

Soil Chemistry

Project Summary

Question:

"What changes in the concentration, oxidation state, and speciation of Sulfur and Phosphorous may be present in the soil of Northern Alberta at various depths as a result of being exposed to heat caused by the Fort McMurray wildfire."

Scan List:

- 1) XRF Wildfire source 1, 2cm
- 2) XRF No Wildfire source 1, 2cm
- 3) XRF Wildfire source 1, 5cm
- 4) XRF No Wildfire source 1, 5cm
- 5) XRF Wildfire source 1, 10cm
- 6) XRF No Wildfire source 1, 10cm
- 7) XANES Sulfur Wildfire source 1, 2cm
- 8) XANES Sulfur No Wildfire source 1, 2cm
- 9) Standards Sulfur Ferric Sulphate
- 10) Standards Sulfur Iron(II) Sulfide
- 11) Standards Sulfur Elemental Sulfur
- 12) Standards Sulfur Potassium Sulphate
- 13) Standards Sulfur Copper Sulfide
- 14) Standards Sulfur Zinc Sulfide
- 15) Standards Sulfur Calcium Sulphate
- 16) XANES Sulfur Wildfire source 1, 5cm
- 17) XANES Sulfur No Wildfire source 1, 5cm
- 18) XANES Sulfur Wildfire source 1, 10cm
- 19) XANES Sulfur No Wildfire source 1, 10cm
- 20) XANES Phosphorous Wildfire source 1, 2cm
- 21) XANES Phosphorous No Wildfire source 1, 2cm
- 22) Standards Phosphorous Potassium Phosphate monobasic
- 23) Standards Phosphorous Ferric Phosphate
- 24) XANES Phosphorous Wildfire source 1, 5cm
- 25) XANES Phosphorous No Wildfire source 1, 5cm
- 26) XANES Phosphorous Wildfire source 1, 10cm
- 27) XANES Phosphorous No Wildfire source 1, 10cm
- 28) *Repeat for Second Wildfire and no wildfire source if there is extra time*

Oxidation States

Sulphate (+6) ex; Ferric Sulphate

Sulfide (-2) ex; Iron(II) Sulfide

Elemental Sulfur (0) ex; Elemental Sulfur

Phosphate (+5) ex; Ferric Phosphate

Our Standards (Bold=Using)

Potassium Phosphate monobasic

Potassium Sulphate

Ferric Sulphate

Calcium Sulphate

Elemental Sulfur

Copper Sulfide

Ferric Phosphate

Iron (II) Sulfide

Zinc Sulfide

Potassium Phosphate dibasic

Calcium Phosphate

Aluminum Phosphate

X-ray Critical Absorption and Emission Energies

Sulfur: K shell emission (eV)

Ka₁	Ka₂	Kb₁
2,307.84	2,306.64	2,464.04

Phosphorus : K shell emission (eV)

Ka₁	Ka₂	Kb₁
2,013.7	2,012.7	2,139.1

Phosphorus XRF ~2.142eV

Sulphur XRF ~2.470eV

XANES Sulphur Standards ~2.4825 KeV (Monochromator calibration)

XANES Phosphorus Standards ~2.1541 KeV (Monochromator calibration)

Notes On Techniques

X-ray Fluorescence (XRF)

XRF is a spectroscopy technique that allows us to view the relative concentration of elements in a sample. A beam of photons(light particles) is sent at the sample at a specific energy level. Electrons that exist at an energy level within the atom but not the highest energy level in the atom may absorb these photons and have enough energy to eject the electrons from the atom. When this happens the atom is left in an excited state and an electron from a higher energy level is sent down to occupy the “core hole,” left by the ejected electron. When that happens a photon is emitted from the atom to conserve energy, this is known as the fluorescent photon, the fluorescent photon has an energy that is equal to the difference in the energy levels

of the electron that came down to fill the core hole and the electron that was ejected from the atom. There are different types of fluorescent photons that correspond to the difference between these energy levels. There is a letter assigned that is dependent on what energy level the core hole is present at. If the core hole is at the lowest energy level then the fluorescent photon is from the edge, the next level is called the edge, and so on. There is then a subscript that is assigned to the letter and further subscripts after that, but the naming is quite tedious. The energy levels of these fluorescent photons is well known which is why they are often times called characteristic X-Rays. The idea behind XRF is to measure the amount of photons absorbed by a detector at certain energies, so you measure counts of photons vs energy of photons. This will create a graph that has many different peaks that correspond to different fluorescent photons and different elements. There will also be a peak at the energy level of the photons that you sent in, this is known as the scatter peak. The scatter peak is the count of photons that were not absorbed by the sample. Here is an example of an XRF graph. (The scatter peak is labeled: Compton)

The higher the peak(more counts) of an element means the more of that element you have in a sample. A common technique used to compare XRF graphs of different samples to evaluate relative concentration is normalizing to the scatter peak. Essentially you divide the counts by the scatter peak counts of both graphs and then graph again so that the scatter peak of both graphs is 1.

X-Ray Absorption Near Edge Structure Spectroscopy (XANES)

XANES is a spectroscopy technique that allows us to see the relative concentration of different oxidation states of a single element. An oxidation state is the charge of an atom due to the number of electrons that are either gained or lost in a bond. Electrons usually exist at well defined energy levels, however when an atom has an oxidation state the electrons exist at a slightly shifted energy level. The idea of XANES is to find the shift and figure out the oxidation state(s) of an element in the sample. To do this, photons are slowly sent in over a range of energy. When the energy of the incoming photons reaches the required energy to eject an electron from a specific energy level from the atom there will be a large increase in the amount of photons absorbed. A XANES graph plots the counts of the photons that are absorbed against the energy level of the photons. Peaks with more counts correspond to oxidation states of higher concentration in the sample.

Linear Combination Fitting (LCF)

LCF is a data analysis technique that is used to find the relative concentrations of chemical species within a sample. In order to accomplish this there are many XANES scans that are needed, a XANES scan of the sample, and XANES scans of standards (standards are known chemical species). LCF is an attempt to add up all of the XANES scans of the standards in such a way that they recreate the XANES scan of the sample. This is done on a computer program(Athena is commonly used) the scans of the standards are given a weighting such that the sum of the weights of the standards are equal to 1. Comparing the weighting that the computer program gives to each standard gives you an idea of the relative concentrations of each species. Larger weighting means a higher concentration.

- Phosphorus (P)

Phosphorus Oxidation States in Organic Compounds

-3	-1	0	+1	+3	+5
PH_3 phosphine R_3P trialkyl phosphines $\text{R}-\text{P}^+(\text{R})_3$ tetraalkyl phosphonium	$\text{R}-\text{P}(\text{R})=\text{O}$ phosphine oxides	P elemental	$\text{R}-\text{P}(\text{R})(\text{OH})_2$ phosphonic acids	$\text{R}-\text{P}(\text{OH})(\text{OR})_2$ phosphonic acids $\text{RO}-\text{P}(\text{OR})_3$ phosphite esters	P_2O_5 $\text{R}-\text{O}-\text{P}(\text{O})(\text{O}-\text{R})_2$ phosphate esters

- Sulfur (S)

Sulfur Oxidation States in Organic Compounds

-2	-1	0	+2	+4	+6
H_2S $\text{R}-\ddot{\text{S}}-\text{H}$ thiols $\text{R}-\ddot{\text{S}}-\text{R}$ sulfides $\text{R}-\text{S}^+(\text{R})_3$ sulfonium ions	$\text{R}-\ddot{\text{S}}-\ddot{\text{S}}-\text{R}$ disulfides	S elemental $\text{R}-\text{S}(=\text{O})-\text{R}$ sulfoxides $\text{R}-\ddot{\text{S}}(\text{OH})_2$ sulfenic acids	$\text{R}-\text{S}(=\text{O})_2-\text{R}$ sulfones $\text{R}-\text{S}(=\text{O})_2-\text{OH}$ sulfinic acids	SO_2 $\text{R}-\text{S}(=\text{O})_2-\text{OH}$ sulfonic acids $\text{R}-\text{O}-\text{S}(=\text{O})_2-\text{O}-\text{R}$ sulfite esters	SO_3 $\text{R}-\text{O}-\text{S}(=\text{O})_2-\text{O}-\text{R}$ sulfate esters

<http://casfs.ucsc.edu/about/publications/Teaching-Organic-Farming/PDF-downloads/2.2-soil-chemistry.pdf>

https://www.firescience.gov/projects/98-S-01/project/Soil_and_Water.pdf

- Relatively insensitive soil properties that do not change until temperatures have reached over about 842 °F (450 °C). This class includes clays, cations (calcium, magnesium, potassium) and other minerals such as manganese.

- Moderately sensitive soil properties that are changed at temperatures between 212 and 752 °F (100 and 400 °C). Materials belonging

to this class include sulfur, organic matter, and soil properties dependent upon organic matter.

- Sensitive soil properties are those that are changed at temperatures less than 212 °F (100 °C). Examples of sensitive materials are living microorganisms (for example, bacteria, fungi, mycorrhizae), plant roots, and seeds. This class also includes many of the biologically mediated nutrient cycling processes in soils.

Threshold for soil Characteristics

Soil wettability: 250 celsius

Soil structure: 300 celsius

Calcite formation: 300-500 celsius

Clay: 460-980 celsius

Sand (quartz): 1,414 celsius

Temperature threshold for soil chemical characteristics

Organic matter 100 celsius

Nitrogen 200 celsius

Sulfur 375 celsius

Phosphorus and potassium 774 celsius

Magnesium 1,107 celsius

Calcium 1,484 celsius

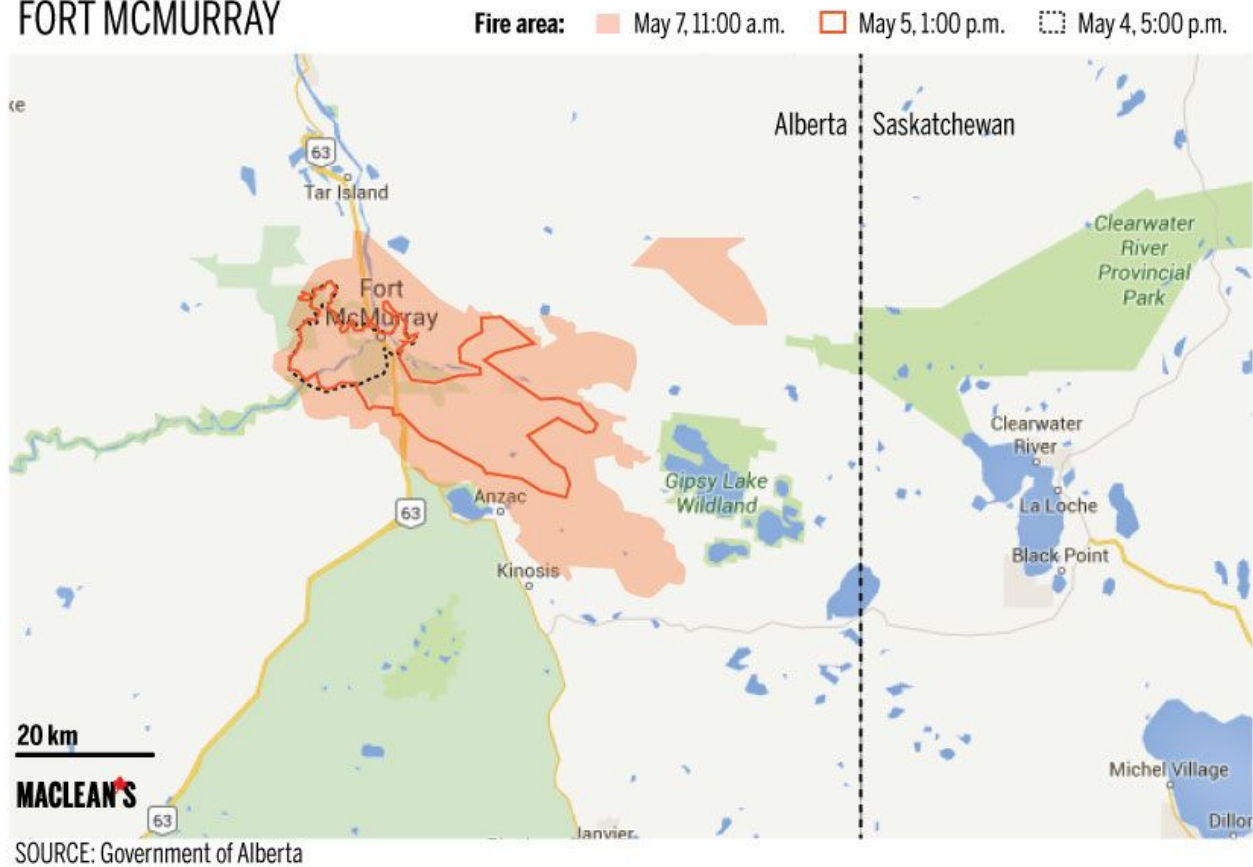
Manganese 1,962 celsius

- Sulfur has been reported as limiting in some coastal forest soils of the Pacific Northwest
- The combustion of organic matter leaves a relatively large amount of highly available P in the surface ash found on the soil surface immediately following fire. This highly available P, however, can be quickly immobilized if calcareous (calcium carbonate) substances are present in the ash and thus can become unavailable for plant growth.
- In summary, many nutrients essential for plant growth including N, P, S, and some cations described earlier are all affected to some extent by fire. Nitrogen is likely the most limiting nutrient in natural systems, followed by P and S. Cations released by burning may affect soil pH and result in the immobilization of P. The role of micronutrients in ecosystem productivity and their relationship to soil heating during fire is for the most part unclear. One study, however, did show that over half of the selenium in burned laboratory samples was recovered in the ash residue.

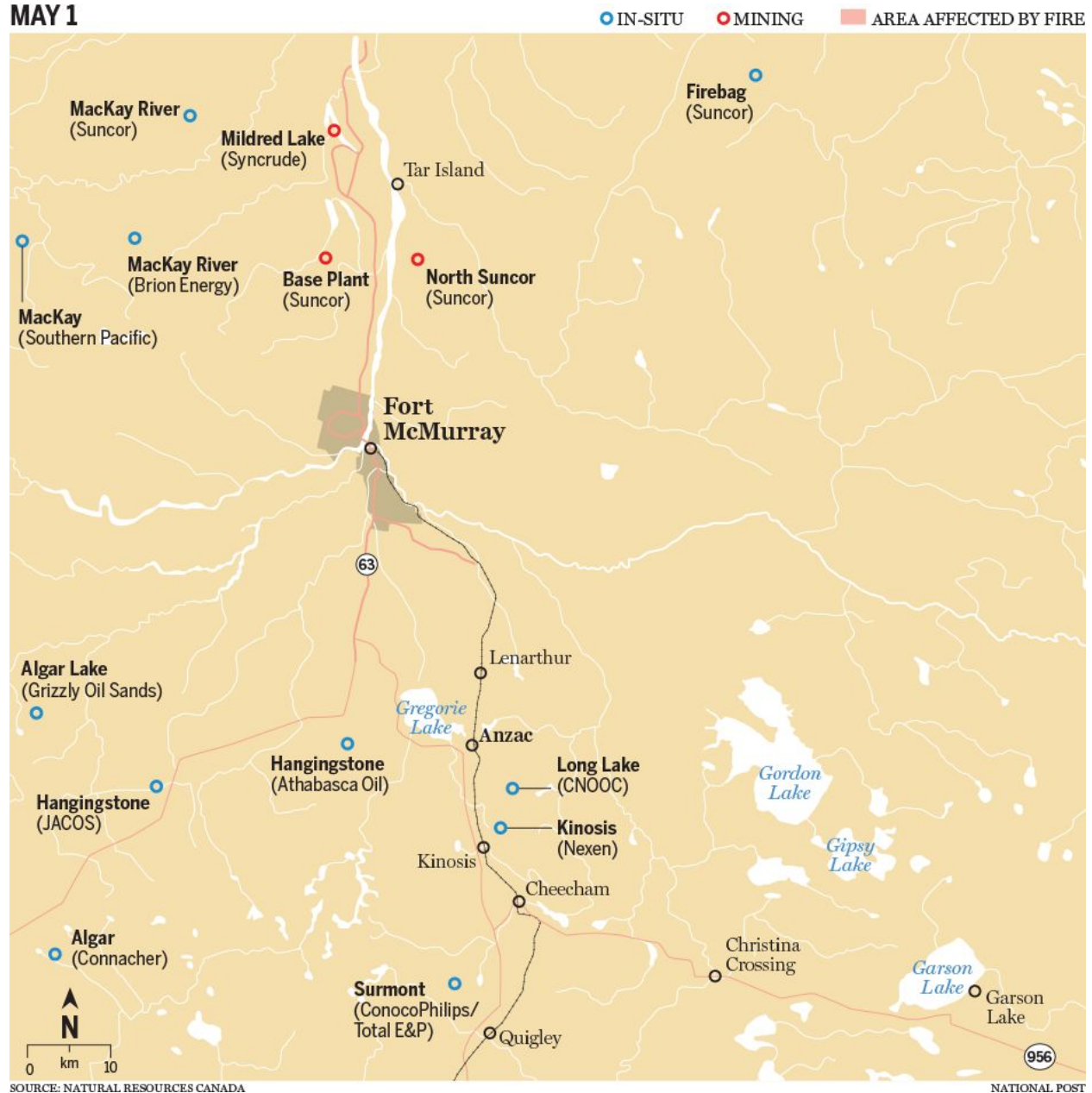
- The nutrients leached from the forest floor and the ash were adsorbed in the mineral soil. Surface soils were found to retain 89 to 98 percent of the nutrients leached from the plant ash (Soto and Diaz-Fierros 1993). As the leachates moved through the mineral soil, the pH of the solution decreased.
- Chemical ions generally become more available in the surface soil as a result of Fire.
- Grove and others (1986) found that immediately after fire, extractable nutrients increased in the 0 to 1.2 inch (0-3 cm) depth. Concentrations of S, NH₄, P, K, Na, zinc (Zn), Ca, and Mg increased. Everything except Zn and organic C increased in terms of total nutrients. At the lower depths sampled, 1.2 to 3.9 inches and 3.9 to 7.9 inches (3-10 and 10-20 cm), only extractable P and K were increased by burning. One year later nutrient levels were still greater than preburn concentrations, but had decreased. A study on an area of pine forest burned by a wildfire reported that in the soil, concentrations of P, Ca, and Mg, aluminum (Al), iron (Fe) had increased in response to different levels of fire severity
- Summary:
 - The most basic soil chemical property affected by soil heating during fires is organic matter. Organic matter not only plays a key role in the chemistry of the soil, but it also affects the physical properties (see chapter 2) and the biological properties (see chapter 4) of soils as well. Soil organic matter plays a key role in nutrient cycling, cation exchange, and water retention in soils. When organic matter is combusted, the stored nutrients are either volatilized or are changed into highly available forms that can be taken up readily by microbial organisms and vegetation. Those available nutrients not immobilized are easily lost by leaching or surface runoff and erosion. Nitrogen is the most important nutrient affected by fire, and it is easily volatilized and lost from the site at relatively low temperatures. The amount of change in organic matter and N is directly related to the magnitude of soil

heating and the severity of the fire. High- and moderate-severity fires cause the greatest losses. Nitrogen loss by volatilization during fires is of particular concern on low-fertility sites because N can only be replaced by N-fixing organisms. Cations are not easily volatilized and usually remain on the site in a highly available form. An abundance of cations can be found in the thick ash layers (or ash-bed) remaining on the soil surface following high-severity fires.

FORT MCMURRAY



MAY 1



<http://news.nationalpost.com/news/canada/watch-the-fort-mcmurray-fire-spread-over-18-days-in-may-beastly-blaze-just-wont-die-growing-to-423000-hectares>

How does fire affect the oxidation/reduction and relative concentrations of sulfur, phosphates and micronutrients in depths of 0,3,5,10,30 cm of areas in the forest that were untouched by human activity and changed through human activity.

<http://www.extension.umn.edu/agriculture/nutrient-management/phosphorus/the-nature-of-phosphorus/>

Phosphorus (P) is an essential element classified as a macronutrient because of the relatively large amounts of P required by plants. Phosphorus is one of the three nutrients generally added to soils in fertilizers. One of the main roles of P in living organisms is in the transfer of energy. Organic compounds that contain P are used to transfer energy from one reaction to drive another reaction within cells. Adequate P availability for plants stimulates early plant growth and hastens maturity. Although P is essential for plant growth, mismanagement of soil P can pose a threat to water quality. The concentration of P is usually sufficiently low in fresh water so that algae growth is limited. When lakes and rivers are polluted with P, excessive growth of algae often results. High levels of algae reduce water clarity and can lead to decreases in available dissolved oxygen as the algae decays, conditions that can be very detrimental to game fish populations.

The phosphorus cycle

The P cycle is similar to several other mineral nutrient cycles in that P exists in soils and minerals, living organisms, and water. Although P is widely distributed in nature, P is not found by itself in elemental form. Elemental P is extremely reactive and will combine with oxygen when exposed to the air. In natural systems like soil and water, P will exist as phosphate, a chemical form in which each P atom is surrounded by 4 oxygen (O) atoms. Orthophosphate, the simplest phosphate, has the chemical formula PO_4^{3-} . In water, orthophosphate mostly exists as H_2PO_4^- in acidic conditions or as HPO_4^{2-} in alkaline conditions.

Phosphate is taken up by plants from soils, utilized by animals that consume plants, and returned to soils as organic residues decay in soils (Figure 1). Much of the phosphate used by living organisms becomes incorporated into organic compounds. When plant materials are returned to the soil, this organic phosphate will slowly be released as inorganic phosphate or be incorporated into more stable organic materials and become part of the soil organic matter. The release of inorganic phosphate from organic phosphates is called mineralization and is caused by microorganisms breaking down organic compounds. The activity of microorganisms is highly influenced by soil temperature and soil moisture. The process is most rapid when soils are warm and moist but well drained. Phosphate can potentially be lost through soil erosion and to a lesser extent to water running over or through the soil.

Many phosphate compounds are not very soluble in water; therefore, most of the phosphate in natural systems exists in solid form. However, soil water and surface water (rivers and lakes) usually contain relatively low concentrations of dissolved (or soluble) phosphorus. Depending on the types of minerals in the area, bodies of water usually contain about 10 ppb or more of dissolved P as orthophosphate. Water bodies may also contain organic P and phosphate attached to small particles of sediment. Total phosphorus in water is all of the phosphorus in solution regardless of its form and is often the form reported in water quality studies. Algal available or bioavailable phosphorus is P that is estimated to be available to organisms like algae that are present in a lake or river. This is usually estimated by a chemical test which is

designed to measure the dissolved P and the particulate P that are easily available. This is a measure of the P that is of immediate concern to water quality.

The word phosphorus or P refers to the element and is also used as a general term when a particular chemical form of P is not being designated. For example, the total P content of a soil or plant material is usually expressed as percent P. However, fertilizer analyses are usually reported as percent P_2O_5 . The phosphate form (P_2O_5) is a chemical produced during fertilizer analysis, but does not exist in either fertilizers or soils.

Forms of phosphorus in soils

In soils P may exist in many different forms. In practical terms, however, P in soils can be thought of existing in 3 "pools":

- solution P
- active P
- fixed P

The solution P pool is very small and will usually contain only a fraction of a pound of P per acre. The solution P will usually be in the orthophosphate form, but small amounts of organic P may exist as well. Plants will only take up P in the orthophosphate form. The solution P pool is important because it is the pool from which plants take up P and is the only pool that has any measurable mobility. Most of the P taken up by a crop during a growing season will probably have moved only an inch or less through the soil to the roots. A growing crop would quickly deplete the P in the soluble P pool if the pool was not being continuously replenished.

The active P pool is P in the solid phase which is relatively easily released to the soil solution, the water surrounding soil particles. As plants take up phosphate, the concentration of phosphate in solution is decreased and some phosphate from the active P pool is released. Because the solution P pool is very small, the active P pool is the main source of available P for crops. The ability of the active P pool to replenish the soil solution P pool in a soil is what makes a soil fertile with respect to phosphate. An acre of land may contain several pounds to a few hundred pounds of P in the active P pool. The active P pool will contain inorganic phosphate that is attached (or adsorbed) to small particles in the soil, phosphate that reacted with elements such as calcium or aluminum to form somewhat soluble solids, and organic P that is easily mineralized. Adsorbed phosphate ions are held on active sites on the surfaces of soil particles. The amount of phosphate adsorbed by soil increases as the amount of phosphate in solution increases and vice versa (Figure 2). Soil particles can act either as a source or a sink of phosphate to the surrounding water depending on conditions. Soil particles with low levels of adsorbed P that are eroded into a body of water with relatively high levels of dissolved phosphate may adsorb phosphate from the water, and vice versa.

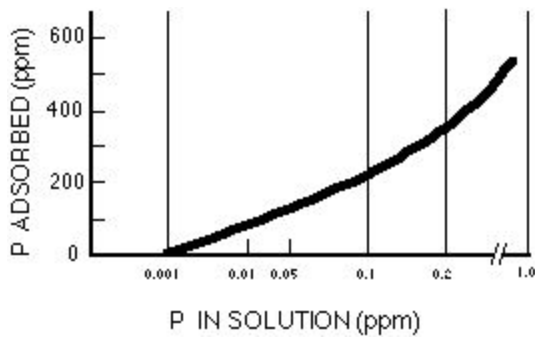


Figure 2. Relationship between P absorbed by soil and P in solution.

The fixed P pool of phosphate will contain inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization by microorganisms in the soil. Phosphate in this pool may remain in soils for years without being made available to plants and may have very little impact on the fertility of a soil. The inorganic phosphate compounds in this fixed P pool are more crystalline in their structure and less soluble than those compounds considered to be in the active P pool. Some slow conversion between the fixed P pool and the active P pool does occur in soils.

Fate of phosphorus added to soils

The phosphate in fertilizers and manure is initially quite soluble and available. Most phosphate fertilizers have been manufactured by treating rock phosphate (the phosphate-bearing mineral that is mined) with acid to make it more soluble. Manure contains soluble phosphate, organic phosphate, and inorganic phosphate compounds that are quite available. When the fertilizer or manure phosphate comes in contact with the soil, various reactions begin occurring that make the phosphate less soluble and less available. The rates and products of these reactions are dependent on such soil conditions as pH, moisture content, temperature, and the minerals already present in the soil.

As a particle of fertilizer comes in contact with the soil, moisture from the soil will begin dissolving the particle. Dissolving of the fertilizer increases the soluble phosphate in the soil solution around the particle and allows the dissolved phosphate to move a short distance away from the fertilizer particle. Movement is slow but may be increased by rainfall or irrigation water flowing through the soil. As phosphate ions in solution slowly migrate away from the fertilizer particle, most of the phosphate will react with the minerals within the soil. Phosphate ions generally react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe), and forming compounds that are solids. The adsorbed phosphate and the newly formed solids are relatively available to meet crop needs.

Gradually reactions occur in which the adsorbed phosphate and the easily dissolved compounds of phosphate form more insoluble compounds that cause the phosphate to be become fixed and unavailable. Over time this results in a decrease in soil test P. The

mechanisms for the changes in phosphate are complex and involve a variety of compounds. In alkaline soils (soil pH greater than 7) Ca is the dominant cation (positive ion) that will react with phosphate. A general sequence of reactions in alkaline soils is the formation of dibasic calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite. The formation of each product results in a decrease in solubility and availability of phosphate. In acidic soils (especially with soil pH less than 5.5) Al is the dominant ion that will react with phosphate. In these soils the first products formed would be amorphous Al and Fe phosphates, as well as some Ca phosphates. The amorphous Al and Fe phosphates gradually change into compounds that resemble crystalline variscite (an Al phosphate) and strengite (an Fe phosphate). Each of these reactions will result in very insoluble compounds of phosphate that are generally not available to plants. Reactions that reduce P availability occur in all ranges of soil pH but can be very pronounced in alkaline soils (pH > 7.3) and in acidic soils (pH < 5.5). Maintaining soil pH between 6 and 7 will generally result in the most efficient use of phosphate (Figure 3).

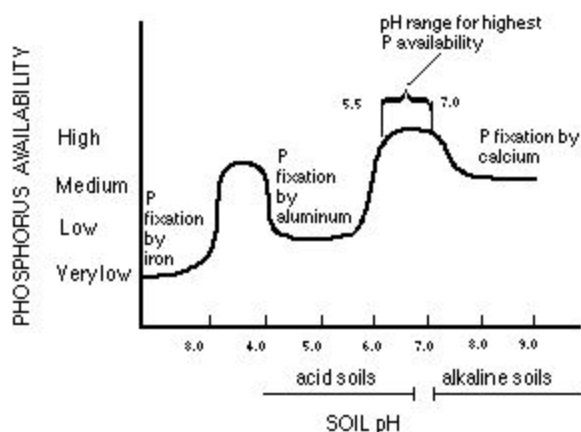


Figure 3. The availability of phosphorus is affected by soil pH.

Adding to the active P pool through fertilization will also increase the amount of fixed P. Depleting the active pool through crop uptake may cause some of the fixed P to slowly become active P. The conversion of available P to fixed P is partially the reason for the low efficiency of P fertilizers. Most of the P fertilizer applied to the soil will not be utilized by the crop in the first season. Continued application of more P than the crops utilize increases the fertility of the soil, but much of the added P becomes fixed and unavailable.

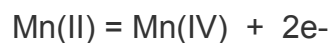
Most fine-to medium-textured soils have large capacities to hold phosphate by adsorption and precipitation. Occasionally the question of how much phosphate a soil can hold is asked, especially when high loading rates of P are expected or have occurred. Soils differ in their phosphate holding capacity. Fine-textured soils can generally hold hundreds of pounds of phosphate per acre, while coarse-textured soils can generally hold much less phosphate due to the more inert character of sand particles as compared to clay particles. In addition the subsoil of many soils often has an even greater capacity to hold phosphate than does the corresponding surface soil. However, an important aspect of the ability of a soil to hold phosphate is that a soil cannot hold increasing amounts of phosphate in the solid phase without also increasing soil solution phosphate (Figure 2). Increased amounts of phosphate in solution will potentially cause more phosphate to be lost to water running over the soil surface or

leaching through the soil. Loading soils with very high levels of phosphate will generally not hurt crops but may result in increased phosphate movement to nearby bodies of water.

Plant nutrients, their chemical symbols, and the ionic forms common in soils and available for plant uptake

Element	Symbol	Ion or molecule
Carbon	C	CO_2 (mostly through leaves)
Hydrogen	H	H^+ , H_2O (water)
Oxygen	O	O^{2-} , OH^- , CO_3^{2-} , SO_4^{2-} , CO_2
Phosphorus	P	H_2PO_4^- , HPO_4^{2-} (phosphates)
Potassium	K	K^+
Nitrogen	N	NH_4^+ , NO_3^- (ammonium, nitrate)
Sulfur	S	SO_4^{2-}
Calcium	Ca	Ca^{2+}
Iron	Fe	Fe^{2+} , Fe^{3+} (ferrous, ferric)
Magnesium	Mg	Mg^{2+}
Boron	B	H_3BO_3 , H_2BO_3^- , B(OH)_4^-
Manganese	Mn	Mn^{2+}
Copper	Cu	Cu^{2+}
Zinc	Zn	Zn^{2+}
Molybdenum	Mo	MoO_4^{2-} (molybdate)
Chlorine	Cl	Cl^- (chloride)

Phosphate ions generally react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe),



Living compounds create energy by oxidizing carbohydrates and reducing oxygen. That is, organisms take electrons from the organic carbon, run it through their metabolic cycles, and then dump the electron to an electron acceptor. When oxygen is not present, microorganisms must seek alternate electron acceptors. The energy gain for the organisms is the energy difference between reduced carbon and the electron acceptor. In order of favorability, electron acceptors are:



A lack of oxygen leads to an *anaerobic* condition and results in the build up of reduced species: Mn(II), N₂, Fe(II), As(III), and S²⁻. When reduced species are build up in the system, it is termed "REDUCED". When O₂ is present with reduced species such as S²⁻, Fe(II), Mn(II), or As(III) it is energetically favorable for oxygen to oxidizing the previous species and thus become reduced to water. Thus, if oxygen is introduced to a 'reduced' system, the reduced species are oxidizes in opposite order:



Iron Cycles:

Iron goes through pronounced changes with redox potential changes.

- Fe(III)-oxides are dominant in oxidized systems
- suboxic soils result in high Fe(II) concentrations
 - * Fe(II) can precipitate as FeCO₃ (siderite)
- in anoxic systems, Fe(II) may precipitate as FeS / FeS₂ (pyrite)
- upon aeration, the reduced Fe forms are oxidized quickly

Manganese Cycles:

Like Fe, Mn goes through extensive changes with redox potential changes.

- Mn-oxides dominate in aerated systems
- Mn(II) is formed upon reduction
- MnCO₃ forms in reduced (suboxic) systems, less likely are MnS but they do form
- oxidation is much slower than for Fe(II) except at mineral surfaces

Sulfur Cycles

- Sulfur goes through dramatic changes in redox cycling. It covers a full 8 electron transfer sequence with most intermediates being possible.
- We usually only consider sulfate and sulfide, but we should look at the other possible oxidation states.
 - Sulfate dominates in oxidized environments
 - anoxic conditions leads to the formation of sulfides and other reduced S forms

- plant tissue degradation leaves many intermediate S oxidation states
- sulfide tends to form strong, insoluble complexes with soft to intermediate acids: Fe(II), Cd, Cu, Pb, Hg, ...
- oxidation of sulfide leads to acidification of many systems (acid mine drainage)

<http://encyclopedia2.thefreedictionary.com/Magnesium+compounds>

<http://extension.missouri.edu/p/G9185>

<https://www.extension.umn.edu/agriculture/nutrient-management/phosphorus/the-nature-of-phosphorus/>

<https://www.ncbi.nlm.nih.gov/pubmed/16899757>

http://journals.lww.com/soilsci/citation/1966/04000/oxidation_and_reduction_of_sulfur_compounds_in.9.aspx

<https://link.springer.com/article/10.1007/BF00201914>

<https://passel.unl.edu/pages/informationmodule.php?idinformationmodule=1130447044&topicorder=3&maxto=7>

<http://www.sciencedirect.com/science/article/pii/S003807177690047X>

<http://www.sciencedirect.com/science/article/pii/S0038071779900555>

<http://pubs.acs.org/doi/abs/10.1021/es500073r>

<http://onlinelibrary.wiley.com/doi/10.1111/j.1469-8137.1996.tb01889.x/pdf>

http://rruff.info/uploads/CM18_157.pdf

<http://www.nrcresearchpress.com/doi/pdf/10.4141/cjss89-074>

Question:

Do the oxidation states and concentration of Sulfur, Phosphorus and potassium change in the soil of Northern Alberta at various depths when exposed to extreme heat caused by wildfire."

Hypothesis:

General: Due to pyrolysis the speciation of phosphorus and sulfur will change; the vast presence of available nutrients after a fire will cause many new chemical bonds to form. There will be a general trend from organic sulfur/phosphorus to inorganic sulfur/phosphorus, as a result their concentrations will increase. Species bond to inorganic elements will be more numerous in the samples affected by wildfire. Although volatilization of these compounds may actually cause a drop in the overall concentrations.

Sulfur: The oxidation states of sulfur are influenced by being in the presence of anaerobic or aerobic environments. Soil with lots of organic matter and nutrient cycles is mostly aerobic, however specific soils can be anaerobic, due to our observations it appears that the samples we collected contain aerobic soil. It can be inferred that this soil will contain more sulfur in the form of sulphate due to the aerobic conditions and plants preference for sulphate forms for uptake. The question arises what happens to

the speciation and concentrations of sulphate after a fire. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures, around 200-300 degrees celsius, wildfires typically reach 1000 degrees, it can be concluded that pyrolysis occurred during the Fort McMurray wildfire. It typically occurs during the charring/burning of wood, which is the main fuel source during a wildfire. It is known that sulfur reacts with oxygen to form gaseous compounds like Dihydrogen sulfide, Sulfur Dioxide, and a few more, these would be released into the air therefore decreasing the concentrations of sulphate in the soil. At the same time the burning of organic matter gives the soil more sulfur. This sulfur will be converted to sulphate and sulfide forms, yet because pyrolysis is an anaerobic process it is hypothesised that more sulfide compounds will form as a result of this process. Therefore it is hypothesised that there will be a greater concentration and abundance of sulfides in the soil after a forest fire; with sulfates and elemental sulfur being more present in the samples not affected by wildfire. However since samples were taken a year after the fire, the concentrations and speciation may be closer to what it was before the fire.

Phosphorus: Phosphorus is most common in phosphate form in soil, it is also taken up by plants in this form. It is to be noted that most phosphate compounds are insoluble, and therefore are found in solid form. It is hypothesised that there will be phosphorus speciation mainly in the form of phosphates in the non-wildfire soil. Post wildfire it is expected that there will be an abundance of phosphorus in the surface, however high temperatures can cause 50 to 60 percent of the total fuel phosphorus to be lost to volatilization. Studies show that a wildfire that produced higher soil temperatures reduced phosphatase activity and increased the mineralization (**Mineralization**; the process through which an organic substance becomes oxidized by inorganic substances) of organic P (organic compounds containing phosphorus), which increased ortho-phosphate P and decreased organic P. It is hypothesised that post wildfire there will be larger concentrations and speciation in the forms of mineralized organic phosphorus, and ortho-phosphates, whereas a decrease in organic phosphorus. The wildfire will cause a change in the speciation of organic phosphates, to inorganic phosphates, also resulting in a change of concentration.

Potassium: The burning of organic matter provides soil with an abundance of nutrients, among these chemical ions are more present. The concentrations of potassium ions are expected to increase, it is also likely that they would form bonds with the available phosphates to create potassium-phosphate compounds, it may also combine to form potassium sulphate, however it is hypothesised that there will be a greater amount of potassium-phosphate compounds, rather than Potassium-Sulphate compounds.

Standards Available:

Potassium Phosphate Monobasic

Potassium Phosphate Dibasic

Potassium Sulphate

Ferric Sulphate

Calcium Sulphate

Elemental Sulfur

Copper Sulfide

- Of Interest:
 - Potassium-magnesium sulfate
 - Ferric phosphate
 - Calcium phosphate
 - Aluminium phosphate
 - Magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$
 - Iron(II) sulfide
 - Zinc sulfide
 -

Sulfur/Phosphorus- Mainly binds with (Al, Ca, Fe, K, Mg, Na, Mn, P, Cr, Co, Cu, Ni, Pb, Sr, V, and Zn

-Question is which combinations are the most common

Notes:

Sulfur: Environmental factors such as temperature, moisture, and pH, as well as microbial population and particle size influence the rate of sulphur oxidation in soil, we will mainly focus on the effects of temperature. Plants normally absorb sulphur in the form of sulphate, and thus the oxidation of sulphide, elemental sulphur and organic sulphur is of prime importance in plant nutrition. Therefore the most common forms of sulfur found in soil will be elemental sulfur, sulfates and sulfides. Sulphides are much more present under anaerobic conditions, whereas sulfates are much more prevalent under aerobic conditions.

- Aluminium oxide appears to have a greater capacity for the absorption of sulphate than has iron oxide
- Under anaerobic conditions sulphate is reduced to sulphide, usually iron sulphide, and as this compound is insoluble it tends to accumulate
- Ferric Sulphate tends to be a common speciation of sulfur
- When in the presence of excess oxygen sulfur tends to react with it to form sulfur dioxide, which is gaseous, this is likely to occur during a forest fire.

Pyrolysis is a type of thermolysis, and is most commonly observed in organic materials exposed to high temperatures. It is one of the processes involved in charring wood, starting at 200–300 °C (390–570 °F).^[1] It also occurs in fires where solid fuels are burning or when vegetation comes into contact with lava in volcanic eruptions. In general, pyrolysis of organic substances produces gas and

liquid products and leaves a solid residue richer in carbon content, char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization.

Phosphorus:

Inorganic phosphates (ferric phosphate, calcium phosphate and aluminium phosphate) and organic forms of phosphorus (inositol hexaphosphate and /glycerophosphate)

*****Chemical ions generally become more available in the surface soil as a result of fire. Grove and others (1986) found that immediately after fire, extractable nutrients increased in the 0 to 1.2 inch (0-3 cm) depth. Concentrations of S, NH₄, P, K, Na, zinc (Zn), Ca, and Mg increased, it can be expected that there will be a greater concentration of oxidation states with these compounds (standards should include compounds between sulfur/phosphorus and these ions.)

Temperature threshold for soil chemical characteristics

Organic matter 100 celsius

Nitrogen 200 celsius

Sulfur 375 celsius

Phosphorus and potassium 774 celsius

Magnesium 1,107 celsius

Calcium 1,484 celsius

Manganese 1,962 celsius

Experiment Procedure

The XRF and XANES scans will be using the low energy crystal. The estimated time for an XRF scan is 5-10 minutes, and for a XANES scan is approximately 20-30 minutes. The XANES data will be analyzed using linear combination fitting.

Samples: (Affected=Wildfire, Unaffected=No Wildfire)

Source 1 (Affected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

Source 2 (Affected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

Source 3 (Affected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

Source 1 (Unaffected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

Source 2 (Unaffected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

Source 3 (Unaffected Region)

- Organic (Surface) Layer
- Mineral Layer (2 cm deep)
- Mineral Layer (5 cm deep)
- Mineral Layer (10 cm deep)

All Possible Standards

Potassium Phosphate monobasic

Potassium Phosphate dibasic

Potassium Sulphate

Ferric Sulphate

Calcium Sulphate

Elemental Sulfur

Copper Sulfide

Potassium Magnesium Sulphate

Ferric Phosphate

Calcium Phosphate

Aluminum Phosphate

Magnesium Phosphate $Mg_3(PO_4)_3$

Iron (II) Sulfide

Zinc Sulfide

We Will be Studying the Oxidation States

Sulphate (+6) using Ferric Sulphate

Sulfide (-2) using Iron(II) Sulfide

Elemental Sulfur (0) using Elemental Sulfur

Phosphate (+5) using Potassium Phosphate monobasic or Ferric Phosphate

Procedure for Comparing Soil Depths

- 1) Run XRF scans on 2 samples, from wildfire source 1 and from no wildfire source 1 at the 2cm depth.
- 2) Run XANES Sulfur scan wildfire source 1 at the 2cm depth.
- 3) Run XANES Sulfur scan no wildfire source 1 at the 2cm depth.
- 4) Run Standards scans for Ferric Sulphate, Iron(II) Sulfide, Elemental Sulfur, Potassium Sulphate, Copper Sulfide, Zinc Sulfide and Calcium Sulphate
- 5) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 5cm depth.
- 6) Run XANES Sulfur scan wildfire source 1 at the 5cm depth.
- 7) Run XANES Sulfur scan no wildfire source 1 at the 5cm depth.
- 8) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 10cm depth.
- 9) Run XANES Sulfur scan wildfire source 1 at the 10cm depth.
- 10) Run XANES Sulfur scan no wildfire source 1 at the 10cm depth.
- 11) Run XANES Phosphorous scan wildfire source 1 at the 2cm depth.
- 12) Run XANES Phosphorous scan no wildfire source 1 at the 2cm depth.
- 13) Run Standards scans for Potassium Phosphate monobasic, Ferric Phosphate
- 14) Run XANES Phosphorous scan wildfire source 1 at the 5cm depth.
- 15) Run XANES Phosphorous scan no wildfire source 1 at the 5cm depth.
- 16) Run XANES Phosphorous scan wildfire source 1 at the 10cm depth.
- 17) Run XANES Phosphorous scan no wildfire source 1 at the 10cm depth.
- 18) *Repeat for Second Wildfire and no wildfire source if there is extra time*

Alt Procedure for Running Sulfur and Phosphorus

- 1) Run XRF scans on 2 samples, from wildfire source 1 and from no wildfire source 1 at the 2cm depth.
- 2) Run XANES Sulfur scan wildfire source 1 at the 2cm depth.
- 3) Run XANES Sulfur scan no wildfire source 1 at the 2cm depth.
- 4) Run XANES Phosphorous scan wildfire source 1 at the 2cm depth.
- 5) Run XANES Phosphorous scan no wildfire source 1 at the 2cm depth.
- 6) Run Standards scans for Ferric Sulphate, Iron(II) Sulfide, Elemental Sulfur, Potassium Phosphate monobasic, Ferric Phosphate, Potassium Sulphate, Copper Sulfide, Zinc Sulfide and Calcium Sulphate
- 7) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 5cm depth.
- 8) Run XANES Sulfur scan wildfire source 1 at the 5cm depth.
- 9) Run XANES Sulfur scan no wildfire source 1 at the 5cm depth.
- 10) Run XANES Phosphorous scan wildfire source 1 at the 5cm depth.
- 11) Run XANES Phosphorous scan no wildfire source 1 at the 5cm depth.

- 12) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 10cm depth.
- 13) Run XANES Sulfur scan wildfire source 1 at the 10cm depth.
- 14) Run XANES Sulfur scan no wildfire source 1 at the 10cm depth.
- 15) Run XANES Phosphorous scan wildfire source 1 at the 10cm depth.
- 16) Run XANES Phosphorous scan no wildfire source 1 at the 10cm depth.
- 17) *Repeat for Second Wildfire and no wildfire source if there is extra time*
- 18) **Repeat for second wildfire and no wildfire sources if time is available***

Potassium Phosphate monobasic

Monopotassium phosphate, MKP, (also potassium dihydrogenphosphate, KDP, or monobasic potassium phosphate), KH_2PO_4 , is a soluble salt of potassium and the dihydrogen phosphate ion. It is a source of phosphorus and potassium. It is also a buffering agent. When used in fertilizer mixtures with urea and ammonium phosphates, it minimizes escape of ammonia by keeping the pH at a relatively low level.

Potassium Sulphate

[http://www.ipni.net/publication/nss.nsf/0/ADD4AB8BDFABE40C852579AF007505D6/\\$FILE/NSS-05%20Potassium%20Sulfate.pdf](http://www.ipni.net/publication/nss.nsf/0/ADD4AB8BDFABE40C852579AF007505D6/$FILE/NSS-05%20Potassium%20Sulfate.pdf)

Ferric Sulphate

Ferric sulfate, or iron (III) sulfate, has the chemical formula $\text{Fe}_2(\text{SO}_4)_3$. It is a yellow crystalline salt that can be prepared from oxidation of [iron \(II\) sulfate](#) or treatment of ferric oxide or [ferric hydroxide](#) with [sulfuric acid](#). Ferric sulfate can be used as a mordant for dyeing purposes or coagulant for industrial wastes. By the FDA, ferric sulfate is a direct food substance affirmed as generally recognized as safe (GRAS). It is added in food products as a flavoring agent.

from DrugBank

FERRIC SULFATE is a yellow crystalline solid or a grayish-white powder. The primary hazard is the threat to the environment. Immediate steps should be taken to limit its spread to the environment. It is used for [water](#) purification, and as a soil conditioner.

Calcium Sulphate

CALCIUM SULFATE is a calcium salt that is used for a variety of purposes including: building materials, as a desiccant, in dentistry as an impression material, cast, or die, and in medicine for immobilizing casts and as a tablet excipient. It exists in various forms and states of hydration. Plaster of Paris is a mixture of powdered and heat-treated gypsum.

from MeSH

CALCIUM SULFATE is an odorless, white powder or colorless, crystalline solid. Crystals sometimes have a blue, gray or reddish tinge or can be brick red. Density: 2.96 g cm^{-3} .

Elemental Sulfur

Sulfur is an essential component of all living cells. It is the seventh or eighth most abundant element in the human body by weight, about equal in abundance to potassium, and slightly greater than sodium and chlorine. A 70 kg (150 lb) human body contains about 140 grams of sulfur.

In plants and animals, the amino acids cysteine and methionine contain most of the sulfur, and the element is present in all polypeptides, proteins, and enzymes that contain these amino acids. In humans, methionine is an essential amino acid that must be ingested. However, save for the vitamins biotin and thiamine, cysteine and all sulfur-containing compounds in the human body can be synthesized from methionine. The enzyme sulfite oxidase is needed for the metabolism of methionine and cysteine in humans and animals.

Copper Sulfide

Contains copper and lead sulfide in copper concentrates. Insoluble in water and denser than water. Primary hazard is to the environment. Immediate steps should be taken to limit spread to the environment. Chemical intermediate byproduct of the manufacturing processes. Chemical and physical properties vary depending on the components present.

Ferric Phosphate

Iron phosphate is a compound that combines phosphorous and oxygen with iron. It can kill slugs and snails when eaten. The toxicity of iron compounds like this depends on the amount of available iron. Iron is an essential mineral for plants and animals. It can be found in the environment, foods, and water. Iron phosphate has been registered for use in pesticide products in the United States since 1997.

Iron (II) Sulfide

Iron(II) Sulfide (Ferrous Sulfide) is a moderately water and acid soluble Iron source for uses compatible with sulfates. Sulfate compounds are salts or esters of sulfuric acid formed by replacing one or both of the hydrogens with a metal. Most metal sulfate compounds are readily soluble in water for uses such as water treatment, unlike fluorides and oxides which tend to be insoluble. Organometallic forms are soluble in organic solutions and sometimes in both aqueous and organic solutions. Metallic ions can also be dispersed utilizing suspended or coated nanoparticles and deposited utilizing sputtering targets and evaporation materials for uses such as solar energy materials and fuel cells. Iron Sulfide is generally immediately available in most volumes. Ultra high purity and high purity compositions improve both optical quality and usefulness as scientific standards. Nanoscale elemental powders and suspensions, as alternative high

surface area forms, may be considered. American Elements produces to many standard grades when applicable, including Mil Spec (military grade); ACS, Reagent and Technical Grade; Food, Agricultural and Pharmaceutical Grade; Optical Grade, USP and EP/BP (European Pharmacopoeia/British Pharmacopoeia) and follows applicable ASTM testing standards. Typical and custom packaging is available. Additional technical, research and safety (MSDS) information is available as is a Reference Calculator for converting relevant units of measurement.

Zinc Sulfide

ZINC SULFIDE is a yellowish-white powder in a liquid. Insoluble in [water](#) and denser than [water](#). Primary hazard is to the environment. Immediate steps should be taken to limit spread to the environment. Easily penetrates the soil to contaminate groundwater and nearby waterways.

Science Permit

Brief Description

The purpose of the proposed experiment is to determine the chemical changes caused by wildfires in ecosystems, specifically Boreal forests. The experiment is designed to gain an understanding of the magnitude and complexity of these chemical changes in the soil. Sulfur and phosphorus will be the primary focus of the study. Examining the speciation, concentration and distribution of these elements in the soil and throughout the various soil horizons will develop an understanding of the soil quality and the effects fire has on the local ecosystem. To test the hypothesis, a series of scans will be conducted on samples of soil, both affected and not affected, at various depths. A few more scans will be taken on standards and compared to other samples to look at any differences between the oxidation states of both, the fire affected and unaffected samples. Upon completion of the experiment, the team hopes the results will help us better understand the positive or negative effects of forest fires on soil chemistry. Specifically in regards to soil nutrients such as sulfur, phosphorous. This study can bring forth new information about the effects of forest fires. This new information can help in the recovery of soil after a forest fire and also make way for more research in this field.

Societal and Economic Impact

The topic of what happens to organic matter when exposed to extreme heat is a complex matter and is not fully understood by soil scientists. In our project we hope to shed a light on the chemical changes in soil when exposed to extreme heat. This information will allow Parks Canada and other environmental studies to better understand the aftermath of fires on the wildlife and the ecosystem affected. The fire in Fort McMurray is an ideal place to gather samples from as it is close to our school in Calgary, and its residents and ecosystem are still

experiencing the impact of the large-scale forest fire in 2016. The project intends to gather more information about this environmental issue that regularly happens throughout Canada and the world.

Value of the Results and Industrial Relevance

Approximately 42% of Canada's landmass is covered in forest, most of which resides in the Boreal Forest located in the northern regions of Alberta and Canada. This forested region serves as a major contributor to Canada's natural resource exports while also being a vast, unique and important ecosystem. Remarkably, Canada's Boreal Forest accounts for 10% of the world's forested land. Forest fires are a common occurrence, functioning as both negative and positive events, ultimately affecting the local ecosystem in one of such ways. These effects can be traced deep into the soil of the affected region. The full extent of the influence of forest fires is currently not well understood; minimal research has been conducted to study the behaviour and potential changes of Sulfur in the soil. Results will enable environmentalists, developers, biologists, and soil scientists to better understand such changes. Additionally, it may aid in the development of products or procedures that can improve forest recovery following a fire. This research may introduce new methods of exportation of Canada's forests; ideally, in a more environmentally friendly manner, while helping to preserve and maintain the forest ecosystem. The aim of this project is to bridge the gap between fire and its relation to soil in forested and non forested areas. Through our results, we hope to expand upon this knowledge and identify other new and key components regarding the influence of forest fires.

Scientific Merit

The 2016 Fort McMurray forest fire was a devastating and costly disaster which burned down thousands of homes, displaced thousands of people, and destroyed hundreds of kilometers of forest. The extent of the damage remains unknown, and little is understood as to whether or not its effects are beneficial for the environment. The 2017-2018 SotB group has decided to examine soil in effort to understand the effects of forest fire on soil chemistry; specifically, we will be looking at the changes in the concentrations and oxidation states of sulfur & phosphorus. We chose a small area in Gregorian Lake Provincial Park to obtain samples; certain areas were unaffected by fire, and other areas weren't, providing a basis for comparison. Samples were taken from 3 areas of affected region, and 3 areas of unaffected regions, each approximately the same relative distance from one another. At each of these areas, 3-4 holes at approximately 20-30cm were dug as a precaution to compare the soil's profiles so as to remain relatively consistent. From these holes, one is to be used to obtain samples. All holes were documented and photographed. Samples were taken as follows: An Organic (surface) Layer, Mineral Layer @ 2cm, Mineral Layer @ 5cm, Mineral Layer @ 10cm. In total this yields 24 samples. These will be narrowed down to the samples that will most likely contain the highest concentrations of the elements and species of interest: sulfur and phosphorous. Sulfur has the largest role in the environment; a possible pollutant and vital nutrient for plant or bacterial growth. Phosphorous is part of a large cycle that carries nutrients throughout the soil and is the

backbone for many chemical processes. We intend to carry out XRF and XANES scans with the low energy crystal using the IDEAS beamline. Sulfur, and phosphorous standards will be used to perform linear combination fitting; this will provide a basis for comparison so we may determine the specific species in our samples. From our research thus far, we predict that the layers closest to the surface will have greater concentrations of each element, and/or will experience the most substantial changes in its soil chemistry. It is likely that there will be change in the amount of elemental sulfur, sulfides and sulphates between the wildfire and no wildfire sources, along with possible variation in the speciation. The results are significant, as they may provide insight into the quality of the soil, and whether fire can affect those characteristics. Soil is relevant to agriculture, mining, water quality and biological processes in the ecosystem. If there is a change in the concentrations, oxidation states and speciation of sulfur and phosphorus in the soil, there may also be a change in the ecosystem and variation of species in the Fort McMurray area.

Past Productivity

In October of 2016, five of the students on this team conducted research at the CLS . The 2016 team worked on a project examining the changes in the concentration and oxidation states of Chromium (VI), Chromium (III) and Arsenic in the tailings ponds of Northern Alberta. The Team discovered that there is not a significant or measurable amount of Chromium (VI) or Arsenic in the tailings ponds. There was evidence that the Chromium (III) species can be found in the tailings ponds. We also concluded that the bitumen extraction process does little to remove this elemental species from the ponds. The poster created for this project won the 2017 Students on the Beamline Poster Contest. Bishop Carroll has been sending a team to the CLS for 7 years straight and has had the privilege to work on a wide range of projects. Previous research has involved heavy metals in cow's milk, and the process of bacteria denaturing naphthenic acid in the tailings ponds.

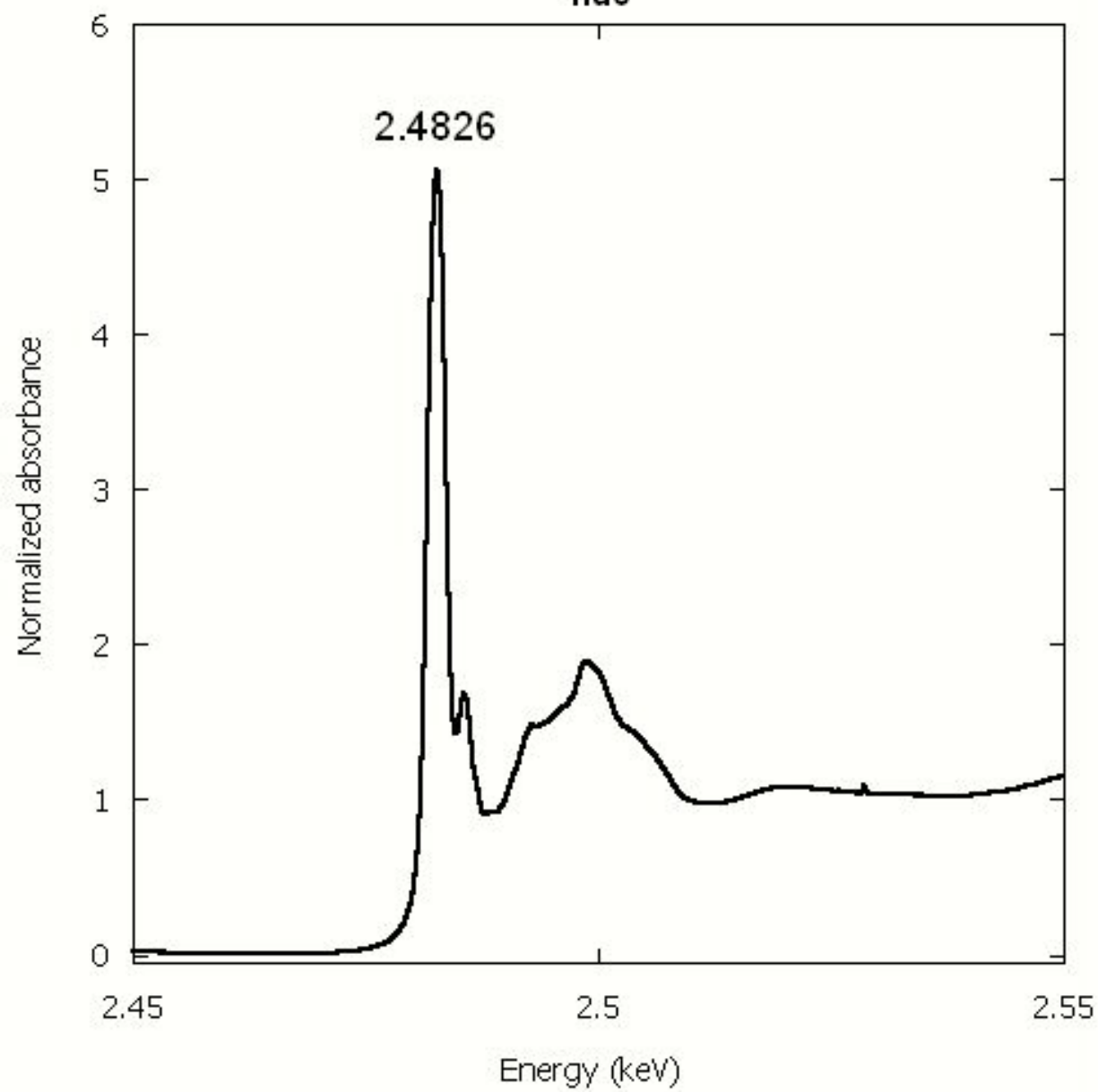
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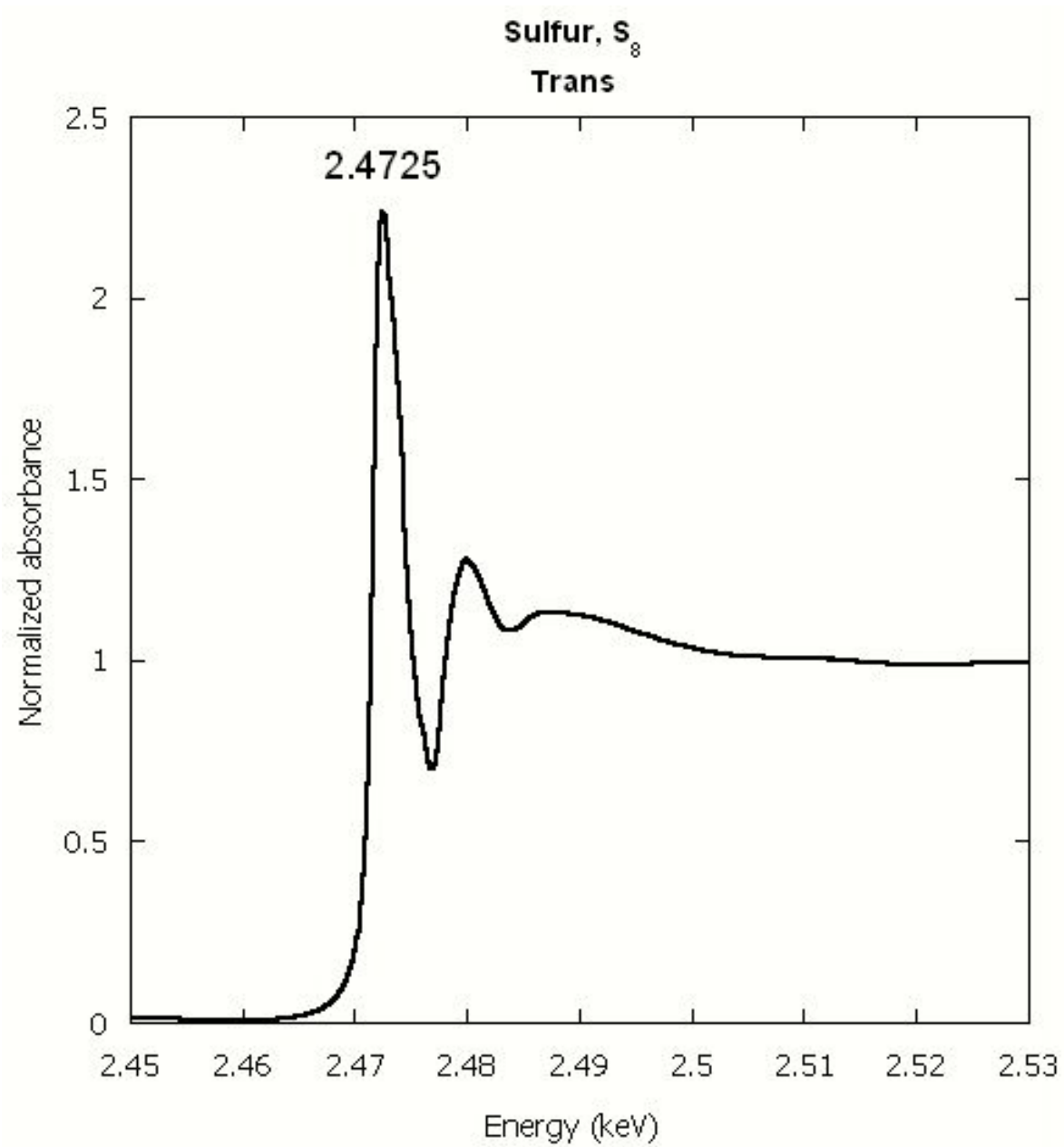
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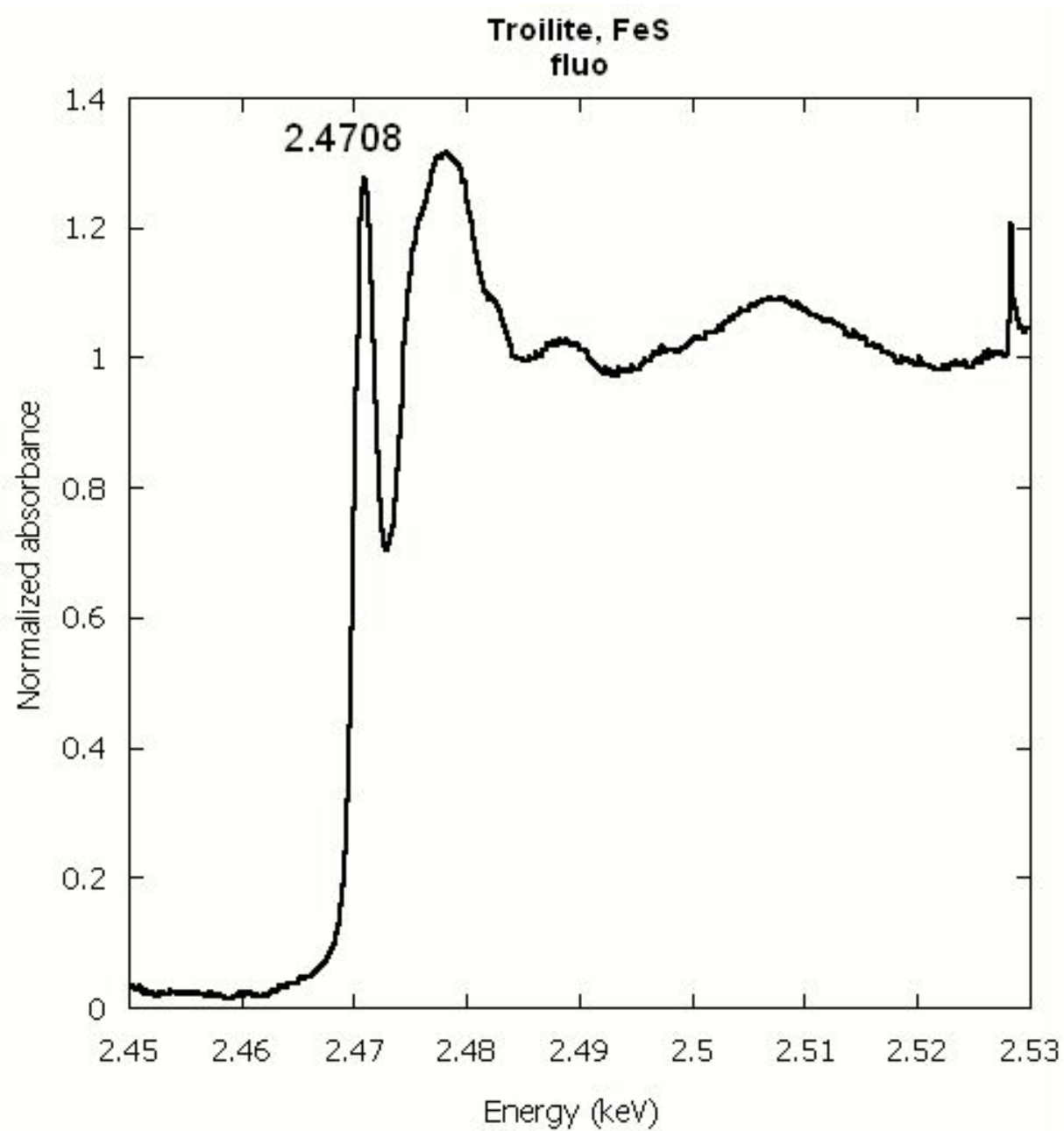
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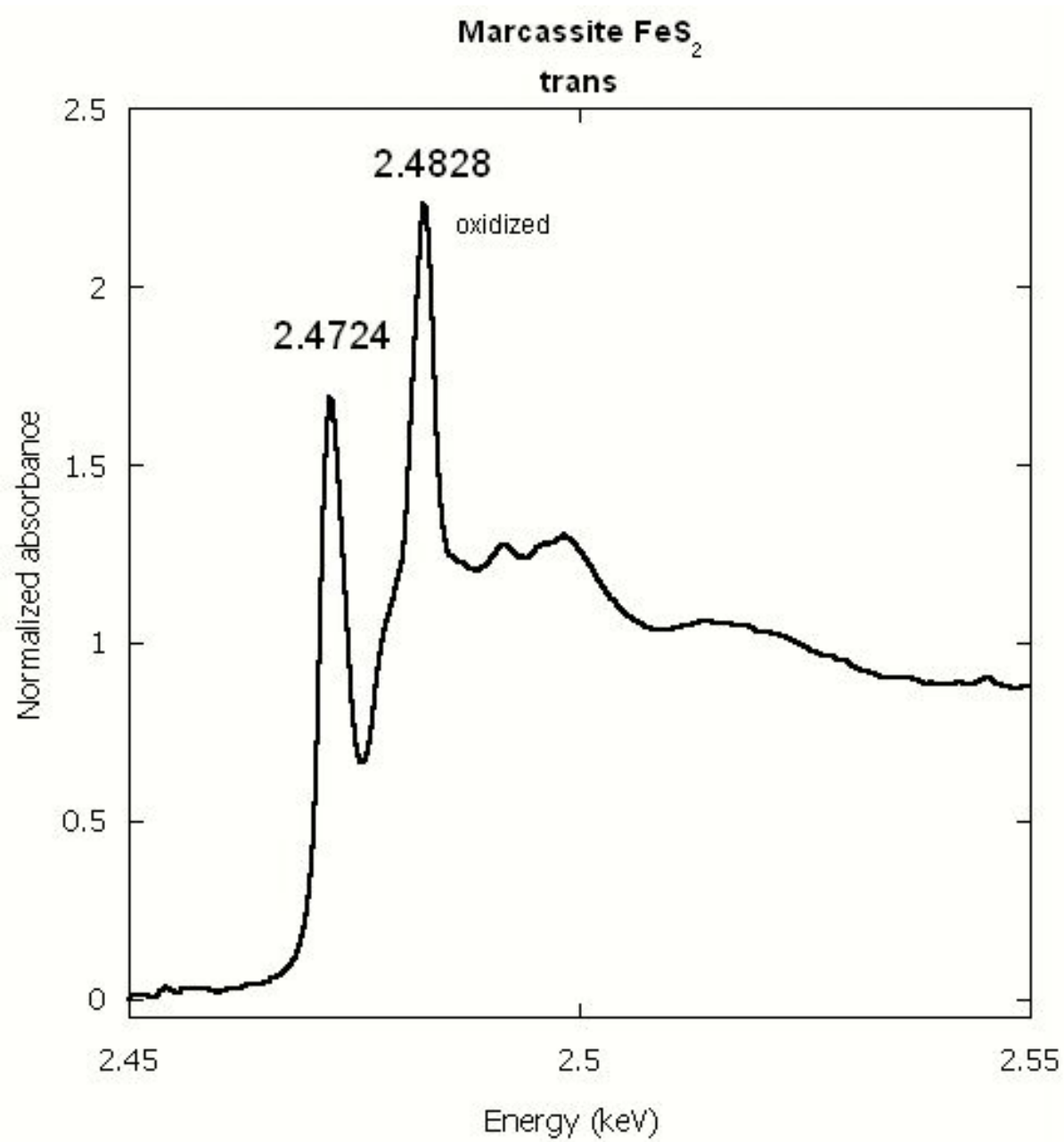
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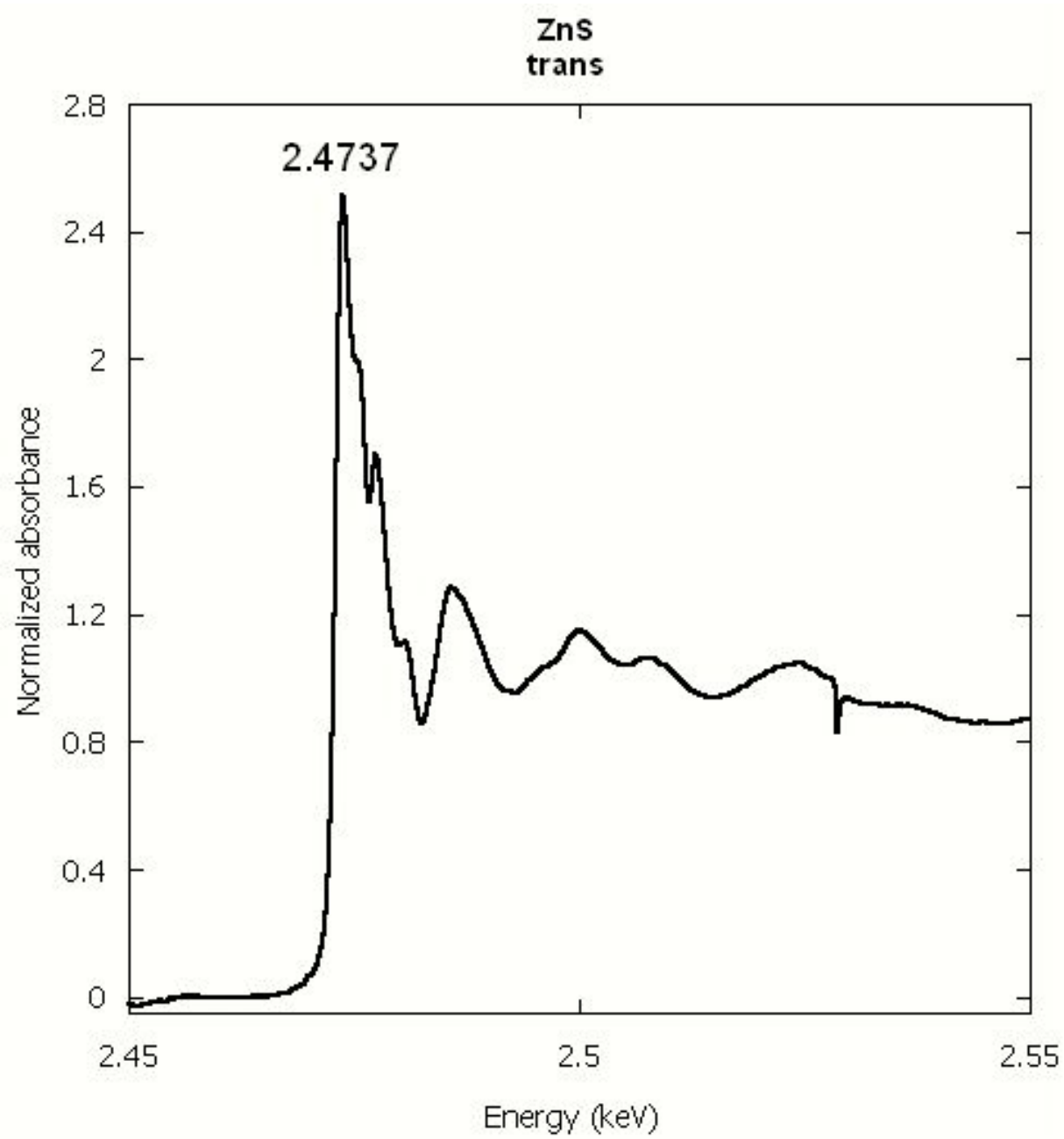
Anhydrite $\text{Ca}(\text{SO}_4)$
fluo











Ferric Phosphate

