

# **RETHINKING SULFIDIZATION AND THE ROLE OF HYDROGEN SULFIDE**

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# Sulfidization – the term

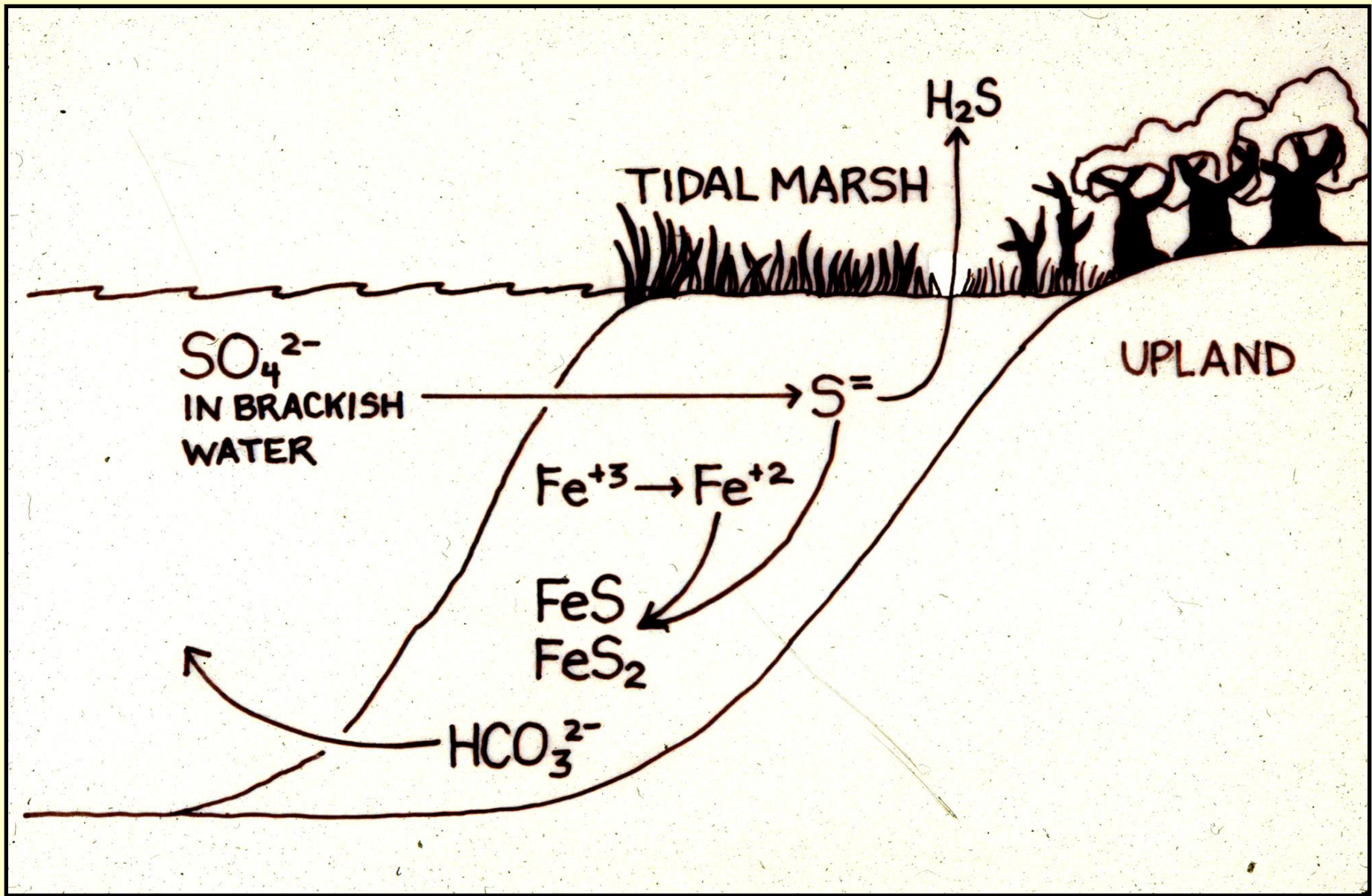
- **The term was conceived and introduced with the help of students in my soil morphology, genesis, and classification course at the University of Maryland in the 1980's as what we called a gross soil genesis process (equivalent to terms such as podzolization, calcification, salinization) to explain the formation of sulfide-bearing soil materials, potential acid sulfate soils and soil materials, however, the concepts were developed by others, going back to the first international acid sulfate symposium/conference, held at Wageningen, The Netherlands, in 1972, 40 years ago.**

# Classic early work by David T. Rickard, reported in Proceedings of the First Symposium (1973)

- Rickard, who did his dissertation work on the subject at University of London, was research fellow, Geologic Institute, Stockholm University, Sweden, at time of his paper for the 1<sup>st</sup> symposium.
- Rickard used the terms sulfidation and pyritization for essentially what in the Fanning and Fanning (1989) book is called sulfidization.

# **Sulfidization – Brief Definiton**

- Set of processes by which sulfide minerals (mainly iron sulfides) form and accumulate in anaerobic soil materials.**
- Occurs most frequently/significantly in marine or estuarine soil environments where large quantities of sulfate sulfur are available from sea water for chemical reduction of S to sulfide and where iron is available in the form of iron oxides or oxyhydroxides, typically in sediments.**



**Idealized diagram for sulfidization in a tidal marsh soil.  
After Fanning and Fanning (1989, page 71, Fig. 10.1).**

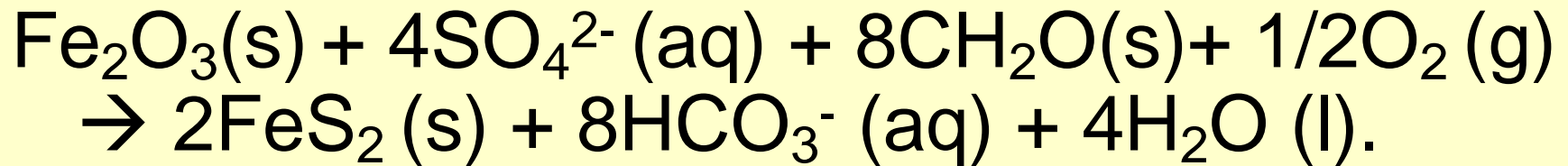




**Chesapeake Bay tidal marsh in which sulfidization occurs. The man likely detected the odor of hydrogen sulfide emanating from the marsh. Tidal flushing supplies sulfate, removes bicarbonate and may supply small amounts of oxygen.**

# Traditional idealized chemical reaction to represent sulfidization

(Pons et al, 1982, Fanning and Fanning, 1989)



Essential ingredients according to Pons et al., 1982

Sulfate – most typically dissolved in sea water.

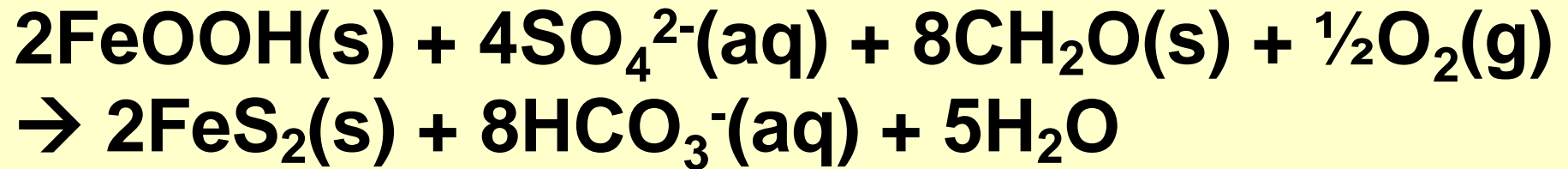
Iron-containing minerals – e.g. iron oxides or oxyhydroxides in sediments.

Metabolizable organic matter – represented here as  $\text{CH}_2\text{O}$ .

Sulfate-reducing bacteria – e.g. *Desulfovibrio desulfuricans*.

Anaerobically alternating with limited aeration.

**Alternative traditional overall sulfidization reaction with iron source as Fe oxyhydroxide instead of as Fe oxide.**





# Some unsatisfactory aspects of the traditional reaction

- 1. The reaction employs oxygen as a reactant in environments such as tidal marshes and subaqueous soils that are considered to be predominantly highly anaerobic.**
- 2. The reduction of both the S and the Fe appear to be by electrons supplied by the oxidation of the organic matter, whereas we now envision reduction of the Fe by sulfide after its production by reduction of sulfate.**

**The succeeding slides  
present a series of reactions  
leading to an alternative  
overall reaction.**

Reduction of sulfate S to sulfide by serving as electron acceptor during oxidation of organic matter

- $\text{SO}_4^{2-}(\text{aq}) + 2\text{CH}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g}) + 2\text{HCO}_3^-(\text{aq})$
- $4\text{SO}_4^{2-}(\text{aq}) + 8\text{CH}_2\text{O}(\text{s}) \rightarrow 4\text{H}_2\text{S}(\text{g}) + 8\text{HCO}_3^-(\text{aq})$
- We envision these rxns to take place primarily microbially. The second (lower) version is the first times 4 -- for combining this rxn with subsequent rxns for new overall sulfidization reaction.



MICROGRAPH OF DESULFOVIBRIO  
AFTER RICKARD (1973)

This slide shows a copy of a picture, stated to be an electronmicrograph of a typical sulfate-reducing bacterium *Desulfovibrio vulgaris*, that reduces sulfate to sulfide as it gets its energy from oxidation of organic matter (after Rickard, 1973, from Proceedings of 1<sup>st</sup> International Acid Sulfate Soils Symposium).

# Production of FeS<sub>2</sub> and FeS by reaction of H<sub>2</sub>S with FeOOH

- **2FeOOH(s) + 3H<sub>2</sub>S(g) → FeS<sub>2</sub>(s) + FeS(s) + 4H<sub>2</sub>O(l), ΔGr° = -1207.719 kJ, highly exothermic. Envisioned to take place primarily as a chemical reaction.**
- **H<sub>2</sub>S reacts very rapidly with moist iron “oxide” bearing soil materials and turns them from reddish or brownish colors to black, see Bohn et al. (1989), other rxns have been proposed.**



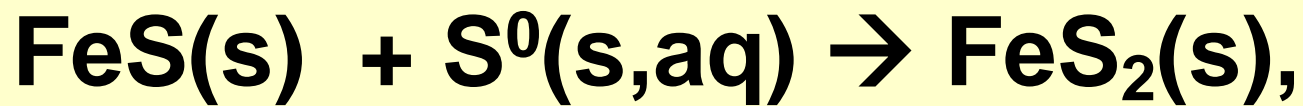
A proposed rxn to convert  
FeS to FeS<sub>2</sub>

- **FeS (s) + H<sub>2</sub>S (g) → FeS<sub>2</sub>(s) + H<sub>2</sub> (g)**
- **ΔG<sub>r</sub><sup>o</sup> = -30.7648 kJ, exothermic**

Addition of 3 reactions (top) to give new overall sulfidization reaction(below)

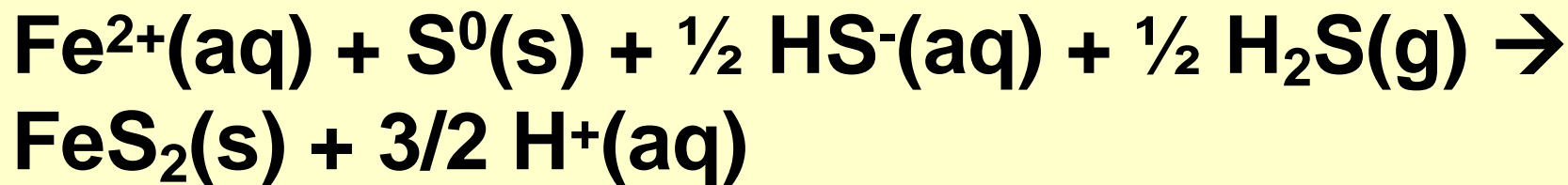
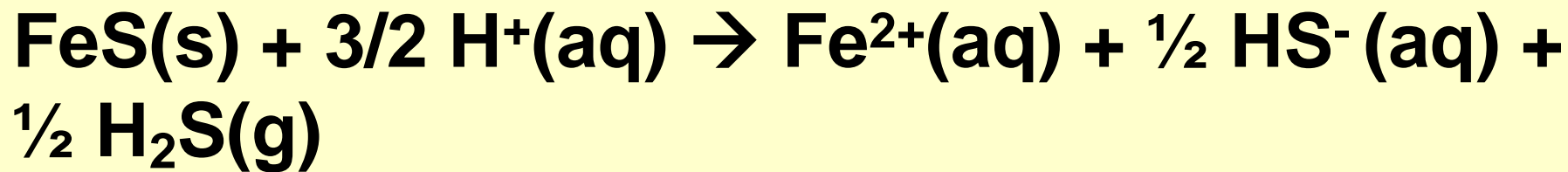
- $4\text{SO}_4^{2-} + 8\text{CH}_2\text{O} \rightarrow 4\text{H}_2\text{S} + 8\text{HCO}_3^-$
  - $2\text{FeOOH} + 3\text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{FeS} + 4\text{H}_2\text{O}$
  - $\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$
- 
- $4\text{SO}_4^{2-}(\text{aq}) + 8\text{CH}_2\text{O}(\text{s}) + 2\text{FeOOH}(\text{s})$   
 $\rightarrow 2\text{FeS}_2(\text{s}) + 8\text{HCO}_3^-(\text{aq}) + \text{H}_2(\text{g}) +$   
 $4\text{H}_2\text{O}(\text{l})$

# Alternative Reaction to convert FeS to FeS<sub>2</sub> proposed by Bruce James

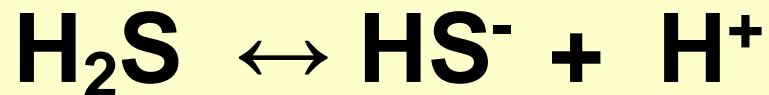


$$\Delta G_r^\circ = -30 \text{ kJ/mol}$$

Bruce got the above reaction by adding together, the two reactions given below



**Succeeding slides provide some evidence for why we think that the conversion of Fe “oxides” to Fe sulfides is by chemical reaction with hydrogen sulfide, or HS<sup>-</sup>, with which H<sub>2</sub>S is in equilibrium,**



# First Evidence

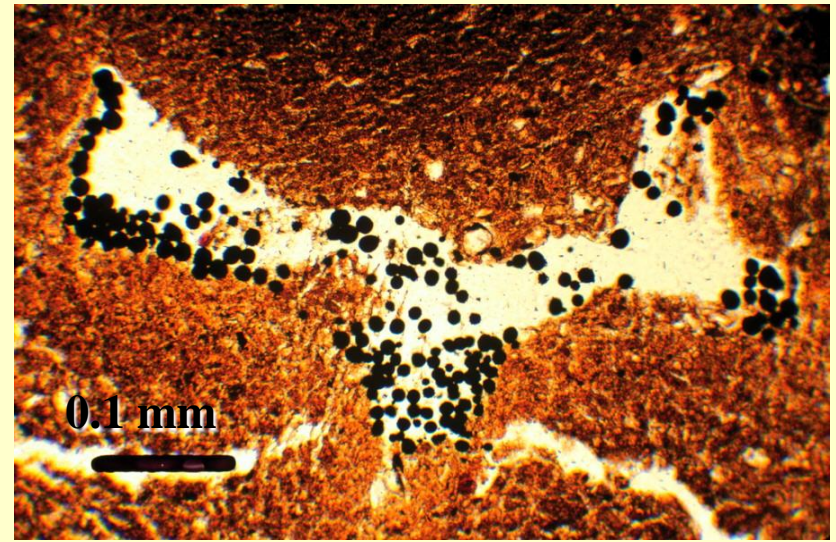
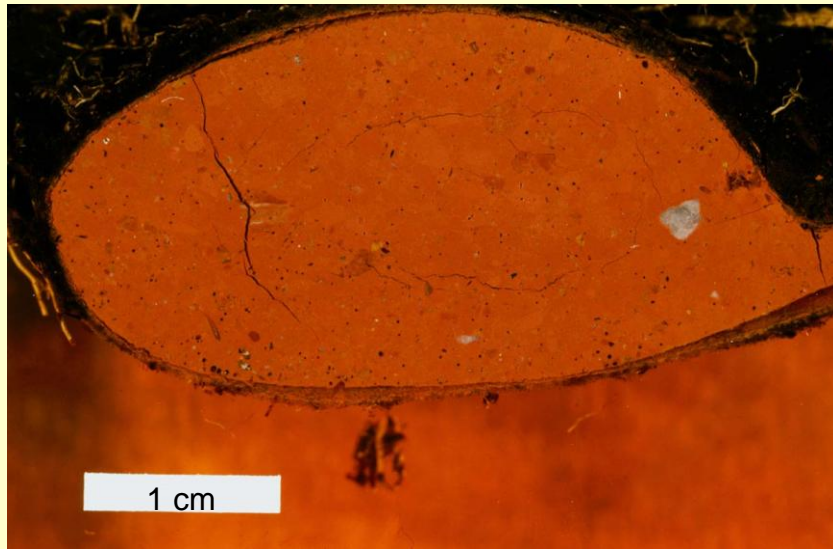
- **Rabenhorst's induced iron sulfide formation in Chesapeake Bay tidal marsh soils, from burial of iron "oxide" bearing soil material (Christiana Bt horizon material) in a *Sulfihemist*, retrieved and examined after 2 years.**
- **Pyrite formed within the soil material, where no organic matter was present, next 2 slides.**



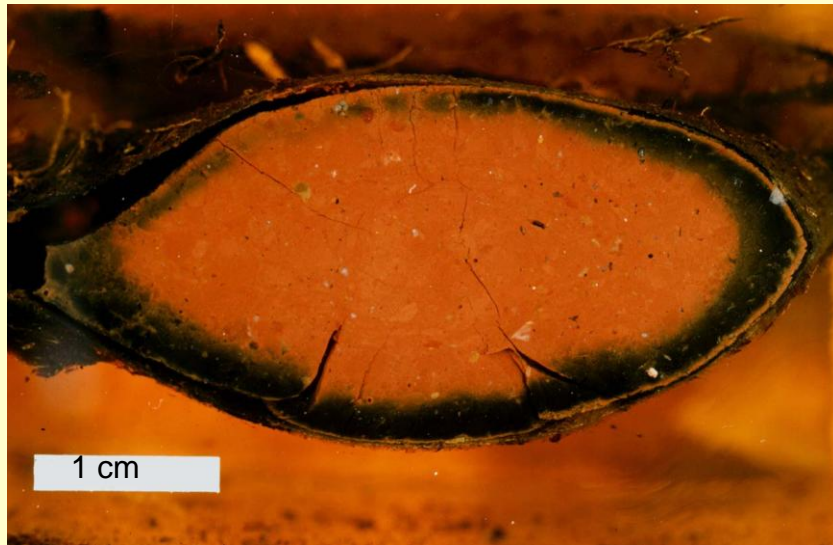


A tidal marsh soil profile in which sulfidization takes place to form iron sulfides. The marks on the tape are 10cm (2.5 inches) apart. The top 45cm of the soil is peat that has accumulated under the anaerobic marsh soil conditions.





**Initial** Development of monosulfide rims (lower left) and even pyrite framboids (upper and lower right). Slide from previous papers.



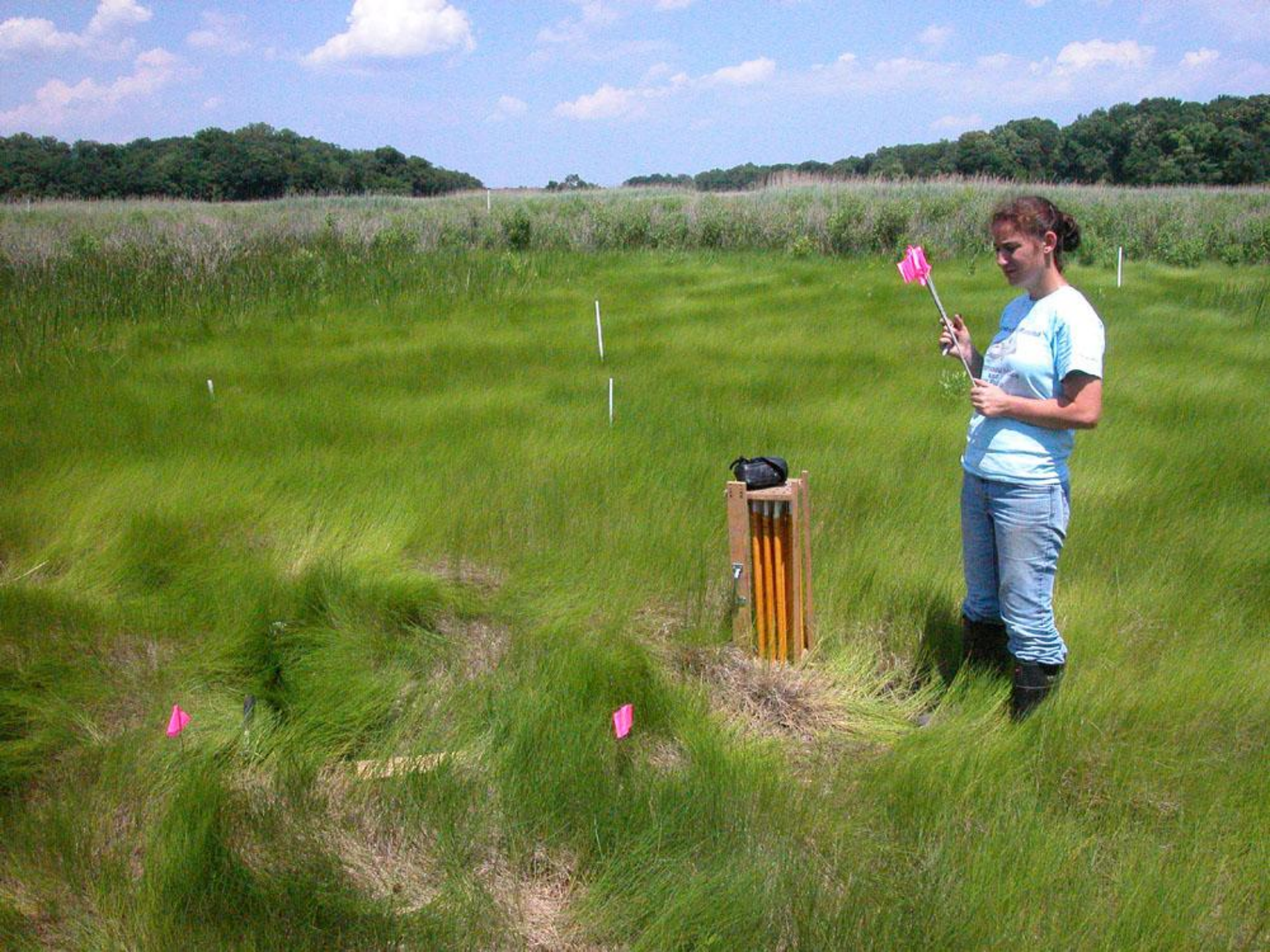
**After 2 years**



# Second Evidence

- **Observations of extremely rapid formation of iron monosulfides on IRIS (indicator of reduction in soils) tubes inserted into tidal marsh and subaqueous soils. The red iron “oxide” coated tubes blacken within 24 hours and in some cases within 5 minutes (see abstract and succeeding slides).**







1 hr

Transquaking  
Typic Sulfihemist  
SERC

24 hr

48 hr

96 hr



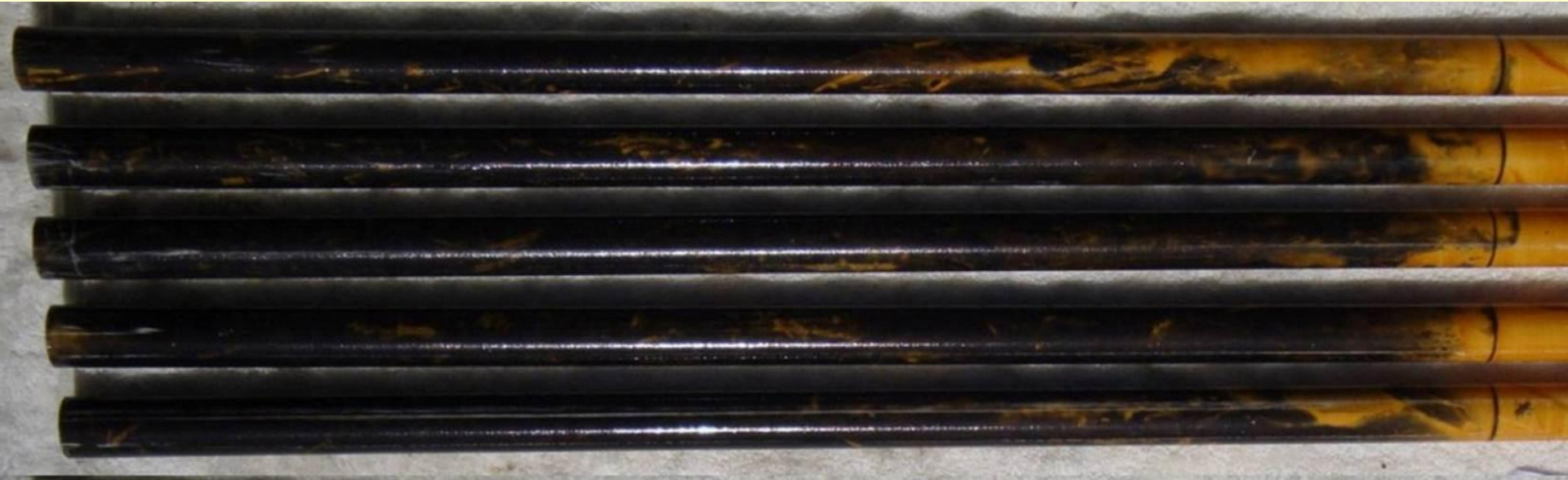


24



Reoxidized (2hrs)

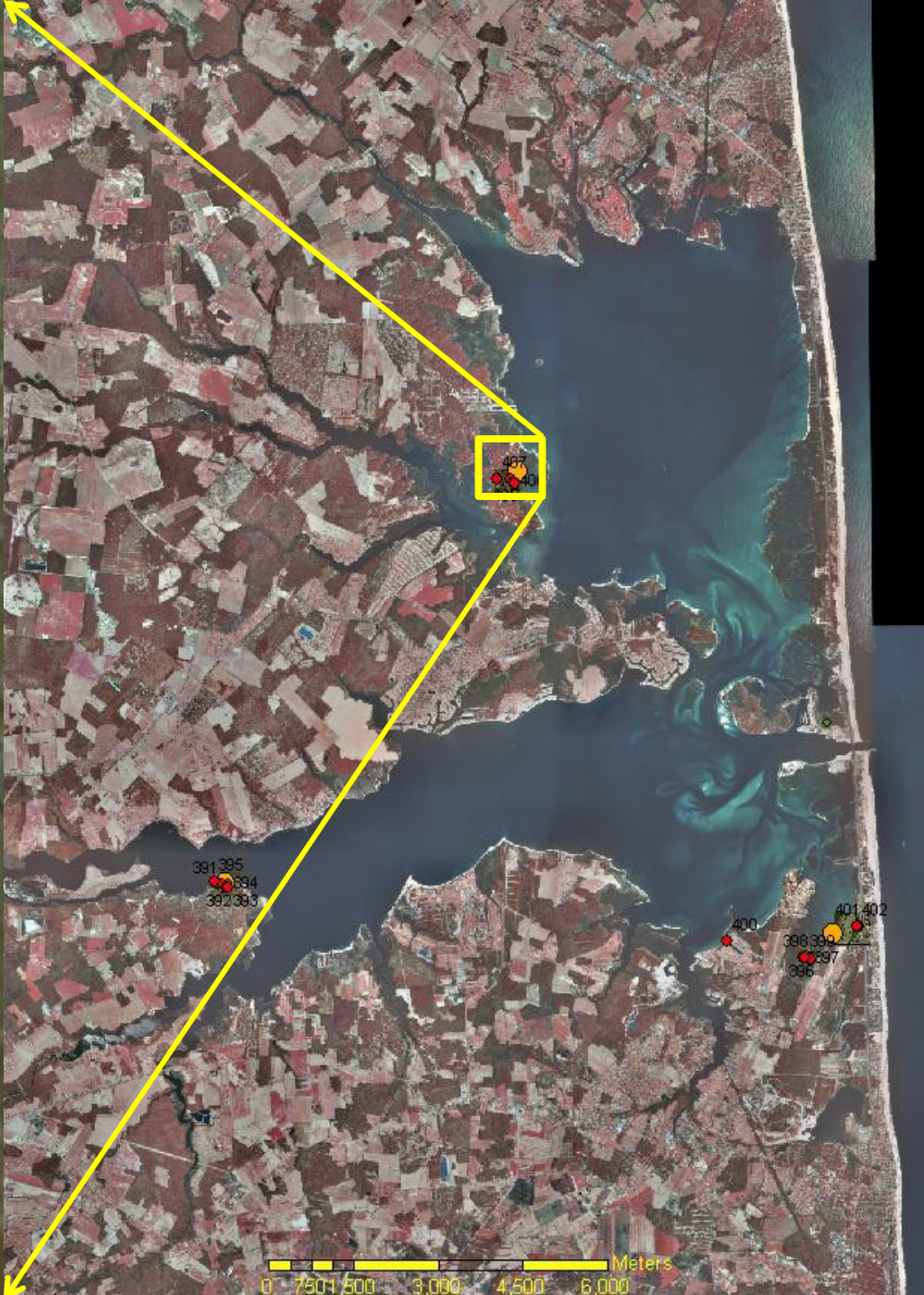
**“Blackened” in only 5 minutes following installation**  
**Suggests porewater sulfide concentration is 5 – 10 mmol S=**



**Broadkill Series**

**Fine-silty, mixed, active, nonacid, mesic *Typic Sulfaquents***







**PHILADELPHIA, PA**  
- START AND END TOUR -

**STOP 9**  
BALTIMORE, MD

**STOP 8**  
UNIVERSITY OF MARYLAND  
AT COLLEGE PARK, MD

**STOP 7**  
PRINCE WILLIAM  
FOREST PARK, VA

**STOP 6**  
GARISONVILLE, VA

**STOP 5**  
STAFFORD COUNTY  
AIRPORT, VA

**POPES CREEK**

**LAPLATA, MD**  
- OVERNIGHT REST STOP -

**STOPS 3 + 4**  
SMITHSONIAN  
ENVIRONMENTAL  
RESEARCH CENTER, MD

**STOP 1**  
REHOBOTH BAY, DE

**STOP 2**  
BLACKWATER  
NATIONAL WILDLIFE REFUGE, MD

**9**

ATLANTIC  
OCEAN

## **Third Evidence, sulfidized/pyritized archeological Native American artifacts.**

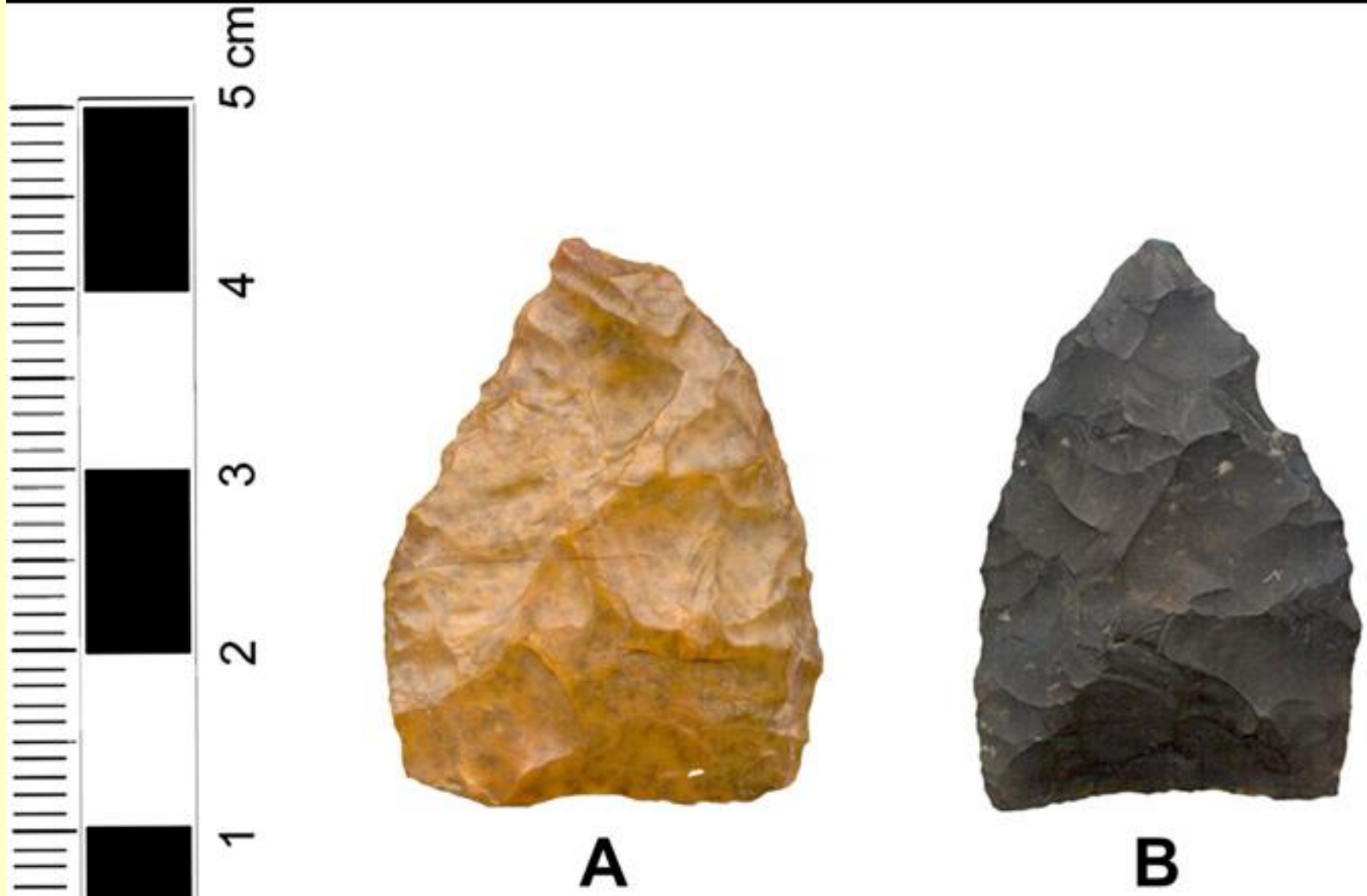
- **Cite Lowery and Wagner (2012) paper, see abstract.**
- **Show some pictures from the paper.**
- **Document presence of pyrite in blackened parts of jasper artifacts by XRD, new data from Rabenhorst.**
- **Cross section of artifact, reddish interior, blackened surface, see abstract.**



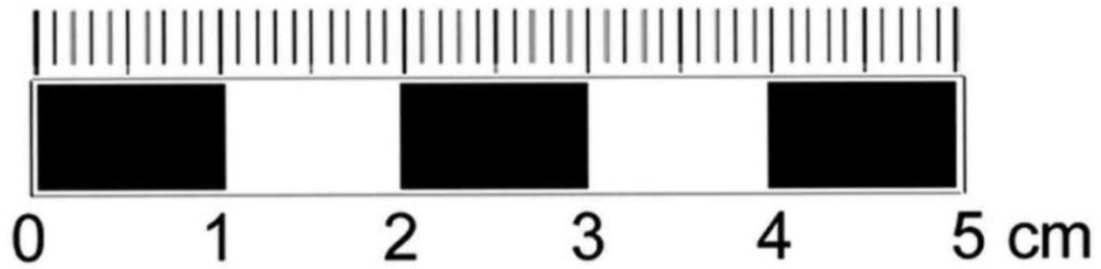
**Lowery, D. and D.P. Wagner. 2012. Geochemical impacts to prehistoric iron-rich siliceous artifacts in the nearshore coastal zone. Journal of Archaeological Science 39:600-607**

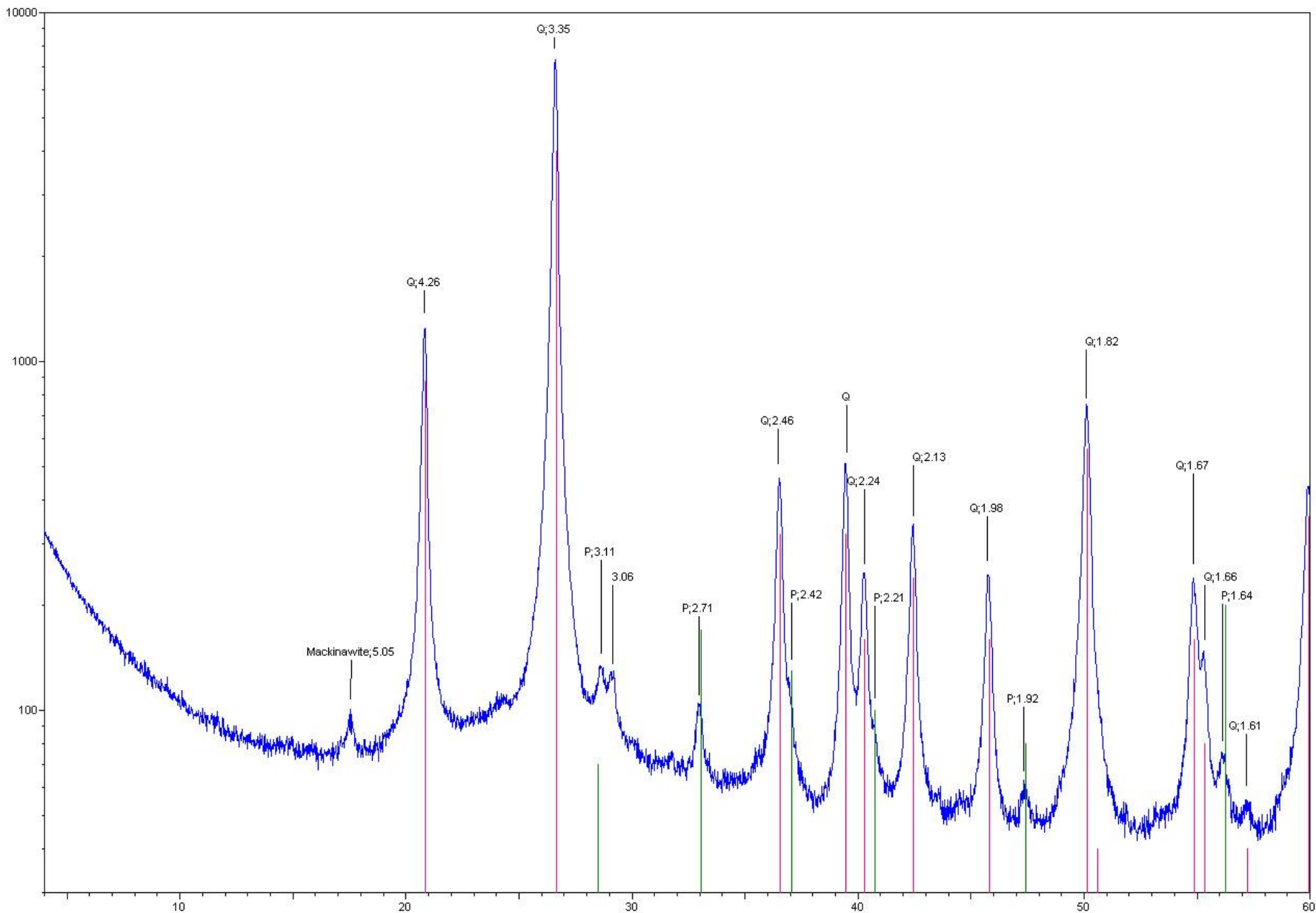


**An assemblage of sulfidized artifacts found at a drowned site (44NH454) in Northampton County, Virginia. Picture taken from paper by Wagner and Lowery in Fall 2011 Pedologue**



**Unsulfidized (A) and sulfidized (B) jasper projectile points. Image copied from Fig. 2 of Lowery and Wagner paper. Black (B) called chert by other scientists.**





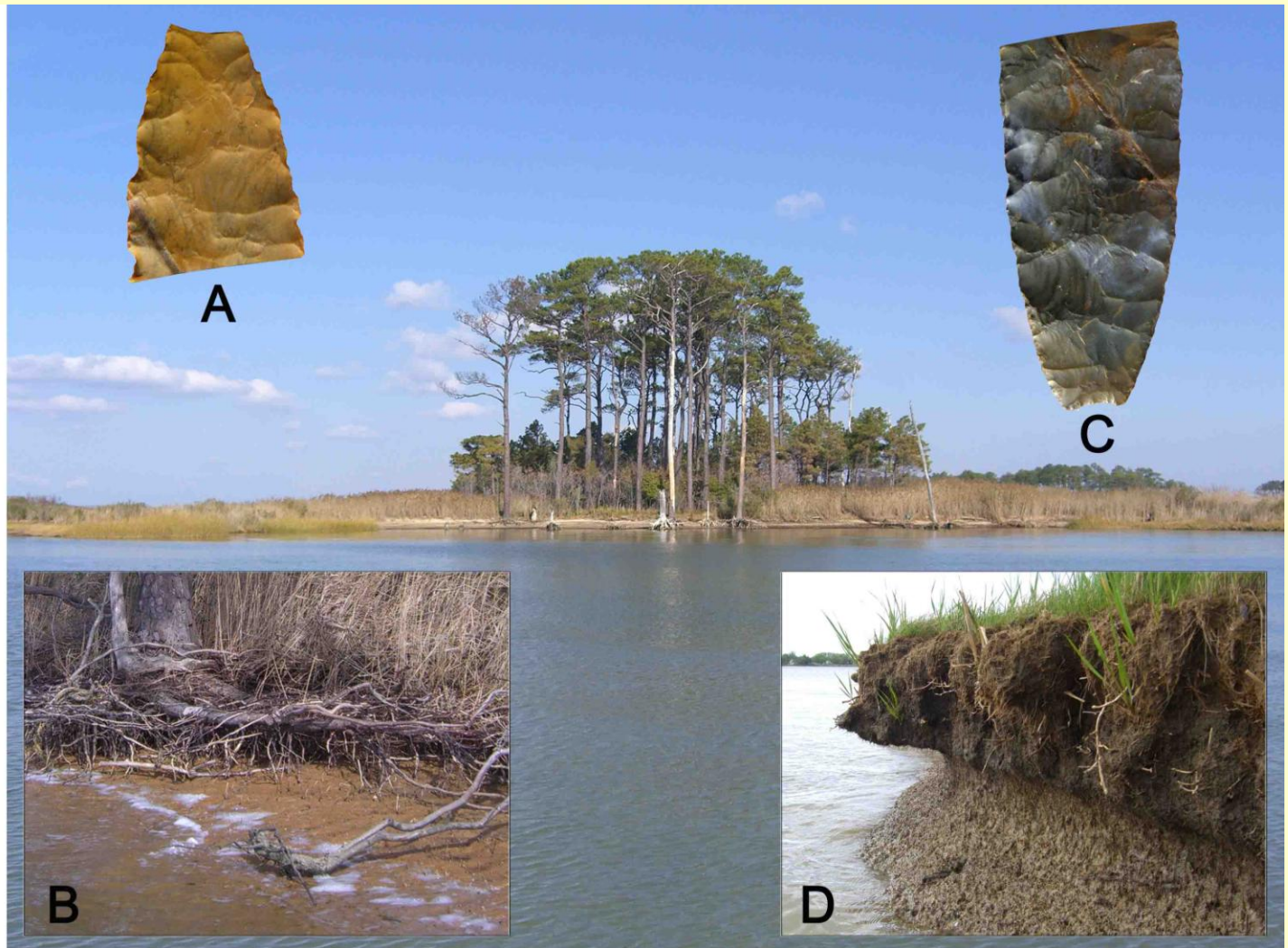
**X-ray diffraction pattern of powder from blacked part of jasper pebble showing peaks of pyrite, quartz (and mackinawite?).**





**Photo of one of the sites, tidally flooded oyster shell kitchen midden in MD, at low tide, where some of the sulfidized artifacts were collected.**





**The effects of tidal marsh geochemical alterations are readily apparent on the basal section of this conjoined jasper biface (left). The distal portion of the biface (A) was found along the eroded forested upland (B). The geochemically altered basal portion of the biface (C) was found along the eroded inundated upland encapsulated by tidal marsh (D).**



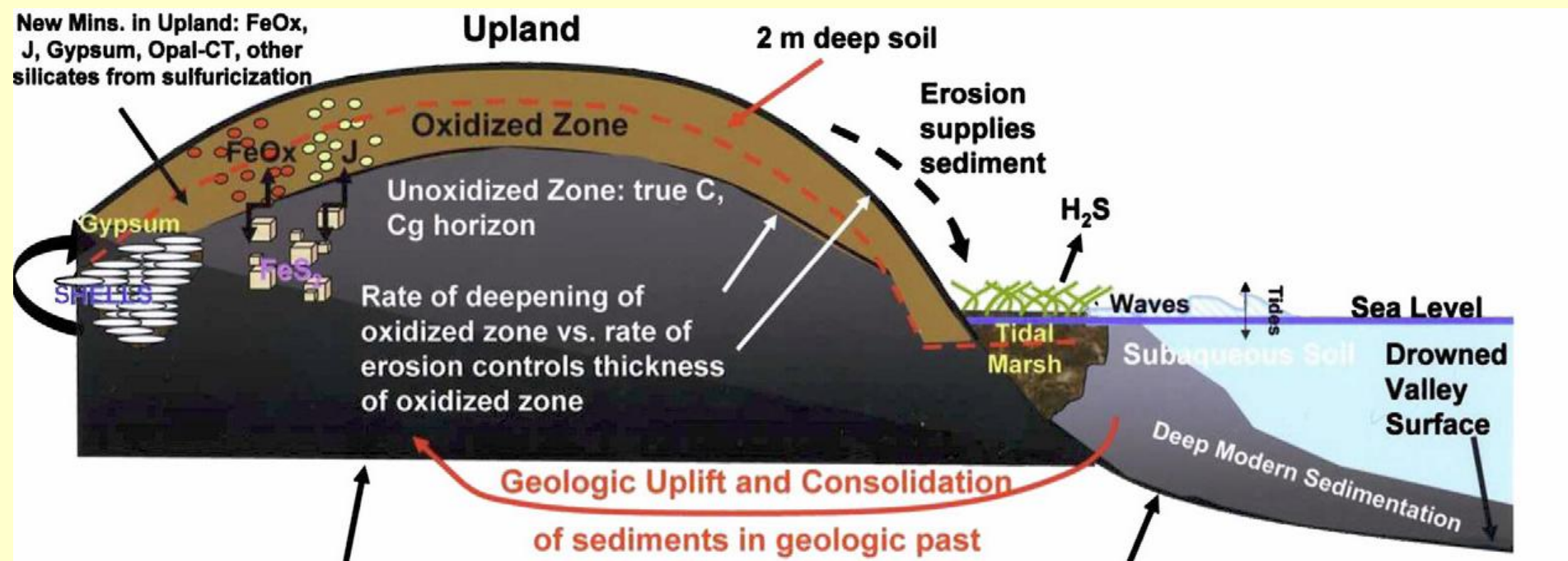
# Summary

- **We present a set of chemical reactions to represent sulfidization leading to a revised overall sulfidization reaction that generates hydrogen as a product instead of consuming oxygen as a reactant (these reactions are in our abstract).**
- **We envision that S of aqueous sulfate in tidal marsh and coastal subaqueous soils is the prime microbial oxidizer of organic matter with  $\text{H}_2\text{S}/\text{HS}^-$  as a product.**
- **We envision that sulfide of  $\text{H}_2\text{S}/\text{HS}^-$  causes the chemical reduction of ferric Fe of iron “oxides” and the precipitation of iron sulfides, monosulfides rapidly and pyrite more slowly.**

# Summary Continued

- **We have documented the (rapid) formation of iron sulfides in iron “oxide” bearing soil materials deliberately (soil materials, IRIS tubes – Rabenhorst’s work) or accidentally (Native American artifacts – Wagner/Lowery) introduced into tidal marsh soils in the Chesapeake Bay/Mid-Atlantic region of the U.S. We think the transformation occurs chemically, although the production of the  $H_2S/HS^-$  is primarily microbial.**

**This slide planned as a new sulfidization diagram, to show production of hydrogen sulfide by reduction of S of sulfate during oxidation (decomposition, respiration) of organic matter in tidal/subaqueous soil environments and reaction of hydrogen sulfide/sulfide with iron oxides/oxyhydroxides to form iron sulfides.**



**Min. Transformations from sulfurization in the land system**

Fe sulfides → FeOx and/or Jarosite

CaCO<sub>3</sub> (calcite/aragonite) → CaSO<sub>4</sub>·2H<sub>2</sub>O (Gypsum)

Silicates (eg. Glauconite) → Opal CT, new Silicates

**Elements incorporated into soil minerals in the sea system**

Fe of FeOx from sediments → Fe Sulfides

Sea water SO<sub>4</sub><sup>2-</sup> → S<sup>2-</sup> → Fe sulfides

Sea water Si → opaline diatoms, glauconite, other silicates?

Sea water Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> → CaCO<sub>3</sub> shells

Sea water K<sup>+</sup> → glauconite

Diagram, Fig. 1 from 2010 Fanning et al. Geoderma vol. 153, pp. 457-464, land sea paper, to show where **sulfidization, right side**, fits into the acid sulfate soils picture.