The James Hutton Institute

Food and Agriculture Organization of the United Nations

GLOSOLAN
Soil spectroscopy training workshops

Interpretation of Mid Infrared Spectra of Soil - Direct Use of Spectra to Provide New Insights

Online webinars

Jean Robertson

GLOBAL SOIL PARTNERSHIP

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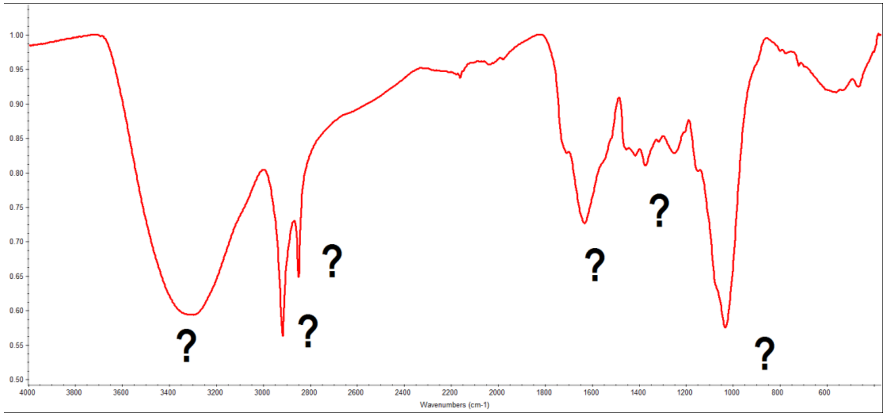
MIR Analysis of Soil



Presentation outline

- Introduction to Infrared (IR) Spectroscopy in the mid infrared (MIR) region and MIR spectra of soil samples
- Applications of MIR Spectroscopic analysis of soil
- How to approach interpretation of MIR spectra of soil: spectral quality, sampling method, sample preparation and interpretation procedure
- Spectral features of organic soils
- Spectral features of mineral soils
- Summary of steps for interpretation of MIR soil spectra

The Infrared (IR) Region

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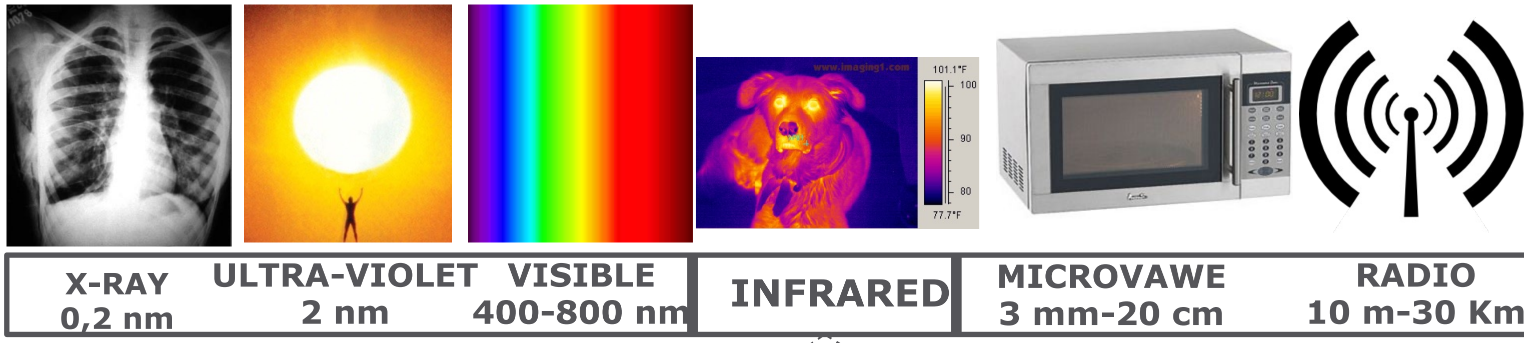
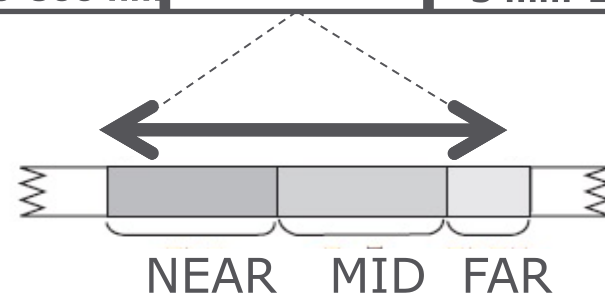




Infrared radiation provides a level of energy that corresponds to that of vibrational energy transitions in molecules hence will be absorbed by molecular inter-atomic vibrations

λ, m (wavelength)
Near -780 to 2500nm **Mid**-2.5 to 25 µm **Far** -30-300 µm

1/λ, cm^{-1} (wavenumber)
Near -12820 to 4000 **Mid**- 4000 to 400 **Far** -400 to 33

IR Spectroscopy

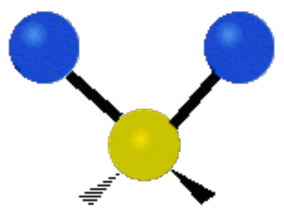
Principles

- Molecules interact with the electric vector of infrared (IR) radiation resulting in absorption at different frequencies

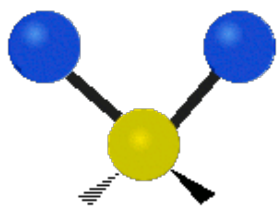
- Compounds require to have covalent bonds and exhibit a change in dipole moment during chemical bond vibrations to be IR active

- Different functional groups absorb at several frequencies involving different types of chemical bond vibrations e.g stretching and bending

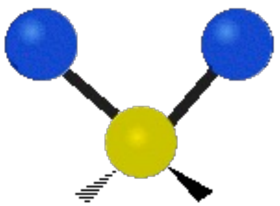
Stretching and Bending molecular vibrations



Symmetric stretching



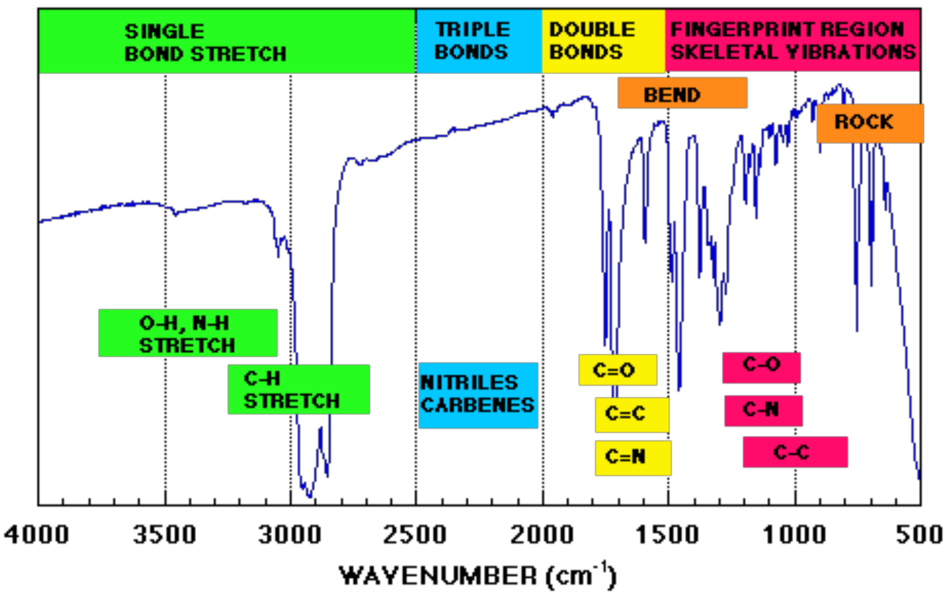
Anti-symmetric stretching

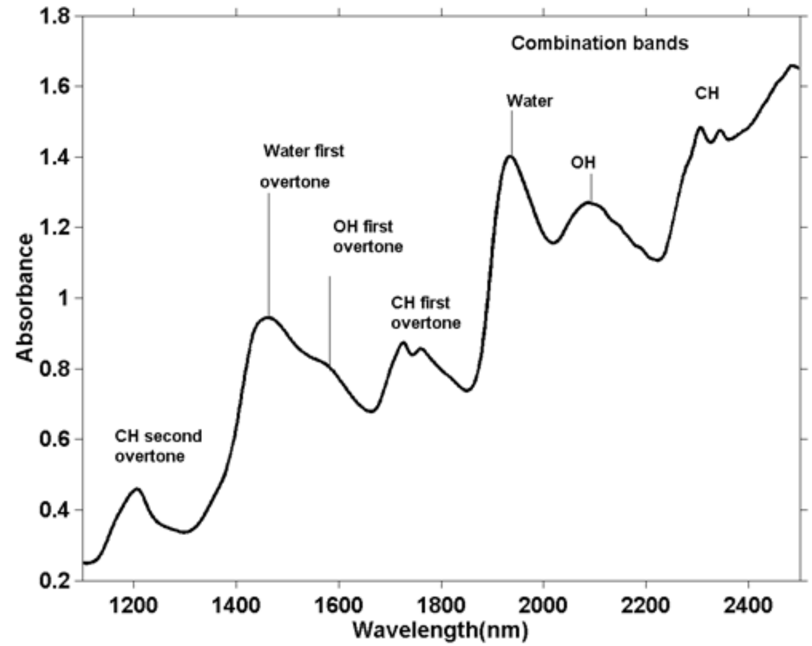


Bending

Water Molecule

MIR vs. NIR





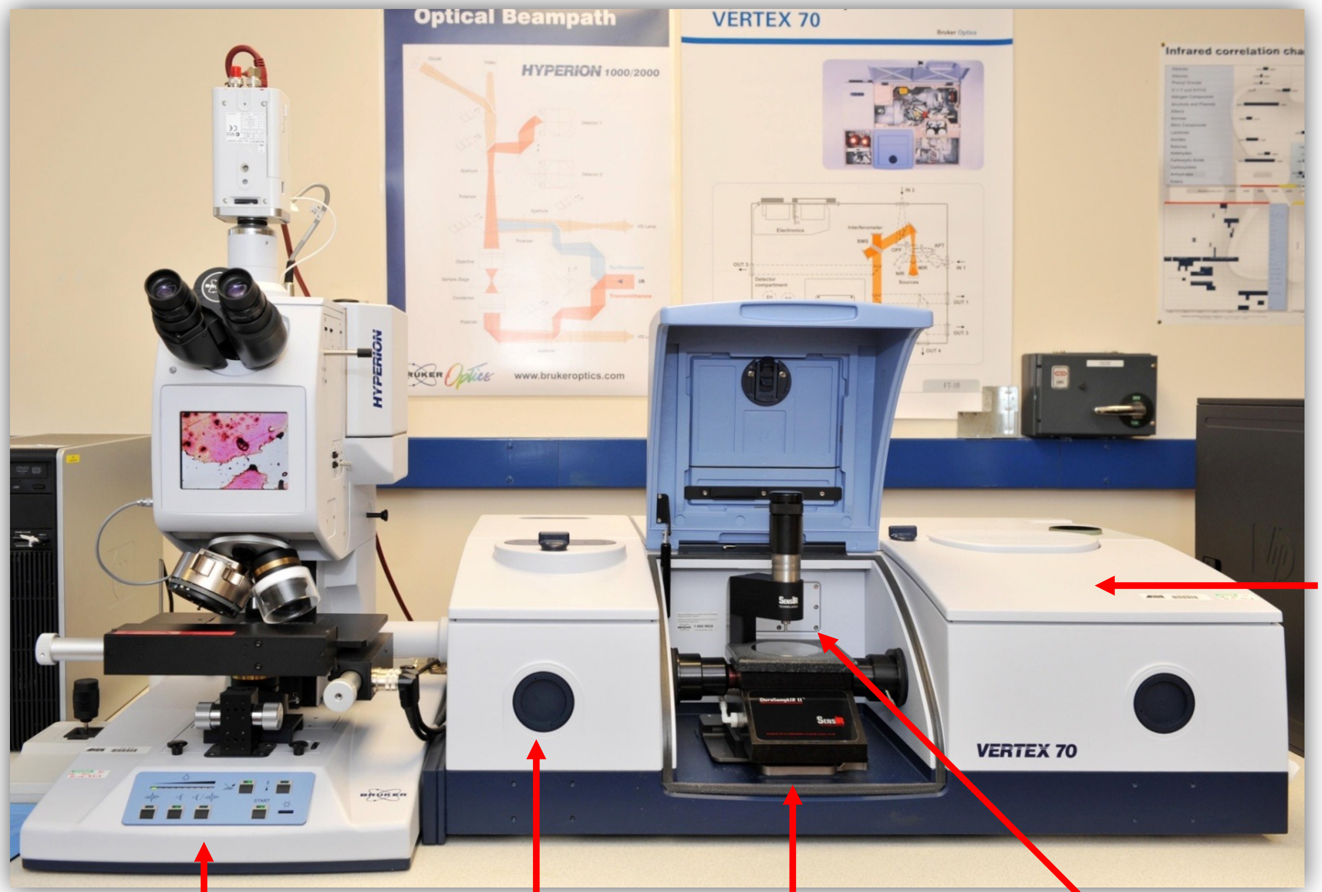
Mid infrared (4000-400 cm^{-1})

- **Fundamental vibrations** of bonds between molecules that absorb IR light
- Spectra provides fingerprint of substances which are more readily interpreted
- More complete profile of inorganic and organic components

Near infrared (1100-2500 nm)

- **Combination bands and overtones of MIR fundamentals**
- Overlooked: complex spectra
- More energetic radiation: allows deeper penetration into sample

FTIR Spectrometer



Source

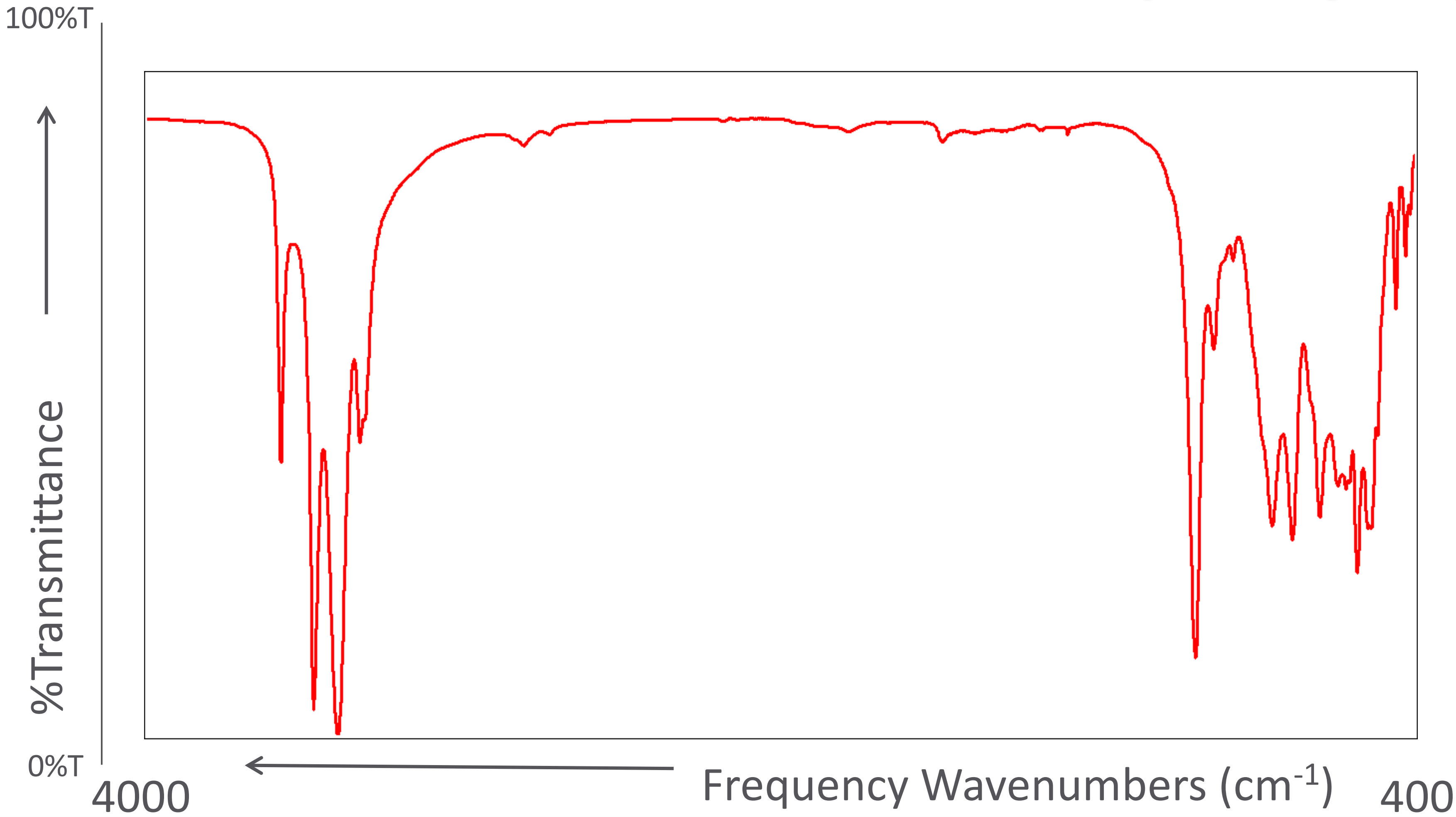
IR Microscope

Detector

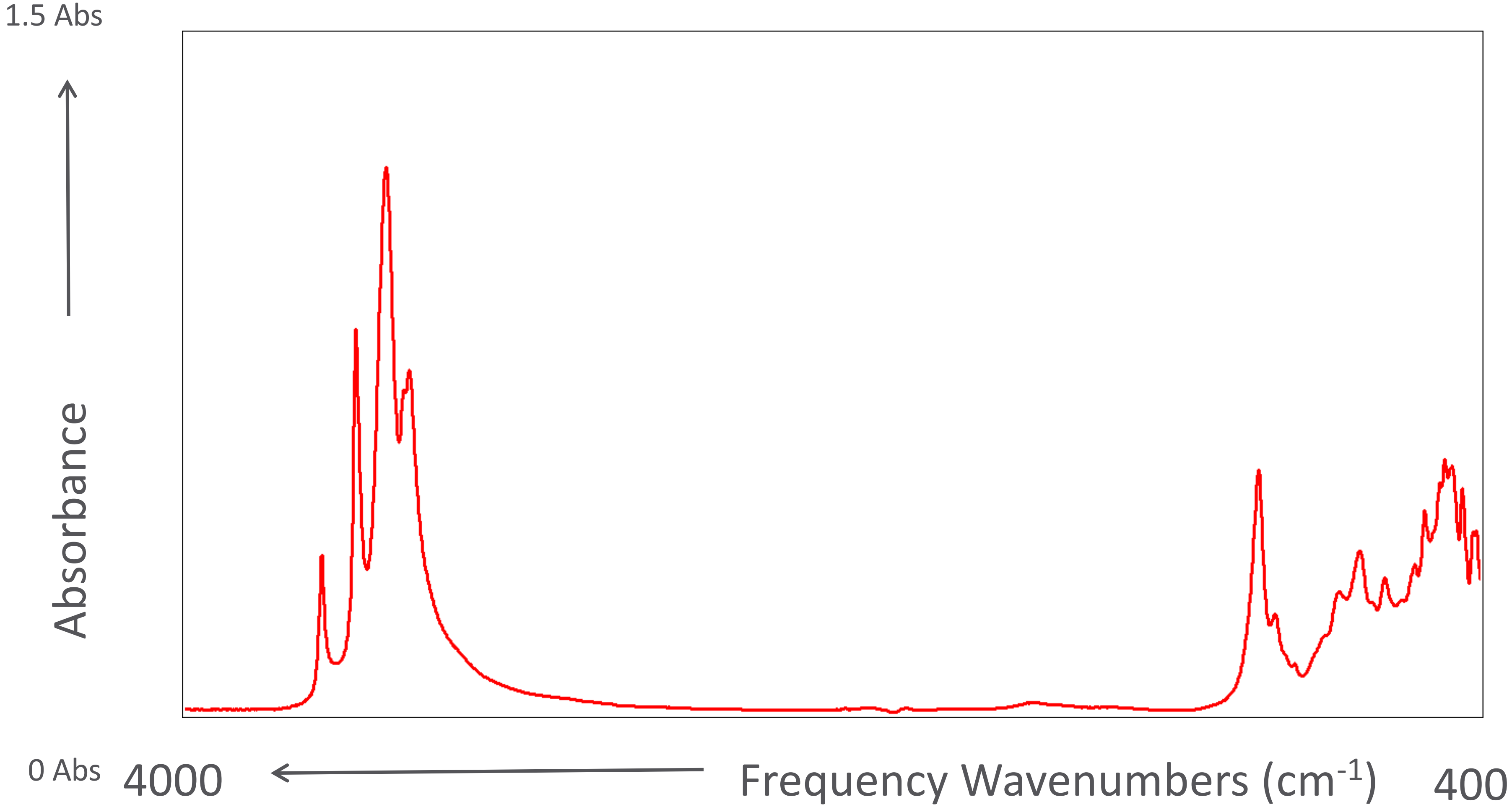
Sample compartment

DATR Sampling accessory

Infrared Spectrum
Plot of Transmittance vs Frequency



Infrared Spectrum
Plot of Absorption vs Frequency

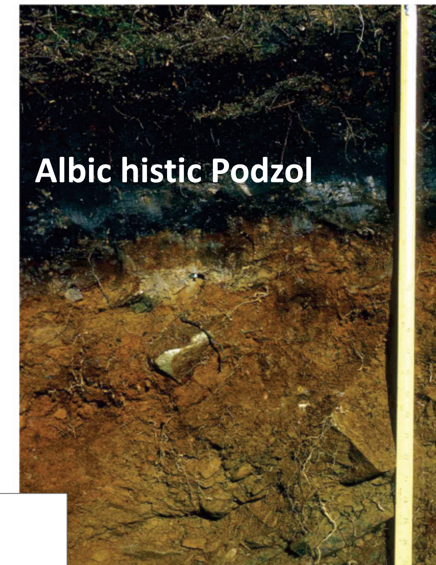


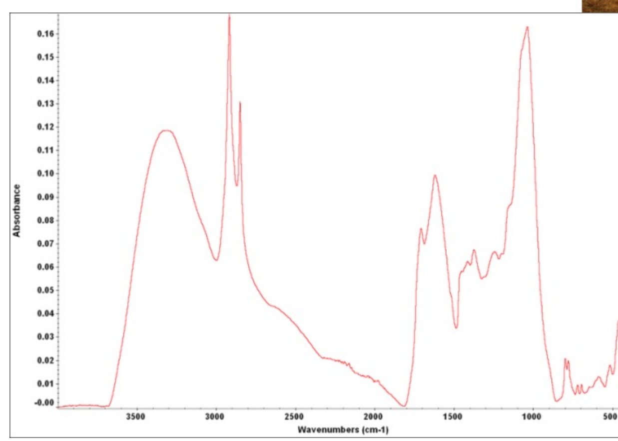
MIR Spectra of Soil Samples

- An FTIR (Fourier Transform Infrared) spectrum in the mid infrared (MIR) region of a soil sample, produced when infrared radiation is absorbed by a soil sample, gives the overall chemical profile of the soil

- Importantly, FTIR spectra can provide information about both the **organic** and **mineral** components of the soil

- Absorption bands in the IR spectrum (4000 to 400 cm^{-1}) relate to fundamental vibrations of the functional groups present in the sample





Robertson et al. (2016)
Spectroscopy Europe Vol 28 no 4

Applications of MIR Spectroscopic Analysis of Soil

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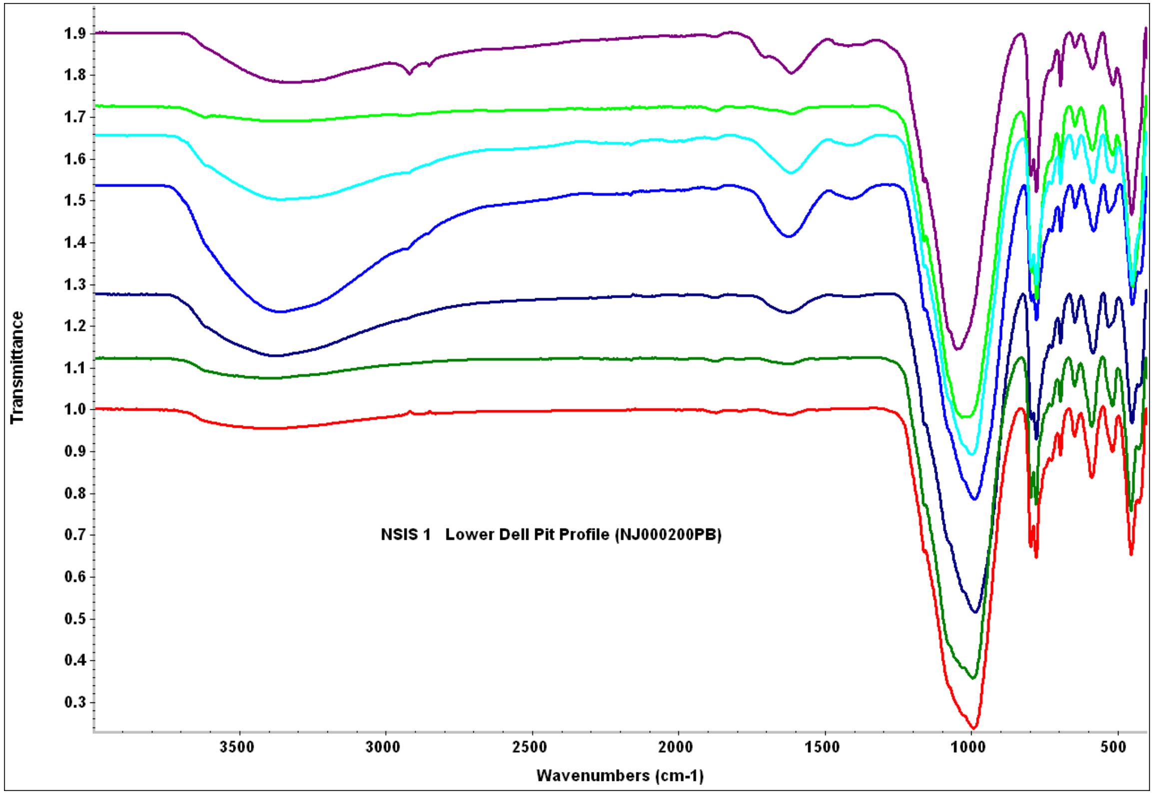
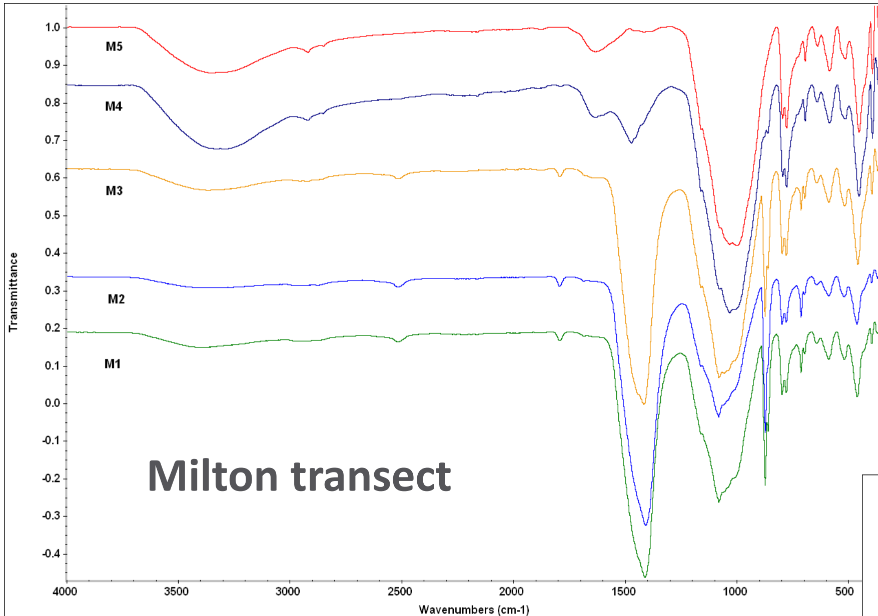
Monitoring changes down a pit profile

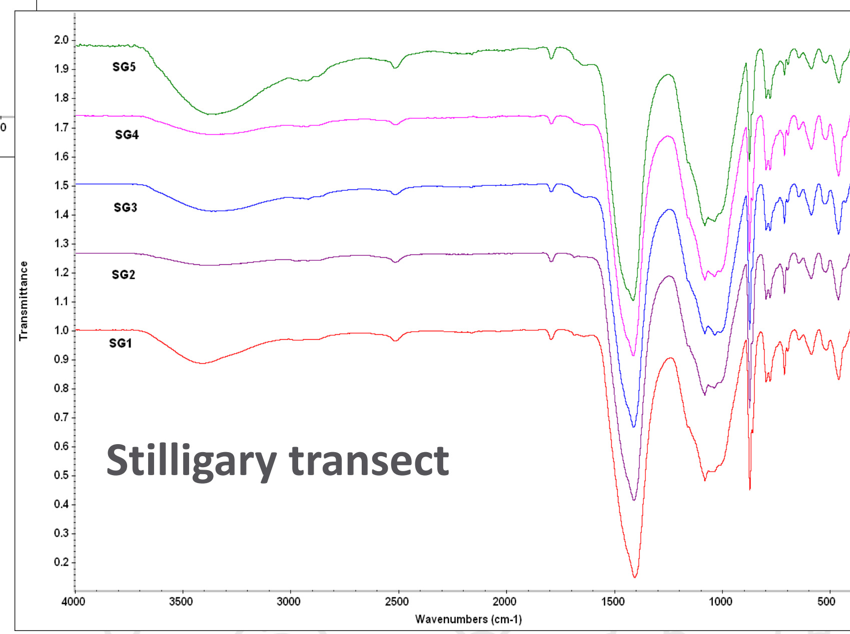


Soil Wind Erosion Studies



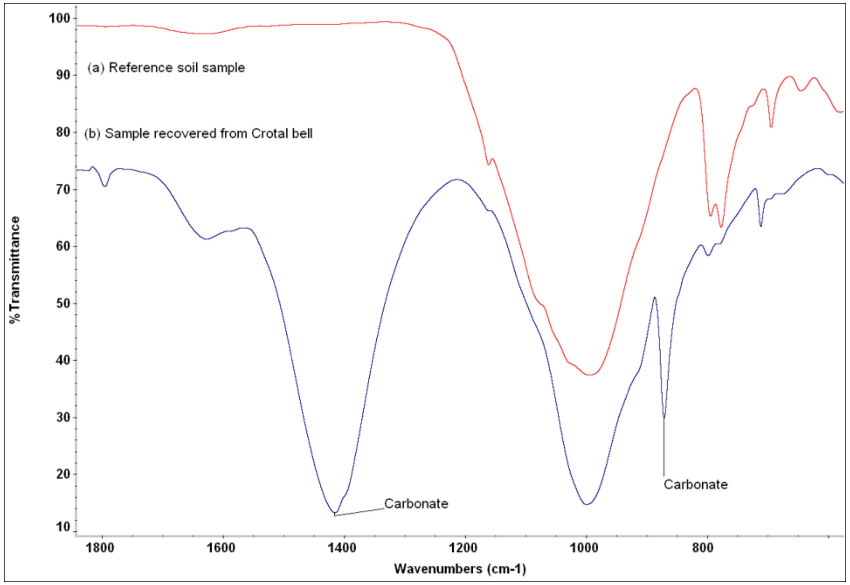
Some transects shows a change from carbonate dominated to purely silicate based soil as you move inland from the coast...

...while others show little change



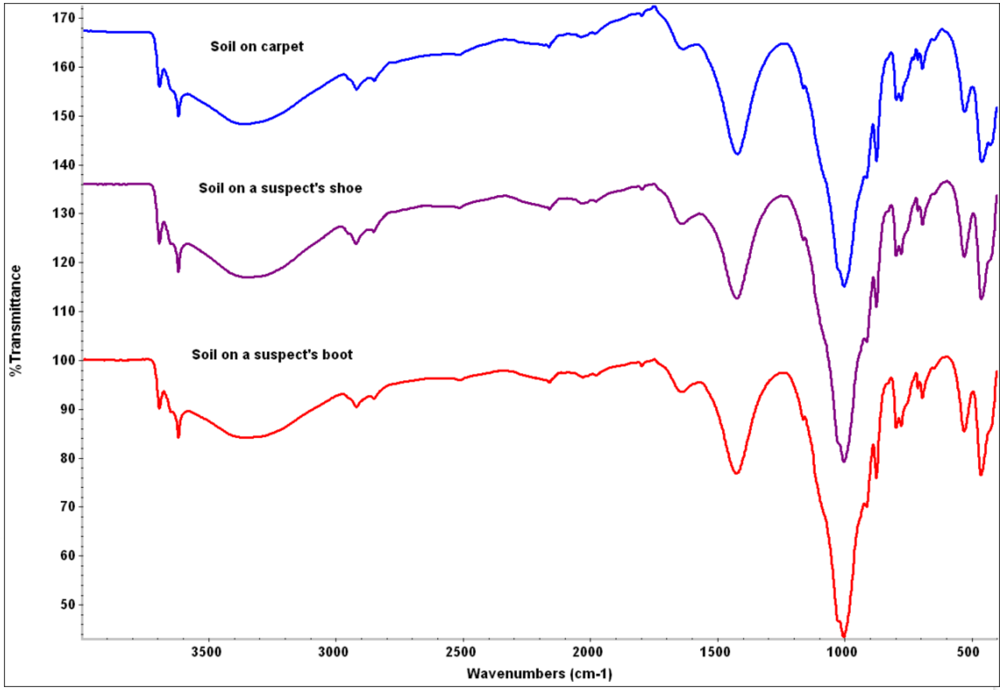
Young et al (2015) Catena 135(December):1 DOI:10.1016/j.catena.2015.06.015

Analysis of Soil for Forensic Investigation



Treasure trove – is this the original burial site of the artefacts?

Crime -can a suspect be linked to the scene of a crime through soil evidence?



Robertson et al. (2015) Spectroscopy “FT-IR Technology for Today’s Spectroscopist” Vol 30 , s8, pp 22-30

Assessment of Peat condition

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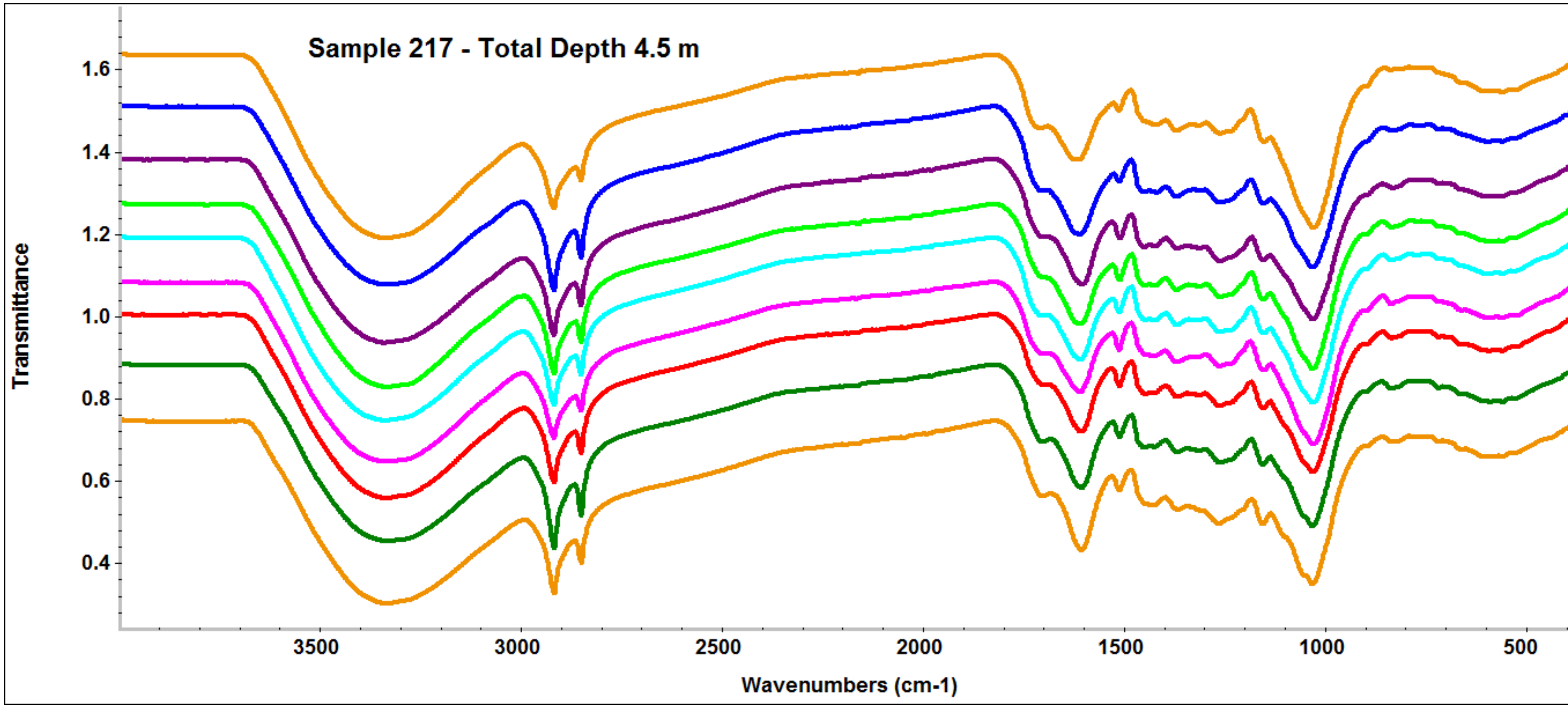

Increasing depth

Characterisation of soil under different long-term treatments

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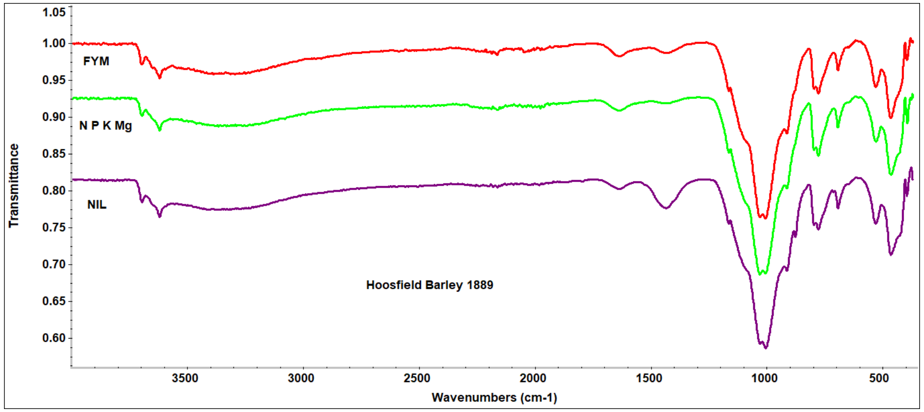
- Characterisation of soil, including the nature of organic matter (SOM), on selected plots of the Broadbalk and Hoosfield long term experiments at Rothamsted
- Variation in two different series of soils which have undergone long-term addition of FYM over time compared with corresponding soils which have had long term N, P, K & Mg addition and unfertilised control
- For each experiment 8 time points over ~150 years were selected for both the FYM, NPKMg and control treatments (48 samples in total)

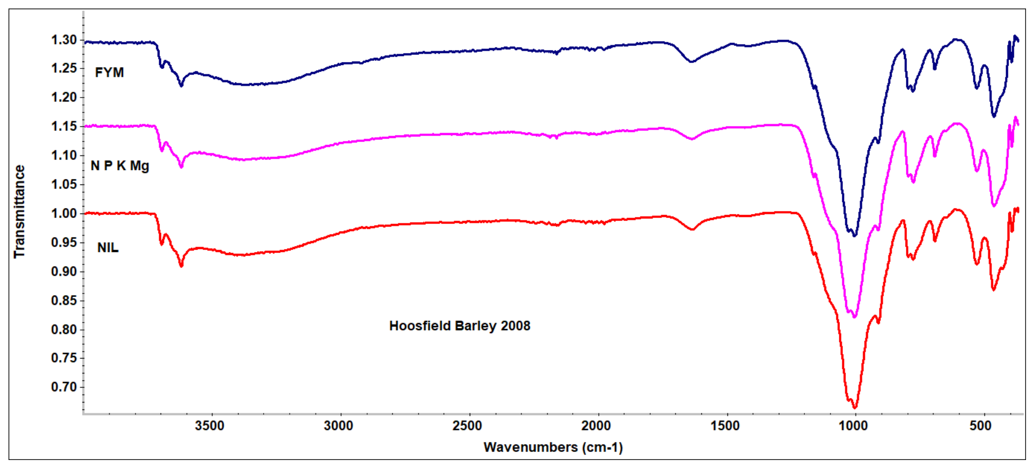
RRes_LTE Guidebook_2018__web AW.pdf (rothamsted.ac.uk)

Preliminary Results – Hoosfield Barley



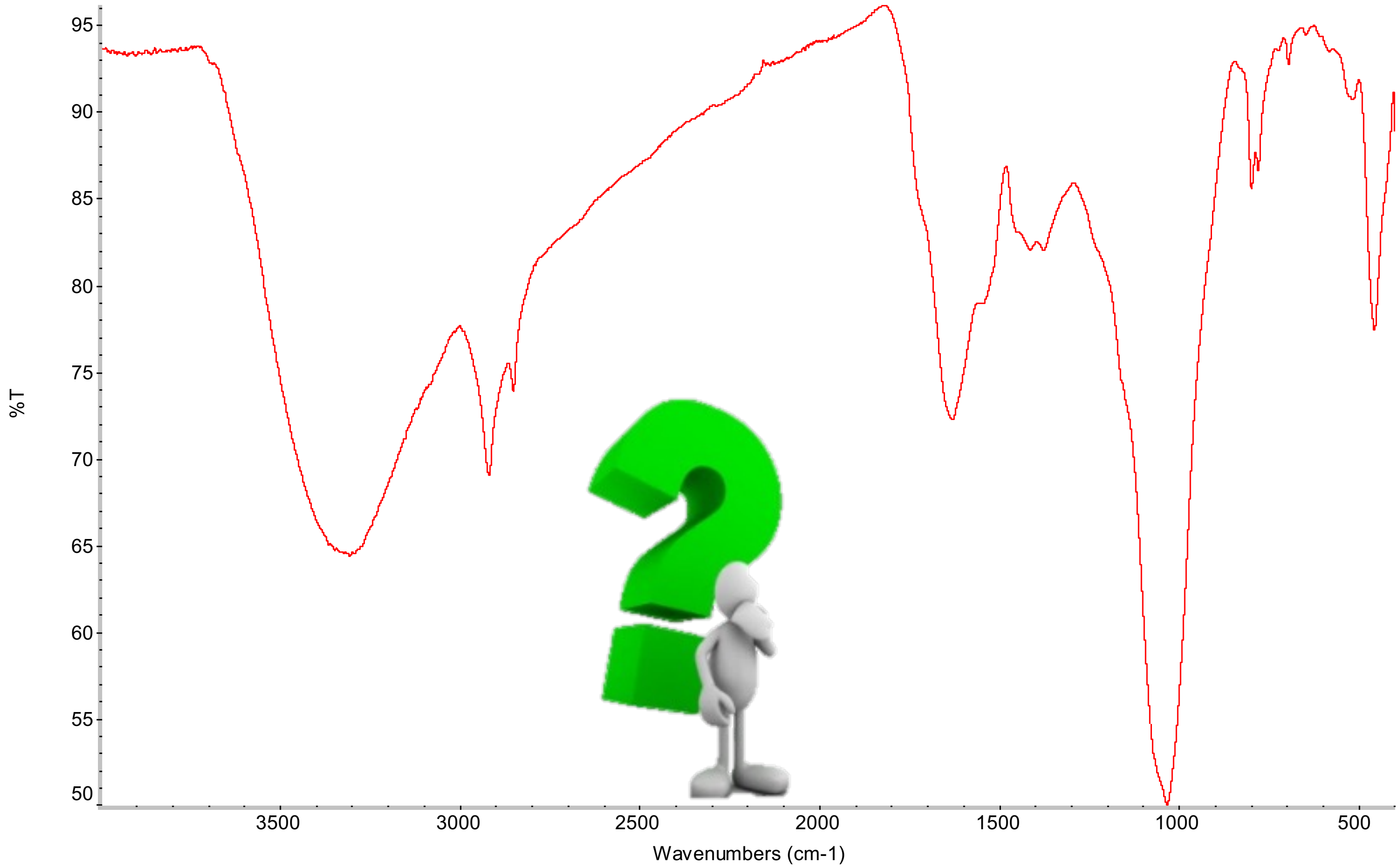
Differences between treatments are subtle but evident

Variations between plots due to sampling date



AHDB Rotations Research Partnership | AHDB

But how do we work out what it all means??



How to Approach Infrared Spectral Interpretation of Soil

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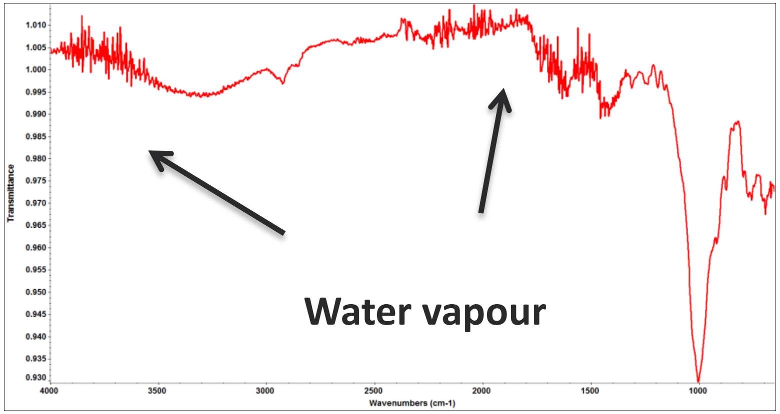
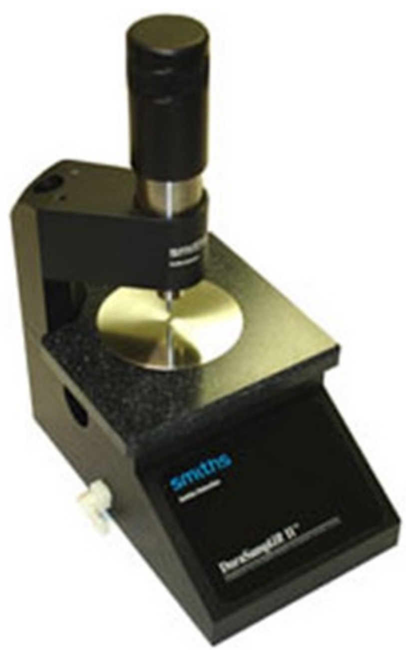
1. Use high quality data, e.g. Good signal/noise ratio, no water vapour spikes or carbon dioxide interference. The most intense band should be less than 2 in absorbance

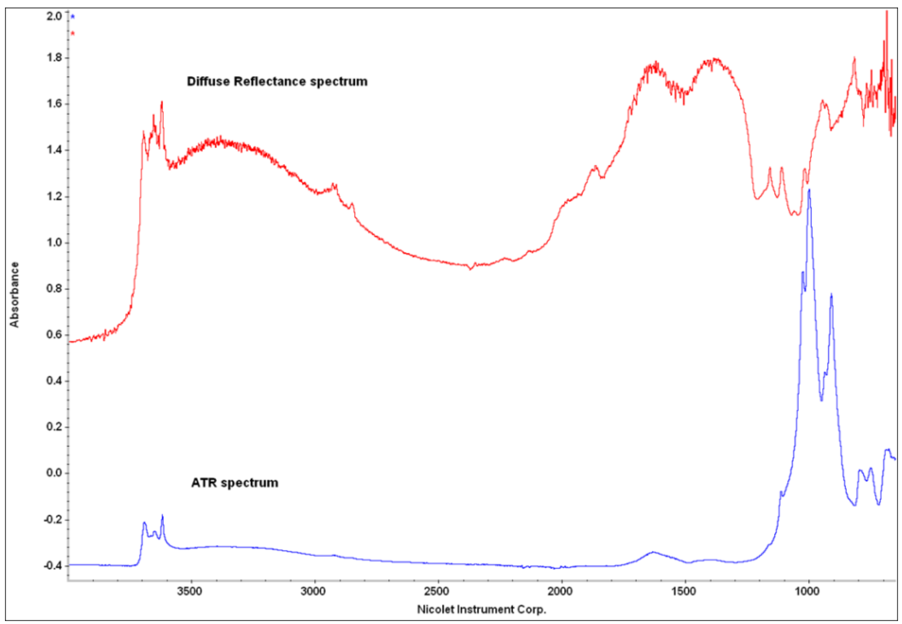


Example of a poor quality spectrum

Different sampling methods for IR spectra

- The FTIR spectra of soil samples can be recorded using a range of different sampling methods: Transmission; Diffuse Reflectance (DRIFTS) and Attenuated Total Reflectance (ATR)
- Both DRIFTS and ATR spectra can also be recorded in the field
- Appearance of the two types of spectra is very different

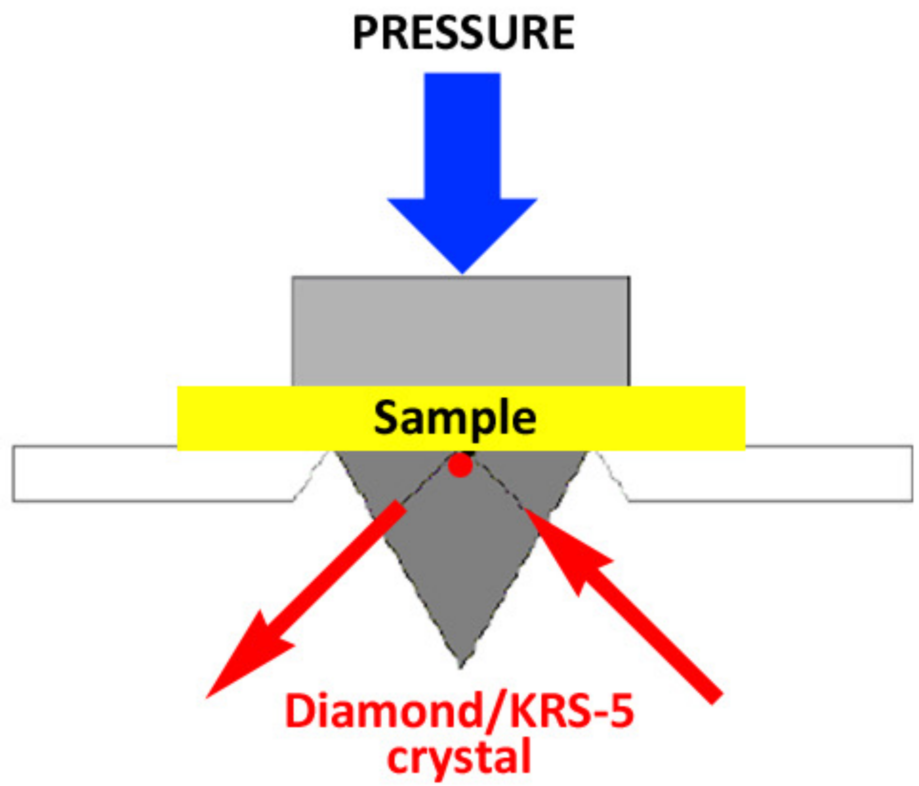




T. Nguyen et al (1991) Aust. J. Soil Res. 29(1), 49–67

Robertson, Wetterlind et al. (2019) Proceedings of the 5th Global Workshop on Proximal Soil Sensing, pp. 59 - 64

Single Reflection Diamond Attenuated Total Reflectance (DATR) Sampling Accessory



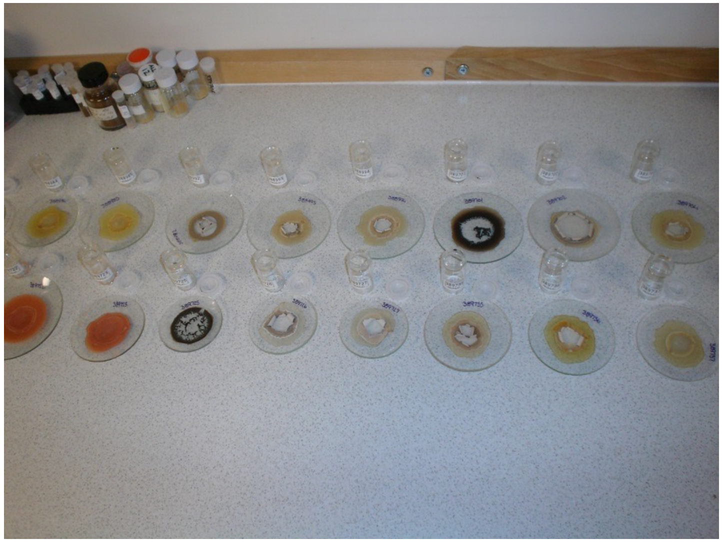
Advantages of DATR Accessory

- Sample can be placed, without processing, on the window
- Non destructive-sample can be recovered
- Economy of sample < 1mg
- Diamond crystal allows analysis of hard particles e.g. quartz
- IR beam only penetrates sample by a few µm- independent of sample thickness – so no absorbance issues
- Spectra are "Transmission like" and easy to interpret
- Optics are all internal so no issue with lighting conditions

Soil Sample Preparation Protocol

- It is very important that spectra are representative and reproducible
- For highest quality FTIR spectra of soil, in the Lab, samples should be dry and milled to < 2µm
- A sample preparation protocol was developed which produced samples with the optimal particle size, whilst avoiding problems of contamination or degradation of the samples:

McCrone milling with the agate barrels (12 minutes milling in water) followed by air drying and lightly grinding (in isopropyl alcohol) with the mortar and pestle gave the best results for the FTIR spectra



Robertson et al. (2013) Proceedings of the 3rd Global Workshop on Proximal Soil Sensing, pp. 182–185.

Milling Trial Results

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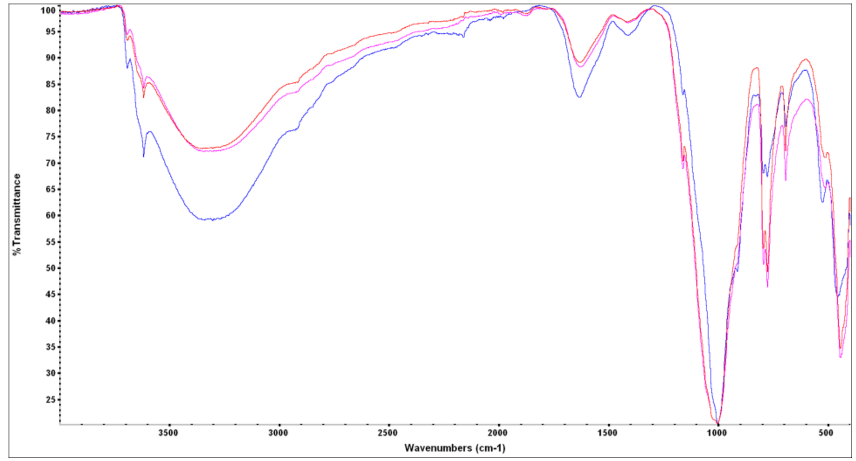
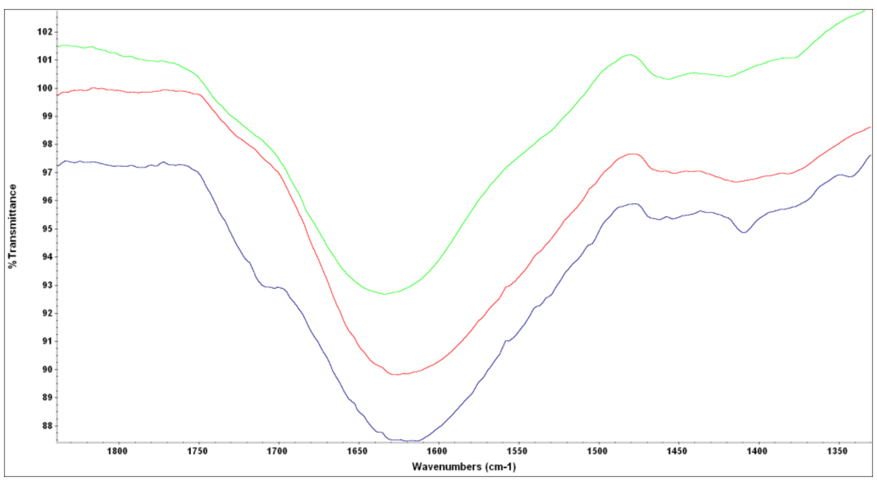
Differences in particle size change spectral pattern



Blue – ball milled 30 sec
Pink – ball milled 10 min
Red – McCrone milled 10 min



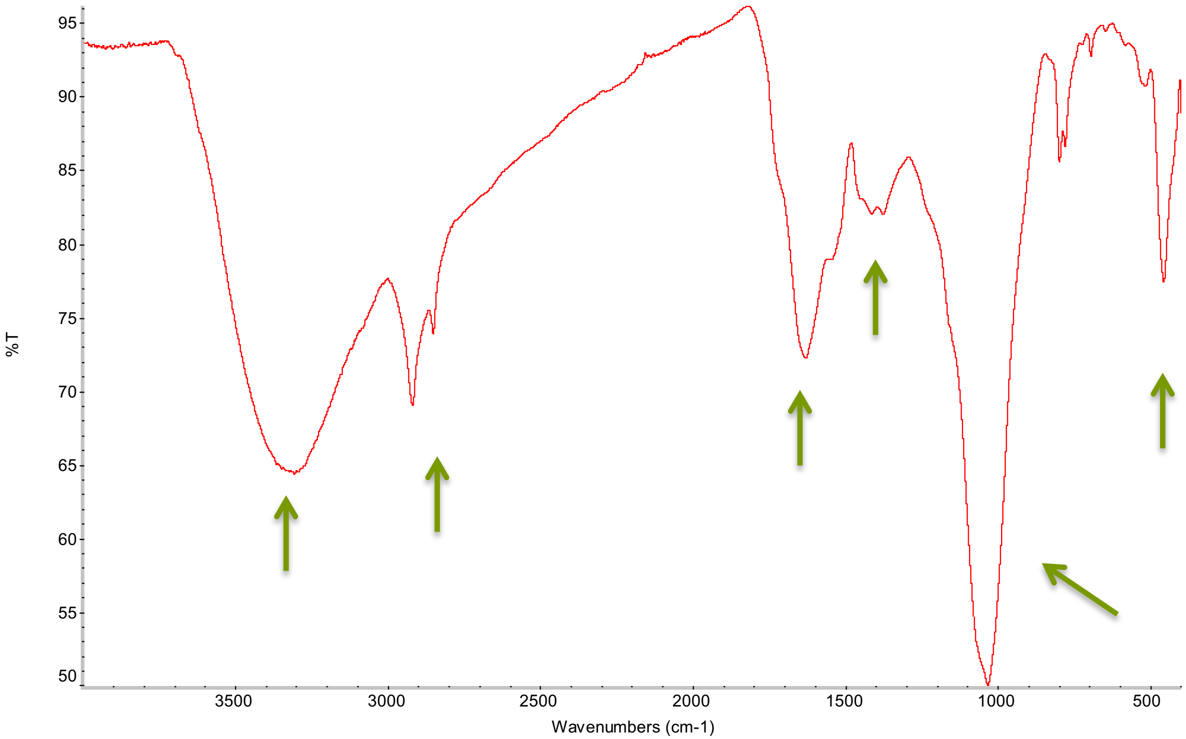
Changes in OM pattern when ball milling with tungsten carbide and water

Green – 30 sec
Red – 1 min
Blue – 10 min

Issues with contamination by agate (ball milling only) and corundum (McCrone mill)

How to Approach Infrared Spectral Interpretation of Soil

2. Look over the spectrum from left to right, noting the frequency (cm^{-1}) of the intense absorption peaks

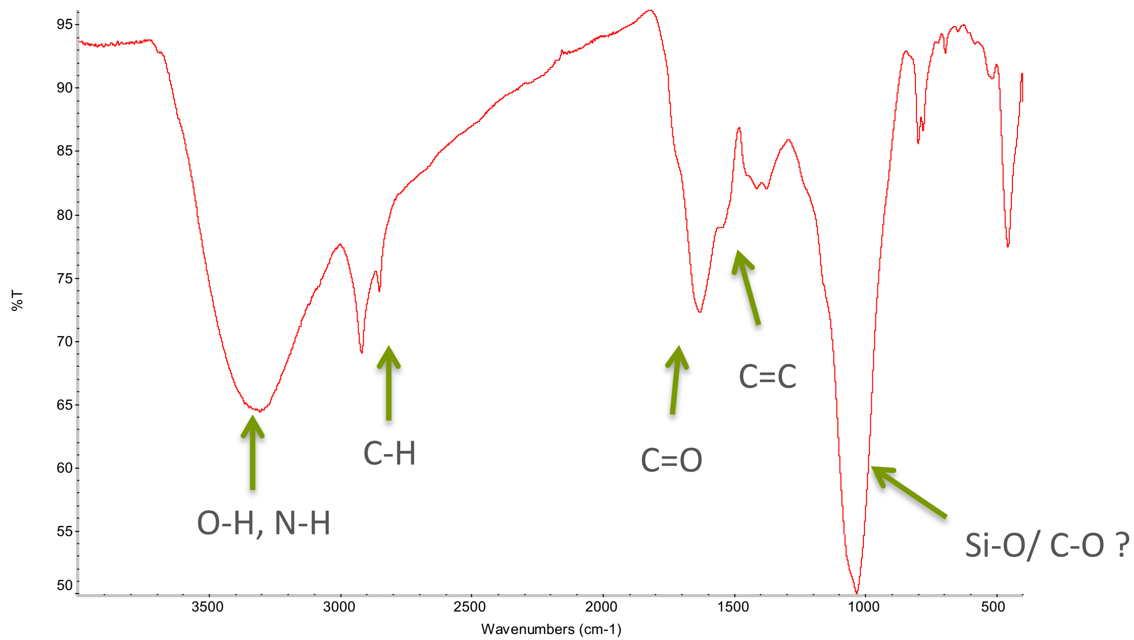


How to Approach Infrared Spectral Interpretation of Soil

3. Taking into account your knowledge of the sample (e.g. is it largely mineral or organic) assign the most intense bands first using correlation tables, or a reliable paper

4. Track down any secondary bands for the functional groups if possible – e.g. for protein/amide there should be amide I and amide II

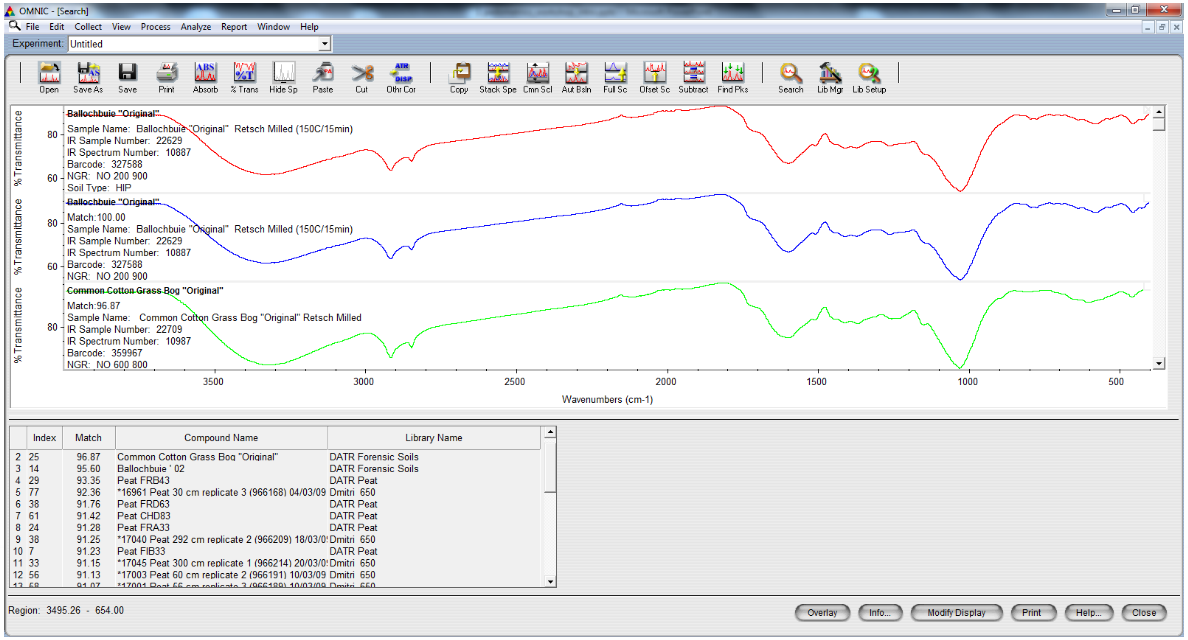
5. Assign other bands as needed



How to Approach Infrared Spectral Interpretation of Soil

6. Write down the SOM functional groups and/or minerals you think exist in the sample

7. Get help from spectral libraries or interpretation software – as soils are very complex mixtures



FTIR-ATR Spectroscopy- Prediction of Soil Organic Carbon

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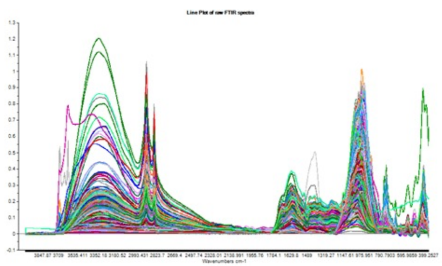
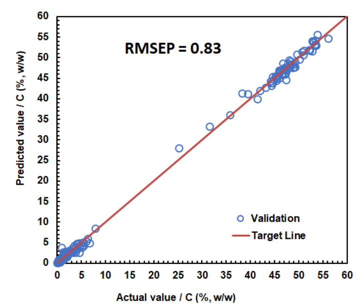
- FTIR-ATR spectra in the MIR region also provide an effective method for rapid and economical monitoring of soil, through prediction of soil parameters
- Statistical methods correlate spectra to soil properties



FTIR spectra of the National Soils Inventory of Scotland dataset



Results for prediction of SOC

- Multiple soil properties can be predicted from a single spectrum (e.g %C, %N, pH, bulk density)
- Accurate predictions of SOC have been achieved using FTIR-ATR in the MIR region
- A combination of interpretation of spectra and development of calibrations makes FTIR-ATR in the MIR region a very powerful tool for soil analysis

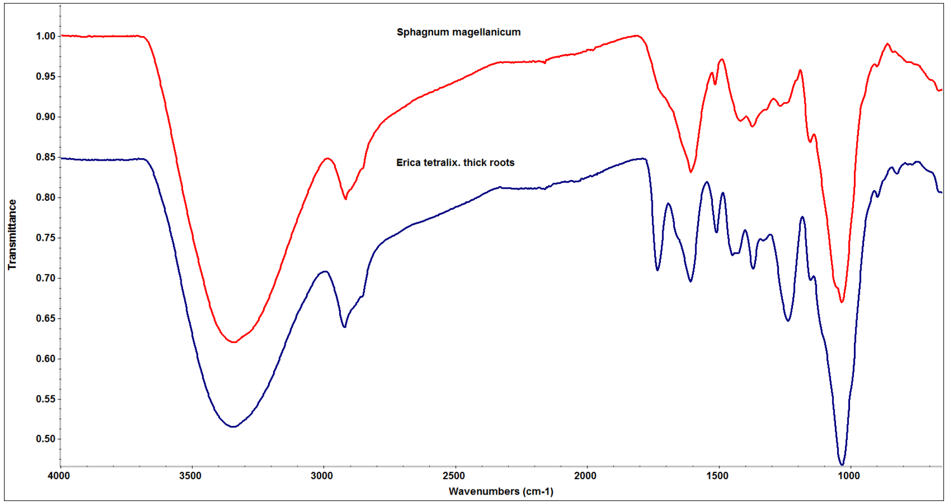
Haghi et al (2021)
Geoderma 396(1):115071
DOI:10.1016/j.geoderma.2021.115071

Spectral features of ORGANIC soils

Organic soils

- Often referred to as peat deposits, organic soils represent accumulations of partly or completely decomposed plant residues formed under anaerobic conditions
- Their spectra are related to that of the un-decomposed vegetation, and peat spectra will differ according to plant population
- The peat spectra will also differ from the vegetation depending on the extent of decomposition

FTIR spectra of two types of un-decomposed vegetation



Chemical characteristics of organic soils - 1

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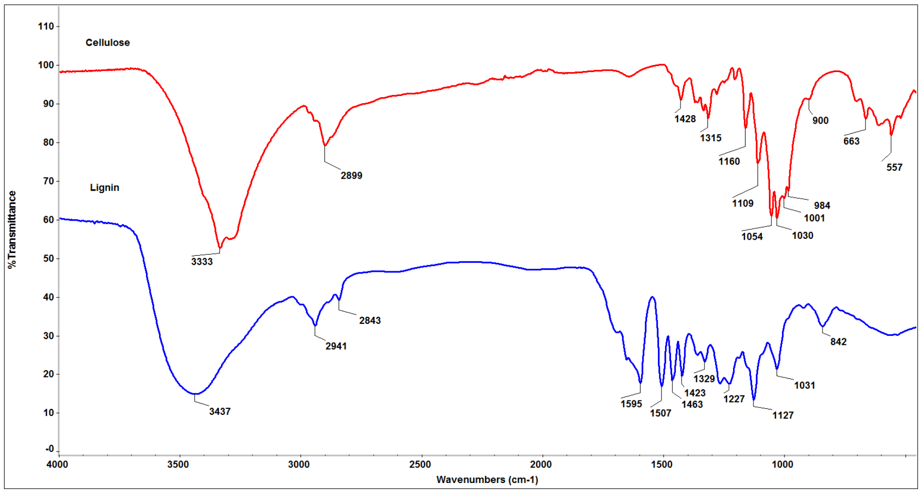
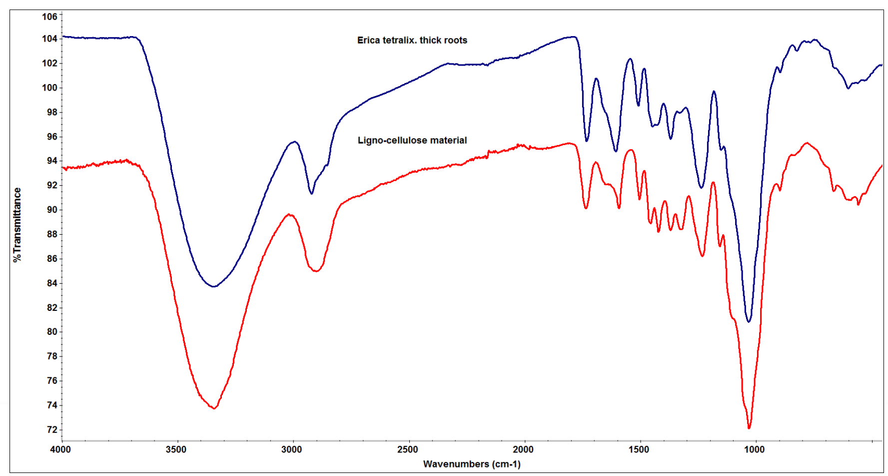


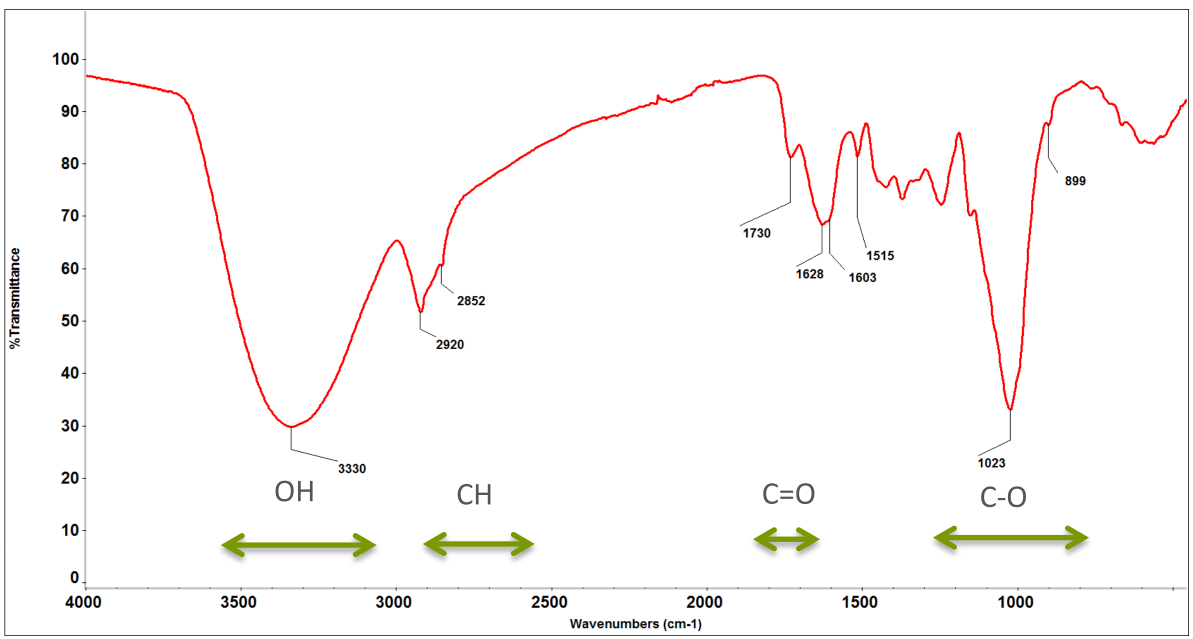
- Cellulose and lignin are major components of plant material
- Key frequencies from their spectra can be identified in spectra of vegetation and peat samples

Comparison is shown between the IR spectrum of ligno-cellulose material and that of Erica roots



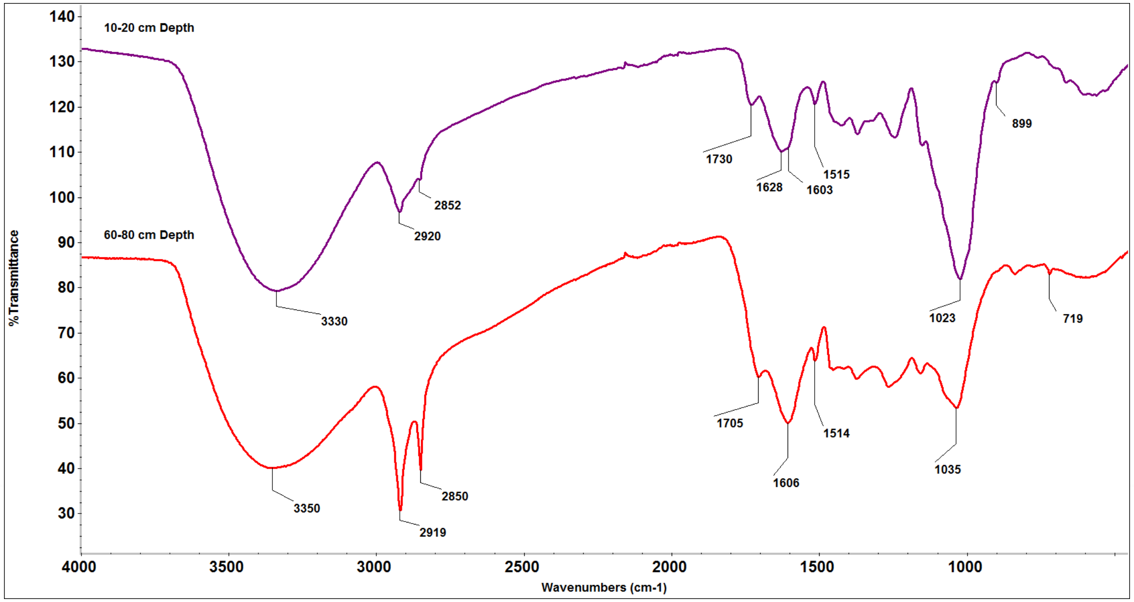
Chemical characteristics of organic soils - 2

- In addition to cellulose (polysaccharide – 1030 cm^{-1} and 3330 cm^{-1}) and lignin (aromatic – 1600, 1510 cm^{-1}) organic soils which are largely un-decomposed (often at the top of the peat) are likely to have other polysaccharides (C-O 1100-900 cm^{-1}), ester (C=O ~1730 cm^{-1})and protein (amide I ~1650 cm-1, amide II ~ 1550cm^{-1}) functional groups identifiable in the spectra
- The CH stretching region (3000 -2800 cm^{-1}) of these soils will show no distinct peaks as the absorption is derived largely from the polysaccharides



Chemical characteristics of organic soils - 3

- Organic soils which are more decomposed (often deeper in the peat) are likely to have reduced polysaccharides (C-O 1100-900 cm^{-1})
- Although some ester may remain, there is likely to be predominantly carboxylic acid present (C=O ~1710 cm^{-1})
- The CH stretching region (3000 -2800 cm^{-1}) of these soils will also show evidence of long chain or waxy compounds with sharp distinct peaks at 2920 cm^{-1} and 2850 cm^{-1} which are derived from CH_2 stretching vibrations. In addition there is a small but sharp CH_2 "wagging" vibration which appears at 720 cm^{-1}

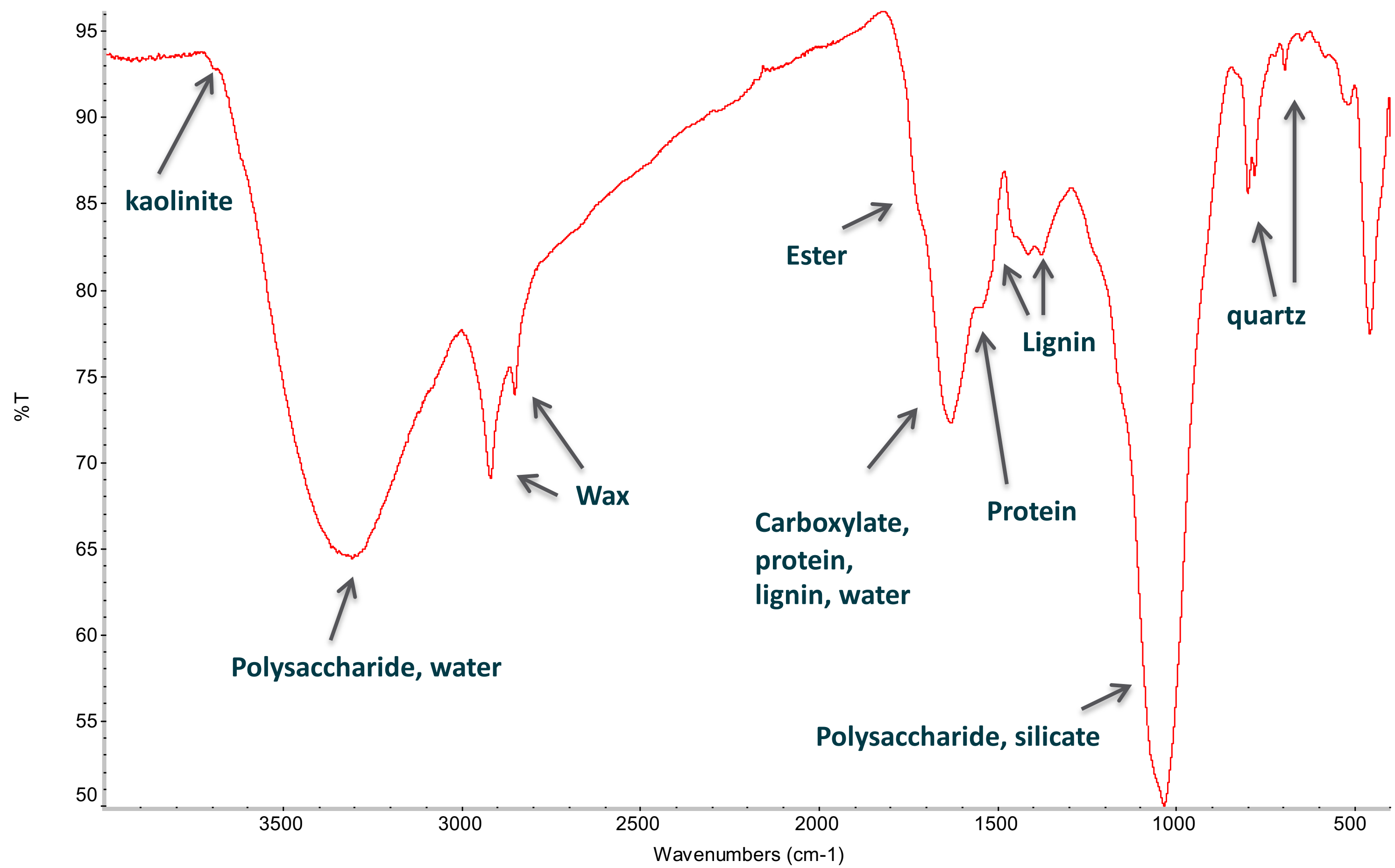


Changes in a Peat with Depth

Minerals in Organic soils

- Although some peat samples may consist entirely of organic matter, many will also contain minerals in different proportions
- Frequently, even in almost pure peat samples, traces of quartz and clay minerals are found
- It is important to bear this in mind when interpreting the spectra as the mineral bands may interfere (e.g. Si-O stretch is in the same region as the C-O stretch of the polysaccharides)

The IR Spectrum of an Organic Soil



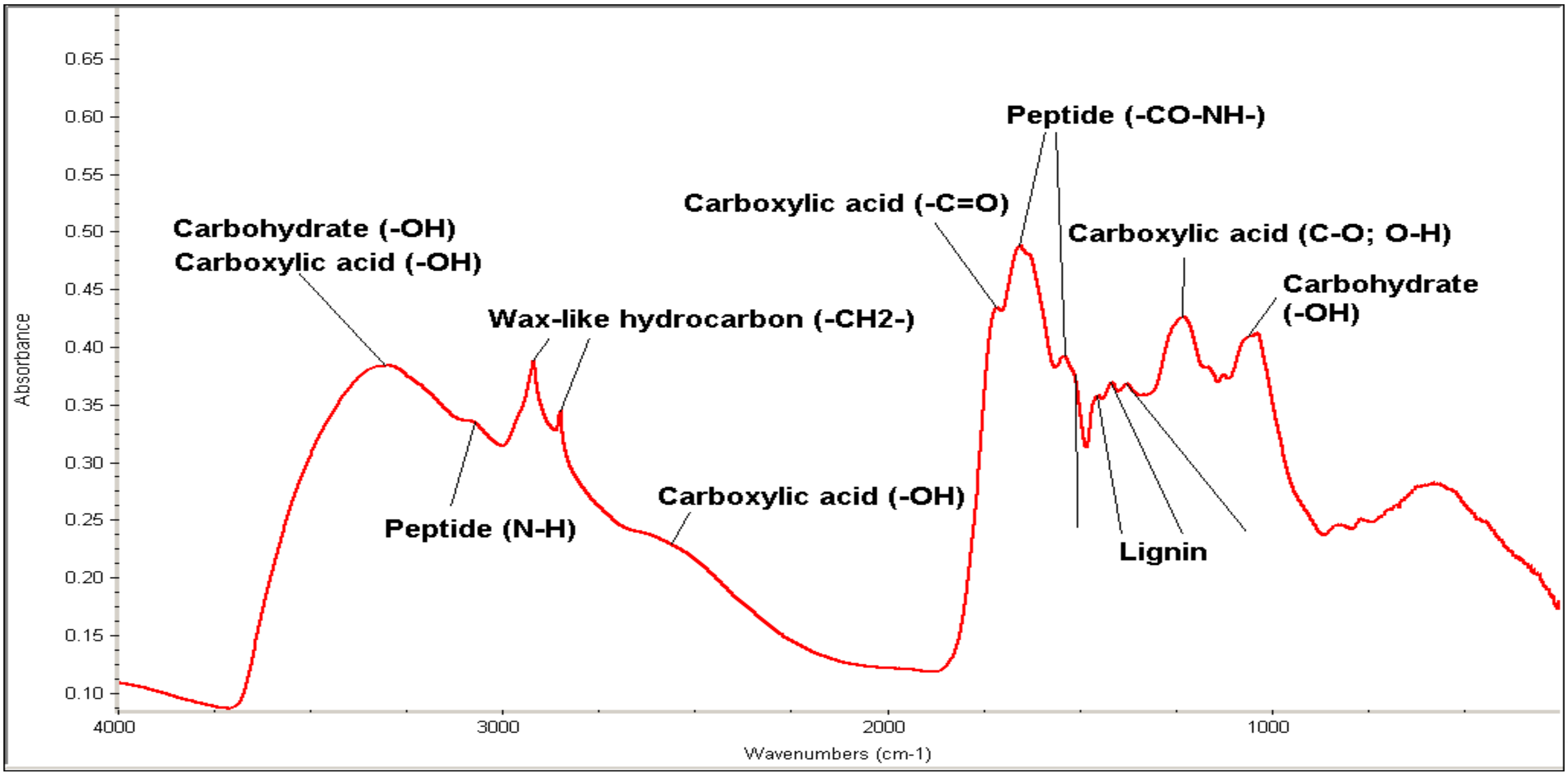
Artz et al. (2008) Soil Biol. Biochem. 40, 515–527 doi: http://dx.doi. org/10.1016/j.soilbio.2007.09.019

Soil Organic Matter (SOM) in Mineral Soils

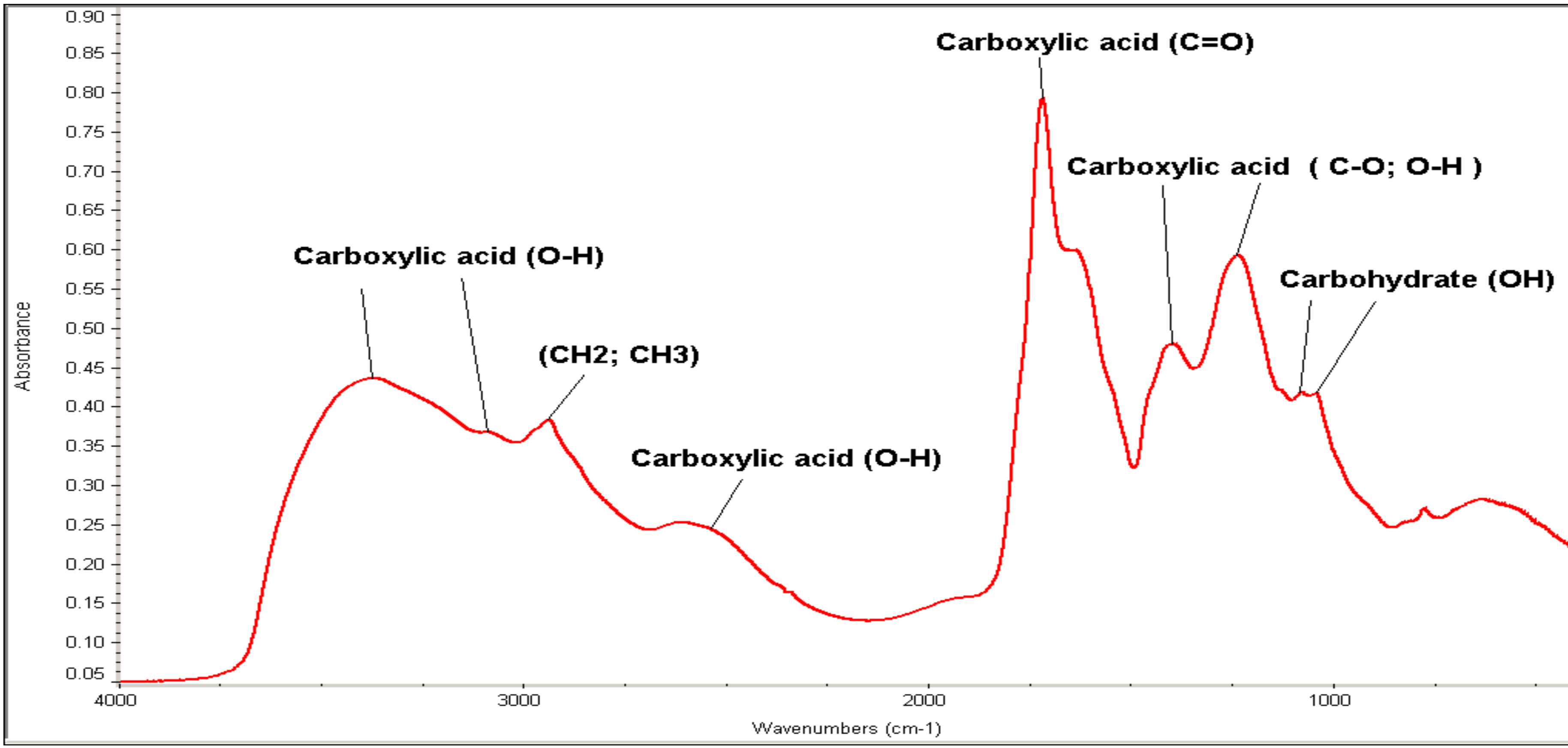
The IR spectrum of a soil sample can rapidly provide an insight into the proportion and nature of SOM present

- Much of the interpretation of spectra of organic soils is also useful in assessing the nature of the SOM in mineral soils
- In the IR spectra of the top horizons, the SOM often still has functional groups which are identifiable
- In lower horizons humification can lead to a smoother profile in the IR spectrum with no distinct bands arising from functional groups discernible
- Broad bands arising from carboxylates can arise in lower horizons

IR Spectrum
Mineral Soil Humic Acid



IR Spectrum
Mineral Soil Fulvic Acid



Spectral features of MINERAL soils

IR Spectra of Mineral Soils - 1

- By definition, mineral soils have low SOM content and so are predominantly inorganic

- Inorganic compounds exhibit an IR spectrum if they contain covalent bonds (or have water of hydration)

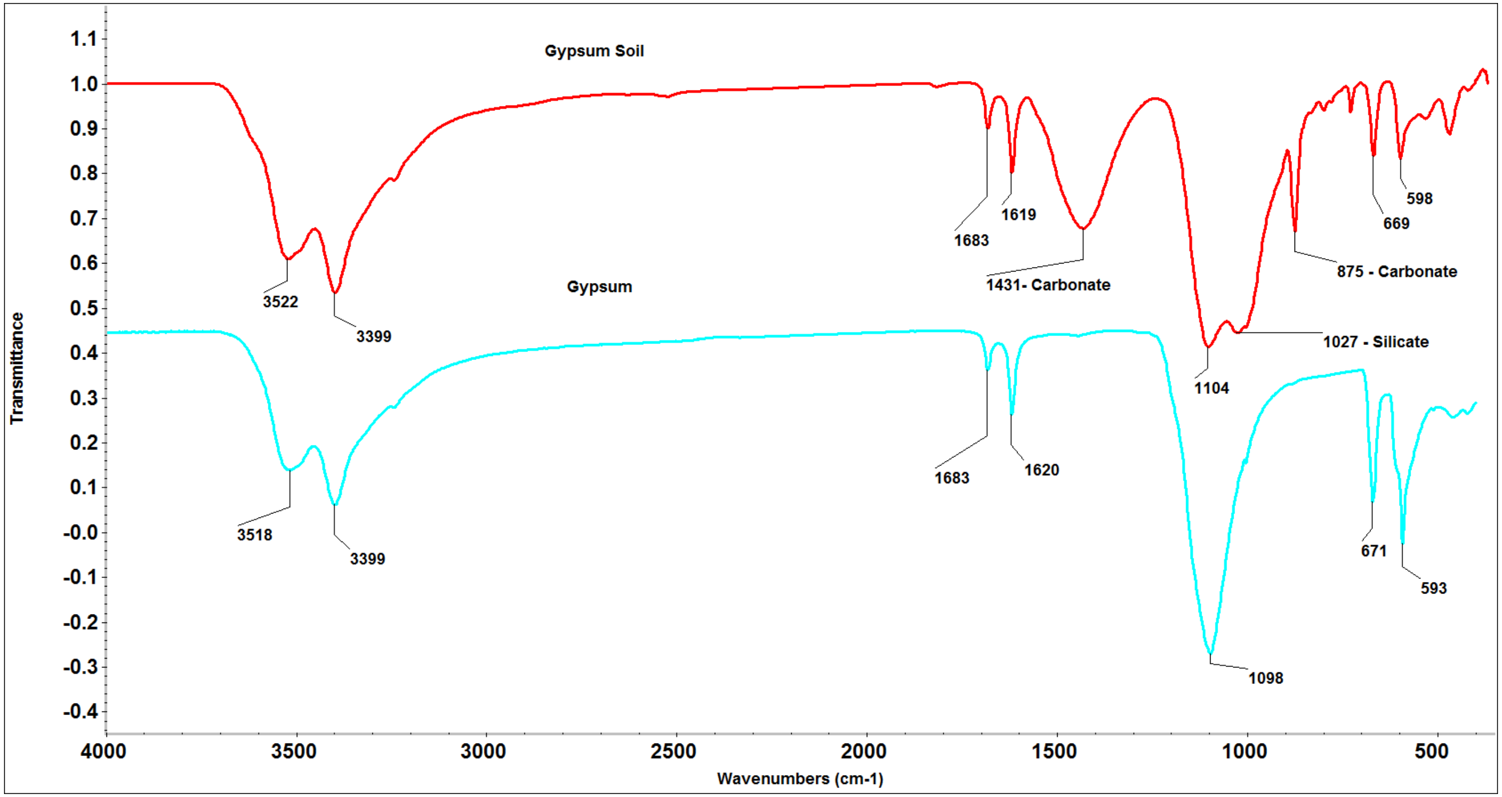
- The majority of minerals in soil do have covalent bonds present e.g Si-O, O-H and CO_3^{2-} (which absorb due to stretching at ~ 1000 cm^{-1}, ~3700 – 3200 cm^{-1} and ~1400 cm^{-1} respectively)

- Frequencies for the bands in the IR spectrum of the minerals can be found in assignment tables

V.C. Farmer, The Infrared Spectra of Minerals. Mineralogical Society, London (1974).

IR Spectra of Mineral Soils - 2

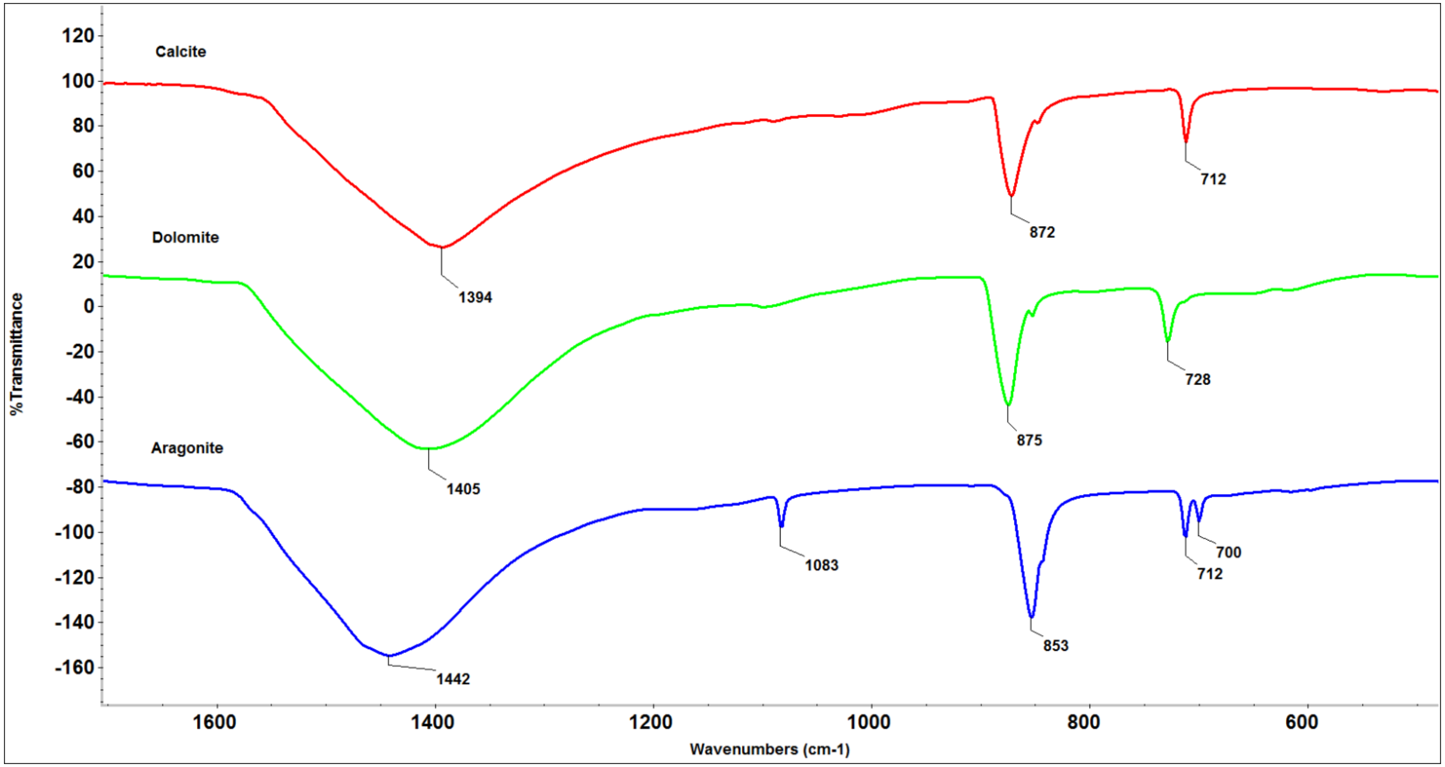
Silicates or carbonates usually dominate, but there are soils with other components e.g. gypsum (calcium sulphate – $CaSO_4 . H_2O$) soils



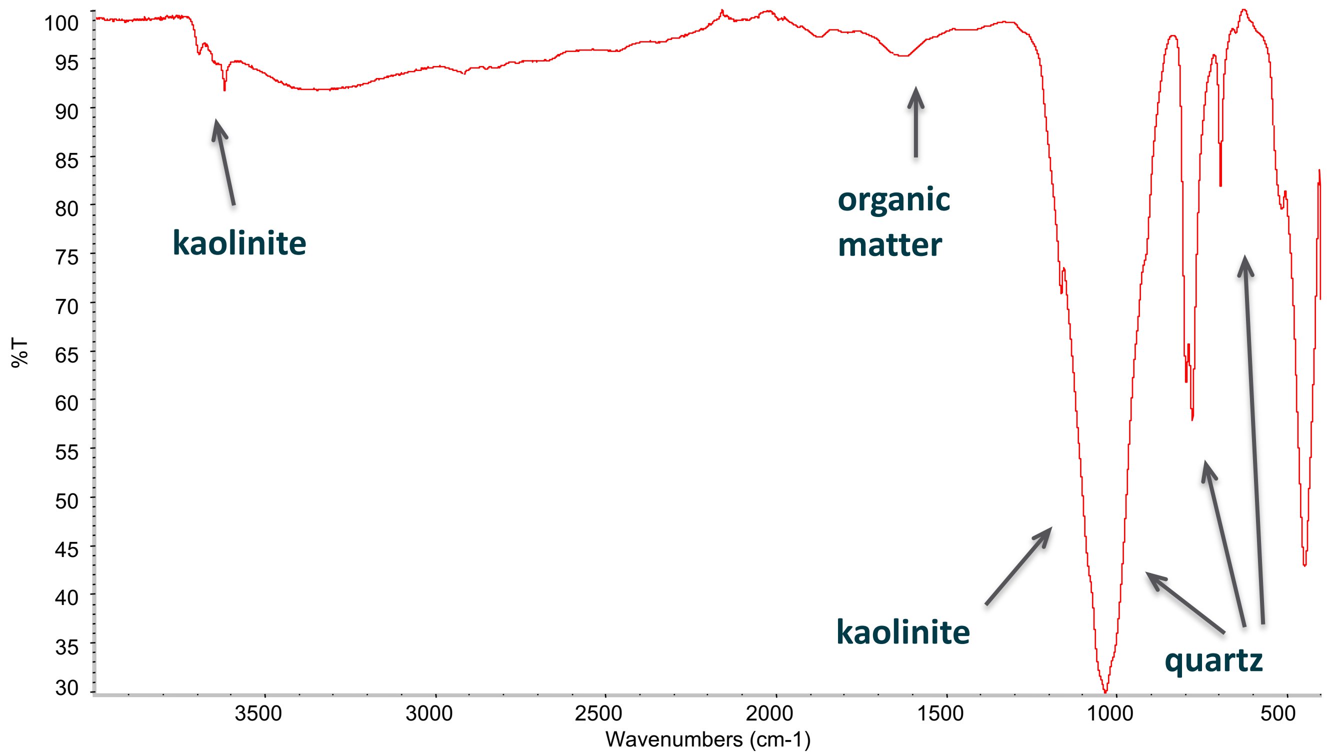
Palacio et al. (2014) PLoS ONE 9(9):e107285.
DOI: 10.1371/journal.pone.0107285

IR Spectra of Mineral Soils - 3

IR spectra can be used to discriminate between the different types of carbonate or silicate minerals present in a soil e.g. whether the carbonate present is calcite, dolomite or aragonite

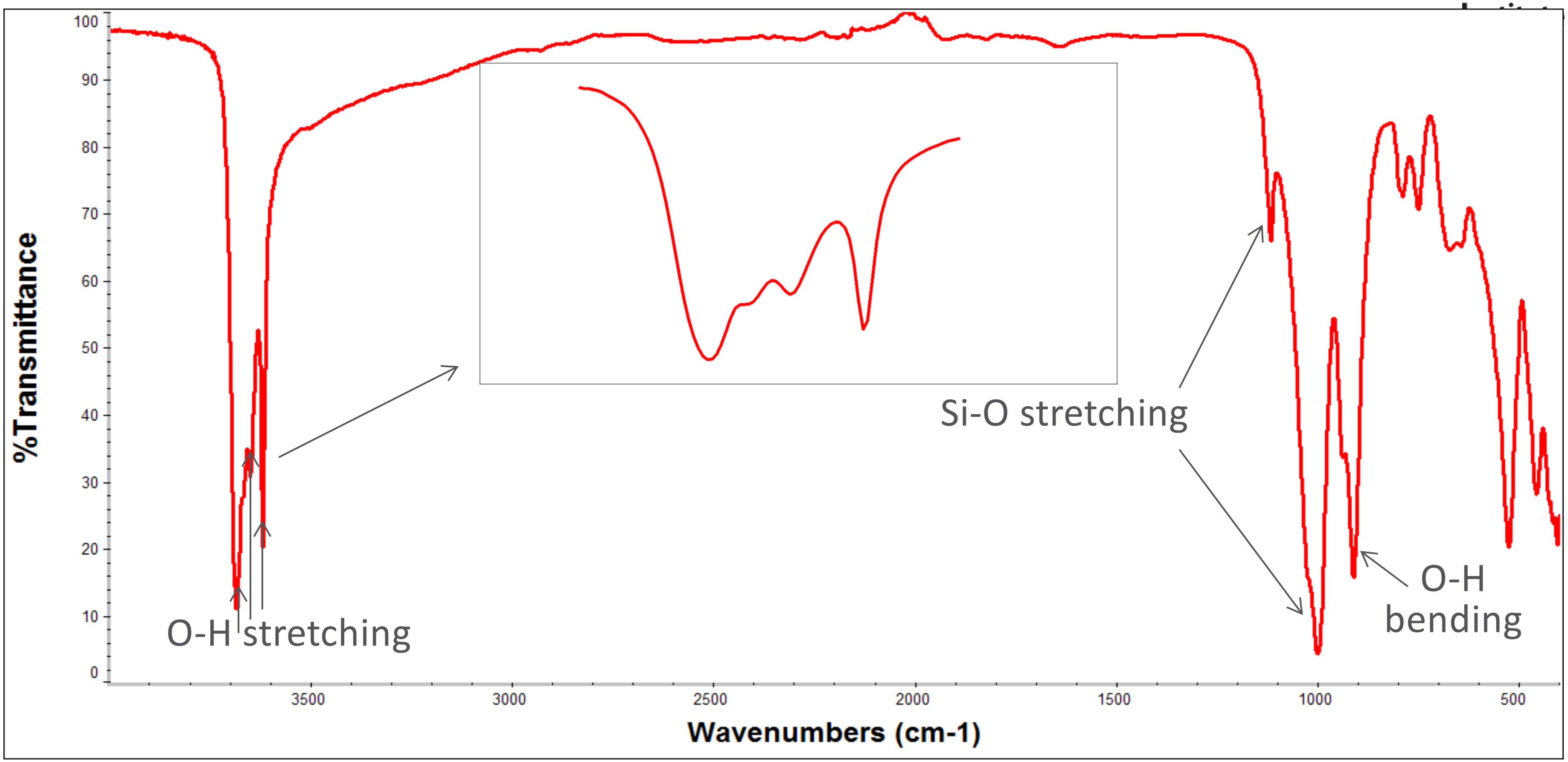


The IR Spectrum of a Mineral Soil



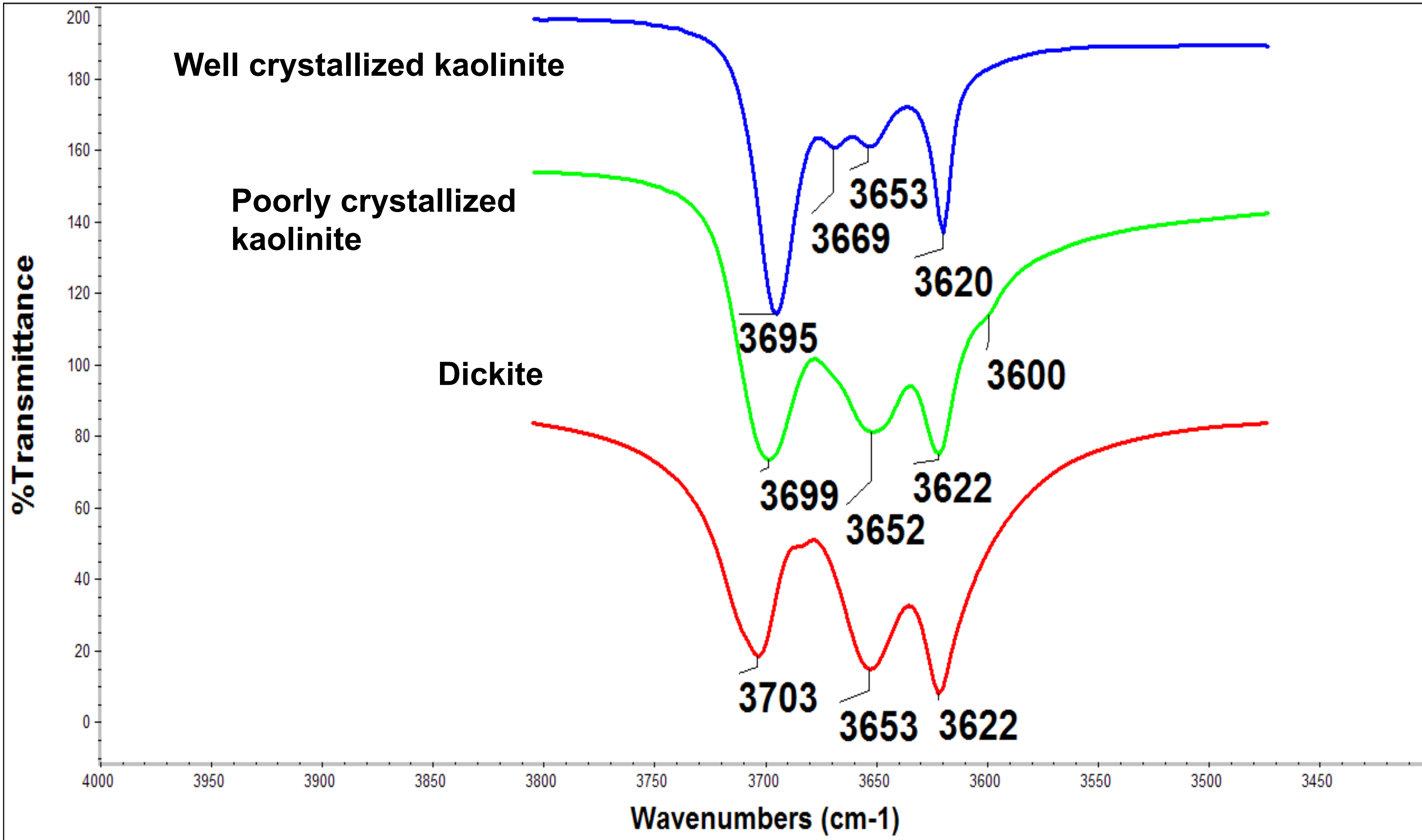
- The IR spectrum of a soil sample provides an instant insight into the geology of the soil, including the proportion and nature of the clay minerals
- Clay minerals can be key to the soil properties so we will consider them in more detail

Interpretation of IR Spectra of Layer Silicate Clay Minerals: Kaolinite-Pure Sample



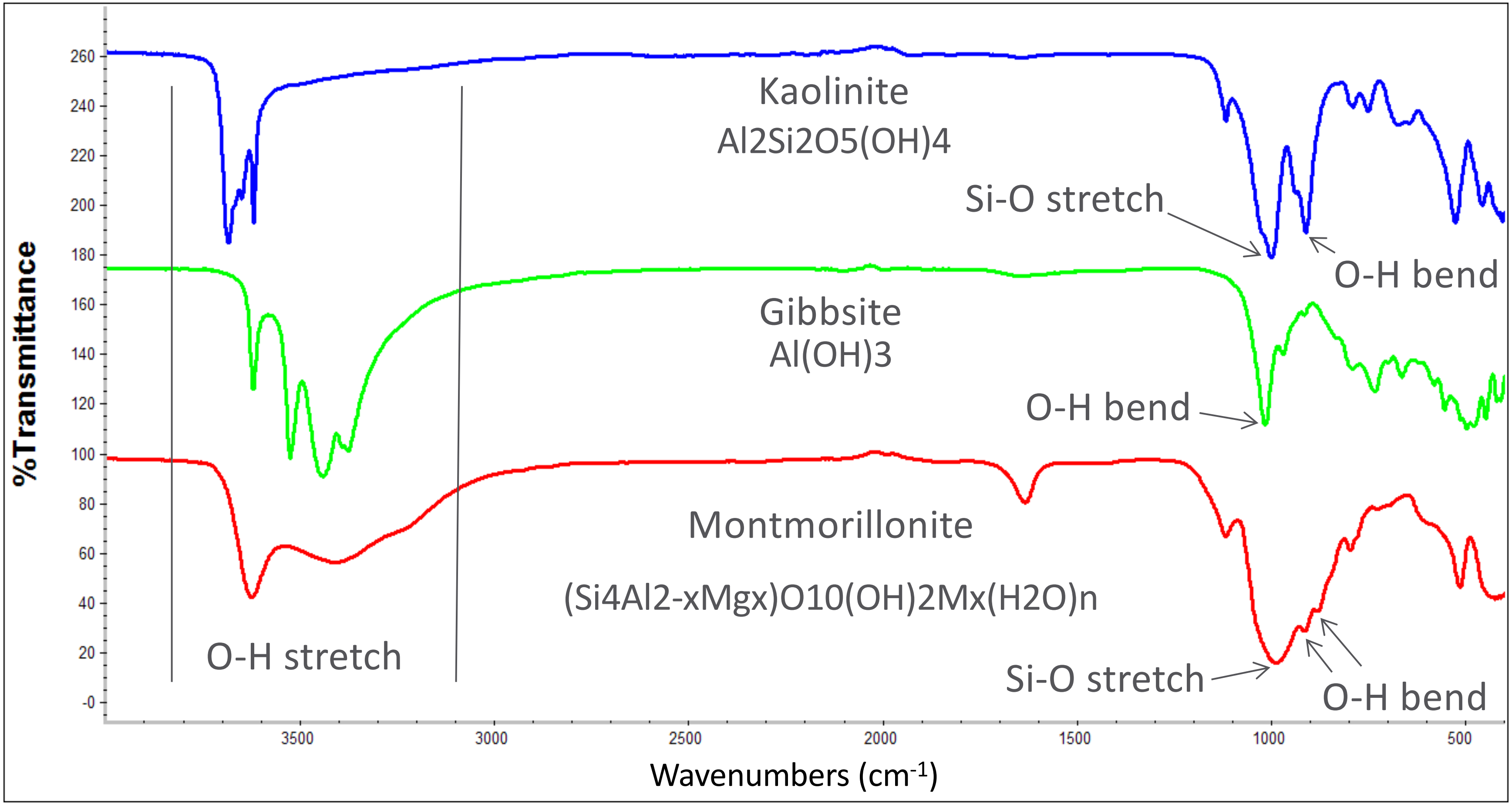
Interpretation of IR spectrum of a single mineral component in a sample is relatively straight forward using searchable mineral IR spectral libraries

Kaolin Minerals - OH Stretching Region



Comparison of Different CLAY Mineral IR Spectra

The James Hutton Institute



Hillier et al. Clay Minerals, (2016) 51, 325–350

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Factors to consider when recording FTIR (MIR) Spectra of soils

- Care must be taken to avoid interference by moisture and CO_2
- Sample preparation methods will affect the spectra produced and a protocol to ensure representative and reproducible spectra should be used
- Different sampling methods (e.g. DRIFTS and ATR) will cause large differences in appearance of spectra which needs to be taken into account when interpreting them

How to Approach Infrared Spectral Interpretation of Soil in MIR Region

1. Use high quality data, e.g. Good signal/noise ratio, no water vapour spikes or carbon dioxide interference. The most intense band should be less than 2 in absorbance

2. Look over the spectrum from left to right, noting the frequency (cm^{-1}) of the intense absorption peaks

3. Taking into account your knowledge of the sample, assign the most intense bands first (using correlation tables)

How to Approach Infrared Spectral Interpretation of Soil in MIR Region

4. Track down the secondary bands for the functional groups if possible

5. Assign other bands as needed

6. Write down the SOM functional groups and/or minerals you think exist in the sample

7. Get help from spectral libraries or interpretation software – as soils are very complex mixtures

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