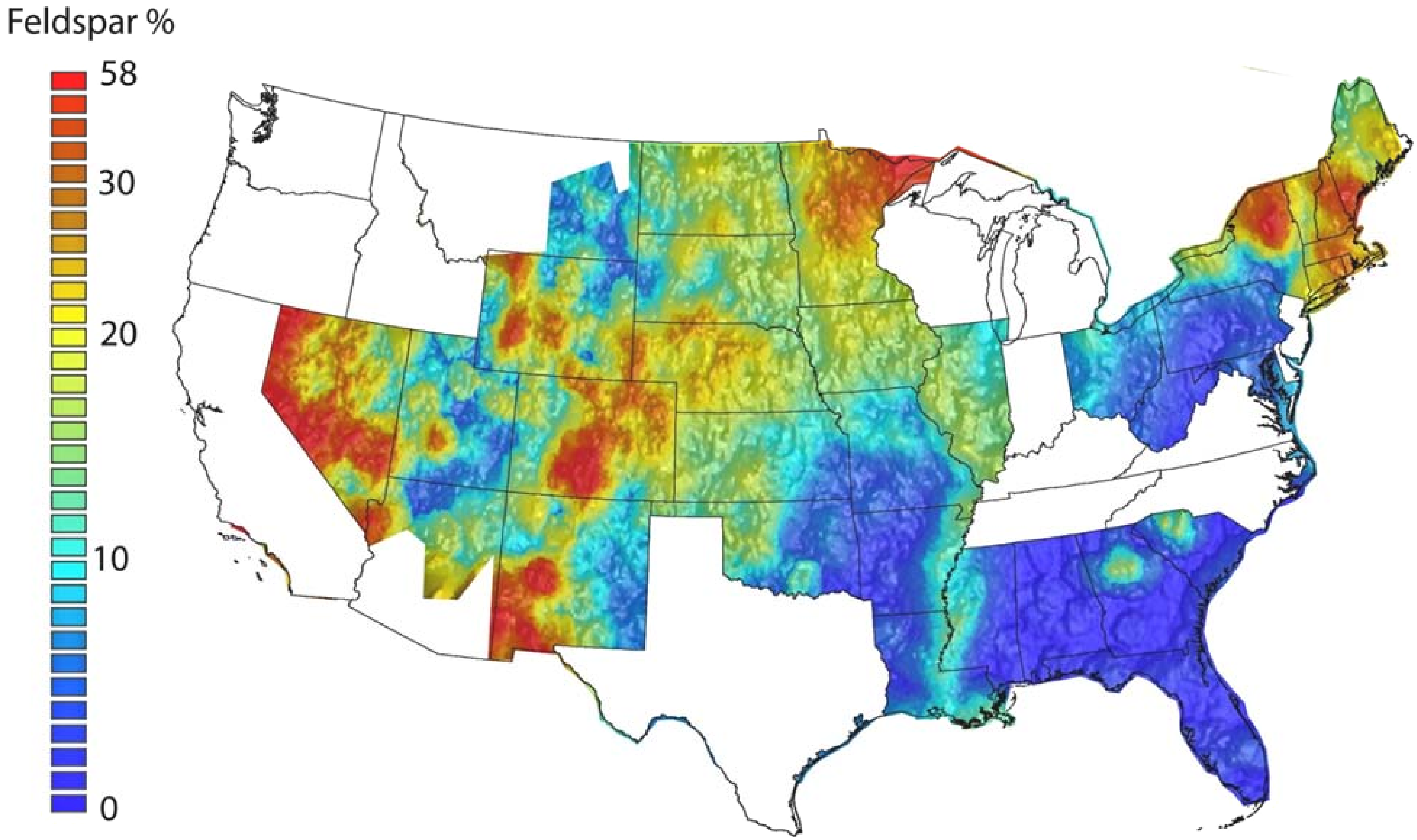
Determine mineralogical residence of various elements

Calculate the effect of quartz dilution on element patterns

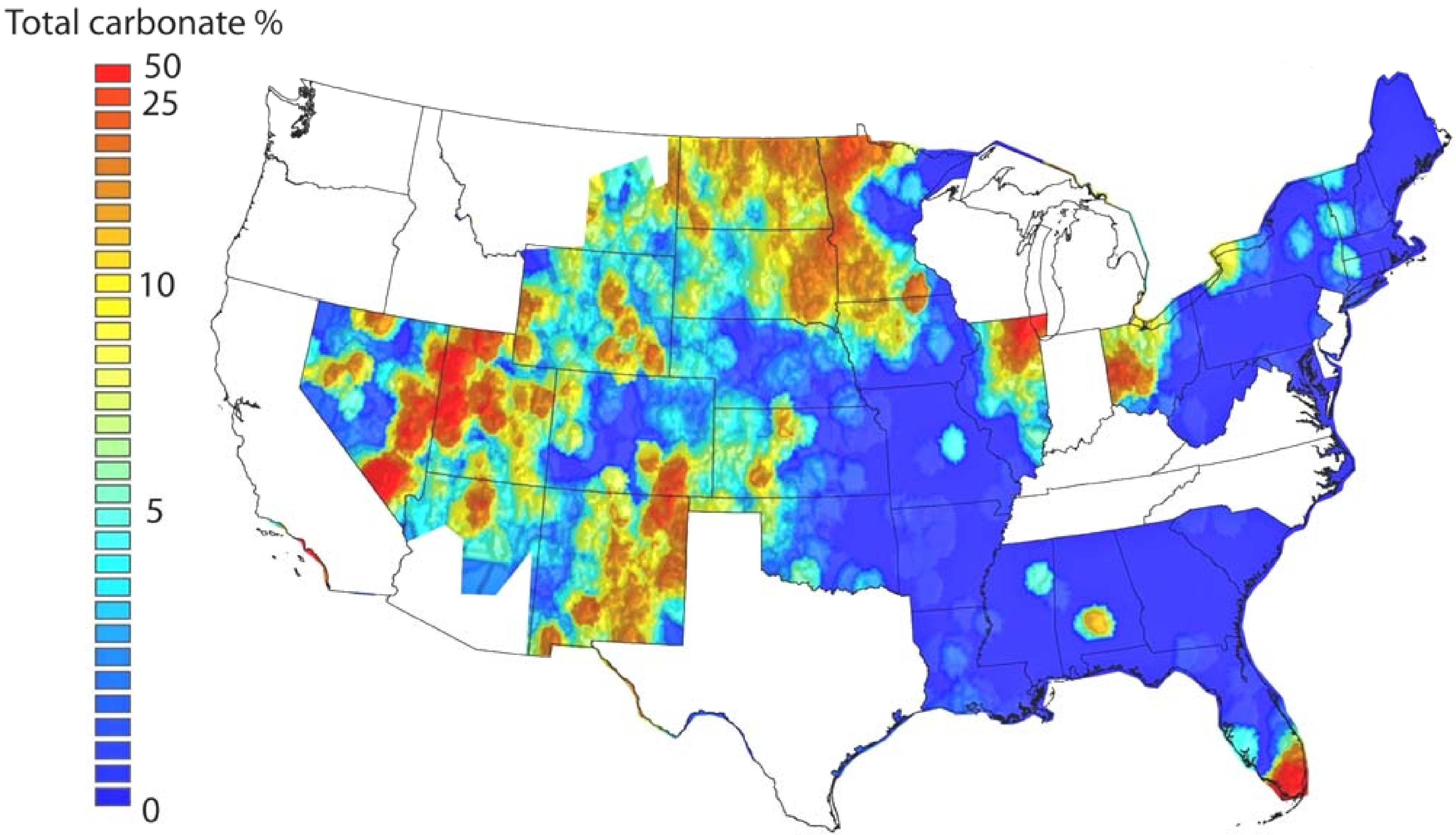
A FEW EXAMPLES



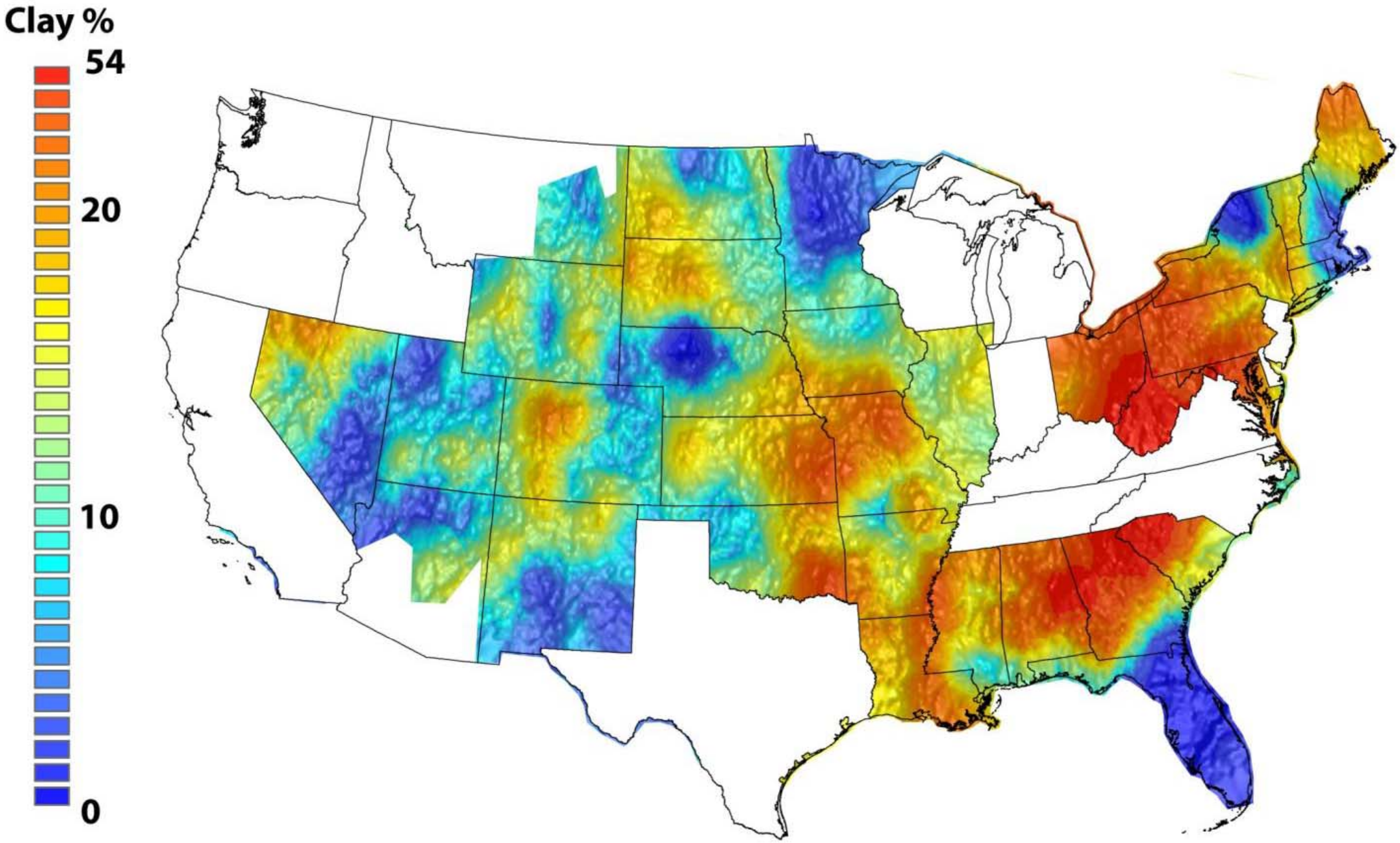
TOTAL FELDSPAR IN C-HORIZON SOIL



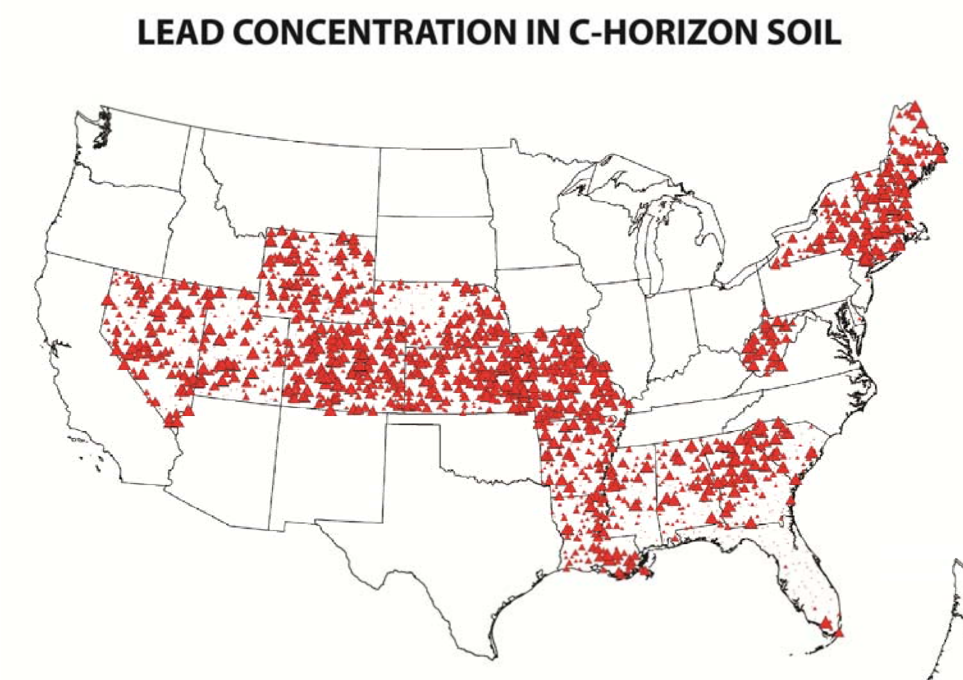
TOTAL CARBONATE MINERALS IN C-HORIZON



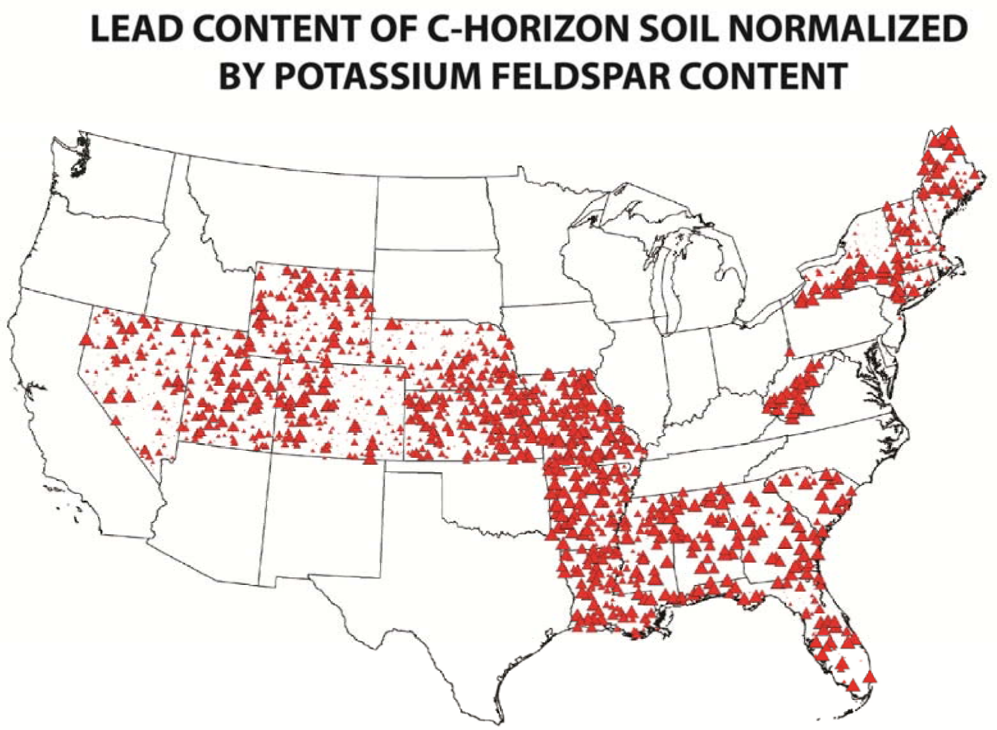
TOTAL CLAY MINERALS IN C-HORIZON



MINERALOGIC RESIDENCE OF TRACE ELEMENTS



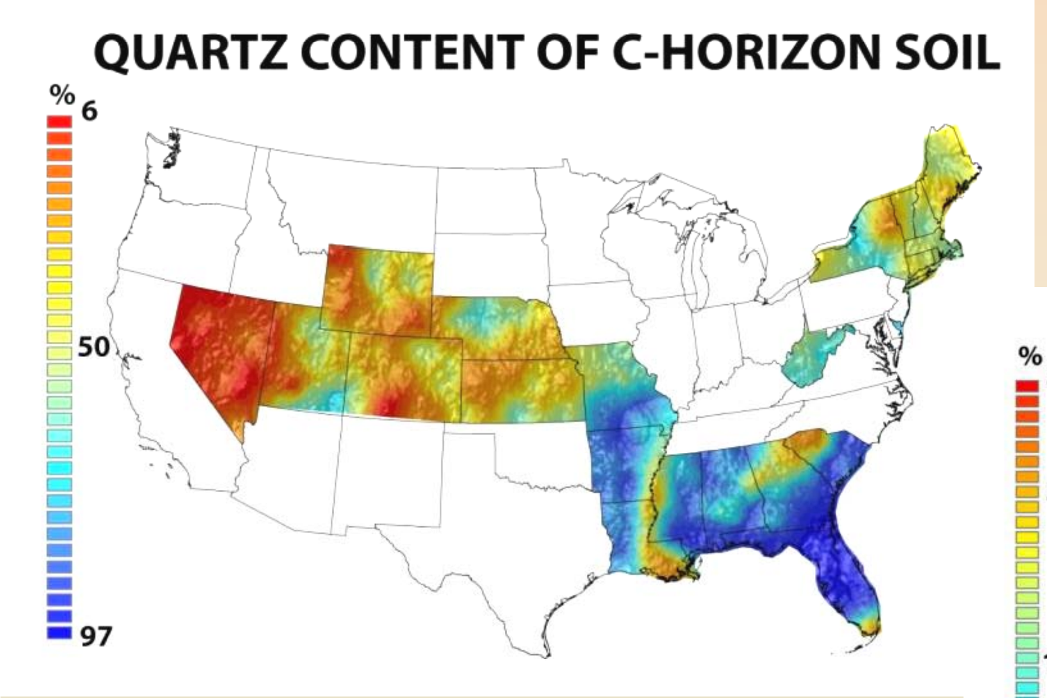
Lead is a common trace element in potassium feldspar where it is relatively immobile in many environments.



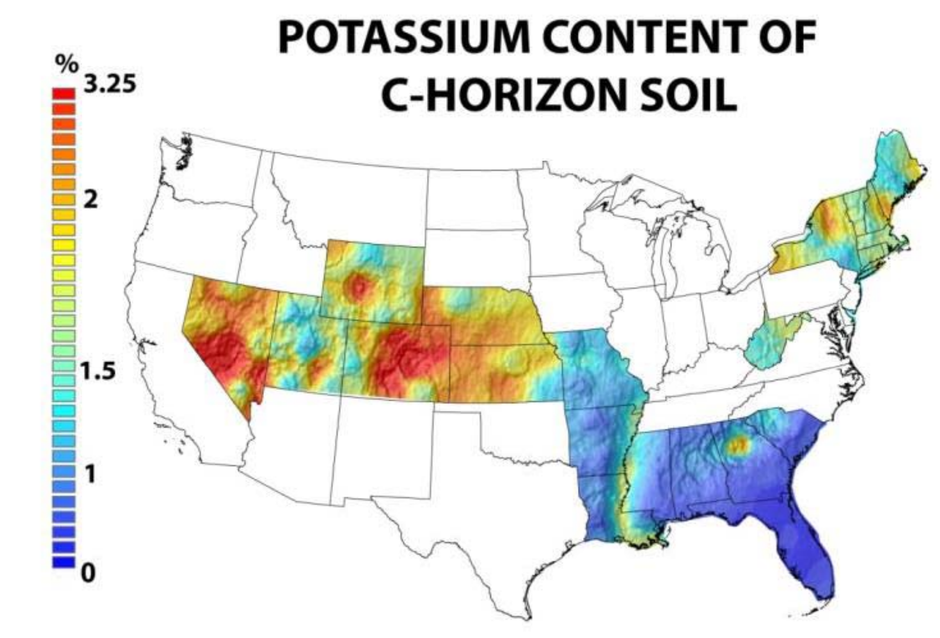
Normalizing lead by potassium feldspar highlights soils where significant amounts of lead reside in other minerals from which it may be more easily mobilized

QUARTZ DILUTION EFFECT

Comparison of quartz content, with inverted color ramp, and potassium content of C-horizon soil

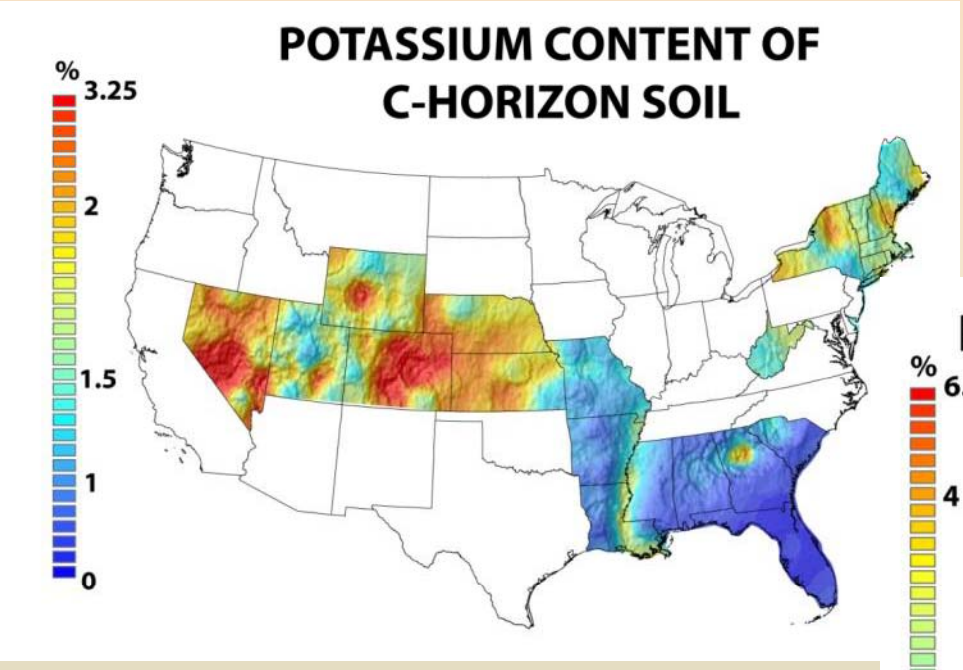


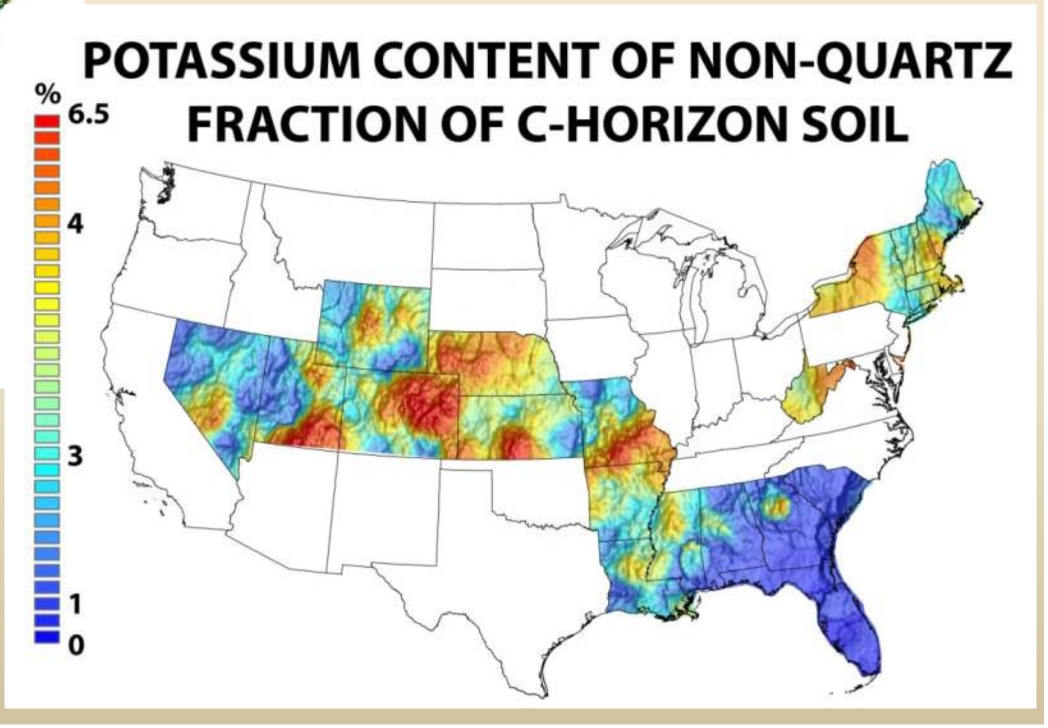
Potassium is just one of many Elements whose distribution mimics the quartz content of the soil.



QUARTZ DILUTION EFFECT

Comparison of potassium content of whole soil sample vs. the quartz-free fraction





CONCLUSIONS

Modern techniques for quantitative x-ray diffraction allow practical development of large data sets for soils and other mineral mixtures.

Such data are important in their own right for issues such as acid buffering capacity of soils and soil behavior controlled by clay content.

When combined with soil chemistry, quantitative soil mineralogy allows a more thorough understanding of the causes and consequences of variations in soil chemistry.