XRF Workshop

Bridging the gap between geology and chemistry

Wednesday, August 9th, 2017

Workshop Materials (1 of 2)

Table of Contents

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Bridging the Gap between Geology & Chemistry

Sponsored by the Western Michigan University, the Michigan Geological Repository for Research and Education, and the U.S. National Science Foundation

This workshop is for educators interested in learning more about the chemistry of geologic materials.

Wednesday, August 9, 2017 (8 am - 5 pm)

Tentative Agenda

8:00-8:20: **Welcome (Steve Kaczmarek)** *Agenda, Safety, & Introductions*

8:20-8:50: **Introduction to Geological Materials (Peter Voice)** *An introduction to rocks, minerals, and their elemental chemistry*

8:50-9:00: Questions/Discussion

9:00-9:30: **Introduction to MI Basin Geology (Bill Harrison)** *An introduction to the common rock types and economic significance of Michigan's geological resources*

9:30-10:00: Questions/Discussion/Bathroom Break

10:00-11:00: **MGRRE Tour (Bill Harrison)** *Walking tour of the core repository*

11:00-11:30: **Introduction to XRF (Steve Kaczmarek)** *An introduction to the physics of XRF*

11:30-11:40: Questions/Discussion

11:40-12:10 **Introduction to XRF Application (Matt Hemenway, Mohamed Al Musawi)** *Student presentations on how XRF is used to solve geological problems in the MI Basin*

12:10-1:00: **Lunch** *Continue with discussions, posters, and complete reimbursement paperwork*

1:00-3:00: **Activity (All)** *Small-team, activity stations with demonstrations and problem sets pertaining to how elemental data can help solve a real-world problems*

1. *Get to Know Your Pet Rock (Kat Rose)*
2. *Powder Problem (Steve Kaczmarek)*
3. *Crime Scene Investigation (Matt Hemenway)*
4. *Bridge to Nowhere (Mohamed Al Musawi)*
5. *Alien Aqua (Charlie Ewing)*
6. *Fossil Free-For-All (Peter Voice)*

3:00-3:15: Break

3:15-4:00: **Team Lesson Planning** *A work session about how to best integrate activities into the classroom*

4:00-4:45: **Discussion & Reflection (Heather Petcovic)** *A discussion about how the activities fit into the framework of Michigan's Science Standards*

4:45-5:00: **Workshop Evaluation and Final Thoughts**

XRF Workshop

Bridging the gap between geology and chemistry

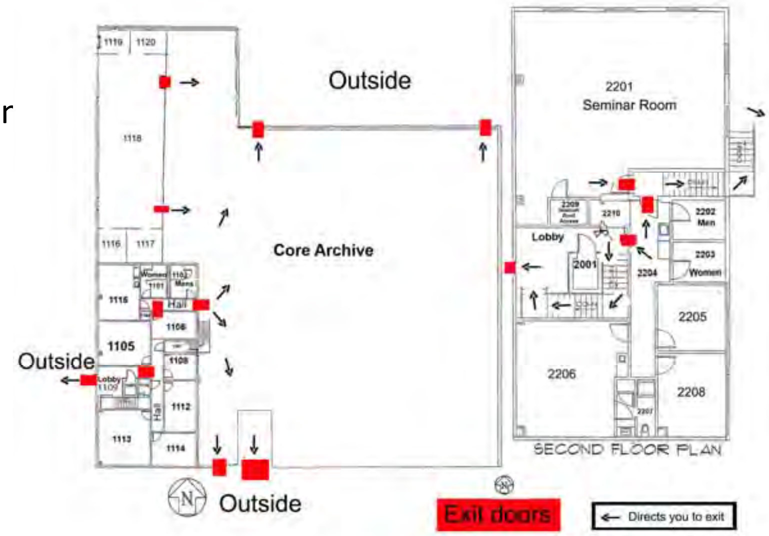
Wednesday, August 9th, 2017

Welcome to MGRRE

https://wmich.edu/michigangeologicalrepository

Safety Information

- Exits
- Equipmer
- Rocks
- People



What we hope to accomplish

- Objectives
  - Increase familiarity with the concept of using geological materials as sources of quantitative chemical data
  - Better appreciate the relationship between common geological materials, their bulk chemical composition, and common societal uses
  - Gain a basic understanding of how X-ray fluorescence spectrometry can be used to determine the chemical composition of geological materials
- Outcomes
  - Be able to apply bulk geochemical data to (i) discriminate between various materials, and (ii) evaluate simple claims about the elemental composition of an object
  - Be able to articulate how geoscientists use analytical instruments to study the composition of geological materials
  - Be able to apply some of the concepts learned in the workshop to develop a classroom exercise whereby students test a claim using bulk elemental data

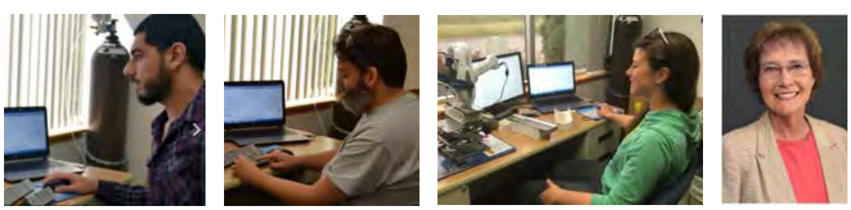
Agenda & Reminders

- Full agenda in booklet
- Summary
  - AM: Lectures, discussions, MGRRE Tour
  - Noon: food, paperwork
  - PM: hands-on activities, discussions
- Please have fun, and ask lots of questions
- Please share your expertise with the team

Facilitator Introductions

- Remember, we are all teachers

S. Kaczmarek H. Petcovic W. Harrison P. Voice M. Hemenway

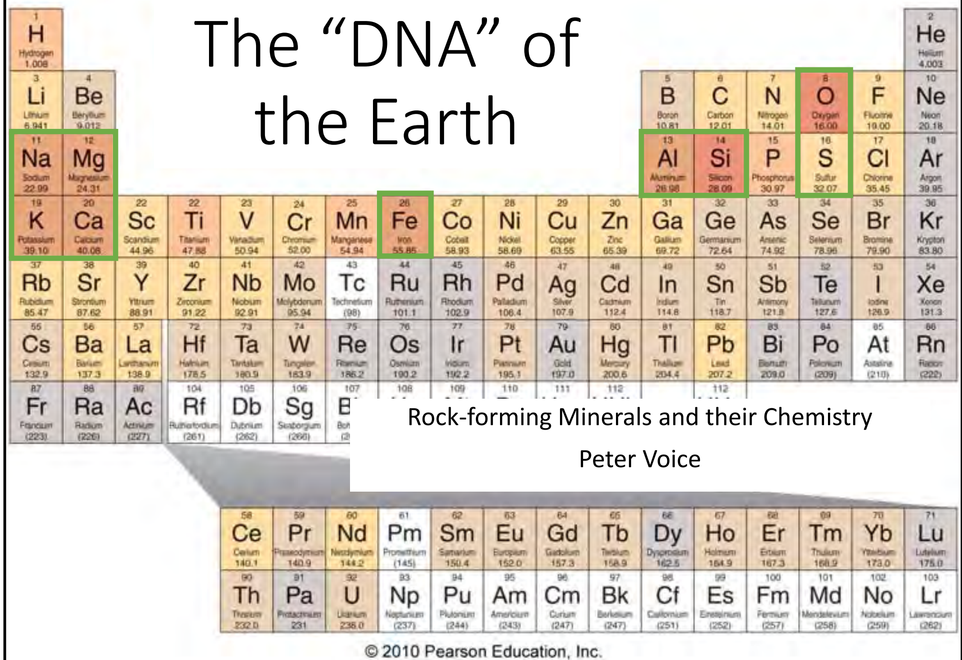


M. Al Musawi C. Ewing K. Rose L. Harrison

The "DNA" of the Earth

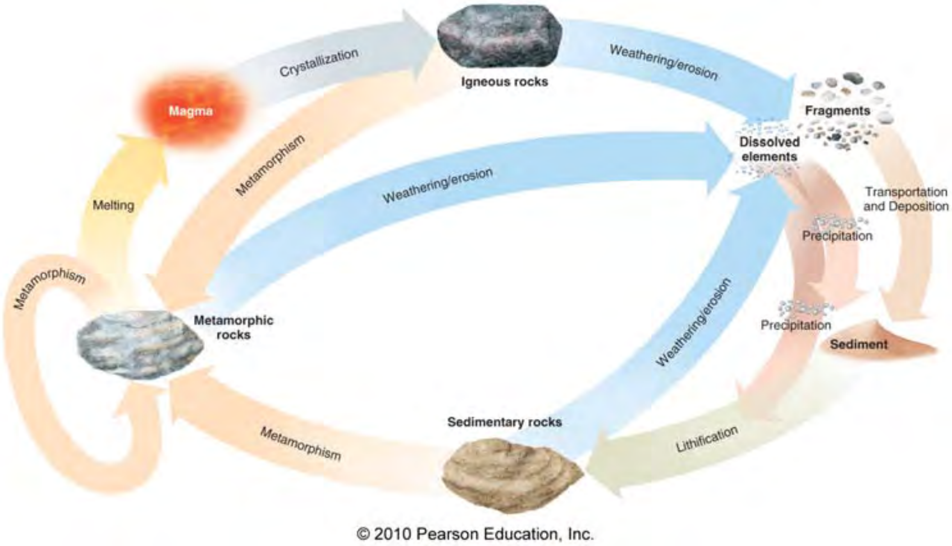
Rock-forming Minerals and their Chemistry

Peter Voice



Minerals and Rocks - A Quick Primer

- **Rock** – aggregates of mineral grains
  - Cemented together – **sedimentary rocks** (recycled rock fragments and skeletal material glued together)
  - Fused through heat and mineral growth (**igneous rocks** – cooled from molten rock; **metamorphic rocks** – rock altered by heat and pressure)
- **Mineral** – an inorganic, crystalline solid with a defined chemical composition
  - Chemical composition – can be fixed or defined as a specific range of compositions
- Minerals are made up of atoms of element(s) bonded together



Rocks – Aggregates of Minerals

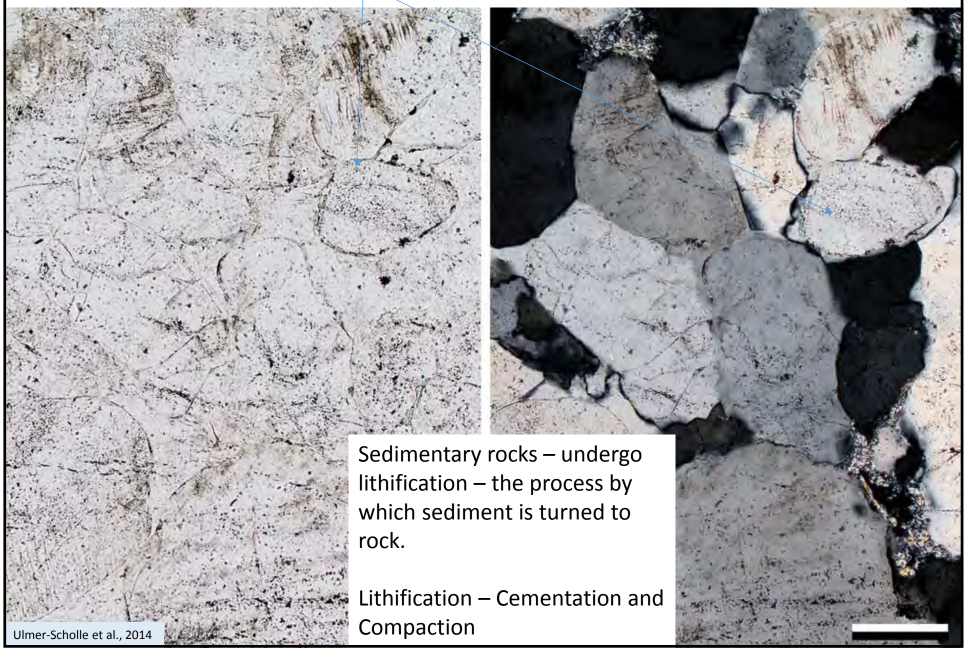
Sedimentary Rocks and Composition

- Classification:
  - Clastic rocks – cemented rocks made up of weathered rock and mineral fragments – subdivided on basis of grain size of particles – shales, sandstones, conglomerates
  - Biochemical rocks – accumulations of skeletal particles or precipitants mediated by organisms – many limestones, "coals"
  - Chemical rocks – precipitate inorganically – oolitic limestones, rock salt, rock gypsum, banded iron formation

Quartz Sandstone

Quartz sand rimmed with quartz cement

Si, O

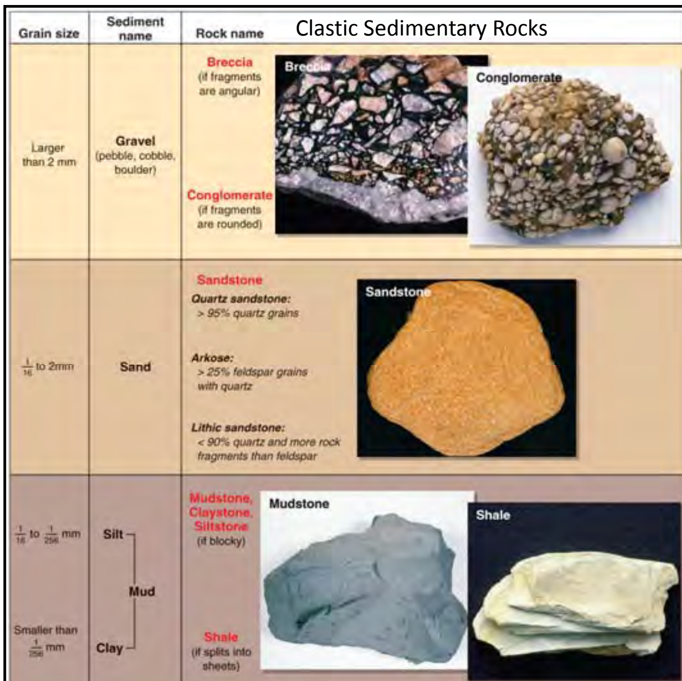


Ulmer-Scholle et al., 2014

Sedimentary rocks – undergo lithification – the process by which sediment is turned to rock.

Lithification – Cementation and Compaction

Clastic Sedimentary Rocks



Grain size	Sediment name	Rock name
Larger than 2 mm	Gravel (pebble, cobble, boulder)	Breccia (if fragments are angular) Conglomerate (if fragments are rounded)
$\frac{1}{16}$ to 2mm	Sand	Sandstone *Quartz sandstone: > 95% quartz grains* *Arkose: > 25% feldspar grains with quartz* *Lithic sandstone: < 90% quartz and more rock fragments than feldspar*
$\frac{1}{16}$ to $\frac{1}{256}$ mm	Silt (Mud)	Mudstone, Claystone, Siltstone (if blocky)
Smaller than $\frac{1}{256}$ mm	Clay (Mud)	Shale (if splits into sheets)

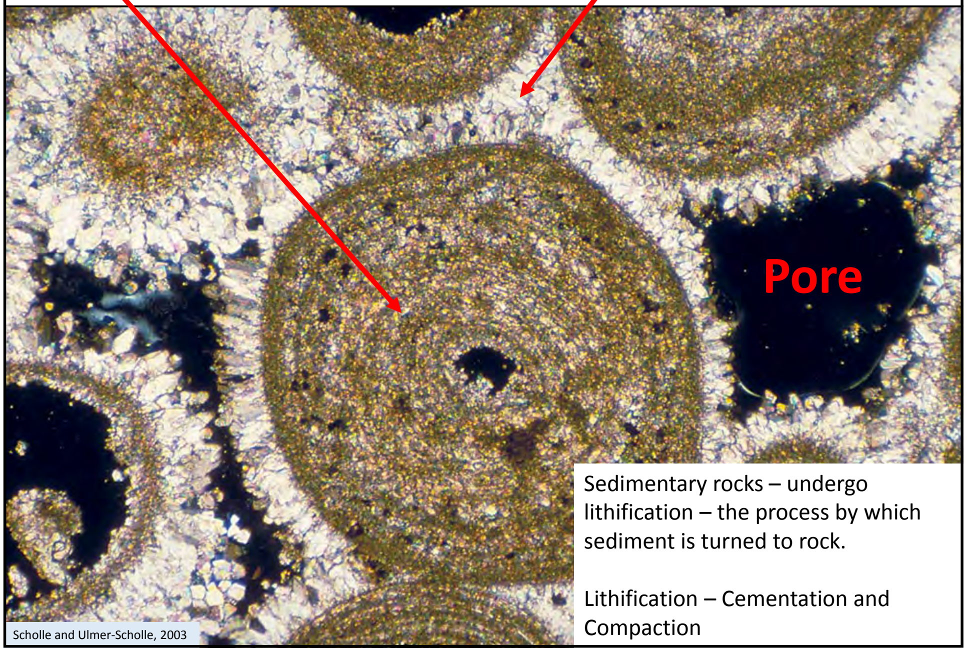
Common minerals – dominantly silicates

Clay minerals, quartz, feldspars

Si, Al, O

+/- Ca, K, Na, Mg, Fe

Ooids **Ca, O, C** Cement **Oolitic Limestone**



Sedimentary rocks – undergo lithification – the process by which sediment is turned to rock.

Lithification – Cementation and Compaction

Limestone and Dolostone – chemical or biochemical

Fossiliferous limestones, oolitic limestones, chalk

Chert – silica – can be biochemical (accumulation of sponge spicules or diatoms) or chemical (some hot spring mineralization)

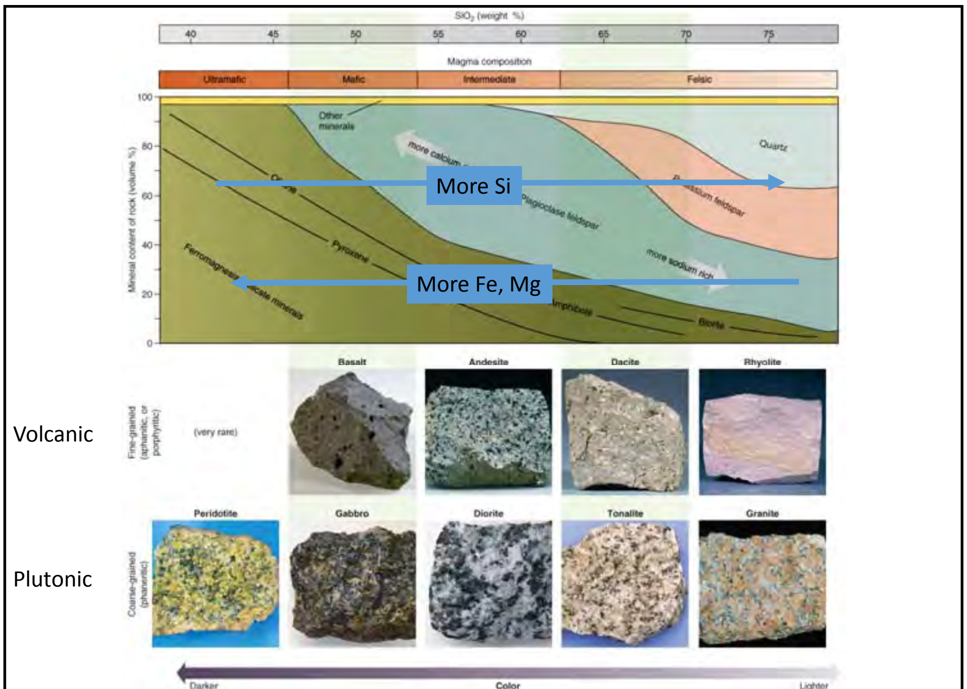
Rock Salt and Rock Gypsum – precipitate from evaporation of seawater

Coal – not a rock – but usually by tradition called a rock – accumulation of degraded organic matter

Even Smaller Number of Basic Elements!

Igneous Rocks and Composition

- Igneous rocks – very rational classification – based on magma composition and grain size
- Magma composition - %silica, Fe and Mg content
  - More Fe-Mg – darker colored rocks
  - More silica – lighter colored rocks
- Grain size – implies cooling rate
  - Finer grained – more rapid cooling (usually volcanic)
  - Coarser grained – slower cooling (usually plutonic)



Metamorphic Rocks and Composition

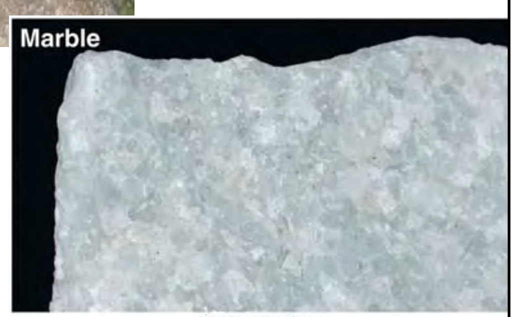
- Metamorphic rocks – lots of classification schemes
- Basic classification – foliated vs. non-foliated
  - Does the rock split into layers or not
  - Then further subdivided on basis of chemistry (mineralogy)

Low-grade dolomitic Marble – preserves 2.3 billion year old structure created by bacteria called a stromatolite

Marbles start out as either limestones or dolomites

Ca, Mg!

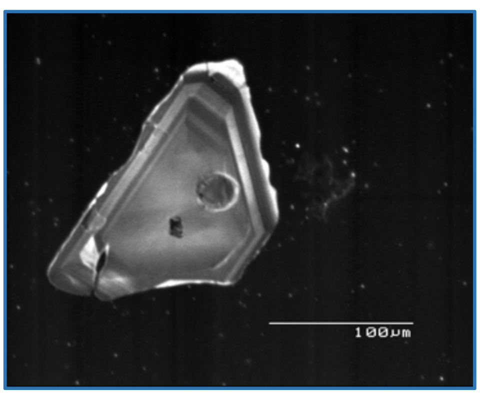
Higher-grade Marble – note primary depositional features are completely obliterated during recrystallization of the calcite



Non-foliated Metamorphic Rock = Marble

Protolith = shales – started as clay-rich rocks. Now higher temperature clays and micas

Foliated Metamorphic Rock = slate

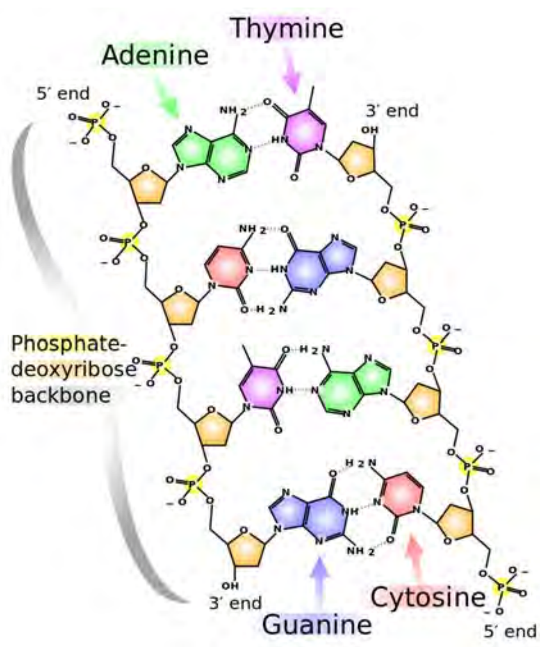


Weathered, detrital Zircon ($ZrSiO_4$) – has enough U (1000's ppm) and Th (100's ppm) to age date!

~5,200 formally named mineral species

Most are quite rare – only a few dozen are common = **Rock-Forming Minerals**

Another ~100 minerals are economically important = **Ore Minerals**



Deoxyribonucleic acid DNA

Made up of C, H, N, P, O

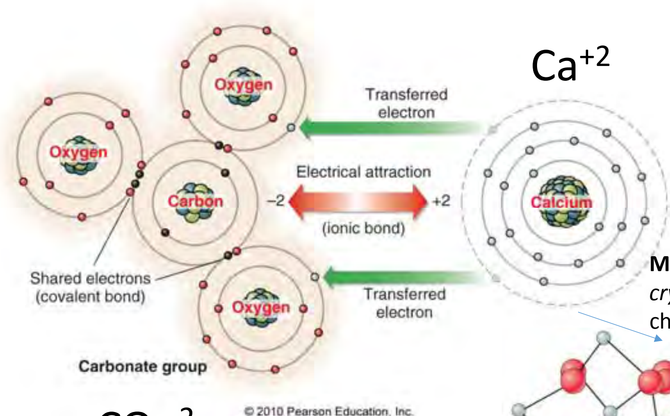
Which combine to form the building blocks:

Phophates

Sugars (deoxyribose)

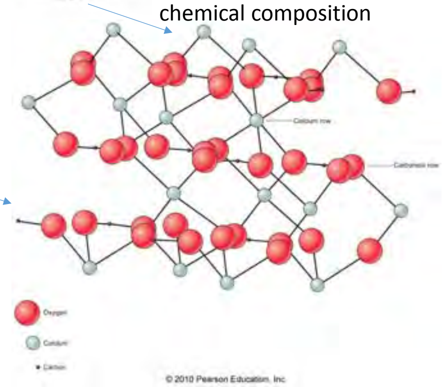
Nitrogenous bases (Adenine, Thymine, Guanine, Cytosine)

Ca^{+2} **Calcite $CaCO_3$**



CO_3^{-2}

Mineral – an inorganic, *crystalline solid* with a defined chemical composition



Many minerals form from ionic bonding of an **anion** and **cation**.

Anions are often more complicated polyatomic species like carbonate, phosphate or sulfate. Cations are usually metals.

Mineral "DNA" - Classification

- *"All the so-called elements of matter are found in the mineral kingdom, either in a pure or combined state; and it is the object of chemical analysis to ascertain the proportions of each in the constitution of the several minerals."*

James Dwight Dana
Manual of Mineralogy
1865 Edition

Early Classification of minerals - based in part on chemical composition! We still use Dana's classification today!

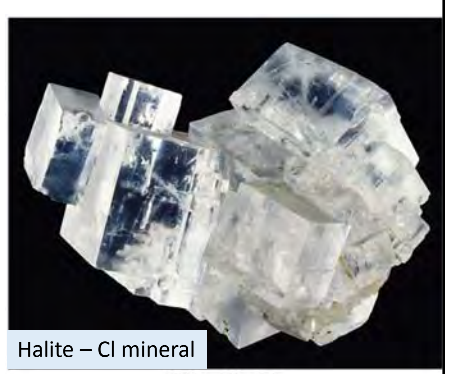
Rock-forming minerals: Silicates

- Silicate minerals have Silicon and Oxygen as part of their chemical composition
- Silicates include two of the most common minerals in the Earth's crust – Feldspar and Quartz

Rock-forming Minerals: Non-silicates

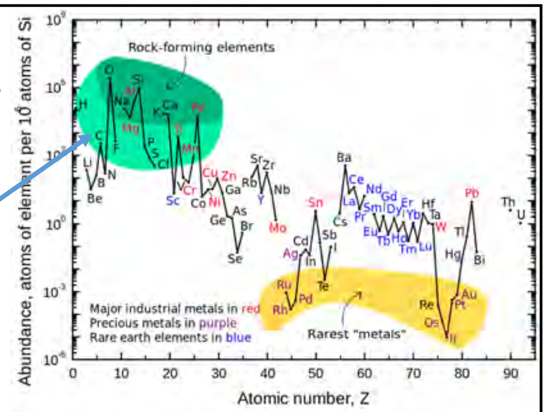
- Often classified based on their chemical composition – especially the dominant anion present in the structure
- Many have important industrial applications or are ore minerals
  - Carbonates (CO_3^{-2}) - Calcite, Dolomite
  - Phosphates (PO_4^{-3}) - apatite
  - Oxides (O^{-2}) – hematite, magnetite, corundum
  - Chlorides (Cl^-) – halite
  - Sulfides (S^{-2}) – pyrite, galena
  - Sulfates (SO_4^{-2}) – gypsum
  - Native Elements – pure elemental materials – Au, Ag, Cu, S, etc.

Sulfide (S) minerals



Mineral "DNA"

- A finite number of elements make up the bulk of the Earth
- So how did they end up here on Earth???



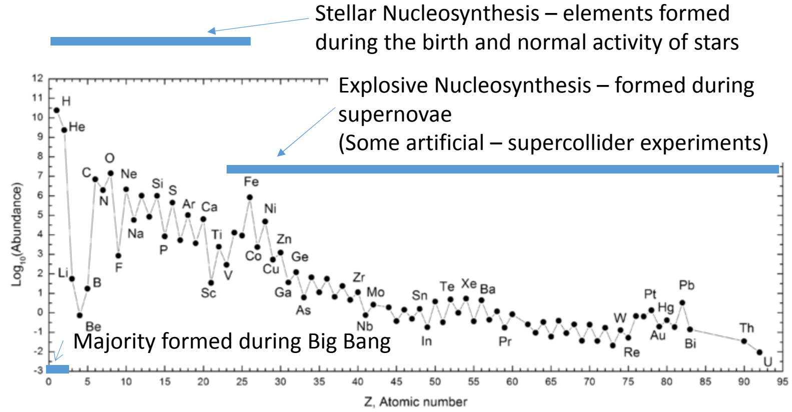
http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements#Earth.27s_crustal_elemental_abundance

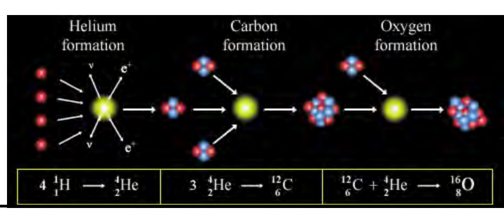
Nucleosynthesis – the formation of new atoms from subatomic particles – develops the 94 naturally occurring elements described on Earth!

Nucleosynthesis

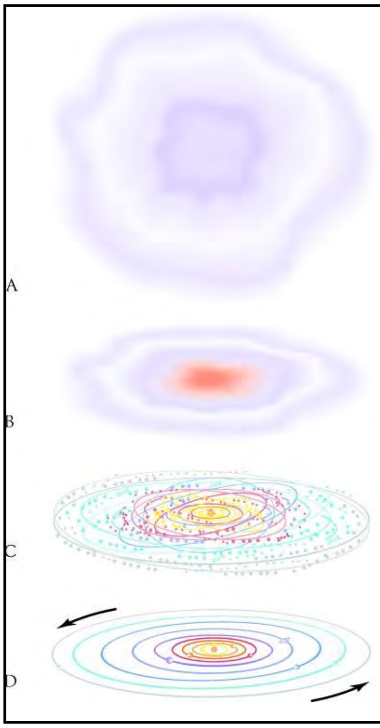
Stellar Nucleosynthesis – elements formed during the birth and normal activity of stars

Explosive Nucleosynthesis – formed during supernovae
(Some artificial – supercollider experiments)





Fusion reactions in the early sun create light elements (Up to Iron)



Accretionary Model – contraction of material to form proto-star and eventually even the Solar system

Supernovae – spread out matter into region forming nebulas. Gravity pulls material into a protostar at center.

Nebula begins to rotate due to balance between gravitational attraction and inertia

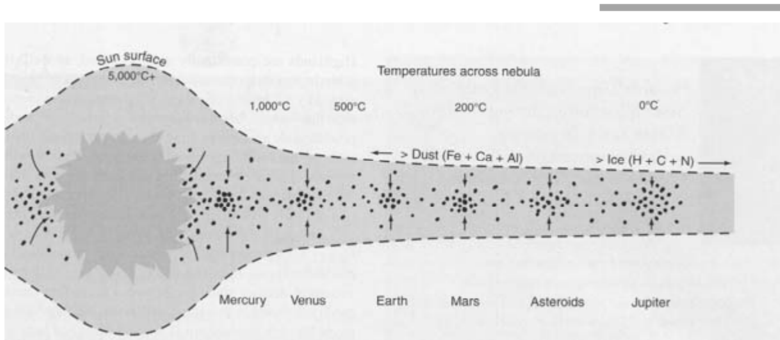
Accretion of larger and larger particles over time, including initial Planetesimals.

Stabilization of Early Planets – Orbits and Shape. Some Planetesimals captured as moons.

H and He

Silicates + light Metals (Ca, Al, Si, ….)

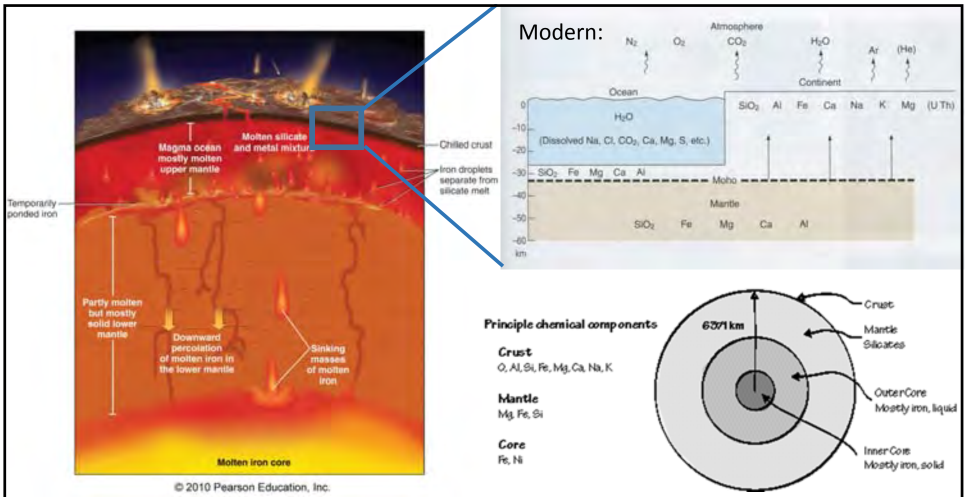
Ice (H, He ±O, C, N…)



Terrestrial Planets

Gas and Ice Planets

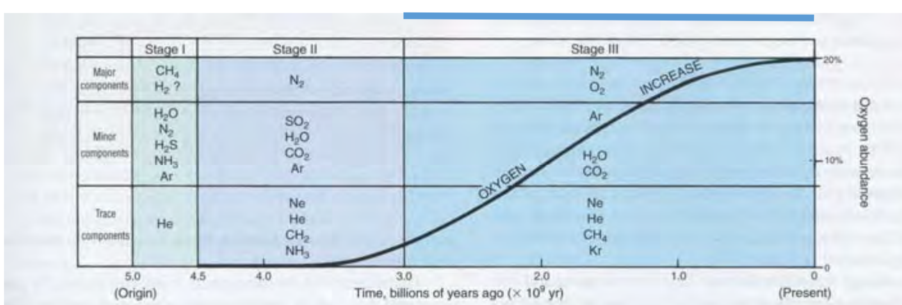
Notice the Compositional Differences across the Solar System.



Planetary Differentiation – explanation for distribution of elements in the Earth's interior

Hematite stable at earth surface

Oxidizing Atmosphere

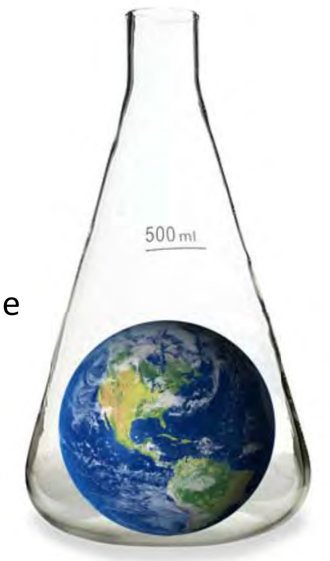


Reducing Atmosphere

Minerals like pyrite (and other sulfides) and siderite stable at earth surface

Impact of the Atmosphere

The chemistry of the Earth is the result of:

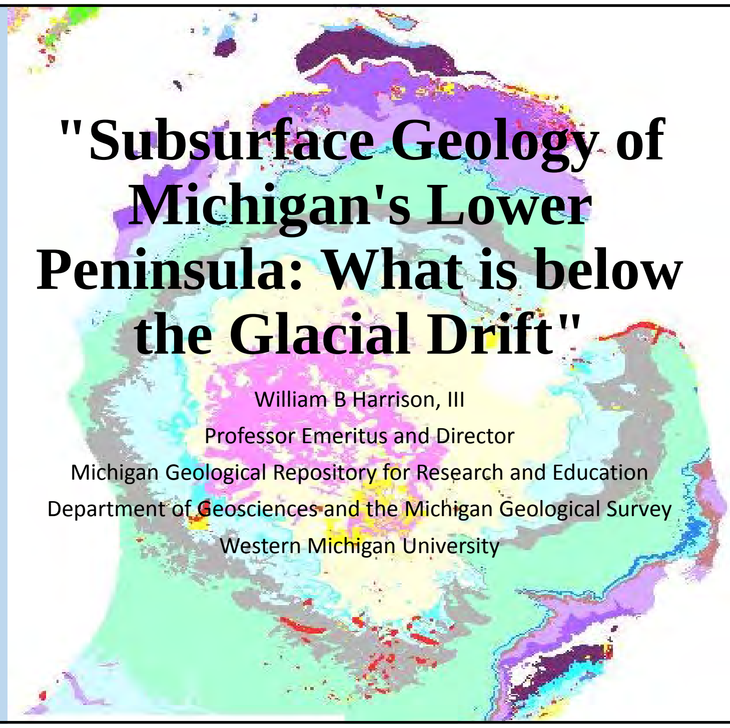


- The material in the nebula that the early solar system formed from
- Compositional Differentiation in the early solar system
- Planetary Differentiation in the early Earth – developed layered Earth (Core-Mantle-Crust)

Key Points

- **Rock** – an aggregate of minerals
  - Composition – based on minerals present
  - Sedimentary rocks
  - Igneous rocks
  - Metamorphic rocks
- **Mineral** – an inorganic, crystalline solid with a *defined chemical composition*
  - Composition – due to environment mineral formed in and available elements
- Minerals are made up of atoms bonded together

Geology ↕ **Chemistry**



"Subsurface Geology of Michigan's Lower Peninsula: What is below the Glacial Drift"

William B Harrison, III
Professor Emeritus and Director
Michigan Geological Repository for Research and Education
Department of Geosciences and the Michigan Geological Survey
Western Michigan University

Geology – The Earth Beneath Our Feet

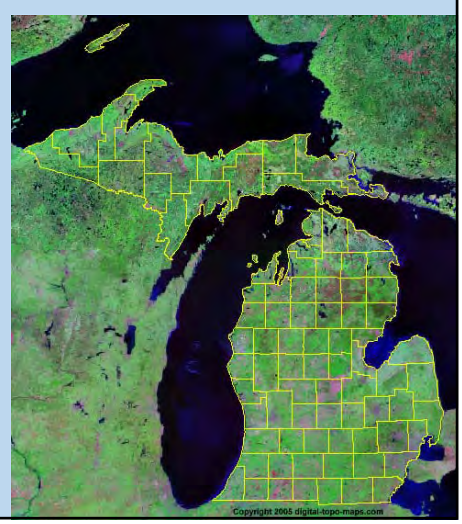
- Geology is the surface of the Earth and the soils, sands, gravels and solid bedrock deeper into the earth
- Sometimes we are interested in what is a few hundred feet down, sometimes thousands of feet down.

How Do We Describe Geologic Materials?

1. Chemical makeup – mineralogy, elements
2. Packages of similar strata – Formations, Groups

How do we know about the Geology of Michigan?

- We look around Michigan and observe the landforms, soils, beaches, etc. at the surface and also look for areas of solid bedrock, mostly along the lake shores, in river valleys and in quarries that we dig. Also we can sample rock layers by drilling wells.

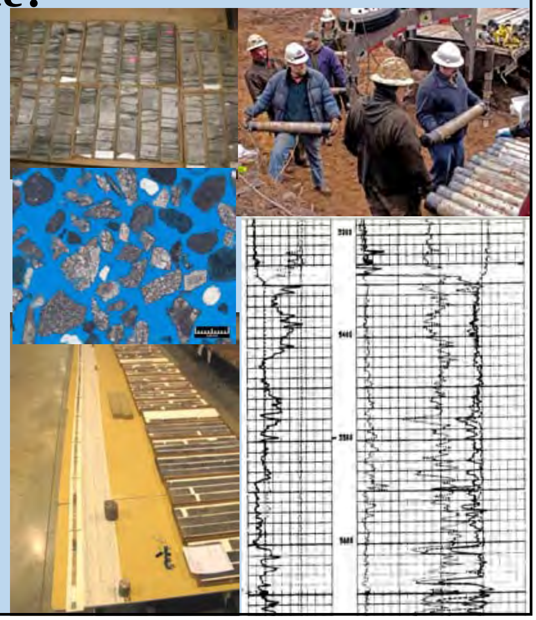


Traverse Lime, near Charlevoix,MI and Squaw Bay, near Alpena, MI

Natural outcrop Grand River Valley Pennsylvanian Sandstones at Grand Ledge, MI

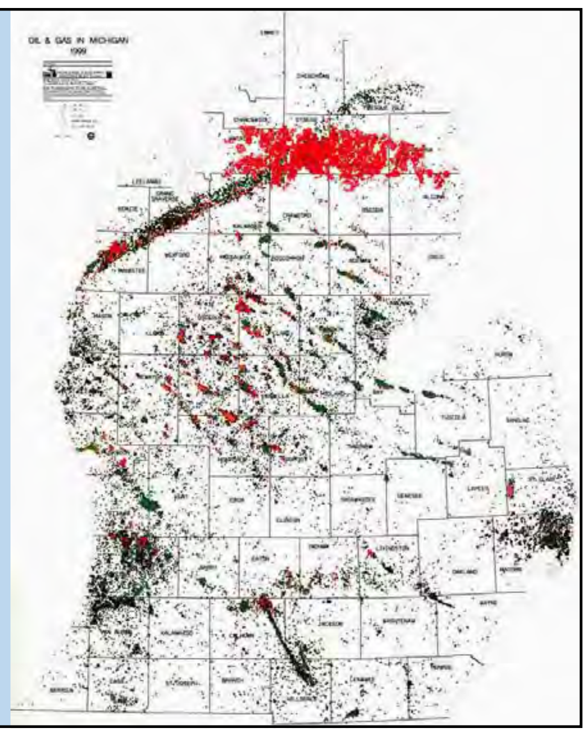
What about deeper rock layers not seen at the surface?

- Deeper layers can be accessed by drilling wells and collecting samples and information during the drilling
- Cores are the best since they represent the actual strata that is drilled through
- Drill cuttings are next best but they are only tiny fragments of the rock formations
- Wireline logs record various properties about the formations, but do not represent actual rock material



Locations of Oil and Gas wells drilled throughout Michigan

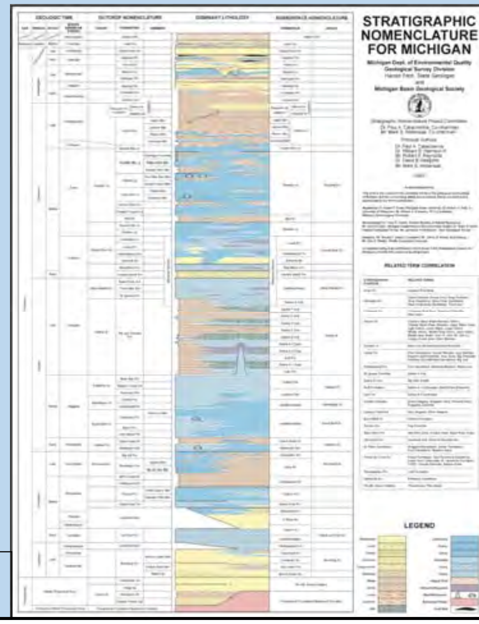
Red – Natural Gas
Green – Oil
Black – Dry hole



Michigan Stratigraphic Column

- Decades of studies of Michigan Geology has produced a similar diagram of the rock layers
- Thickness of this entire column can be up to 16,000 feet in the center of the State
- Packages of strata that are similar and have distinct lithology, mineralogy, elemental composition

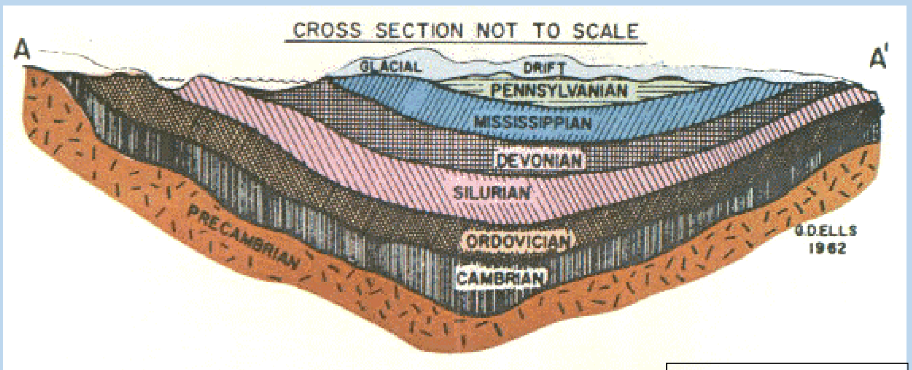
From Michigan Basin Geological Society and Michigan Geological Survey, 2000



Michigan Subsurface Geology

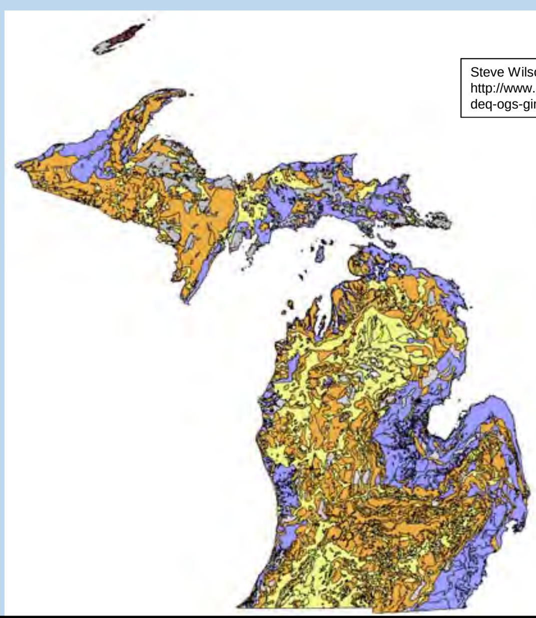
- Geologic strata in the Michigan Basin range in age from Pleistocene glacial drift and the youngest Jurassic-aged bedrock through Cambrian to Pennsylvanian sedimentary bedrock that reaches a maximum thickness of about 16,000 feet in the basin center
- Strata thin and are eroded to progressively older units moving toward the basin margins
- Data from several hundred thousand shallow water wells and over 77,000 oil and gas and mineral wells
- Data includes logs, drill cuttings samples and cores, as well as limited seismic profiles and gravity and magnetic geophysical measurements

Geologic Cross Section of Michigan



From Michigan Oil and Gas News

Glacial Geology in Michigan



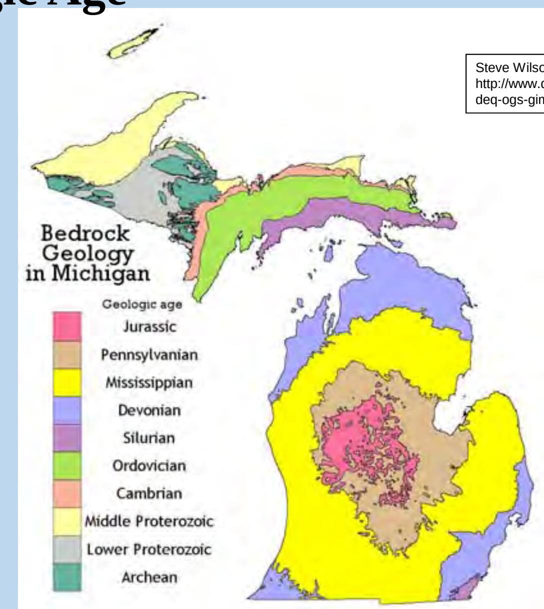
Steve Wilson, 2006
http://www.deq.state.mi.us/documents/deq-ogs-gimdl-GTLH_geo.pdf

Glacial Gravel Quarry, near Petoskey, MI

Variation in Geology around the State

- The thickness and types of geologic materials vary from region to region in Michigan
- The thickest column of these formations is in Central Michigan and thinning occurs towards the edges
- Surface geology may vary, especially in the Upper Peninsula
- Types of rocks deeper in the subsurface may change around the State

Bedrock Geology of Michigan by Geologic Age



Steve Wilson, 2006
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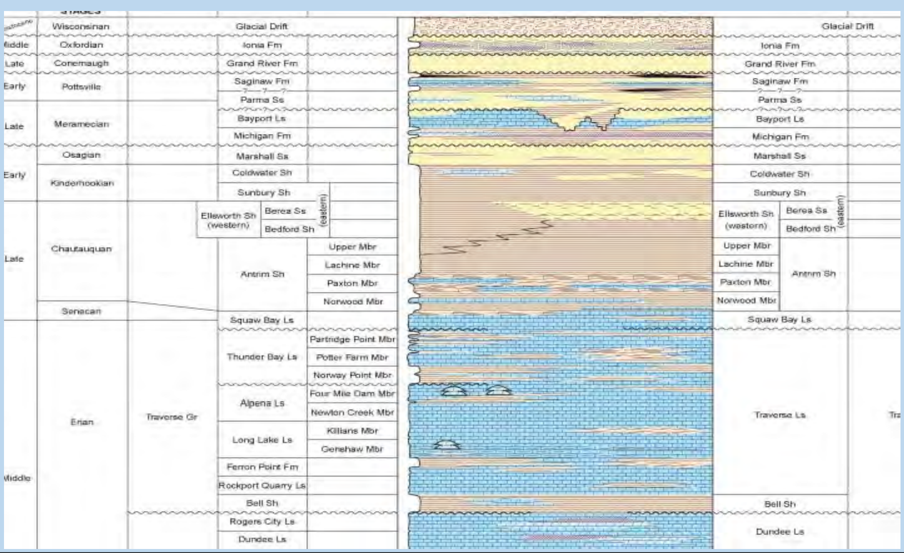
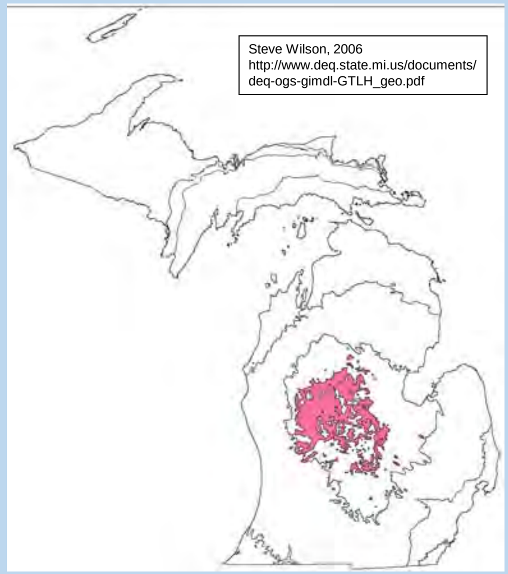
Michigan Stratigraphic Column - Devonian, Mississippian, Pennsylvanian, Jurassic and Pleistocene



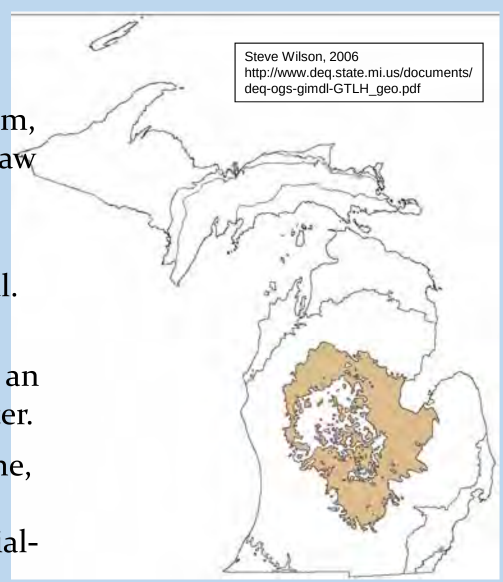
Jurassic Subcrop

- Jurassic outcrops are not found in Michigan, strata is only known from oil and gas drilling samples that contain fossil spores and pollen of Jurassic age.
- Ionia Sandstone is only known formation.
- Lithology is medium to fine red sandstone probably deposited in a terrestrial setting.



Pennsylvanian Subcrop

- Isolated outcrops occur in Arenac, Branch, Calhoun, Clinton, Eaton, Huron, Ingham, Ionia, Jackson, Ottawa, Saginaw and Shiawassee counties.
- Major natural resources are limestone, sandstone and coal.
- Several units are regional bedrock aquifers and serve as an important source of fresh water.
- Lithology is mixed sandstone, shale, siltstone, coal and limestone deposited in a fluvial-deltaic setting.



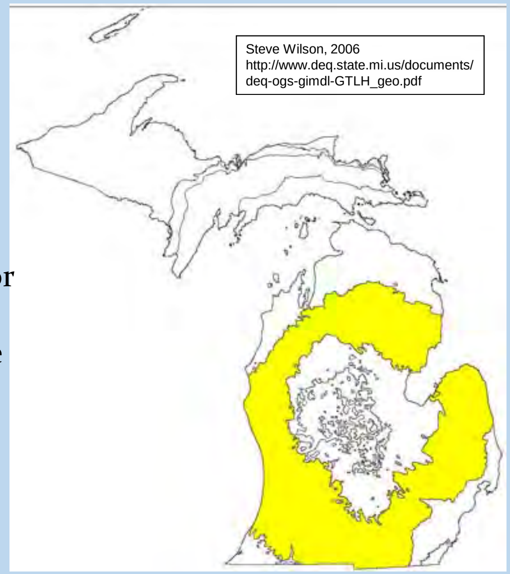
Pennsylvanian Sandstones at Grand Ledge, MI

http://www.msstate.edu/dept/geosciences/CT/TIG/WEBSITES/LOCAL/Summer2003/Fessenden_Lisa/7day1.html

Core Samples – Pennsylvanian Ss.
Wells drilled into shallow subsurface, ~250 ft. near Mason Michigan

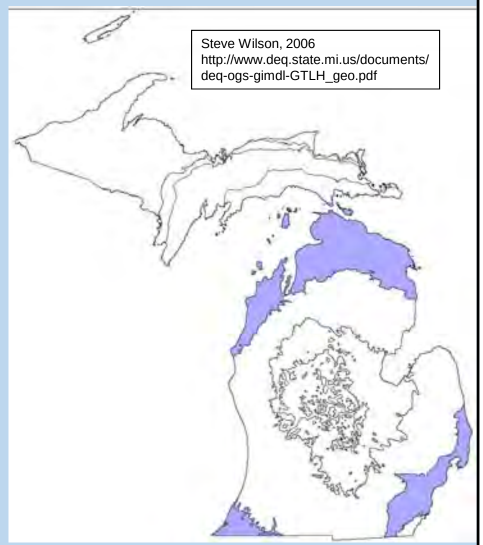
Mississippian Subcrop

- Largest area of subcrop for any geological system in the Lower Peninsula.
- Major natural resources are limestone and fine-grained sandstone.
- Marshall Sandstone is major regional bedrock aquifer and serves as an important source of fresh water.
- Lithology is mixed sandstone, shale, siltstone, coal and limestone deposited in a shallow marine setting.



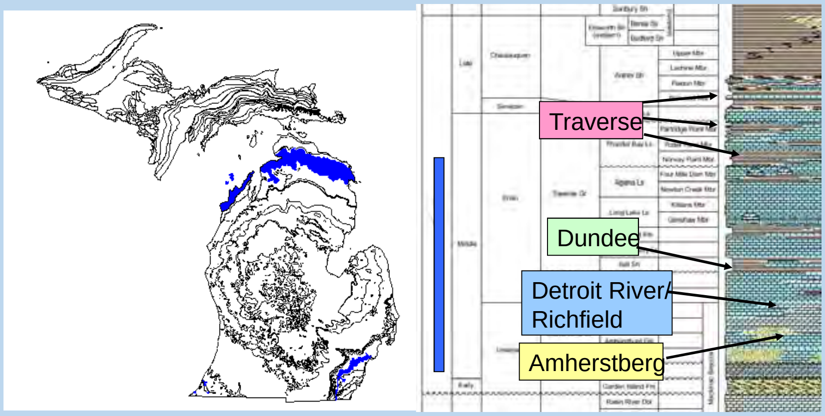
Devonian Subcrop

- Natural outcrops and quarries are relatively abundant, especially near the Great Lakes margins. Bedrock is commonly near the surface, with thin glacial veneer.
- Major natural resources are limestone and a few clay shales.
- Fractured and karsted Limestone are regional bedrock aquifer in northern L.P.
- Lithology is mostly Limestone and Dolomite with minor shale, evaporites and sandstone.



Antrim Shale Localities near Norwood, MI and Kettle Point, Ontario, CA

Middle Devonian Rocks in Michigan



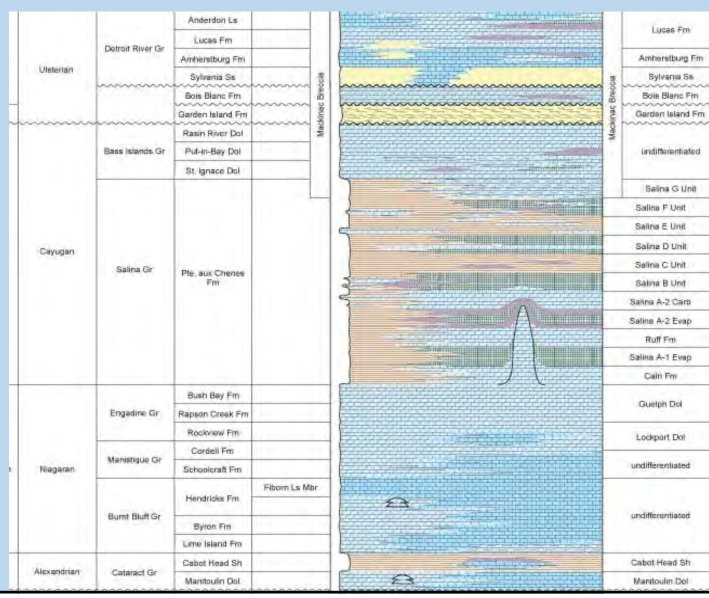
Middle Devonian reservoirs include Traverse Limestone, Dundee Formation, Detroit River Group and Amherstberg Fm. Subcrop of these rocks shown

From Michigan Geological Survey Presentation – "The Rock Cycle"

Traverse Lime, near Charlevoix,MI and Squaw Bay, near Alpena, MI

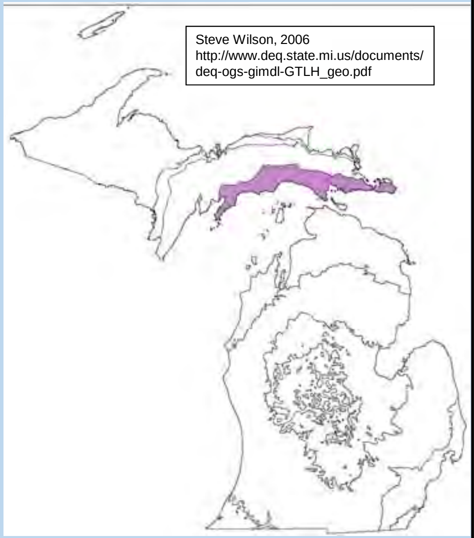
Rogers City and Dundee Limestones, Near Rogers City, MI

Michigan Stratigraphic Column – Silurian and Devonian



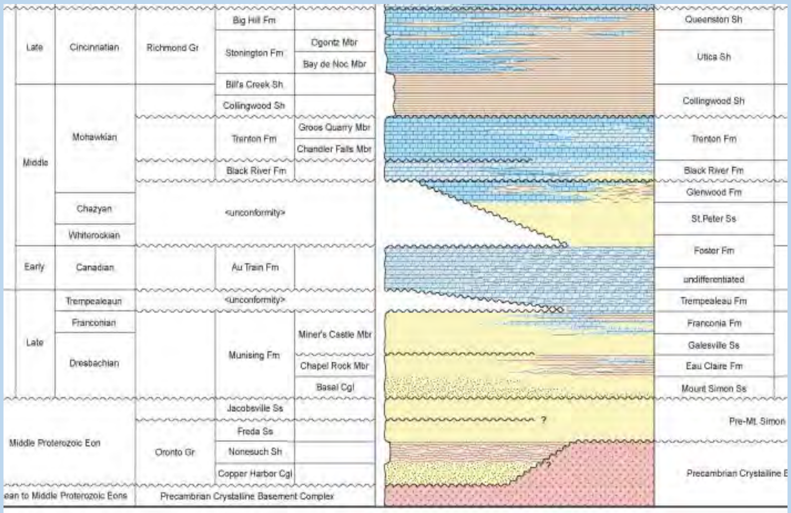
Silurian Subcrop

- Natural outcrops and quarries are fairly common in southeastern U.P. Bedrock is commonly near the surface, with thin glacial veneer.
- Major natural resources are limestone and dolomite near surface and salt in subsurface.
- Fractured and karsted Limestone and dolomite are regional bedrock aquifer in southeastern U.P.
- Lithology is mostly Limestone and Dolomite with minor shale and abundant basinal evaporites.



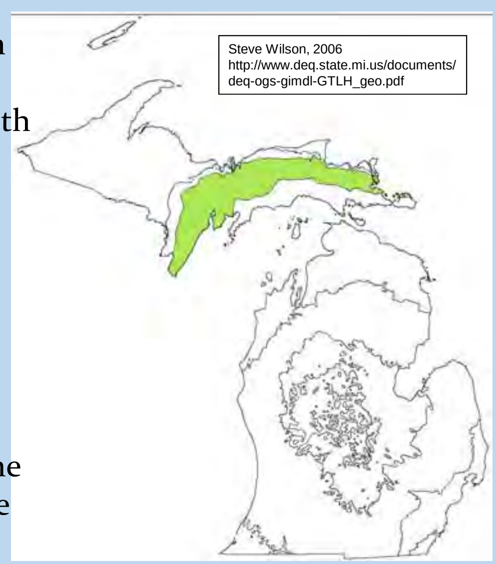
Silurian Engadine Fm. Northeast of St. Ignace, MI

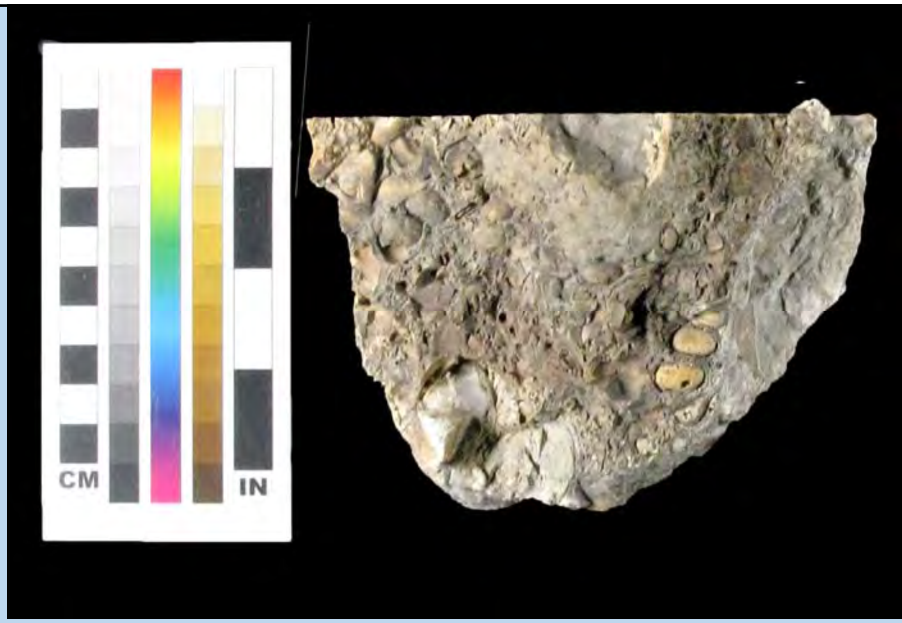
Michigan Stratigraphic Column – Cambrian and Ordovician



Ordovician Subcrop

- Natural outcrops uncommon in central U.P. Bedrock is commonly near the surface, with thin glacial veneer.
- Major natural resources are limestone and dolomite.
- Fractured and karsted Limestone and dolomite are regional bedrock aquifer in central U.P.
- Lithology is mostly Limestone and Dolomite with minor shale and sandy dolomite.





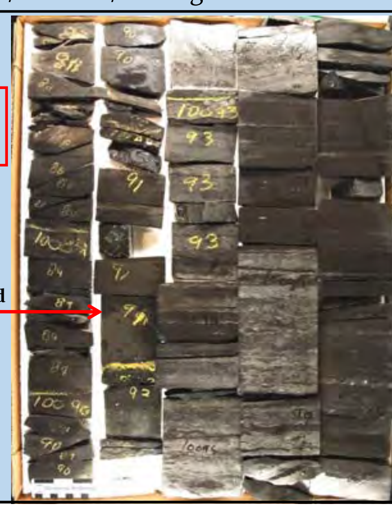
Snails and other fossils in the Ogontz Member, Stonington Formation – near Stonington, MI

Collingwood and Utica Shale in Core from Central Michigan Basin

Utica Shale

Utica /Trenton/Collingwood Contact

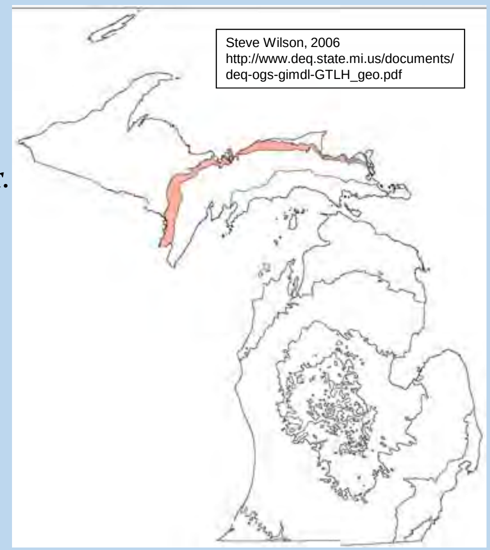
JEM-Weingartz #1-7A Core Clare Co., MI



Hardground contact

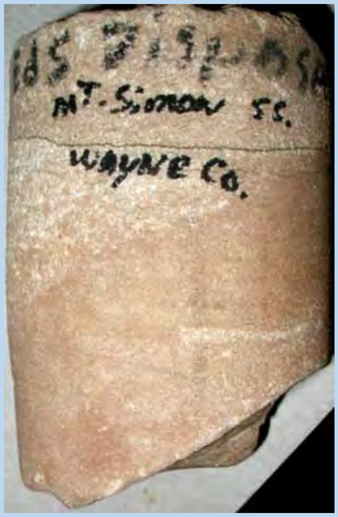
Cambrian Subcrop

- Natural outcrops abundant along Lake Superior shoreline. Bedrock is commonly near the surface, with thin glacial veneer. Major waterfall forming unit in U.P.
- Major potential natural resource is Sandstone.
- Sandstone is local bedrock aquifer in northern U.P.
- Lithology is predominately Sandstone.



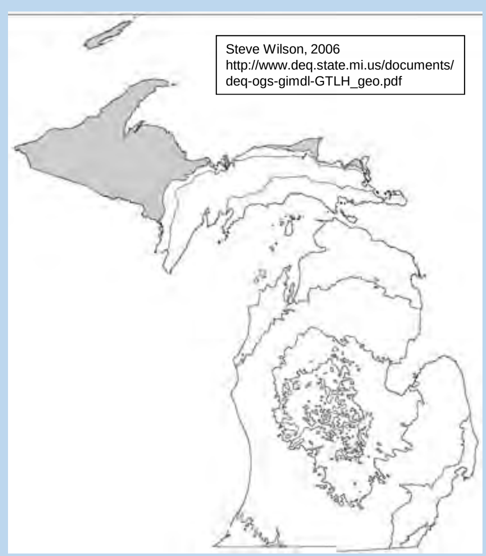
Munising Ss. Pictured Rocks National Lakeshore

Mt Simon Ss. in SE Lower Michigan



Pre-Cambrian Subcrop and Outcrop

- Natural outcrops and mines abundant in western U.P.
- Major source of metallic ores, especially iron and copper.
- Generally poor local bedrock aquifer.
- Lithology is varied, mostly crystalline igneous and metamorphic along with sediments and metasediments.



Pristine, feldspathic porphyritic granite

Cupp #1, 1547.8 m (5078 ft), St. Joseph County, MI

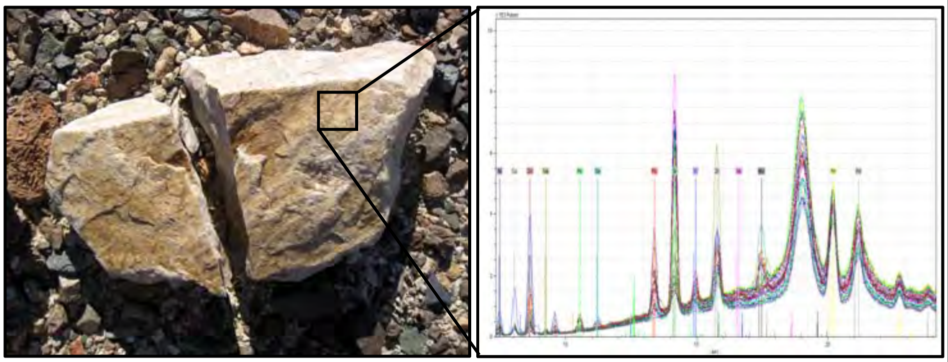
MGRRE at W.M.U. in Kalamazoo, MI Houses Michigan Subsurface Data

MGRRE Collections

- Over 500,000 feet of Michigan Cores
- 25,000 wells of Drill cuttings (Over 20 million ft of drilled interval)
- More than 35,000 wells with Wireline logs
- Petroleum engineering and geochemical data, maps

A Very Brief Introduction to XRF Spectroscopy

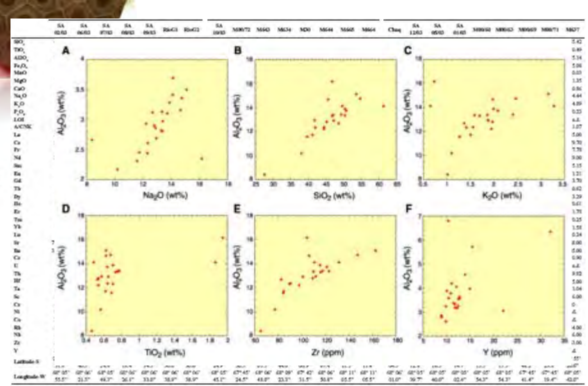
Steve Kaczmarek



The geology-chemistry link

- What most people see…
  - Rocks

- What we see….
  - Geochemical Data
    - Elemental
    - Isotope

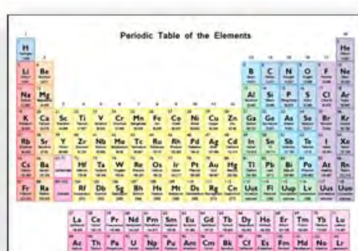


Why is geochemical data useful?

- Chemical composition of material reflects formation conditions/depositional environment
  - Elemental data – the chemistry of the environment
    - Fluid/magma composition
  - Isotope – what conditions of the environment
    - Temperature, evaporation, pressure

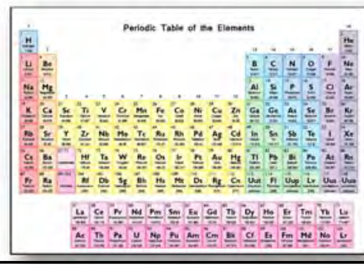
How do we extract geochemical data from rocks?

- Many approaches & tools in our belt
  - Atomic absorption
  - Optical emission
  - Liquid/gas chromatography
  - Mass spectrometry
  - **X-ray fluorescence spectroscopy**
    - Elemental composition of sample



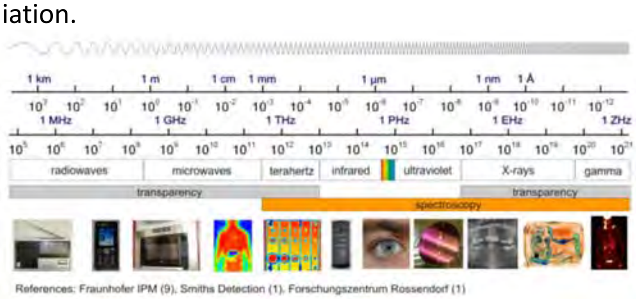
Lecture objectives

- Understand:
- what XRF spectroscopy is,
- the basic physics of XRF,
- how XRF is used,
- limitations of XRF



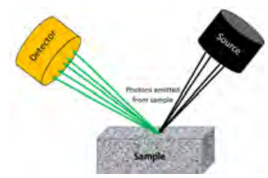
Definitions

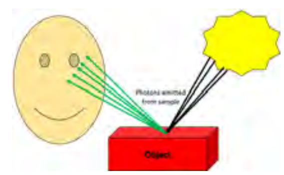
- **Spectroscopy**: investigation and measurement of *spectra* produced when matter interacts with or emits electromagnetic radiation.
- **Spectra**: plural form of *spectrum*.
- **Spectrum**: the entire range of wavelengths of *electromagnetic* radiation.



- **XRF Spectroscopy**: measures energy released by interactions between a sample and millions of high-energy photons

Fundamentals





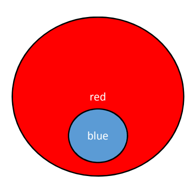
- Photons *emitted* from source
  - Sun (infrared – ultraviolet)
  - Incandescent bulb (mostly infrared)
  - Fluorescent bulb (red – violet)
  - XRF tube (X-rays)
- Photons *interact* with molecules in sample
  - Reflected (white/color), absorbed (black), or scattered
- Reflected photons observed by detector
  - Eyes (red, green, blue cones)
  - XRF detector
- Information is processed
  - Brain takes information and we see color
- Source, object of interaction, & detector determine what photons can be "seen"
  - 3 sources of subjectivity
  - Everyday examples
- If variations in source and detector can be eliminated (i.e. instrument parameters controlled), then detected variations in reflected photon can be attributed to sample composition
  - This is what you do with the XRF
    - Voltage, current, time, filter, atmosphere

What's a photon, you ask…

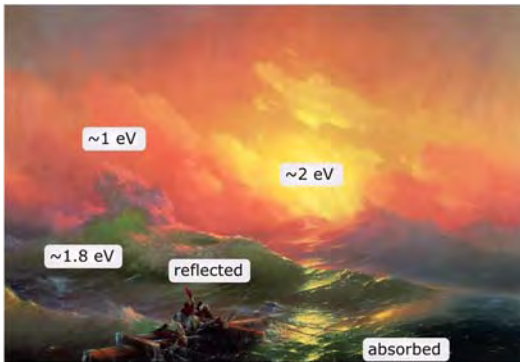
- Nobody really knows exactly what it is…

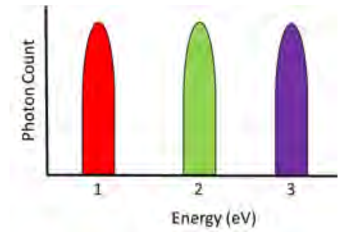
"Discrete packets (quanta) of electromagnetic radiation"

- We do have a handle on some of its properties
- No mass, but carry a force…
- Move at speed of light (*c*) in free space
- Can exhibit characteristics of a wave or a particle but is neither
  - Long scientific debate…..
- Slowed or absorbed when interacts with matter



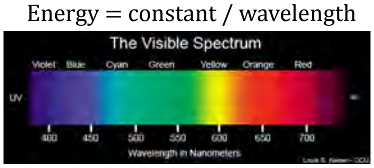
- Best to think about photons in terms of a diameter
- Importantly, photons contain distinguishing information upon return to detector





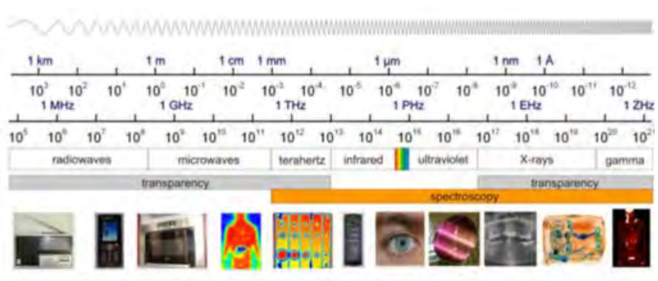
Assumptions?

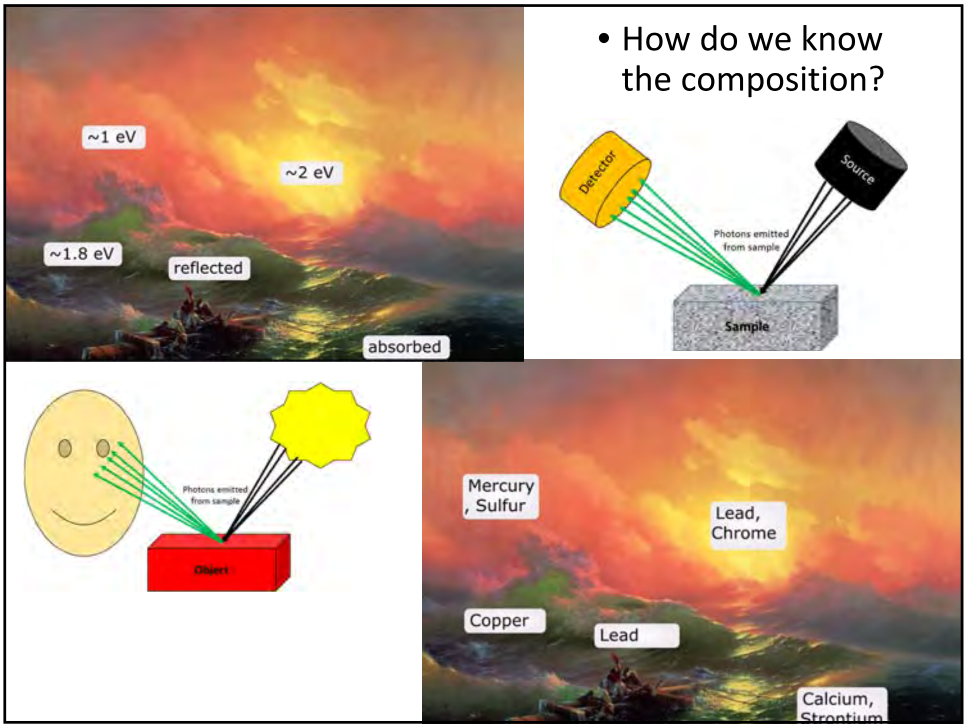
Energy = constant / wavelength



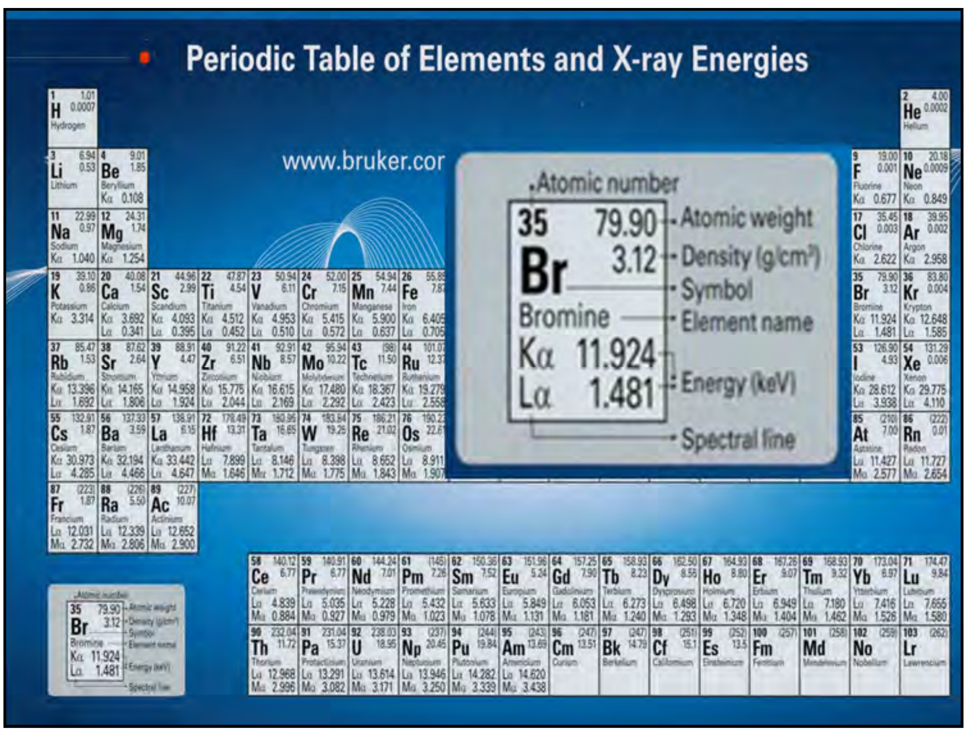
X-ray fluorescence

- High-energy photons emitted from EM source
  - Rh anode (others: Cu, Mo, Cr, etc.)
  - 1 – 40 KeV (cf. ~1-3 eV visible light)
  - Higher energies can interact with the interior of the sample (cf. not just the outer layer with visible light)
    - Yields atomic information (i.e. elemental data)



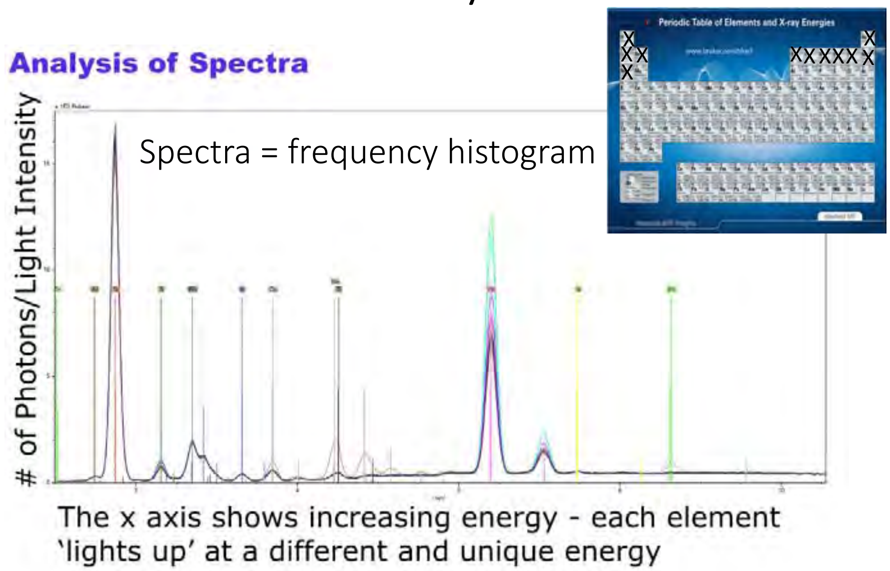


• How do we know the composition?
~1 eV
~2 eV
~1.8 eV
reflected
absorbed
Detector
Source
Photons emitted from sample
Sample
Photons emitted from sample
Object
Mercury, Sulfur
Lead, Chrome
Copper
Lead
Calcium, Strontium

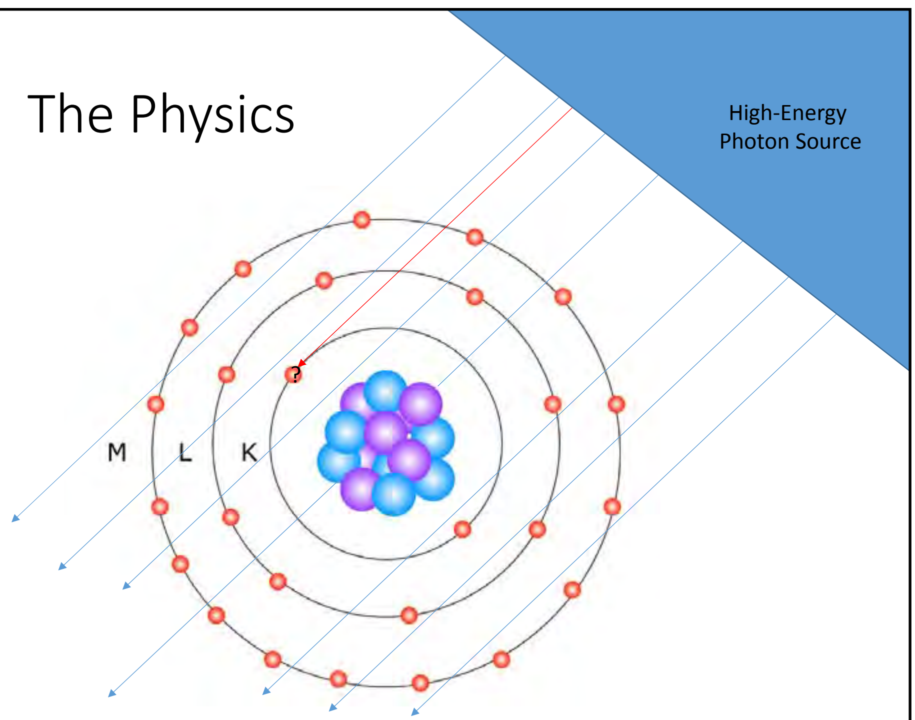


Periodic Table of Elements and X-ray Energies
www.bruker.cor
Atomic number
35 79.90 Atomic weight
Br 3.12 Density (g/cm³)
Symbol
Bromine Element name
Kα 11.924
Lα 1.481 Energy (keV)
Spectral line

What is recorded by the detector

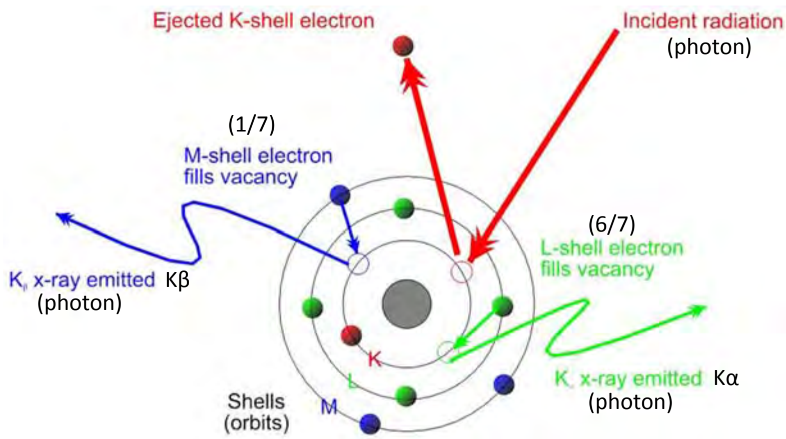


The Physics



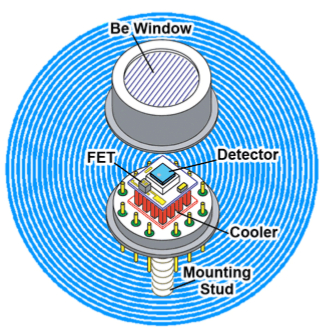
Photon-Sample Interaction

Photon interaction with sample produces "fluorescence"

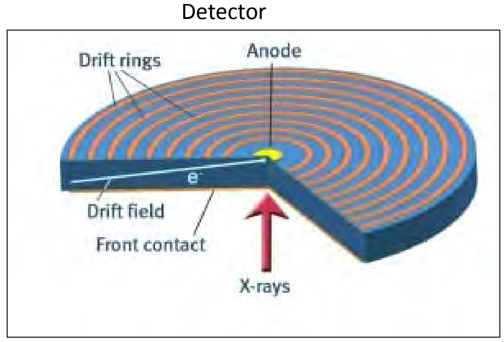


Emitted photons hit detector & specific energies are recorded

- 140 eV-resolution Si-drift detector



Detector



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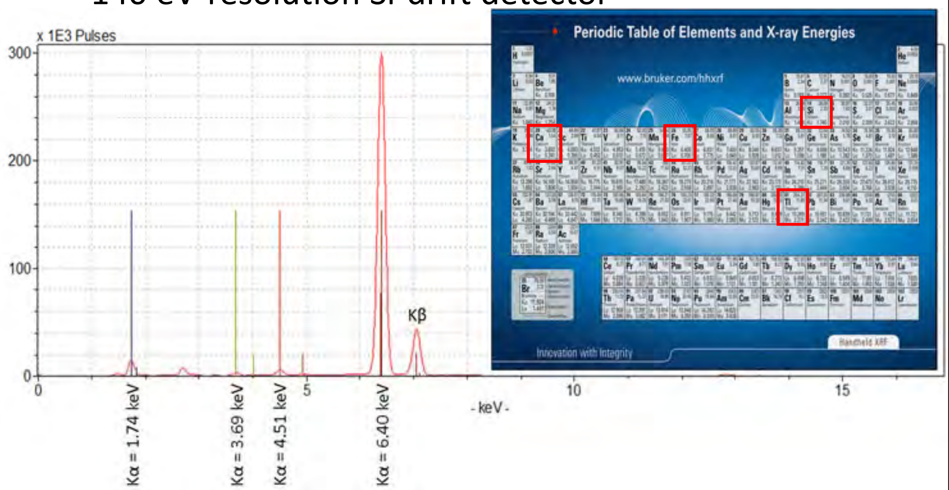


How XRF is used by geoscientists

- Identify elements of interest (economic minerals)
  - Gold, silver, copper
- Identify proxy elements (indicators of special environments/conditions)
  - Mo, Ti, U
- Identify changes in mineralogy
  - E.g., clays, quartz, calcite, dolomite, gypsum, pyrite
- Looks for systematic trends spatially and temporally (stratigraphically)
  - Changes
- Be sure to visit the student posters

Advantages & Limitations

- Non-Destructive
- Liquids, solids, and thin films
- Sample Prep: minimal
- Rapid and inexpensive
- Easy, but requires understanding

- New tool in geological studies
- Matrix effects common
- Calibration needed
- Sample variables
- Health considerations

Hazards of X-rays

- X-rays are energetic electromagnetic radiation that ionize matter by ejecting electrons from atoms
- Ionizing radiation deposits energy at the molecular level, causing cellular chemical changes, and thus biological changes. Damage is not caused by heating, but by molecular changes.
- The extent of ionization, absorption, and molecular change depends on the quality (spectral distribution) and quantity (flux & intensity) of the radiation.

Summary

- Geochemical data is critical for geoscientists
- XRF is one of many tools to extract elemental data
- XRF spectroscopy works by shooting high-energy EM at a sample and recording the energy released during electron interactions
- The energies of the returning EM depend on the elemental composition of the sample

The life of a scientist sounds way more fun when you describe it like you're a six year old.

Additional Resources

- http://www.xrf.guru/
- https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/tracer-5i/overview.html

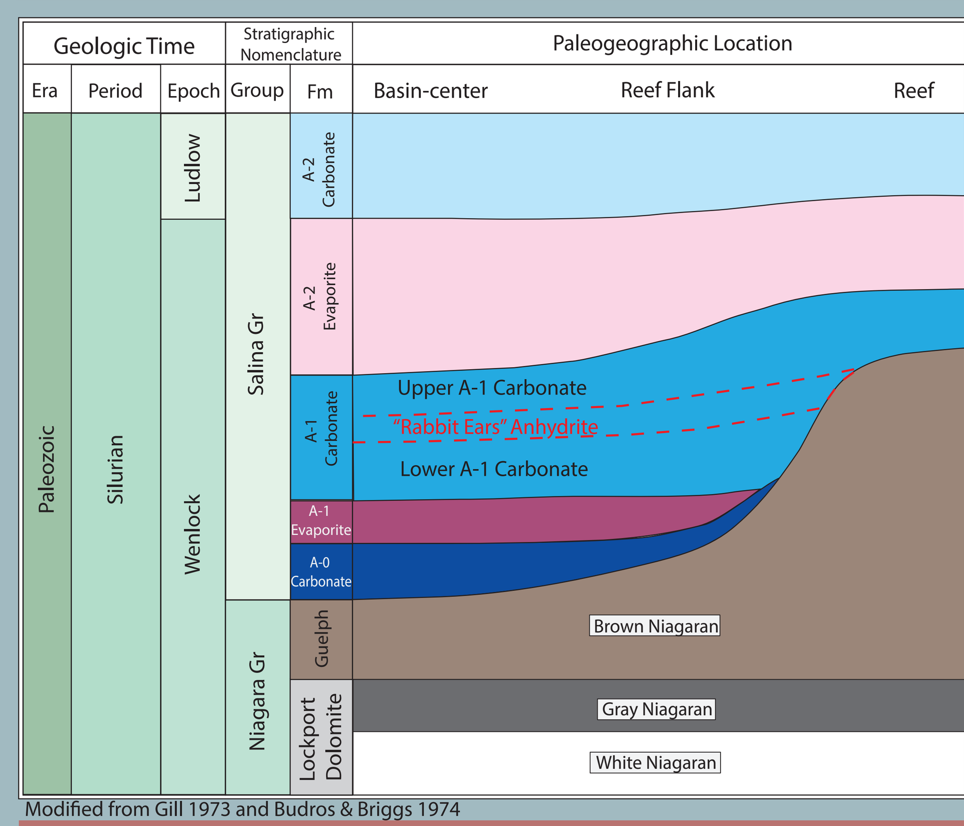
WESTERN MICHIGAN UNIVERSITY
Department of Geosciences

Chemostratigraphic analysis of the Silurian-aged, Salina A-1 Carbonate using handheld ED-XRF

Matthew A. Hemenway, Stephen E. Kaczmarek, and Katherine G. Rose
Western Michigan Univeristy, Kalamazoo, Michigan

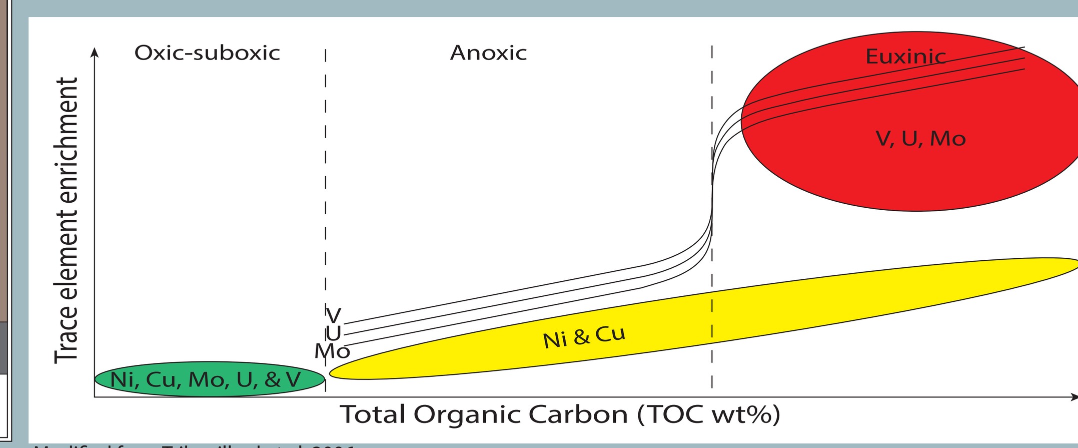
Abstract:
Previous studies of the Silurian-aged, Salina A-1 Carbonate (A1) focus primarily on its stratigraphic relationship with the underlying Niagaran reef complexes. The A1 is conventionally interpreted as a shallow water deposit. More recently, new data supports water depths much greater than previously interpreted (>100 m). These data include facies analysis from a basin-center core and associated elemental data. What remains unknown is: (1) the extent of geochemical variability in A1 basin-center facies, (2) the extent to which chemofacies can be correlated throughout the basin center, and (3) what fundamental sedimentological and diagenetic processes cause the observed elemental variations. In this study, handheld x-ray fluorescence spectrometery (HHXRF) will be used to evaluate the following hypotheses: (1) Elevated concentrations of TOC and trace elements commonly used as paleoredox proxies in deep-water siliciclastic mudrocks, also exhibit a positive correlation in basin center facies of the A-1 Carbonate. (2) Unique geochemical signatures (chemofacies) can be identified and correlated between basin-center wells. (3) Vertical chemofacies variations reflect changes in relative sea-level, redox, and sedimentation through time. These hypotheses will be tested by collecting high-resolution elemental concentration data in multiple drill cores from basin-center locations in an attempt to correlate chemofacies and to test the existing depositional and sequence stratigraphic model for the A1.

Background



Modified from Gill 1973 and Budros & Briggs 1974

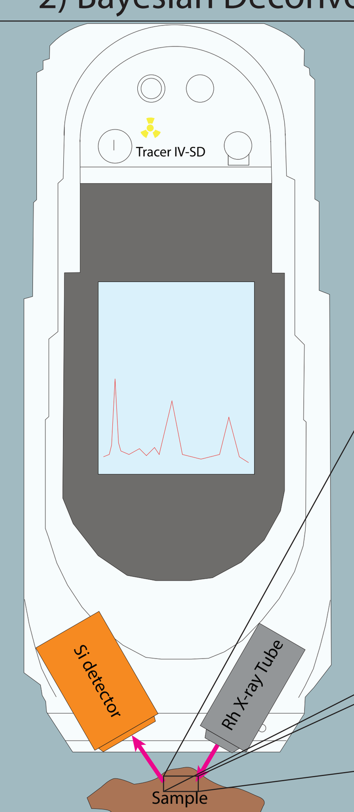
- A-1 Carbonate significant part of the reservoir and the source rock for the largest play in the Michigan Basin (>500 Mmbls oil & 3 Tcf gas; Gardner & Bray 1985, Garrett 2016)
-Rine et al. 2017 incorporated HHXRF into facies analysis; interpreted much greater water depths in the basin center
Research Questions:
1) What is the extent of geochemical variability in the basin center?
2) Can basin center chemofacies be correlated?
3) What sedimentological/diagenetic processes control chemofacies?



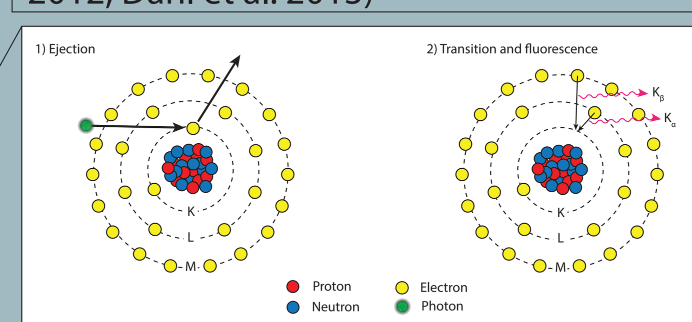
Modified from Tribovillard et al. 2006

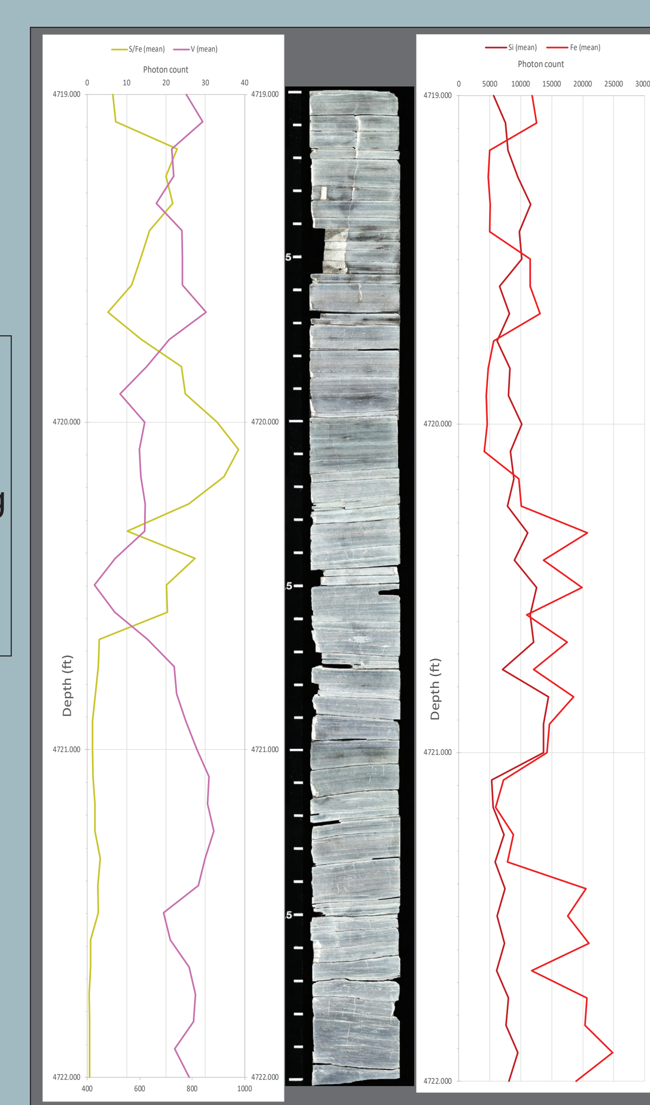
Methods: HHXRF in Mudrocks

XRF Theory
3 component system:
1) Source, 2) Sample, 3) Detector
Data processing
1) Quantification with WD-XRF & ICP-MS (absolute)
2) Bayesian Deconvolution (relative)

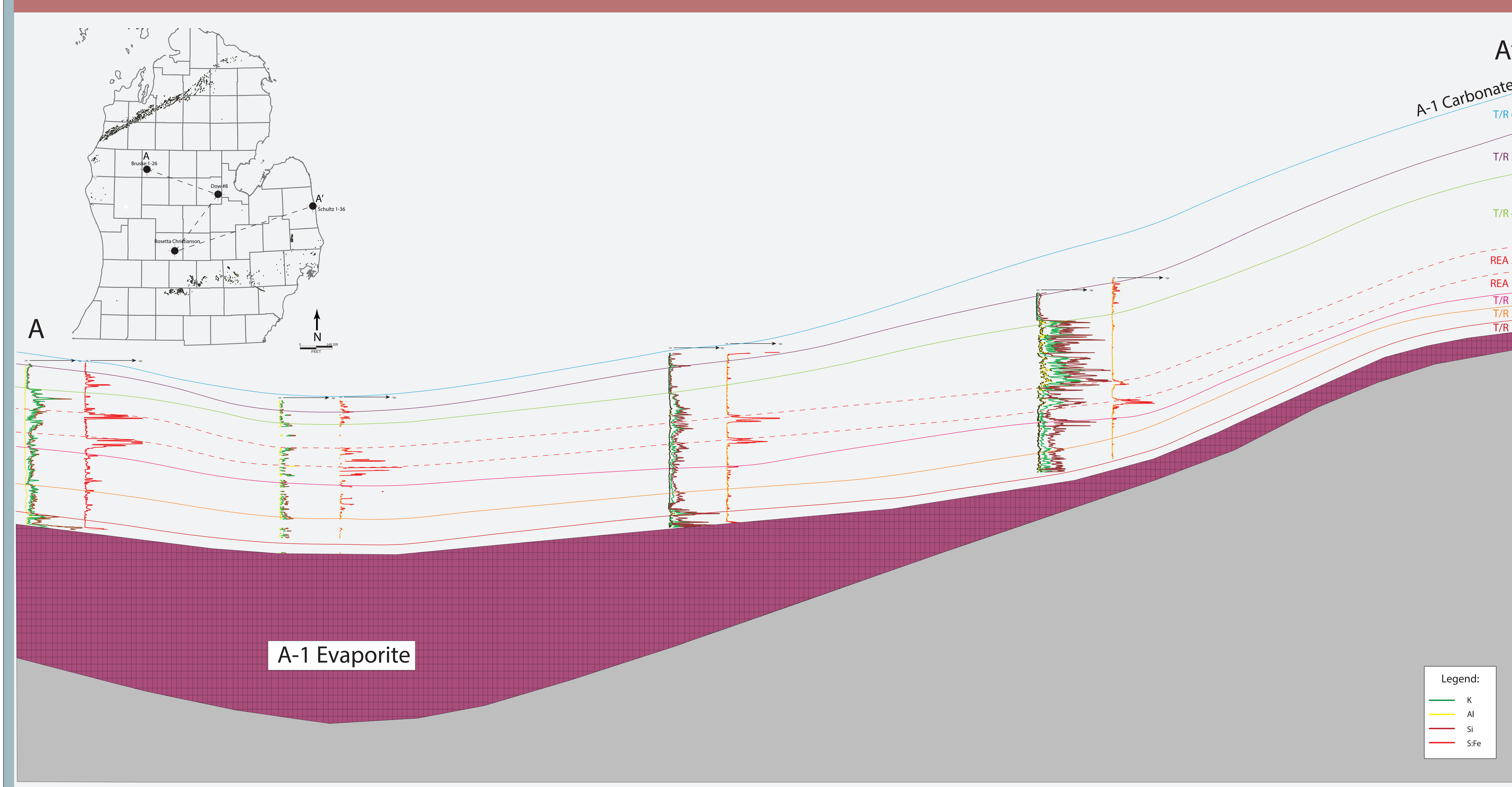


Applications in sedimentology and stratigraphy
-Used to measure elemental concentrations in texturally homogenous mudrocks
-Unique chemical signatures used for correlation and building sequence stratigraphic model (Turner et al. 2016)
-Identification of paleoredox proxy elements (Algeo & Rowe 2012, Dahl et al. 2013)

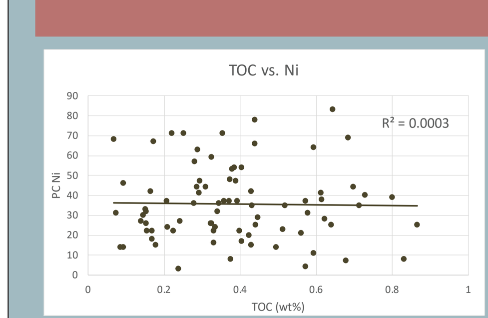


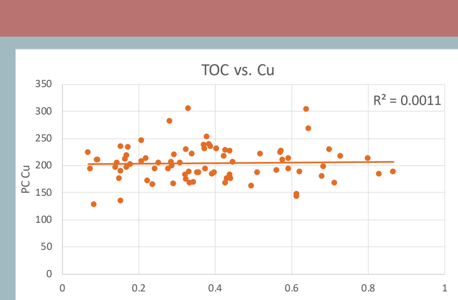


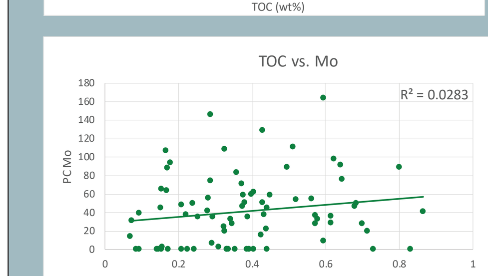
Results: Chemofacies & Sequence Correlation

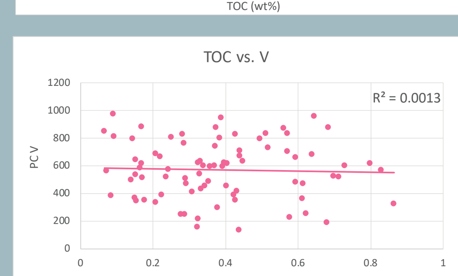


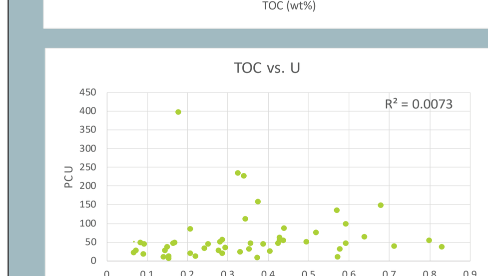
Results: TOC and Trace Elements

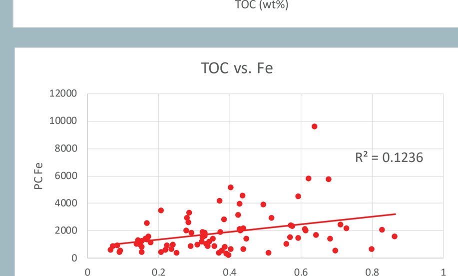












- Very weak correlation between TOC and trace elements used as paleoredox proxies (Reference).

- Fe displays the best correlation; likely represents pyrite.

Possible Explanations:

1) A-1 Carbonate mature to post-mature = lowered present day TOC and/or A-1 Carbonate TOC values too low

2) Hydrothermal alteration (Katz et al. 2016)

3) Restriction from the open ocean = limited trace element source from sea water

Discussion

1) Elevated concentrations of TOC and paleoredox proxy elements do not exhibit a positive relationship in the A-1 Carbonate.

2) Unique chemofacies can be correlated between basin center wells
-Si, Al, K, S, Fe, Sr, Ca, Mg, and V displayed correlative trends.
-Future work:
Cluster analysis using Schumberger TechLog to determine additional elemental relationships

3) Vertical chemofacies variations likely reflect changes in relative sea-level and sedimentation in the A-1 Carbonate
-Siliciclastic proxies and S:Fe ratio used to identify 6 transgressive-regressive cycles
-Future work:
Thin sections, XRD, and SEM in order to determine the mineralogical and diagenetic associations of elements identified with the HHXRF

Sequence Stratigraphy and Depositional Facies Model of the Burnt Bluff Group, Michigan Basin, USA

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Michigan Geological Repository for Research and Education
Department of Geosciences

Abstract

The Burnt Bluff Group (BBG) is one of several hydrocarbon-producing carbonate units in the Michigan Basin. The BBG lithology composed of limestones and dolostones, and it is early Silurian in age. According to USGS assessment 2015, BBG contains 43.8 BCGF of gas. Since the late 1970's, the BBG has produced 30.7 MCF of natural gas.

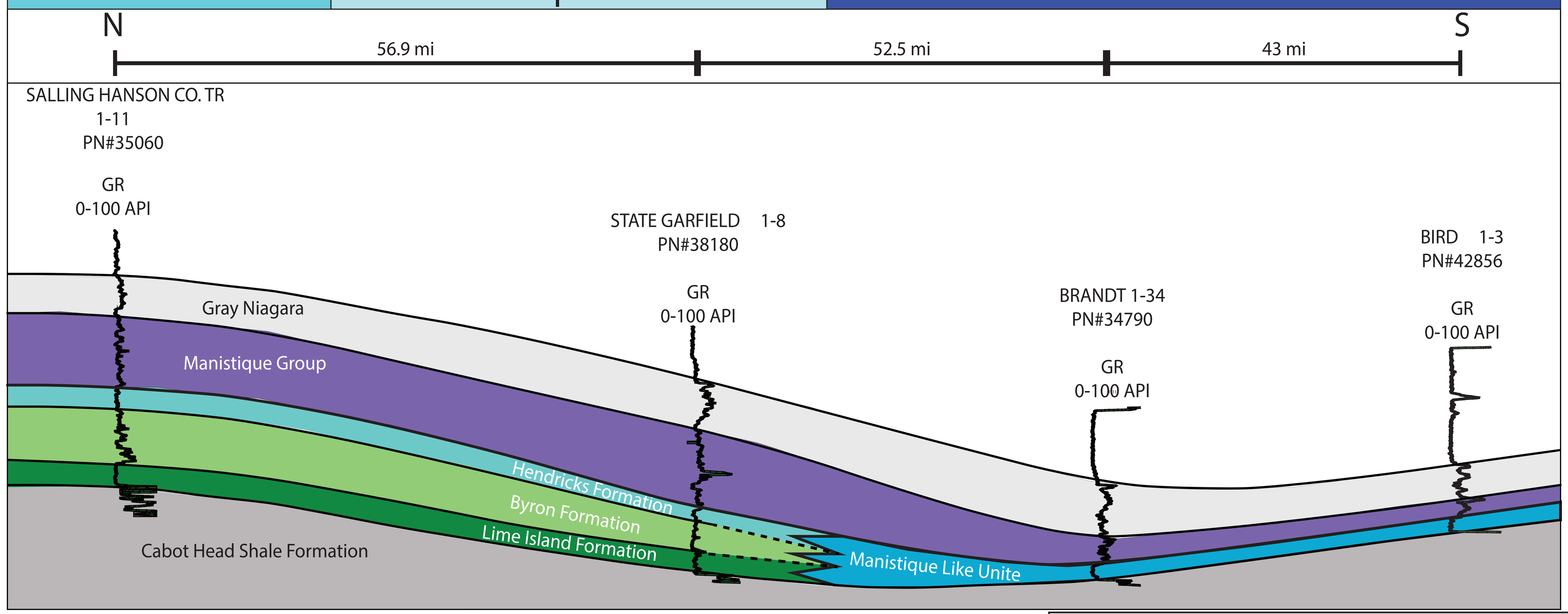
Hydrocarbon production from the BBG is modest. As such, studies of the sedimentology, stratigraphy, and diagenesis of the BBG have been limited in scope. The current study aims to augment this limited understanding of BBG geology by developing a detailed sedimentological and stratigraphic framework using detailed core descriptions, biostratigraphic data (conodonts), thin section petrography, geophysical wireline logs, Carbon stable Isotopes, and X-ray fluorescence elemental data (handheld XRF).

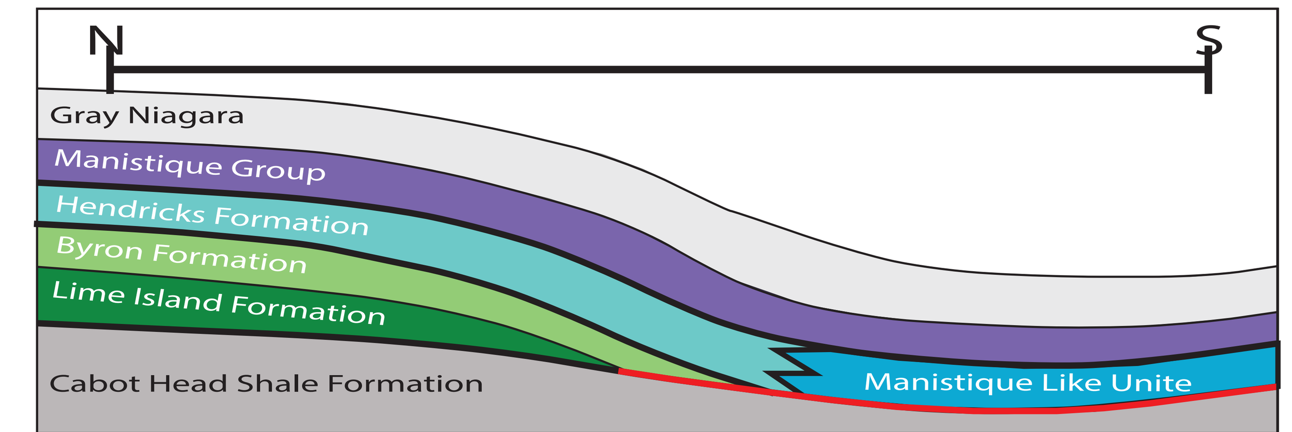
BBG in North, NE and NW parts of basin consist of three formations, these formations lumped together into one unit in the central basin. Accordingly, the objectives of this study are to:

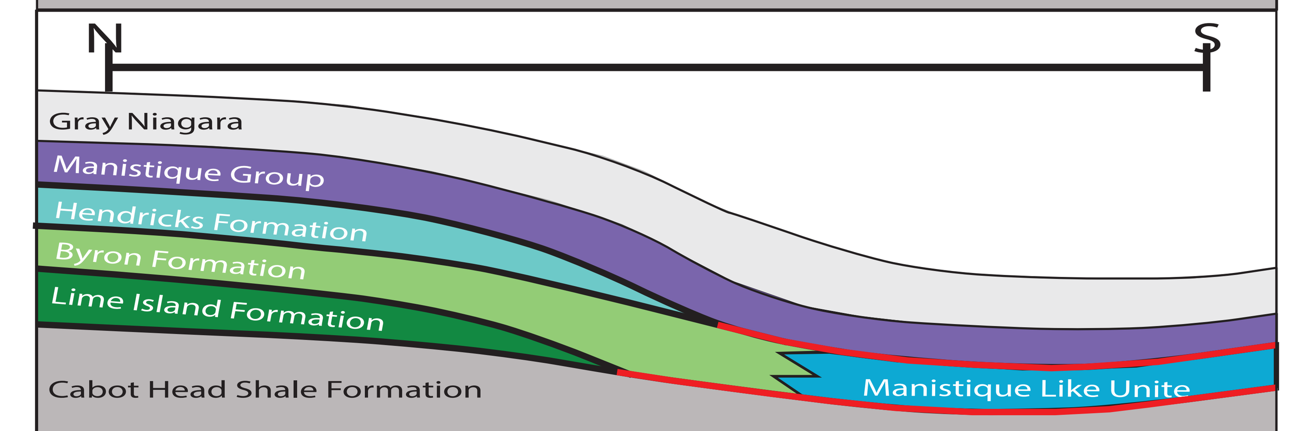
1) Construct age relationship of the BBG units across the basin.
2) Identify the internal facies stacking architecture to identify chronostratigraphic units.
3) Correlate these sequence stratigraphic units to understand the depositional evolution of the basin.

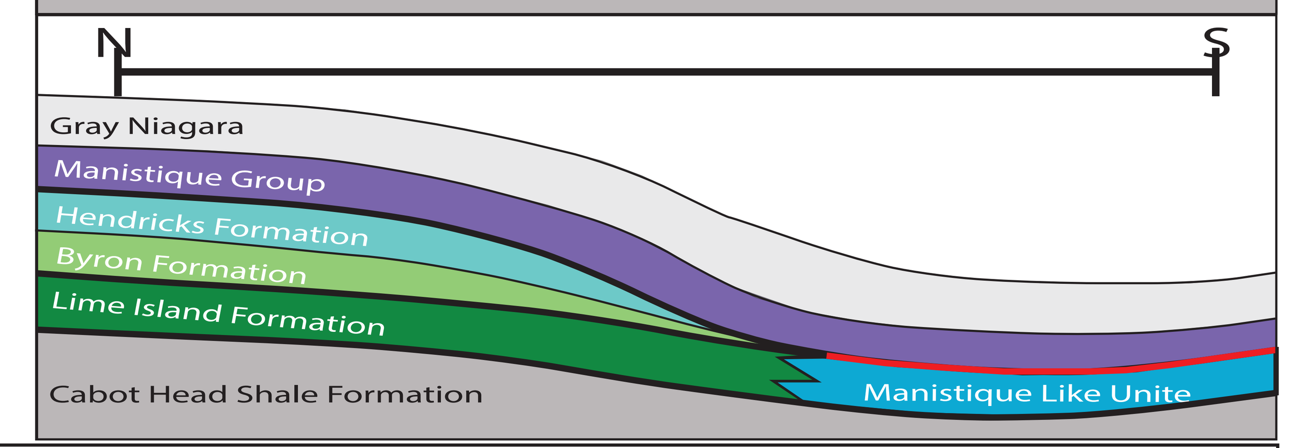
This study will help provide a firmer understanding of the petroleum system within the BBG and will offer valuable context for temporally adjacent stratigraphic units in the Michigan Basin. The findings will also provide information about the areal extent of the various lithofacies with the basin, thus making it possible to identify of new hydrocarbon fields in the BBG.

North-South Structural cross-section, Late Silurian-Michigan basin





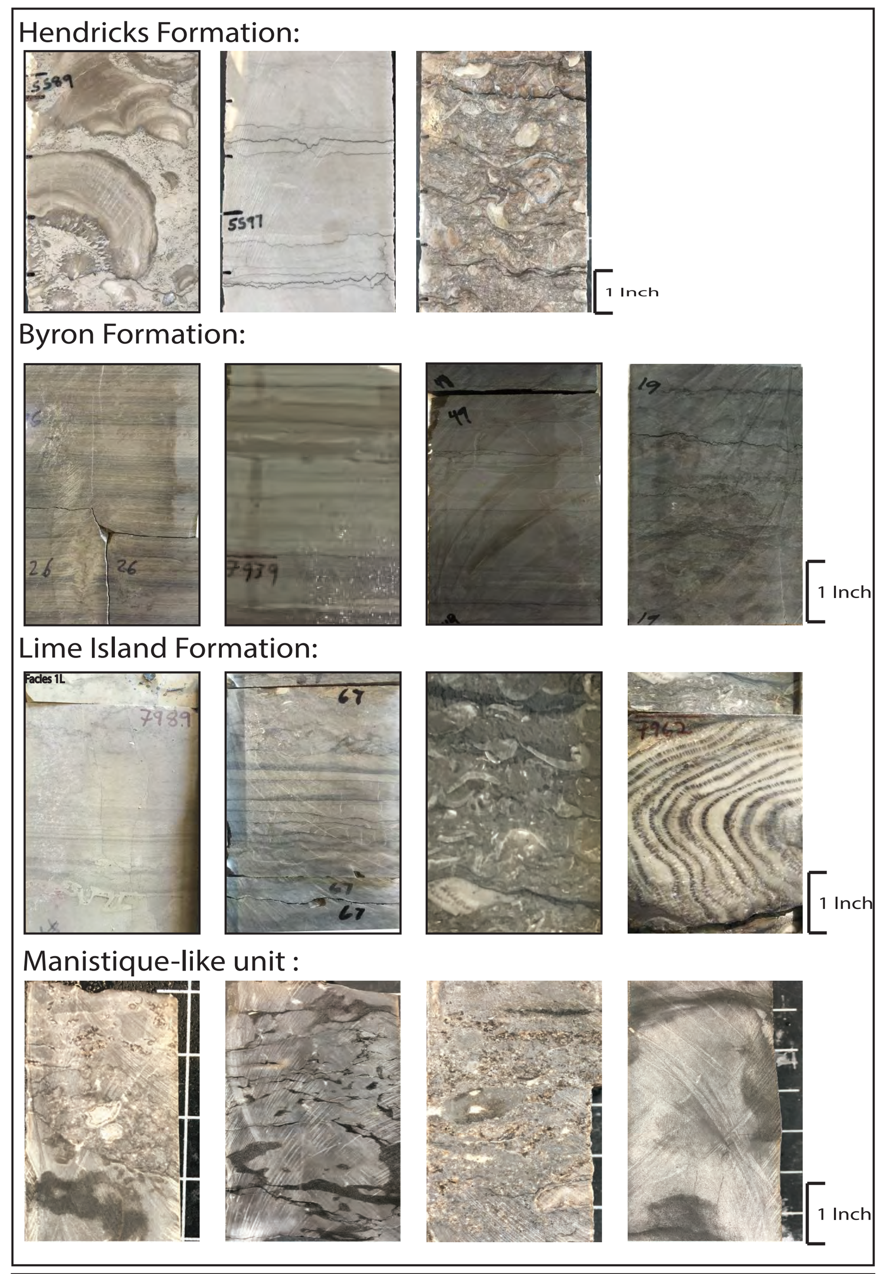




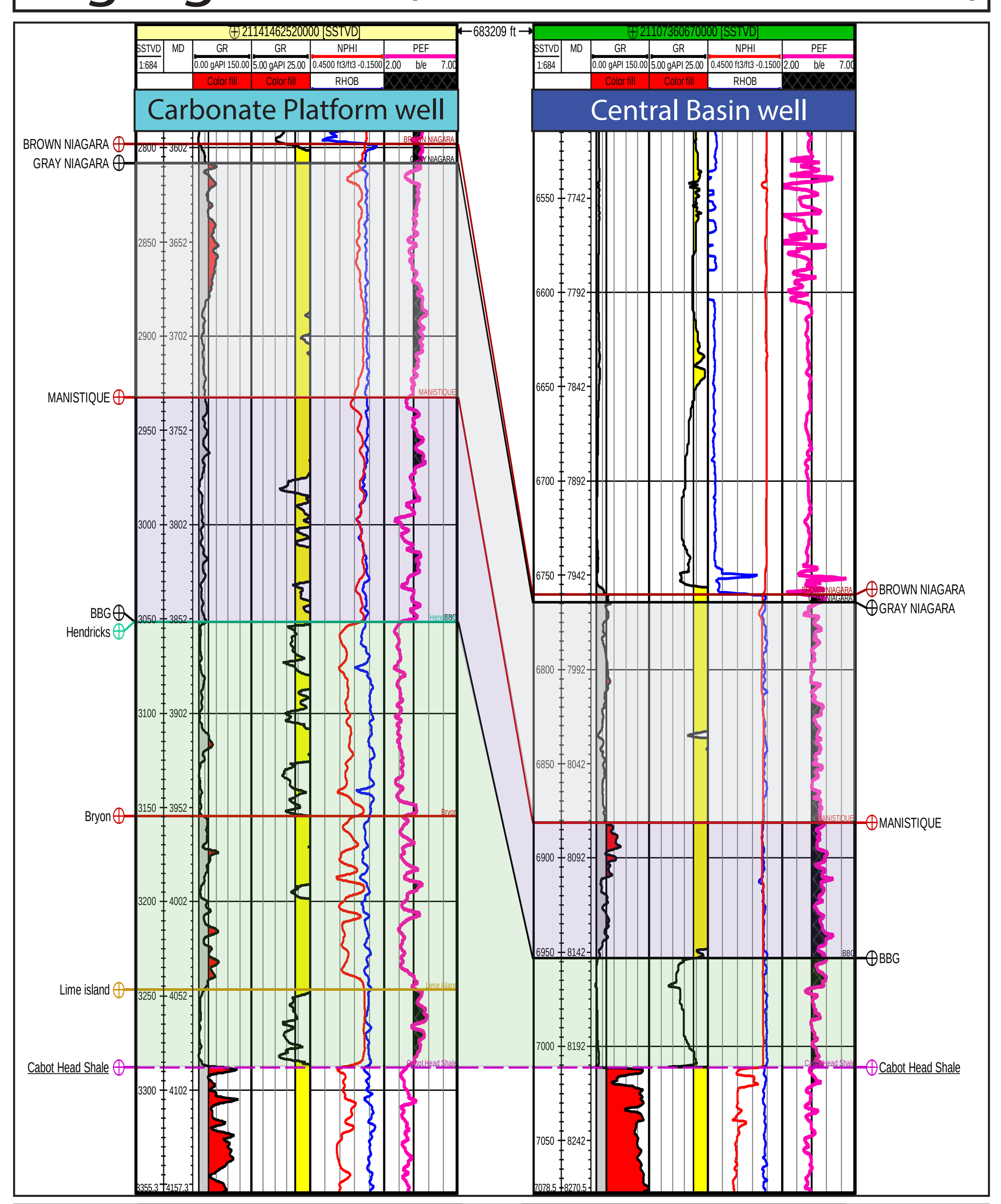
Geological background

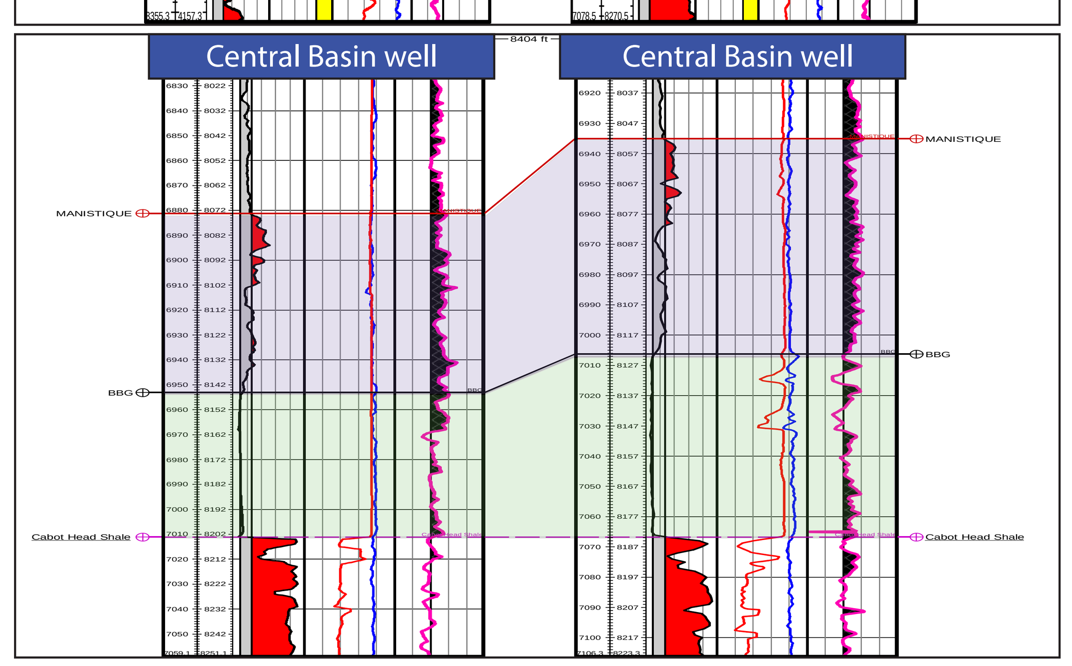
Geologic Time				Lithostratigraphic Nomenclature		
Period	Epoch	N.A. Stages	I.C.S. Stages	Group	Formation L.P.	Formation U.P.
Silurian	Late	Cayugan	Pridoli	Bass Islands Gp.	Undiff.	Raisin River Dol.
						Put-in-Bay Dol.
						St. Ignace Dol.
			Ludfordian	Salina Gp.	G-Unit	Pte. aux Chênes Fm.
					F-Unit	
					E-Unit	
					D-Unit	
					C-Unit	
					B-Unit	
	Early	Niagaran	Gorstian		A-2 Carbonate	
			Homerian		A-2 Evaporite	
					A-2 Carbonate	
					A-1 Evaporite	
					A-0 Carbonate	
				Niagara Gp.	Guelph Dol.	Engadine Gp.: Bush Bay Fm.
						Rapson Creek Fm.
			Sheinwoodian		Lockport Dol.	Rockview Fm.
			Telychian	Manistique Gp.	Cordell Fm.	
					Schoolcraft Fm.	
			Aeronian	*Burnt Bluff Gp.*	*Hendricks Fm.*	
					Byron Fm.	
		Medinan	Rhuddanian		*Lime Island Fm.*	
				Cataract Gp.	Cabot Head Sh.	
					Manitoulin Dol.	

Facies Identified

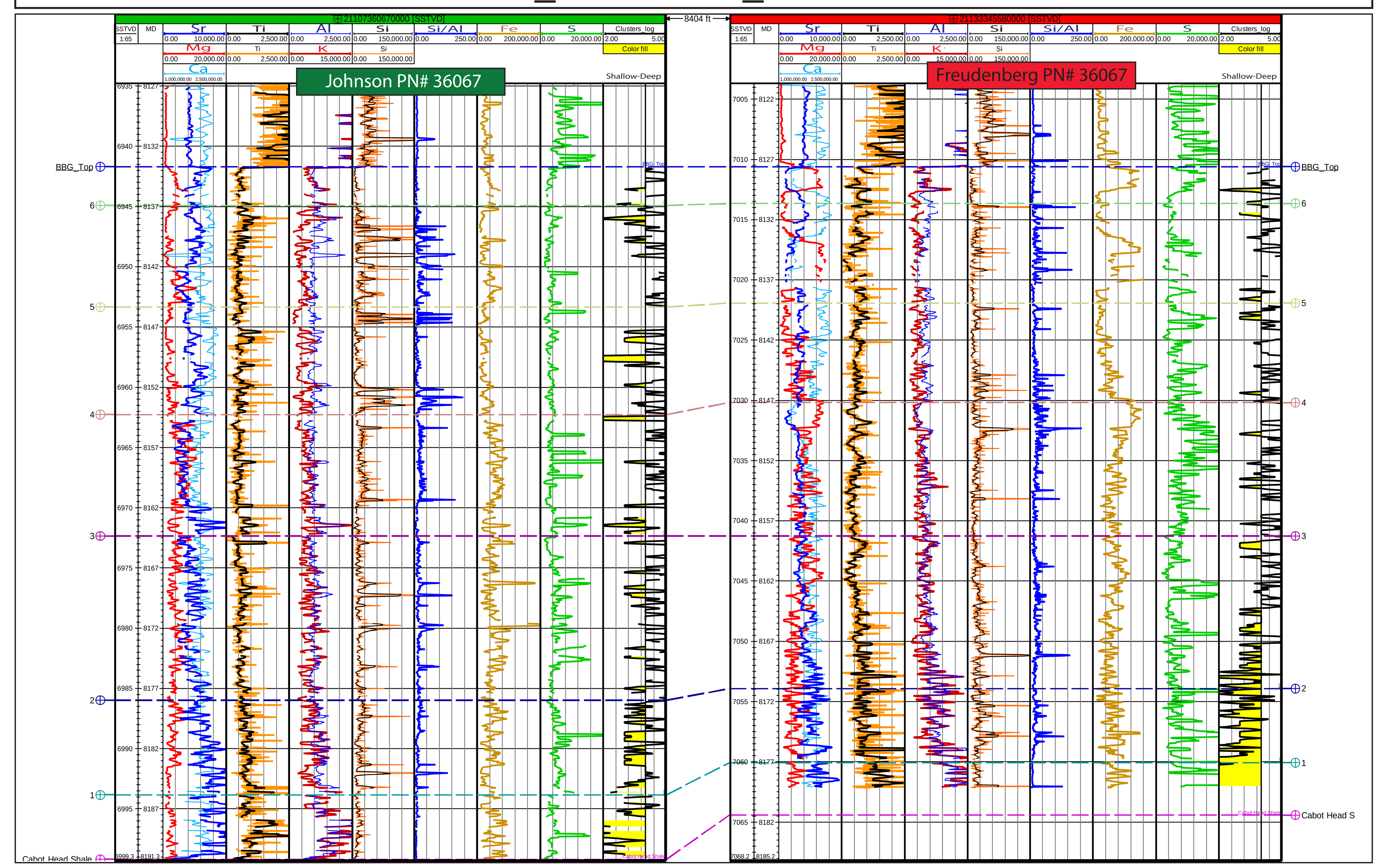


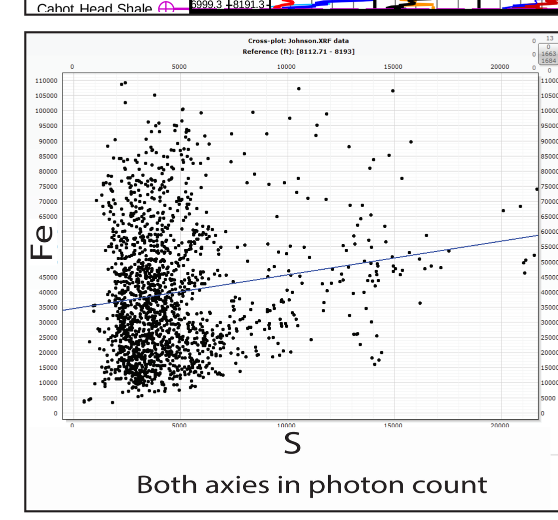
Log Signature (different locations in the Basin)

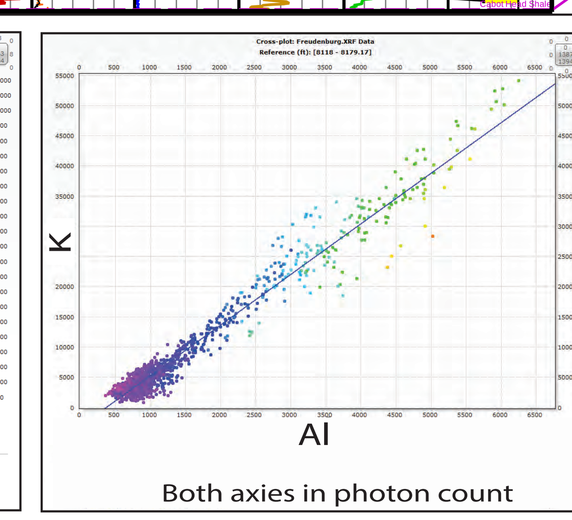


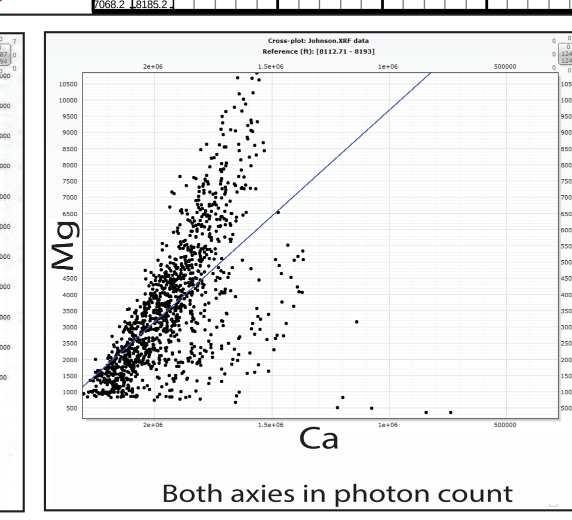


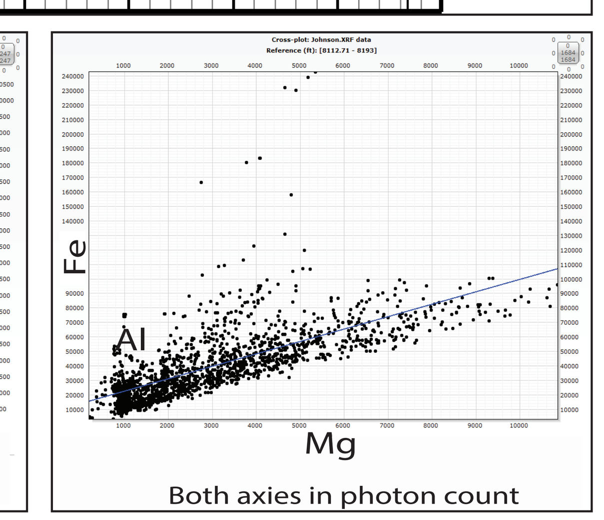
XRF data_correlation_central basin wells



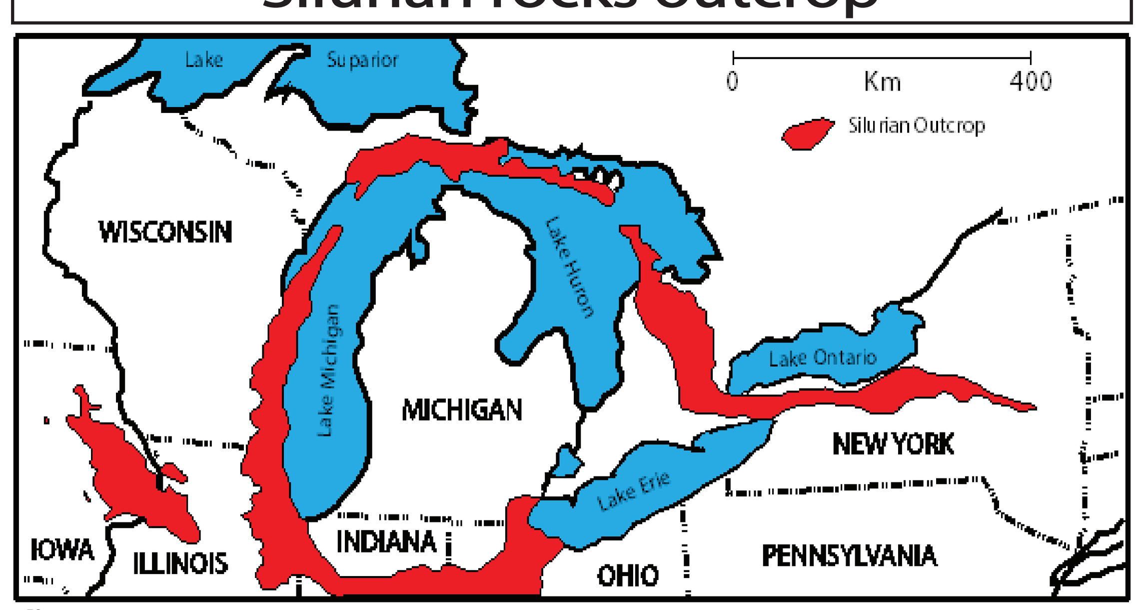




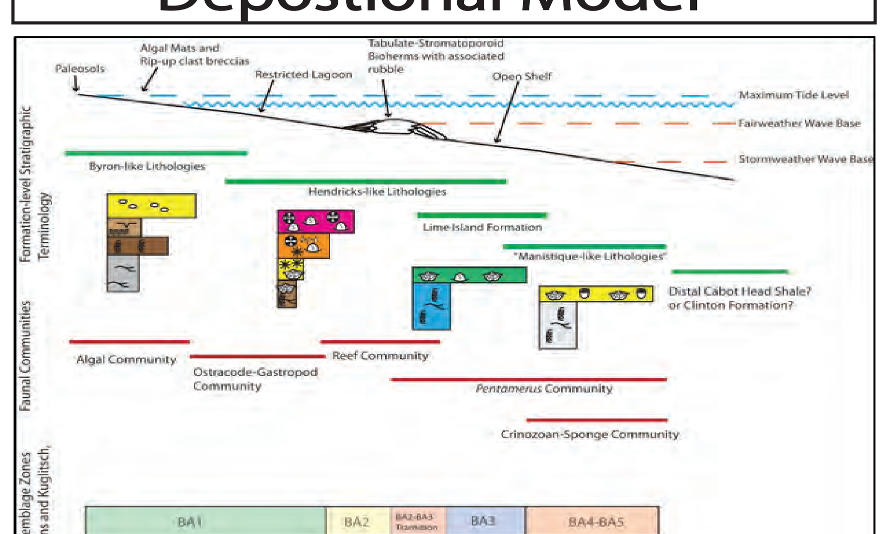




Silurian rocks outcrop



Depostional Model



Voice et al (in press)

Powder Problem

Objectives

The objective of this activity is to identify rock powders based only on their major element compositions as determined by XRF.

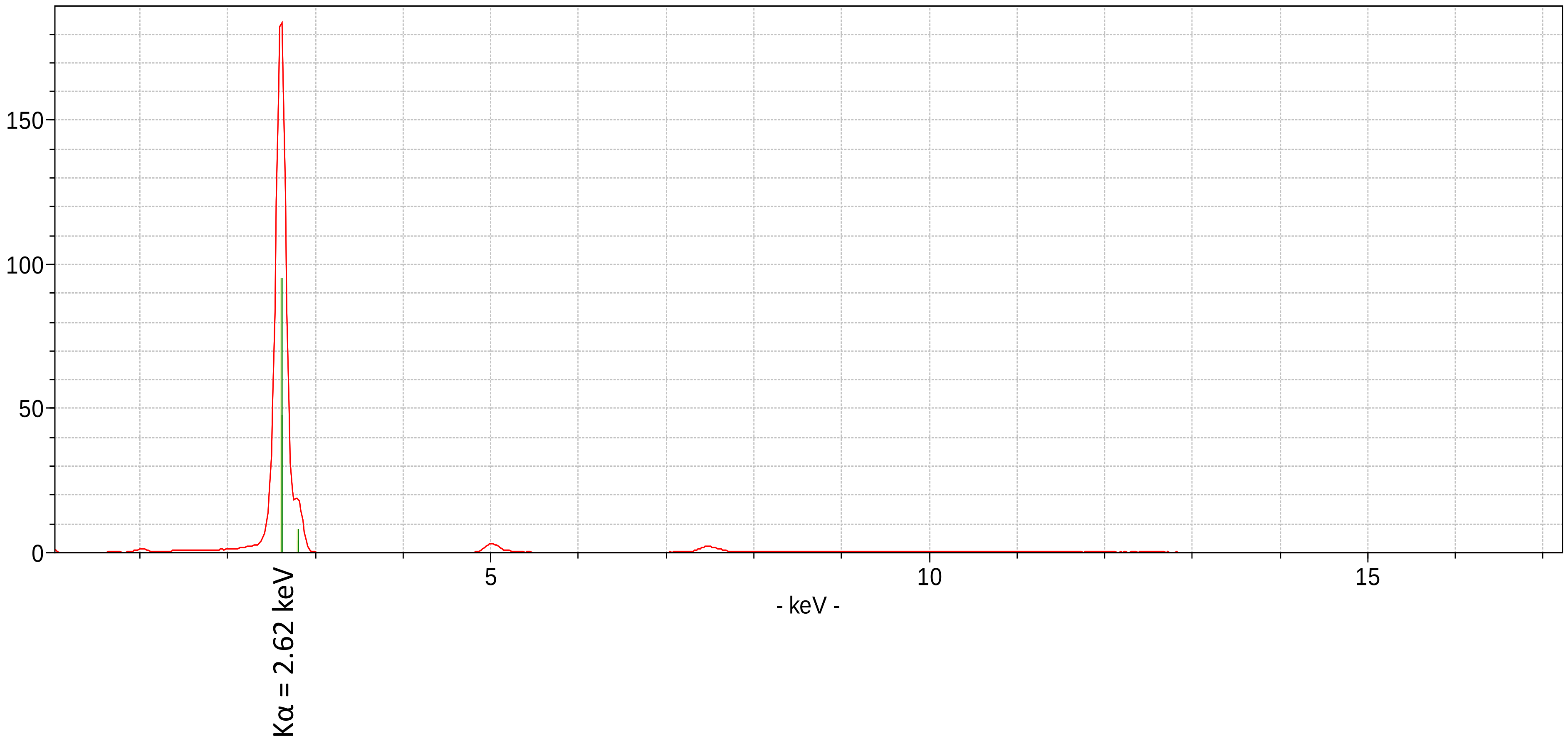
Instructions

A set of rocks commonly found in the Michigan Basin has been provided (Table 1). These rocks have been powdered and placed into the vials labeled A-F. The whole rocks are fairly easy to tell apart, but as you can see, it is quite difficult to discriminate between the white powders (except the hematite, of course). Use the raw XRF spectra provided to match the powdered samples to their whole rock counterparts. The first step is to identify the major K-alpha fluorescence peaks in the XRF spectra. Next, use the major elemental compositions of the powders to match them with the rocks listed below.

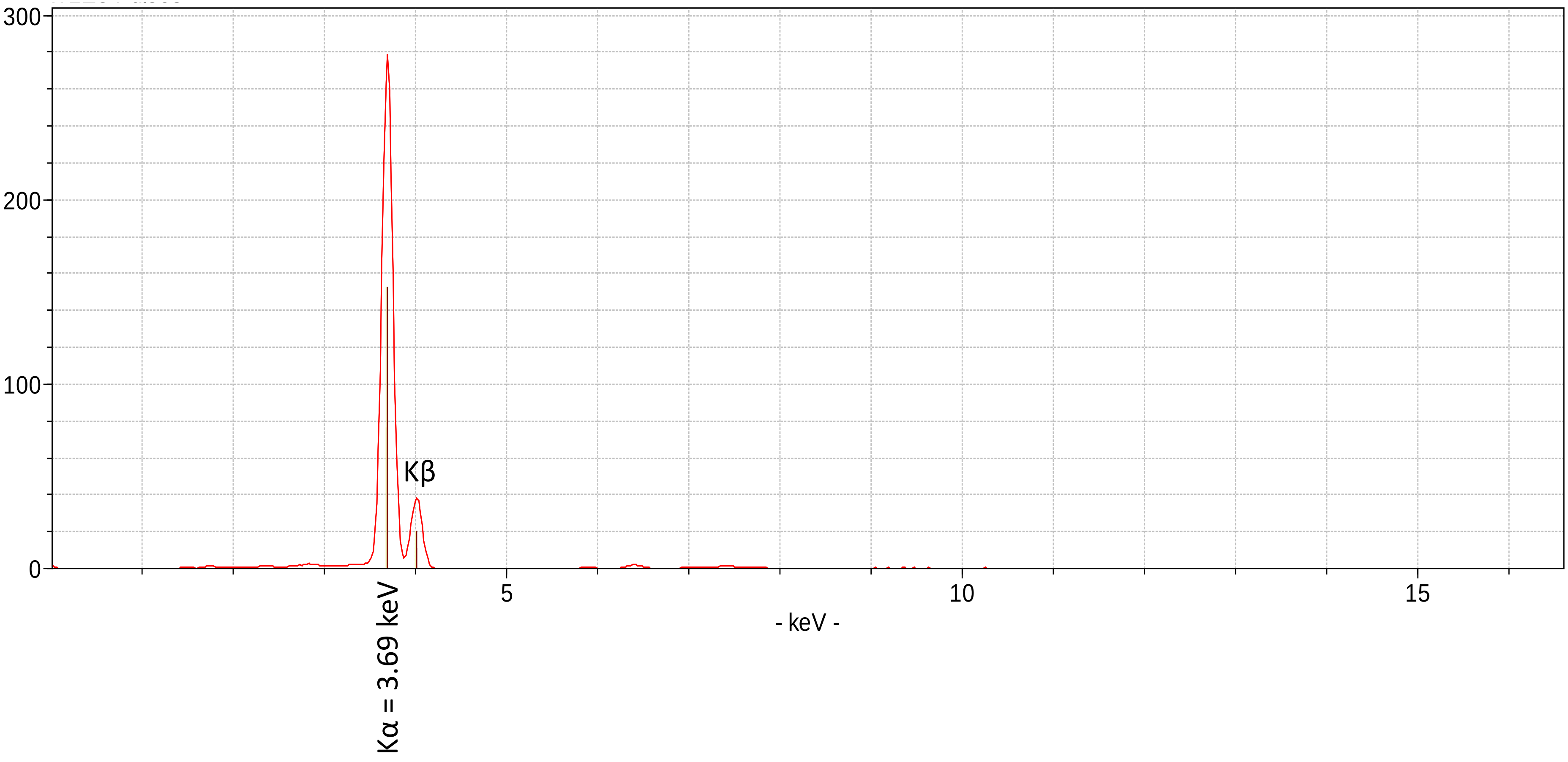
Table 1. Common Rocks in the Michigan Basin

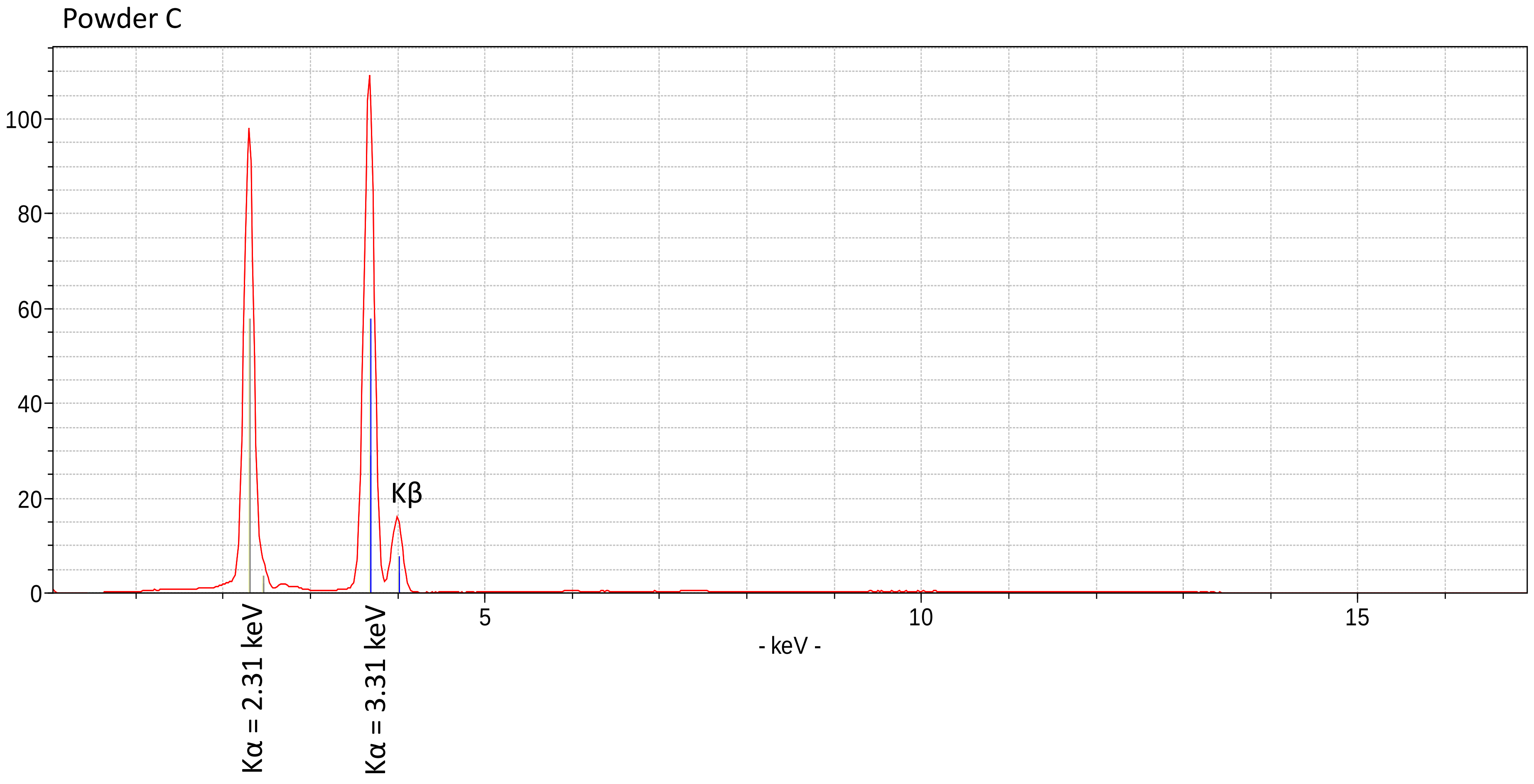
Rock Name	*Mineralogy*	*Chemical Formula*	*Chemical name*
Limestone	calcite, aragonite	$CaCO_3$	calcium carbonate
Dolostone	dolomite	$CaMg(CO_3)_2$	calcium-magnesium carbonate
Rock Salt	halite	NaCl	sodium chloride
Rock Gypsum	gypsum	$CaSO_4$	calcium sulfate
Sandstone	quartz	SiO_2	silicon dioxide
Specular Hematite	hematite, mica	Fe_2O_3	iron oxide

Powder A

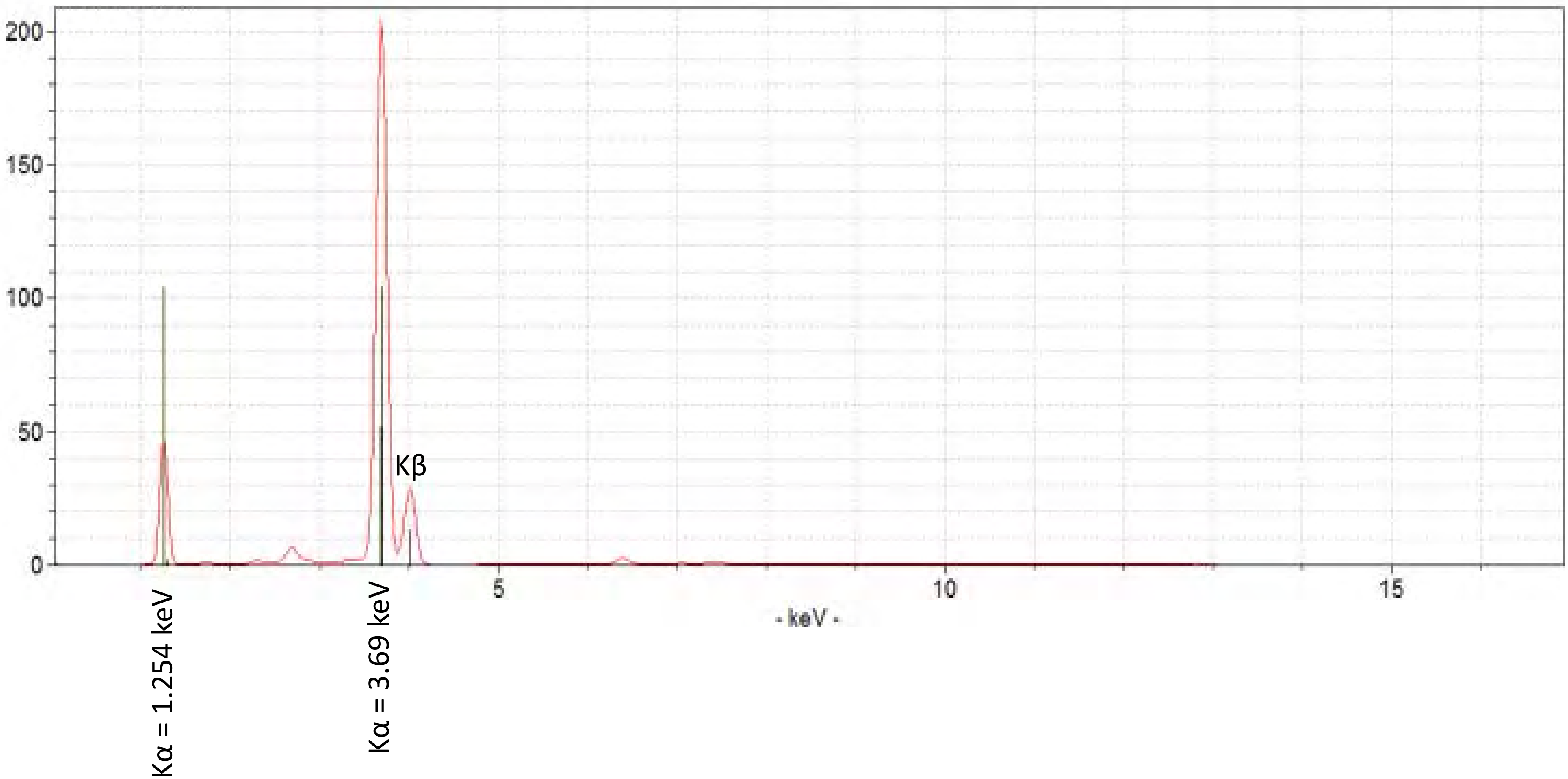


Powder B

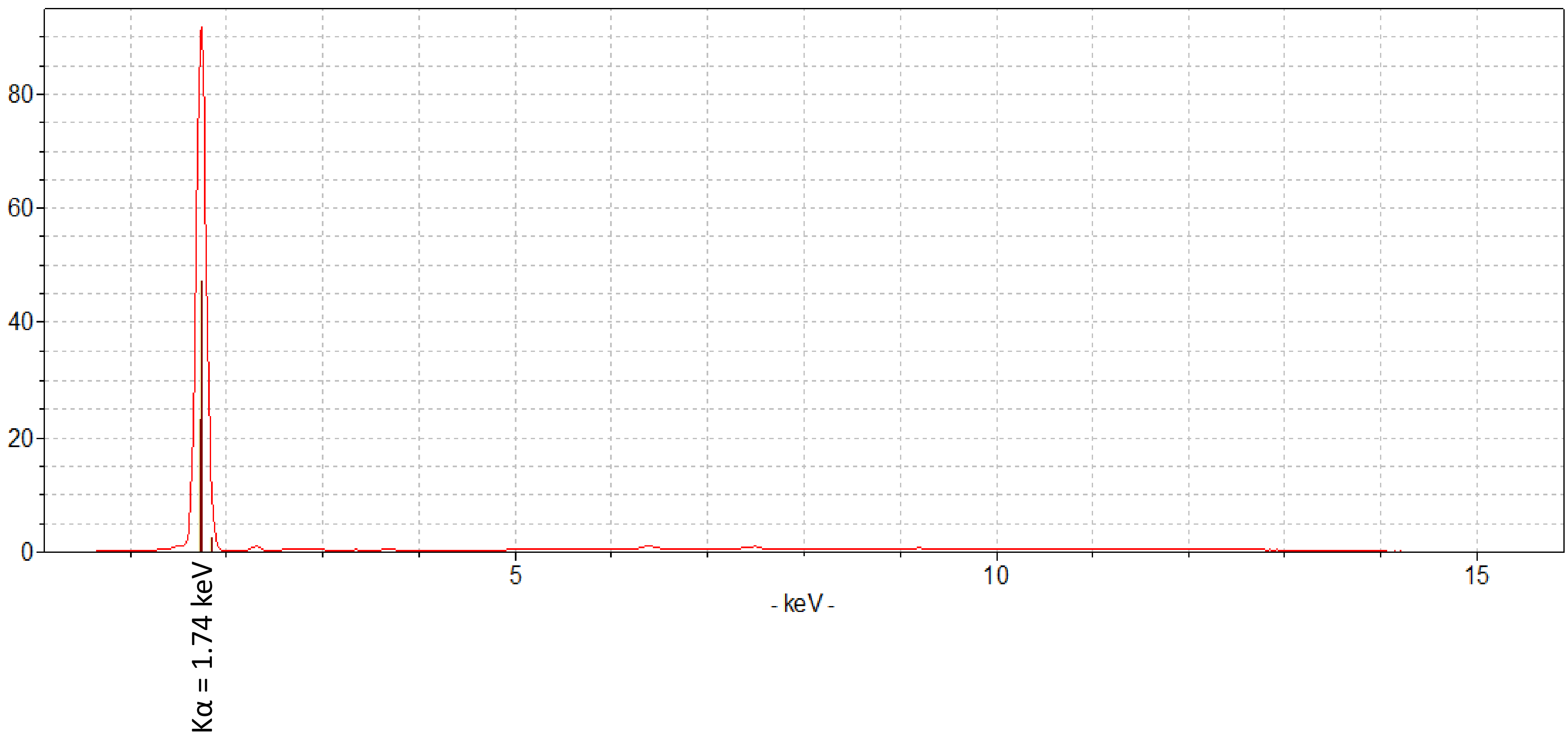



Powder C
100
80
60
40
20
0
Kβ
5
10
15
- keV -
Kα = 2.31 keV
Kα = 3.31 keV

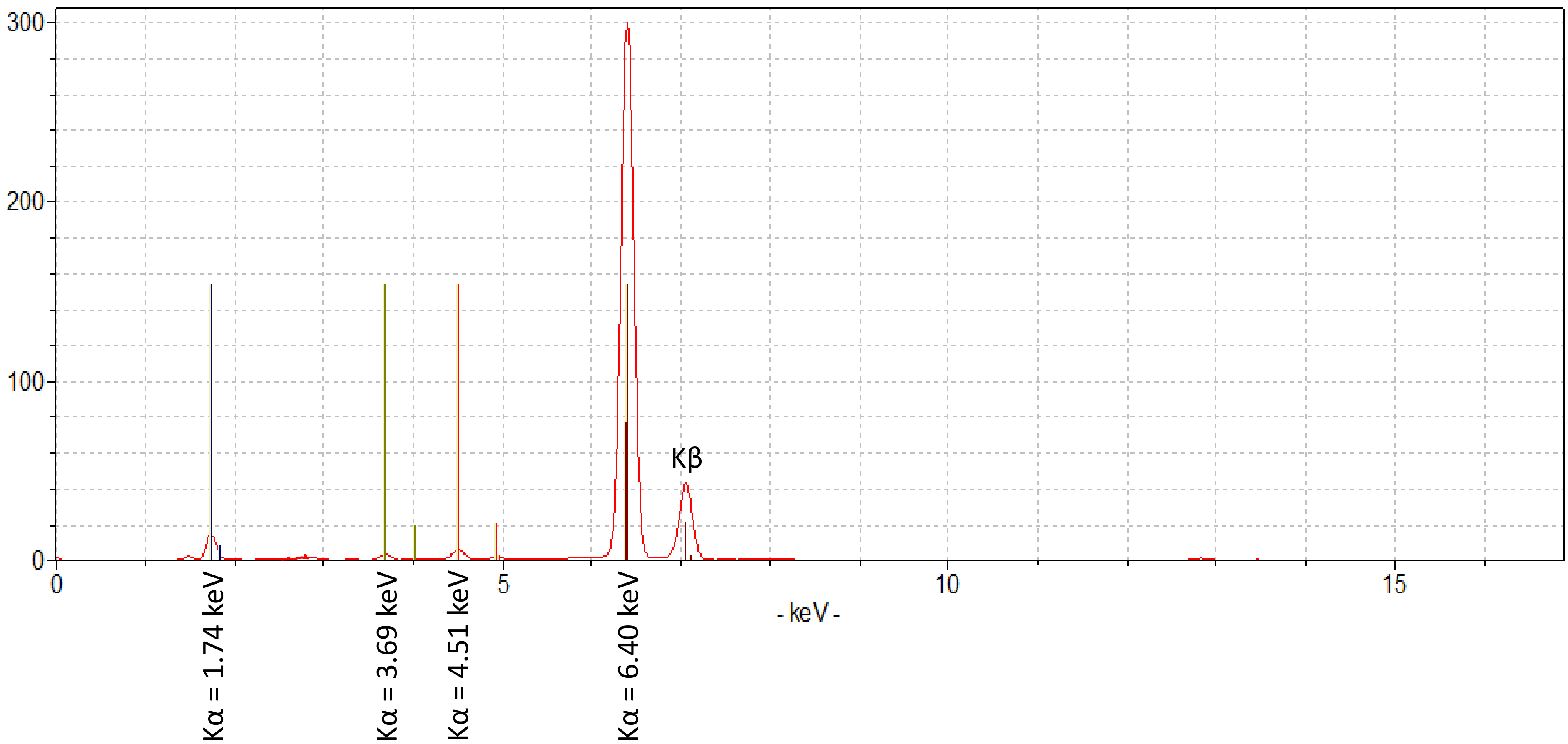
Powder D



Powder E



Powder F


300
200
100
0
Kβ
0
5
10
15
- keV -
Kα = 1.74 keV
Kα = 3.69 keV
Kα = 4.51 keV
Kα = 6.40 keV

www.bruker.com/hhxrf

1 **H** 1.01 0.0007 Hydrogen																	2 **He** 4.00 0.0002 Helium
3 **Li** 6.94 0.53 Lithium	4 **Be** 9.01 1.85 Beryllium Kα 0.108											5 **B** 10.81 2.34 Boron Kα 0.183	6 **C** 12.01 2.27 Carbon Kα 0.277	7 **N** 14.01 0.001 Nitrogen Kα 0.392	8 **O** 16.00 0.001 Oxygen Kα 0.525	9 **F** 19.00 0.001 Fluorine Kα 0.677	10 **Ne** 20.18 0.0009 Neon Kα 0.849
11 **Na** 22.99 0.97 Sodium Kα 1.040	12 **Mg** 24.31 1.74 Magnesium Kα 1.254											13 **Al** 26.98 2.70 Aluminium Kα 1.486	14 **Si** 28.09 2.33 Silicon Kα 1.740	15 **P** 30.97 1.82 Phosphorus Kα 2.010	16 **S** 32.07 2.07 Sulfur Kα 2.309	17 **Cl** 35.45 0.003 Chlorine Kα 2.622	18 **Ar** 39.95 0.002 Argon Kα 2.958
19 **K** 39.10 0.86 Potassium Kα 3.314	20 **Ca** 40.08 1.54 Calcium Kα 3.692 Lα 0.341	21 **Sc** 44.96 2.99 Scandium Kα 4.093 Lα 0.395	22 **Ti** 47.87 4.54 Titanium Kα 4.512 Lα 0.452	23 **V** 50.94 6.11 Vanadium Kα 4.953 Lα 0.510	24 **Cr** 52.00 7.15 Chromium Kα 5.415 Lα 0.572	25 **Mn** 54.94 7.44 Manganese Kα 5.900 Lα 0.637	26 **Fe** 55.85 7.87 Iron Kα 6.405 Lα 0.705	27 **Co** 58.93 8.86 Cobalt Kα 6.931 Lα 0.775	28 **Ni** 58.69 8.91 Nickel Kα 7.480 Lα 0.849	29 **Cu** 63.55 8.93 Copper Kα 8.046 Lα 0.928	30 **Zn** 65.38 7.13 Zinc Kα 8.637 Lα 1.012	31 **Ga** 69.72 5.91 Gallium Kα 9.251 Lα 1.098	32 **Ge** 72.64 5.32 Germanium Kα 9.886 Lα 1.188	33 **As** 74.92 5.78 Arsenic Kα 10.543 Lα 1.282	34 **Se** 78.96 4.81 Selenium Kα 11.224 Lα 1.379	35 **Br** 79.90 3.12 Bromine Kα 11.924 Lα 1.481	36 **Kr** 83.80 0.004 Krypton Kα 12.648 Lα 1.585
37 **Rb** 85.47 1.53 Rubidium Kα 13.396 Lα 1.692	38 **Sr** 87.62 2.64 Strontium Kα 14.165 Lα 1.806	39 **Y** 88.91 4.47 Yttrium Kα 14.958 Lα 1.924	40 **Zr** 91.22 6.51 Zirconium Kα 15.775 Lα 2.044	41 **Nb** 92.91 8.57 Niobium Kα 16.615 Lα 2.169	42 **Mo** 95.94 10.22 Molybdenum Kα 17.480 Lα 2.292	43 **Tc** (98) 11.50 Technetium Kα 18.367 Lα 2.423	44 **Ru** 101.07 12.37 Ruthenium Kα 19.279 Lα 2.558	45 **Rh** 102.91 12.41 Rhodium Kα 20.216 Lα 2.697	46 **Pd** 106.42 12.02 Palladium Kα 21.177 Lα 2.838	47 **Ag** 107.87 10.50 Silver Kα 22.163 Lα 2.983	48 **Cd** 112.41 8.69 Cadmium Kα 23.173 Lα 3.133	49 **In** 114.82 7.31 Indium Kα 24.210 Lα 3.286	50 **Sn** 118.71 7.29 Tin Kα 25.271 Lα 3.444	51 **Sb** 121.76 6.69 Antimony Kα 26.359 Lα 3.604	52 **Te** 127.60 6.23 Tellurium Kα 27.473 Lα 3.768	53 **I** 126.90 4.93 Iodine Kα 28.612 Lα 3.938	54 **Xe** 131.29 0.006 Xenon Kα 29.775 Lα 4.110
55 **Cs** 132.91 1.87 Cesium Kα 30.973 Lα 4.285	56 **Ba** 137.33 3.59 Barium Kα 32.194 Lα 4.466	57 **La** 138.91 6.15 Lanthanum Kα 33.442 Lα 4.647	72 **Hf** 178.49 13.31 Hafnium Lα 7.899 Mα 1.646	73 **Ta** 180.95 16.65 Tantalum Lα 8.146 Mα 1.712	74 **W** 183.84 19.25 Tungsten Lα 8.398 Mα 1.775	75 **Re** 186.21 21.02 Rhenium Lα 8.652 Mα 1.843	76 **Os** 190.23 22.61 Osmium Lα 8.911 Mα 1.907	77 **Ir** 192.22 22.65 Iridium Lα 9.175 Mα 1.980	78 **Pt** 195.08 21.46 Platinum Lα 9.442 Mα 2.050	79 **Au** 196.97 19.28 Gold Lα 9.713 Mα 2.123	80 **Hg** 200.59 13.53 Mercury Lα 9.989 Mα 2.195	81 **Tl** 204.37 11.85 Thallium Lα 10.269 Mα 2.271	82 **Pb** 207.20 11.34 Lead Lα 10.551 Mα 2.342	83 **Bi** 208.98 9.81 Bismuth Lα 10.839 Mα 2.423	84 **Po** (209) 9.32 Polonium Lα 11.131 Mα 2.499	85 **At** (210) 7.00 Astatine Lα 11.427 Mα 2.577	86 **Rn** (222) 0.01 Radon Lα 11.727 Mα 2.654
87 **Fr** (223) 1.87 Francium Lα 12.031 Mα 2.732	88 **Ra** (226) 5.50 Radium Lα 12.339 Mα 2.806	89 **Ac** (227) 10.07 Actinium Lα 12.652 Mα 2.900															

The Chemistry of Fossils – a Guide to the Fossilization Process

What is a fossil?

Fossils are:

- The remains of ancient organisms
  - Bones, teeth (hard parts)
  - Tissues, hair, feathers (soft parts)
- The traces of ancient organisms
  - Footprints, nests, etc. – preserve behavior but not the actual organism
- At least 10,000 years old – younger materials are studied by Archaeologists, while Paleontologists study fossils

How do fossils form?

Paleontologists have defined several fossilization processes:

1. **Recrystallization** – the original shell material is still present, but the bio-minerals have been altered by pressure and heat in the burial environment – crystals generally become larger filling the original porosity in the shell.
2. Replacement – the original shell material is slowly dissolved away to be replaced by new minerals precipitated from the groundwater passing through the fossil.
    a. **Permineralization** – very slow replacement – preserves incredibly fine details – down to the cellular level
    b. **Petrifaction** – more rapid process – preserves coarse features of the organism
3. Molds and Casts – a **mold** forms when a shell leaves an imprint in sediment, before being leached away. Sometime later, the void left behind can fill with other sediment to form a replica of the shell – called the **cast**.
4. Carbonization – very common process for plants and other soft-bodied organisms. As the plant is buried to deeper depths, the pressures cook off volatile compounds – converting the plant to pure carbon (graphite). These fossils are called **carbon films**, because the compression flattens the organism into a sheet.

The Chemistry of Fossils – a Guide to the Fossilization Process

Activity 1 – Fossil vs. Not a Fossil

Materials Needed:

You may want several sets so that you can break your classroom into multiple groups.

Several fossils – corals, brachiopods, trilobites, etc.

A piece of petrified wood

Modern shells – snails, coral fragments, etc.

A feather

A marble

A stone – a piece of granite or marble would work (use a rock type that is not fossiliferous!)

A bag to hold the samples

Activity – have each group take a set of samples. Using the criteria of what a fossil is, have the children sort the samples into fossils vs. not fossils. After they have sorted the objects, check their identifications – and for mislabeled objects try to stress the criteria.

For a more advanced group, see if they can also determine the style of preservation for the fossils.

Activity 2 – Molds and Casts

Materials Needed:

> Some random modern shells – a good mix of ornamentation is recommended
>
> Play-dough
>
> Optional – also provide a display fossil that is an actual mold (note this should be kept well away from play-dough – as younger kids will attempt to make molds of real fossils in the play-dough)

Activity – this activity is geared towards younger students, but is worth doing at all levels. The play-dough simulates muddy sediment on a lake bottom. Have the students gently press the shells into the play-dough, then remove the shells. An imprint will be left behind, which is the mold.

Activity 3 – Chemistry of Fossils

Materials Needed:

Photoset of fossils with different styles of preservation (in digital materials) or alternatively your own fossils that match the styles of preservation

The chemical data (in digital materials)

Background information:

Biominerals – minerals secreted by organisms as part of their hard parts (bones, shells, teeth, etc.)

Only a few common biominerals:

$CaCO_3$ – calcite or aragonite - Most marine organisms (snails, clams, corals) – sometimes with a matrix of organic matter (crustaceans, trilobites)

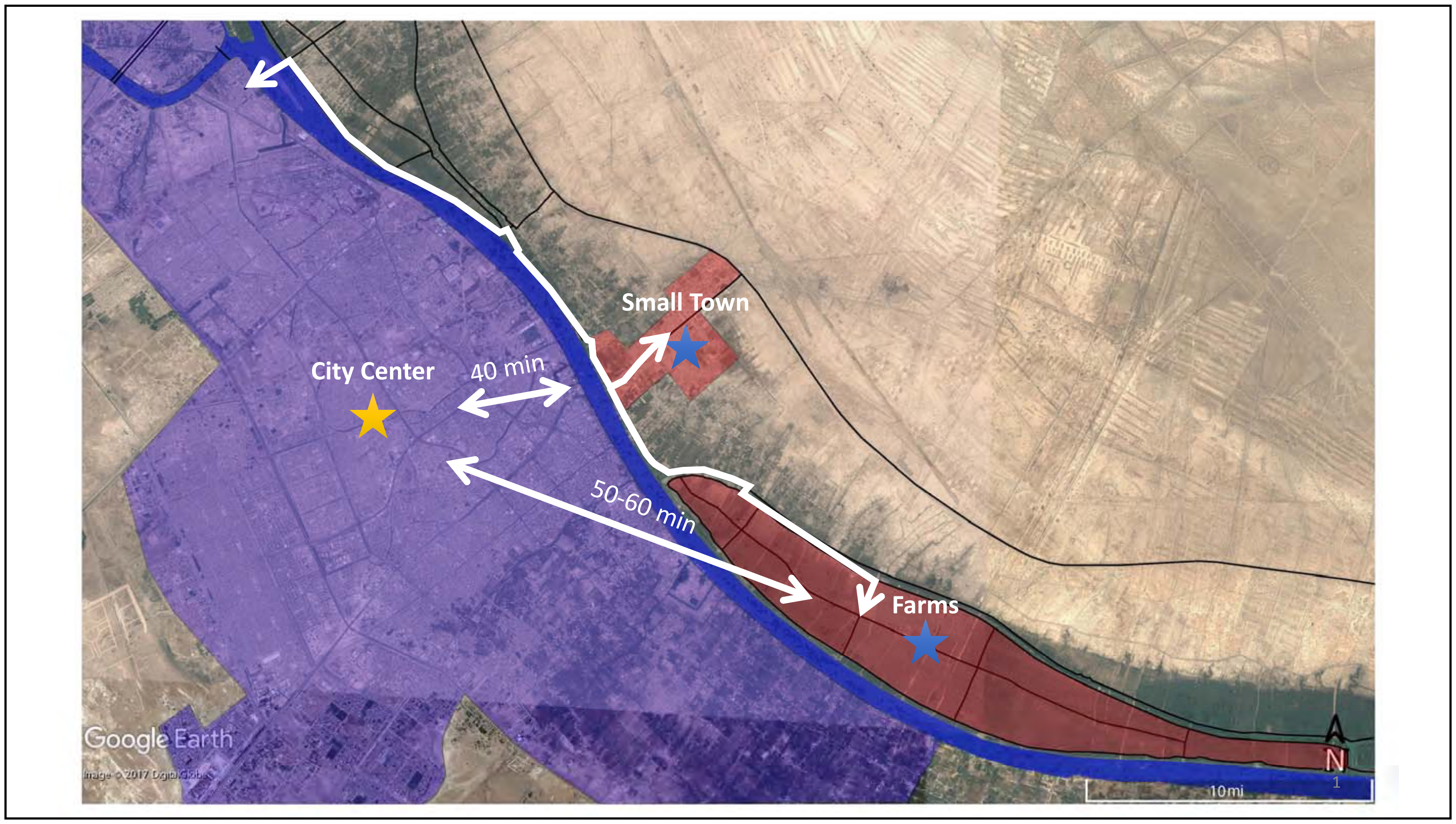
SiO_2 – silica – some sponges, and some plankton (diatoms, radiolarians)

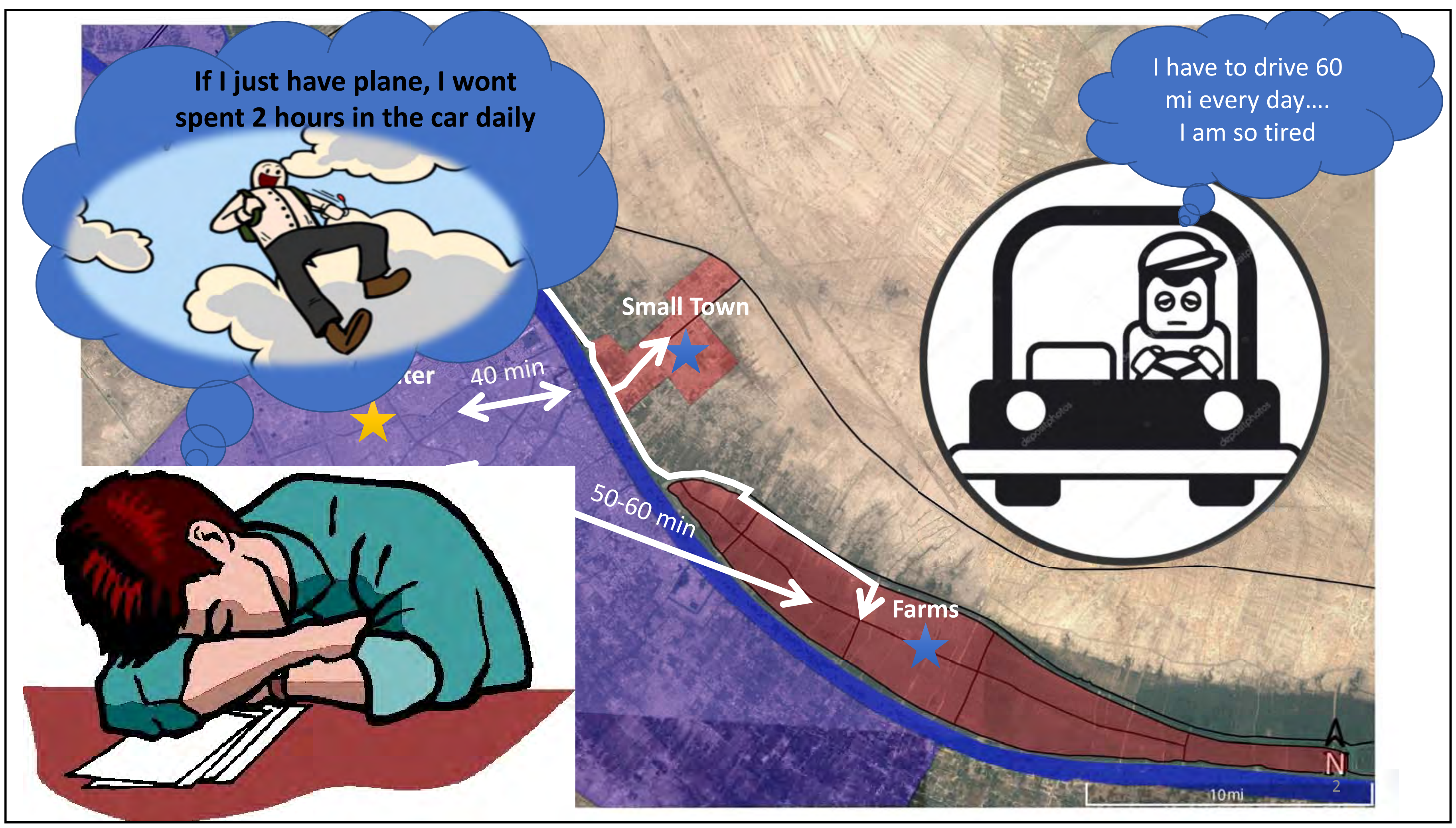
$Ca_5(PO_4)_3(F,Cl,OH)$ – apatite – vertebrates secrete bone and teeth – in marine realm: fish and marine mammals (whales)

Activity – the four fossils analyzed include a fossil horse tooth, two brachiopods with varying degree of replacement with Pyrite (FeS_2), and a piece of petrified wood. Have the students examine the pictures of the fossils and the corresponding XRF data. Then have them answer the following questions:

1. Brachipods have shells made of calcite ($CaCO_3$), what elements are present in the spectrum for each brachiopod? What styles of preservation do the brachiopods exhibit?
2. What is wood made of? Based on the spectrum, what elements is the petrified wood made of now? What style of preservation does the wood exhibit?
3. What kind of biomineral should the teeth of a mammal like a horse exhibit? Does the spectrum reflect the chemistry of the original biomineral, or has the tooth been replaced (fully or partially) with some new mineral?

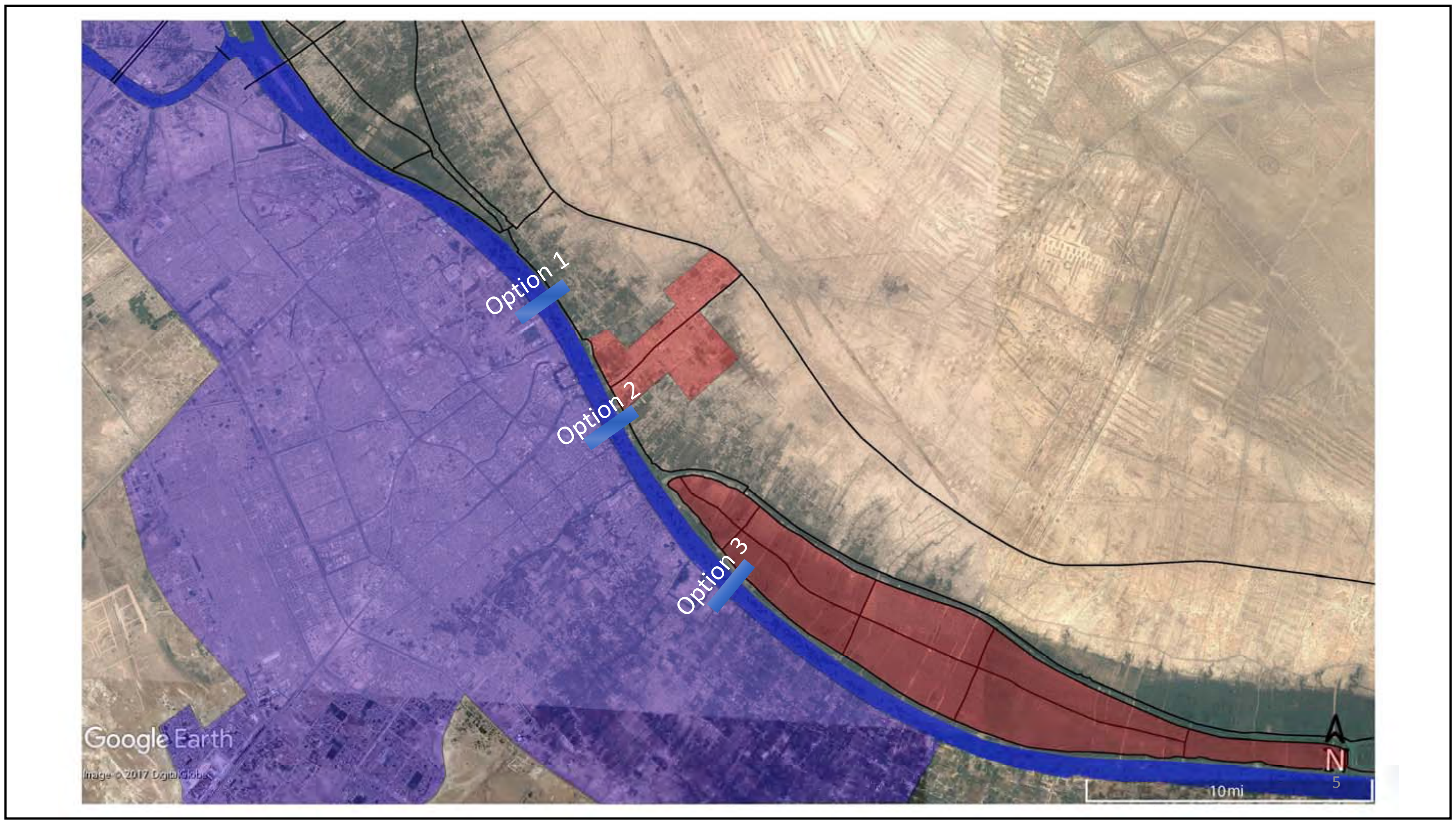
Bridge to Nowhere


Small Town
City Center
40 min
50-60 min
Farms
Google Earth
N
10mi
1

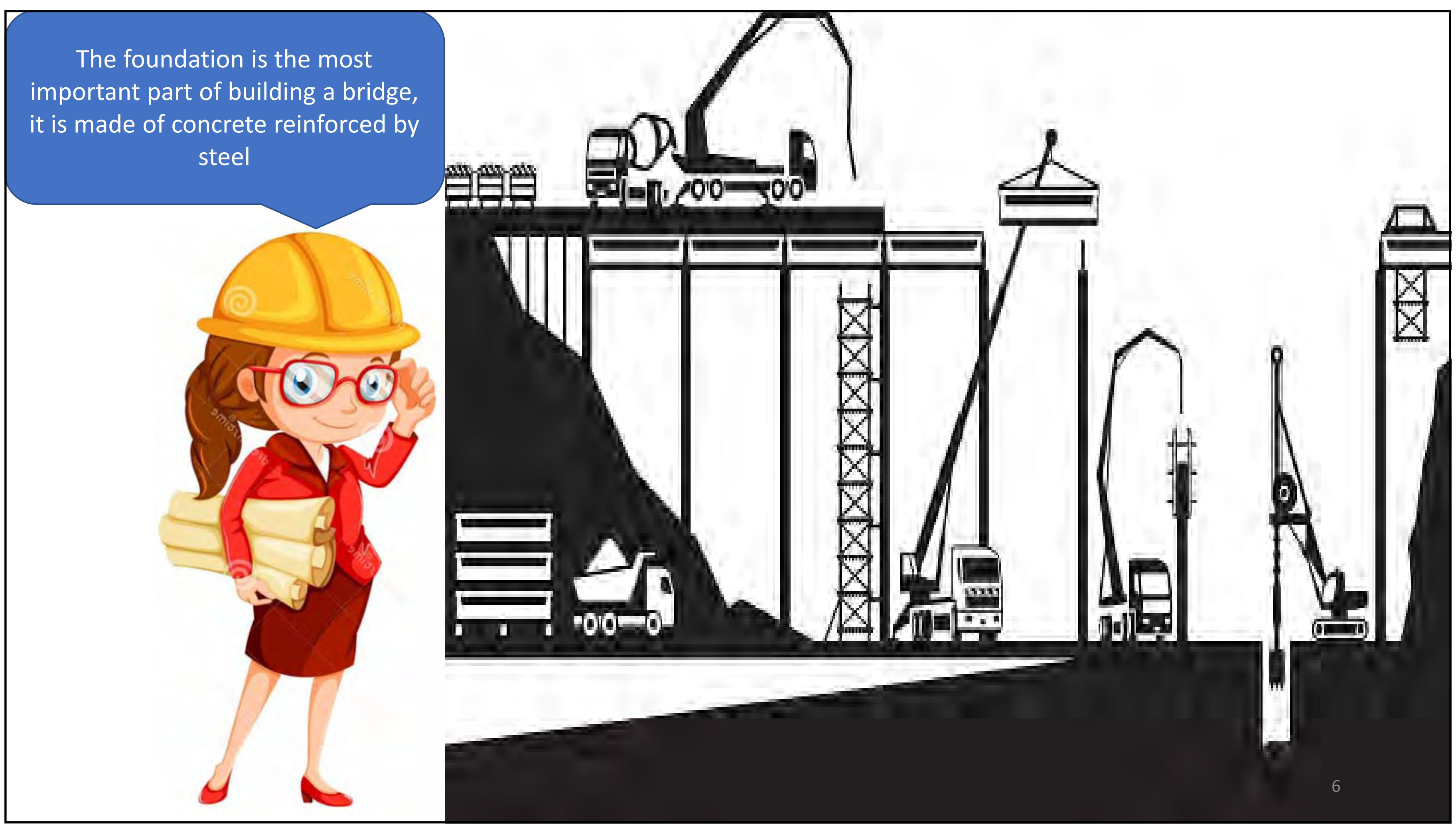

If I just have plane, I wont spent 2 hours in the car daily
I have to drive 60 mi every day…. I am so tired
Small Town
40 min
50-60 min
Farms
N
10mi
2


Bridge
Bridge
Google Earth
10mi
N


City agreed to build new bridge in to connect the town to City
I have three different location where we can build the new Bridge… What do you think the best location is? Why?
N



Option 1
Option 2
Option 3
Google Earth
N
10mi
5



The foundation is the most important part of building a bridge, it is made of concrete reinforced by steel
6

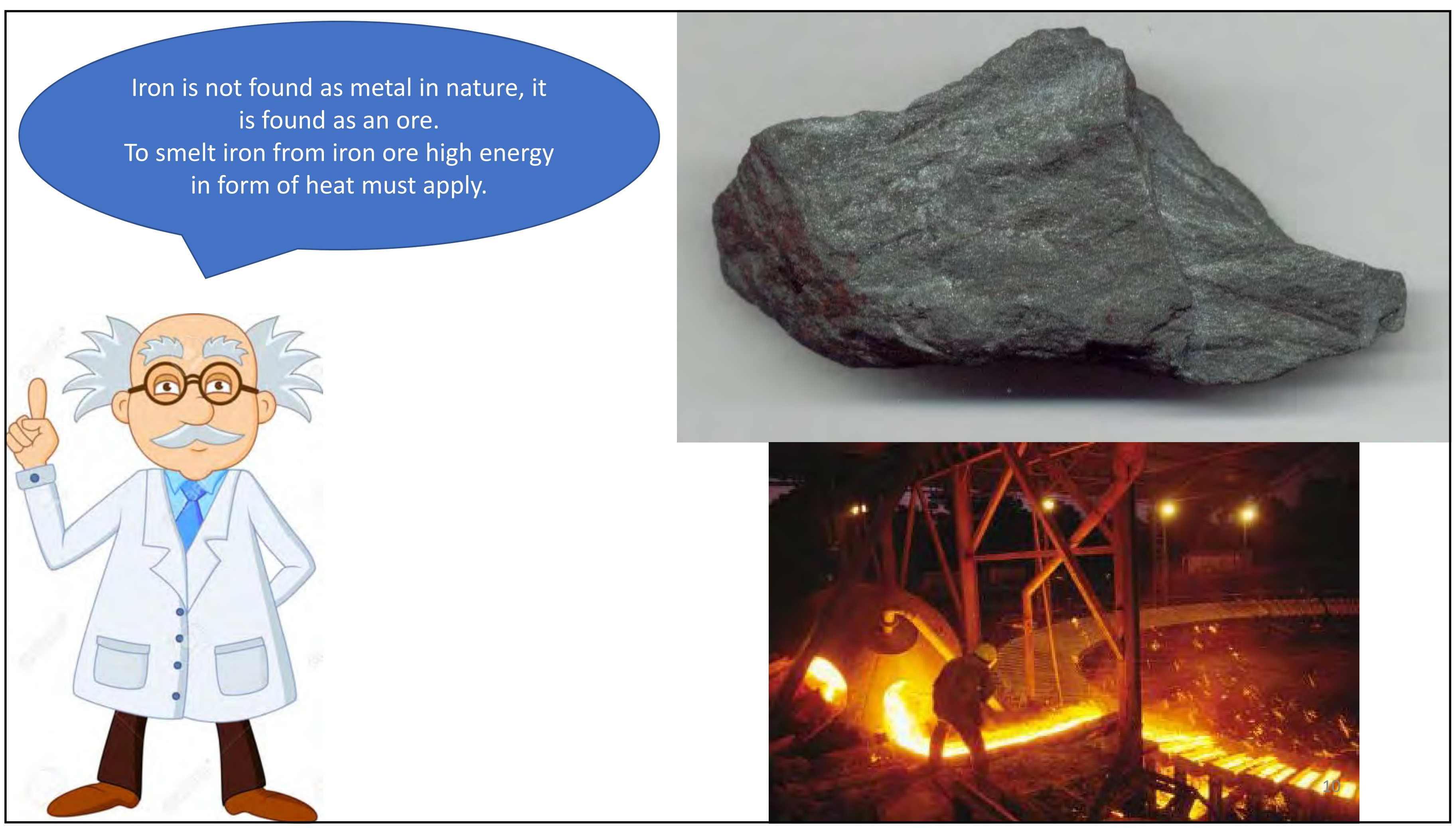
These are some examples…

7

These are some examples…

8

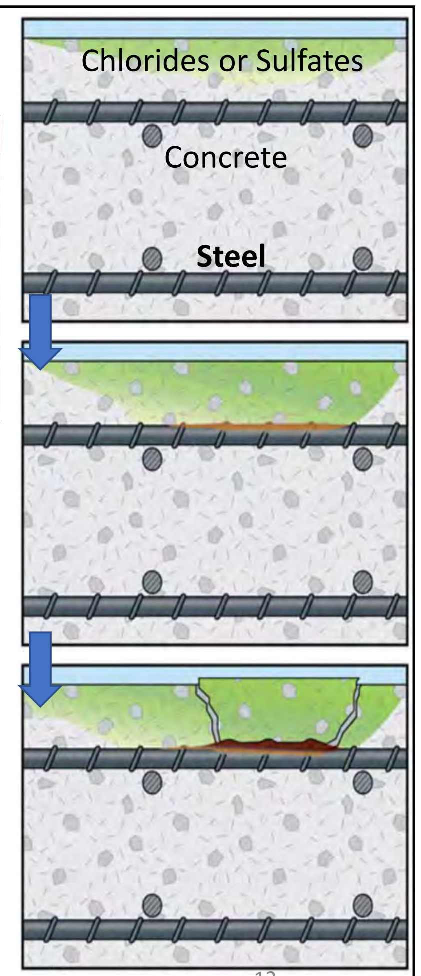

These are some examples…
9


Iron is not found as metal in nature, it is found as an ore.
To smelt iron from iron ore high energy in form of heat must apply.

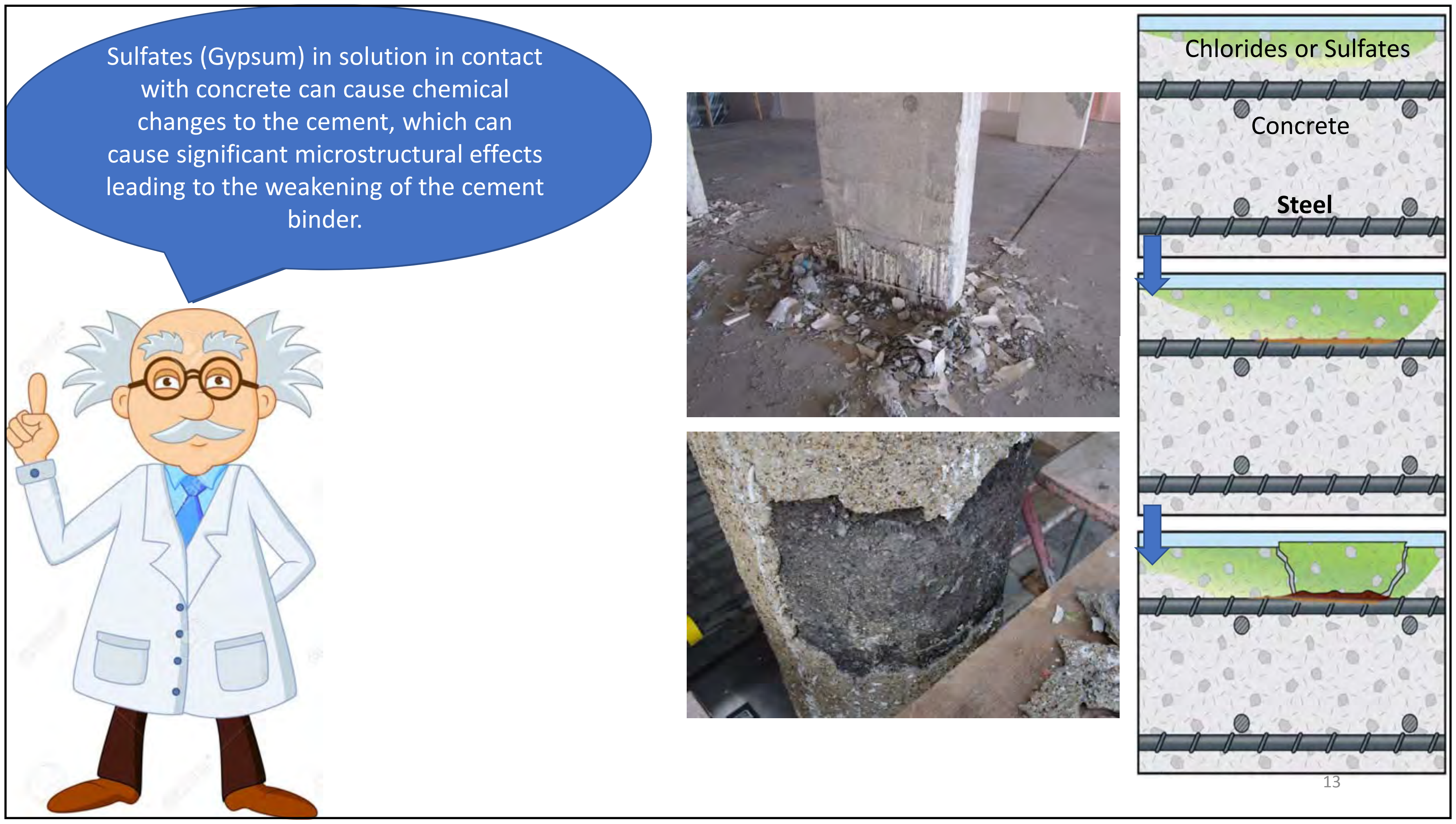
Iron always wants to go back to old form (as in Ore), and this is why it rusts.

11

Chlorides (CaCl & NaCl (halite)) have been shown to leach calcium hydroxide and cause chemical change in Portland cement. Leading to loss strength as well as attacking the steel reinforcement present in most concrete

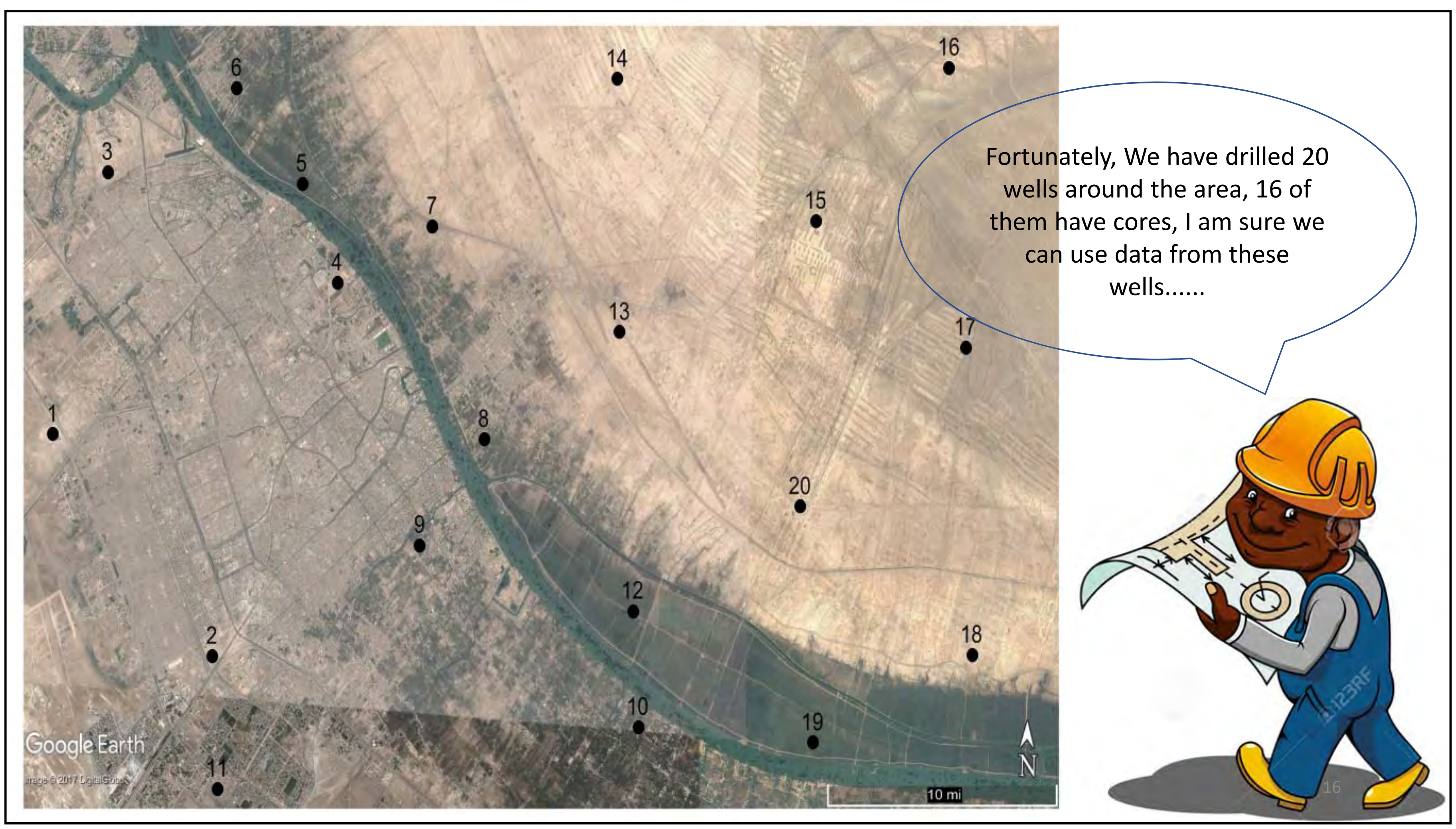


12


Sulfates (Gypsum) in solution in contact with concrete can cause chemical changes to the cement, which can cause significant microstructural effects leading to the weakening of the cement binder.
Chlorides or Sulfates
Concrete
Steel
13


Carbone steel are passive to corrosion in alkaline environment and behave like stainless steel.
Chlorides or Sulfates
Concrete
Steel
14


So... a Good location will have low concentration of Chlorides and Sulfates also low PH value (alkaline environment).
Chlorides or Sulfates
Concrete
Steel
15


Fortunately, We have drilled 20 wells around the area, 16 of them have cores, I am sure we can use data from these wells......
1
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Google Earth
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16

That is great, We can run the Hand held XRF on cores to identify elements concentration in the area to decide the best location to build the bridge

304SS

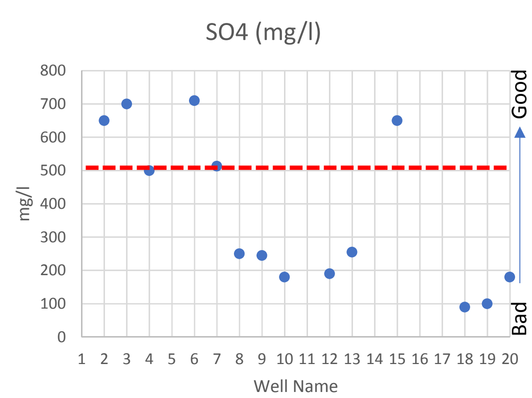
42 Match 9.6 01-04 22:38
Time 2.0

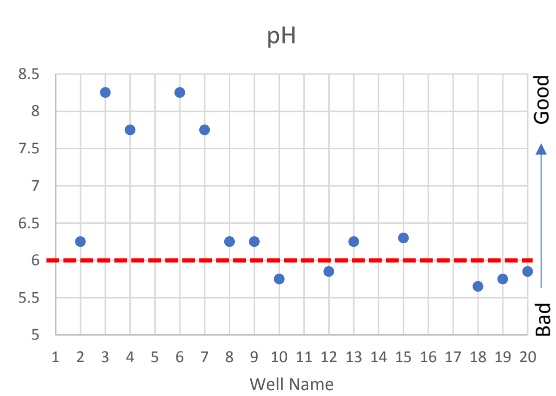
El	Min	%	Max	+/-
Fe	66.35	71.80	74.00	0.37
Cr	18.00	18.05	20.00	0.16
Ni	8.00	8.36	10.50	0.16
Mn	0.00	1.22	2.00	0.09
Cu	0.00	0.17	0.50	0.03
Mo	0.00	0.13	0.50	0.01
Co		0.28		0.03

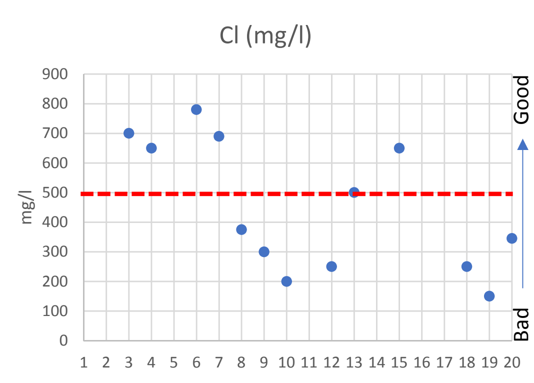
Elemental data

17

These are some information you should use in order to pick the right location to build the new bridge







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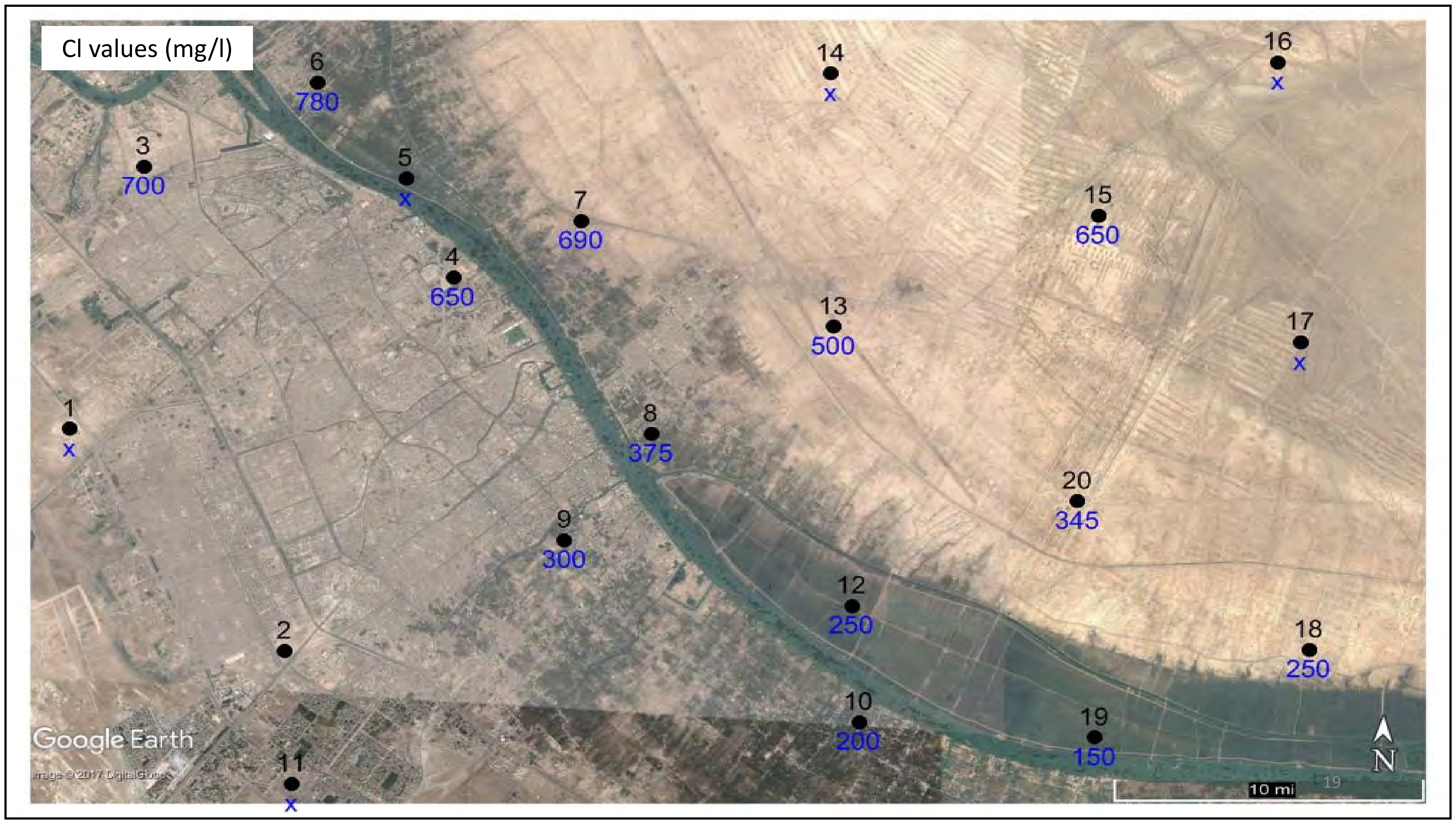
Cl values (mg/l)
6
780
3
700
5
x
7
690
4
650
14
x
16
x
15
650
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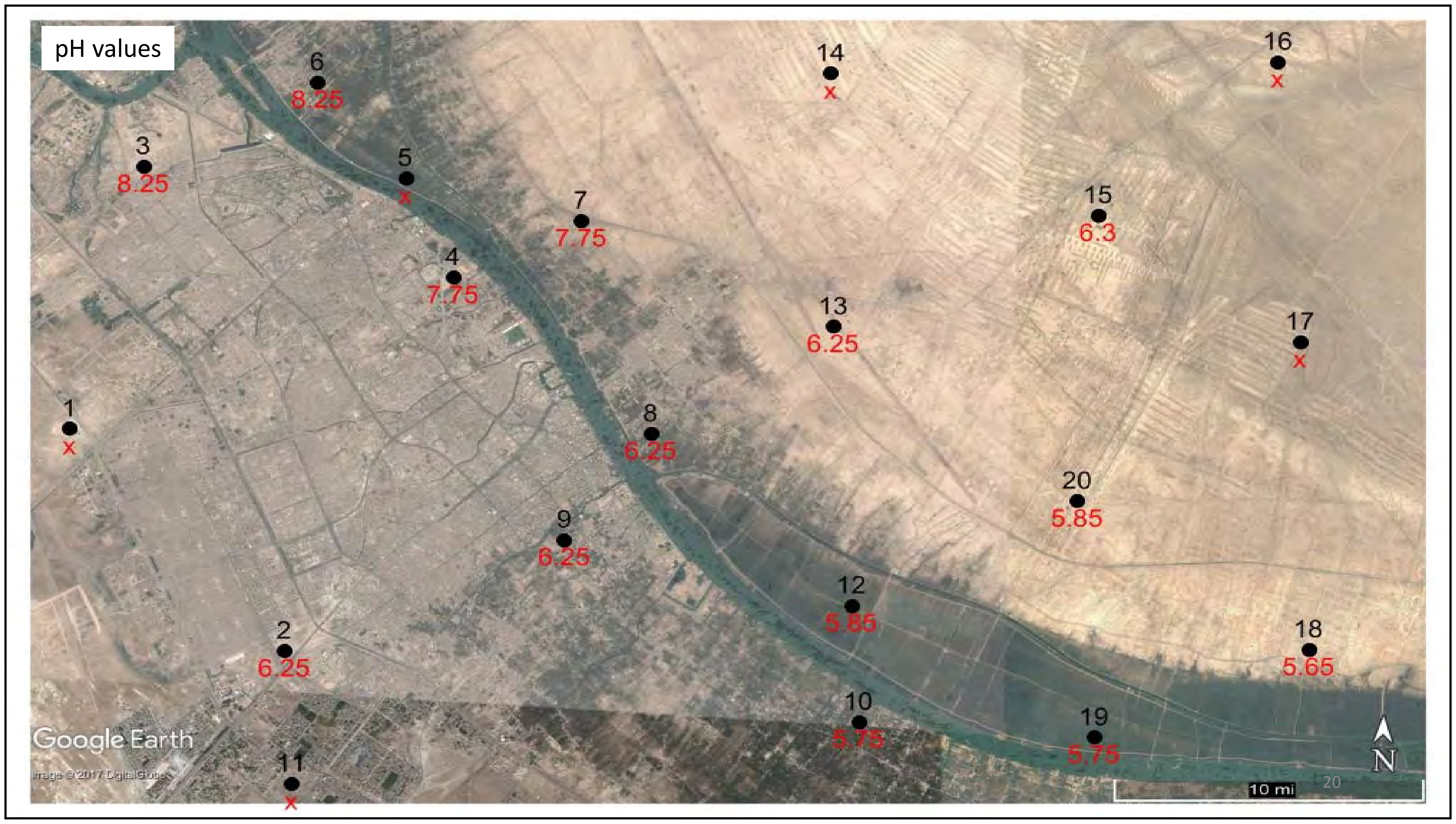
500
17
x
1
x
8
375
20
345
9
300
12
250
2
18
250
10
200
19
150
11
x
Google Earth
10 mi
N


pH values
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3
8.25
5
x
7
7.75
4
7.75
14
x
16
x
15
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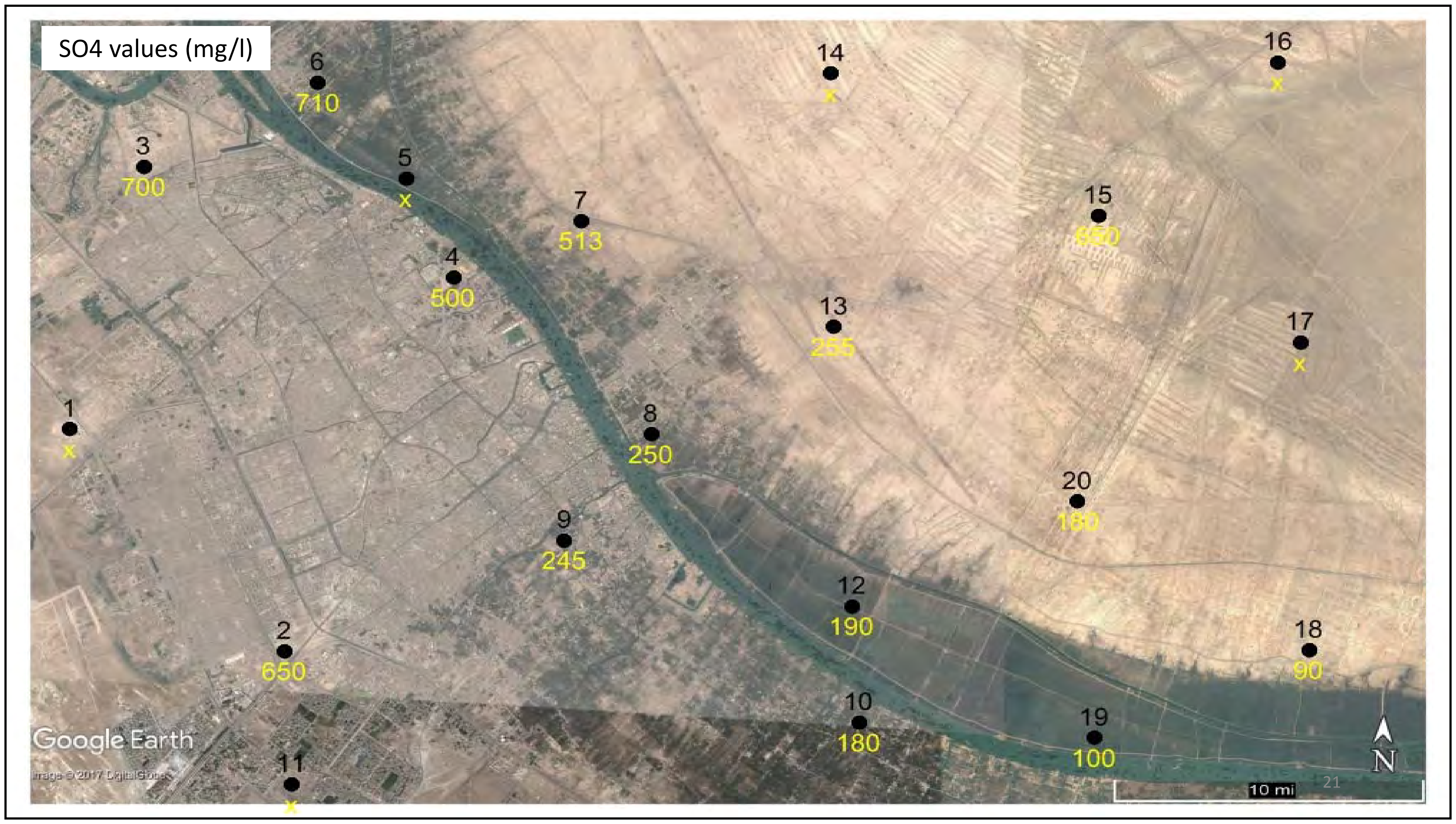
6.25
17
x
1
x
8
6.25
20
5.85
9
6.25
12
5.65
2
6.25
18
5.65
10
5.75
19
5.75
11
x
Google Earth
10 mi
N


SO4 values (mg/l)
1
x
2
650
3
700
4
500
5
x
6
710
7
513
8
250
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10
180
11
x
12
190
13
255
14
x
15
650
16
x
17
x
18
90
19
100
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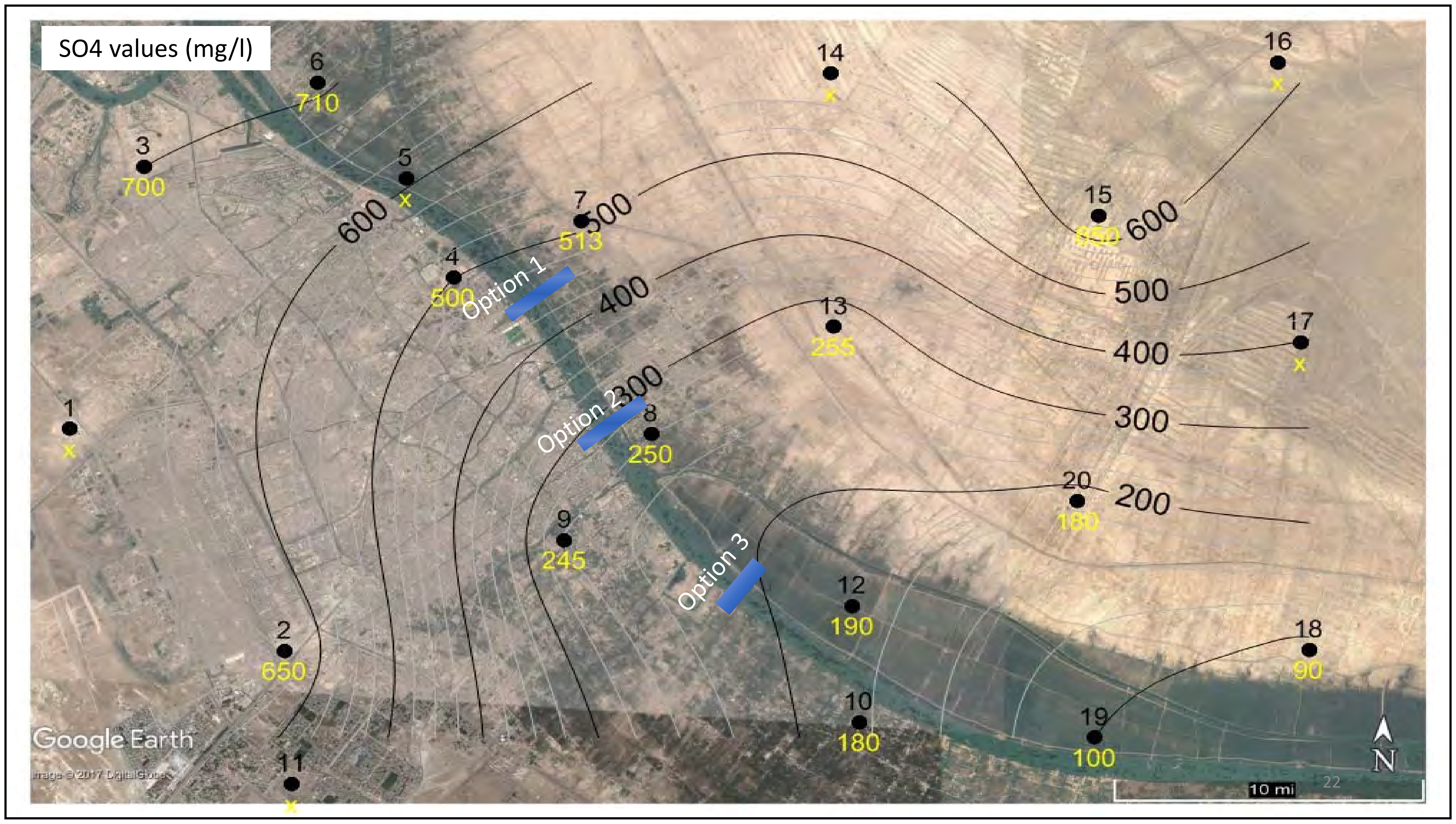
180
Google Earth
N
10 mi


SO4 values (mg/l)
1
x
2
650
3
700
4
500
5
x
6
710
7
513
8
250
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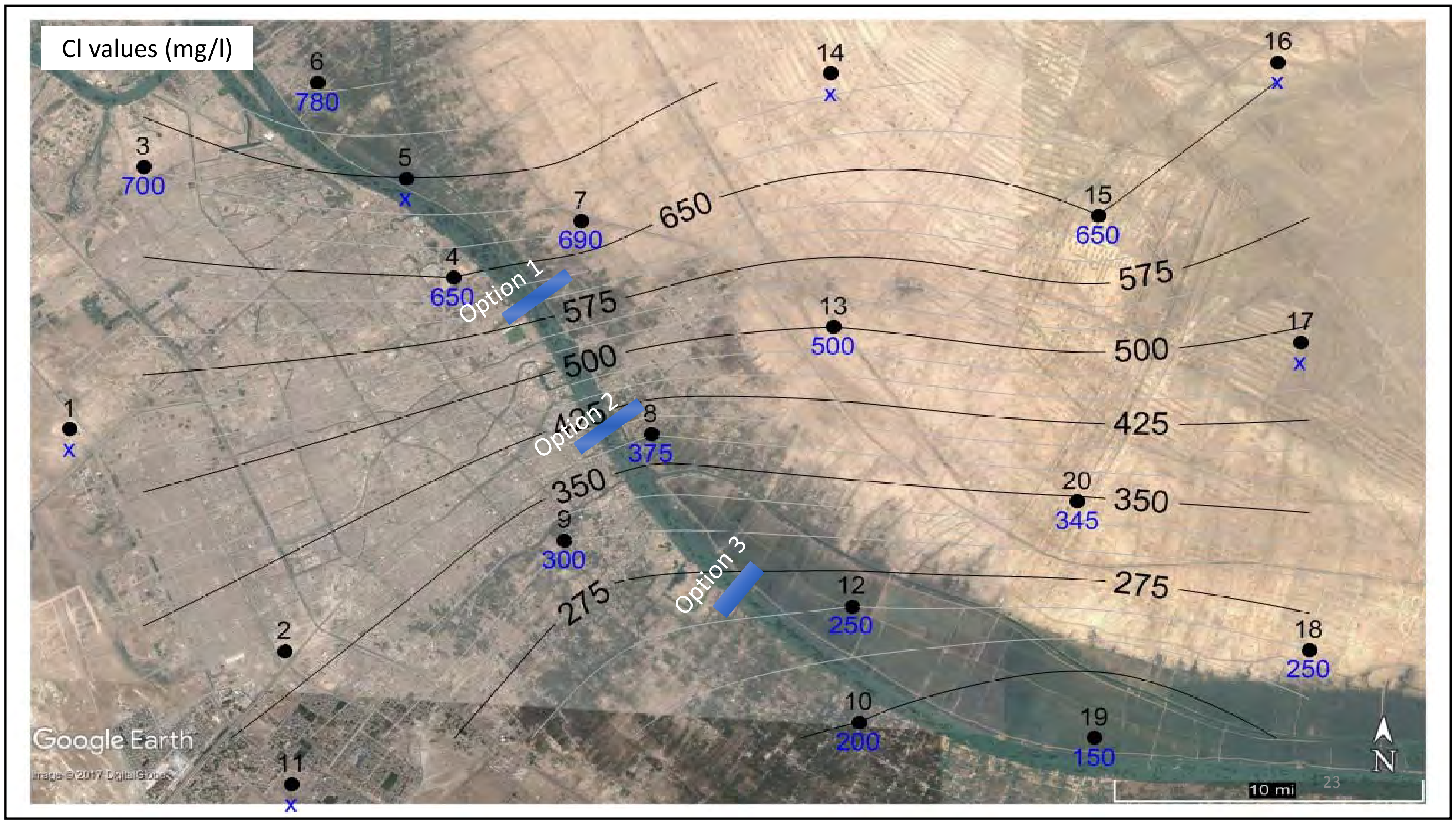
10
180
11
x
12
190
13
255
14
x
15
650
16
x
17
x
18
90
19
100
20
180
600
500
400
300
200
Option 1
Option 2
Option 3
Google Earth
N
10 mi


Cl values (mg/l)
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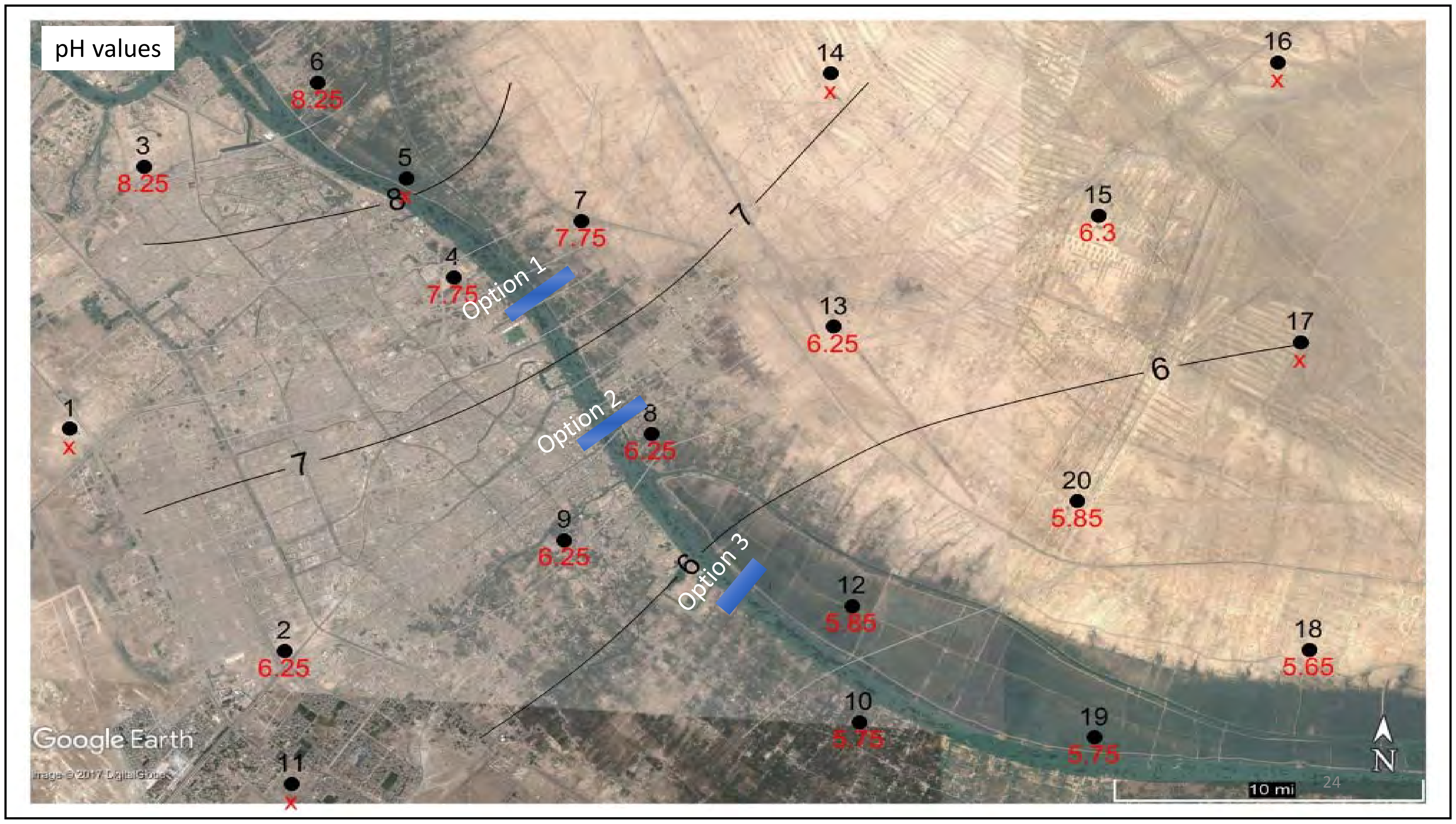
780
14
x
16
x
3
700
5
x
7
690
650
15
650
4
650
Option 1
575
575
13
500
17
x
500
500
1
x
Option 2
425
8
375
425
20
345
350
350
9
300
Option 3
275
12
250
275
18
250
2
10
200
19
150
11
x
Google Earth
10 mi
N


pH values
6
8.25
14
x
16
x
3
8.25
5
8
7
7.75
7
15
6.3
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7.75
Option 1
13
6.25
17
x
6
1
x
7
Option 2
8
6.25
20
5.85
9
6.25
6
Option 3
12
5.65
18
5.65
2
6.25
10
5.75
19
5.75
11
x
Google Earth
10 mi
N

Pet Rock

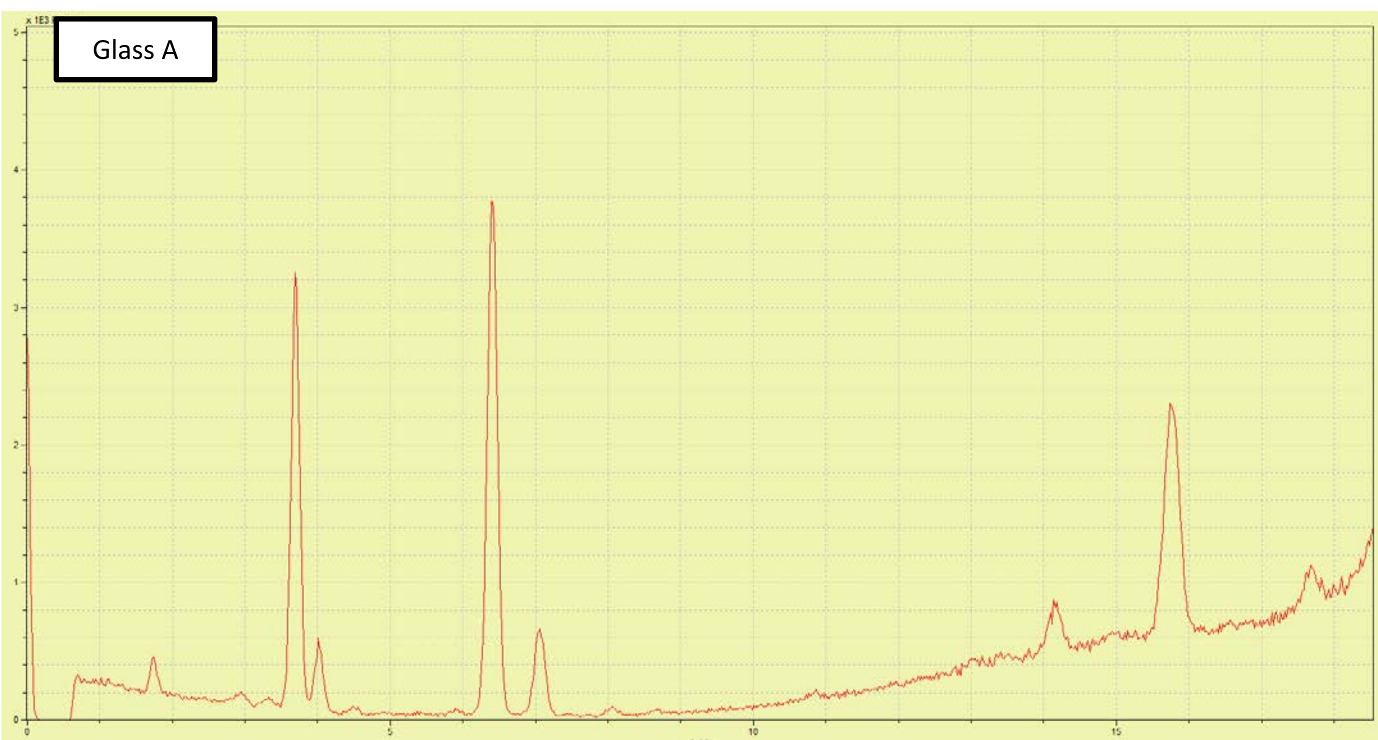
You were invited to bring your favorite rock along to the workshop. If you did, great! Use the ED-XRF to analyze its major elemental composition. Is your rock compositionally homogeneous? Can you tell what type of rock it is based on its elemental composition? What is unique about its elemental composition? If you forgot to bring your pet rock, feel free to ask Kat to analyze something else that you brought along. Most things are fair game!

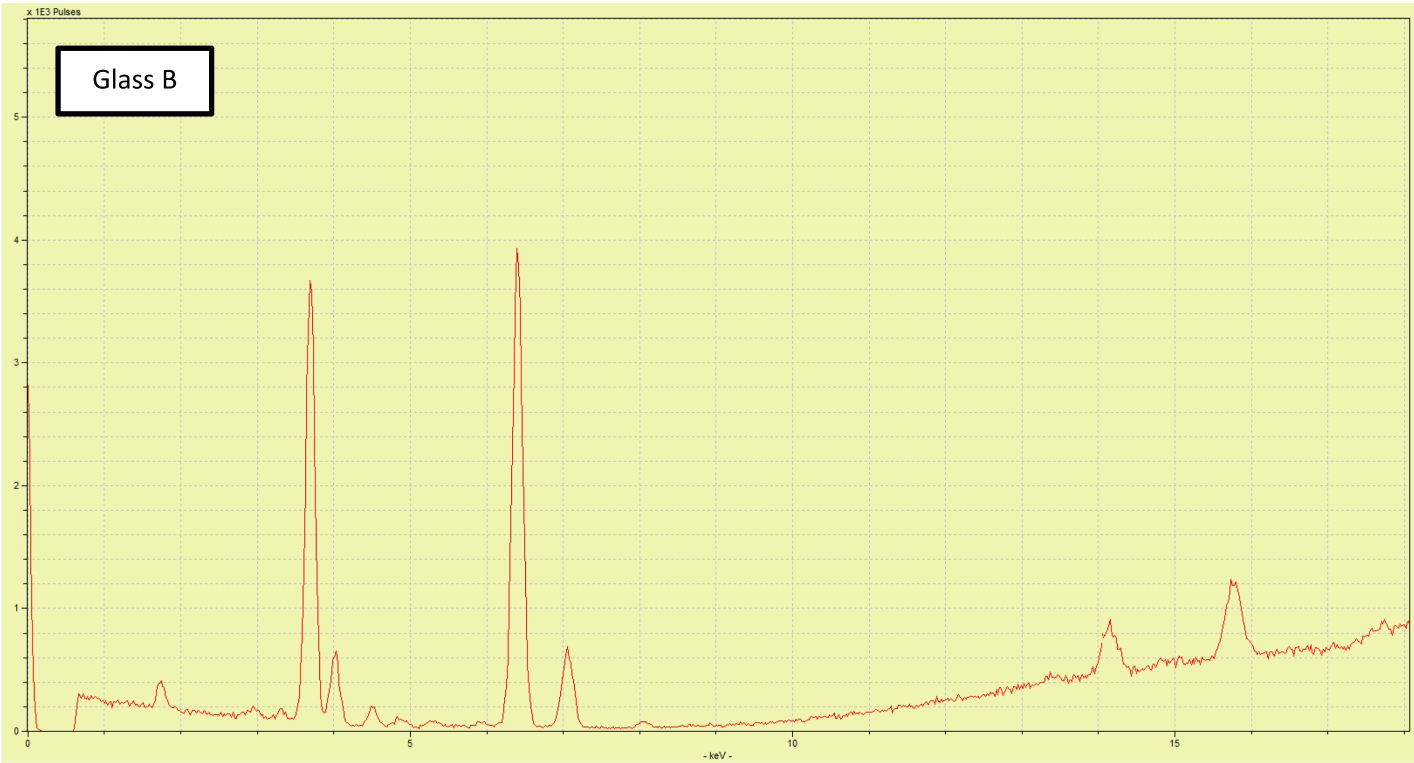
Forensic X-ray Fluorescence: Hit-and-Run

Forensic scientists collect and analyze evidence at crime scenes to determine link between people and places. Essentially, they help to answer the question of who was there and what happened. Often the types of evidence that forensic scientists work with cannot be seen with the unaided eye and require tools such as “black lights” and X-ray Fluorescence (XRF). One way XRF is used in forensics is to identify various trace elements found in glass. Since glass is derived from sand and sandstone, it contains the unique trace elements from the source sand. Forensic scientists use the glass’s trace element “fingerprint” to identify where the car was manufactured and if it has any link to a crime scene.

Image that you’re a forensic scientist whose task it is to determine what happened in a hit-and-run car accident. At the crime scene, microscopic glass fragments from the car’s windshield are found on the victim’s body (Glass A). The police locate an abandon car with serious damage that fits a witness’s description. The owner of the vehicle (i.e. suspect #1) claims his vehicle was stolen earlier that night and he wasn’t involved with the accident. After obtaining a search warrant, your team searches the suspect’s home and collects a small glass fragment embedded in the suspect’s jacket (Glass B).

Both glass samples have been analyzed with the handheld XRF to determine their trace element compositions. Here are the resulting spectra:

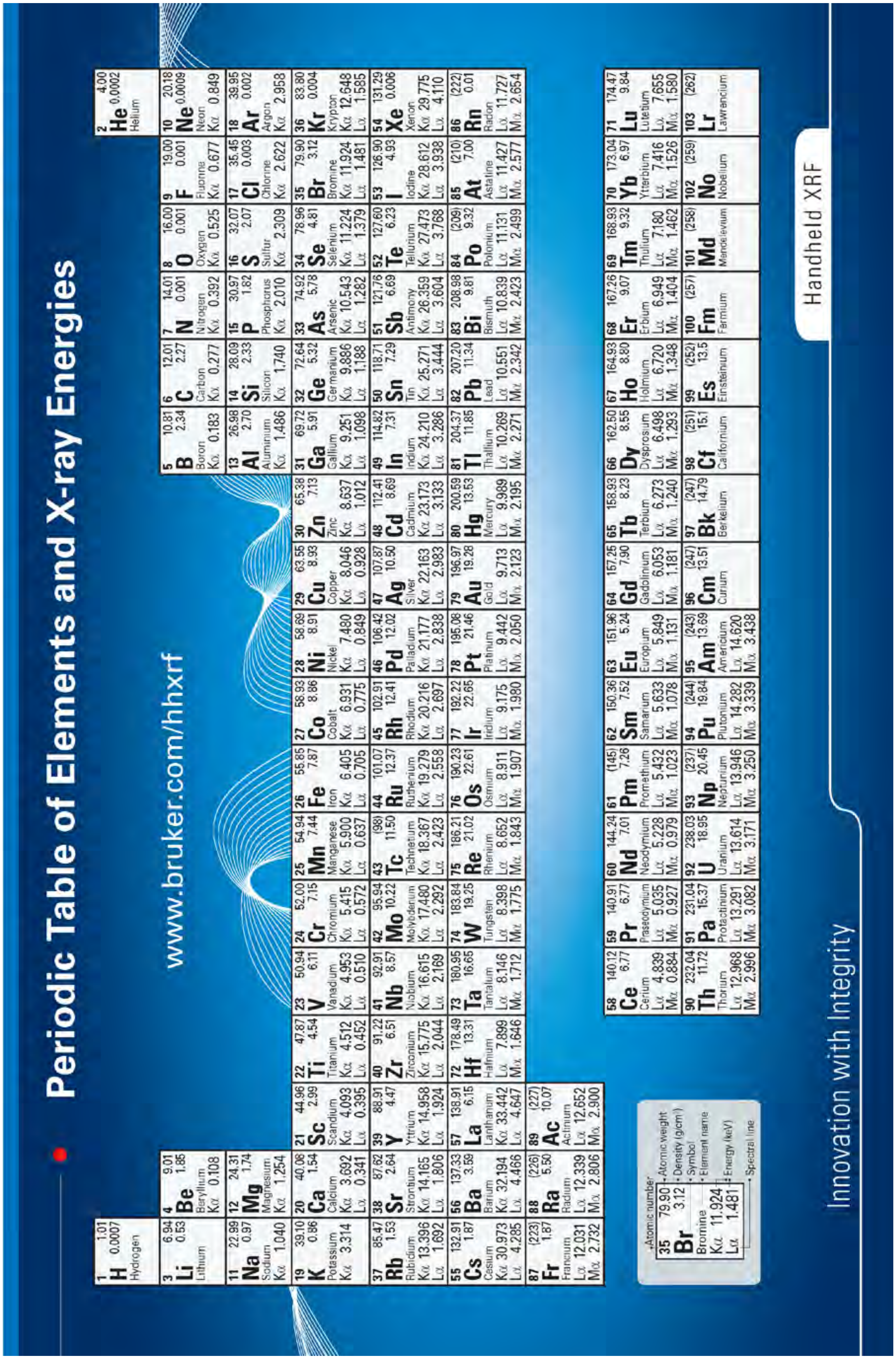




1) Using the periodic table with the various X-ray energies shown (page 3) and the elemental components of glass provided, identify all the elements in the two glass samples (Label each peak with its respective element).

2) What elements do the glass samples have in common? What elements are unique? Do these samples have the same origin?

3) Is there enough evidence to say the suspect was or wasn't involved in the crime?



Periodic Table of Elements and X-ray Energies
www.bruker.com/hhxrf
Handheld XRF
Innovation with Integrity

Alien Aqua

As a mission commander in the Galactic Federation, you and your team have been sent to an abandoned mining planet to investigate sources of raw materials. After beaming down, you suddenly lose communication with your ship and realize you have very limited supplies. You and your crew have easily identified a location to establish a temporary shelter, but there is only enough drinking water to last one day. You don't know how long you'll be stranded, so you must find an adequate water source. Luckily for your crew, this planet has vast groundwater resources. The problem is that past mining activities have resulted in various levels of contamination of these resources.

Your handheld XRF device can detect trace elements in water samples, but the automatic setting has been disabled due to lack of communication with your ship's network. You'll have to use the manual mode.

While your crew established a shelter, you collect and analyze the chemical composition of five water samples. As a reference, you've also collected an XRF analysis of the drinking water that you brought along. See figures 1-6 below.

Using the old reference documentation stored on your handheld computer, evaluate the toxicity of the water sample. See the blue table of elements on the last page of this exercise for spectral peak indices. Table 1 is a list of elements that are harmful to humans in even small quantities. Table 2 is a list of elements that can be harmful to humans is consumed in very high quantities.

TABLE 1	TABLE 2
Arsenic	Copper
Barium	Iron
Cadmium	Manganese
Lead	Tin
Mercury	Silver
Uranium	Zinc

To determine if the water samples are suitable for drinking, you must first determine what elements are represented by the peaks on your XRF readouts. Your device is equipped with a filter to specialize in analyzing heavy metals, such as those listed in the tables above.

To identify the element associated with each peak, you must first determine the energy (eV) of the peaks. To do this, measure from zero, at the left, to the midpoint of the peak. Then match the peak energy (eV) with the element data on the blue periodic table. Identify peaks between 3.5 keV and 16 keV.

As mission commander, it is your responsibility to find the best drinking water option in order to save your team from almost certain peril. You don't know how long you will be stuck here, so determine how many are drinkable so you can have multiple options.

Activity Questions:

1) Which water samples appear safe to drink? Why?

2) Order the water samples from most safe to least safe.

3) Do you think XRF technology is sufficient in the detection of drinkable water? Why or why not?

Post Exercise Questions:

4) What challenges did you encounter using the XRF in manual mode?

5) What other contaminants might exist that cannot be detected by XRF in manual mode?

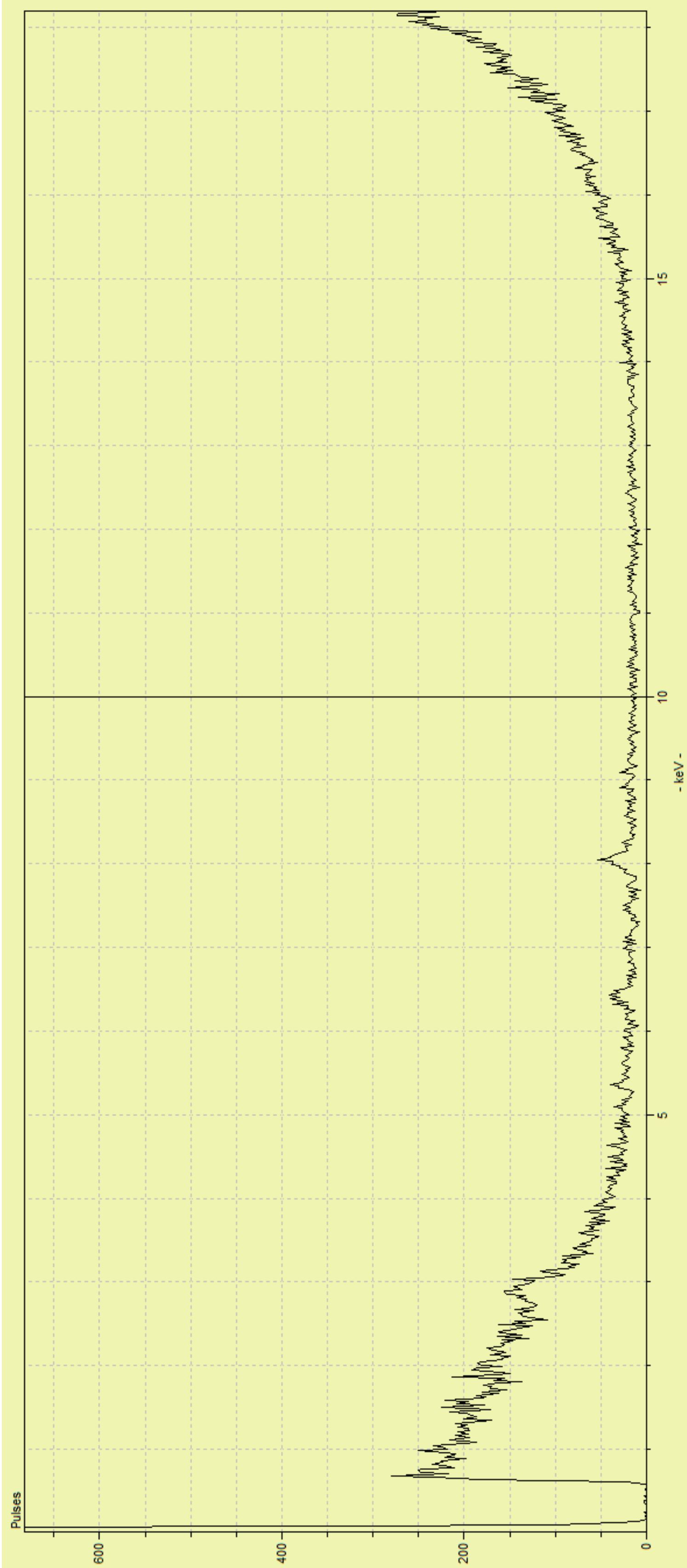


Figure 1: Water carried from your ship. This water has passed standards tests of the Galactic Federation.

Sample #1

Identify the peaks near 6 and 8 keV to get an idea of what is a safe level for those minerals.

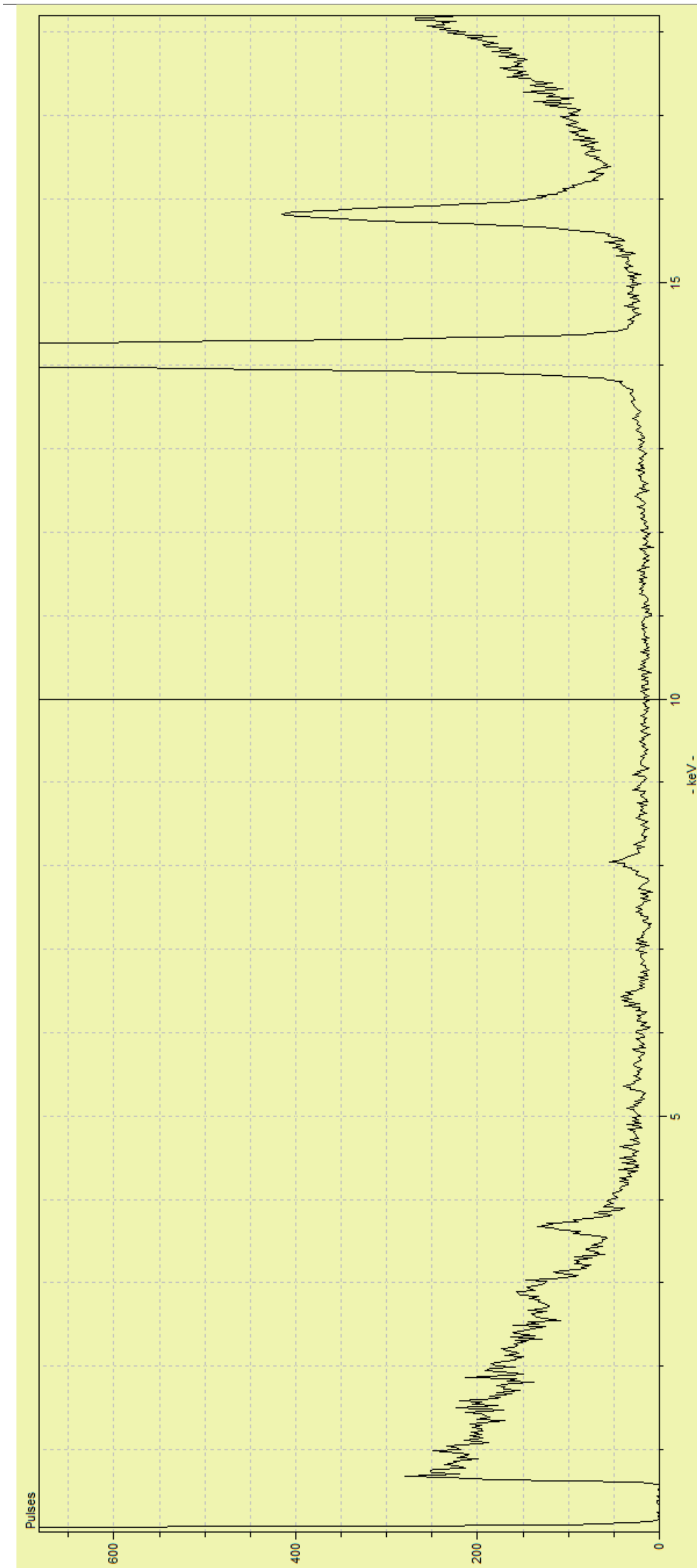


Figure 2: Water from a nearby cave.

Sample #2

The water is clear and has no odor, but imparts a slightly bluish tint when light passes through.

Identify all the elements in this sample between 3.5-16 keV. Is this water safer to drink?

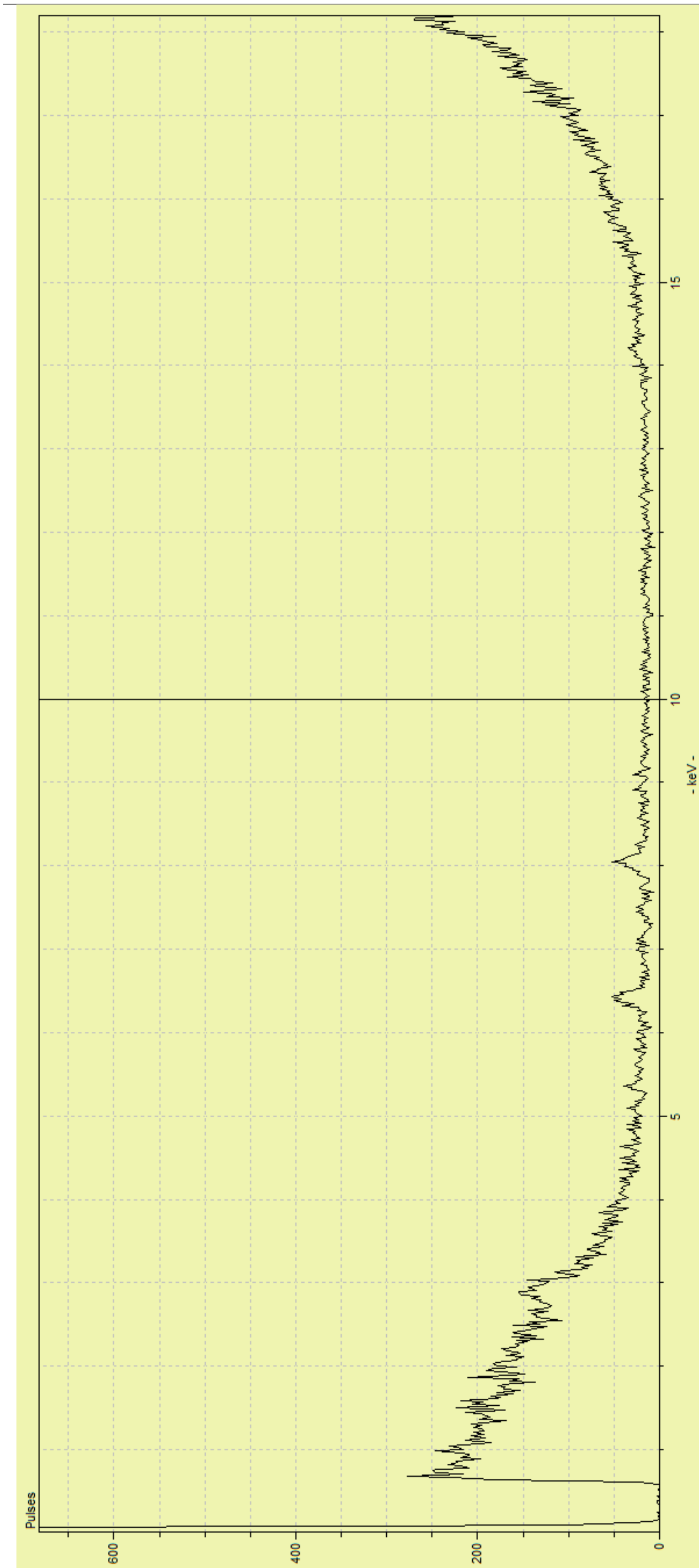


Figure 3: Water from a volcanic ash field.

Sample #3

The water is cloudy, and slightly yellow but has no odor.

Identify all the elements in this sample between 3.5-16 keV. Is this water safer to drink?

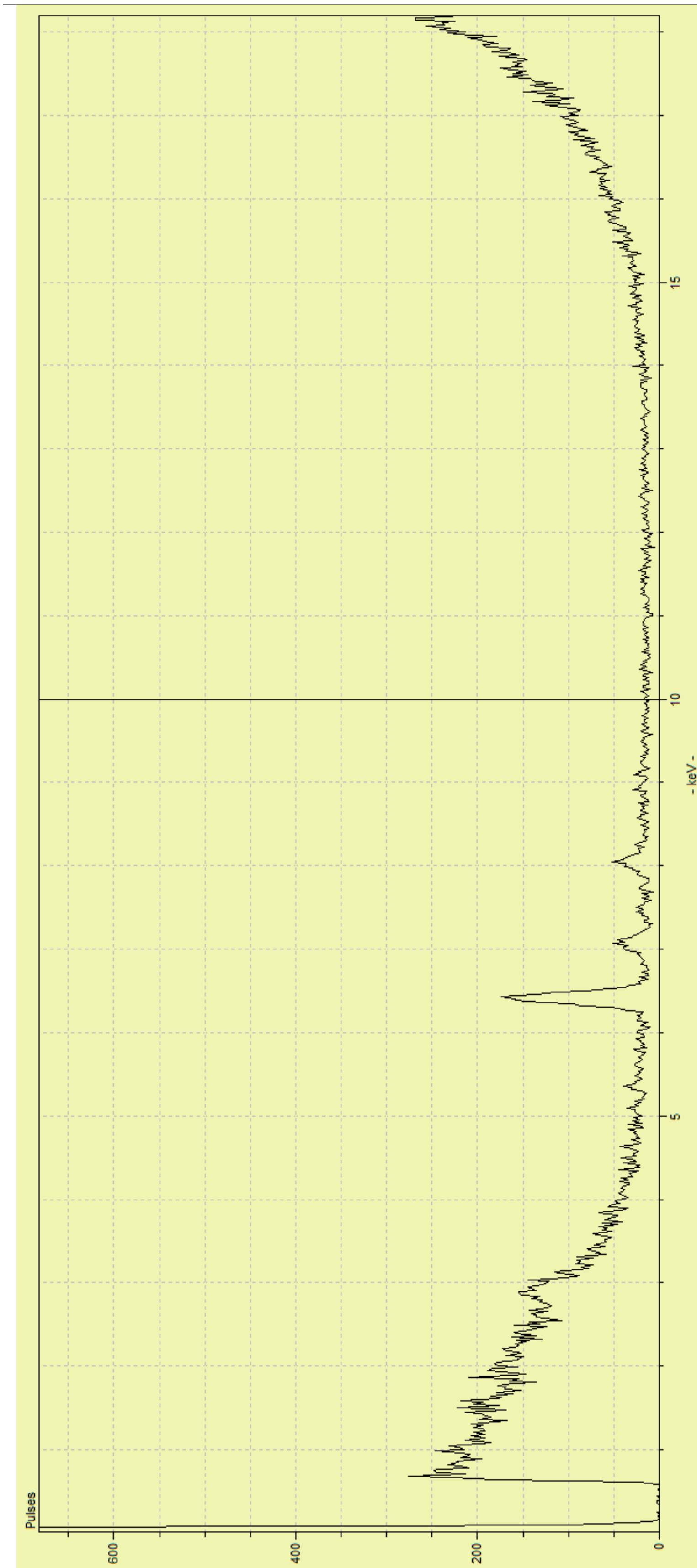


Figure 4: Smelly water collected from geyser.

Sample #4

This water smells of rotten eggs, but is otherwise clear. Nobody really wants to collect it.

Identify all the elements in this sample between 3.5-16 keV. Is this water safer to drink?

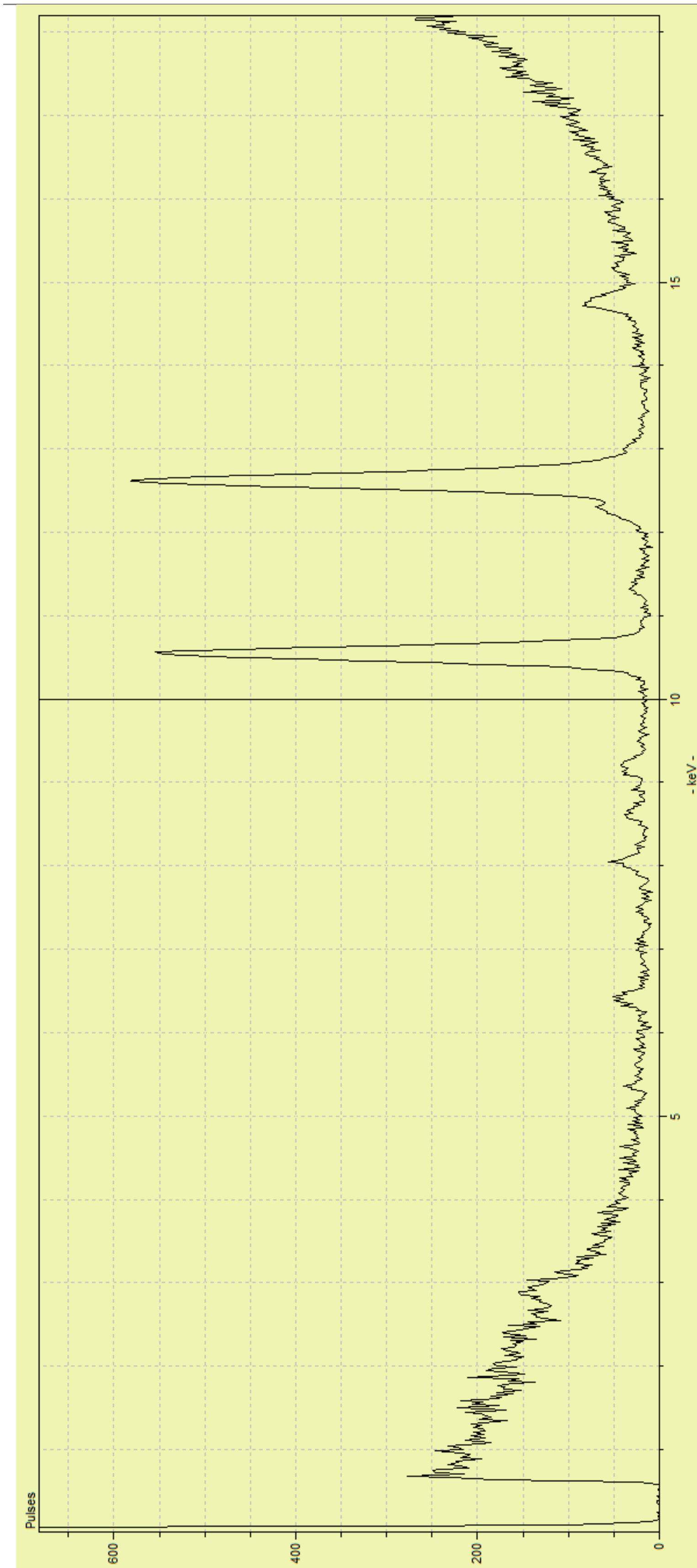


Figure 5: Water from near the mine site.

Sample #5

Identify all the elements in this sample between 3.5-16 keV. Is this water safer to drink?

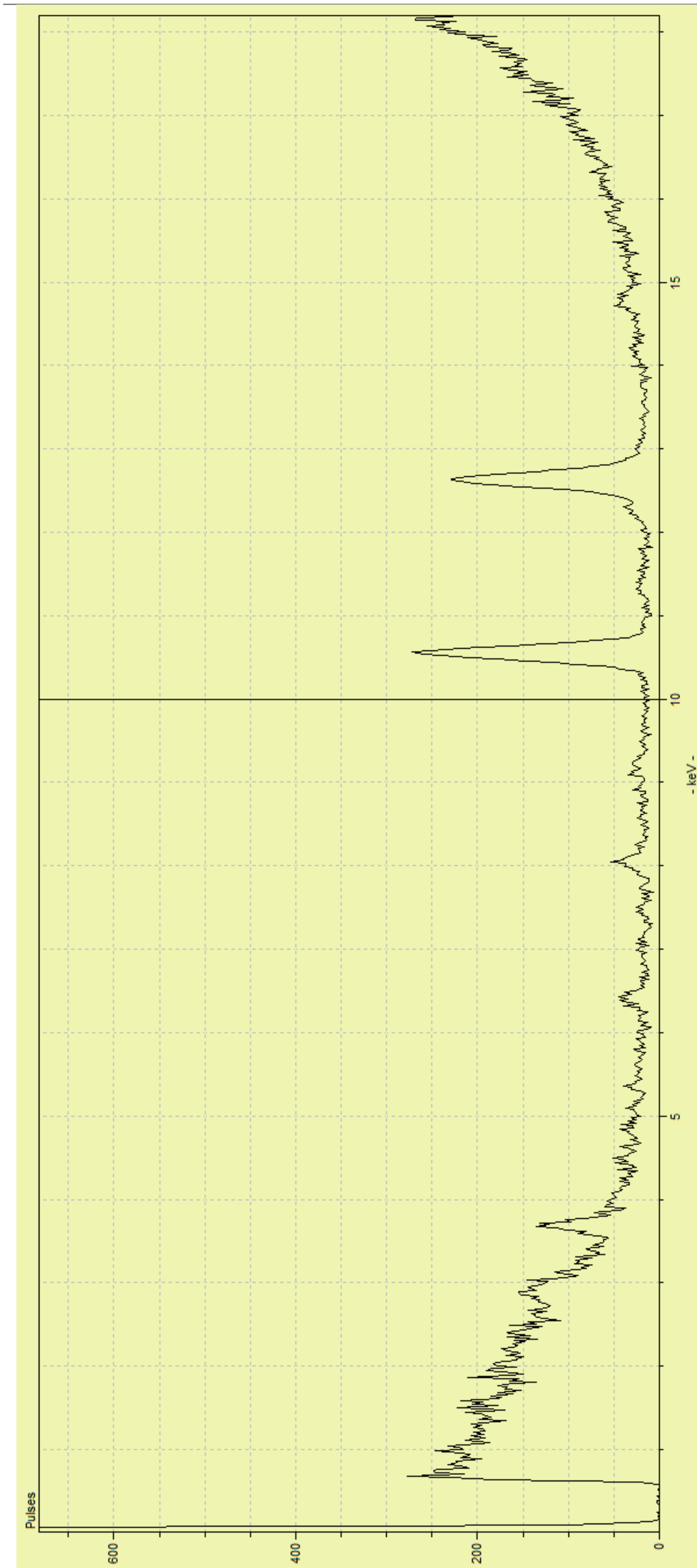


Figure 6: Water from a beautiful, golden crystal cave near the mine site.

Sample #6

Identify all the elements in this sample between 3.5-16 keV. Is this water safer to drink?

BRUKER

Periodic Table of Elements and X-ray Energies

www.bruker.com/hhxrf

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.01 0.0007 Hydrogen																	2 He 4.00 0.0002 Helium
3 Li 6.94 0.53 Lithium	4 Be 9.01 1.85 Beryllium Kα 0.108											5 B 10.81 2.34 Boron Kα 0.183	6 C 12.01 2.27 Carbon Kα 0.277	7 N 14.01 0.001 Nitrogen Kα 0.392	8 O 16.00 0.001 Oxygen Kα 0.525	9 F 19.00 0.001 Fluorine Kα 0.677	10 Ne 20.18 0.0009 Neon Kα 0.849
11 Na 22.99 0.97 Sodium Kα 1.040	12 Mg 24.31 1.74 Magnesium Kα 1.254											13 Al 26.98 2.70 Aluminium Kα 1.486	14 Si 28.09 2.33 Silicon Kα 1.740	15 P 30.97 1.82 Phosphorus Kα 2.010	16 S 32.07 2.07 Sulfur Kα 2.309	17 Cl 35.45 0.003 Chlorine Kα 2.622	18 Ar 39.95 0.002 Argon Kα 2.958
19 K 39.10 0.86 Potassium Kα 3.314	20 Ca 40.08 1.54 Calcium Kα 3.692 Lα 0.341	21 Sc 44.96 2.99 Scandium Kα 4.093 Lα 0.395	22 Ti 47.87 4.54 Titanium Kα 4.512 Lα 0.452	23 V 50.94 6.11 Vanadium Kα 4.953 Lα 0.510	24 Cr 52.00 7.15 Chromium Kα 5.415 Lα 0.572	25 Mn 54.94 7.44 Manganese Kα 5.900 Lα 0.637	26 Fe 55.85 7.87 Iron Kα 6.405 Lα 0.705	27 Co 58.93 8.86 Cobalt Kα 6.931 Lα 0.775	28 Ni 58.69 8.91 Nickel Kα 7.480 Lα 0.849	29 Cu 63.55 8.93 Copper Kα 8.046 Lα 0.928	30 Zn 65.38 7.13 Zinc Kα 8.637 Lα 1.012	31 Ga 69.72 5.91 Gallium Kα 9.251 Lα 1.098	32 Ge 72.64 5.32 Germanium Kα 9.886 Lα 1.188	33 As 74.92 5.78 Arsenic Kα 10.543 Lα 1.282	34 Se 78.96 4.81 Selenium Kα 11.224 Lα 1.379	35 Br 79.90 3.12 Bromine Kα 11.924 Lα 1.481	36 Kr 83.80 0.004 Krypton Kα 12.648 Lα 1.585
37 Rb 85.47 1.53 Rubidium Kα 13.396 Lα 1.692	38 Sr 87.62 2.64 Strontium Kα 14.165 Lα 1.806	39 Y 88.91 4.47 Yttrium Kα 14.958 Lα 1.924	40 Zr 91.22 6.51 Zirconium Kα 15.775 Lα 2.044	41 Nb 92.91 8.57 Niobium Kα 16.615 Lα 2.169	42 Mo 95.94 10.22 Molybdenum Kα 17.480 Lα 2.292	43 Tc (98) 11.50 Technetium Kα 18.367 Lα 2.423	44 Ru 101.07 12.37 Ruthenium Kα 19.279 Lα 2.558	45 Rh 102.91 12.41 Rhodium Kα 20.216 Lα 2.697	46 Pd 106.42 12.02 Palladium Kα 21.177 Lα 2.838	47 Ag 107.87 10.50 Silver Kα 22.163 Lα 2.983	48 Cd 112.41 8.69 Cadmium Kα 23.173 Lα 3.133	49 In 114.82 7.31 Indium Kα 24.210 Lα 3.286	50 Sn 118.71 7.29 Tin Kα 25.271 Lα 3.444	51 Sb 121.76 6.69 Antimony Kα 26.359 Lα 3.604	52 Te 127.60 6.23 Tellurium Kα 27.473 Lα 3.768	53 I 126.90 4.93 Iodine Kα 28.612 Lα 3.938	54 Xe 131.29 0.006 Xenon Kα 29.775 Lα 4.110
55 Cs 132.91 1.87 Cesium Kα 30.973 Lα 4.285	56 Ba 137.33 3.59 Barium Kα 32.194 Lα 4.466	57 La 138.91 6.15 Lanthanum Kα 33.442 Lα 4.647	72 Hf 178.49 13.31 Hafnium Lα 7.899 Mα 1.646	73 Ta 180.95 16.65 Tantalum Lα 8.146 Mα 1.712	74 W 183.84 19.25 Tungsten Lα 8.398 Mα 1.775	75 Re 186.21 21.02 Rhenium Lα 8.652 Mα 1.843	76 Os 190.23 22.61 Osmium Lα 8.911 Mα 1.907	77 Ir 192.22 22.65 Iridium Lα 9.175 Mα 1.980	78 Pt 195.08 21.46 Platinum Lα 9.442 Mα 2.050	79 Au 196.97 19.28 Gold Lα 9.713 Mα 2.123	80 Hg 200.59 13.53 Mercury Lα 9.989 Mα 2.195	81 Tl 204.37 11.85 Thallium Lα 10.269 Mα 2.271	82 Pb 207.20 11.34 Lead Lα 10.551 Mα 2.342	83 Bi 208.98 9.81 Bismuth Lα 10.839 Mα 2.423	84 Po (209) 9.32 Polonium Lα 11.131 Mα 2.499	85 At (210) 7.00 Astatine Lα 11.427 Mα 2.577	86 Rn (222) 0.01 Radon Lα 11.727 Mα 2.654
87 Fr (223) 1.87 Francium Lα 12.031 Mα 2.732	88 Ra (226) 5.50 Radium Lα 12.339 Mα 2.806	89 Ac (227) 10.07 Actinium Lα 12.652 Mα 2.900															
				58 Ce 140.12 6.77 Cerium Lα 4.839 Mα 0.884	59 Pr 140.91 6.77 Praseodymium Lα 5.035 Mα 0.927	60 Nd 144.24 7.01 Neodymium Lα 5.228 Mα 0.979	61 Pm (145) 7.26 Promethium Lα 5.432 Mα 1.023	62 Sm 150.36 7.52 Samarium Lα 5.633 Mα 1.078	63 Eu 151.96 5.24 Europium Lα 5.849 Mα 1.131	64 Gd 157.25 7.90 Gadolinium Lα 6.053 Mα 1.181	65 Tb 158.93 8.23 Terbium Lα 6.273 Mα 1.240	66 Dy 162.50 8.55 Dysprosium Lα 6.498 Mα 1.293	67 Ho 164.93 8.80 Holmium Lα 6.720 Mα 1.348	68 Er 167.26 9.07 Erbium Lα 6.949 Mα 1.404	69 Tm 168.93 9.32 Thulium Lα 7.180 Mα 1.462	70 Yb 173.04 6.97 Ytterbium Lα 7.416 Mα 1.526	71 Lu 174.47 9.84 Lutetium Lα 7.655 Mα 1.580
				90 Th 232.04 11.72 Thorium Lα 12.968 Mα 2.996	91 Pa 231.04 15.37 Protactinium Lα 13.291 Mα 3.032	92 U 238.03 18.95 Uranium Lα 13.614 Mα 3.171	93 Np (237) 20.45 Neptunium Lα 13.946 Mα 3.250	94 Pu (244) 19.84 Plutonium Lα 14.282 Mα 3.339	95 Am (243) 13.69 Americium Lα 14.620 Mα 3.438	96 Cm (247) 13.51 Curium	97 Bk (247) 14.79 Berkelium	98 Cf (251) 15.1 Californium	99 Es (252) 13.5 Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (262) Lawrencium

Key:
- 35 – Atomic number
- 79.90 – Atomic weight
- 3.12 – Density (g/cm³)
- Br – Symbol
- Bromine – Element name
- Kα 11.924, Lα 1.481 – Energy (keV)
- Kα, Lα – Spectral line

Handheld XRF

Innovation with Integrity