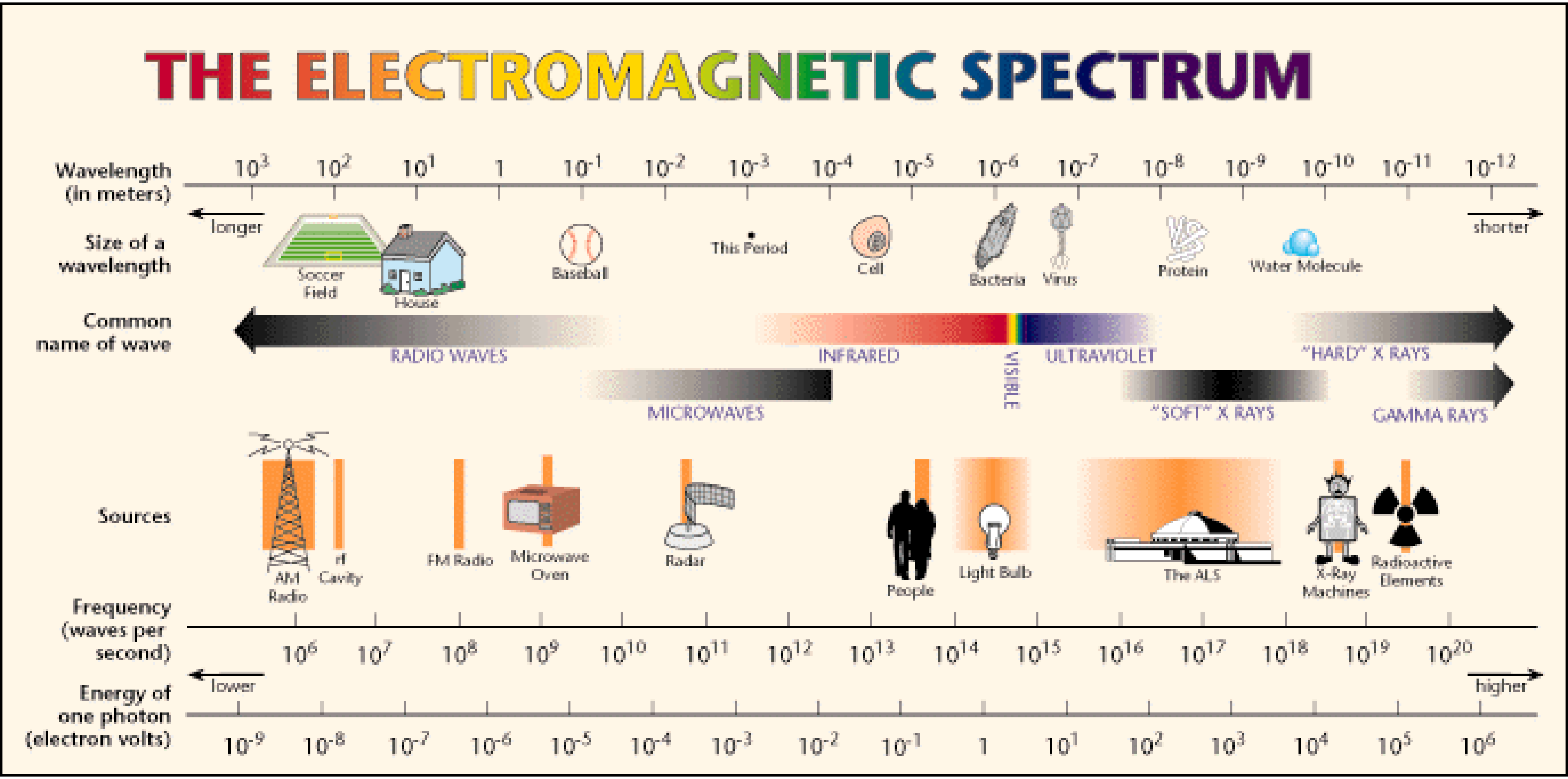
‘Wet’ Chemical Techniques

- One technique to analyze the chemistry of a mineral is to dissolve it
  - Water, Strong acids/bases, hydrofluoric acid, oxidants, fluxes of other material dissolve mineral
  - Analyze the chemical constituents now dissolved in the resulting solution
  - Spectroscopy (often using Inductively coupled plasma (ICP) or flame) to ionize the atoms and investigate the effects of/on visible light.

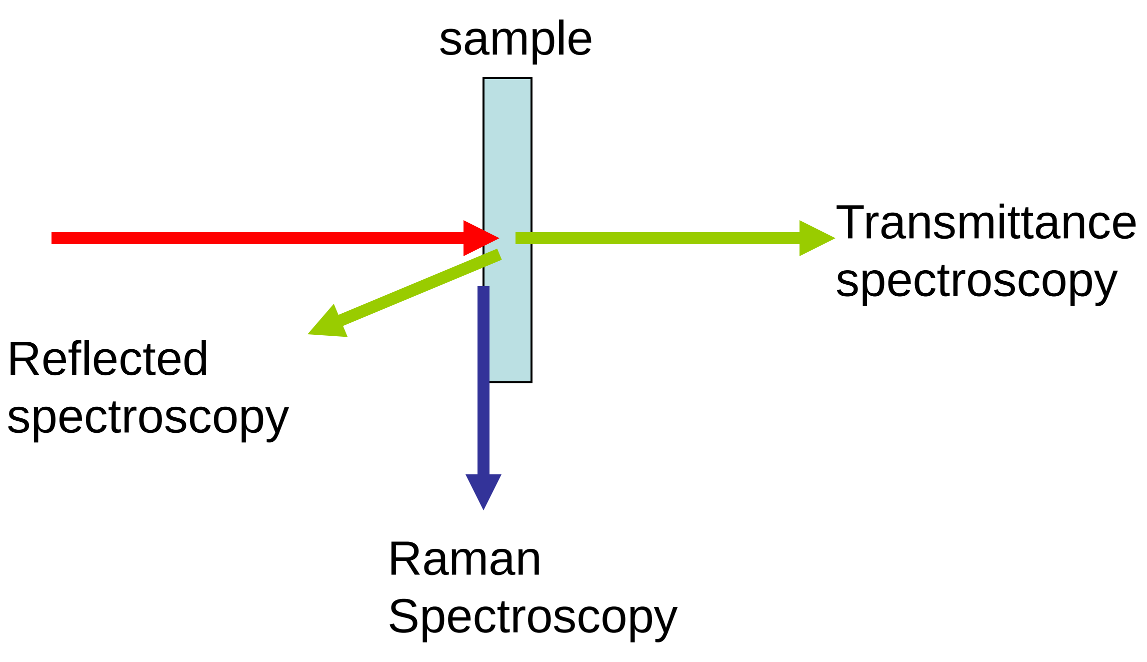


Planck's law: $E=h\nu = hc/\lambda$

Where ν is frequency, λ is wavelength, h is Planck's constant, and c is the speed of light

Spectroscopy

- Exactly how energy is absorbed and reflected, transmitted, or refracted changes the info and is determined by different techniques



Analytical Techniques for Minerals

- XRD (X-ray diffraction) is one of the most powerful tools for mineral identification, structural/chemical refinement, and size determination – we will study it in detail (both lecture and lab).
- Microscopy – Optical techniques are another very powerful tool for mineral identification, identification of physical/ chemical ‘history’ of minerals/rocks, and mineral association which we will also study in detail (both lecture and lab)

Analytical Techniques for Minerals

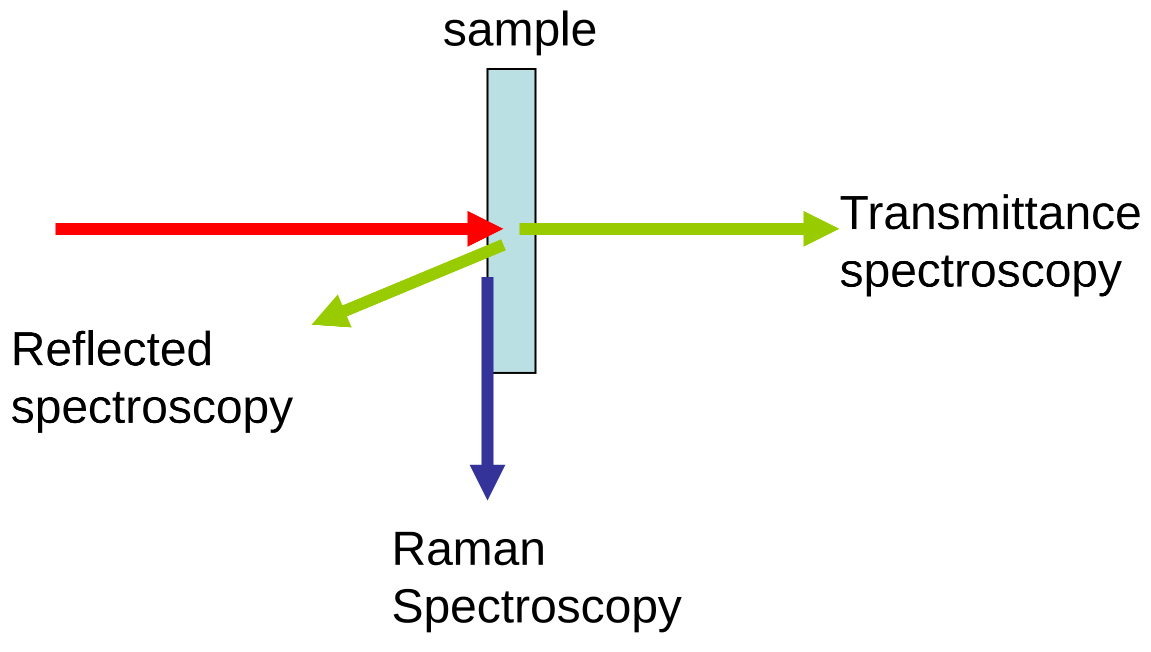
- Spectroscopy – different methods of studying how different parts of the electromagnetic spectrum (of which visible light is a small part) are affected by minerals
- Electron microscopy – look at techniques which utilize how electrons (shot through a sample of mineral) interact with minerals – imaging possible to very small sizes
- Scanned-proximity probe microscopy techniques – look at forces between probe tip and sample to measure a property (height, optical absorption, magnetism, etc)

More analytical techniques

- Sychrotron – Different techniques (many similar to spectroscopic techniques) that utilize particles accelerated to very high speeds and energies and how they interact with minerals
- Magnetic – different techniques that utilize the magnetic properties of minerals
- Size – techniques to determine the sizes of different minerals
- Chemistry/isotopes – techniques to probe chemical and isotopic signatures in minerals

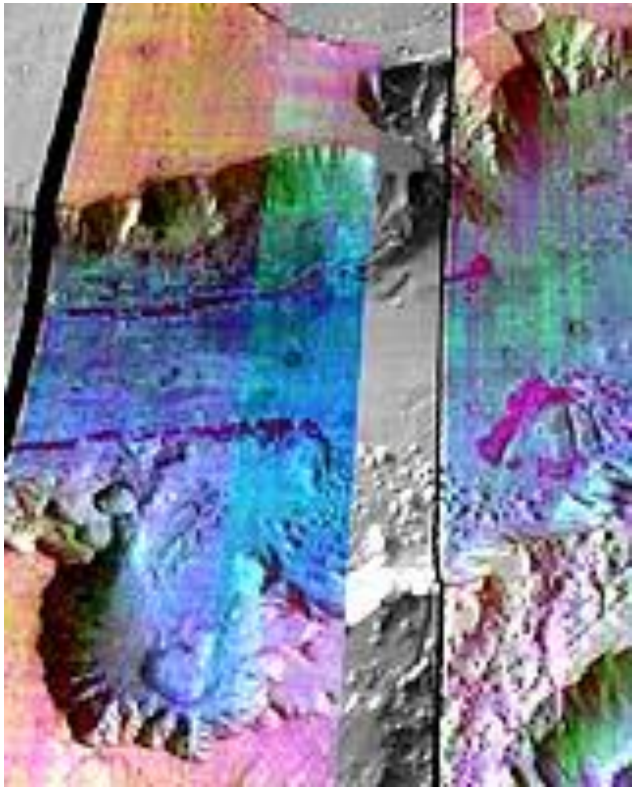
Spectroscopy

- Exactly how light is absorbed and reflected, transmitted, or refracted changes the info and is determined by different techniques



Light Source

- Light shining on a sample can come from different places (in lab from a light, on a plane from a laser array, or from earth shining on Mars from a big laser)
- Can ‘tune’ these to any wavelength or range of wavelengths



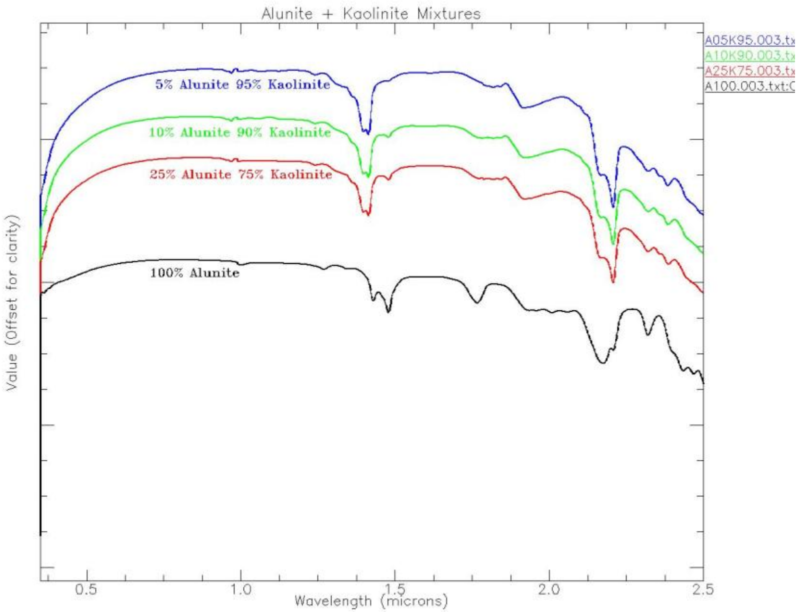
IR image of Mars
Olivine is purple

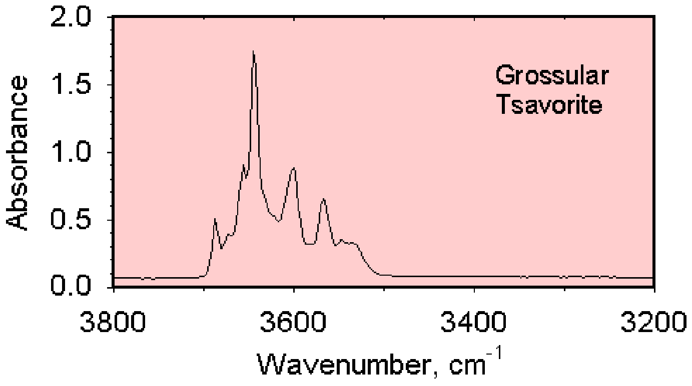
Causes of Absorption

- Molecular or atomic orbitals absorb light, kicks e^- from stable to excited state
- Charge transfer or radiation (color centers)
- Vibrational processes – a bond vibrates at a specific frequency → only specific bonds can do absorb IR though (IR active)

Reflectance Spectroscopy

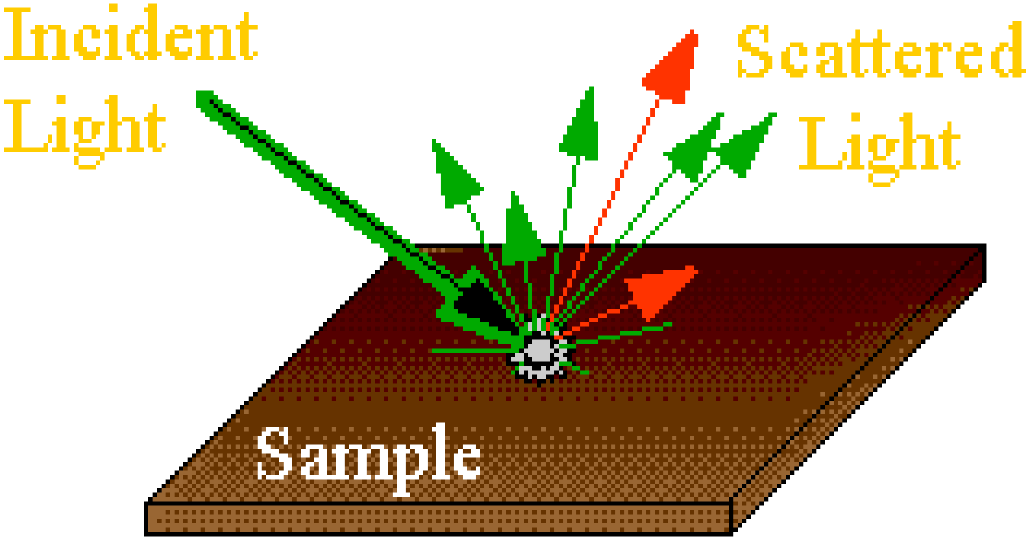
- Non-destructive form of analysis, used to ‘see’ some of the chemistry, bonding
- Spectroscopy is particularly good at detecting water and OH groups in minerals (especially in IR)
- Good at differentiating between different clays because it detects OH groups well





Raman Spectroscopy

- Another kind of spectroscopy which looks at a scattering effect and what that tells us about the chemistry, oxidation state, and relative proportions of different ions

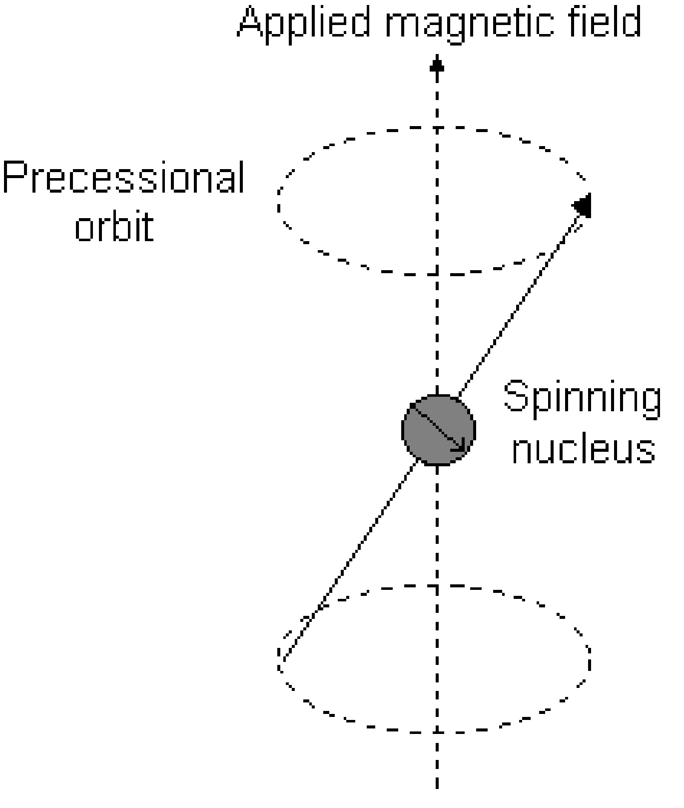


Mössbauer Spectroscopy

- Special effect, restricted to specific isotopes of certain elements which causes a very characteristic emission (after getting hit with a beam of gamma radiation) which is sensitive to the bonding environment of that isotope (only ^{57}Co, ^{57}Fe, ^{129}I, ^{119}Sn, ^{121}Sb)
- Generally used to study Fe – tells us about how Fe is bonded and it's oxidation state

Nuclear Magnetic Resonance Spectroscopy (NMR)

- NMR is useful for determining short range cation ordering in minerals.
- The NMR spectrometer can be tuned to examine the nucleus of mineralogical interest (e.g. aluminosilicates (27Al, 29Si, 23Na) oxides (17O, 25Mg, etc.), phosphates (31P), hydrous minerals (1H, 19F)).
- NMR is particularly useful for cations that can not be distinguished by X-ray methods, such as Si/Al ordering in aluminosilicates

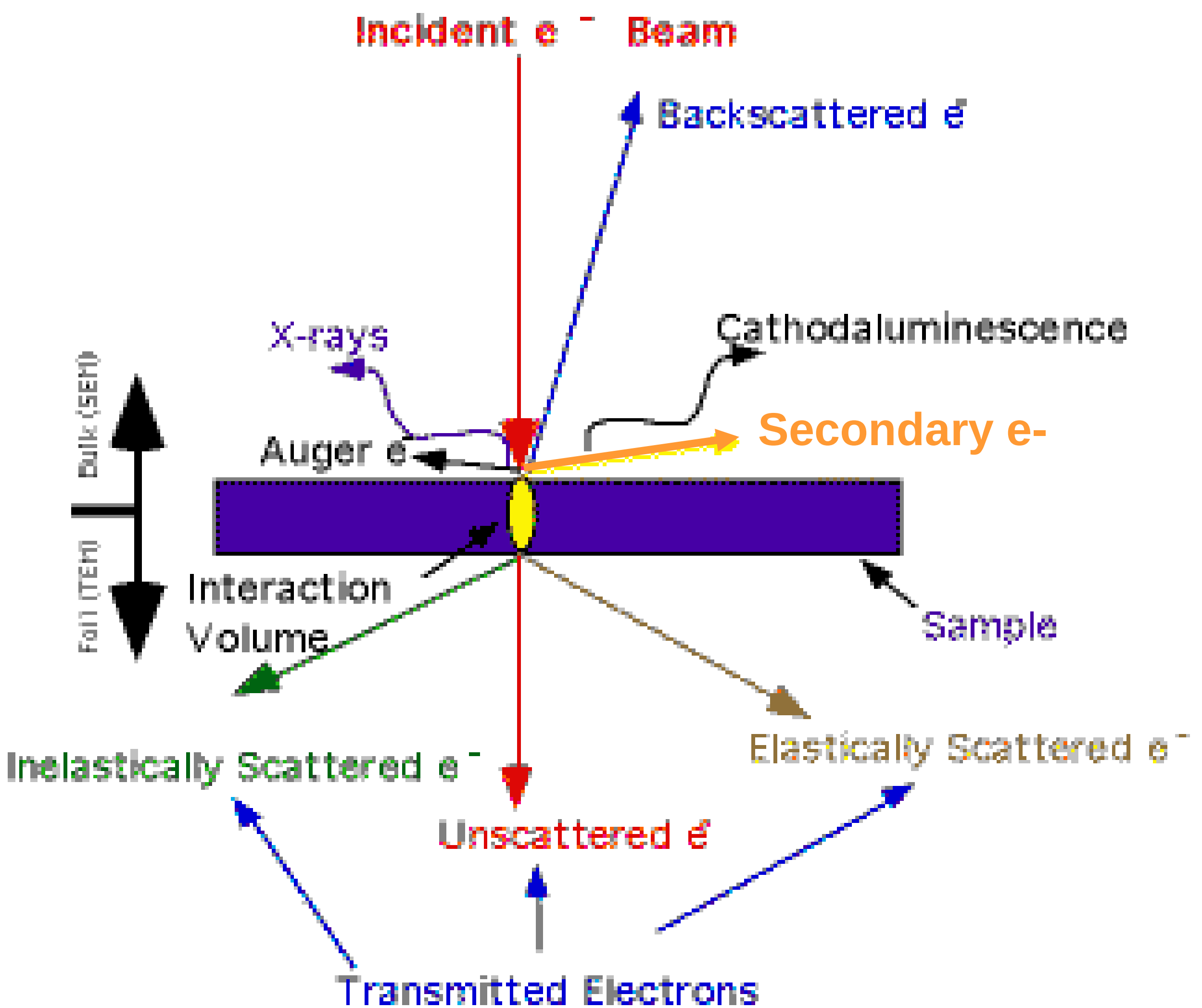


Electron Microscopy

- What we can see using visible light is limited at the small end of spatial scales by the wavelength of light (hundreds of nanometers)
- To image things smaller than this, need to use energy of smaller wavelengths
- Because energy is inversely proportional to wavelength ($E=hc/\lambda$), higher energy particles have smaller wavelengths and can image smaller things (e^- are easy to generate and accelerate → faster particle has more energy)

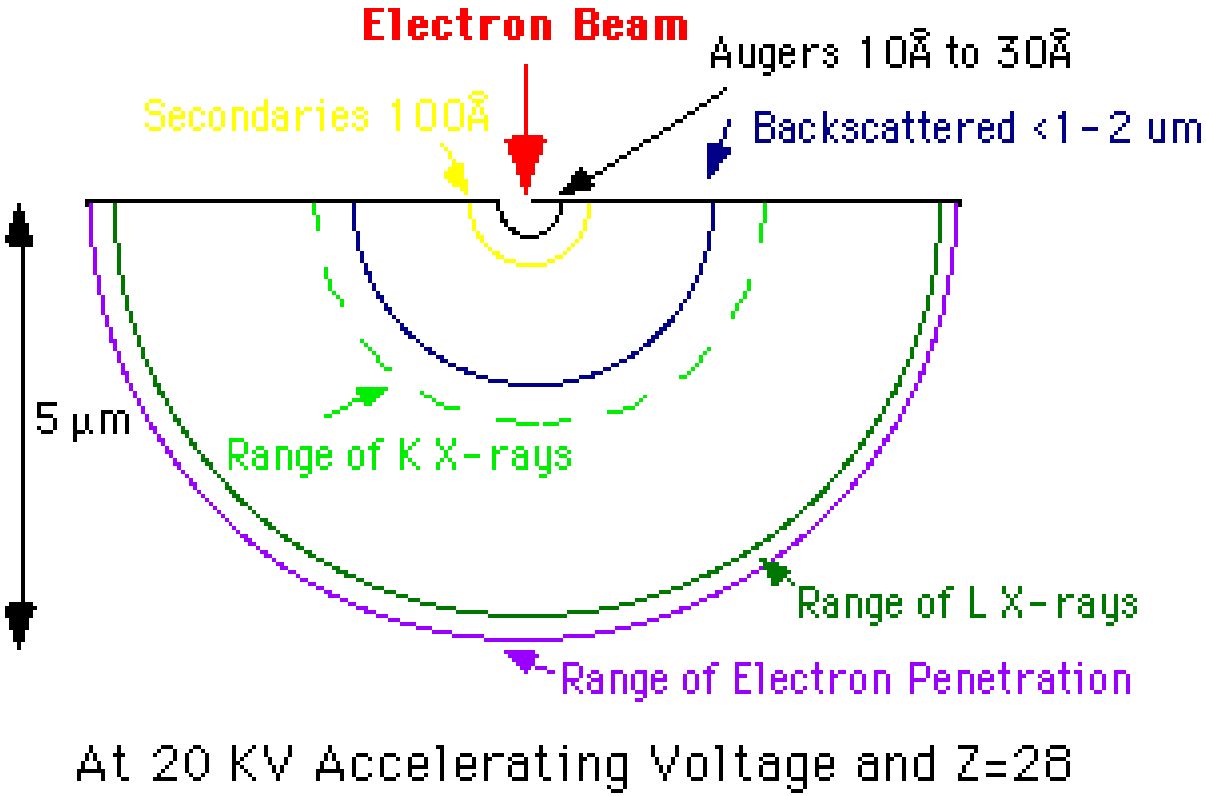
Electron Microscopy/ Spectroscopy

- Interaction of electrons with a sample



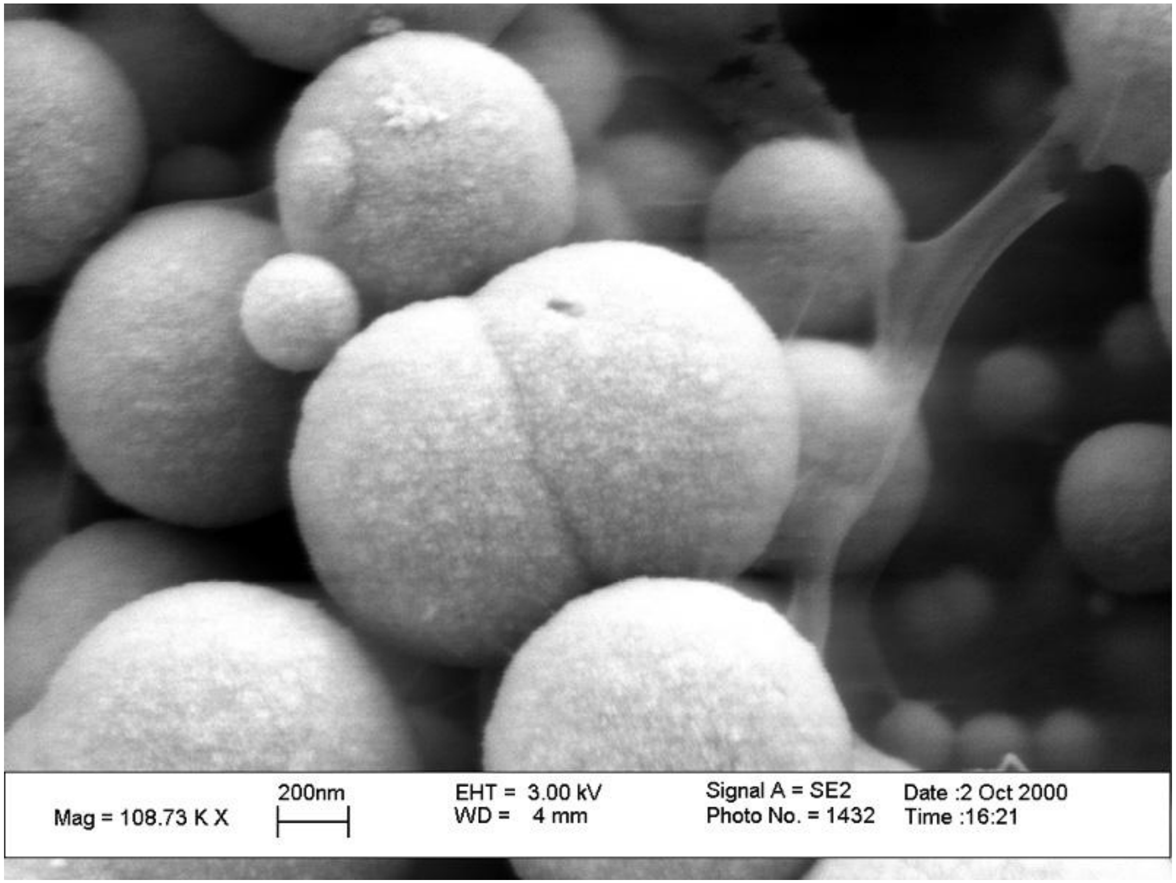
e- penetration into a sample

- Details dependent on mineral composition and accelerating voltage of e- beam, but for SEM applications:



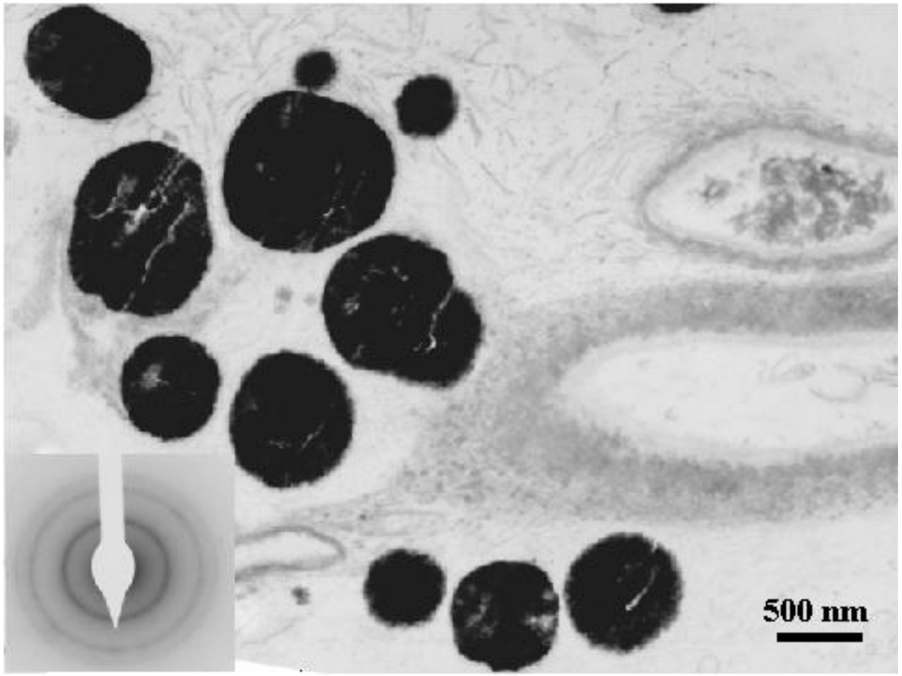
SEM – what do we get?

- Topography (surface picture) – commonly enhanced by ‘sputtering’ (coating) the sample with gold or carbon



TEM (+ HRSTEM) – What do we get?

- 'See' smallest features with this – sub-nm!
- **Morphology** – size, shape, arrangement of particles on scale of atomic diameters
- **Crystallographic information** – from diffracted electrons, get arrangement and order of atoms as well as detection of atomic-scale defects
- **Compositional information** – Chemical identity, including redox speciation (distinguish Fe^{2+} and Fe^{3+} for instance)



Electron Microprobe

- Very similar to SEM and TEM in many respects, but utilizes ‘thick sections’ and a set of detectors which measure the emitted X-Rays from e^- bombardment and excitation more accurately than the detectors used in SEM or TEM analyses
- These detectors are wavelength dispersive spectrometry (WDS) detectors, there are usually an array of 3-5 which record over some range of wavelength much more accurately than the EDX detector available with SEM and TEM instruments

Synchrotrons

- A synchrotron is a ring which uses magnets and electrodes to accelerate x-rays or light to nearly the speed of light
- These extremely bright sources have widened the range of information which we can use traditional spectroscopy, diffraction, and even microscopy techniques for

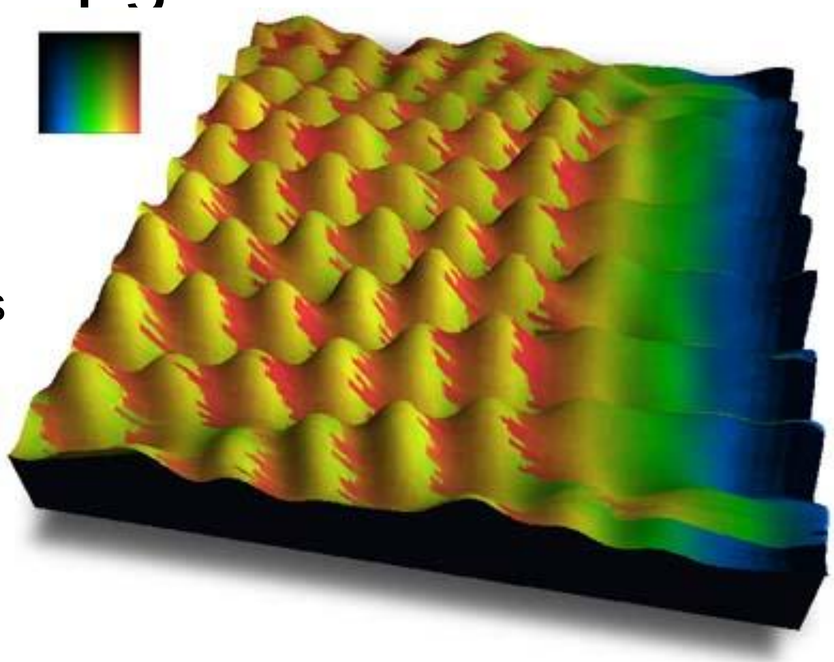
National Synchrotron Light Source (NSLS)

XANES and EXAFS

- X-ray adsorption near-edge spectroscopy and Extended X-ray adsorption Fine Structure, commonly done with synchrotron radiation because the higher energy X-ray yields more precise data
- X-ray techniques which look at the fine details of X-ray interactions with minerals
- Sensitive to oxidation states and specific bonding environments

Atomic Force Microscopy (AFM)

- Can be done in water or air (unlike SEM/TEM which requires a vacuum)
- The probe is attached to a cantilever spring, in which the force 'sensed' is measured
- Get topograpgic information at an atomic scale



Scanning tunneling microscopy (STM) is the precursor to this technique, and is still used to yield similar information

2.5 nm^2 rendering of a surface – what are the bumps??