Acid Generation Potential of Earthen Materials

USGS

Why do we care?
The Bad:

- Causes serious water quality problems.
- Causes serious soil fertility problems.
- Costly to clean up.
- Clean ups usually require long-term maintenance.

USGS

Why do we care?
The Good:

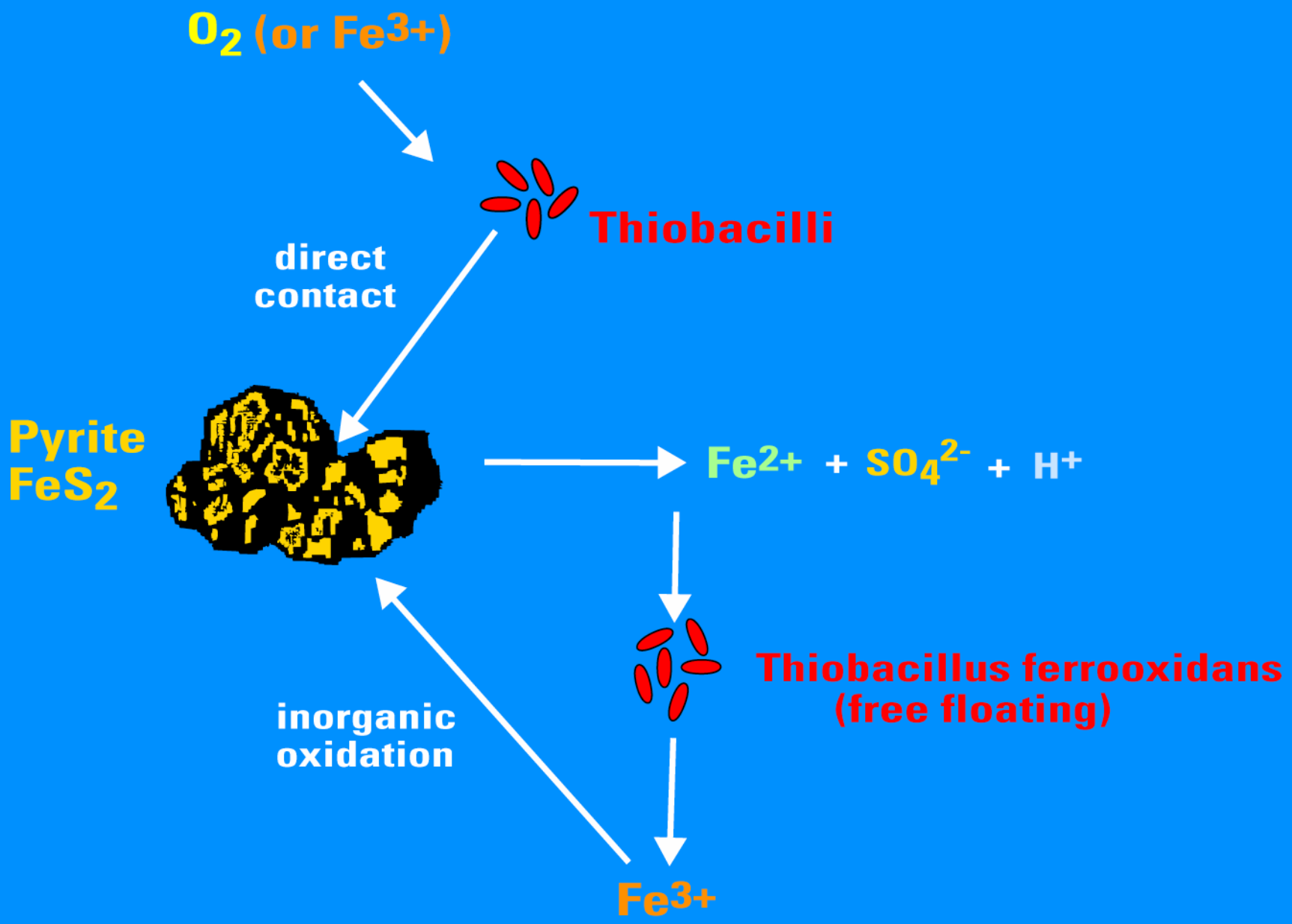
- Enriches metal ore bodies.
- Produces iron-rich soils which are fertile.

What earthen materials display the problem?

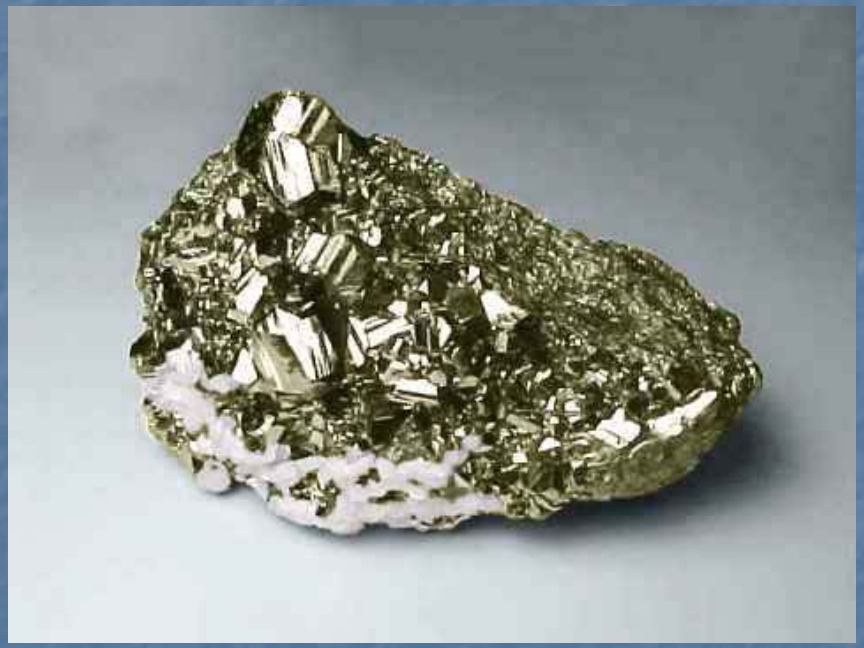
- Coal, base metal, and precious metal mine waste.
- Iron sulfide-rich estuarine marine sediments.
- Iron sulfide-rich metamorphic rocks (e.g., slates, phyllites).
- Iron sulfide-rich sedimentary rocks (e.g., pyritic sandstones).
- Hydrothermally altered rock.

What is the primary cause?

- Iron sulfide mineral oxidation catalyzed by bacteria.
- Iron sulfide minerals responsible: acid volatile sulfide > marcasite > pyrrhotite > pyrite.
- Other sulfide minerals: copper, nickel, mercury, etc. sulfides do not oxidize readily in air and water to produce acid. However, ferric iron from iron sulfide oxidation will oxidize them to produce mine waters rich in heavy metals, mercury, arsenic, etc.


O_2 (or Fe^{3+})
Thiobacilli
direct
contact
Pyrite
FeS_2
$Fe^{2+} + SO_4^{2-} + H^+$
Thiobacillus ferrooxidans
(free floating)
inorganic
oxidation
Fe^{3+}

Iron sulfides



What is the secondary cause?

- Acid release from iron sulfate salt dissolution.
- Rapid - Melanterite, rozenite, szomolnokite, romerite, copiapite, etc.
- Slow - Alunite-jarosite
- Dry mine waste may contain iron sulfate salts that are an easily released source of stored acid.

Iron sulfate salts

Coquimbite, $Fe^{III}_2(SO_4)_3 \cdot 9H_2O$

Rhomboclase
$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$

IRON-SULFATE MINERALS

MINERAL	FORMULA
Fe^{II}	
Melanterite	$Fe^{II}SO_4 \cdot 7H_2O$
Rozenite	$Fe^{II}SO_4 \cdot 4H_2O$
Szomolnokite	$Fe^{II}SO_4 \cdot H_2O$
Halotrichite-Pickeringite	$(Fe^{II},Mg)Al_2(SO_4)_4 \cdot 22H_2O$
Mixed Fe^{II}-Fe^{III}	
Copiapite	$Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Bilinite	$Fe^{II}Fe^{III}_2(SO_4)_4 \cdot 22H_2O$
Römerite	$Fe^{II}Fe^{III}_2(SO_4)_4 \cdot 14H_2O$
Voltaite	$K_2Fe^{II}_5Fe^{III}_4(SO_4)_{12} \cdot 18H_2O$
Fe^{III}	
Coquimbite	$Fe^{III}_2(SO_4)_3 \cdot 9H_2O$
Kornelite	$Fe^{III}_2(SO_4)_3 \cdot 7H_2O$
Rhomboclase	$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$
Ferricopiapite	$Fe^{III}_5(SO_4)_6O(OH) \cdot 20H_2O$

Natural Buffers

- Carbonate Minerals provide rapid buffering.
  - Calcite > dolomite > magnesite > ankerite.
- Silicate Minerals provide slow buffering (about 7 orders of magnitude slower than carbonates).
  - Feldspars, olivine

Acid Generation in the field

Iron sulfate salts on a road cut.

Copiapite-group minerals growing on pyrite, Iron Mountain, CA

In summary
All Iron sulfide minerals generate acid “Sooner” or “Later”

- “Sooner” causes serious water quality problems because a lot of acid is generated over a short time. Natural neutralization or assimilation cannot keep up.
- “Sooner” results from: low crystallinity, high surface area, impurities (e.g., arsenic in pyrite), lattice defects, strong oxidizing conditions.
- “Later” causes no or limited to water quality problems because acid is produced over a time span sufficient for neutralization or assimilation by the environment.
- “Later” results from: high crystallinity, low surface area, high purity, defect-free lattice, reducing conditions.

Discussion?