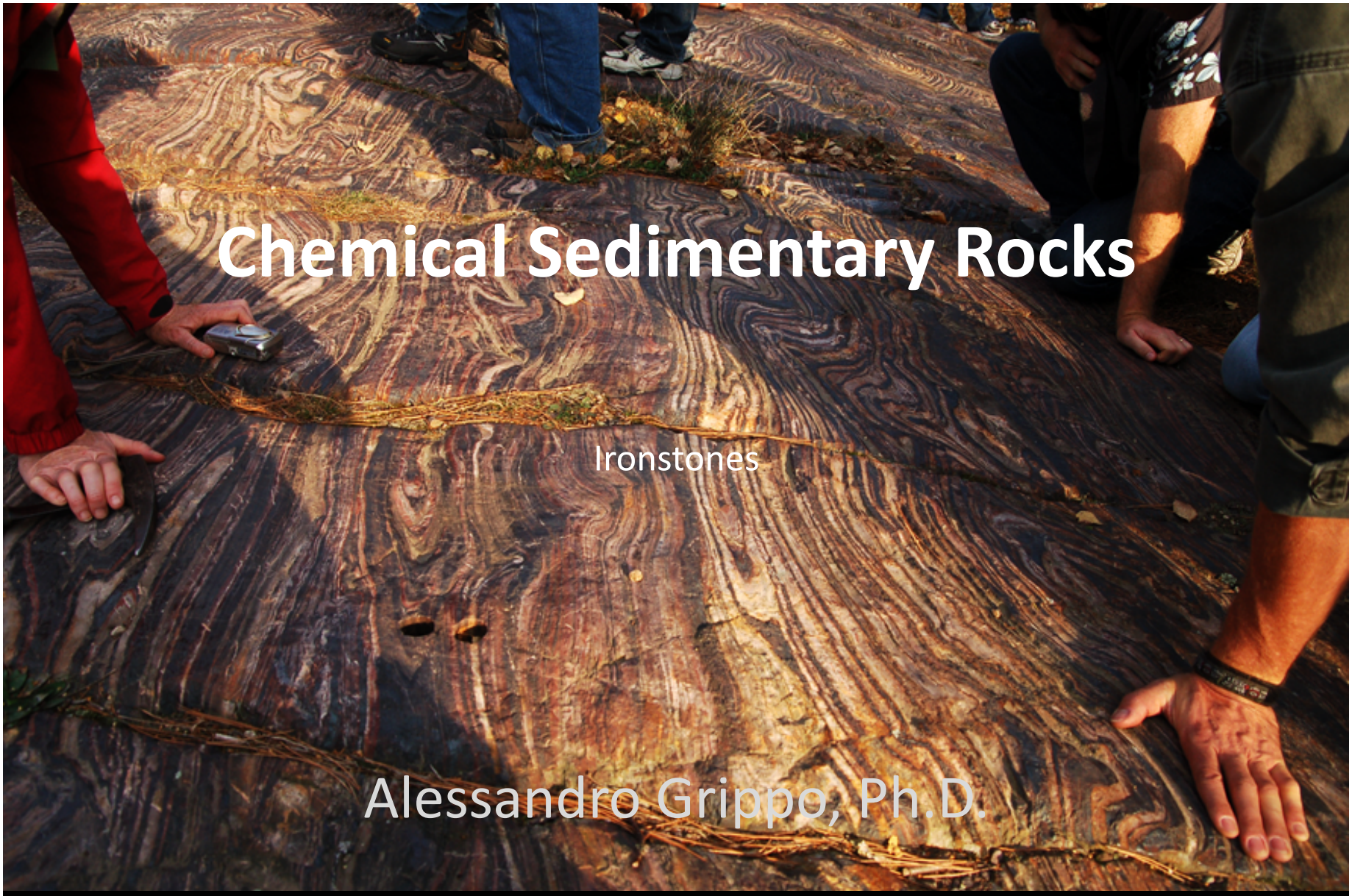


Chemical Sedimentary Rocks

Ironstones

Alessandro Grippo, Ph.D.

Banded Iron Formations, Soudan Mine, Soudan, Minnesota

Chemical Sedimentary Rocks

from inorganic precipitation from solution

- The dissolved components (ions) that precipitate to form iron-rich sedimentary rocks and evaporites originate from weathering of pre-existing rocks and minerals

- Even if together these two rock groups only make up 2% of sedimentary rocks, they are major sources of iron, many salts, and other chemicals

Water chemistry

ION name	ION Chemical formula	River Water dissolved solids (%) Salinity = 0.012%	Seawater dissolved solids (%) Salinity = 3.5%
Bicarbonate and Carbonate	$(HCO_3)^-$ $(CO_3)^{2-}$	48.6	0.4
Calcium	Ca^{2+}	12.4	1.2
Silica	H_4SiO_4	10.8	<0.01
Sulfate	$(SO_4)^{2-}$	9.3	7.7
Chlorine	Cl^-	6.5	55.0
Sodium	Na^+	5.2	30.6
Magnesium	Mg^{2-}	3.4	3.7
Potassium	K^+	1.9	1.1
Iron	Fe^{2+}, Fe^{3+}	0.6	<0.01
Aluminum	$Al(OH)_4$	0.2	<0.01
Nitrate	NO_3^-	0.8	<0.01
TOTAL		**99.7**	**99.7**

What do we get form the previous table?

- Carbonate, bicarbonate, calcium, silica, are much more common in freshwater than in sea water
- That means that, as soon as they get to the oceans, they are used faster than others
- Iron is rare in the ocean
- Sodium and chlorine are not really used in the ocean and the only way out is through evaporation
  - That explains their high concentration in sea water

Iron-Rich Sedimentary Rocks

- Most iron (Fe) dissolved in freshwater comes from weathering of igneous Fe-rich minerals

- Ionic iron occurs in two forms
  - Ferrous iron, Fe^{2+}, relatively soluble
  - Ferric iron, Fe^{3+}, essentially insoluble

- In presence of oxygen, ferrous iron oxidizes ("rusts") to ferric iron
  - That is, with oxygen, iron leaves water and turns into a solid clump of hematite, Fe_2O_3

- Because oxygen is abundant in today's Earth's atmosphere, the predominant form of iron is the insoluble ferrous iron

- At the beginning of Earth history, oxygen was not present in Earth's atmosphere
  - There were no iron oxides!

- Upon entering the ocean, iron-rich materials crystallize, grow together and settle to the ocean bottom

- Almost all sedimentary rocks (sandstones, shales, limestones) contain some iron but…

- An iron-rich sedimentary rock is defined by a total iron content that exceeds 15%

Two main kinds of iron-rich sedimentary rocks

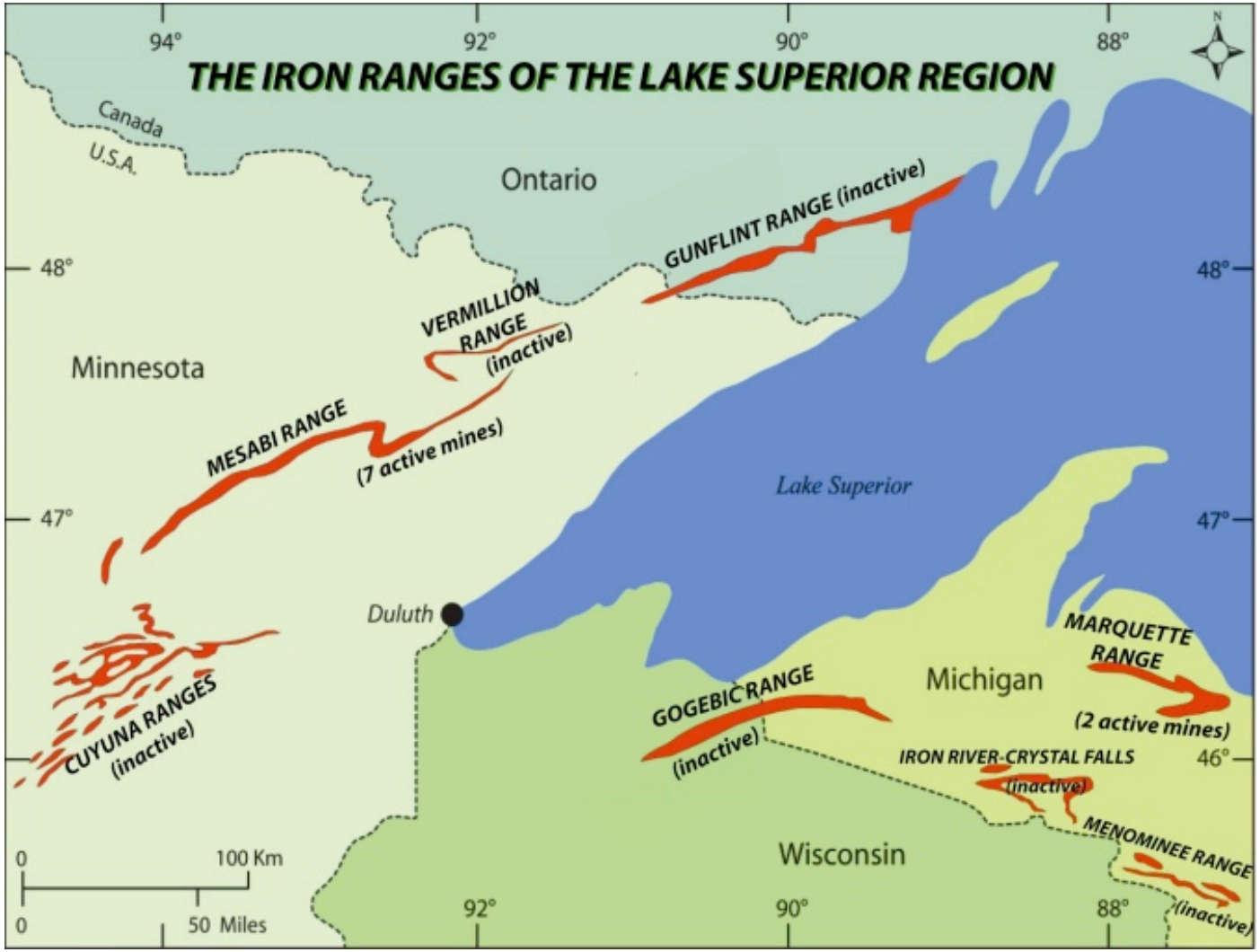
- Precambrian **Banded Iron Formations** (BIFs)
- Phanerozoic **Ironstones**

- These two categories make up only for 1% of the sedimentary record but are of enormous economic importance

Presence of abundant Fe in the “iron ranges” of Minnesota, Ontario, upper Michigan was crucial to the industrial growth of the U.S. in the late 1800s

An iron mine turned tourist attraction in the Mesabi Range of Minnesota
Virginia, Minnesota

Iron Ranges

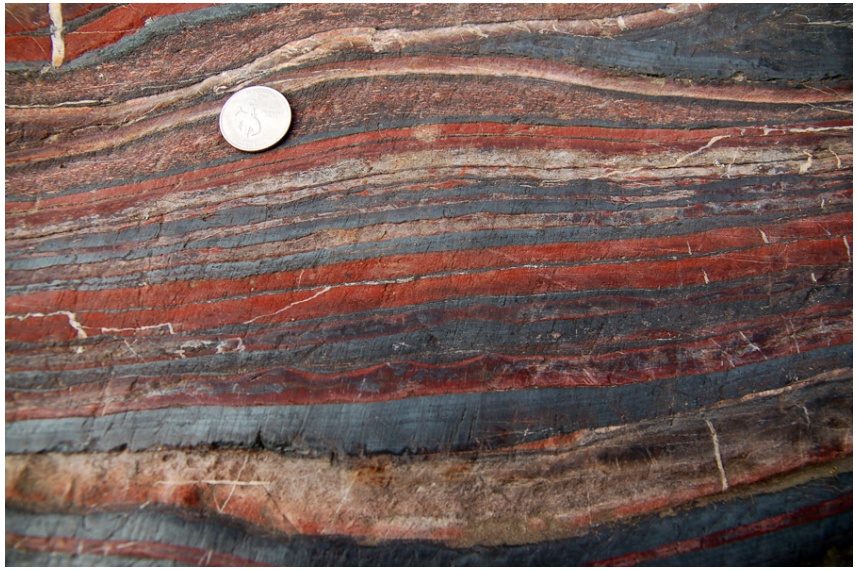

THE IRON RANGES OF THE LAKE SUPERIOR REGION
94°
92°
90°
88°
N
Canada
U.S.A.
Ontario
48°
GUNFLINT RANGE (inactive)
VERMILLION RANGE (inactive)
Minnesota
MESABI RANGE
(7 active mines)
47°
Lake Superior
Duluth
CUYUNA RANGES (inactive)
MARQUETTE RANGE
(2 active mines)
Michigan
GOGEBIC RANGE (inactive)
IRON RIVER-CRYSTAL FALLS (inactive)
46°
MENOMINEE RANGE (inactive)
Wisconsin
0
100 Km
0
50 Miles

Precambrian BIFs

- Cm-thick interlayered alternating bands of gray to black cherts and reddish iron-rich minerals
  - What is the origin of chert?
- Chemical precipitates, maybe aided by bacterial activity
- Texture of these rocks shows that iron was transported in solution, not as a precipitate
- That means that iron could not rust
- That is only possible in an anaerobic Precambrian atmosphere

different Precambrian Fe-rich rocks

before the Great Oxidation Event:
Bibawik Iron Formation
Eveleth, Minnesota



After the Great Oxidation event:
Banded Iron Formations
Soudan, Minnesota

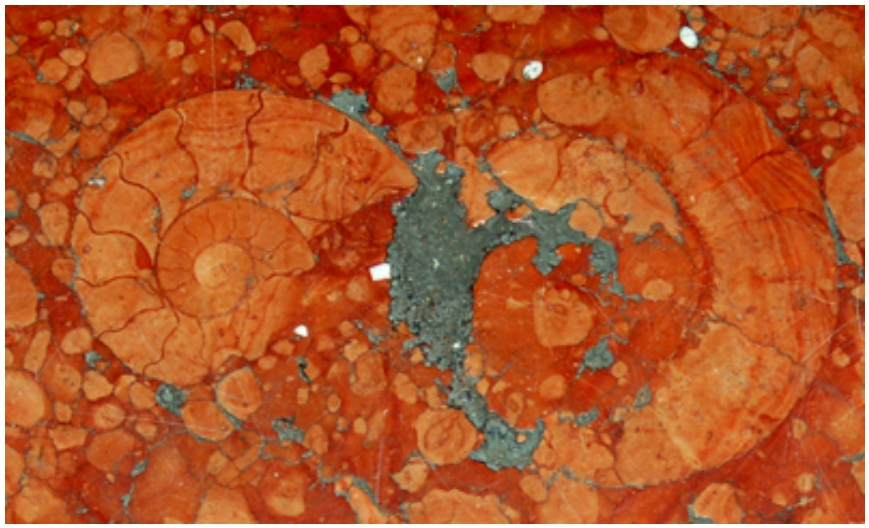
Phanerozoic Ironstones

- These are mostly conventional mudstones (and sandstones) in which a high percentage of iron is concentrated

- Less common than BIFs but easier to explain
  - Likely formed by erosion and deposition of laterites, associated to a low depositional rate of clastic sediment

- Ironstones formed specifically during peak greenhouse times
  - Ordovician, Silurian, Devonian
  - Jurassic, Cretaceous

  - Extreme weathering of lateritic soils
  - Enormous amount of Fe-rich sediment carried to a higher sea level ocean
  - At times associated with black shales



Jurassic Rosso Ammonitico Formation
("Ammonitic Red" Formation)
from the Venetian Alps, Italy

This rock is an iron-rich marl (a mixture of mud and lime) that contains several fossil ammonites and that has been used since Roman times for monuments and decoration.

Downtown pedestrian walkway
Bologna, Italy

Other iron-rich sedimentary rocks

Pyrite-rich black shales

- Black shales and black limestones contain a lot of organic matter
- That happens in absence of oxygen at the ocean bottom, which occurs during peak greenhouse times or in parts of the ocean with limited (restricted) water circulation
- In this case, the iron mineral pyrite (FeS_2) can be commonly found
- Pyrite was also present in the Precambrian but is less common today

Pyrite crystals

Pyritized trilobite fossil
from Ordovician Beecher's Bed, New York
(also seen in *Fossil Ecosystems of North America*

Pyrite concretions within black shales
From Devonian New Albany Shales,
Indianapolis, Indiana

Other iron-rich sedimentary rocks

Manganese nodules

- Irregularly shaped, fist-sized lumps of manganese, iron, and other metals, often with layered internal structure
- Scattered across lake bottoms and parts of the ocean floor (abyssal plain and flanks of M.O.R.)
- Unsure why they are not buried by seafloor sediments
  - Form in absence of other types of sediment
  - Bacterial action?
  - Very slow accumulation rates
  - Form in spurts, rather than steadily
  - Concentric growth
  - Fe and Mn likely from submarine hydrothermal activity

Manganese nodules showing concentric growth rings

Why are these rocks red?
Is that hematite? Are these ironstones?

This is a section of Zion National Park. Like many other rocks on the Colorado Plateau, these sandstones show a red coloration. Many of these rocks though are not considered to be ironstones because their color is given by the sandstone cement rather by the rock itself. That is, the rock is a clastic sedimentary rock (a very mature quartz sandstone) kept together by a red hematite cement

Zion National Park, Utah

next: evaporites

- While iron-rich rocks form directly in ocean water because Fe “rusts”…
- Sodium, chlorine, and sulfate ions take a different road….