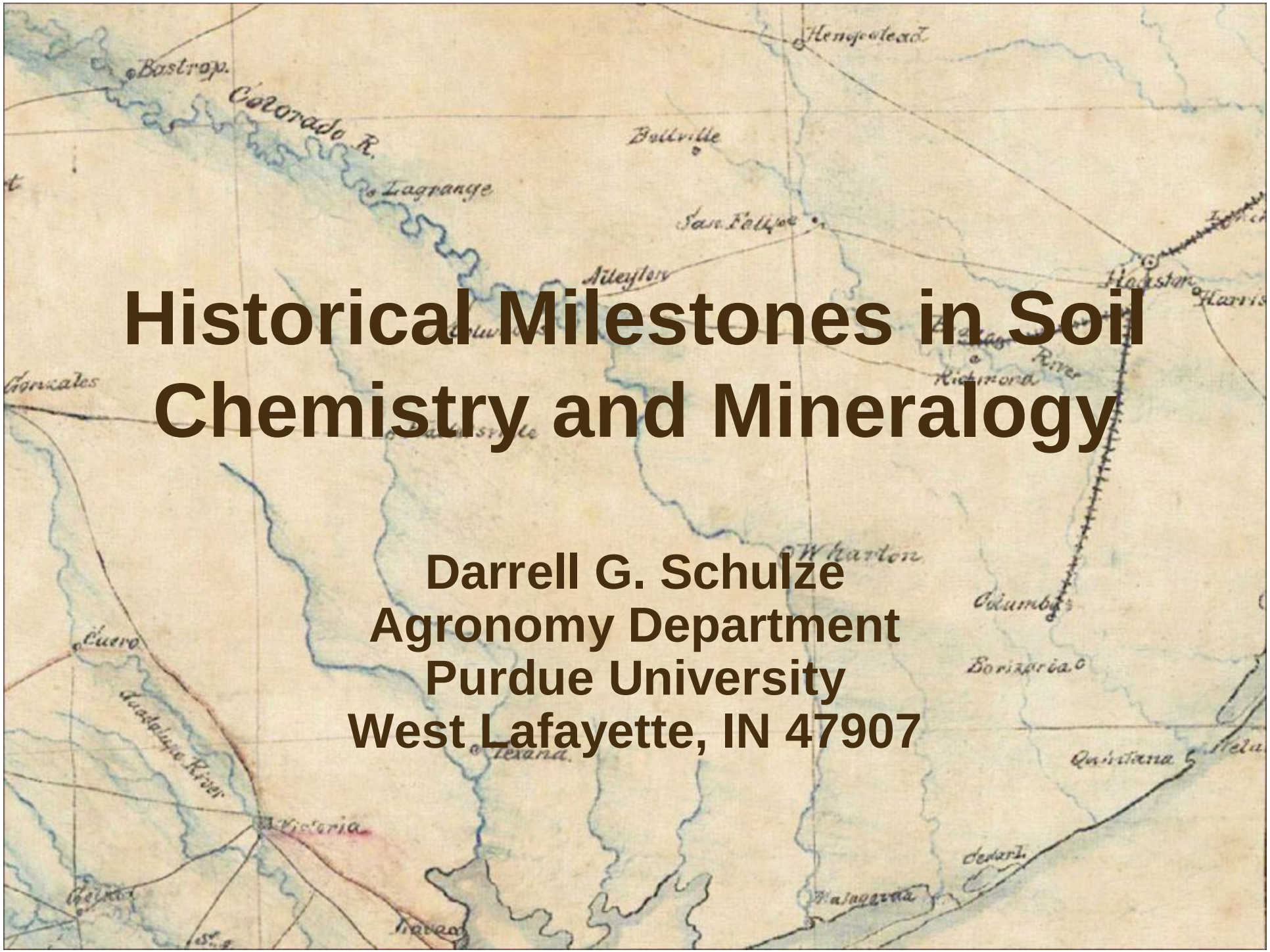


Historical Milestones in Soil Chemistry and Mineralogy

Darrell G. Schulze
Agronomy Department
Purdue University
West Lafayette, IN 47907

- G. W. Thomas. 1977. **Historical developments in soil chemistry: Ion exchange.** Soil Sci. Soc. Am. J. 41:230-238.
- R. E. Grim. 1968. **Concepts of the composition of clay materials.** Chapter 2 in *Clay mineralogy*, 2nd Ed. McGraw-Hill Book Co., New York.

Milestones

- Discovery of
  - Cation exchange properties of soils
  - Crystalline nature of soil clay minerals
  - Aluminum toxicity in soils

Cation Exchange Properties of Soils

Henry Stephen Thompson

- member, Royal Agricultural Society of England
- 1845, concerns about manure
  - loss of volatile ammonia from manure tanks and manure heaps
    - Experiments with H_2SO_4 + $CaSO_4$ or $FeSO_4$
      - $(NH_4)_2SO_4$ formed
    - “I was aware that the soil had a certain power of retaining ammonia.”
    - Will the soluble $(NH_4)_2SO_4$ be retained by soil?

- Loss of volatile and soluble fertilizers from large manure heaps
  - “I was desirous of ascertaining whether it would it be safe to plough manure in at any time during the winter when it was taken out of the yard.”
- Sought help from Joseph Spence, a chemist

- 4 Leaching experiments, summer 1845
- Experiment 1
  - "a light sandy loam of good quality, lying on the new red sandstone formation"
    - Percolator A – $(NH_4)_2SO_4$
    - Percolator B – $(NH_4)_2CO_3$
  - Leachate: $CaSO_4$, $(NH_4)_2SO_4$, NH_4Cl
- Experiment 2
  - like1, but leachate poured back on soil
  - similar results

- Experiment 3
  - "a black soil (from the bottom of an old stick heap)"
    - Percolator A – $(NH_4)_2SO_4$
    - Percolator B – $(NH_4)_2CO_3$
  - Leachate: $CaSO_4$, silica, some ammonia salts
- Experiment 4
  - "a strong clay soil"
  - very little mineral material in leachate

- “My main objective in making these experiments had now been obtained, and I had convince myself that either sandy, clayey, or black vegetable soil possessed the power of retaining a much larger amount of ammoniacal salt than they received in the most liberal manuring.”

- H. S. Thompson. 1850. *On the Absorbent Power of Soils*, J. Roy. Agric. Soc. England, 11:68-74.
  - "This set of experiments … may perhaps be regarded with some interest as the first discovery of a highly important property of soils, the knowledge of which can hardly fail to be beneficial to agriculture."
- ~1848, mentioned work to J. Thomas Way

John Thomas Way

- Consulting Chemist to the Royal Agricultural Society of England
- *On the Power of Soils to Absorb Manure*
  - Lecture to Royal Ag. Society, Spring 1850
  - Publication by same name in journal

- “The Members have already been favored by Professor Way with three very interesting lectures during the present year: the first on Guano, … the second on the adsorptive powers of soil in reference to manure, … the third, on butter and cheese making. In consequence of the great interest excited by Professor Way’s second lecture, he kindly consented to repeat its delivery, …”

On the Power of Soils to Absorb Manure

- J. Thomas Way. 1850. J. Roy. Agric. Soc. England, 11:313-379.
- 66 pages, details of 96 experiments

Way's Experiments

- Leaching of various solutions through columns of soil or clay

- Sorption of aqueous NH_3
  - NH_4OH solution
  - Ammonia smell removed
- Was NH_3 solution displacing water?
  - NaCl solution
  - Cl^- passed through immediately

- Sorption of aqueous NH_3
  - different soils, clays
    - Mr. Pusey's soil, Mr. Huxtable's soil, white "plastic clay" used for pottery
  - different exposure times, sand alone, dried soil (~150° C), burnt (calcined) soil and clay (powdered brick, powdered tobacco pipes), clays and soil digested with acid
  - Sorption
    - due to the *clay*
    - very rapid
    - not a condensation reaction
    - reduced by heating for some but not all clays

- Sorption of NH_4HCO_3
  - ammonia smell removed
  - sorbed from both NH_4HCO_3 & NH_4OH
- Sorption of $(NH_4)_2SO_4$
  - ammonium sorbed
  - $CaSO_4$ released
  - “… we meet with a remarkable circumstance. Sulphate of ammonia obeys the law of absorption so far as the ammonia is concerned, but its acid unites with lime, and comes through in solution.”

- Sorption of NH_4NO_3
  - NH_4^+ absorbed
  - NO_3^- passed through
- Sorption of NH_4Cl
- Sorption of KOH, $KHCO_3$, KNO_4, KCl, K_2SO_4, $NaSO_4$
- Sorption of $Ca(OH)_2$ (lime water)
  - Ca was arrested
  - attributed to formation of $CaCO_3$
- Sorption of $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$

- Sorption of Na_3PO_4, Peruvian guano ash
  - PO_4^{3-} retained from both
  - attributed to retention as calcium phosphate
- concerned with preferential flow
- quantitative sorption experiments

- Adsorption of “Organic Matters”
  - filtering putrid urine
    - “highly offensive stinking tank water”
    - “… ultimately more than 1 ounce of it passed, *quite clear*, free from smell or *taste*, except a peculiar *earthy* smell and taste derived from the soil.” (italics are Way’s)
  - stinking flax water
  - London sewer water
- displacement of Na from a Na-bentonite?

- “… we find that the soil retains the greater part – in most cases the whole – of those ingredients of manure upon which we are accustomed to place the most value.”

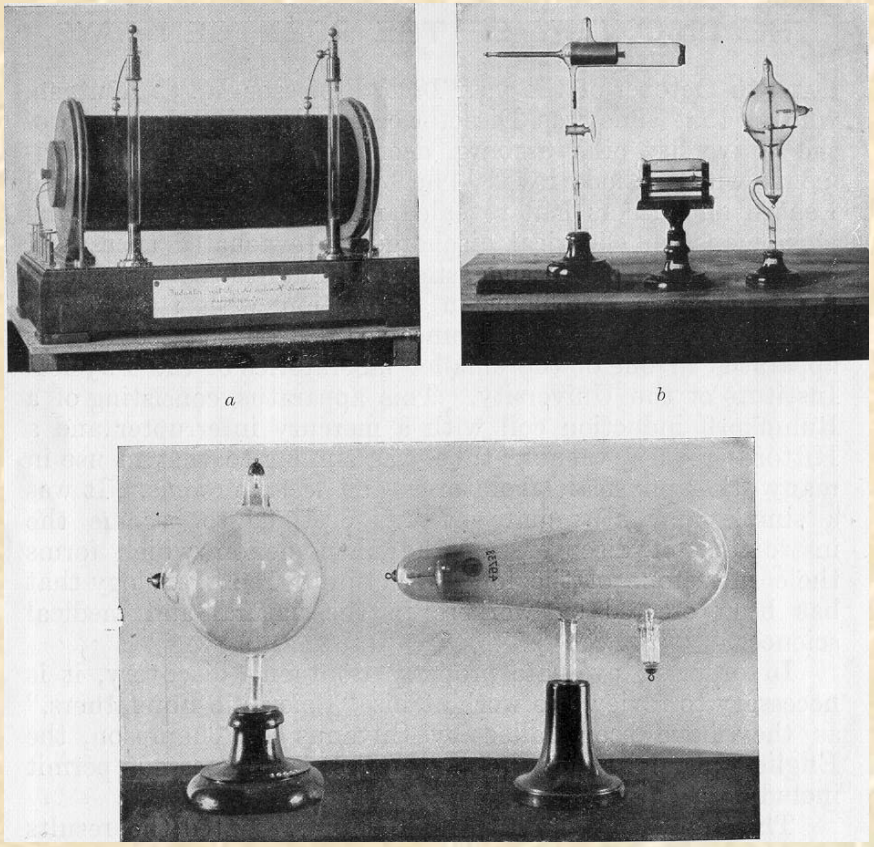
- “I shall forbear in the present paper from giving any very precise opinion as to the cause of the absorbent power which we have been studying.”
  J. Thomas Way. 1850. J. Roy. Agric. Soc. England, 11:313-379.

- On the power of soils to absorb manure (second paper). J. Roy. Agric. Soc. England, 13:123-143 (1852)
  - prepared synthetic aluminosilicates (zeolites?)
  - no convincing determination of the cause of the sorptive powers

Crystalline Nature of Soil Clay Minerals

Wilhelm Conrad Röntgen Discovers X-rays

Friday evening, November 8, 1895



“Eine Neue Art von Strahlen”, Dec. 28, 1895

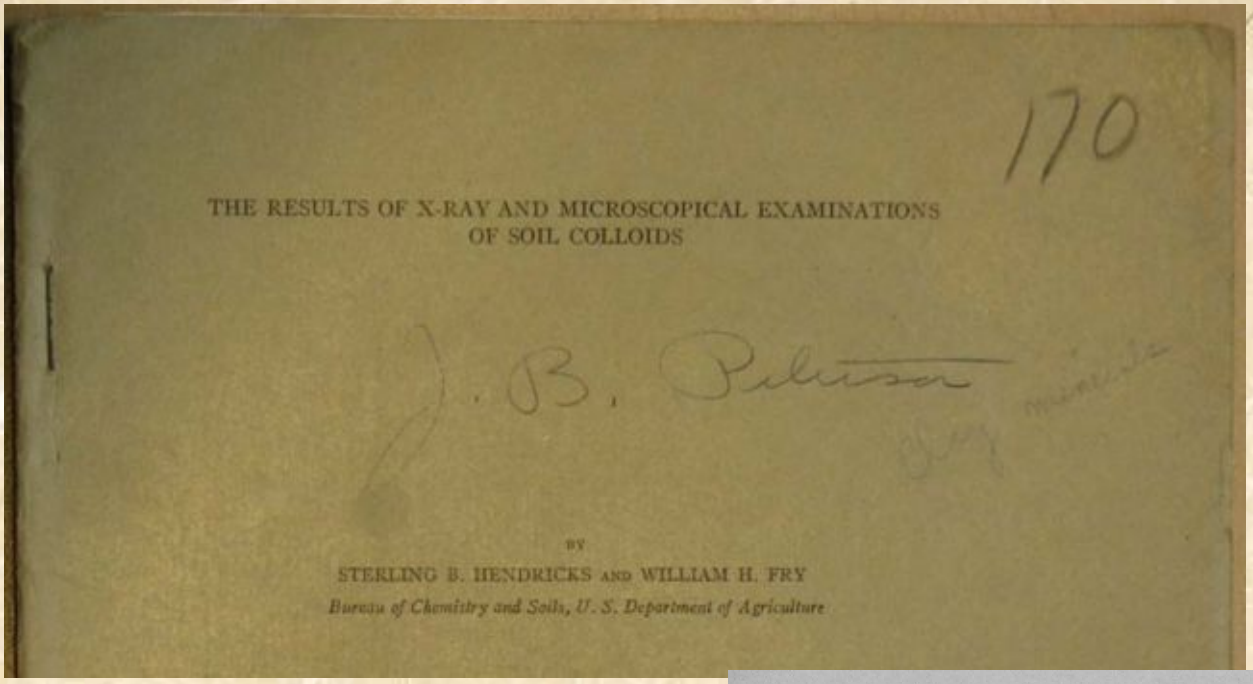
Frau Röntgen’s Hand, December 22, 1895

Discovery of X-ray Diffraction

- Max von Laue
  - develops theory, winter1912
  - decisive experiment
    - Walter Friedrich, Paul Knipping, Max von Laue
- crystals have periodic structures, x-rays are waves
- communicated to the Bavarian Academy of Sciences, June 8 and July 6, 1912
  - published in the *Proceedings of the Bavarian Academy of Sciences*

The Crystalline Nature of Clays

- first x-ray diffraction patterns of clay materials – clays are crystalline
  - A. Hadding (Sweden), 1923
  - F. Rinne (Germany), 1924
- establishment of soil clays as crystalline
  - S. B. Hendricks and W. H. Fry (USDA)
    - Soil Sci. 29:457-478 (1930)
  - W. P. Kelley, W. H. Dore, and S. M. Brown
    - Soil Sci. 31:25-45 (1932)



THE RESULTS OF X-RAY AND MICROSCOPICAL EXAMINATIONS OF SOIL COLLOIDS

170

BY

STERLING B. HENDRICKS AND WILLIAM H. FRY

Bureau of Chemistry and Soils, U. S. Department of Agriculture

Soil clays are discovered to be crystalline …

… 70 years after Thompson and Way's discovery of cation exchange

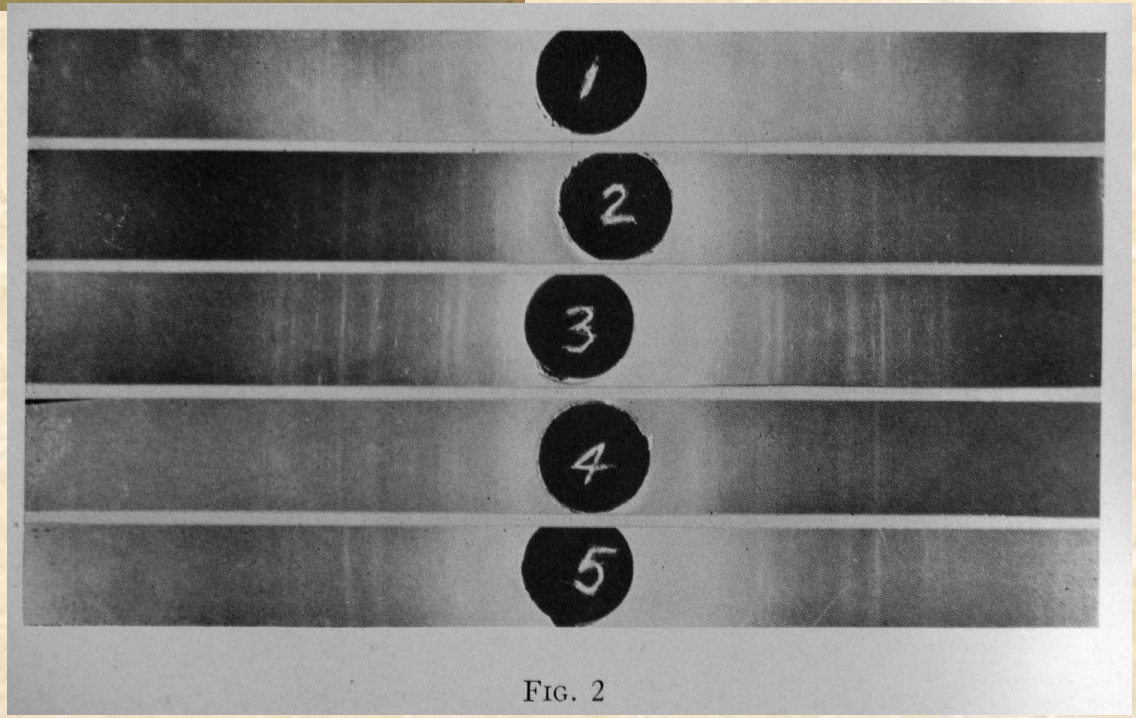


FIG. 2

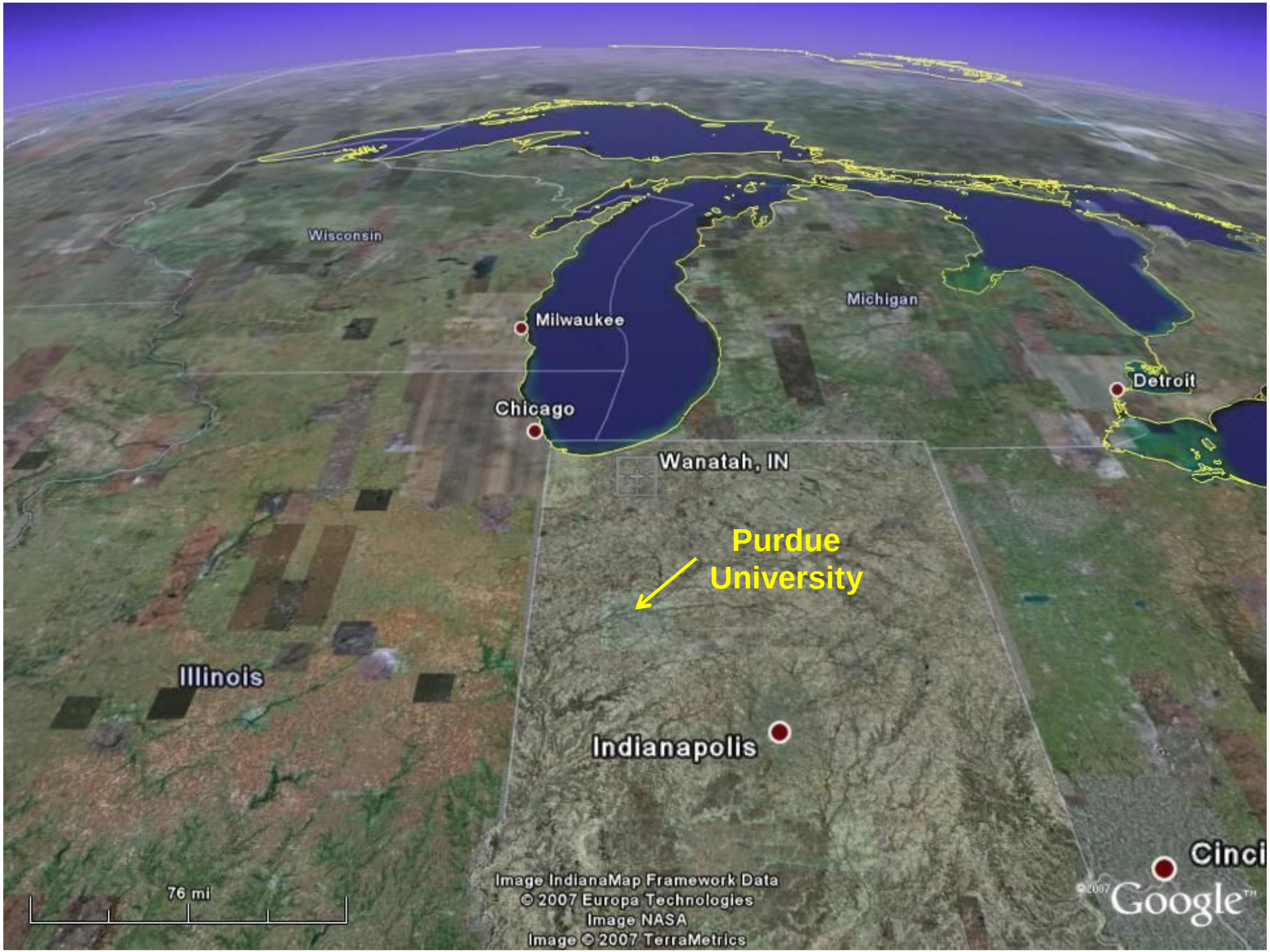
Aluminum Toxicity in Soils

Samuel D. Conner 1872 - 1936

Purdue University 1899 – 1936
Department of Agronomy 1912 - 1936

Bogus Soils!

- 1895, H. A. Huston, Purdue AES Bull. 57, *The Improvement of Unproductive Black Soils*
- “bogus” = unproductive spots in the field
- usually
  - sandy, peaty mineral soils; mucks (Saprists)
  - poor drainage, serious K deficiency, or both
- bogus soils near Wanatah, IN different
  - did not respond to
    - drainage or K fertilization
    - “any fertilizer or manure treatment”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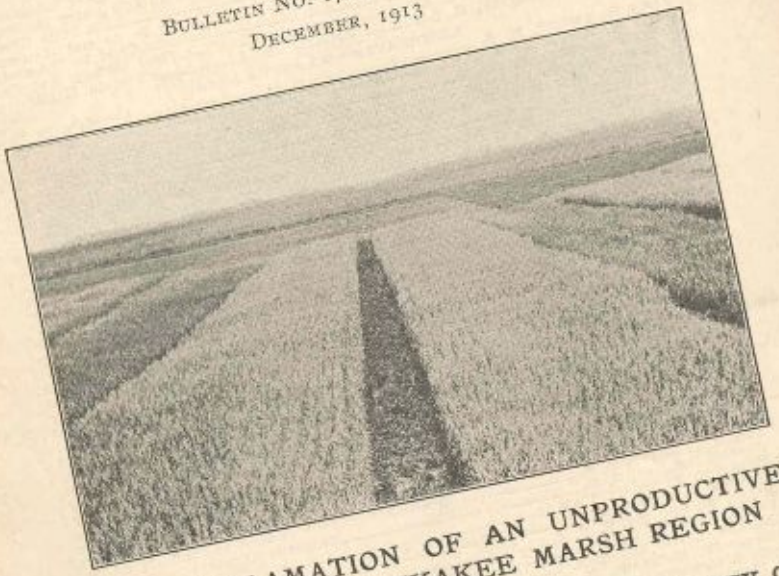


THE RECLAMATION OF AN UNPRODUCTIVE SOIL OF THE KANKAKEE MARSH REGION

SOIL ACIDITY, NITRIFICATION, AND THE TOXICITY OF SOLUBLE SALTS OF ALUMINUM

Published by the Station:
LAFAYETTE, INDIANA
U. S. A.

Abbott, Conner, & Smalley. 1913. Observations on “bogus” or unproductive soils

- “It is generally possible to identify this type of soil even in virgin prairie by the inferior native vegetation.”

- “… dewberries (*Rubus Canadensis*), red sorrel (*Rumex acetosella*), pine weed (*Hypericum gentianoides*), wild flax (*Koellia flexuosa*), various mosses, and a few inferior grasses and sedges cover the ground.”

- “In the worst places considerable areas of nearly bare ground are found.”

“Corn fails to grow normally …. The roots of the dwarfed corn plants which survive present a peculiar gnarled appearance …. Clovers refuse to grow at all.”

“Wheat in the Wanatah experimental field in 1911”

Untreated

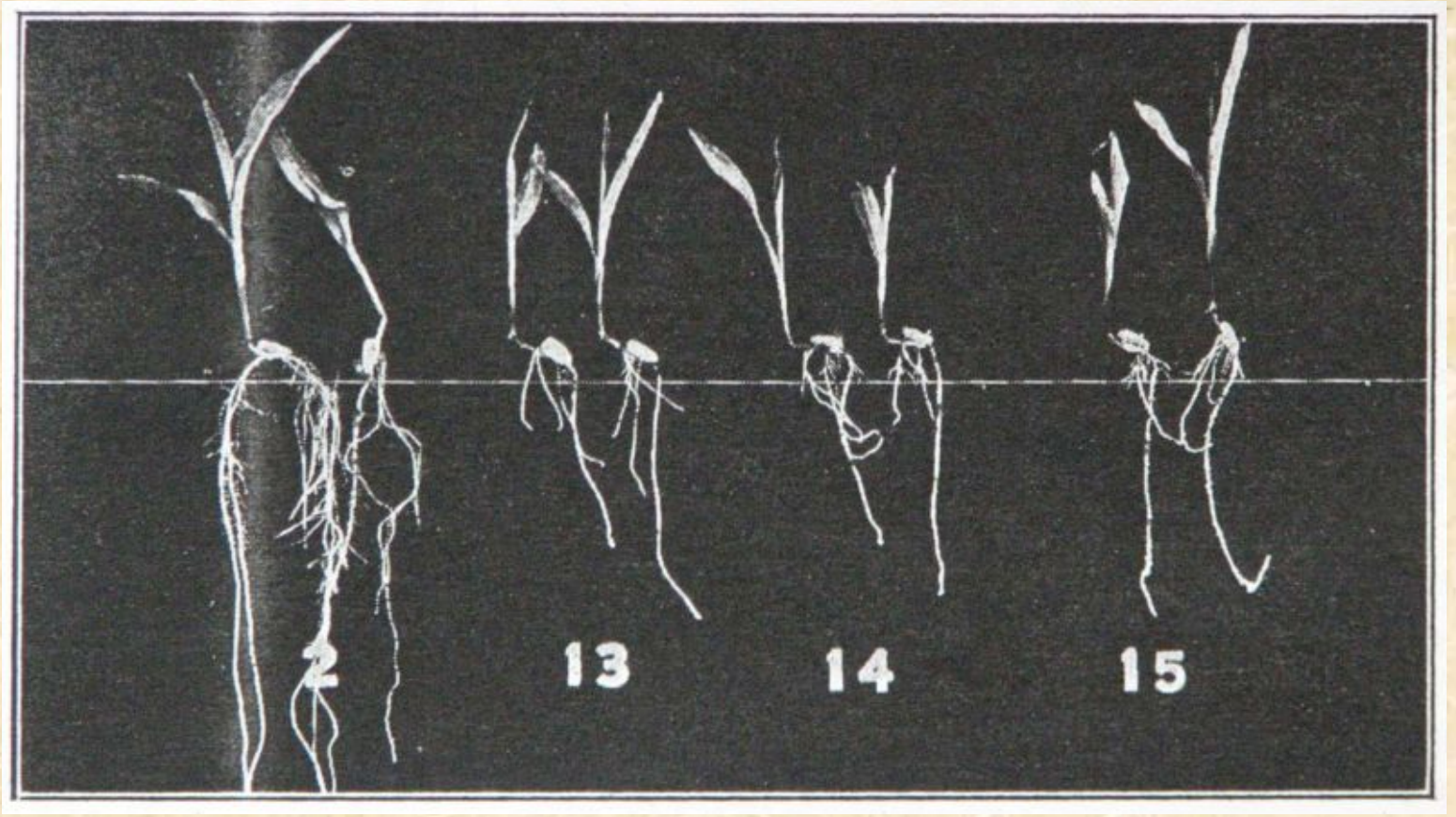
“Corn fails to grow normally …. The roots of the dwarfed corn plants which survive present a peculiar gnarled appearance …. Clovers refuse to grow at all.”

“Wheat in the Wanatah experimental field in 1911”

Lime + Fertilizer

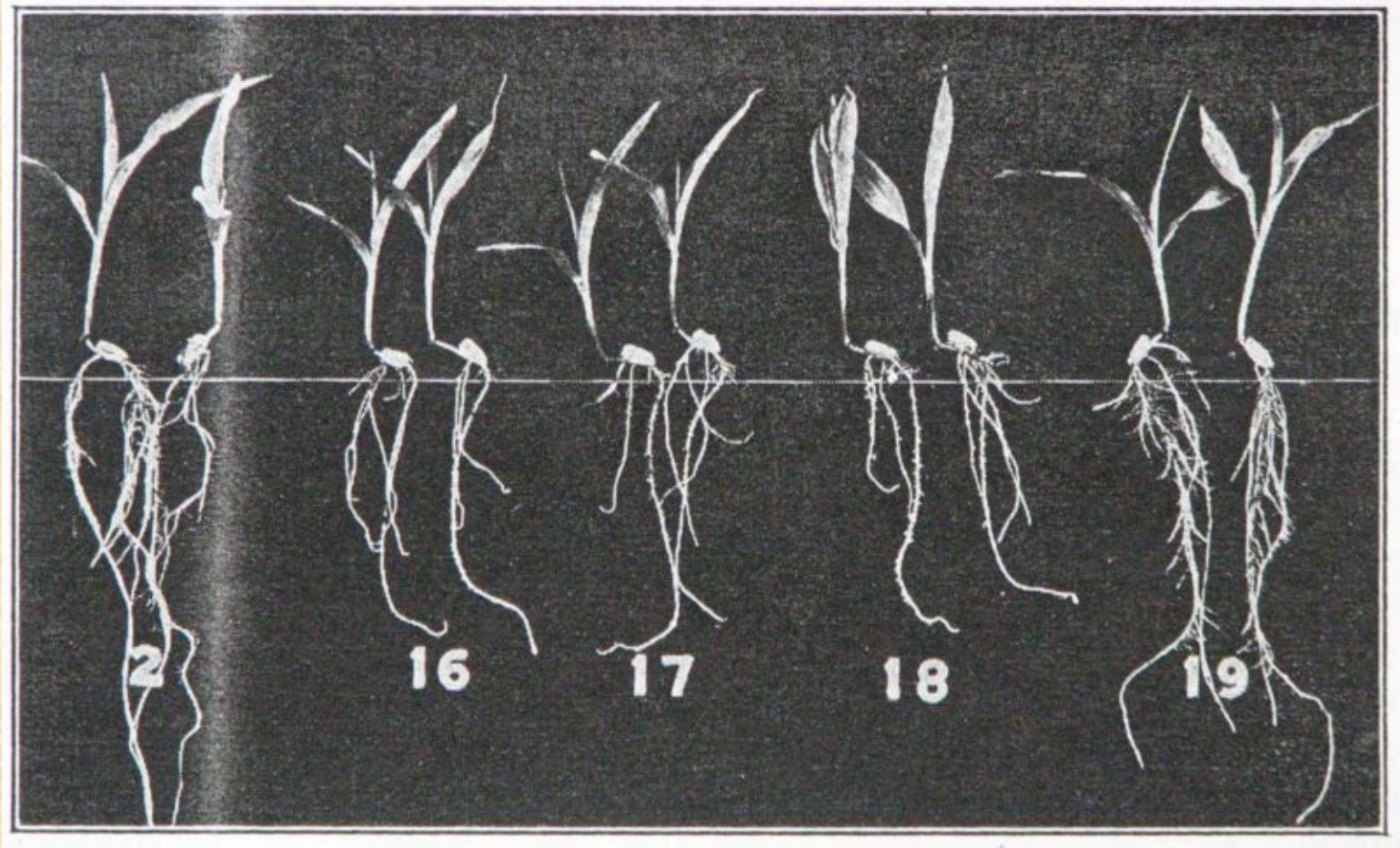
Untreated

Effect of $Al(NO_3)_3$ on Growth



control (nut. soln.)	0.01N $Al(NO_3)_3$	0.002N $Al(NO_3)_3$	0.001N $Al(NO_3)_3$

Effect of Soil Extract on Growth



control (nut. soln.)	0.033N soil ext.	0.002N soil ext.	0.001N soil ext.	0.033N soil ext.+$CaCO_3$

Abbott, Conner, & Smalley. 1913.

- identified Al-toxicity as the cause of the unproductive soil
- the first ever to show that soluble Al in soils was toxic to plants in the field

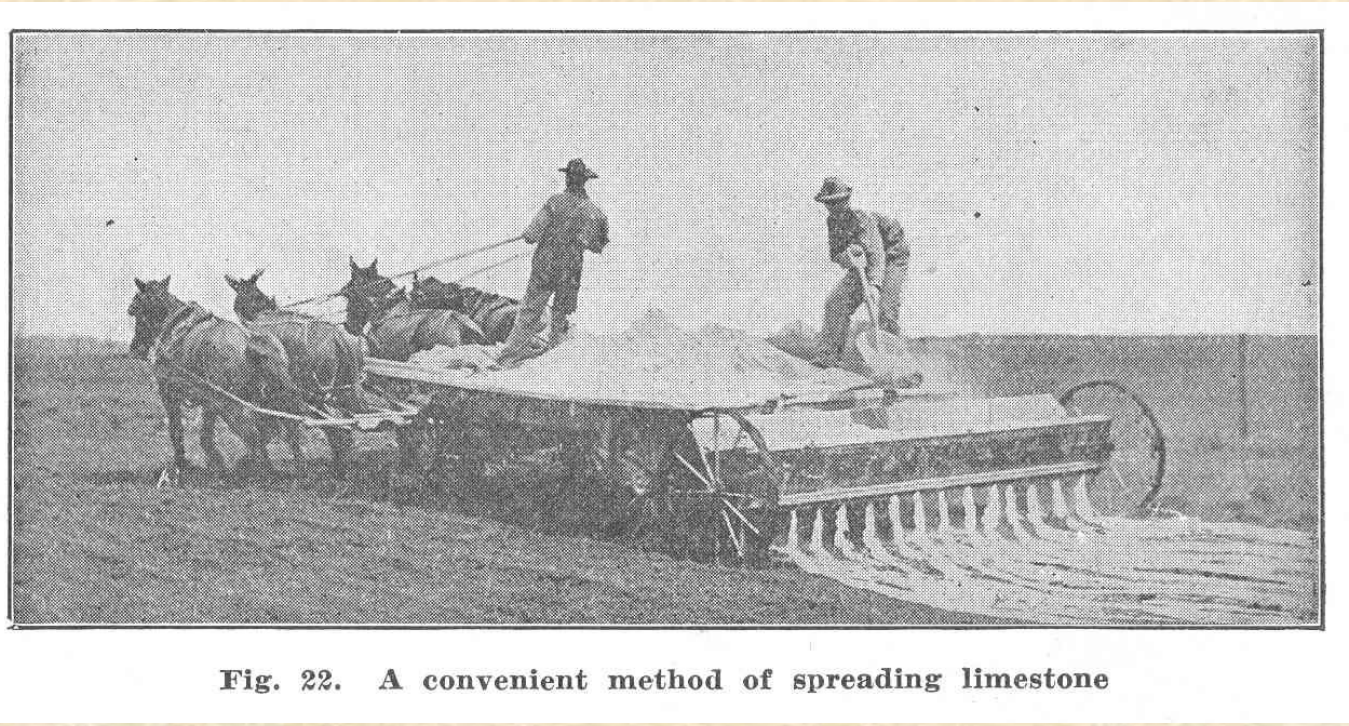


Fig. 22. A convenient method of spreading limestone

Samuel D. Conner 1872 - 1936

Purdue University 1899 – 1936
Department of Agronomy 1912 - 1936

Conner's Obituary:

"His discovery in 1912 of aluminum toxicity under certain soil conditions … [was a] noteworthy result of his work."

Milestones

- Discovery of
  - Cation exchange properties of soils
  - Crystalline nature of soil clay minerals
  - Aluminum toxicity in soils

Thank You!