NEAR INFRARED SPECTROSCOPY

Reflectance Spectroscopy

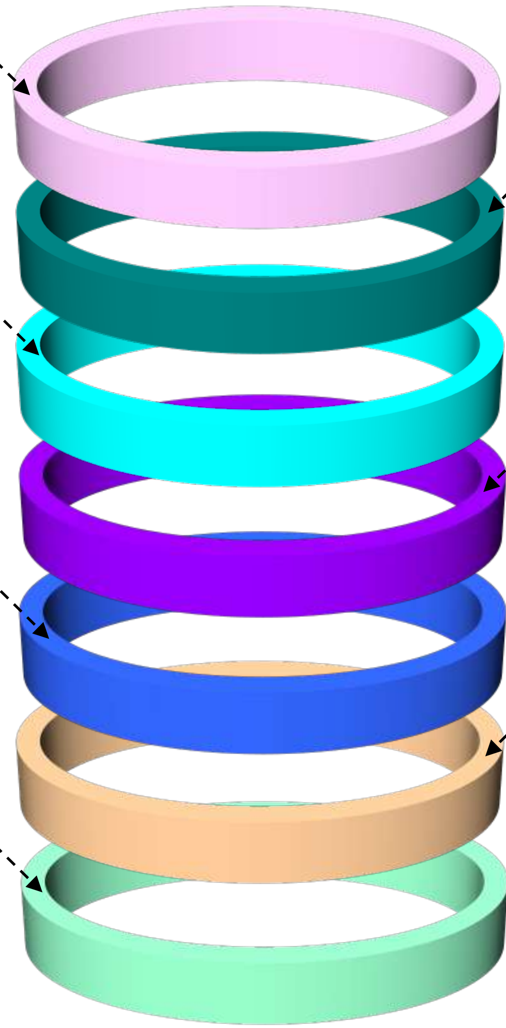
Maria Kokkaliari, *BSc, MSc Geologist,*

PhD Candidate

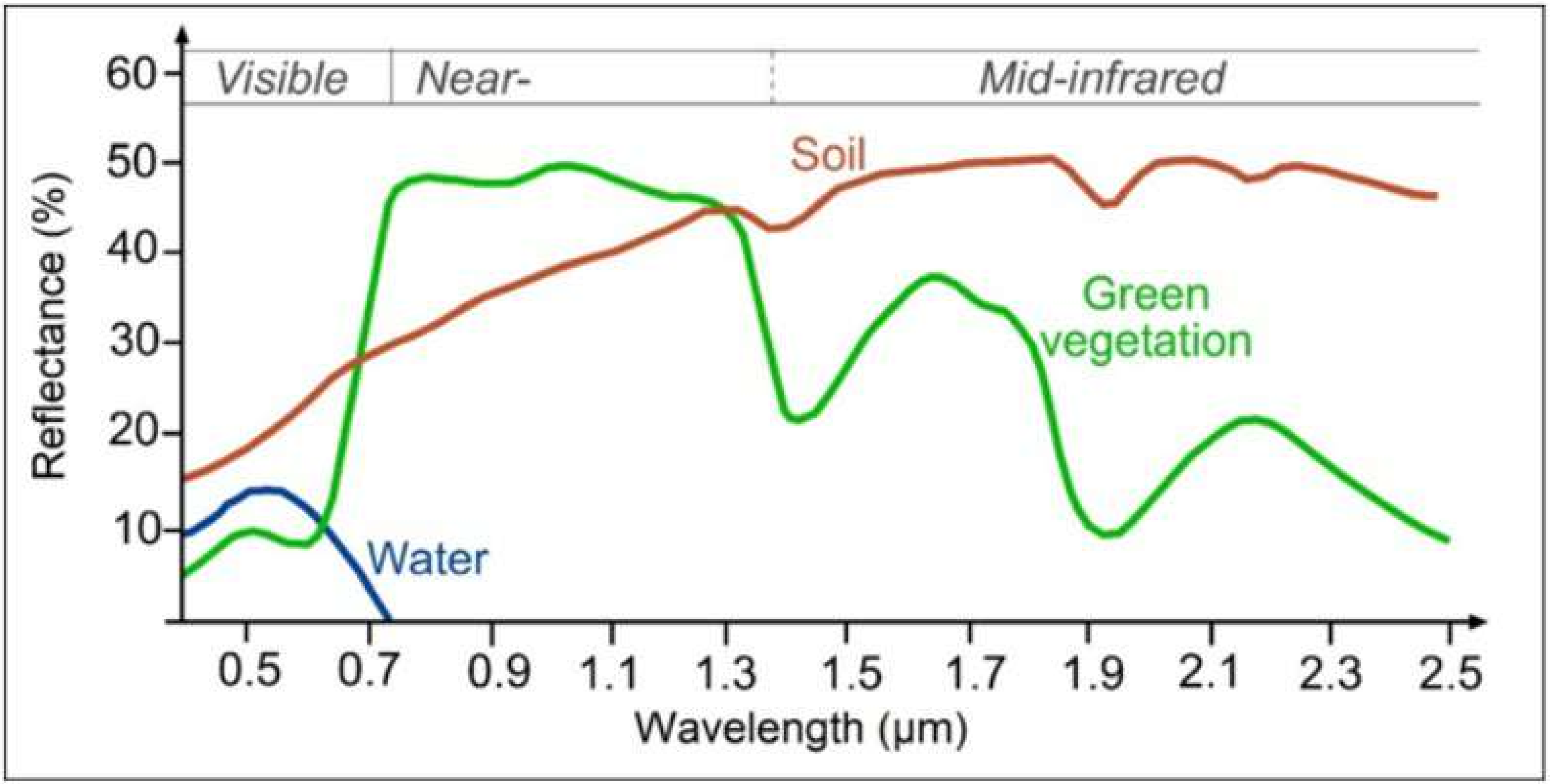
Department of Geology, University of Patras, Greece

Supervisor: ***Ioannis Iliopoulos****, Professor*

Table of contents:



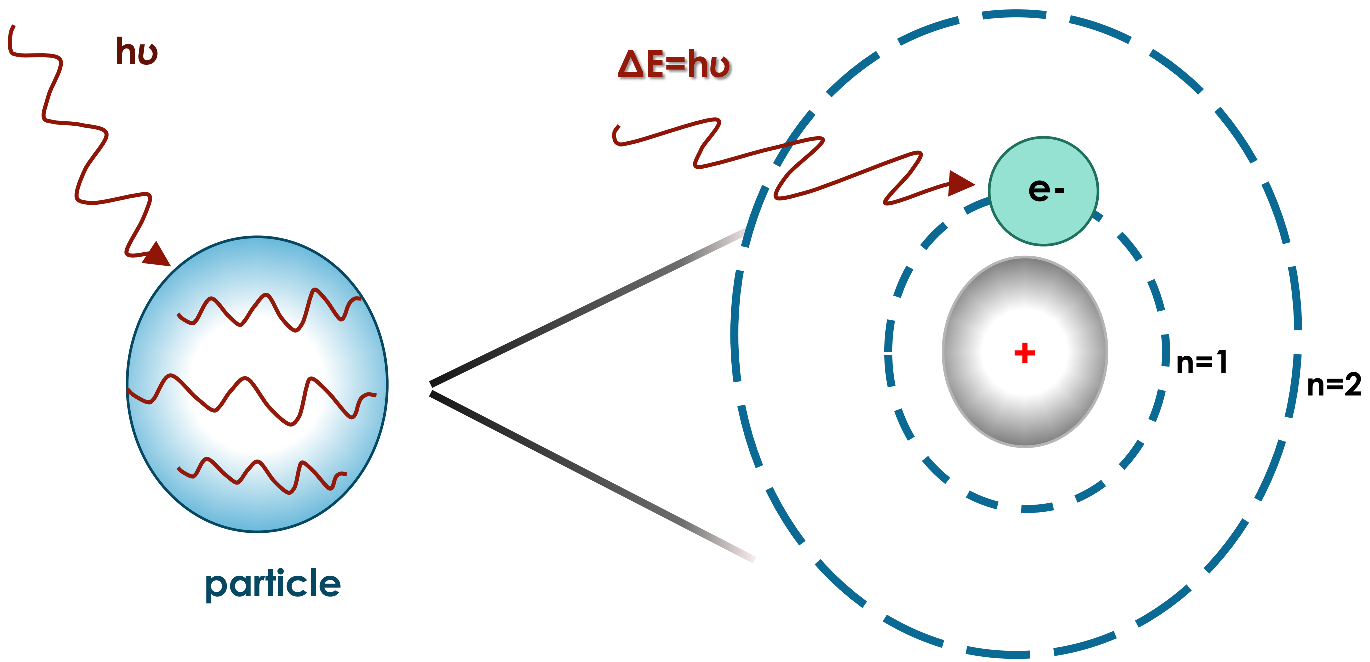
Η μέθοδος αυτή έγινε ιδιαίτερα δημοφιλής και ουσιαστικά άρχισε να ανακαλύπτεται παράλληλα με τις μεθόδους τηλεπισκόπησης.



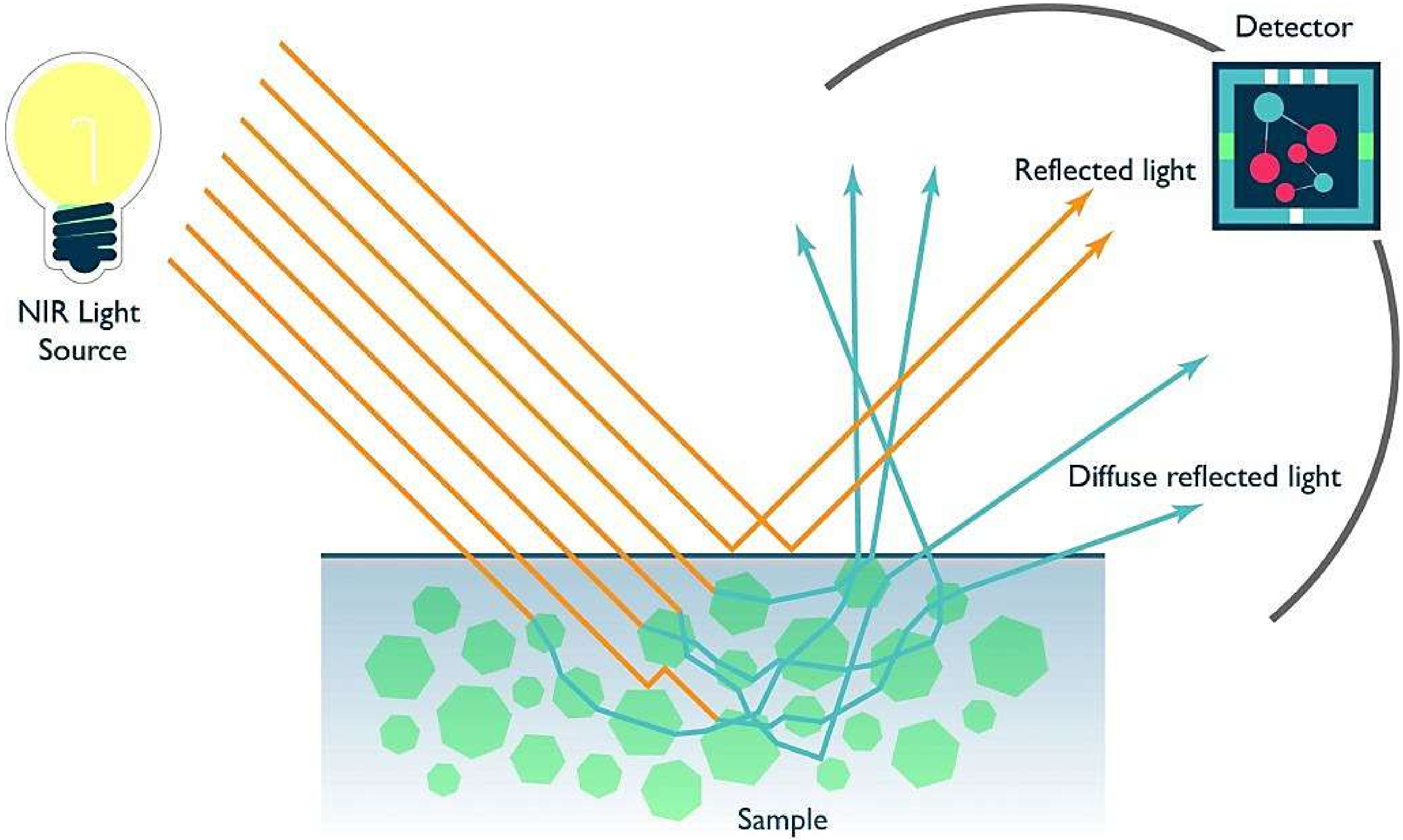
Συνδυαστική πληροφορία των καμπυλών φασματικής ανάκλασης για τη βλάστηση, το έδαφος, το νερό και τα φασματικά κανάλια του World View 2

S P E C T R O S C O P Y is the study of Interaction of ***Electromagnetic radiation*** with ***matter***

Reflectance spectroscopy can be defined as the technique that uses the energy in certain wavelength regions of the electromagnetic spectrum to analyze minerals (Hunt, 1977 and Goetz, et al., 1982).



Diffuse reflectance spectroscopy



LAMBERT – BEER LAW:

$$A = -\log \frac{I_t}{I_o} = \varepsilon\, c\, l$$

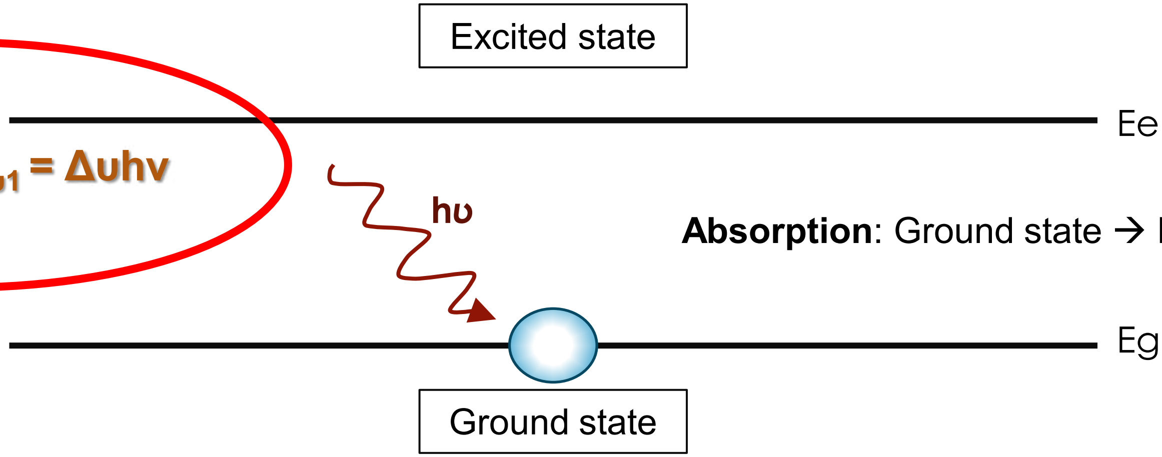
- A is the absorbance
- I_o is the intensity of the incident light
- I_t is the intensity of the transmitted light
- ε is the molar absorption coefficient ($M^{-1}\ cm^{-1}$)
- c is the molar concentration (M)
- l is the optical path length (cm)

S P E C T R O S C O P Y is the study of Interaction of ***Electromagnetic radiation*** with ***matter***

Interaction of Electromagnetic Waves with matter

- Absorption
- Emission

$$\Delta E = E_{\upsilon 2} - E_{\upsilon 1} = \Delta \upsilon h\nu$$



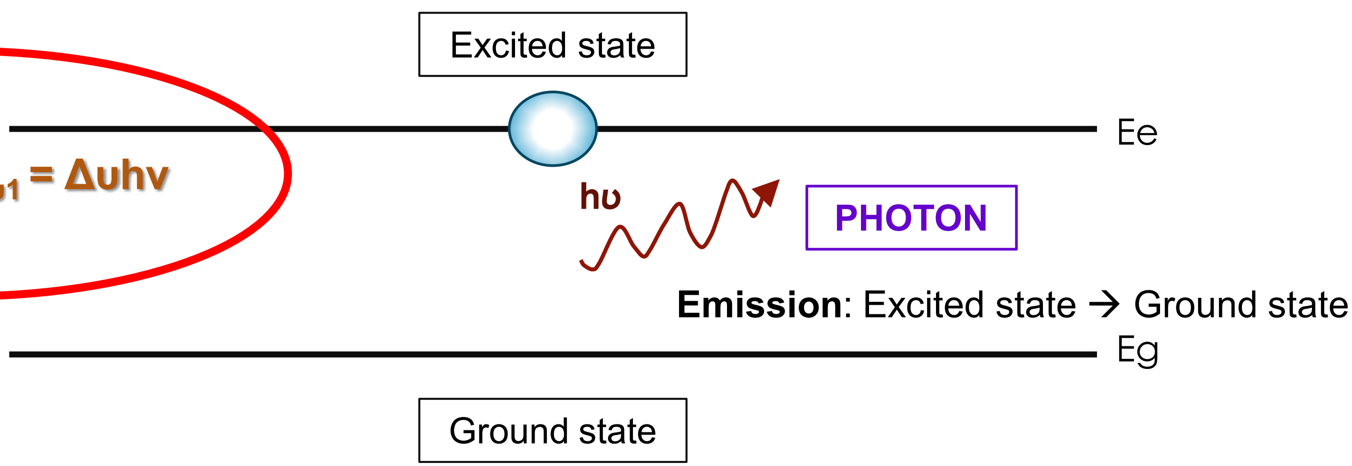
Absorption: Ground state → Excited state

S P E C T R O S C O P Y is the study of Interaction of ***Electromagnetic radiation*** with ***matter***

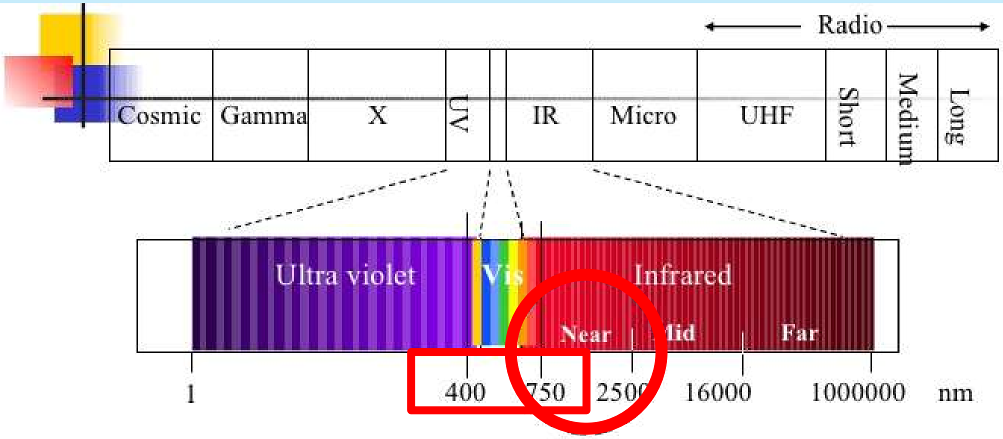
Interaction of Electromagnetic Waves with matter

- Absorption
- Emission

$$\Delta E = E_{\upsilon 2} - E_{\upsilon 1} = \Delta \upsilon h\nu$$

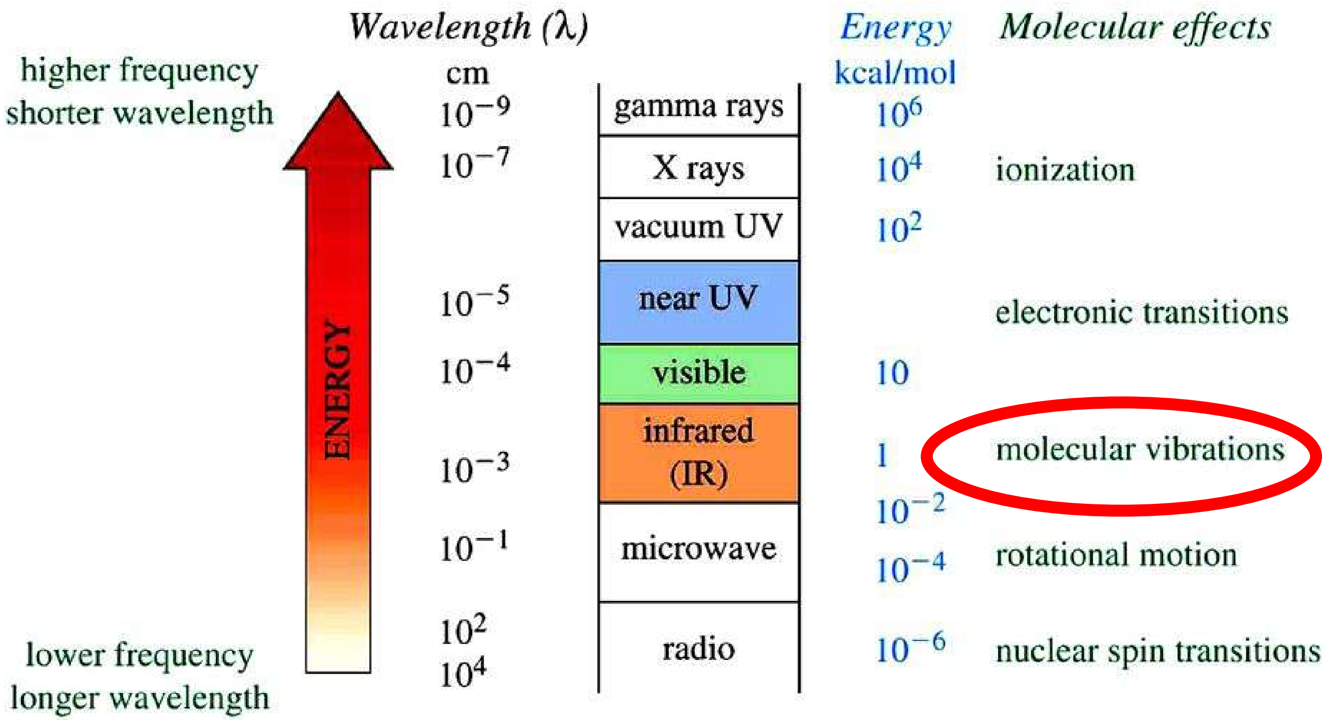


The electromagnetic spectrum



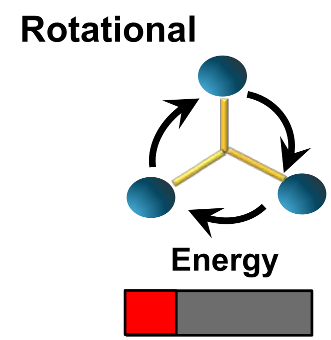
- The NIR spectrum extends from ≈ 800nm – 2500nm.

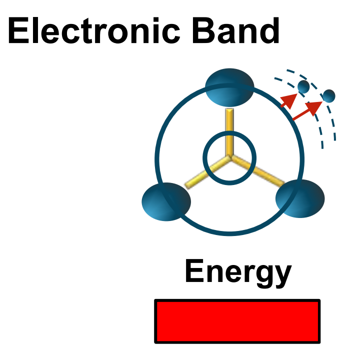
EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES

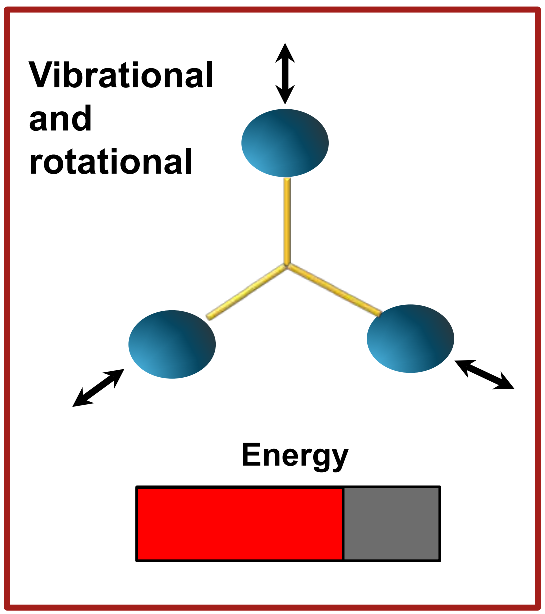


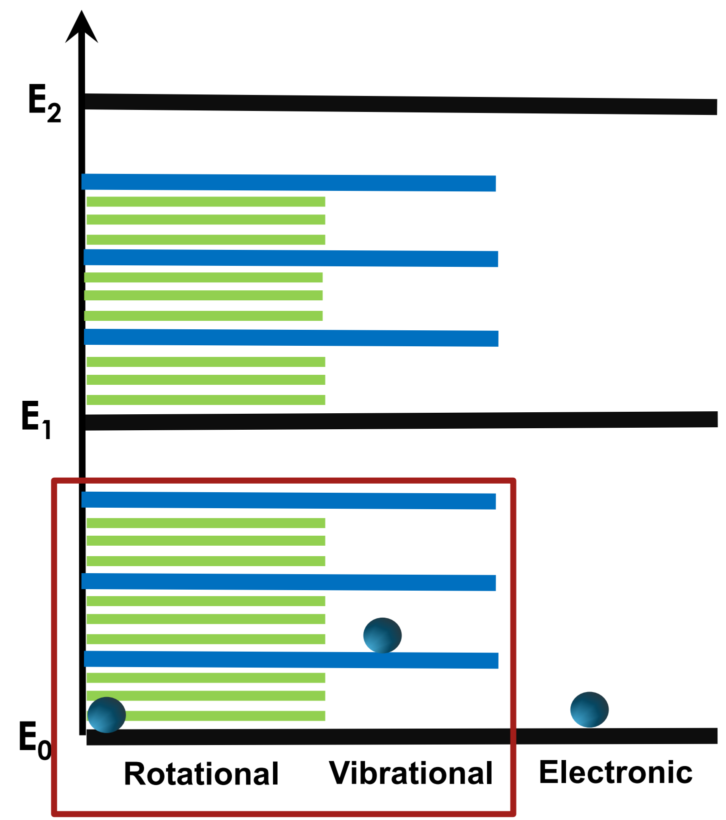
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

Types of molecular spectra



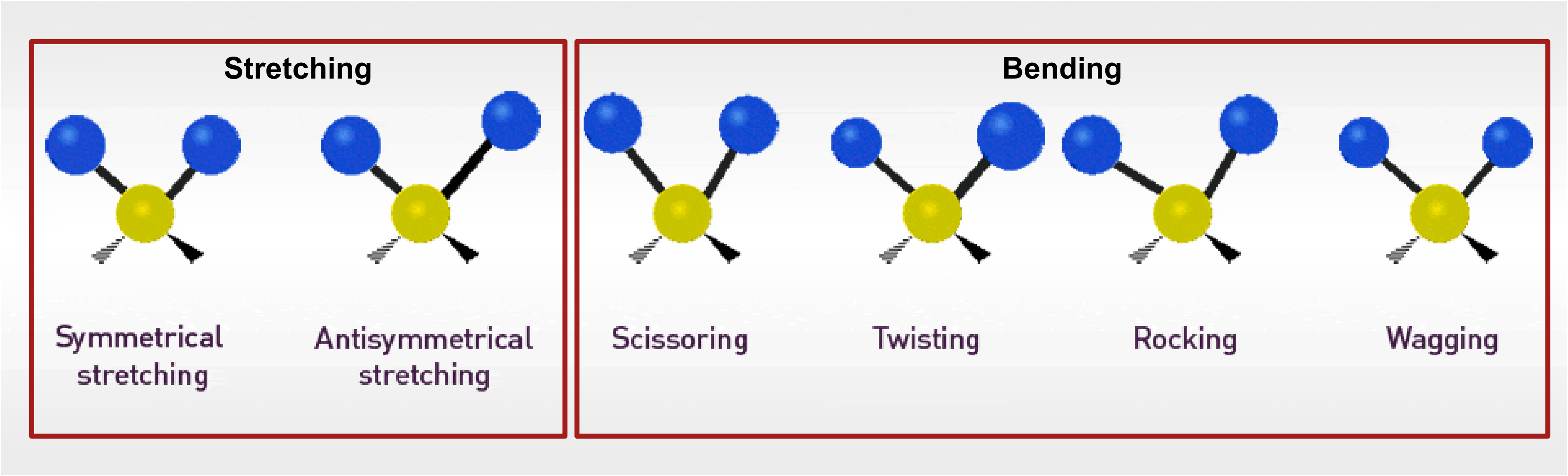






Types of vibration

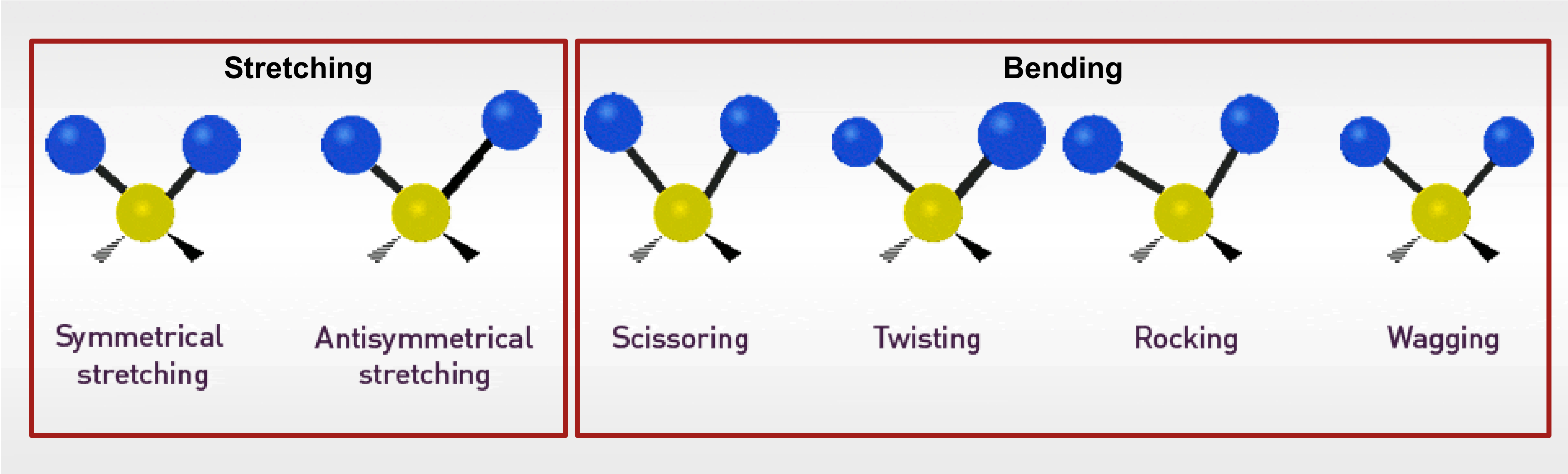
Molecular vibration occurs when the atoms of a molecule are in periodic motion while at the same time the molecule performs continuous linear and rotational motion. **Near infrared spectroscopy measures the vibrational energy of the bond between the atoms and the molecules**. The bonds will vibrate differently - at discrete wavelengths, as a function of their length.



Types of vibration

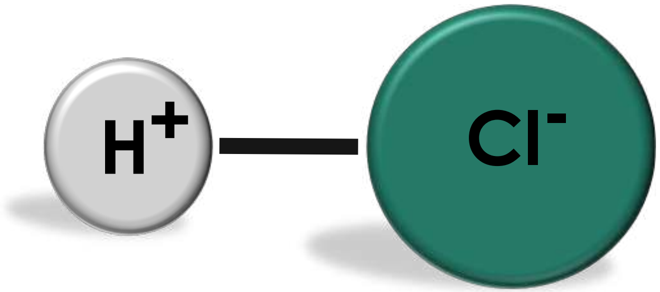
Molecular vibration → internal movements of atoms such as changing the length and the angle of the bond

The relative positions of atoms in a molecule are not perfectly defined but fluctuate constantly as a result of the many different types of vibrations and rotations around their bonds with the molecule.



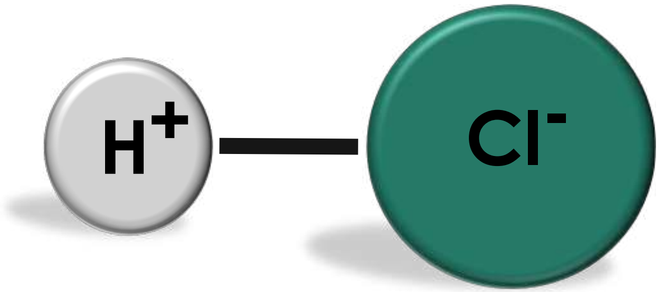
Absorption of NIR

- Change in dipole moment → result from rotational and molecular vibrations
- Dipole moment depends on the value of the charge difference and the distance between the two charged center
- When a molecule vibrates, there is a constant change in dipole moment and a field is created which interacts with the electromagnetic field of the radiation.



Absorption of NIR

- If the frequency of the radiation coincides with the frequency of a normal vibration of the molecule → a pure energy transfer will follow.
- Change in the amplitude of the molecular vibration → radiation will be absorbed.
- Not all types of vibration can be detected in the infrared!!!! → The symmetrical movements are not detectable (O_2, N_2 or Cl_2)



HARMONIC OSCILLATOR

<u>Hook's Law</u>

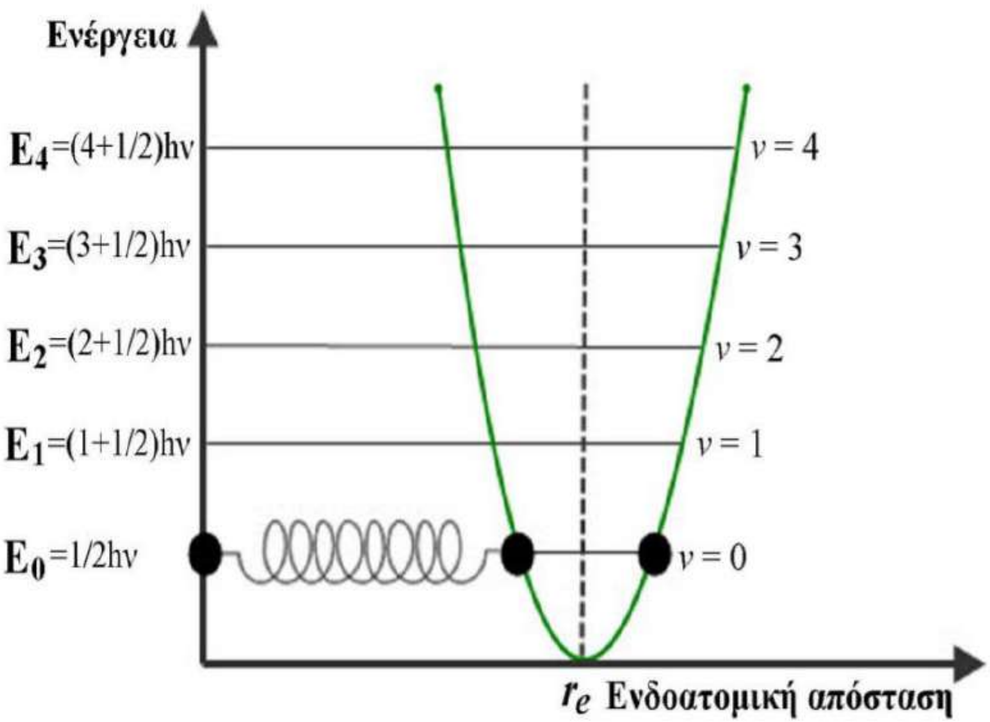
$$V(x) = \frac{1}{2}kx^2$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

<u>Vibrational Energy</u>

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)h\nu$$

$$\omega = \nu/c,$$



$$\omega = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

υ: vibrational quantum number,
h: Planck constant
v: frequency
k: is a positive real number
μ: reduced mass of the system
c: light speed

Vibrational processes

Absorption features in NIR: composition

Vibrational state transitions

Overtones and combination features

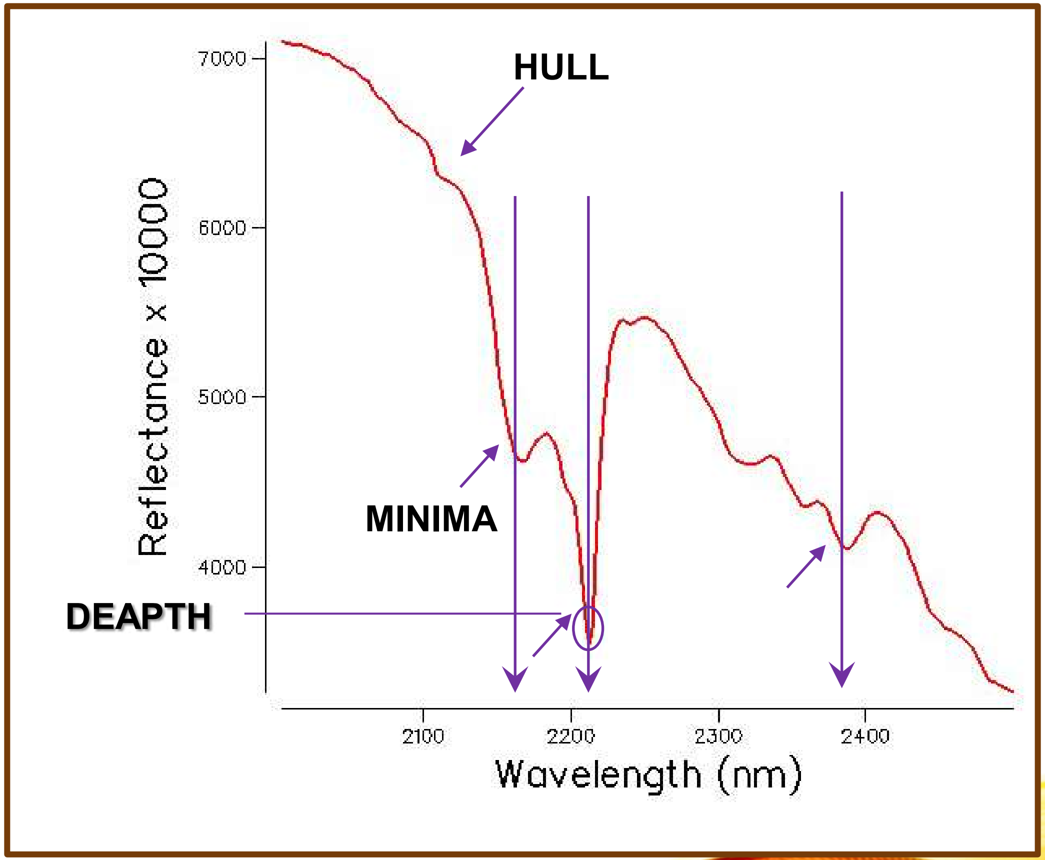
REFLECTANCE SPECTRUM

Fundamentals: vibrational motions between components

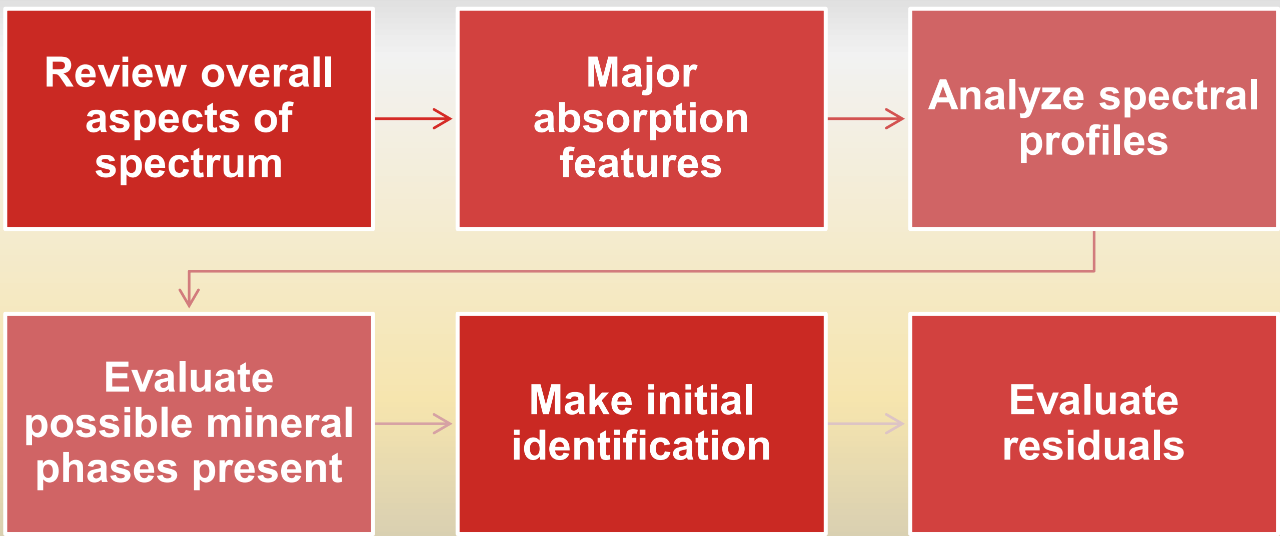
Overtone: fundamental mode that is exited with two or more quanta of energy

Combination: when more than two or more fundamental vibrations are excited simultaneously.

Absorption feature with its components



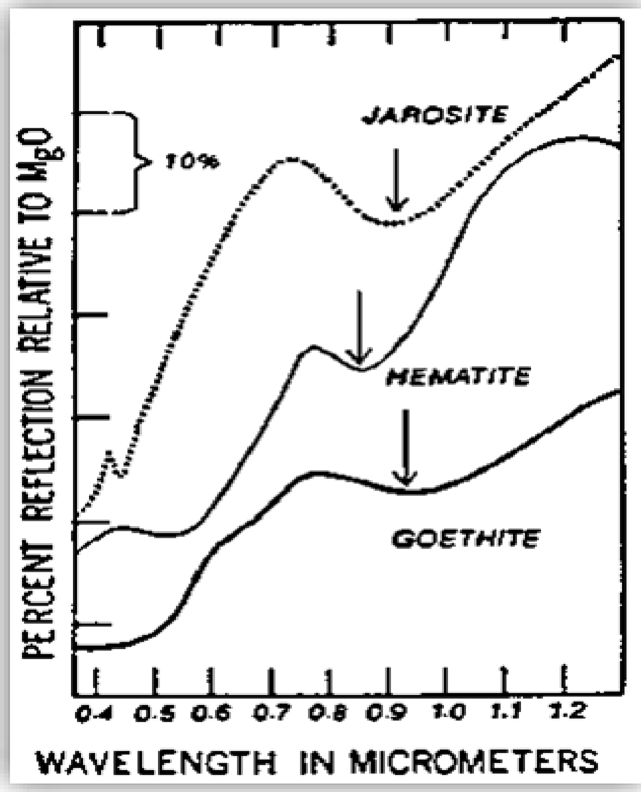
Mineral identification steps

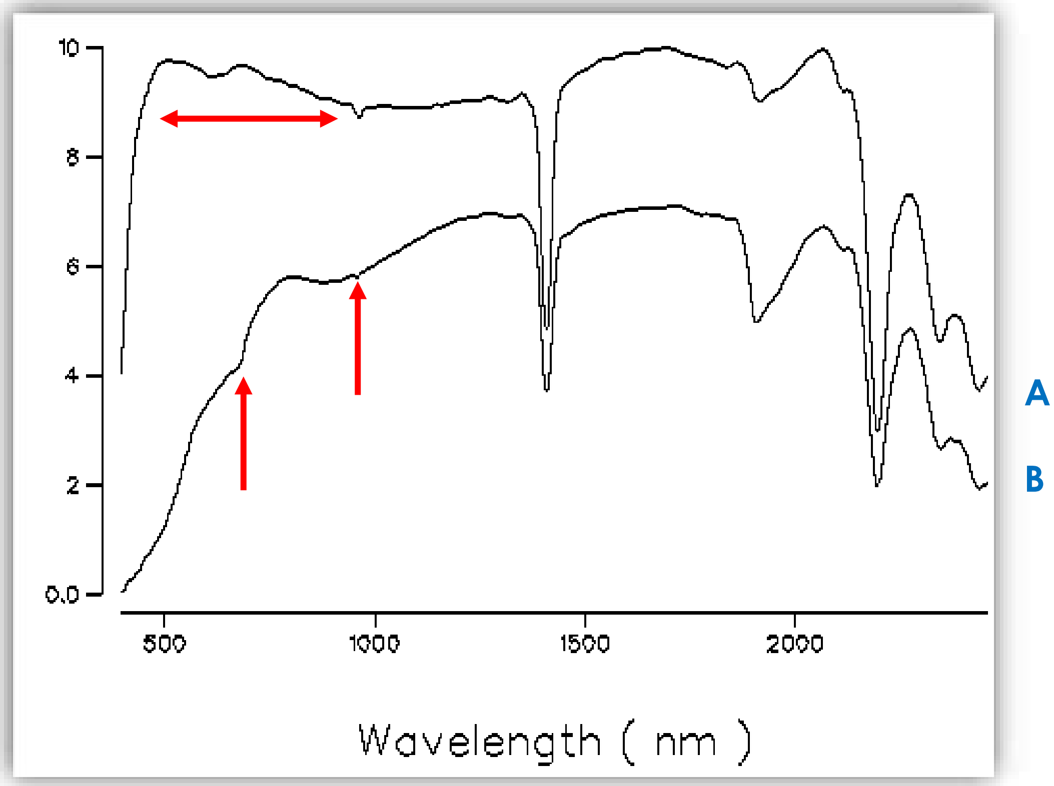


Major absorption features

Position	Mechanism	Mineral group
~ 1.4 μm	OH and WATER	Clays, Sulfates, Hydroxides, Zeolites
~ 1.56 μm	NH_4	NH_4 Species
~ 1.8 μm	OH	Sulfates
~ 1.9	MOLECULAR WATER	Smectite
~ 2.02, 2.12 μm	NH_4	NH_4 Species
~ 2.2 μm	Al – OH	Clays, Amphiboles, Sulfates, Micas
~ 2.35 μm	CO_3^{-2}	Carbonates

Contribution of the visible region



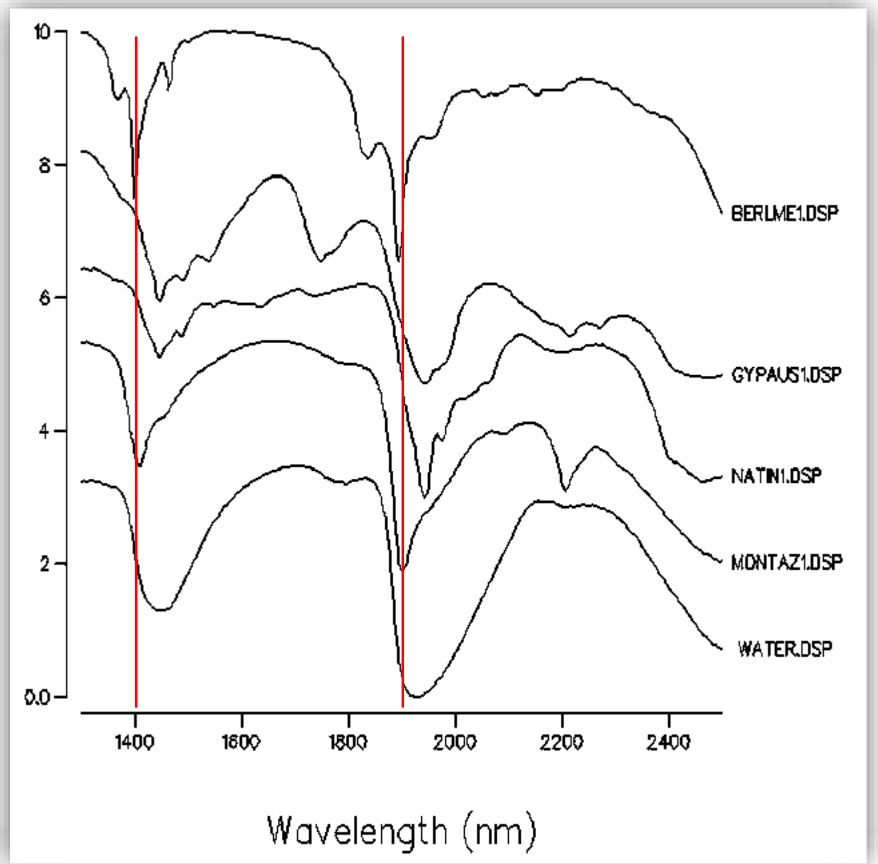


Two different illites

A: illite B: illite with maghemite

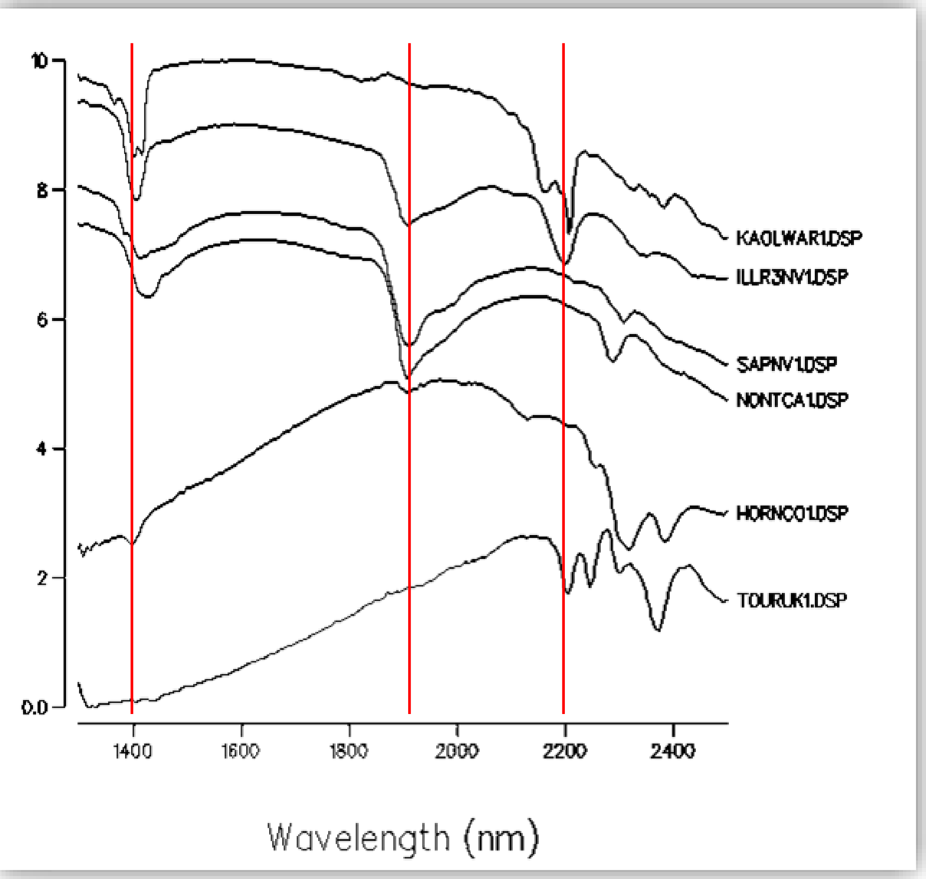
Water vs hydroxyl site occupancy

- ❖ 1.4 and 1.9 μm features are diagnostic of the presence of water
- ❖ Broad features → water molecules occupy unordered, multiple, non-equivalent sites



Water vs hydroxyl site occupancy

- ❖ Only one infrared active stretching mode fundamental, located at ~2.75µm
- ❖ Micas, clays and amphiboles all contain well-resolved, intense OH features, especially in the 2.2 µm region



The presence of iron

A: Chamosite

B: Biotite

C: Hornblende

D: Uralite

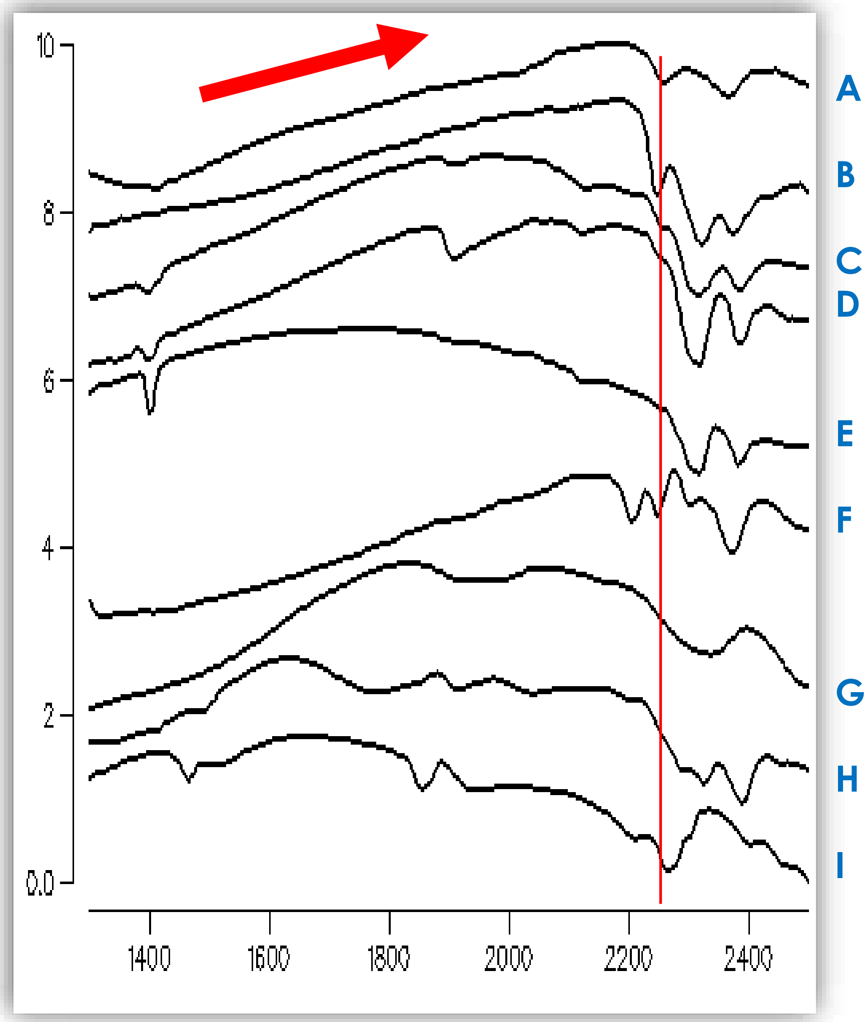
E: Actinolite

F: Tourmaline

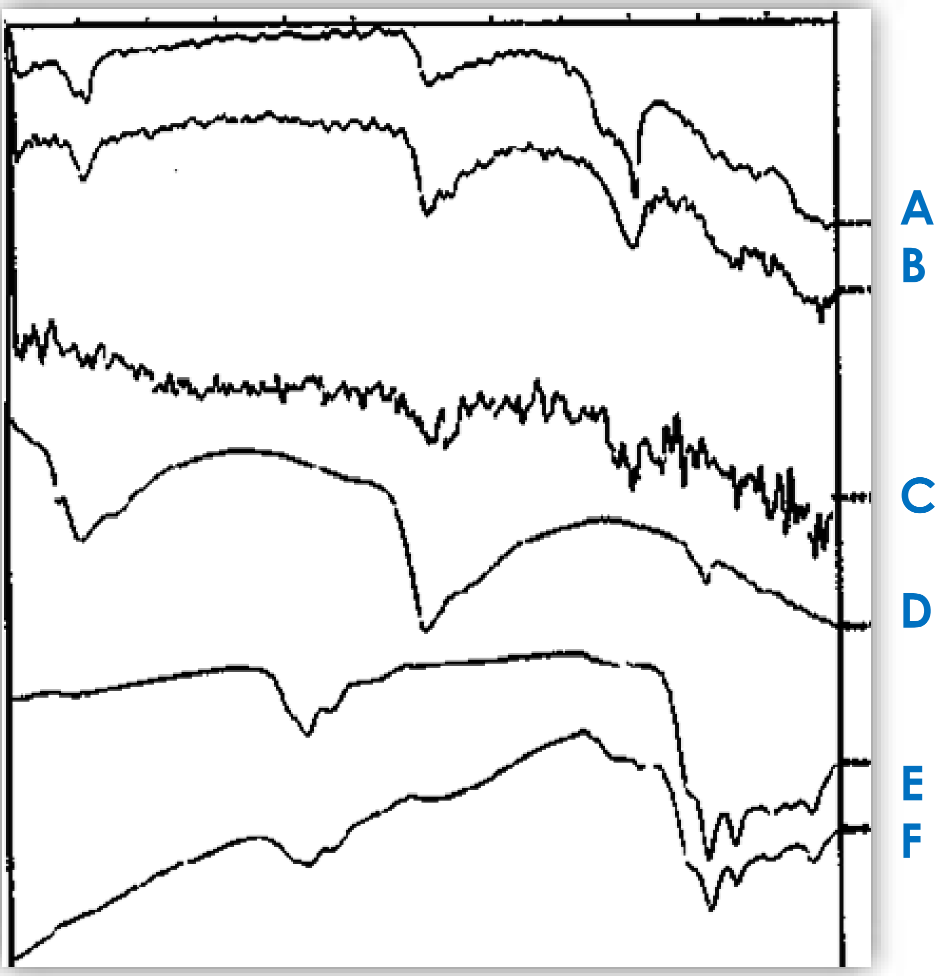
G: Siderite

H: Chloritoid

I: Jarosite



Low reflectance, noise, organics



A: Coal 1-2 %

B: Coal ~4 %

C: Coal 7-8 %

D: Coal very thin sample

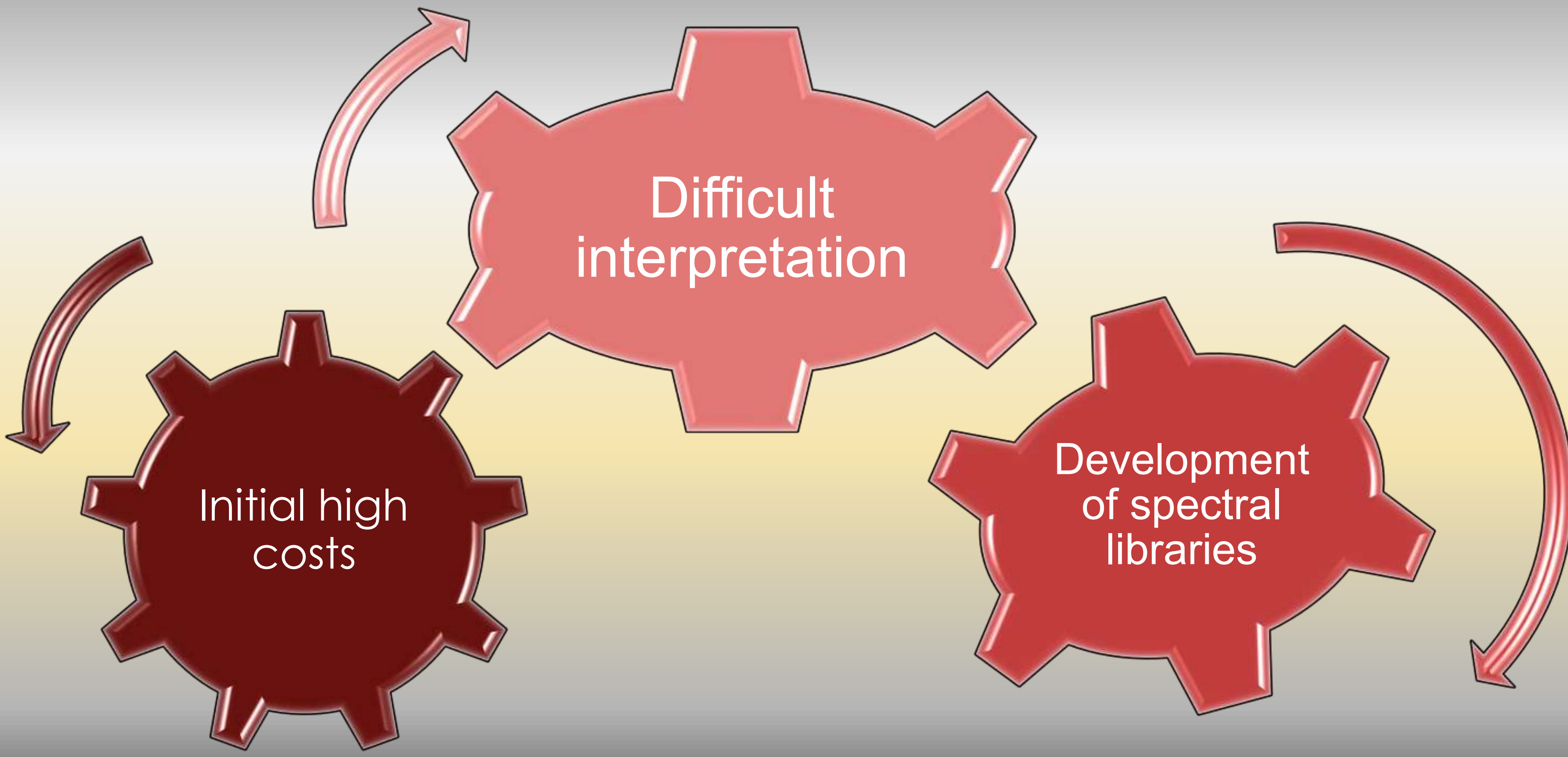
E, F: Organics

EQUIPMENT

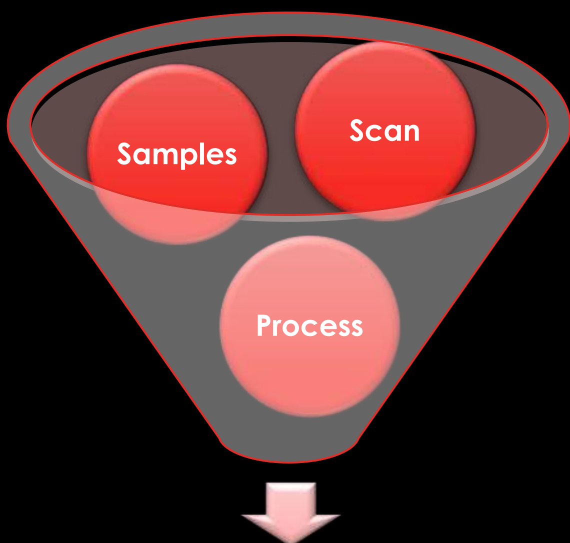
Types of sample media

- Argillized samples
- White rocks or altered white areas
- From veins and outward of them
- Fresh vs Weathered material
- Fracture Surfaces
- Porphyritic rocks
- Breccias

LIMITATIONS OF NIR SPECTROSCOPY



DEVELOPING A SPECTRAL LIBRARY



Libraries!!!

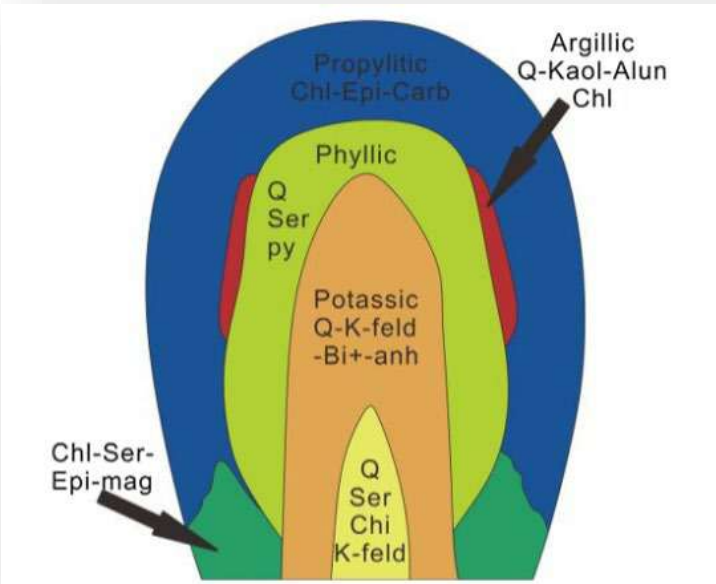
ADVANTAGES OF NIR - SPECTROSCOPY

- Less time consuming
- Very small amount of sample is required
- Non-destructive method !!!
- Cost economical in the long run
- No trace-method but brilliant for bulk
- Important for field analyses !!!

APPLICATIONS

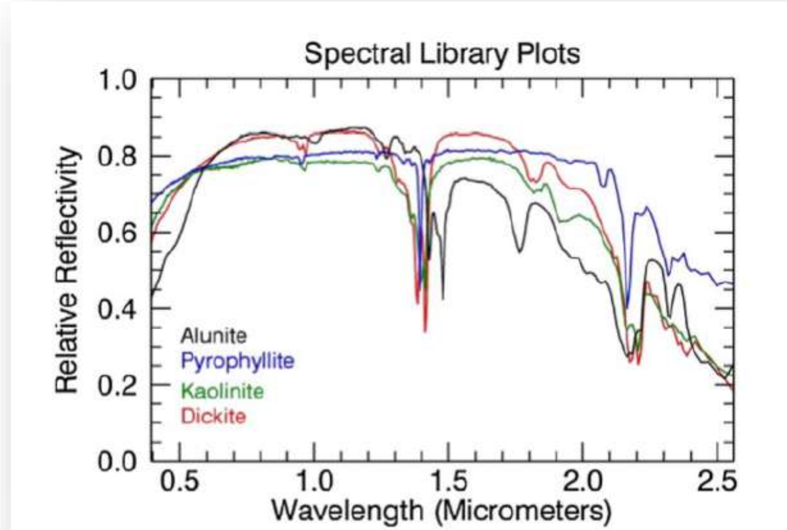
Crop management	**Soil quality monitoring**	**Soil carbon assessment**	**Food industry**
Pharmarceuticals	**Petrochemistry & Biofuel analysis**	**Ore geology**	**Polymer**
Remote monitoring	**Materials Science**	**Archaeometry**	**Metamorphic Geology**

WANG ET AL. 2020



PCA Eigenvalue matrix for propylitization alteration.

Eigenvalues	Band 1	Band 5	Band 8	Band 9
PC1	0.999690	0.017451	0.014487	0.010260
PC2	−0.024877	0.715931	0.552558	0.426032
PC3	−0.000618	−0.691210	0.646342	0.323219
PC4	0.000641	−0.096784	−0.526034	0.844938



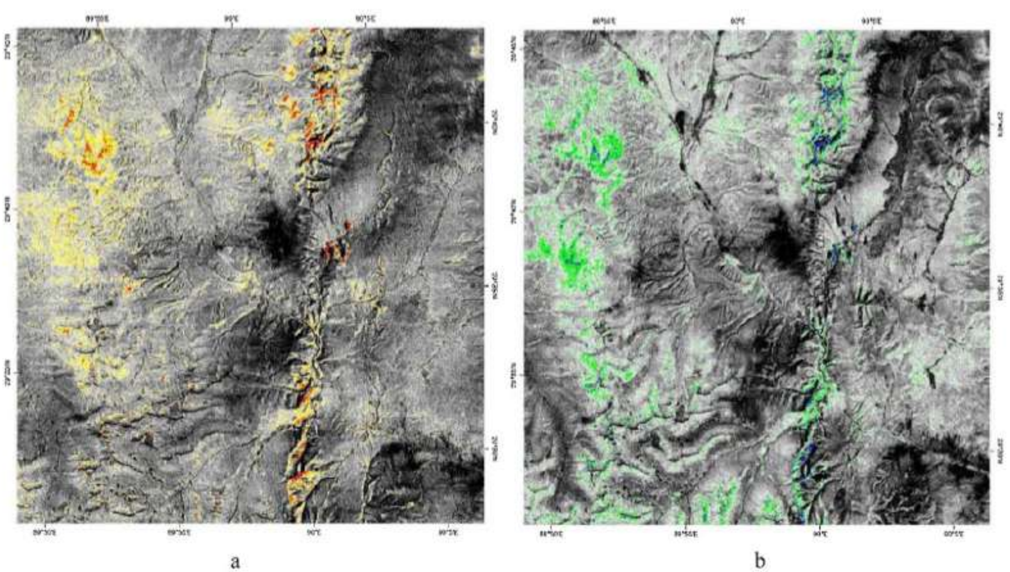
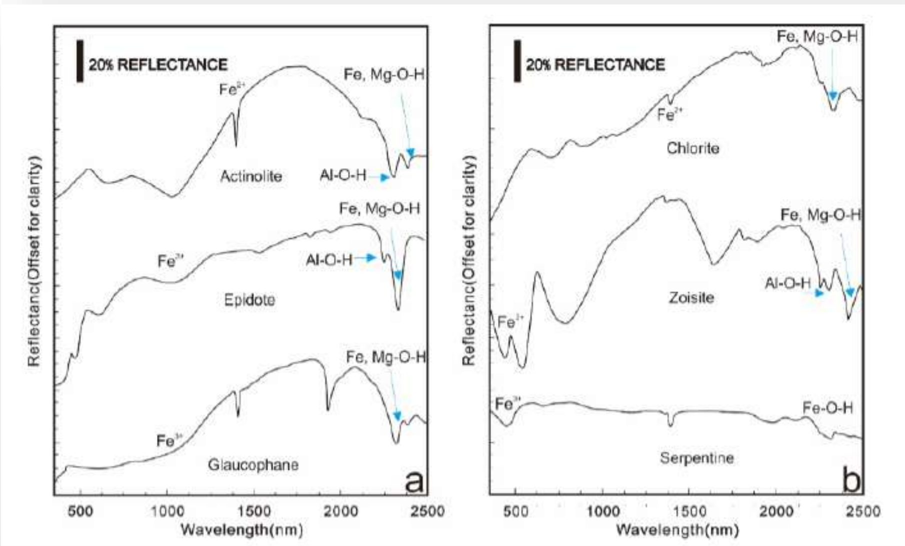
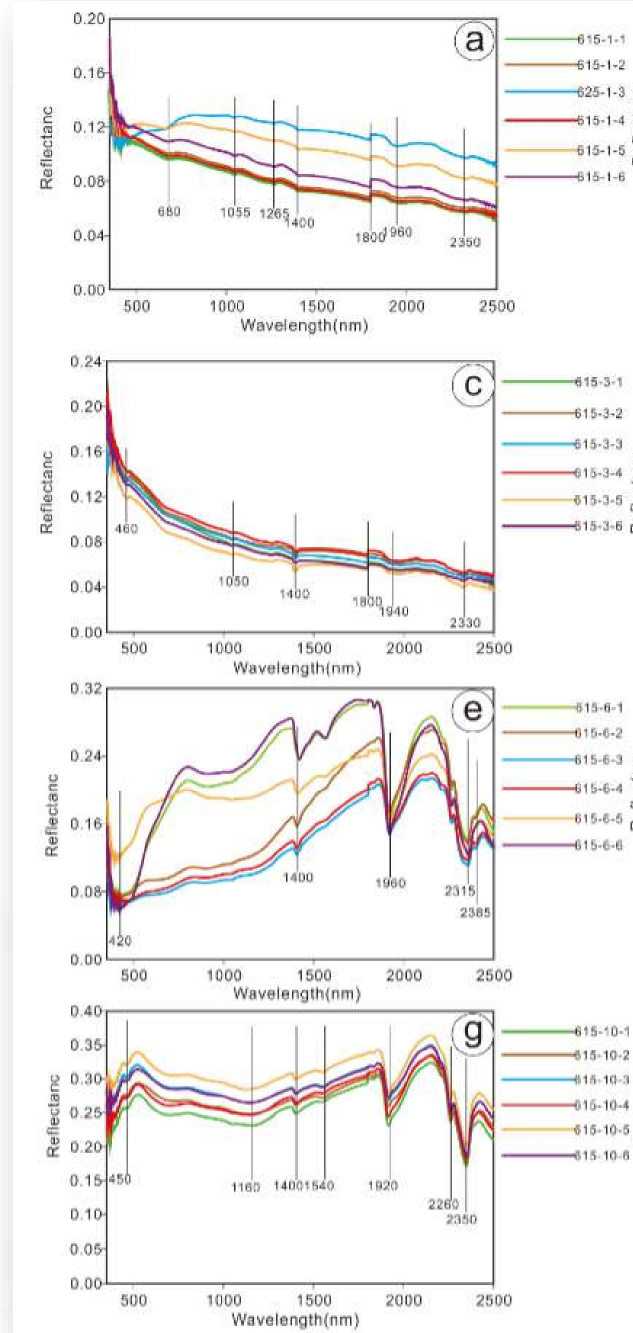


Fig. 6. PCA results for argilization and propylitization. (a) Argillization alteration, yellow: slight, red: severe, (b) Propylitization alteration, green: slight blue: severe. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

SHI ET AL. 2018



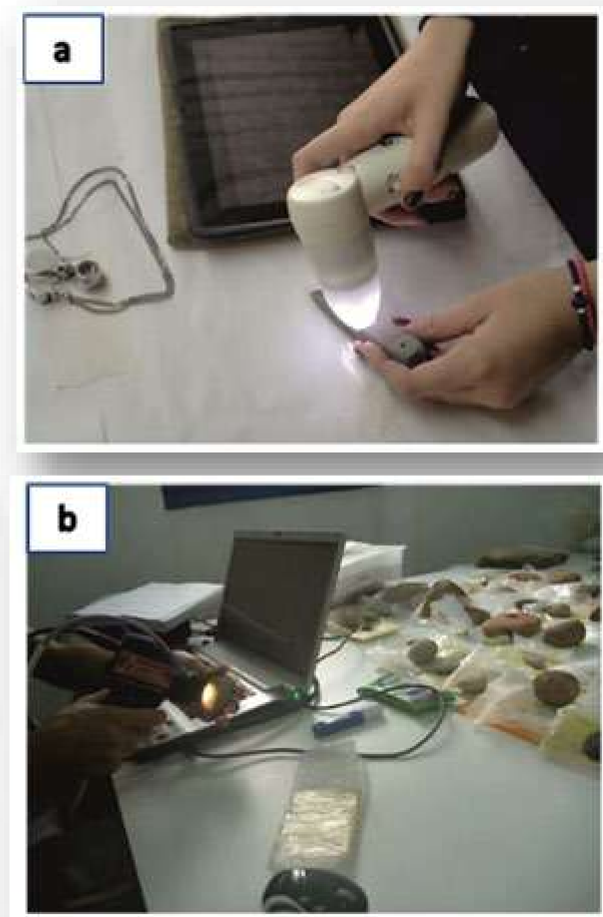


KOKKALIARI ET AL. 2022

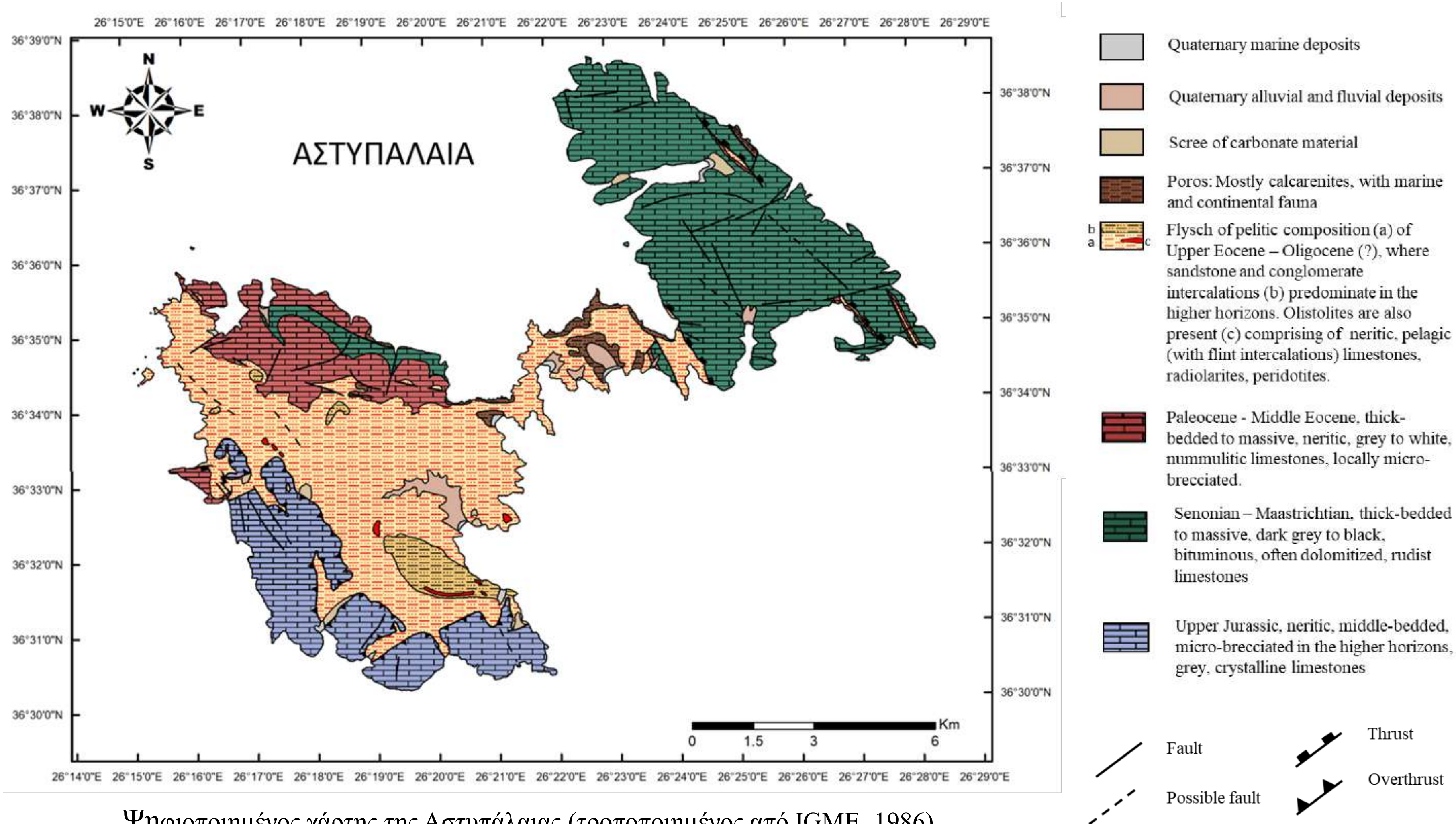
The lithic artefacts

A total of 190 stone tools were found during an extensive study on the Vathy Peninsula, from 2011 to 2015.

KOKKALIARI ET AL. 2022

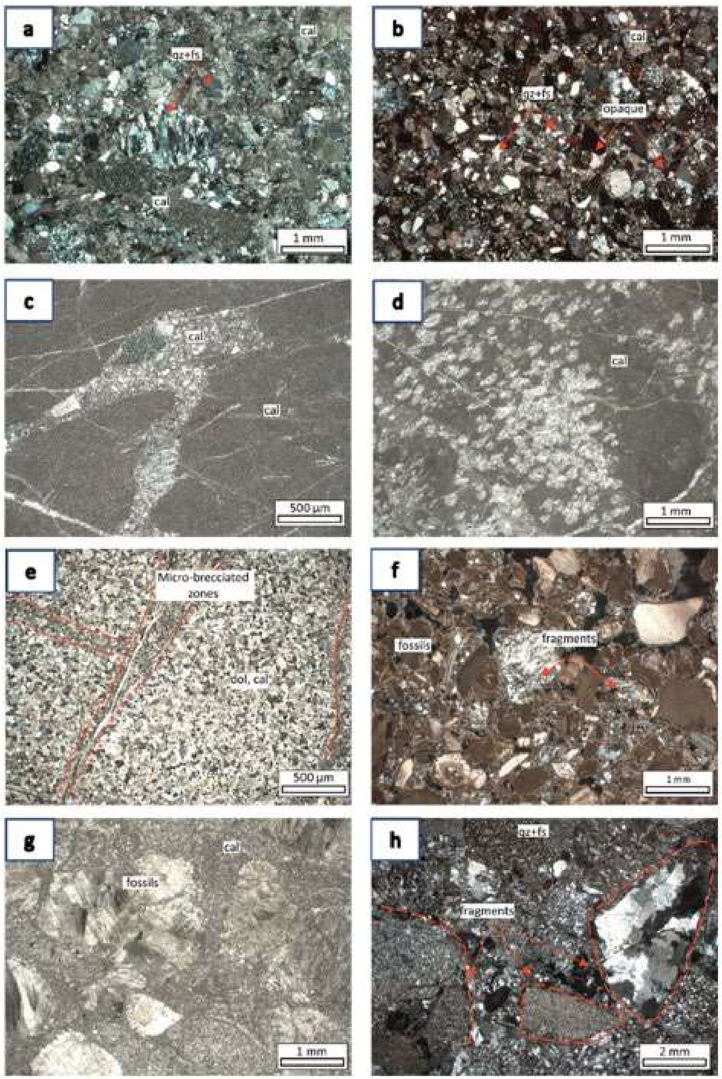


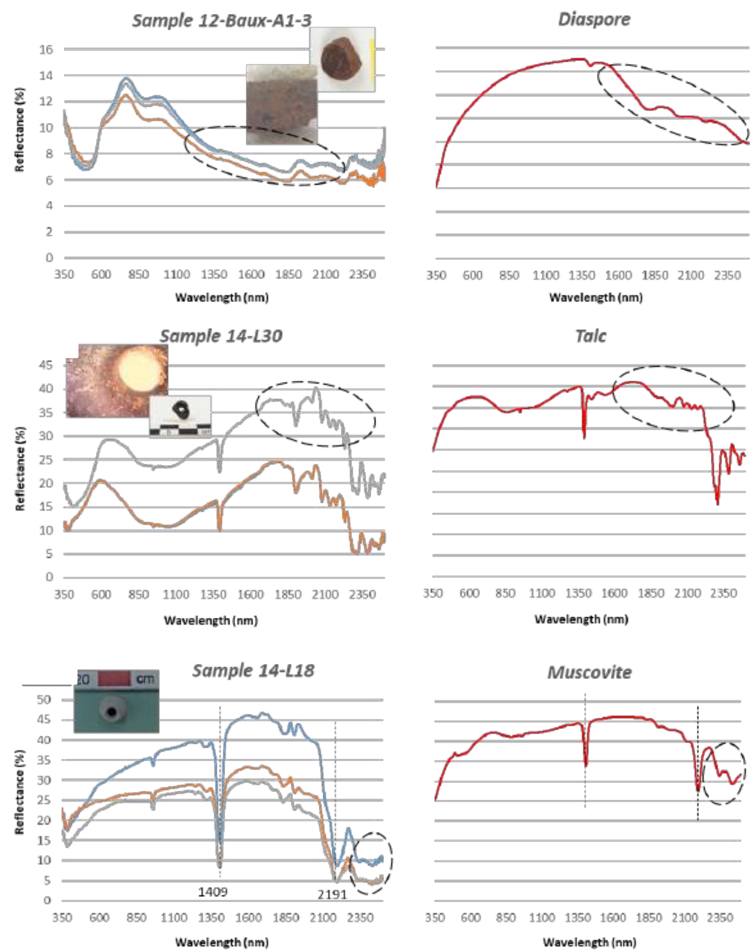
Geologic Structure of Astypalaia Island



Ψηφιοποιημένος χάρτης της Αστυπάλαιας (τροποποιημένος από IGME, 1986)

KOKKALIARI ET AL. 2022





MAIN RAW MATERIALS THAT WERE IDENTIFIED

Local

Sandstones (calcitic)

Mudstoned

Clay schists

Limestones

Imported???

Pumice

Volcanic Rocks (rhyodacites to andesites, tuffs)

Non-local

Chalcedony

Bauxite

Meta-Bauxite

Steatite

Paragonite

THANK YOU FOR YOUR ATTENTION