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The Abdus Salam International Centre for Theoretical Physics

IAEA International Atomic Energy Agency

unesco United Nations Educational, Scientific and Cultural Organization

Obtaining and Understanding Geochemical and Petrological Data for Studying the Thermal- Compositional Structure of Lithospheric Mantle: Part 2A.

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Department of Earth Sciences – University of Cambridge

Aims and Motivation for Part 2.

Obtaining and Understanding Geochemical Data for Studying the Mantle

- Understand the basic analytical techniques (EPMA) that can be used to measure the chemical compositions of mineral
- Understand why the chemical compositions of minerals vary within the lithospheric mantle
- Understand the basics of geothermobarometry for obtaining pressures and temperatures of rocks and minerals from the lithospheric mantle
- Understand some of the uses of geothermobarometry pressure and temperature estimates for studying the mantle

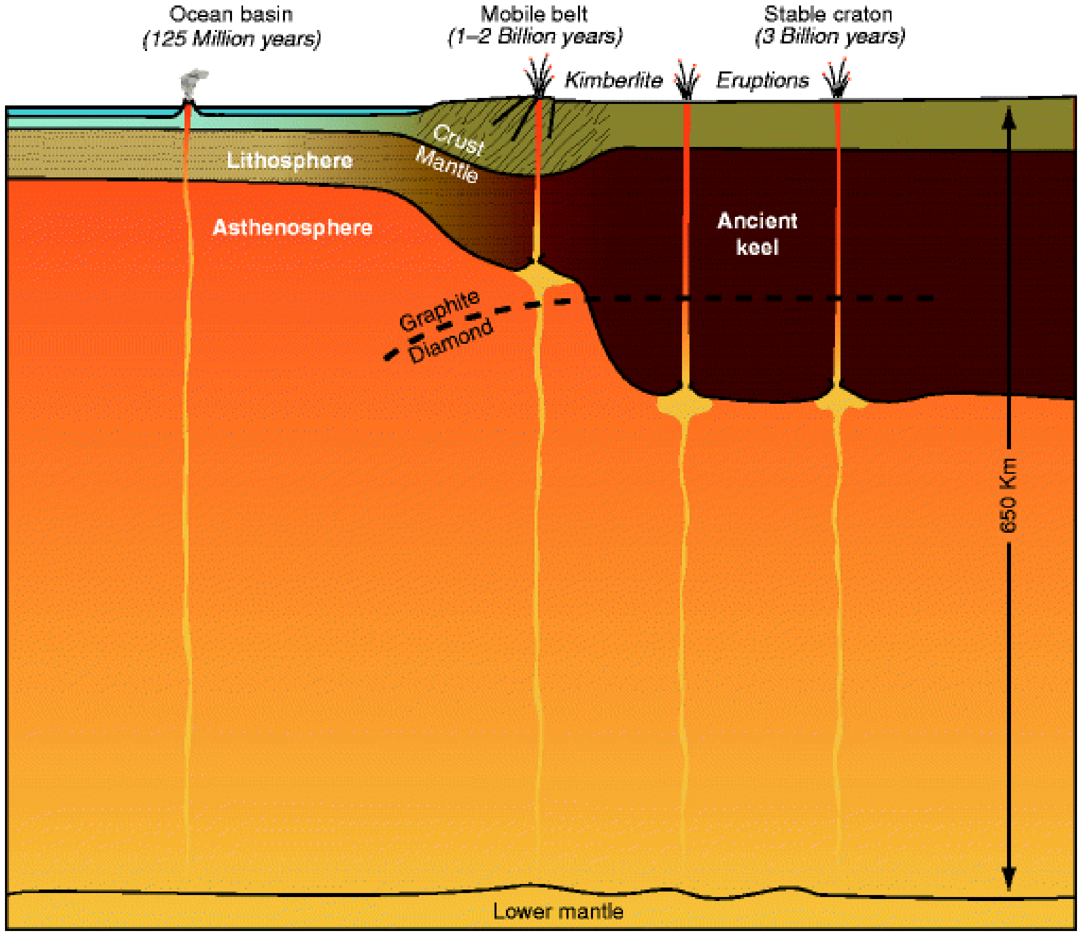
Recommended Reading:

- Pearson, D. G., D. Canil, and S. B. Shirey. "Mantle samples included in volcanic rocks: xenoliths and diamonds." *Treatise on geochemistry* 2 (2003): 568.
- Winter, John DuNann. *Principles of igneous and metamorphic petrology*. Vol. 2. Harlow, UK: Pearson education, 2014.

Studying Lithospheric Mantle with Geochemical Data

Quantitative concentrations of the chemical compositions of rocks and minerals **are crucial** for studying the geochemistry and petrology of the lithospheric mantle:

- Pressure and temperature estimates
- Paleogeotherm models
- Composition and lithology of mantle
- Deep H_2O and CO_2 cycles
- Metal sources and budgets
- Geophysical anomalies (MLD and LAB)
- Constraints for geodynamic models



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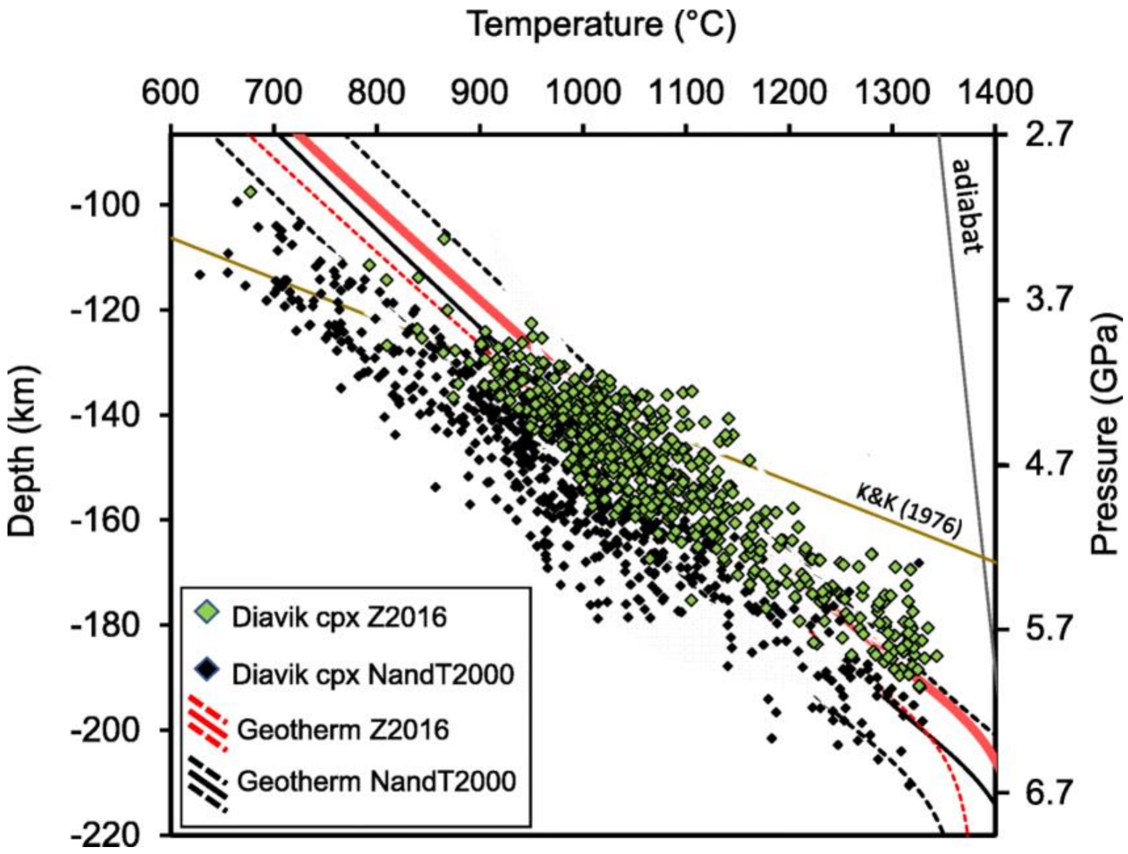

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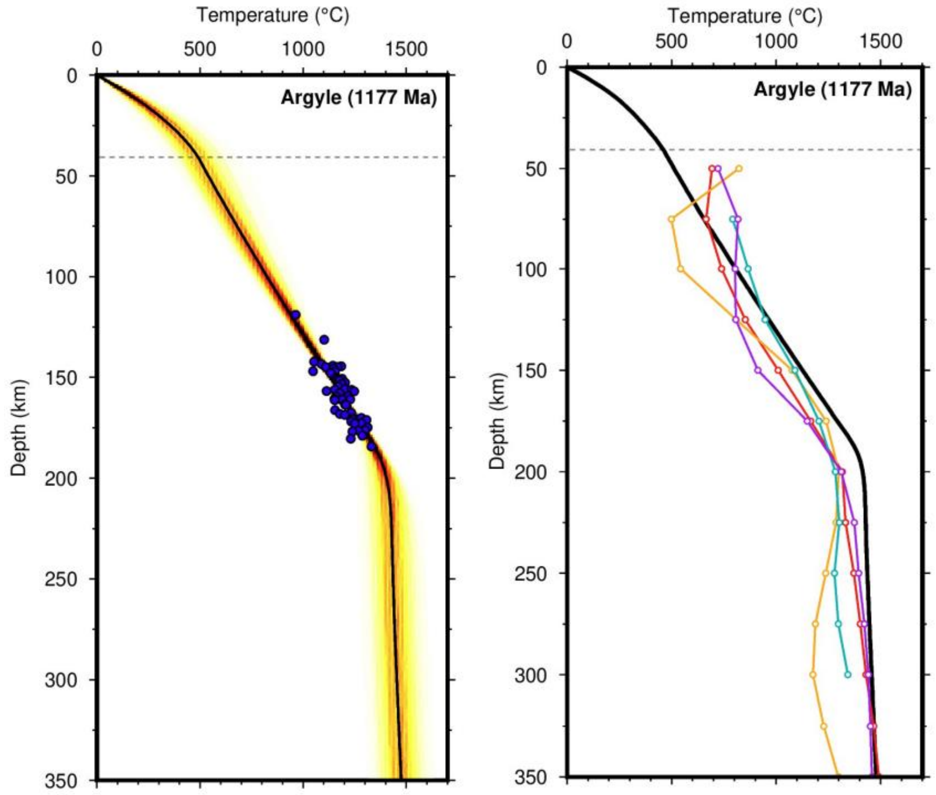

Representative geothermal gradient (yellow) fit to xenolith pressure-temperature estimates. After Hoggard et al. (2020)

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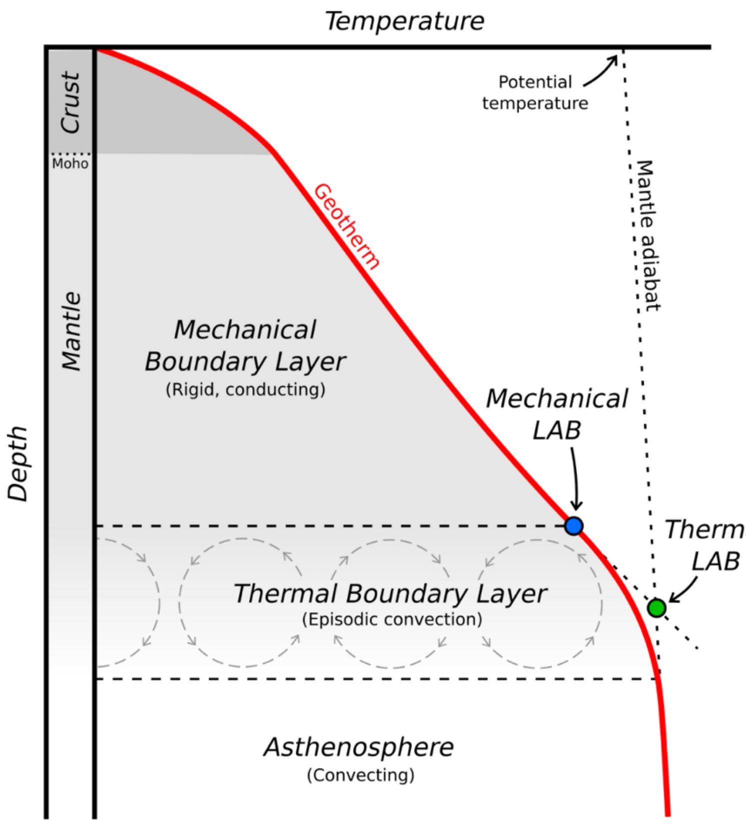

Representative geothermal gradient. After Hoggard et al. (pers. comms). Note that the LAB is the point where the paleogeotherm intersects the mantle adiabat.

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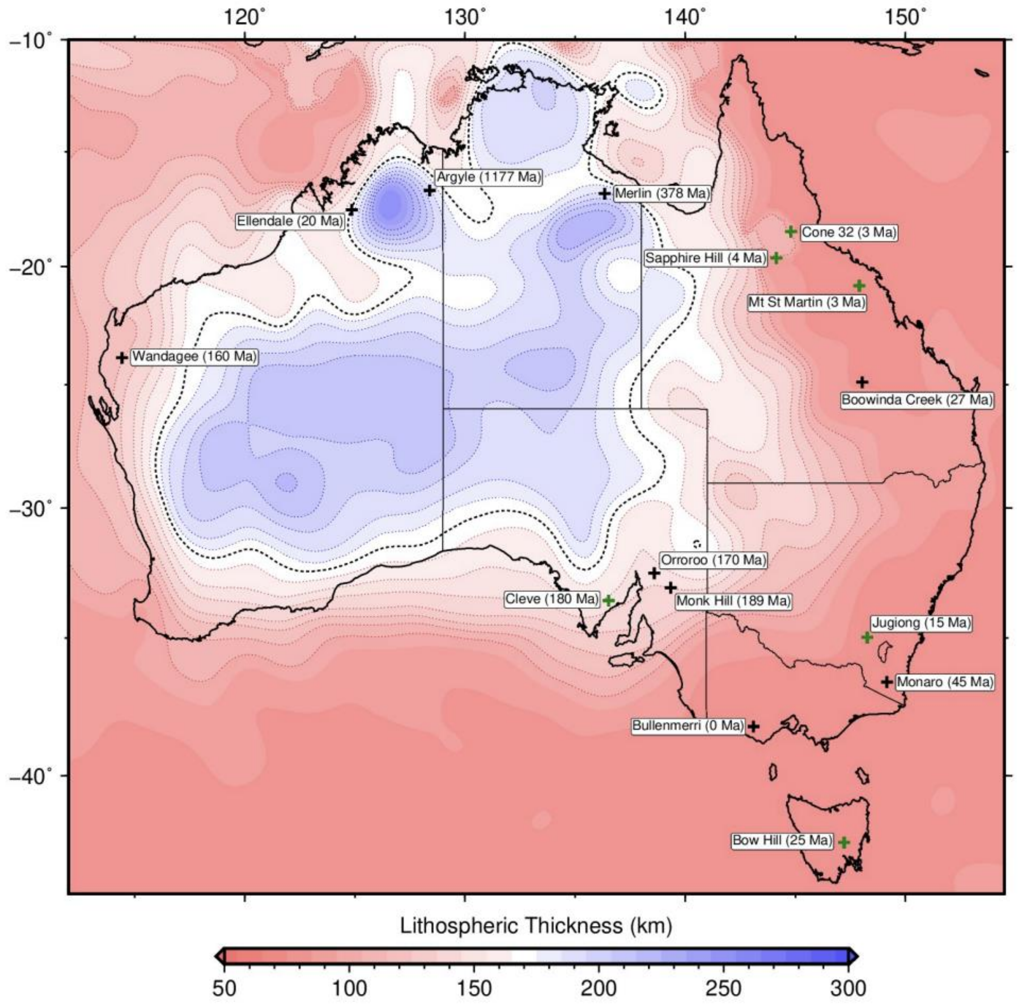

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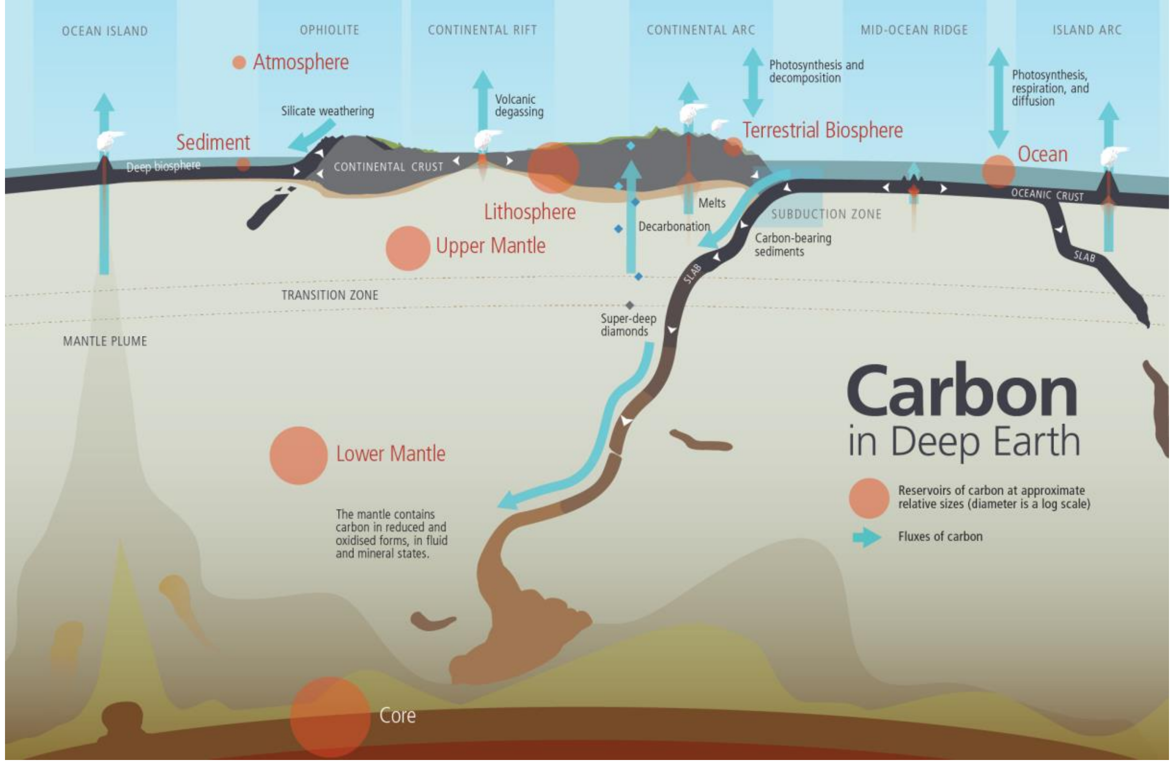

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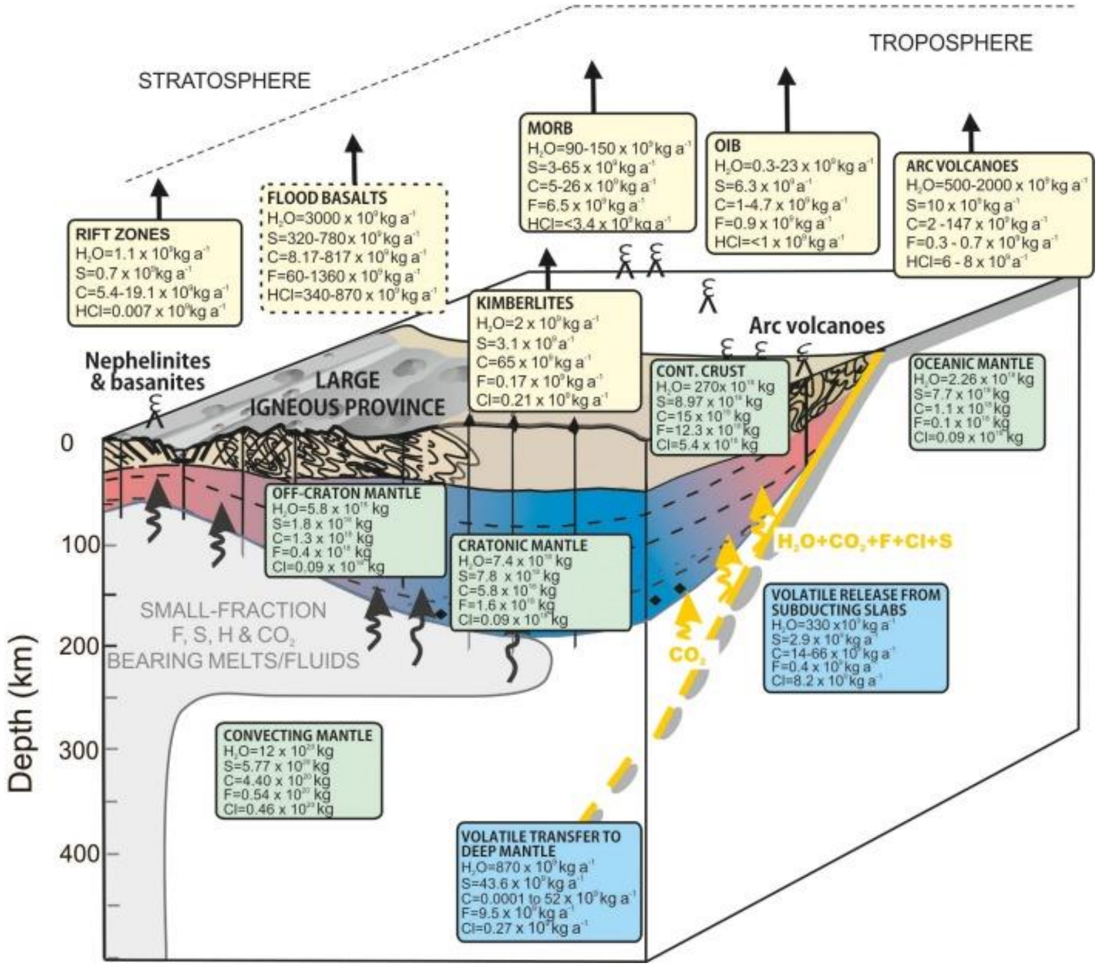

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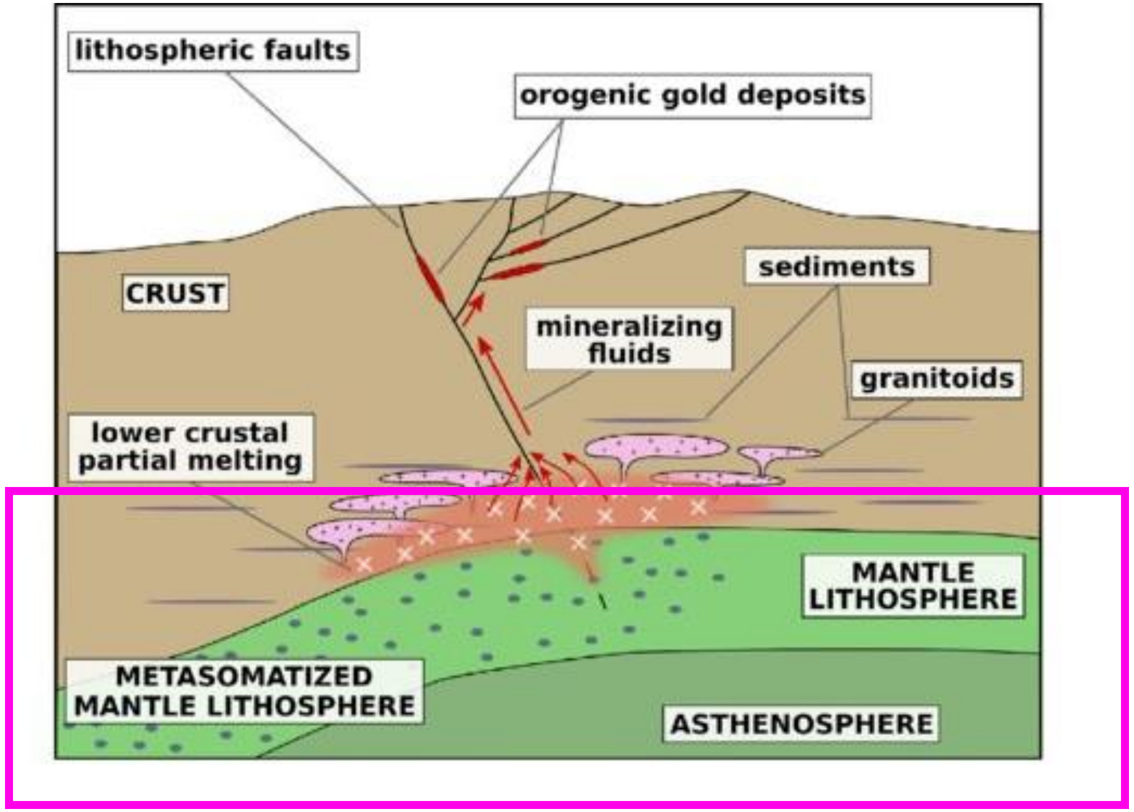

Schematic sketch illustrating the proposed model for the origin of mineralizing fluids of Neoarchean orogenic gold deposits in the Yilgarn Craton. After Caruso et al. (2022).

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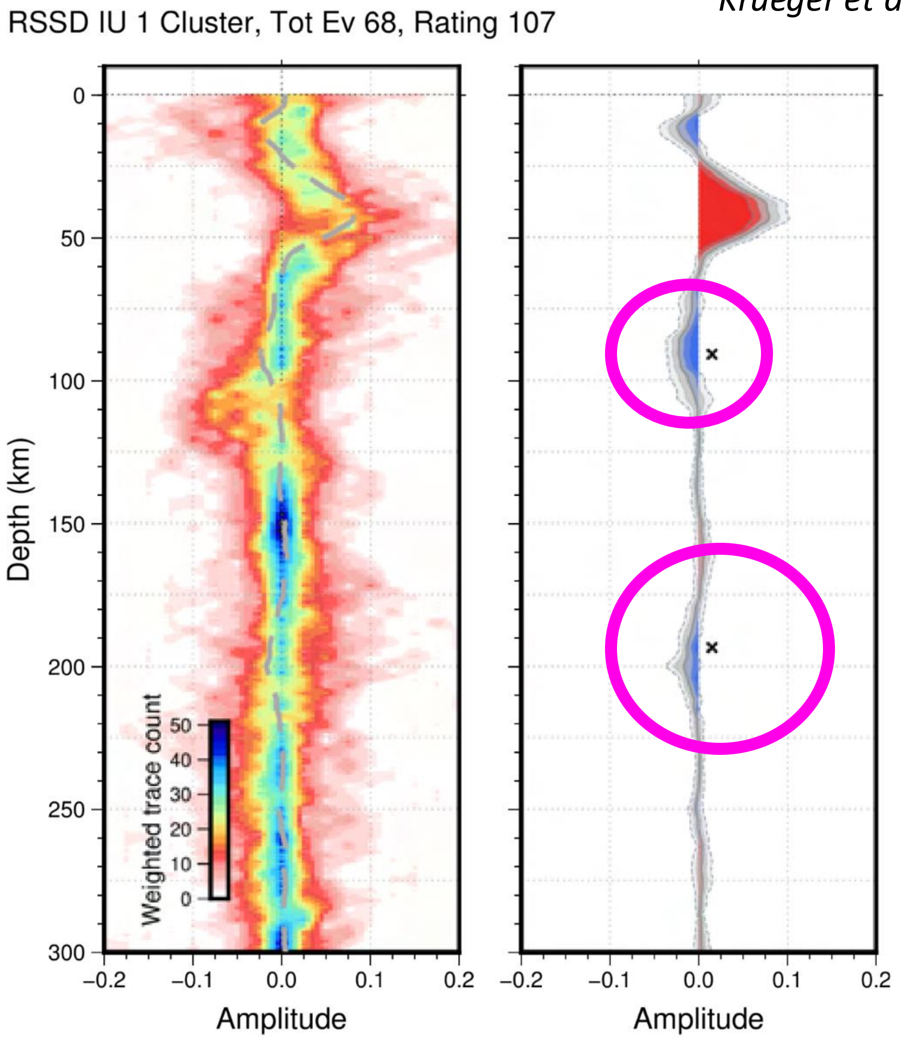
Krueger et al. (2021)



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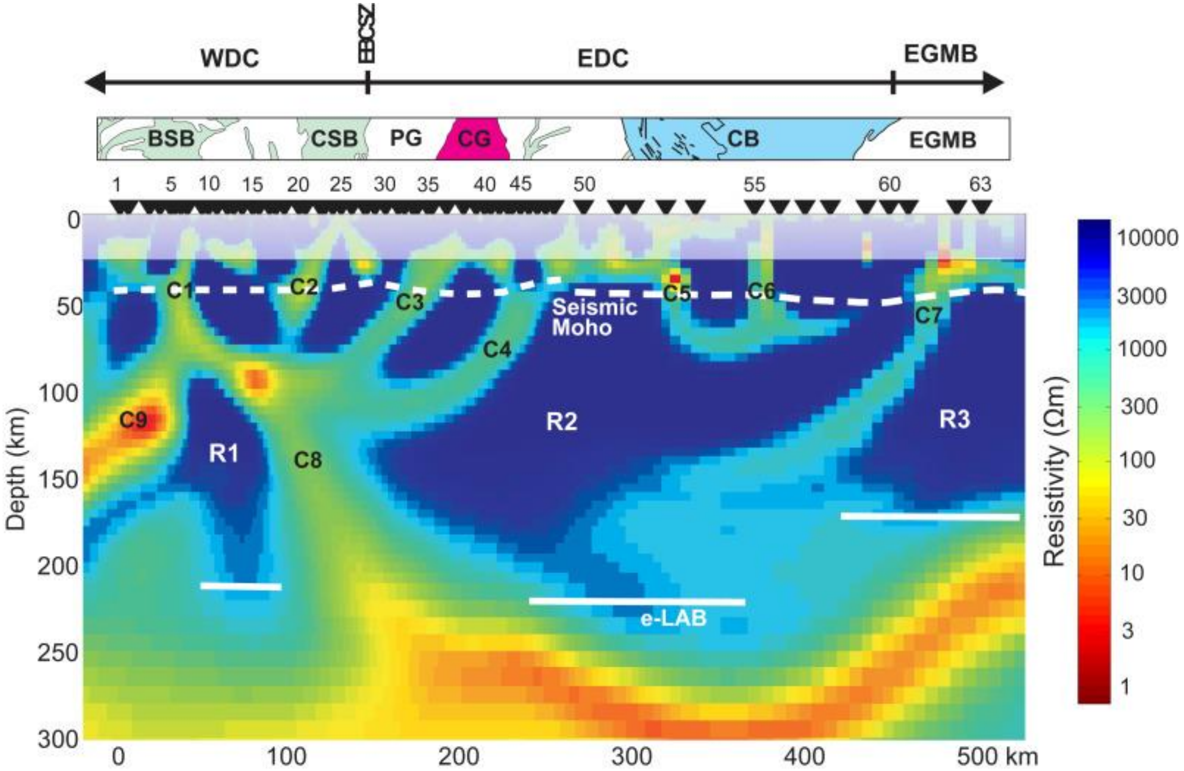


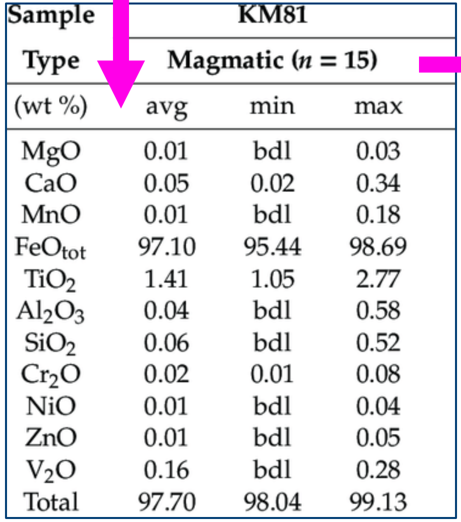
2-D resistivity model derived from the joint inversion of MT and tipper responses and the surface geology along the profile. After Malleswari et al. (2019).

Studying Lithospheric Mantle with Geochemical Data

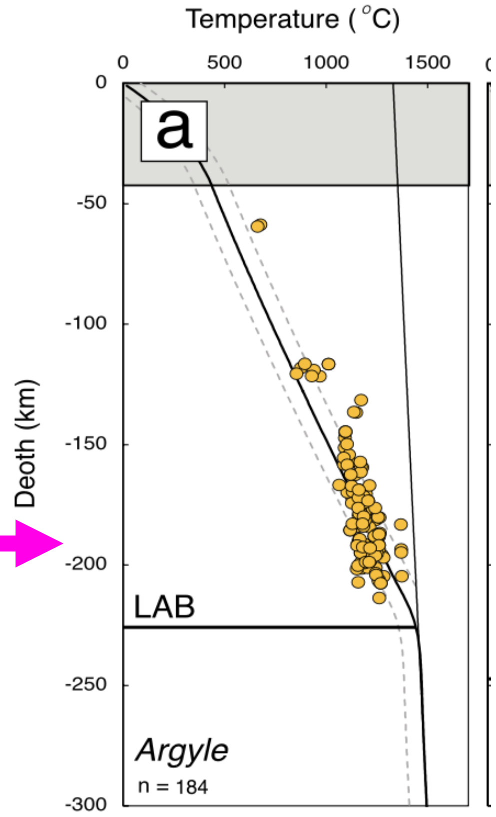
Before we go into detail on how geochemical and petrological data can be used to the study the composition and structure of the lithosphere, **we must first have a basic grasp on how geochemical data is obtained using common analytical techniques**…

How do we go from having a physical rock sample (mantle xenolith) to obtaining quantitative geochemical concentrations that can be used for calculating pressures and temperatures and paleogeotherm modeling

Help better understand geochemical data and where it comes from



Sample	KM81		
Type	Magmatic (n = 15)		
(wt %)	avg	min	max
MgO	0.01	bdl	0.03
CaO	0.05	0.02	0.34
MnO	0.01	bdl	0.18
FeO_{tot}	97.10	95.44	98.69
TiO_2	1.41	1.05	2.77
Al_2O_3	0.04	bdl	0.58
SiO_2	0.06	bdl	0.52
Cr_2O	0.02	0.01	0.08
NiO	0.01	bdl	0.04
ZnO	0.01	bdl	0.05
V_2O	0.16	bdl	0.28
Total	97.70	98.04	99.13



Studying Lithospheric Mantle with Geochemical Data

Geochemical data can be obtained **for individual minerals** of for the **entire rock** (usually requires dissolution or crushing). There are many different types of geochemical data that can be obtained for rocks and minerals from the lithospheric mantle. **Common types of geochemical data includes:**

- **Major and minor oxides**
  SiO_2, TiO_2, Al_2O_3…. (wt%; weight percent)
  High abundance and usually easy to measure. *Common geochemical building blocks*

- **Trace elements**
  Co, Ni, V, Sc…. (ppm; parts per million)
  Low abundance. Sometimes challenging to measure. Special techniques required.

- **Isotopes (stable, radiogenic, heavy and light)**
  ^{12}C, ^{13}C, ^{238}U, ^{206}Pb, ^{40}K, ^{40}Ar…. (ppm to ppt)
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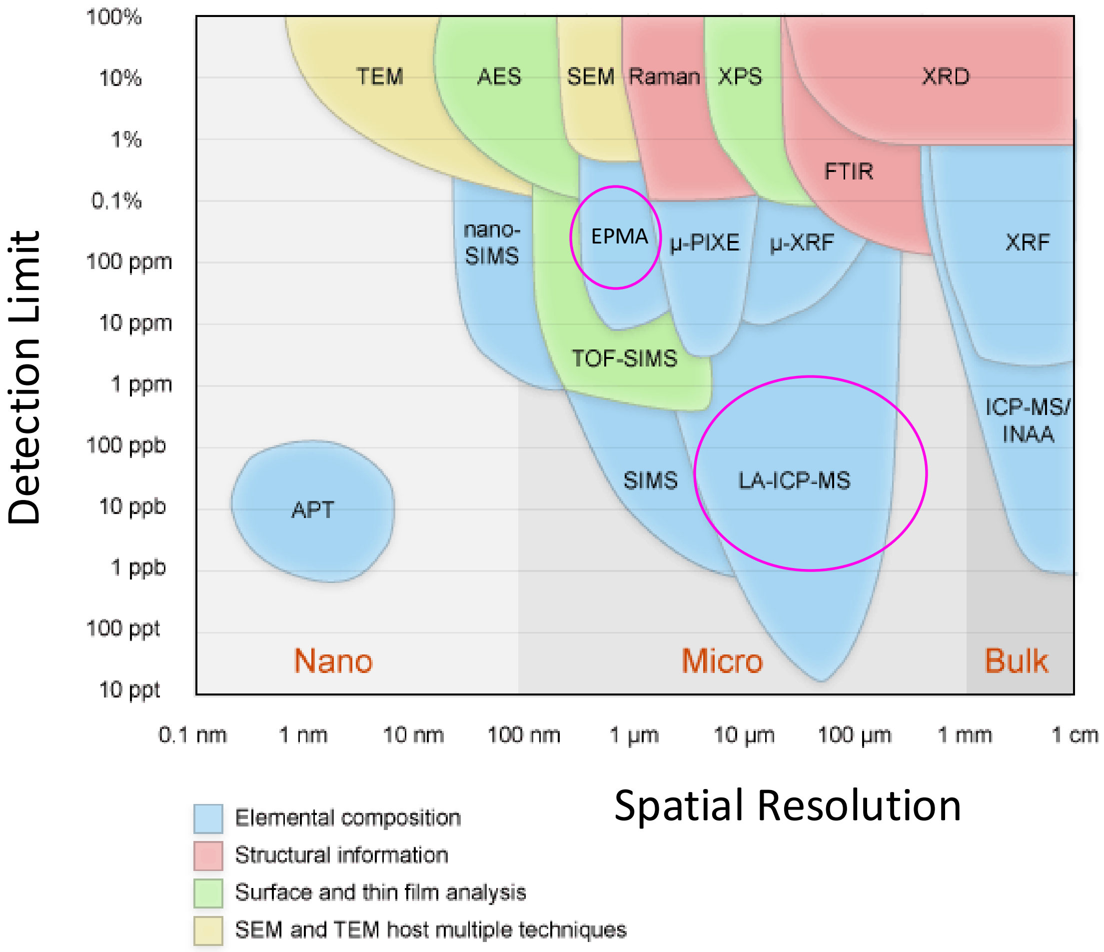
Studying Lithospheric Mantle with Geochemical Data

How do we obtain geochemical data for rocks and minerals from the lithospheric mantle?

The best technique depends on the type of data you want. There is not one techniques that fits all…

Trade off between **spatial resolution** (what do I want to measure and how small) and **detection limit** (how precise do I want the chemical concentrations)

common techniques are **EPMA** and **LA-ICP-MS**



Studying Lithospheric Mantle with Geochemical Data

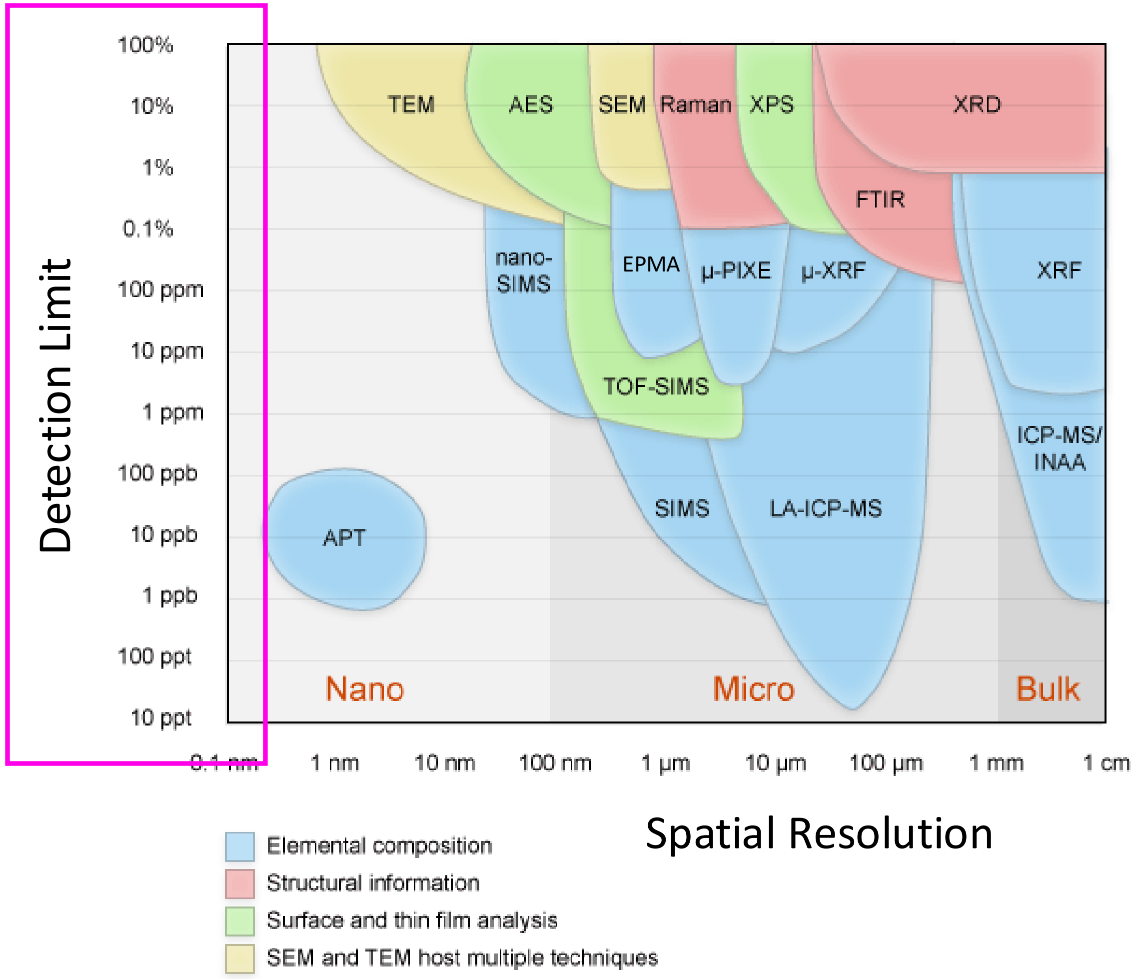
Understanding **Geochemical Concentrations** of elements and oxides:

wt% (weigh percent)
ppm (parts per million)
ppb (parts per billion)
ppt (parts per trillion)

Units of Concentration

1 wt% = 10,000 ppm

The units of concentration simply refer to how much of that element or oxide is present within the analyzed area



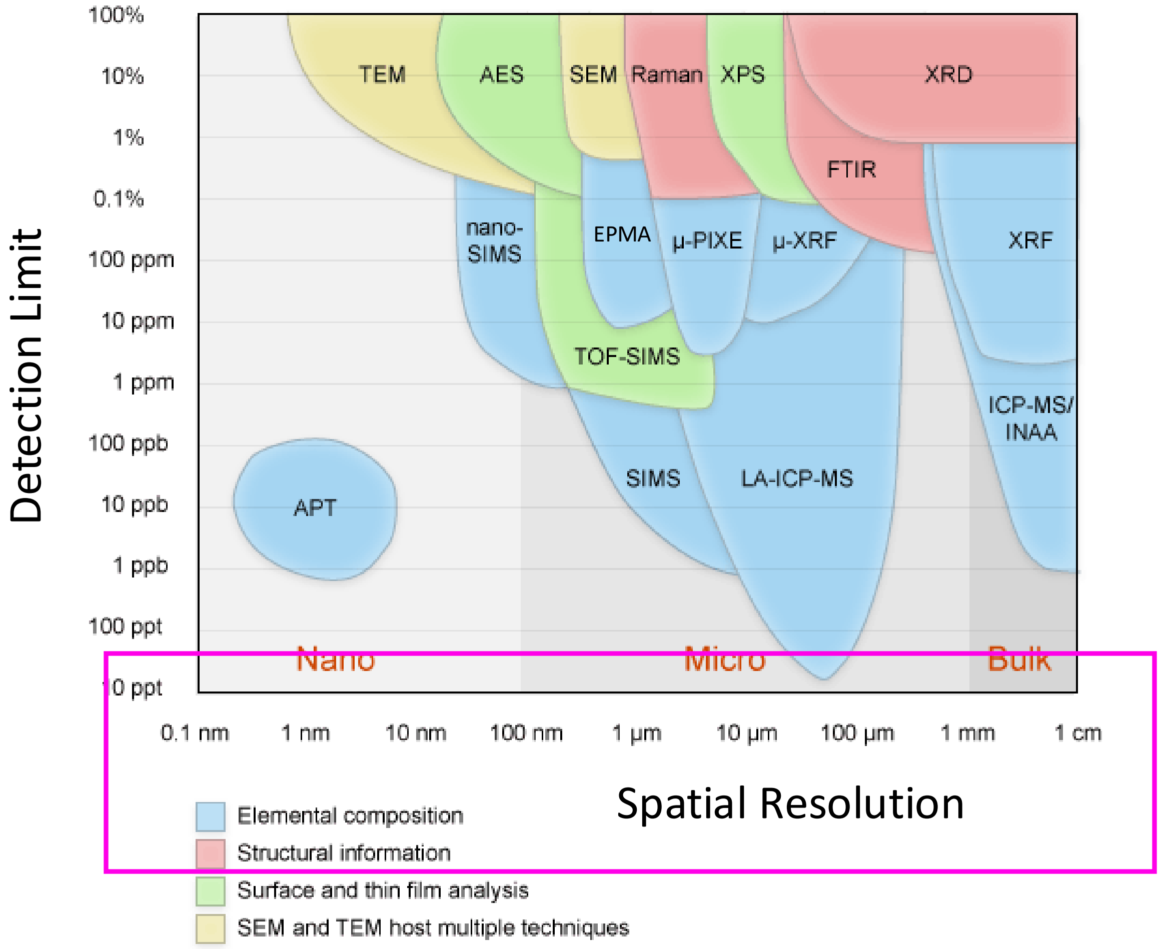
Studying Lithospheric Mantle with Geochemical Data

Understanding **Spatial Resolution** of geochemical measurements:

Most measurements are conducted on a small portion of a mineral – petrologist and geochemistry are typically interested in the grain to sub-grain scale

Most mineral grains are >1 mm in size. Geochemical analyses by EPMA and LA-ICP-MS occur on scales of 1 um to 100 um.

1 cm = 10000 um (microns)



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Studying Lithospheric Mantle with Geochemical Data

EPMA: Electron Probe Microscopy

Detection Limit: about 1 wt% to 10 ppm

Spatial Resolution: 1 to 5 um

Suitable for measuring the chemical compositions of major and minor elements in minerals (particularly silicate minerals). Good for measuring the common elements that are in high abundance (SiO_2, Al_2O_3, Cr_2O_3...).

LA-ICP-MS: Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Detection Limit: about 100 ppm to 1 ppb

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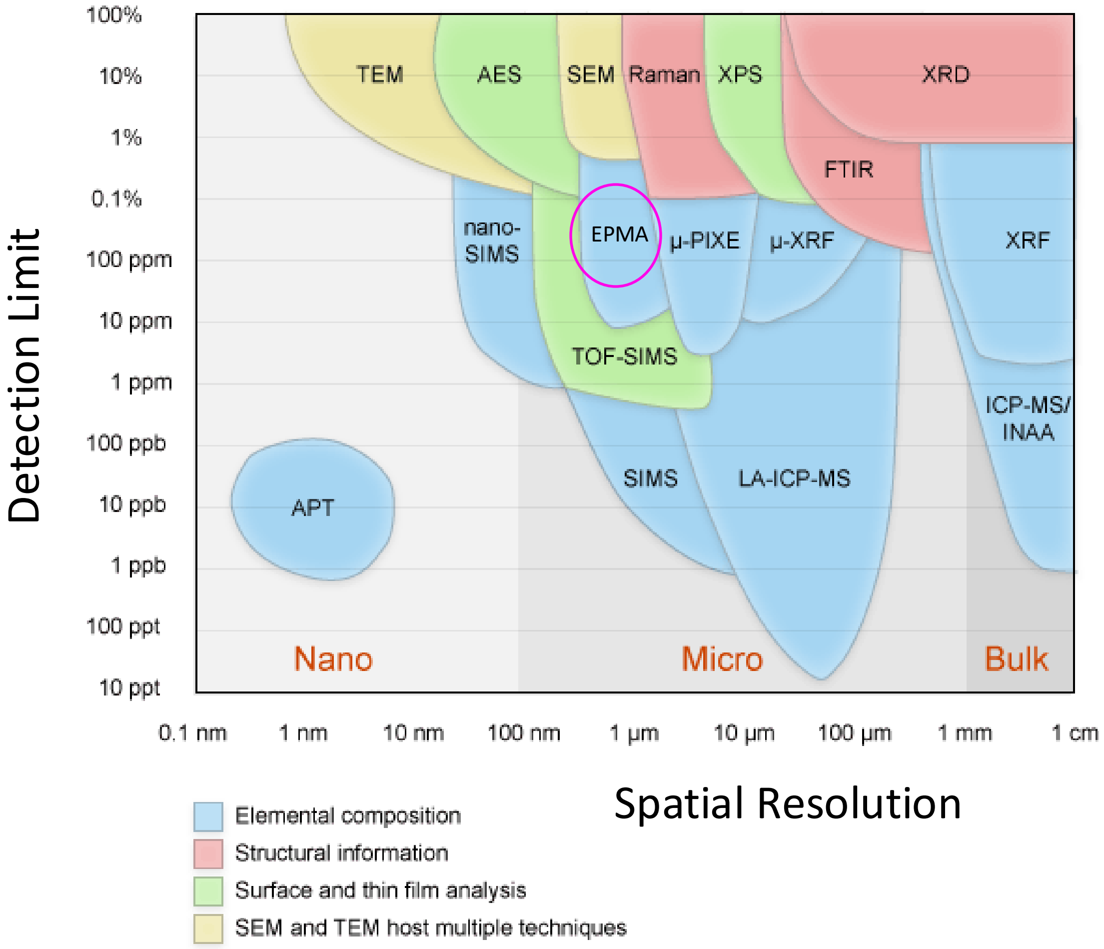
Suitable for measuring the chemical compositions of trace elements in minerals. Good for measuring the less common elements that are in low abundance (Zr, Y, Cu, Co, Rb, Sr...).



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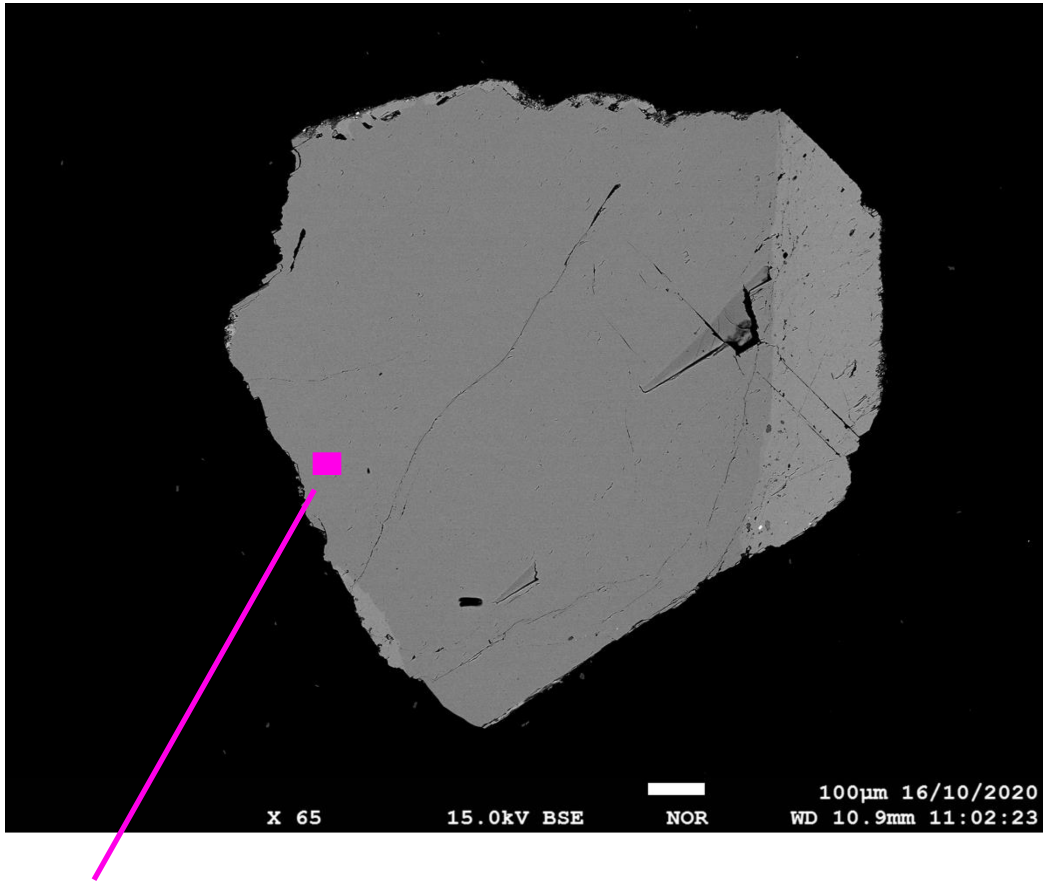

Typical spatial resolution for chemical measurements by electron probe microanalysis

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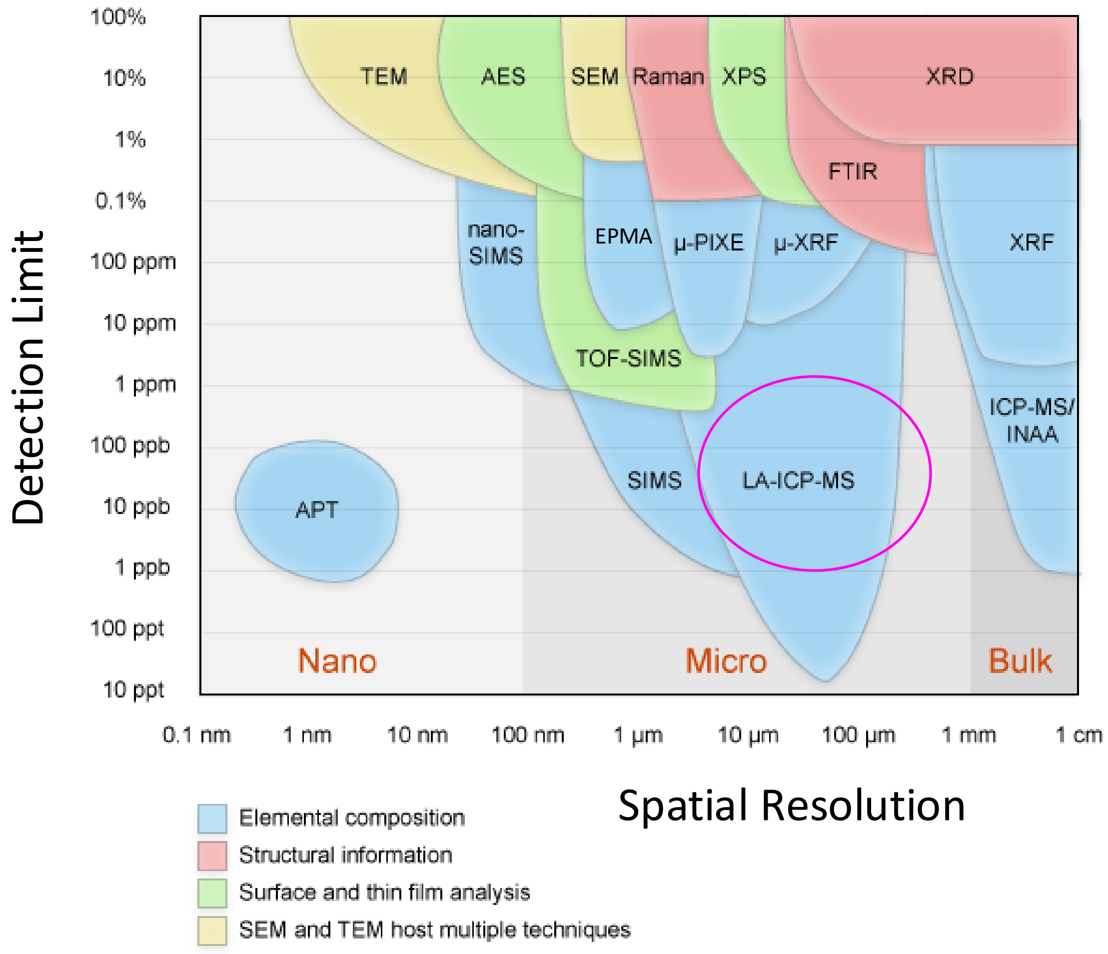

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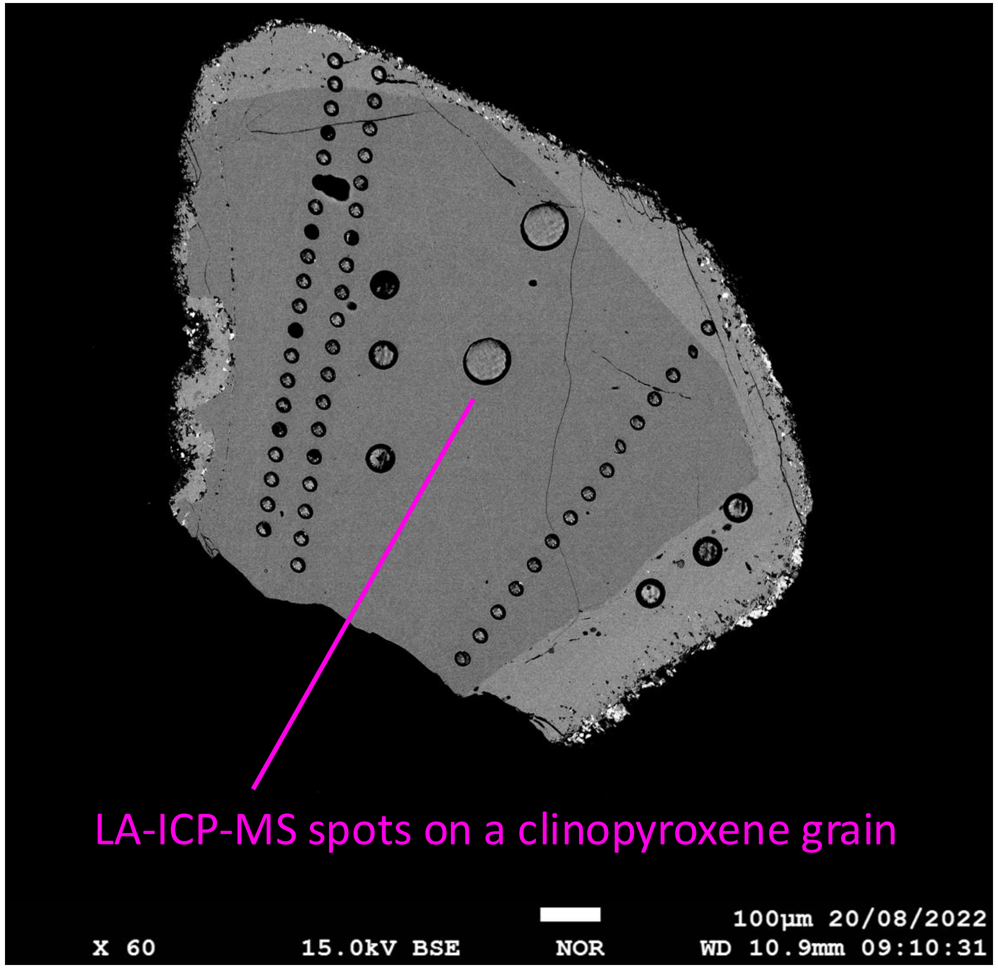

LA-ICP-MS spots on a clinopyroxene grain

Quick break for Questions…..

Electron Probe Microanalyzer (EPMA)

- A quantitative technique that uses X-rays emitted from minerals
- Measures chemical compositions of minerals at a microscale (um)
- Can be used for imaging at microscale
- Uses wavelength dispersive spectroscopy
- Generally considered non-destructive (i.e., your mineral won't be destroyed)
- Historically a tool for geological and material sciences

Image of an electron probe microanalyzer. Yale University.

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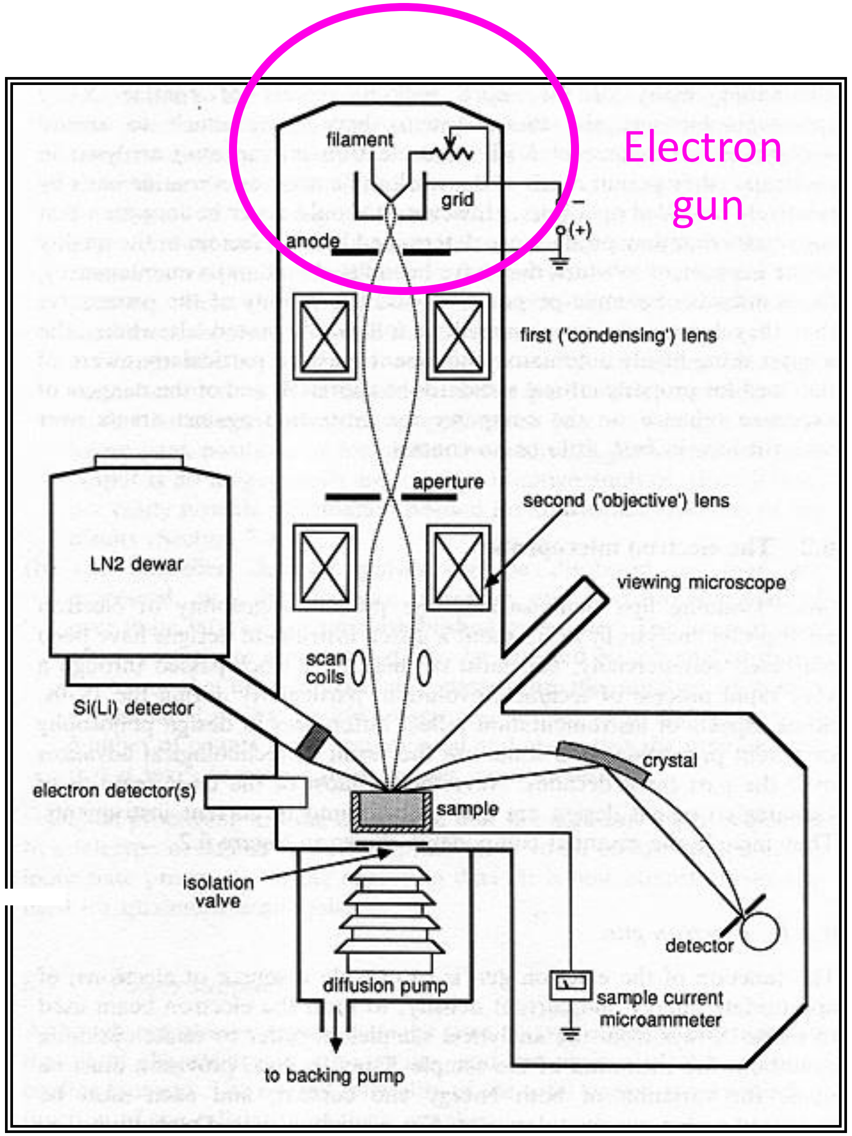
wt%	Olivine	Clino	Ortho	Spinel
SiO_2	42.77	53.78	56.45	0.33
MgO	55.19	25.32	34.39	24.24
CaO	0.34	12.91	2.86	0.22
Al_2O_3	0.13	4.82	3.91	31.75
Cr_2O_3	0.34	2.01	1.64	42.49
Na_2O	0.01	0.10	0.03	0.01
Total	98.82	99.07	98.99	99.31

An example of the types of geochemical data that are obtain from an EPMA. This table shows the measured wt% of different oxides within the measured minerals.

Electron Probe Microanalyzer (EPMA)

An **Electron Probe Microanalyzer** has several important components that are used for chemical analyses and imaging:

- **Electron gun (source of energy needed for imaging and chemical analyses)**
- Sample chamber (vacuum chamber where the specimen is held)
- Electron detectors (used for imaging)
- Crystal (used to diffract X-rays to detector)
- X-ray detectors (used for chemical analyses)



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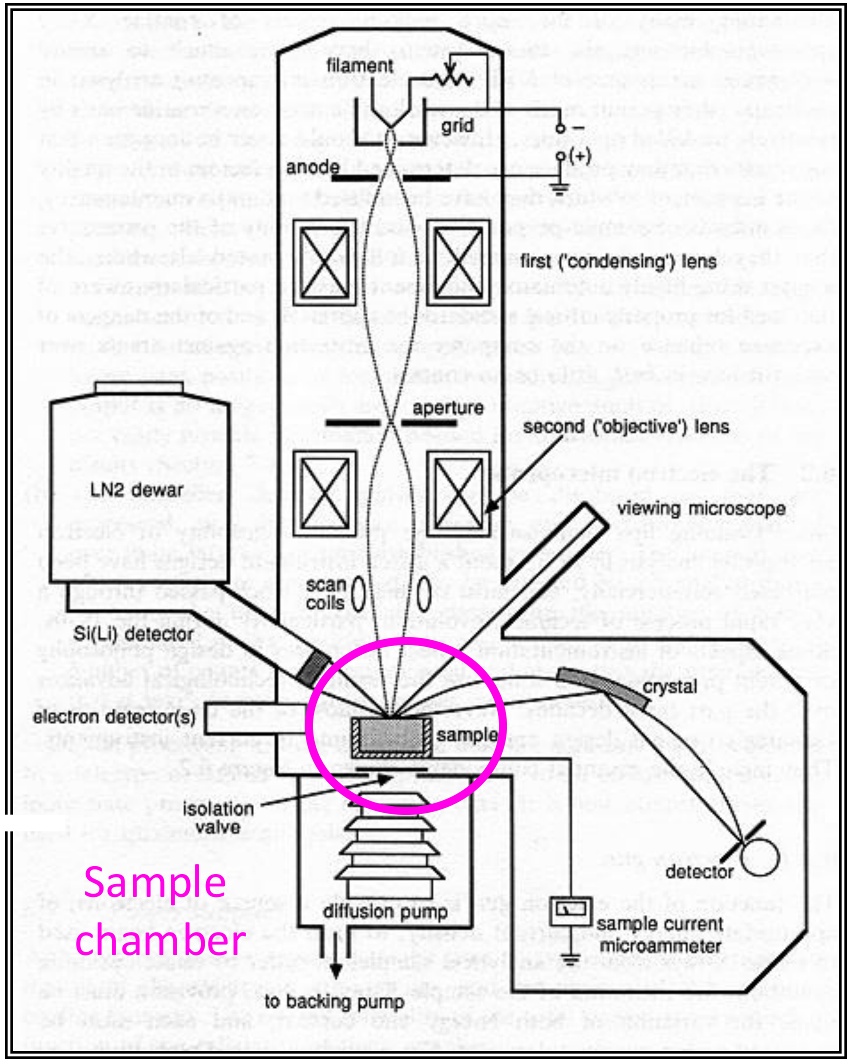

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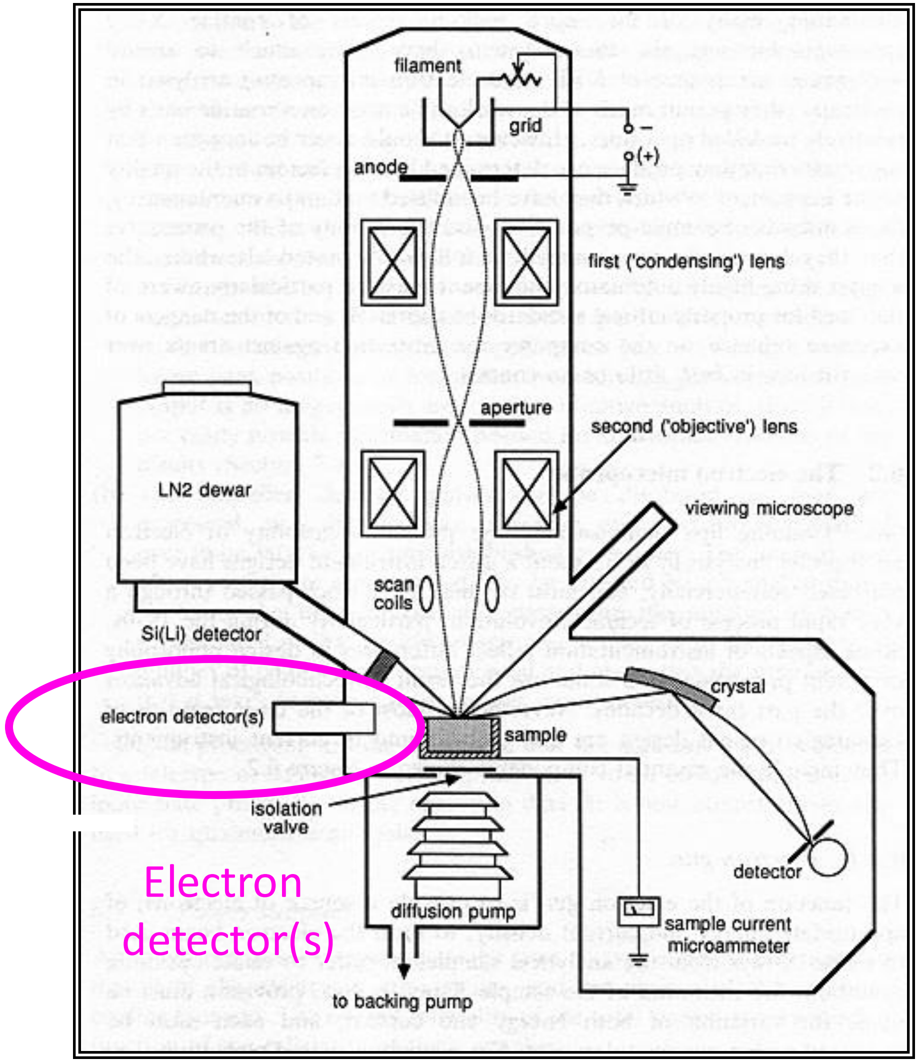

Electron detector(s)

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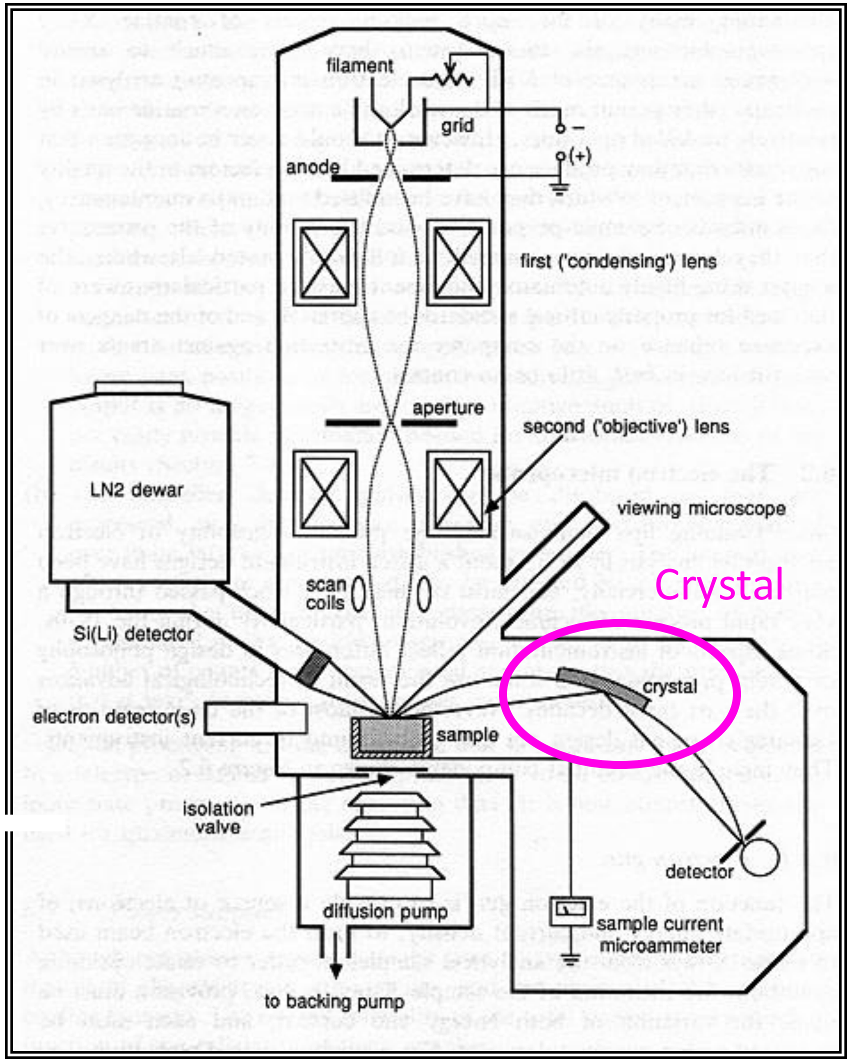

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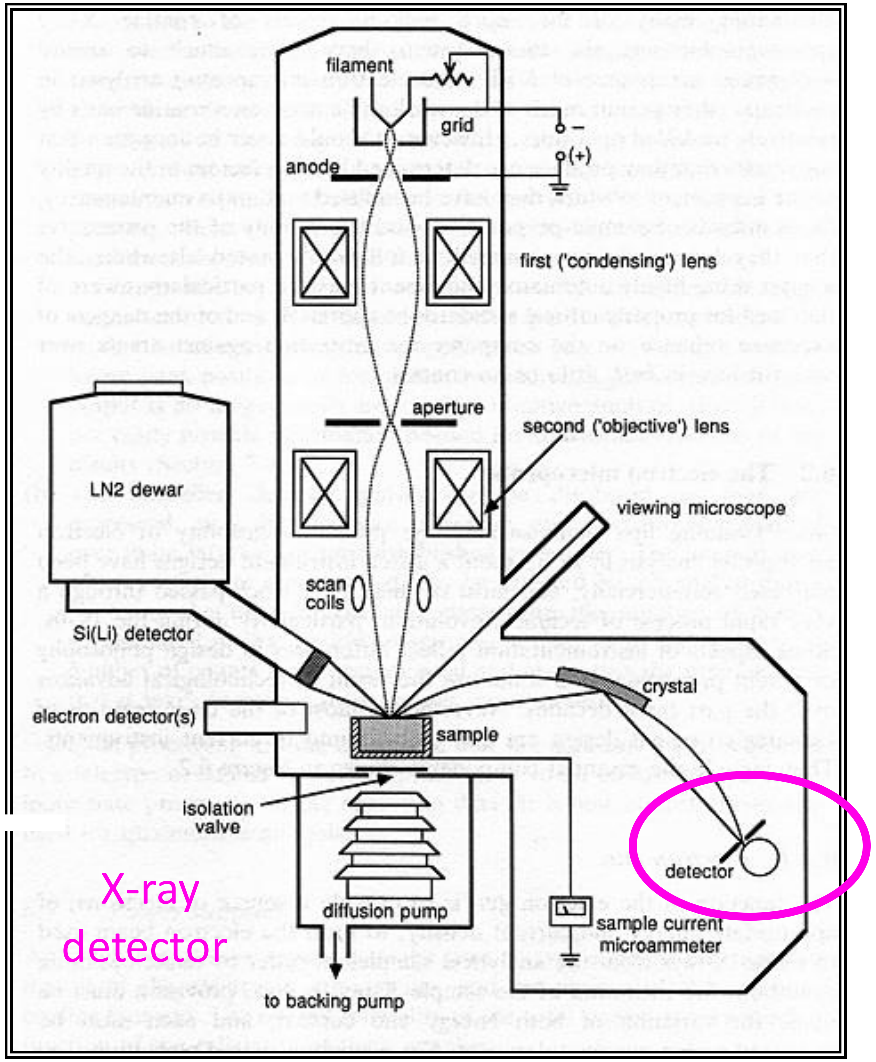
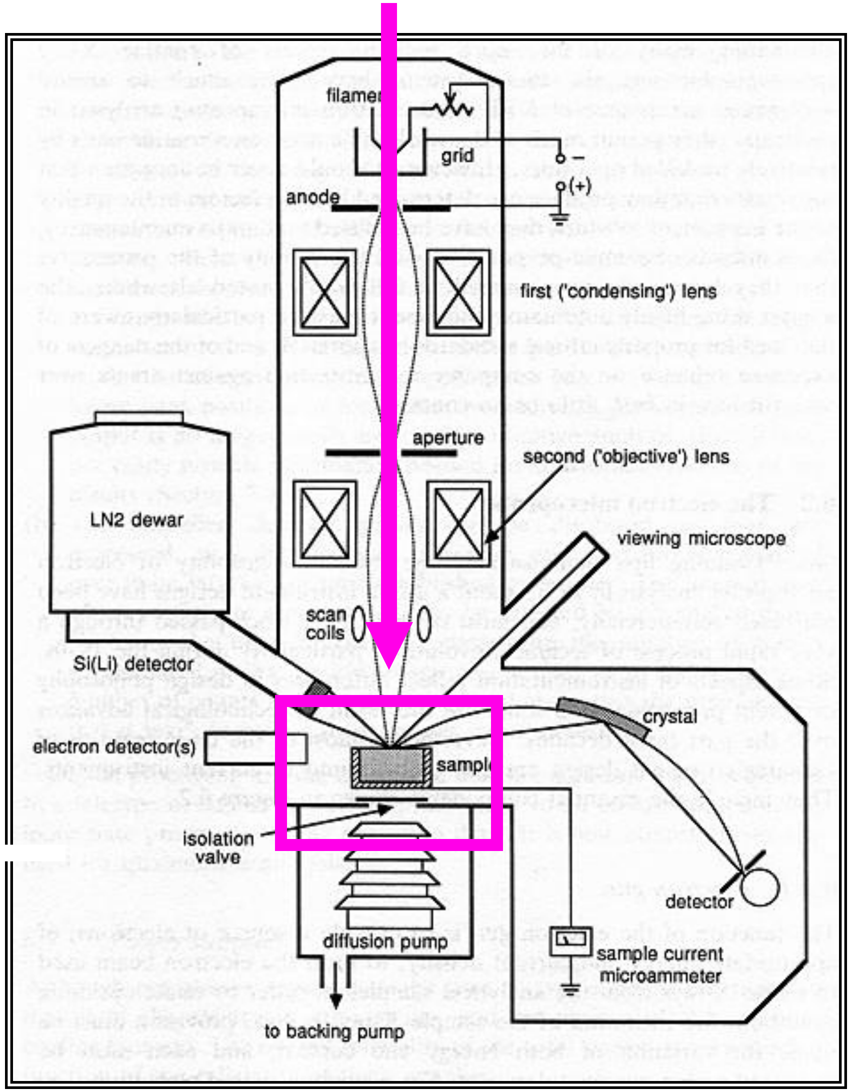


Electron Probe Microanalyzer (EPMA)

A narrow and focused beam of electrons (1 to 20 um) is shot from the electron gun. The accelerating voltage and beam size can be varied

The electrons interact with the sample and generate several products that can be used for quantifying chemical compositions and high-resolution imaging:

- X-rays
- Secondary electrons
- Back-scattered electron
- Cathodoluminescence



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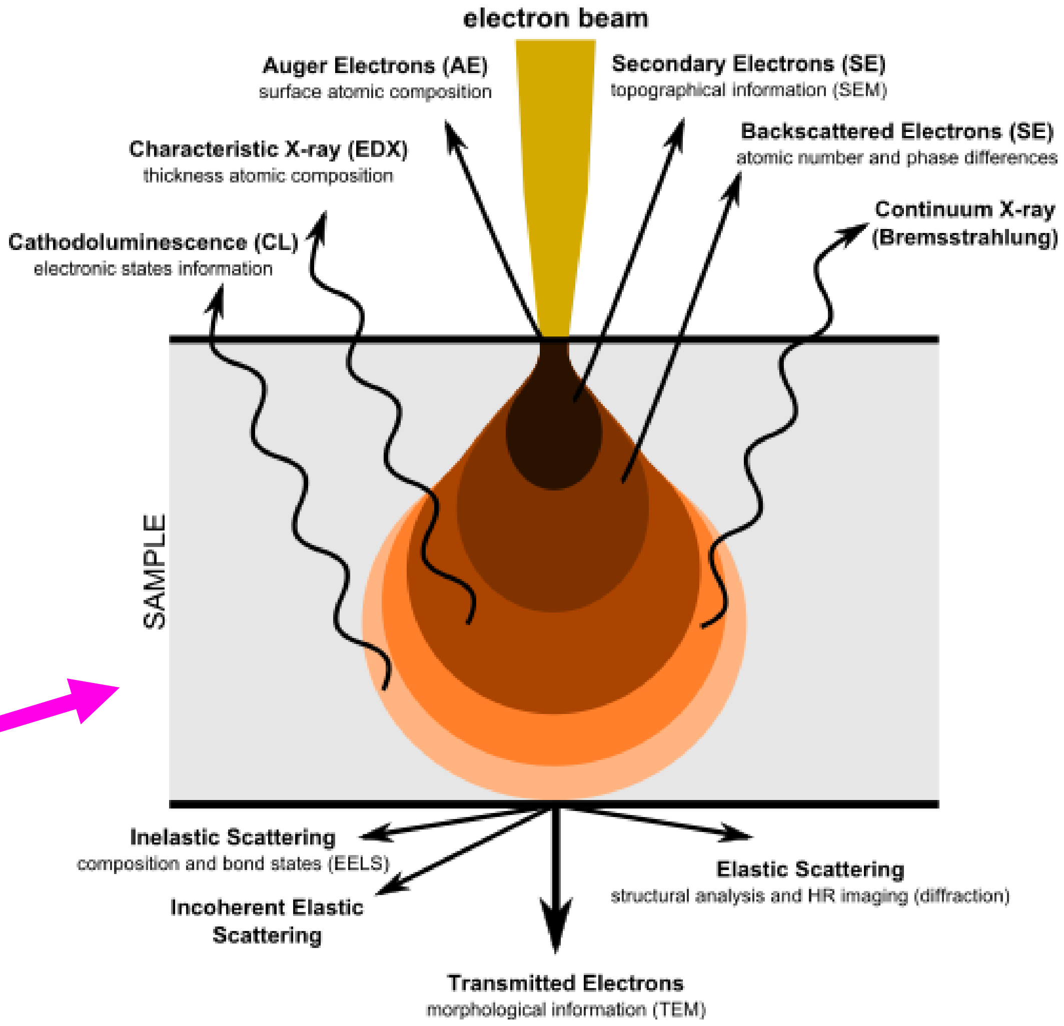
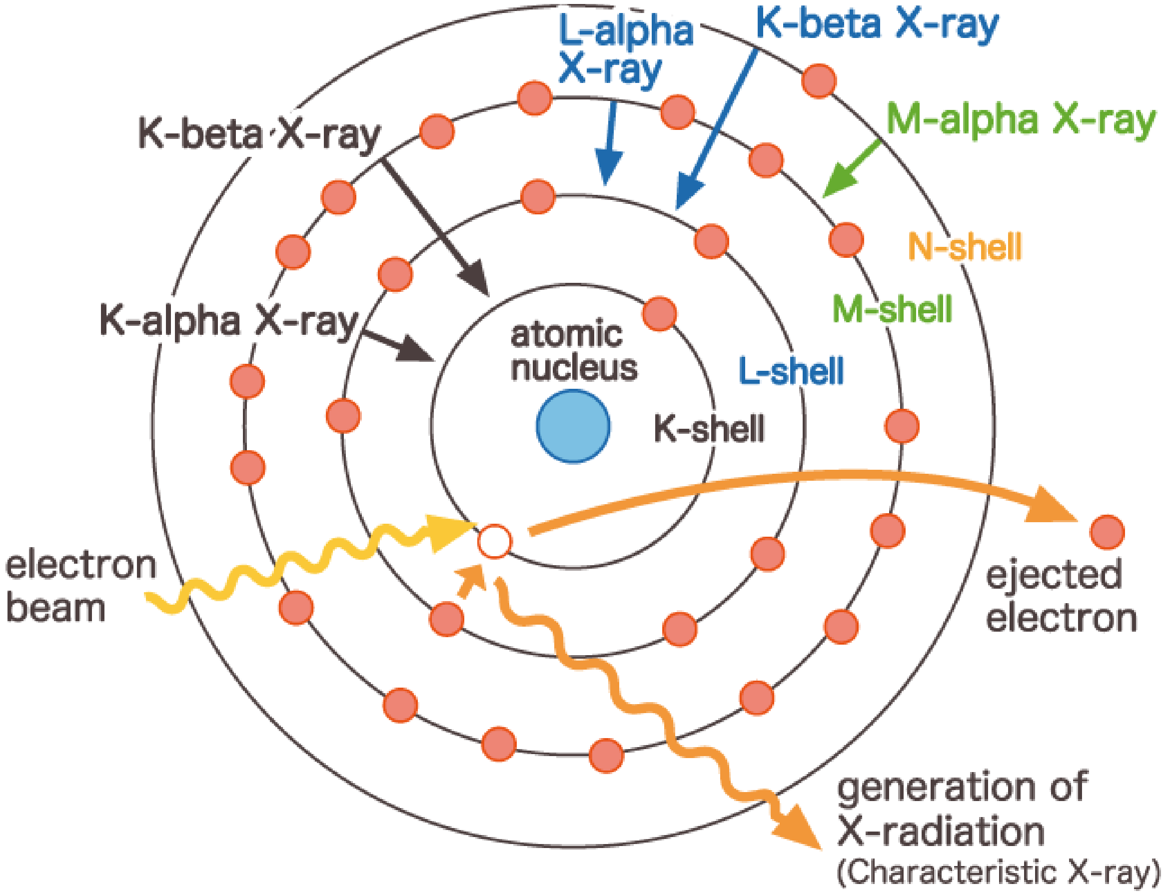


Electron Probe Microanalyzer (EPMA)

X-rays emissions are most important because they can be used to quantify the chemical composition of the sample.

X-ray emission works by:

Electrons from the gun (incident electrons) hit and eject an electron belonging to the inner shell of an atom from the sample. An electron from the outer shell of the atom moves down to fill the empty space. This transition is associated with an X-ray emission that is characteristic of the atom

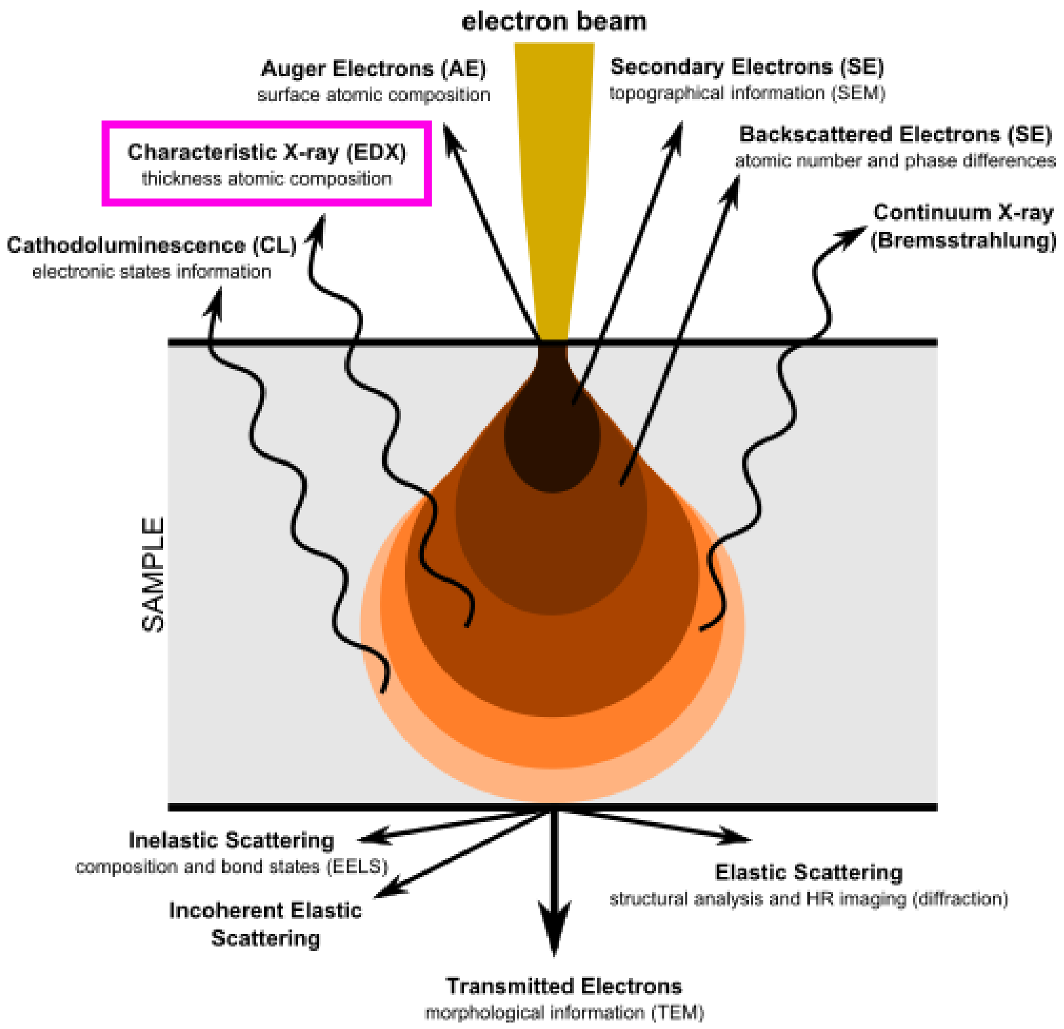


Electron Probe Microanalyzer (EPMA)

X-ray diffraction within the EPMA:

The emitted X-rays are diffracted by a crystal that is within the spectrometer. The angle of diffraction is characteristic of the element. Most EPMA's have four different crystals that are optimized for different X-rays.

The diffracted X-rays enter a detector where they interact with a Nobel gas (usually Xe or Ar). The interaction between the X-rays and the gas causes ionization. The electron generated by the process binds to a wire that can be used to quantify the X-ray counts.



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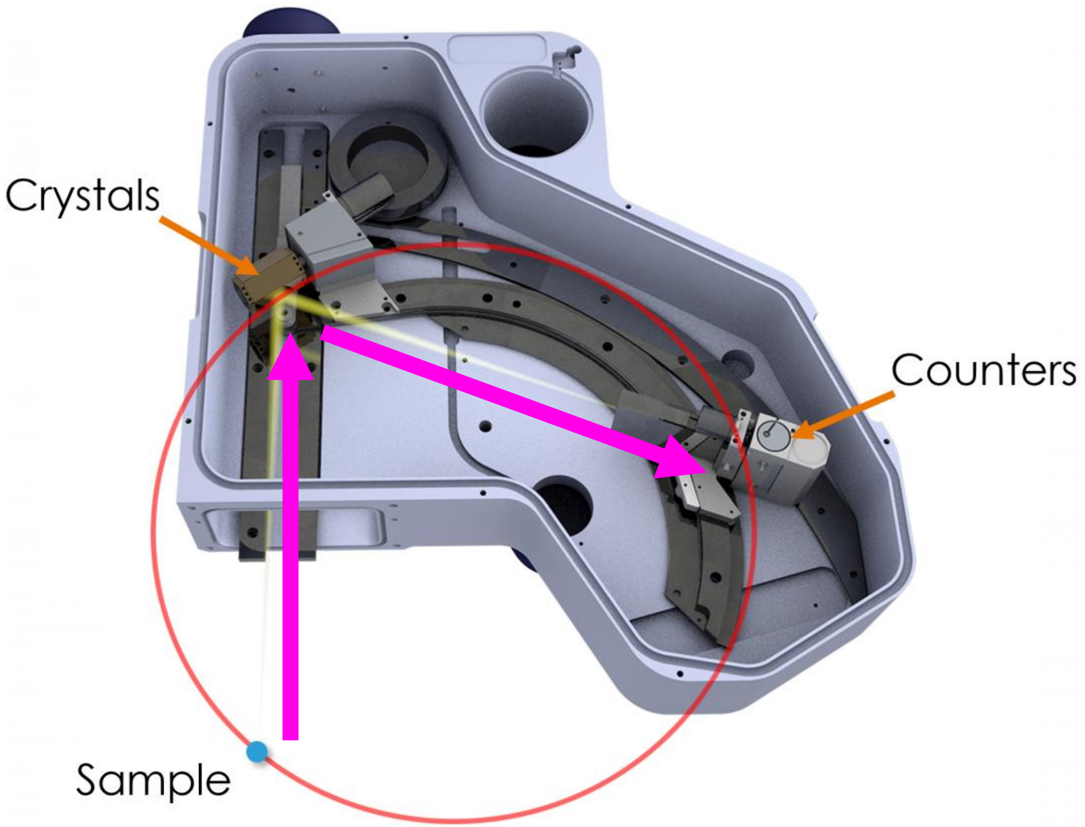

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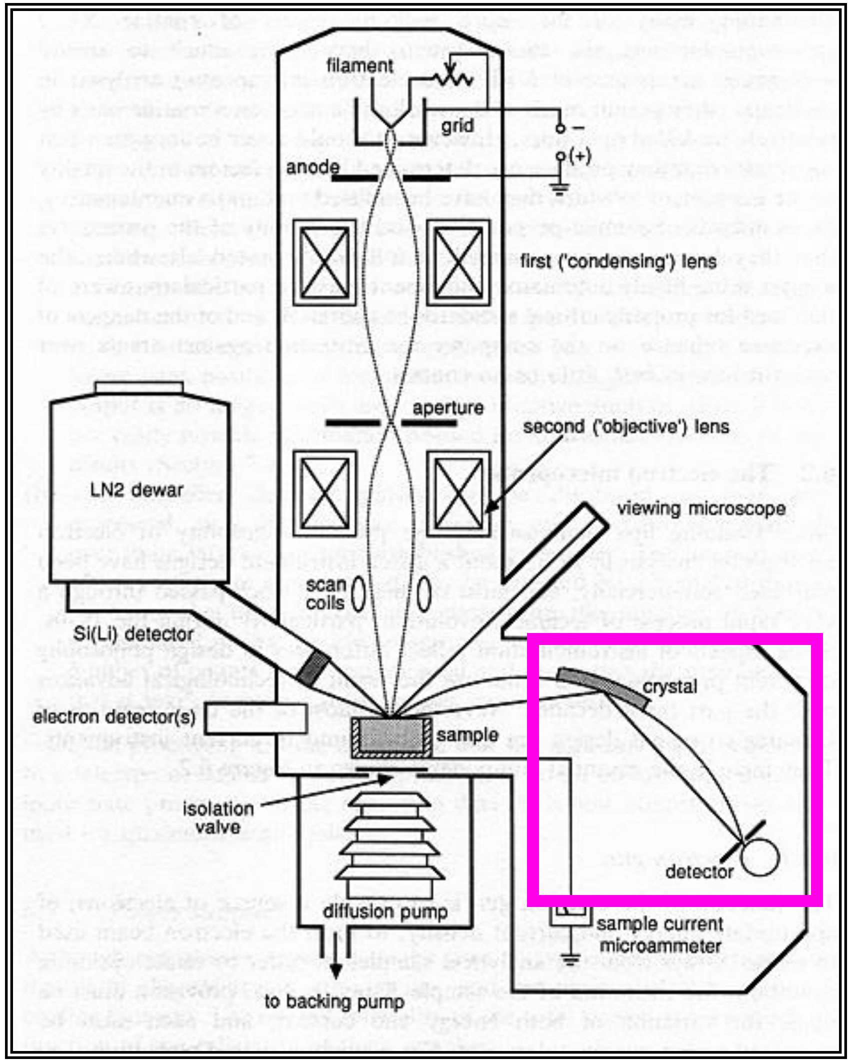
The emitted X-rays are diffracted by a crystal that is within the spectrometer. The angle of diffraction is characteristic of the element. Most EPMA's have four different crystals that are optimized for different X-rays.

The diffracted X-rays enter a detector where they interact with a Nobel gas (usually Xe or Ar). The interaction between the X-rays and the gas causes ionization. The electron generated by the process binds to a wire that can be used to quantify the X-ray counts.



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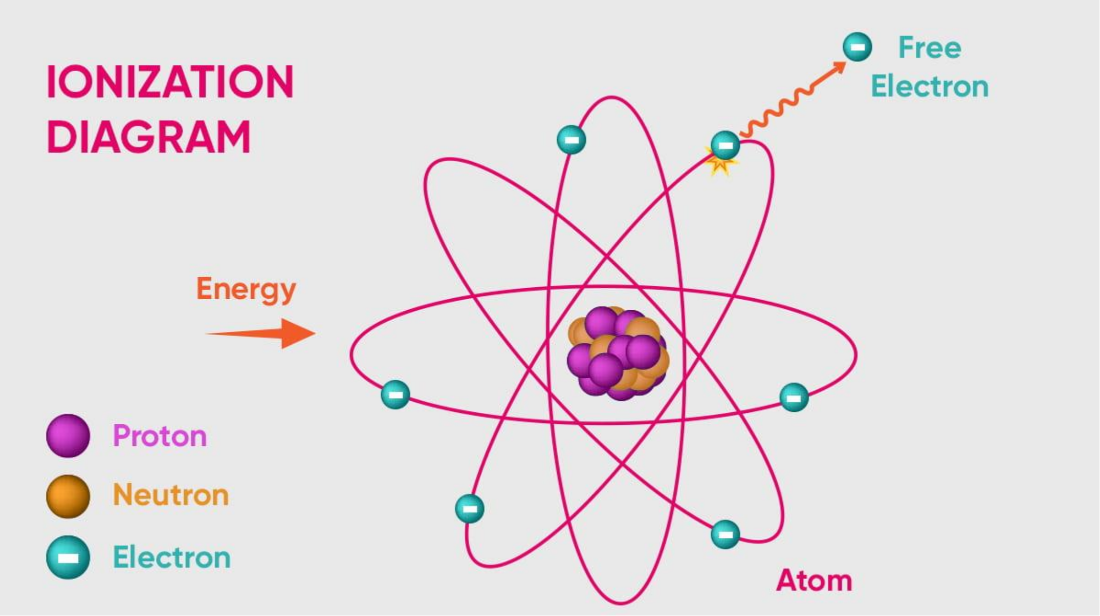


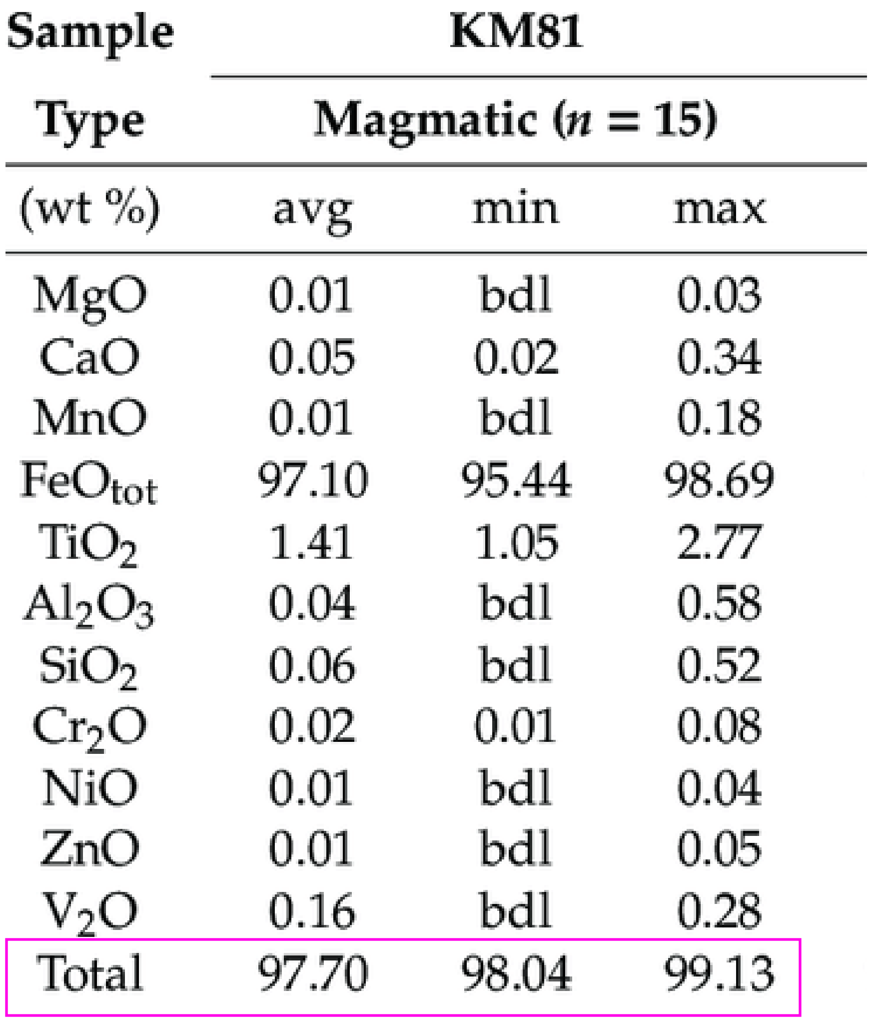
The Xe or Ar gases in the detector are ionized by the X-rays. This processes results in a free electron which can be detected and used for characterization.

Electron Probe Microanalyzer (EPMA)

X-ray diffraction within the EPMA:

After the analyses are finished and the data is processes as part of the measurement – the X-ray counts are reported as concentrations of the oxides within the sample. The concentrations are reported as wt% (i.e., how much CaO % is present within the analyzed section of the sample…). The concentrations are not in moles or cations but can be easily converted to these values

Why might the total concentration of the oxides be <100 wt%?



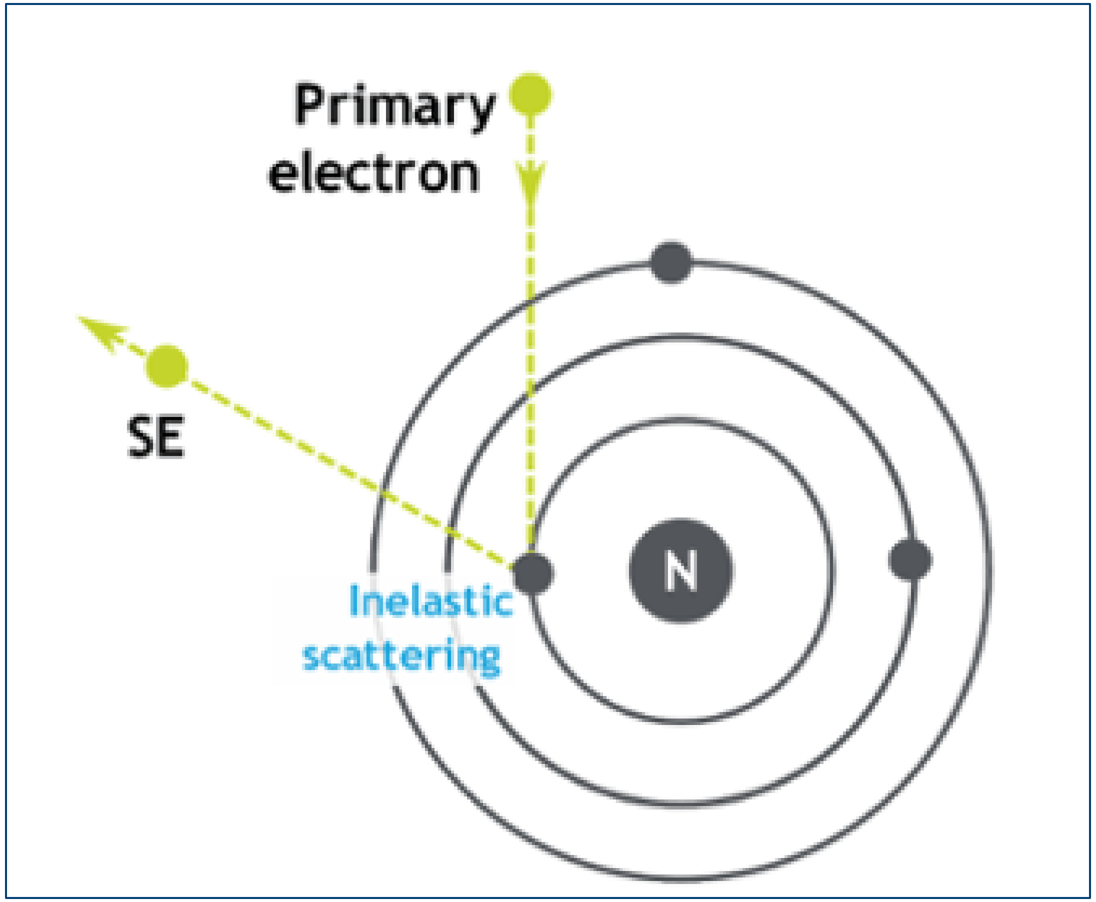
Sample	KM81		
Type	Magmatic ($n = 15$)		
(wt %)	avg	min	max
MgO	0.01	bdl	0.03
CaO	0.05	0.02	0.34
MnO	0.01	bdl	0.18
FeO_{tot}	97.10	95.44	98.69
TiO_2	1.41	1.05	2.77
Al_2O_3	0.04	bdl	0.58
SiO_2	0.06	bdl	0.52
Cr_2O	0.02	0.01	0.08
NiO	0.01	bdl	0.04
ZnO	0.01	bdl	0.05
V_2O	0.16	bdl	0.28
Total	97.70	98.04	99.13

Electron Probe Microanalyzer (EPMA)

Secondary electrons are useful for imaging of the sample – particularly topography

Secondary electrons (SE) work by:

The electrons that are ejected from the electron shells of an atom caused by the gun - constitute secondary electrons. They are generally low energy and are **produced near the surface of a sample**. They are collected and analyzed in an electron detector which can be used to determine the surface and topography of a sample



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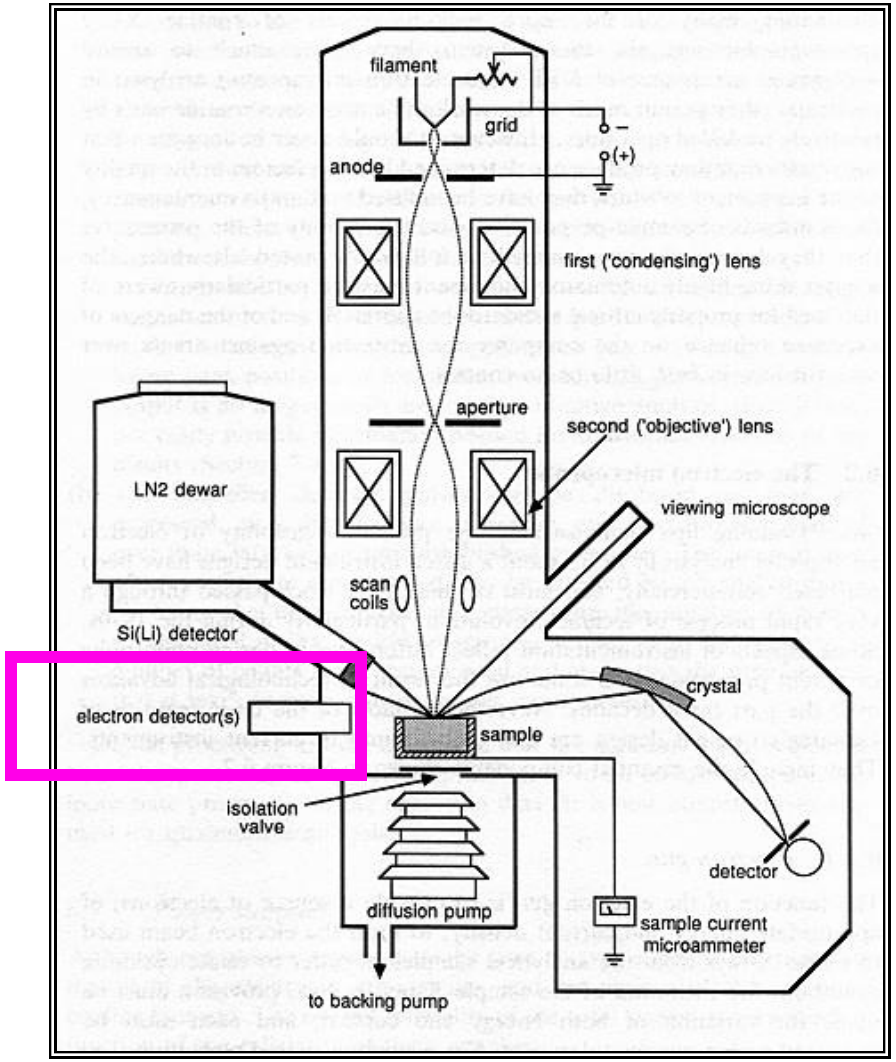
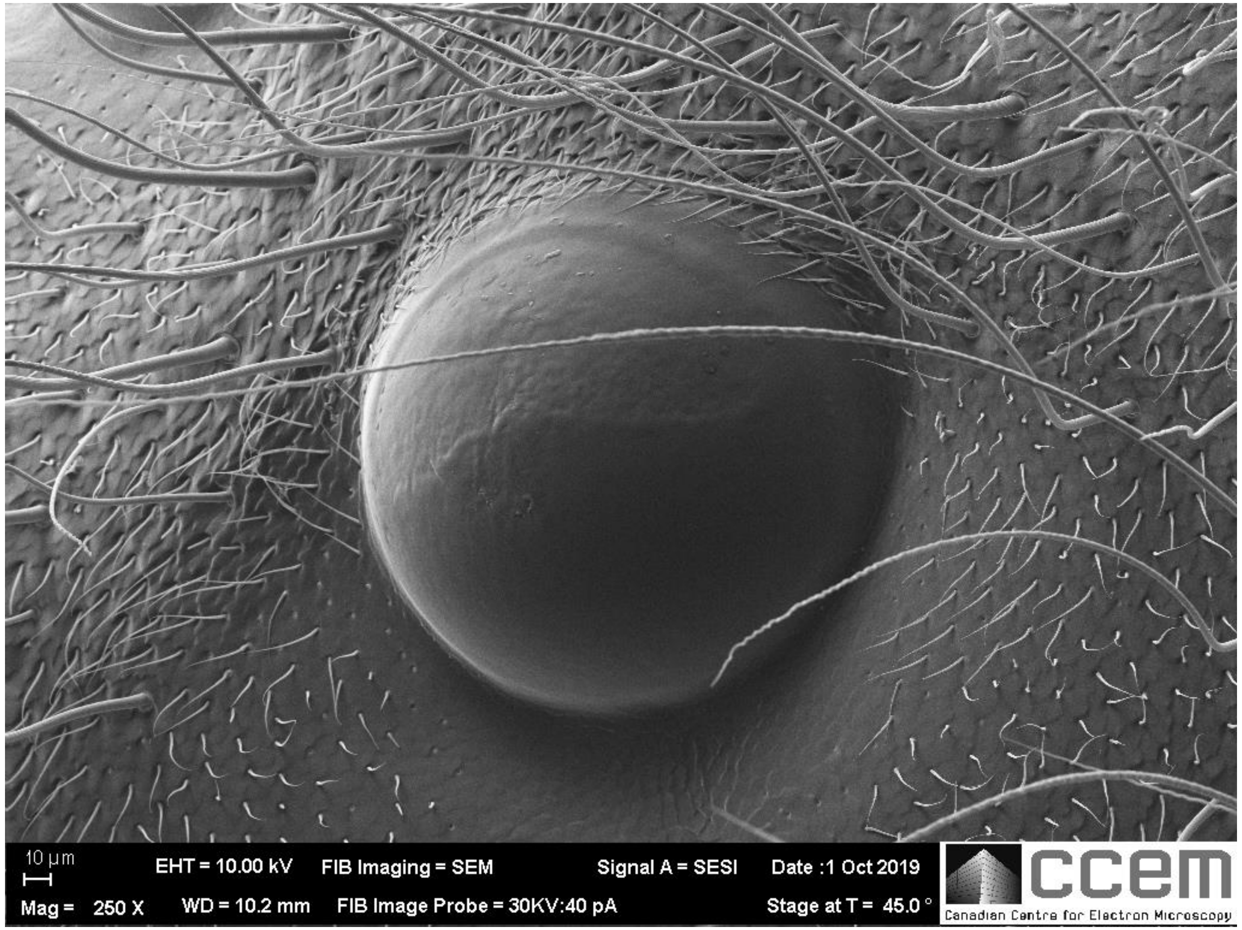
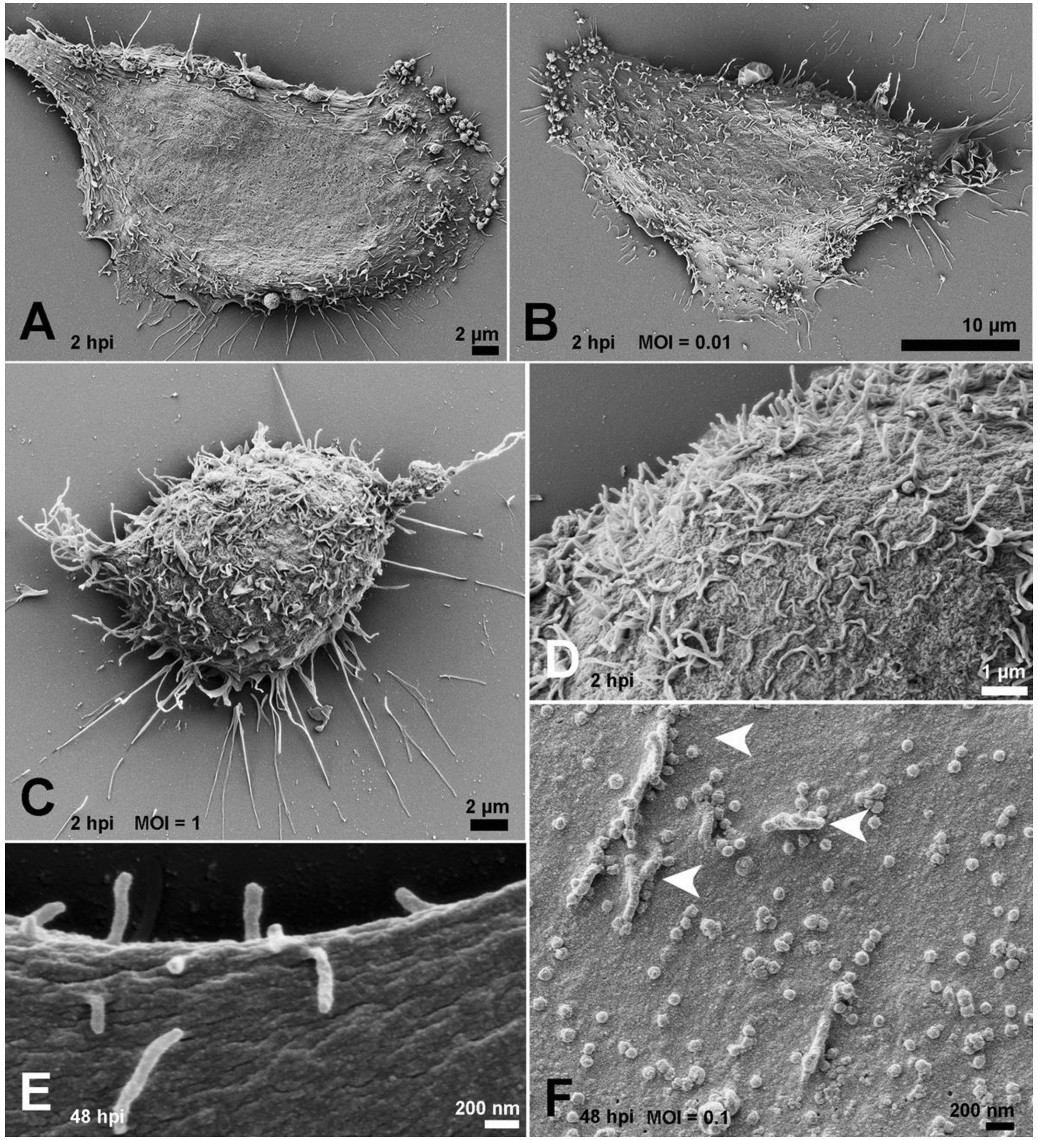


SE Images of various rock samples



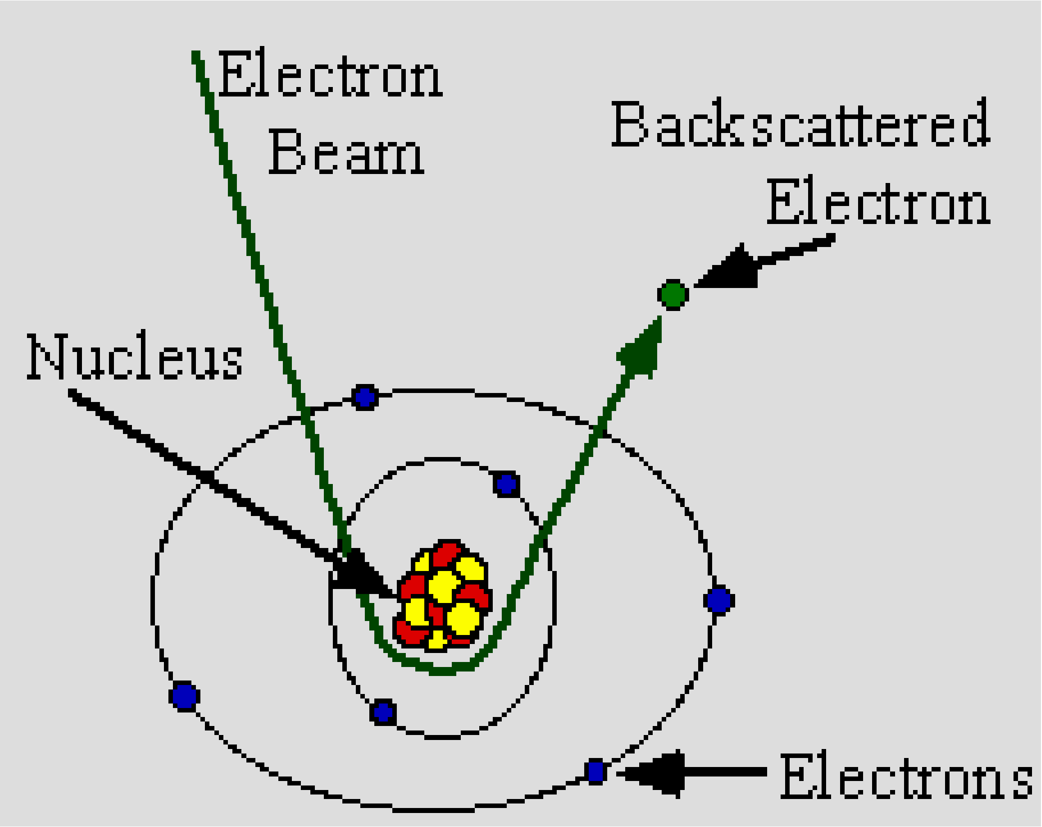


Electron Probe Microanalyzer (EPMA)

Back-scattered electrons are also useful for imaging of the sample – particularly composition

Back-scattered electrons (BSE) works by:

Electrons from the gun hit the nucleus of the atom and scatter in a different trajectory and emerge on the surface of the sample. Atoms with a larger nucleus (heavier elements) will deflect electrons more strongly than lighter elements. BSE are analyzed in an electron detector and can be used to determine the surface of a sample and its composition



Cartoon image showing the generation of back-scattered electrons. After Iowa State

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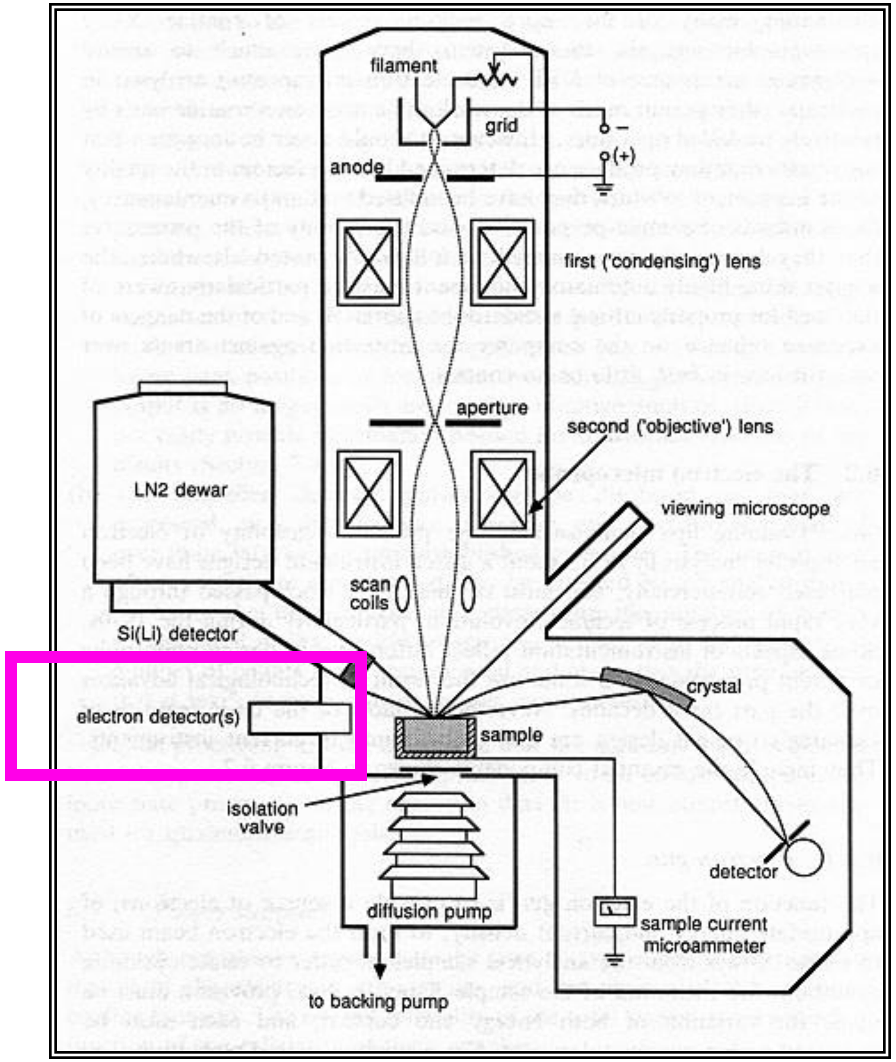
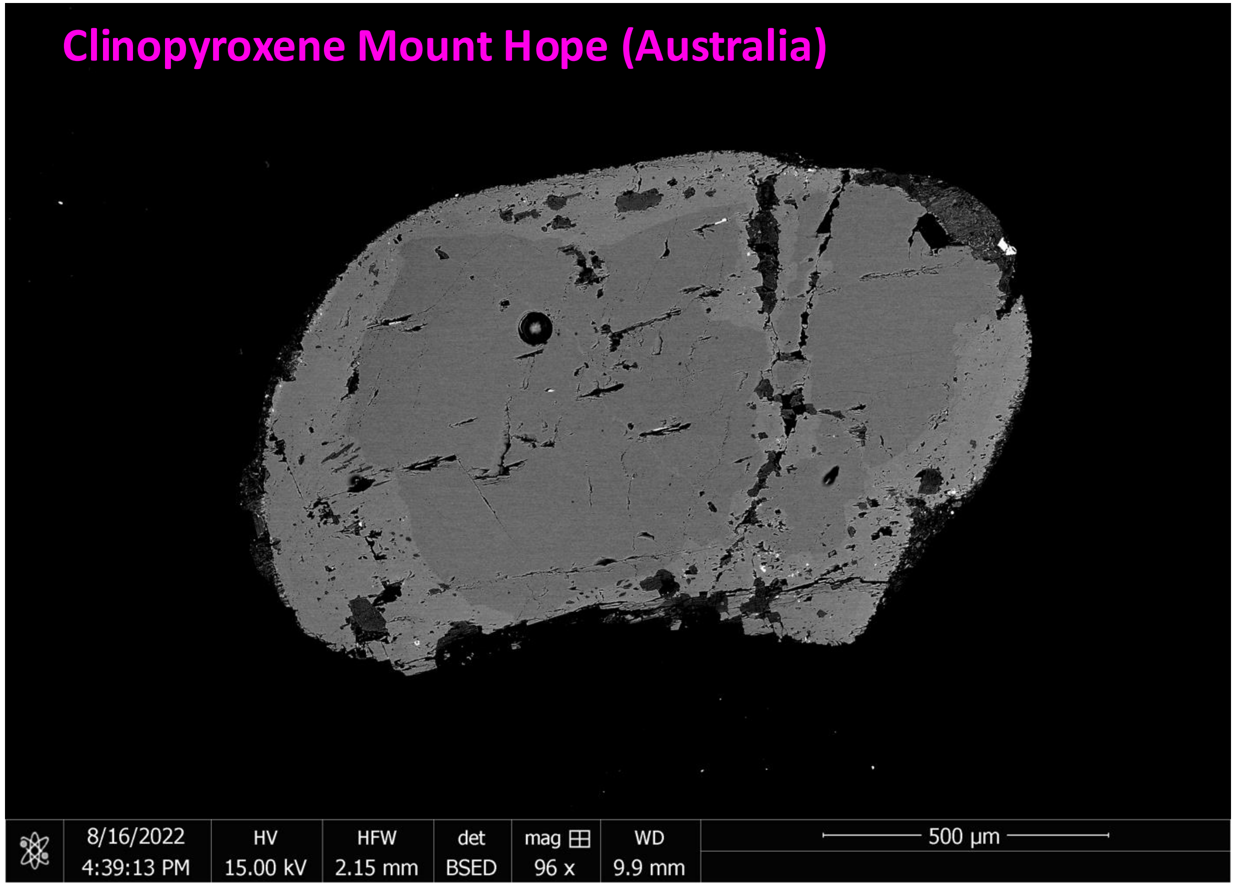
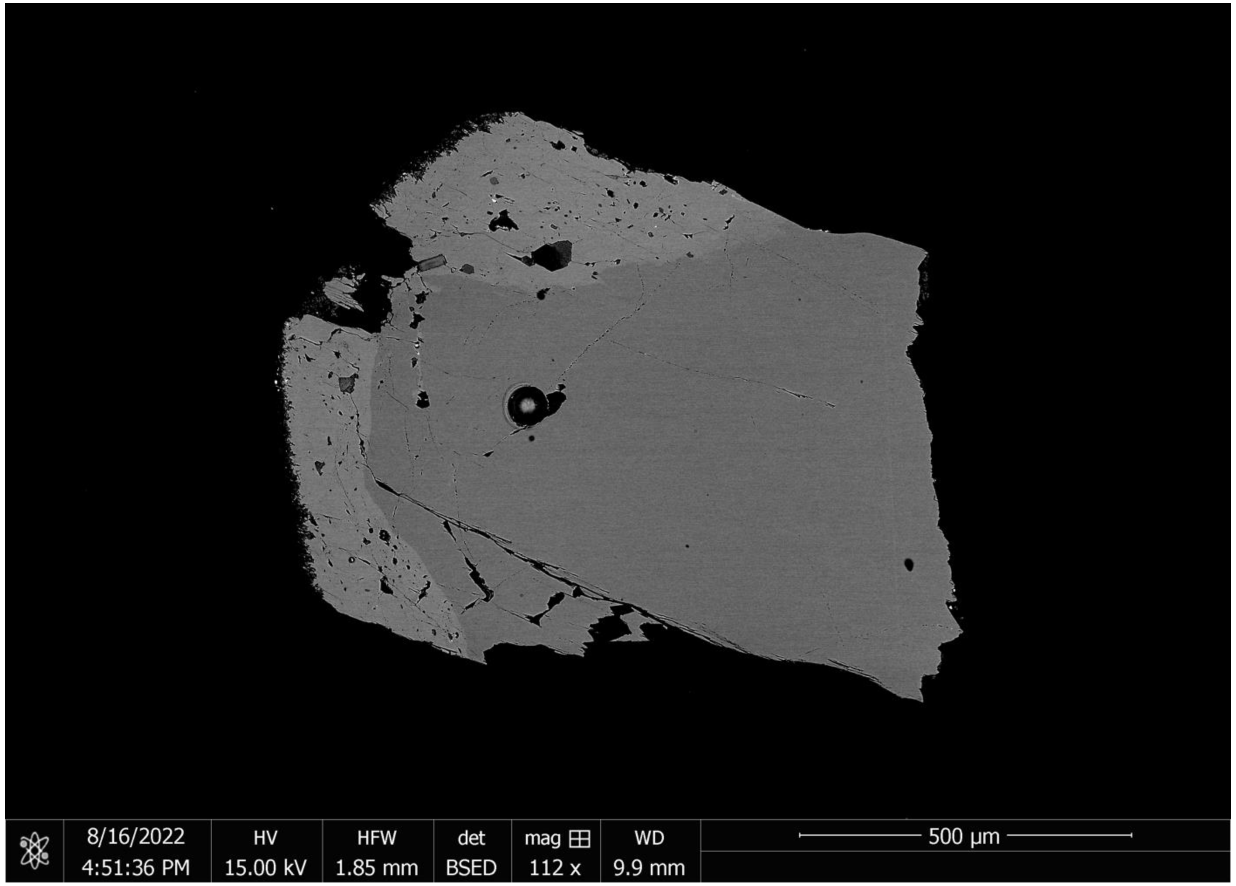


BSE Images of various rock samples





Lighter areas are parts of the minerals that have more heavy elements present (in comparison to darker areas)

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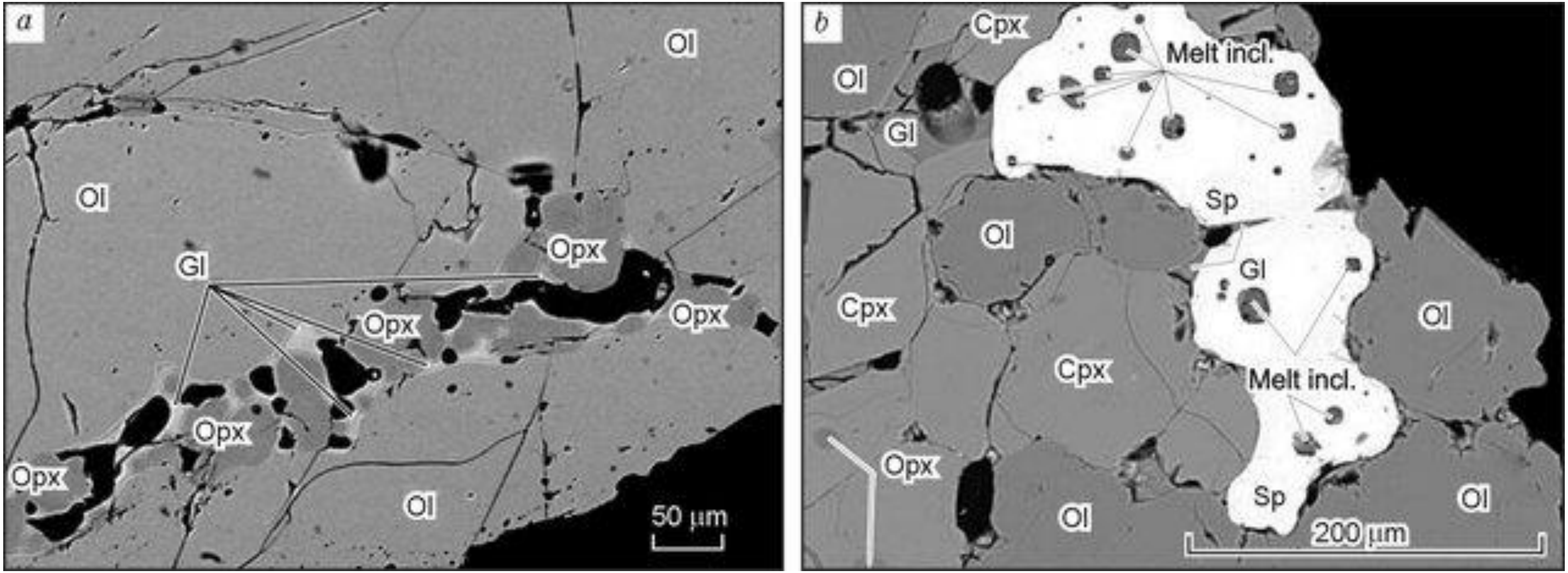

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Scanning Electron Microscopy (SEM)

A powerful imaging technique that produces a largely magified image (up to 650,00 times) by using electrons and X-rays instead of light.

Electron Probe Microanalyzer (EPMA)

What can I put in an EPMA:

Some minor sample preparation is required for EPMA. The samples cannot be conductive within the sample chamber and need to be polished. Most samples require a thin carbon film on surface.

Suitable samples:

Small epoxy mounts of grains or rock chips
Thin slices of rock (thin sections) on glass slides

Unsuitable samples:

Large and porous rock fragments
Unsupported rock fragments
Organic material (no plants)

Individual grains of clinopyroxene that are held in an epoxy mount. The grains are polished and cannot fall out. The mount will be coated with a thin film of carbon before EPMA.

2.5 cm

Small fragments of mantle xenoliths (garnet lherzolites) that are held in a dried epoxy mount that has been finely polished. The samples cannot fall out and will be coated with a carbon film before EPMA.

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Thin section slide of a mantle xenolith in a basalt volcanic rock

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Loose rocks fragments of mantle xenolith. A loose rock is too large and will not fit into the sample chamber. You may also risk damaging the internal part of the EPMA including the detectors. The rough and unpolished surfaces will also prevent accurate imaging and detection of X-rays.

Porous and organic-rich sedimentary rock. The porosity will prevent the chamber from going into vacuum. Organic material will contaminate inside of the EPMA.

Geothermobarometry: Obtaining Estimates of Pressure and Temperatures from Geochemical Data: Part 2B.

Dr. Zachary J. Sudholz (zs441@cam.ac.uk)

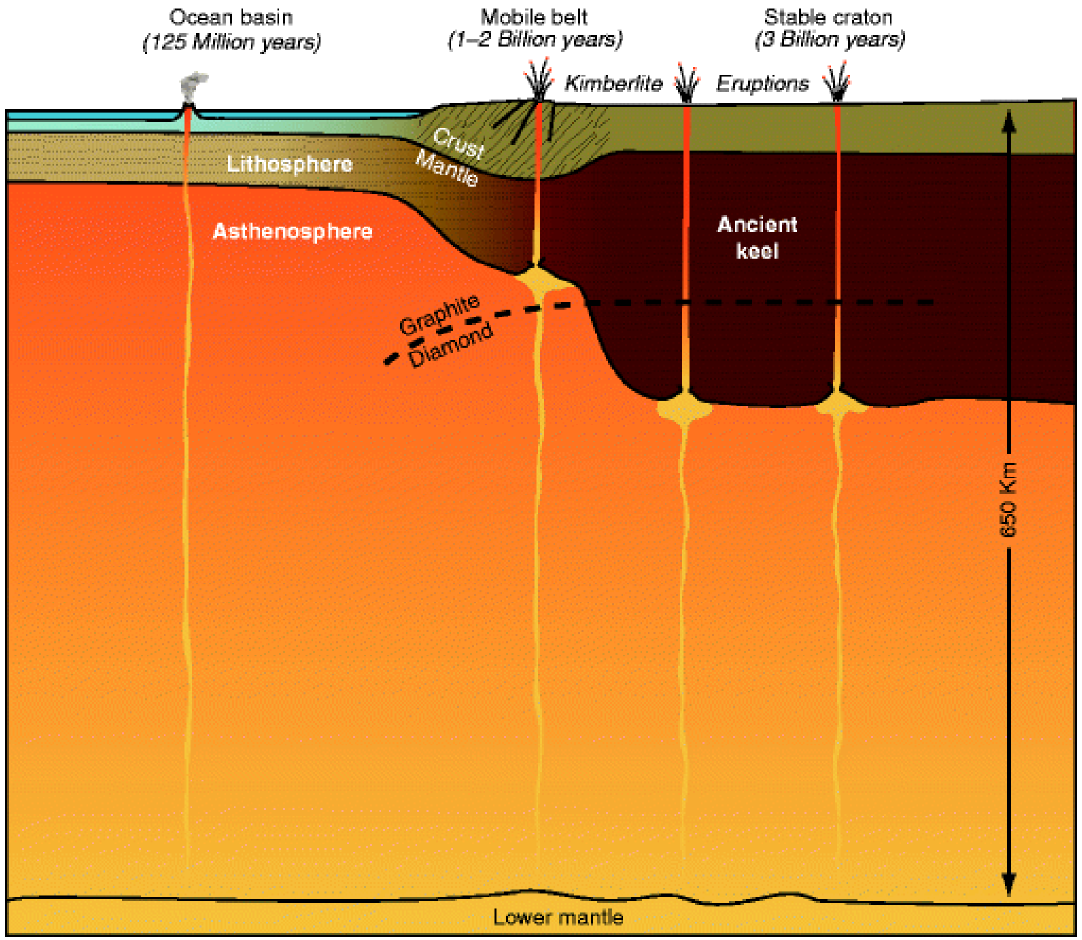
Department of Earth Sciences – University of Cambridge

Geothermobarometry

One of the most important pieces of data that can be obtained from chemical concentrations of rocks and minerals **are pressure and temperature estimates**

Pressure and temperature estimates of rocks and minerals help petrologists determine **WHERE** in the mantle a particular sample was derived from

Volcanic eruptions can often have thousands of mantle xenoliths (pieces of the mantle brought to surface) – what pressure and temperature did each of these pieces come from?



Geothermobarometry

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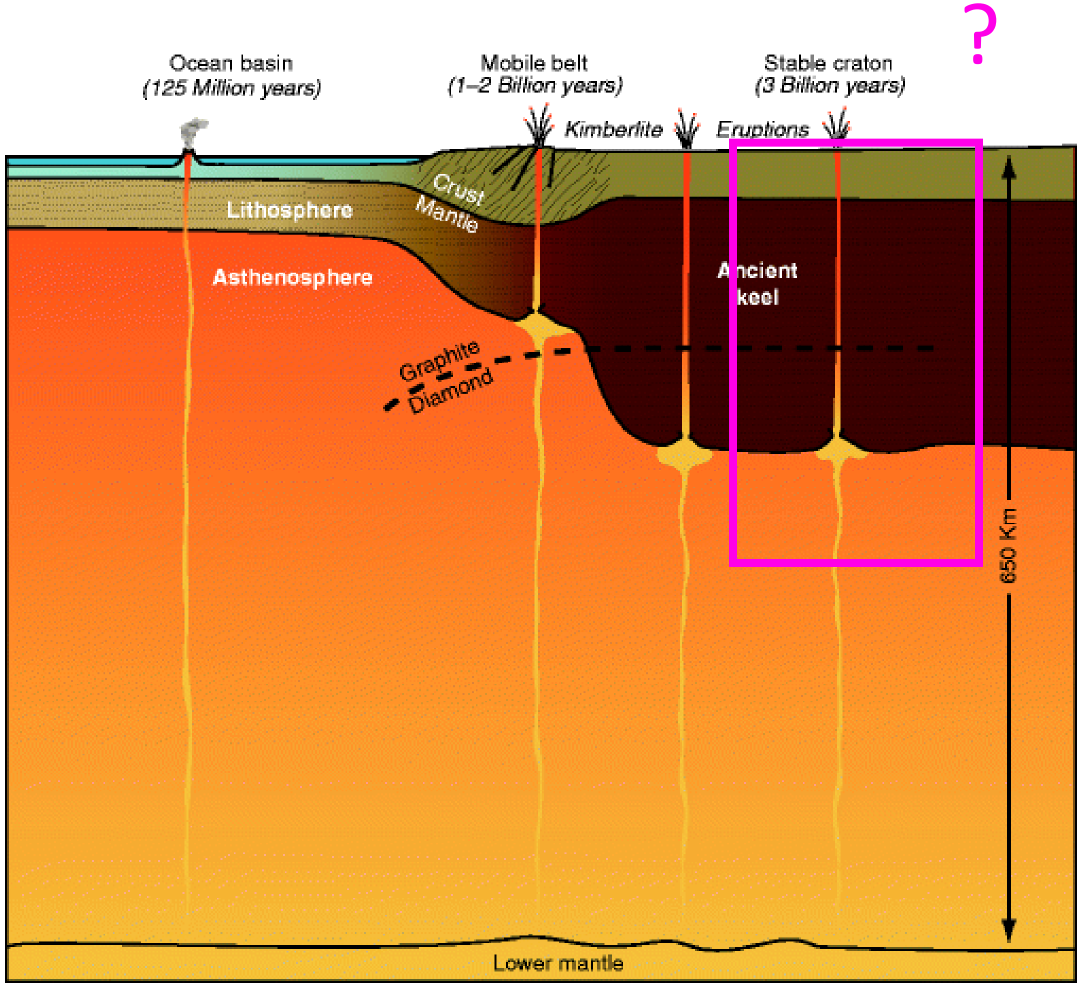

Geothermobarometry

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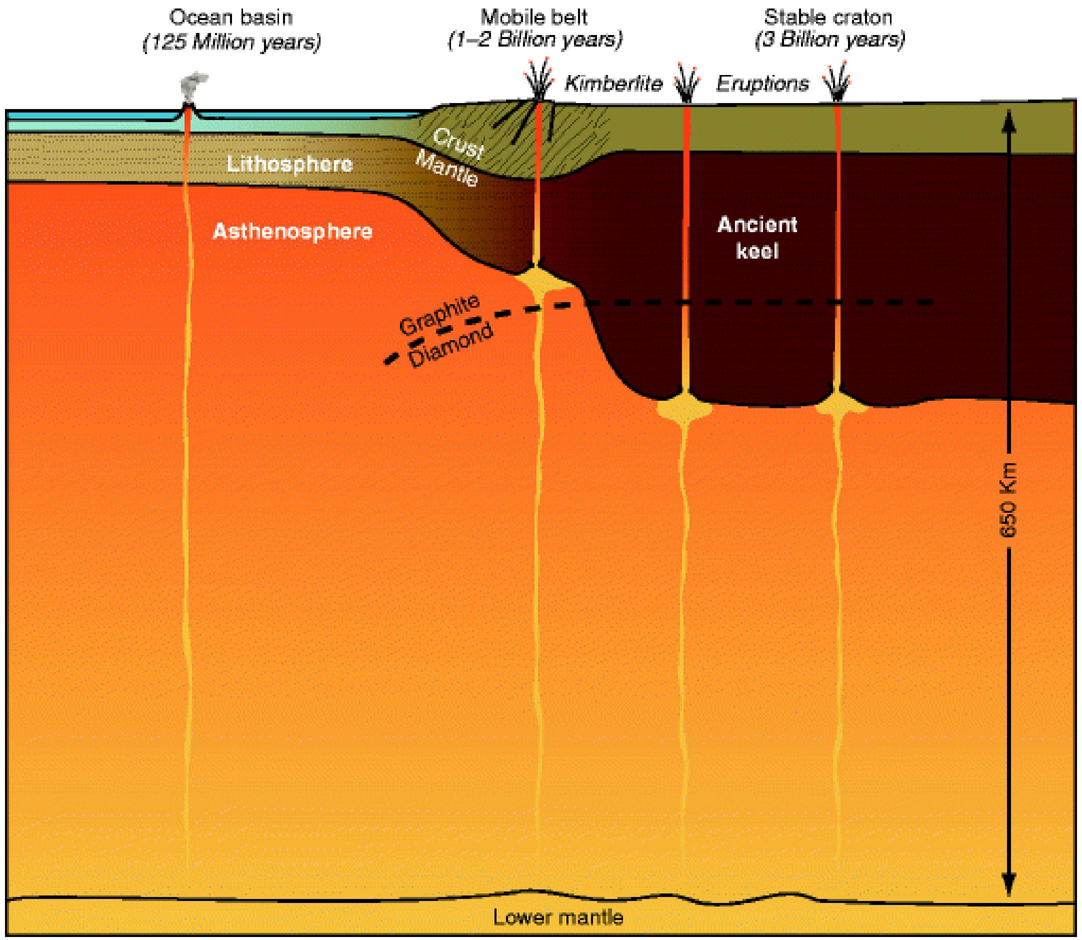
Pressure and temperature estimates of rocks and minerals help petrologists determine **WHERE** in the mantle a particular sample was derived from

We can determine the pressure and temperature of samples using a petrological technique called geothermobarometry which used the chemical compositions of rocks and minerals to back-calculate pressure and temperature

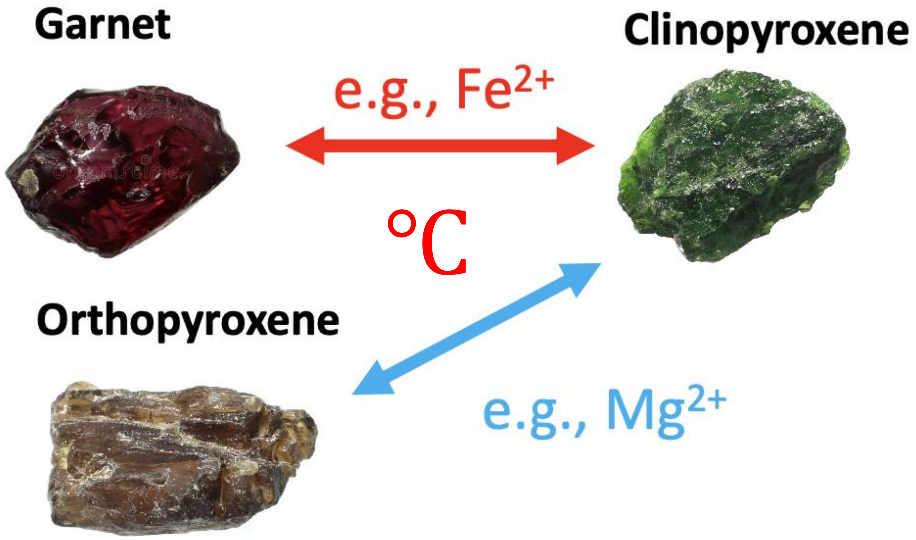


Geothermobarometry

The chemical compositions of minerals may vary due to changes in pressure and temperature. The changes in chemical composition are accommodated by chemical exchange reactions that occur between different minerals

These reactions can be studied theoretically (using thermodynamics) or using experimental petrology

The change in chemical composition because of these pressure-temperature dependent reactions **occurs primarily to help maintain a state of geochemical equilibrium within the lithospheric mantle**



The exchange of Fe and Mg between garnet and clinopyroxene is known to be temperature dependent and is a useful geothermometer!

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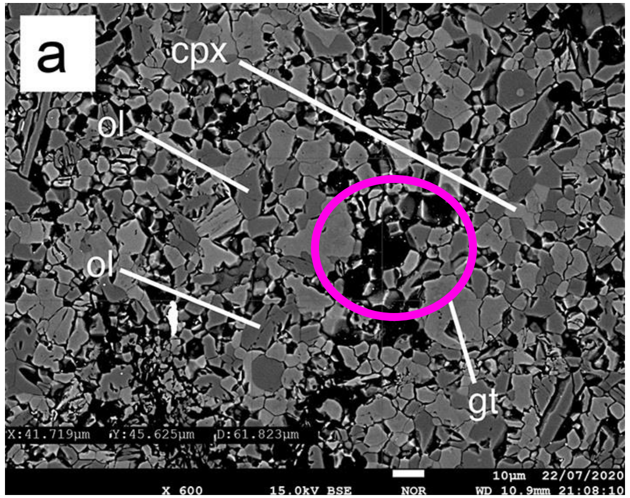

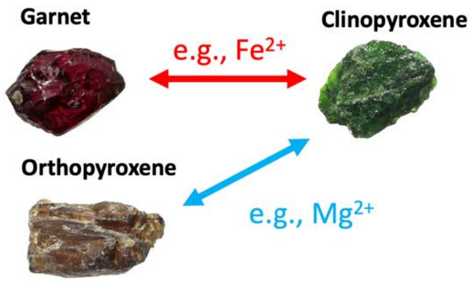

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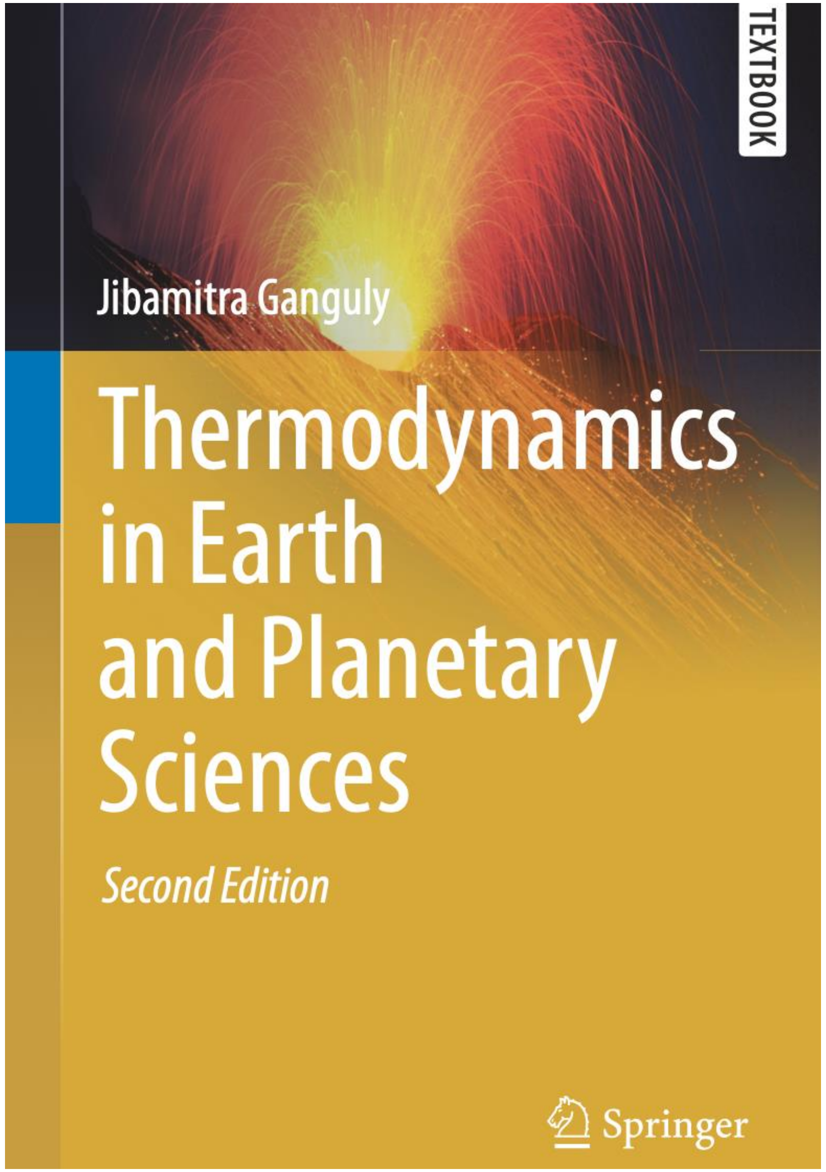


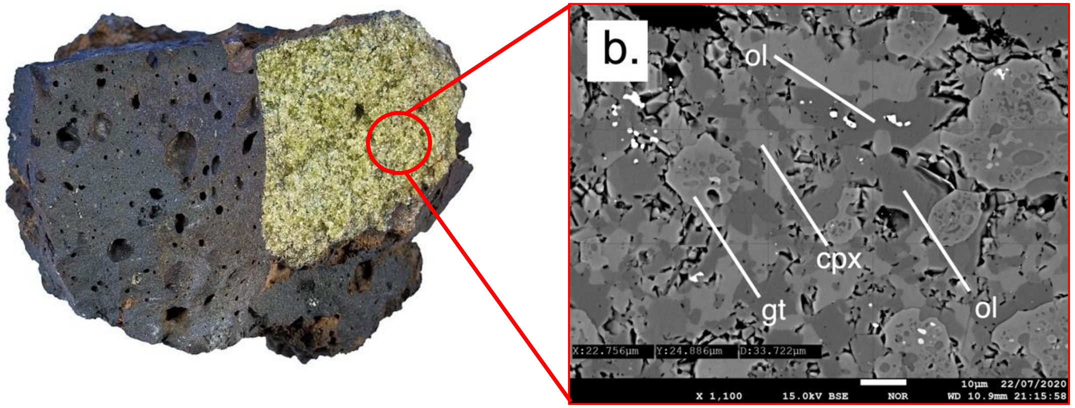
Geothermobarometry

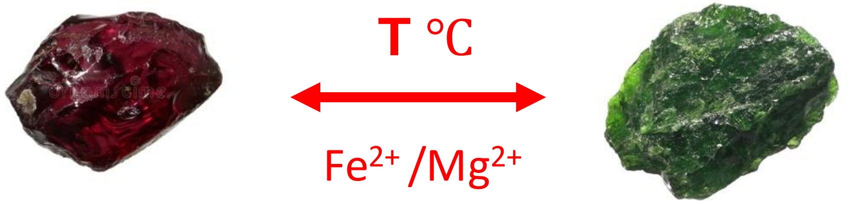
Geothermobarometers are equations that back-calculate the pressures and/or temperatures of rocks and minerals based on their chemical compositions

Geothermobarometers are initially calibrated by experimentally synthetizing minerals at different pressures and temperatures. Pressure and temperature dependent variations in chemical composition can be analyzed using an EPMA

Conduct 10’s or 100’s of experiments to monitor how the chemical compositions change as a function of pressure and temperature. Use the relationship from this data to establish equations and models to estimate PT of natural samples.

Garnet-clinopyroxene Fe-Mg exchange geothermometer





T °C

Fe^{2+}/Mg^{2+}

Garnet

Clinopyroxene

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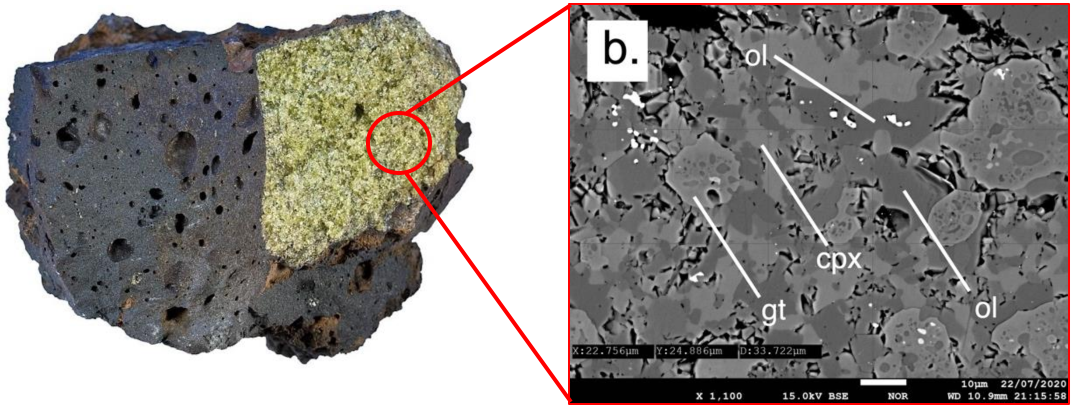

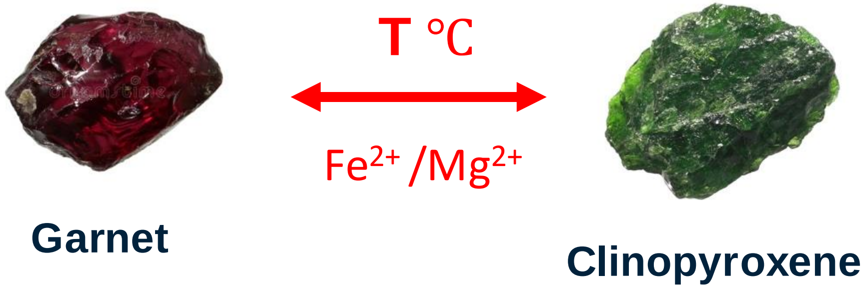

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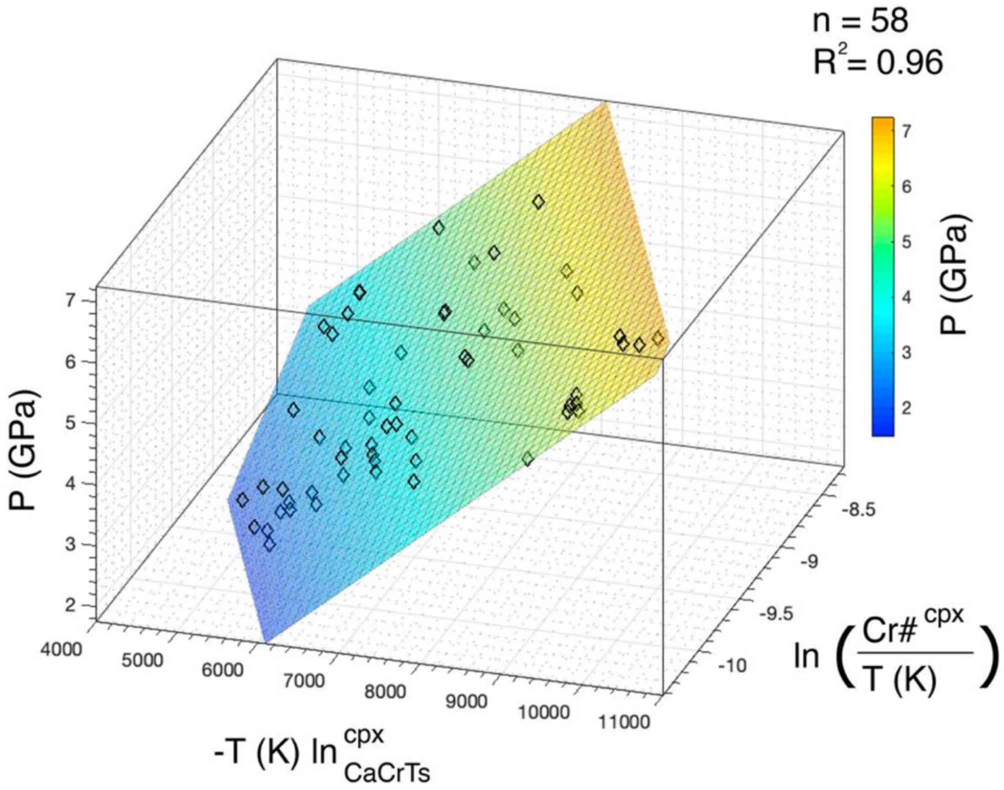

If we conduct enough experiments at a wide pressure and temperature range – it is possible to develop an equation that describes the relationship between PT and composition. After Sudholz et al. (2021)

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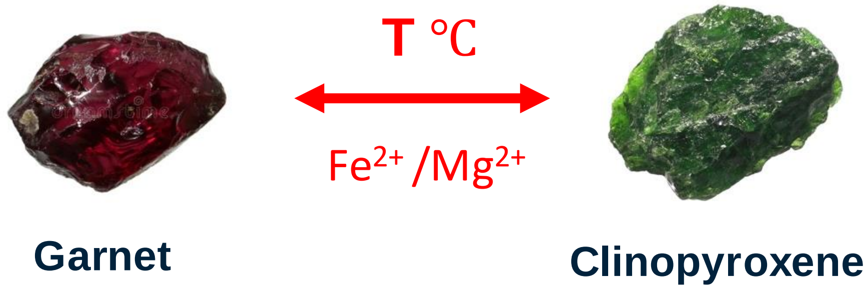

Mg Grt + Fe Cpx = Fe Garnet + Mg Cpx

$$X_{Mg}^{Garnet} = \frac{Mg}{Ca + Mg + Fe} \qquad Kd = \frac{X_{Fe}^{Garnet}}{X_{Mg}^{Garnet}} \cdot \frac{X_{Mg}^{Clino}}{X_{Fe}^{Clino}}$$

$$T(K) = \frac{3104 \cdot X_{Ca}^{Garnet} + 3030 + 10.86 \cdot P(kbar)}{\ln Kd + 1.903}$$

Geothermobarometry

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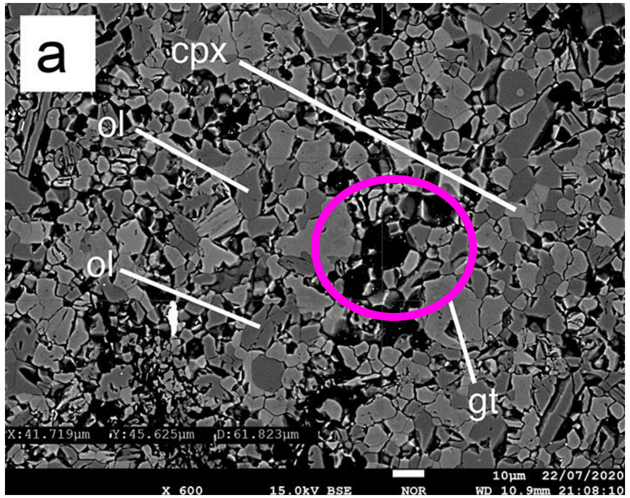

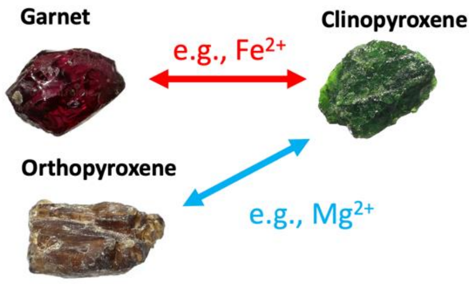

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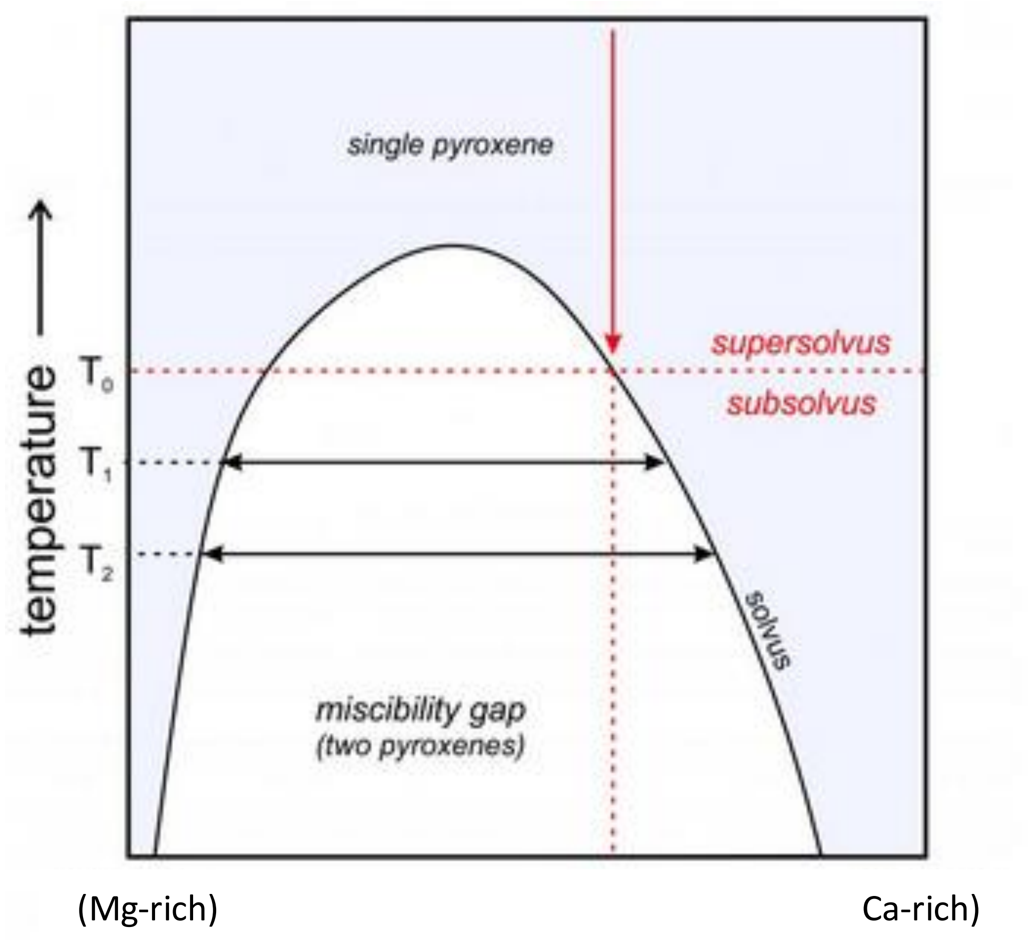
Measure experimental compositions on the electron microprobe to see how the compositions of the experimental minerals varies due to changes in the experimental pressure and temperature for different sets of experiments.

Geothermobarometry

There are over 100 calibrated geothermobarometers suitable for different mantle lithologies and minerals:

Two-pyroxene solvus geothermometers:
Two-pyroxene solvus geothermometry is a method used to estimate the temperature of two coexisting pyroxenes (clinopyroxene and orthopyroxene). It is based on the principle that the chemical compositions of clinopyroxene (Cpx) and orthopyroxene (Opx) change as a function of temperature, specifically in terms of their mutual solubility or the distribution of Fe^{2+} Ca^{2+}, and Mg^{2+} between them. This relationship can be used to infer the temperature of formation



Pyroxene solvus. Note that the Mg and Ca concentrations of ortho- and clinopyroxene change as a function of temperature.

Geothermobarometry

$$T(°C) = \frac{\left(24787 + 678 \cdot \left(\frac{P}{10}\right)\right)}{15.67 + 14.37 \cdot Ti^{cpx} + 3.69 \cdot Fe^{cpx} - 3.25 \cdot (Al^{cpx} + Cr^{cpx} - Na^{cpx}) + \ln Kd} - 273$$

$$\ln Kd = \left(\ln\left(\frac{a^{En}_{cpx}}{a^{En}_{opx}}\right)\right)^2$$

$$a^{En}_{cpx} = (1 - Ca^{cpx} - Na^{cpx}) \cdot (1 - Al^{VI}{}^{cpx} - Cr^{cpx} - Ti^{cpx}) \cdot (1 - \frac{Al^{IV}{}^{cpx}}{2})^2$$

$$Al^{VI}{}^{cpx} = \left(\frac{Al^{cpx}}{2} - \frac{Cr^{cpx}}{2} - Ti^{cpx} + \frac{Na^{cpx}}{2}\right)$$

$$Al^{IV}{}^{cpx} = \left(\frac{Al^{cpx}}{2} + \frac{Cr^{cpx}}{2} + Ti^{cpx} - \frac{Na^{cpx}}{2}\right)$$

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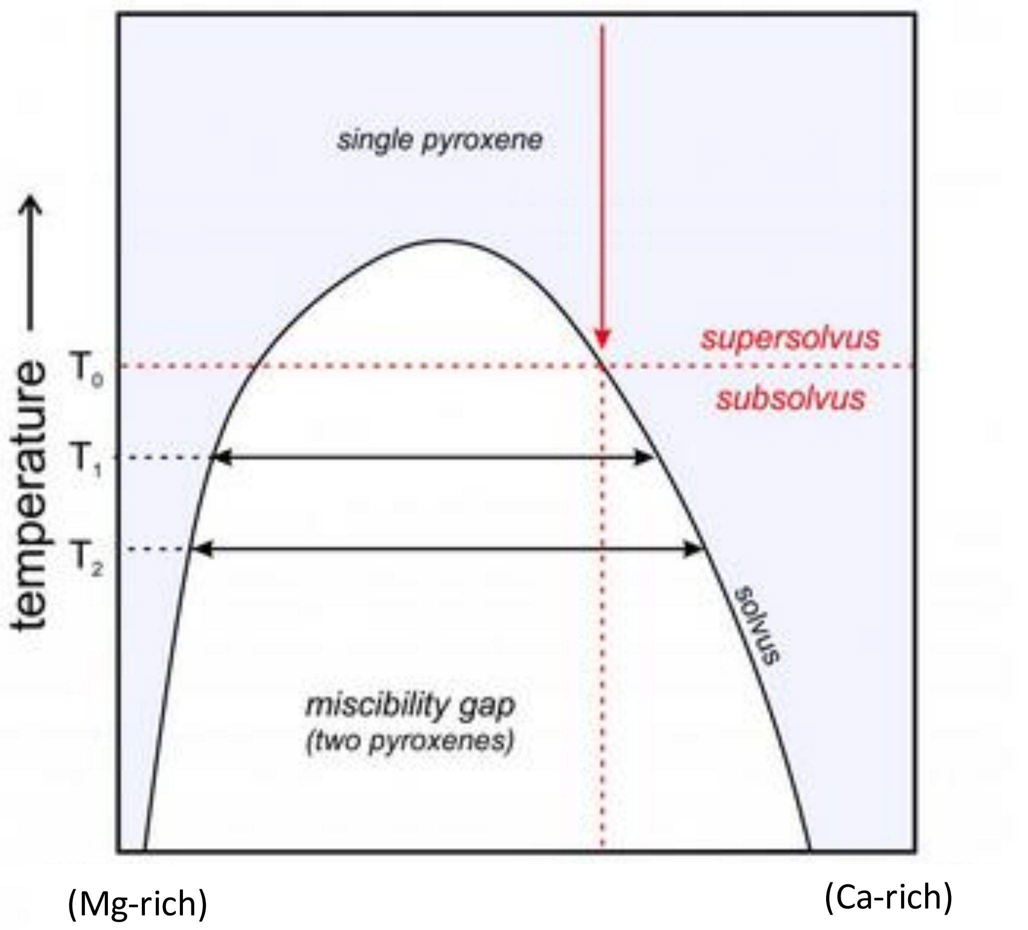


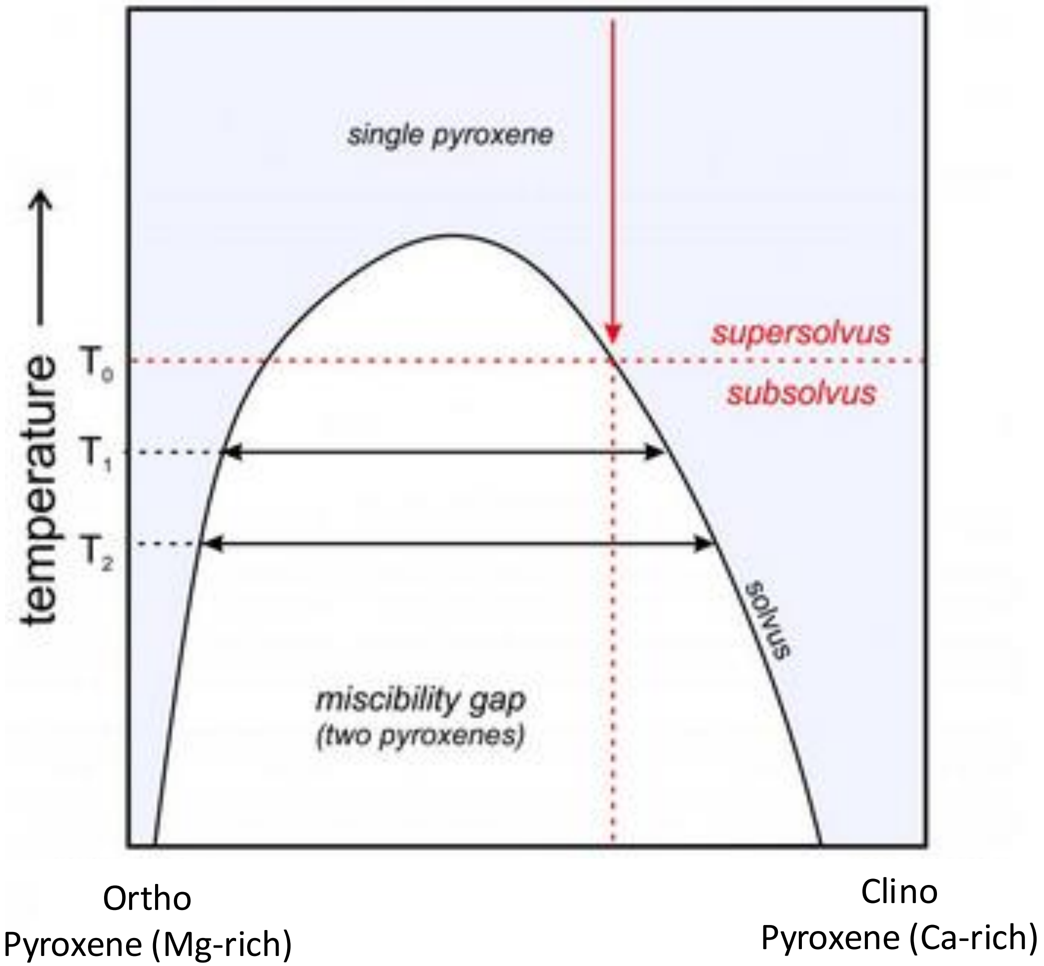
Pyroxene solvus. Note that the Mg and Ca concentrations of ortho- and clinopyroxene change as a function of temperature.

Geothermobarometry

There are over 100 calibrated geothermobarometers suitable for different mantle lithologies and minerals:

Two-pyroxene solvus geothermometers:
Based on temperature dependent variations in Ca, Fe, Mg in ortho- and clinopyroxene

- Suitable for wide temperature ranges (700 to 1450 °C) and relatively pressure insensitive
- Uncertainty on temperature estimates of <40 °C
- Requires compositional data for ortho- and clinopyroxene (limited to lherzolites)
- Used by Priestly et al. (2018; 2024) for LAB models of tomography data



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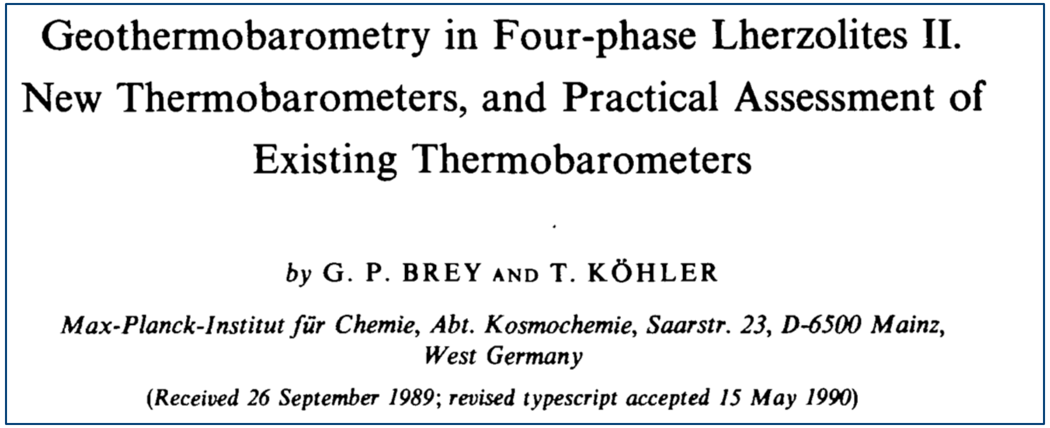
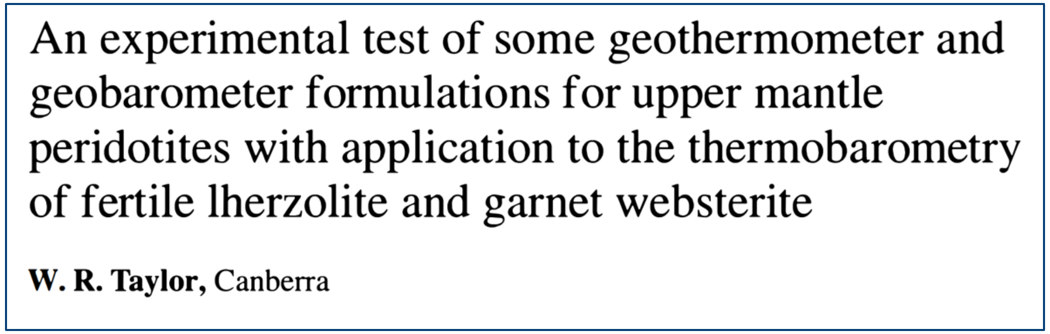


Geothermobarometry in Four-phase Lherzolites II.
New Thermobarometers, and Practical Assessment of
Existing Thermobarometers

by G. P. BREY AND T. KÖHLER

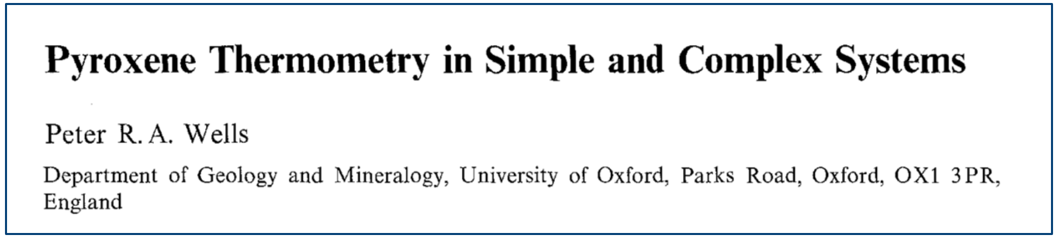
Max-Planck-Institut für Chemie, Abt. Kosmochemie, Saarstr. 23, D-6500 Mainz, West Germany

(*Received 26 September 1989; revised typescript accepted 15 May 1990*)



An experimental test of some geothermometer and geobarometer formulations for upper mantle peridotites with application to the thermobarometry of fertile lherzolite and garnet websterite

W. R. Taylor, Canberra



Pyroxene Thermometry in Simple and Complex Systems

Peter R. A. Wells

Department of Geology and Mineralogy, University of Oxford, Parks Road, Oxford, OX1 3PR, England

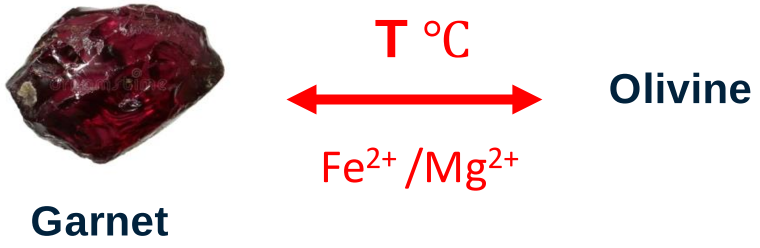
Geothermobarometry

Fe-Mg exchange geothermometers:
Based on the exchange of Fe and Mg between garnet and various mantle minerals (opx, grt, olv etc.)

Fe^{2+} and Mg^{2+} can substitute for one another in the crystal structures of mantle minerals because they have similar ionic radii and charges.

At equilibrium, the distribution of Fe^{2+} and Mg^{2+} between the minerals is controlled by temperature, with the ratio of Fe to Mg in each mineral phase shifting as the temperature changes.

There are several calibrations of Fe-Mg exchange geothermometers for mantle minerals



$$X_{Mg}^{Garnet} + X_{Fe}^{Olv} = X_{Fe}^{Garnet} + X_{Mg}^{Olv}$$

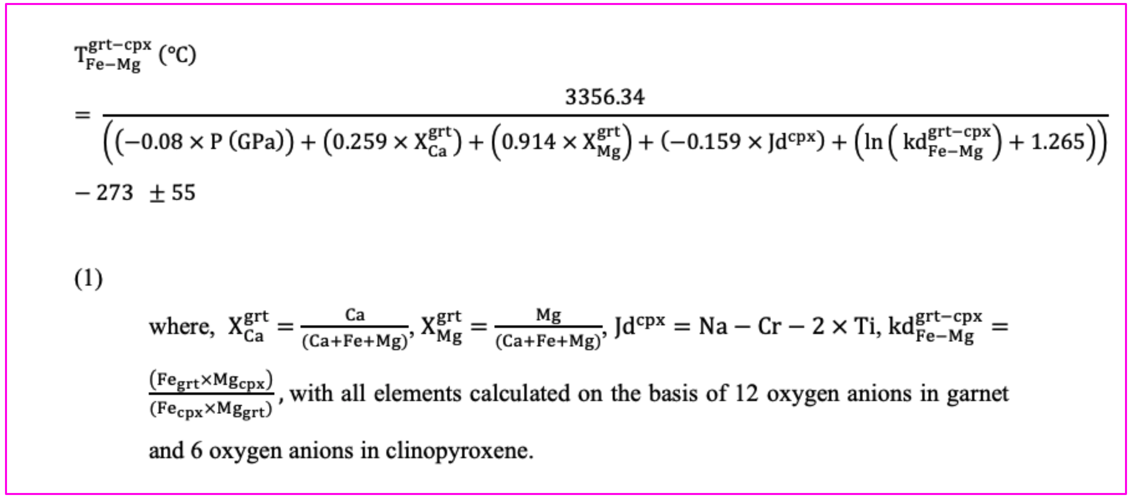
$$Kd = \frac{X_{Fe}^{Garnet}}{X_{Mg}^{Garnet}} \cdot \frac{X_{Mg}^{Olv}}{X_{Fe}^{Olv}}$$

$$\Delta G = \Delta H - T\,\Delta S$$
$$\Delta G = RTlnKd$$

ΔG = Gibbs Free Energy
ΔH = Enthalpy change
ΔS = Entropy change
T = Temperature
R = Gas constant

Possible to use Kd of Temperature dependent reaction to solve for T using principles of equilibrium thermodynamics

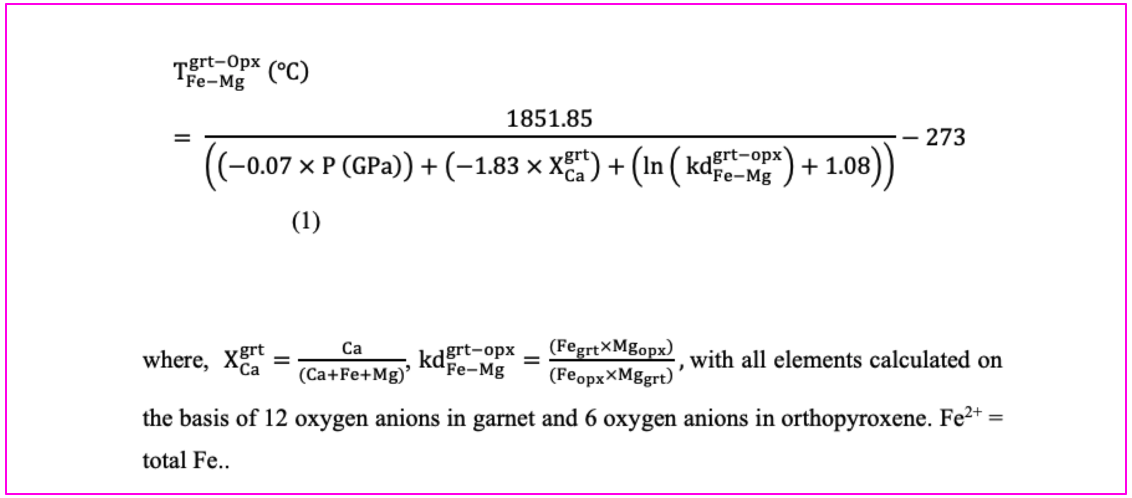
Geothermobarometry



$$T^{grt-cpx}_{Fe-Mg}\,(^{\circ}C) = \frac{3356.34}{\left((-0.08\times P\,(GPa)) + (0.259\times X^{grt}_{Ca}) + (0.914\times X^{grt}_{Mg}) + (-0.159\times Jd^{cpx}) + \left(\ln\left(kd^{grt-cpx}_{Fe-Mg}\right) + 1.265\right)\right)} - 273 \quad \pm 55$$

(1)

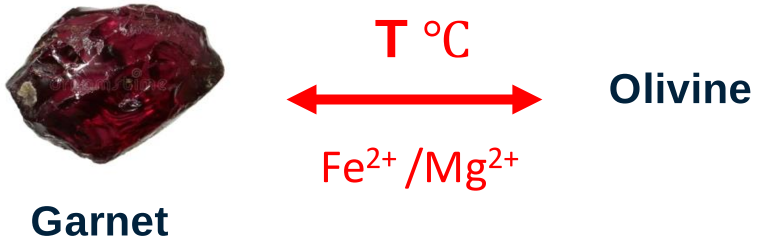
where, $X^{grt}_{Ca} = \frac{Ca}{(Ca+Fe+Mg)}$, $X^{grt}_{Mg} = \frac{Mg}{(Ca+Fe+Mg)}$, $Jd^{cpx} = Na - Cr - 2\times Ti$, $kd^{grt-cpx}_{Fe-Mg} = \frac{(Fe_{grt}\times Mg_{cpx})}{(Fe_{cpx}\times Mg_{grt})}$, with all elements calculated on the basis of 12 oxygen anions in garnet and 6 oxygen anions in clinopyroxene.



$$T^{grt-Opx}_{Fe-Mg}\,(^{\circ}C) = \frac{1851.85}{\left((-0.07\times P\,(GPa)) + (-1.83\times X^{grt}_{Ca}) + \left(\ln\left(kd^{grt-opx}_{Fe-Mg}\right) + 1.08\right)\right)} - 273$$

(1)

where, $X^{grt}_{Ca} = \frac{Ca}{(Ca+Fe+Mg)}$, $kd^{grt-opx}_{Fe-Mg} = \frac{(Fe_{grt}\times Mg_{opx})}{(Fe_{opx}\times Mg_{grt})}$, with all elements calculated on the basis of 12 oxygen anions in garnet and 6 oxygen anions in orthopyroxene. Fe^{2+} = total Fe..



$$X^{Garnet}_{Mg} + X^{Olv}_{Fe} = X^{Garnet}_{Fe} + X^{Olv}_{Mg}$$

$$Kd = \frac{X^{Garnet}_{Fe}}{X^{Garnet}_{Mg}} \cdot \frac{X^{Olv}_{Mg}}{X^{Olv}_{Fe}}$$

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T = Temperature
R = Gas constant

Possible to use Kd of Temperature dependent reaction to solve for T using principles of equilibrium thermodynamics

Geothermobarometry

There are over 100 calibrated geothermobarometers suitable for different mantle lithologies and minerals:

Fe-Mg exchange geothermometers:
Based on the exchange of Fe and Mg between garnet and various mantle minerals (opx, grt, olv etc.)

- Suitable for wide temperature ranges (700 to 1450 °C)
- Uncertainty on temperature estimates of >75 °C
- Requires compositional data for garnet and other phases (suitable for various peridotites)
- Sensitive to pressure and changes in the oxidation state of Fe^{2+} to Fe^{3+}

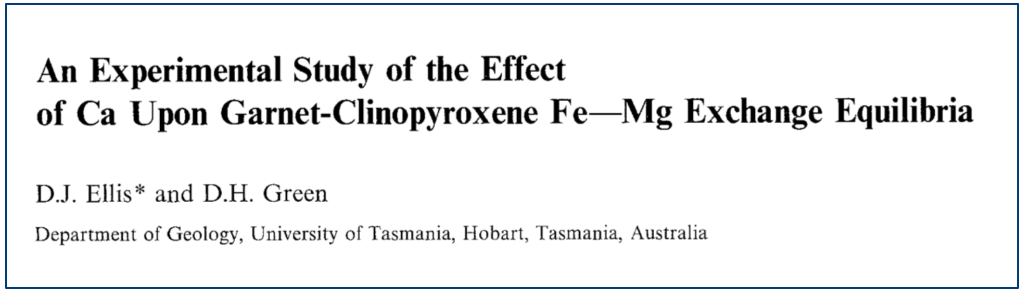
Garnet

T °C ↔ Fe^{2+}/Mg^{2+}

Olivine

Orthopyroxene

Clinopyroxene



An Experimental Study of the Effect of Ca Upon Garnet-Clinopyroxene Fe—Mg Exchange Equilibria

D.J. Ellis* and D.H. Green

Department of Geology, University of Tasmania, Hobart, Tasmania, Australia

An Experimental Study of Fe–Mg Partitioning Between Garnet and Olivine and Its Calibration as a Geothermometer

Hugh St.C. O'Neill* and B.J. Wood

Department of Geology, University of Manchester, Manchester M13 9PL, England

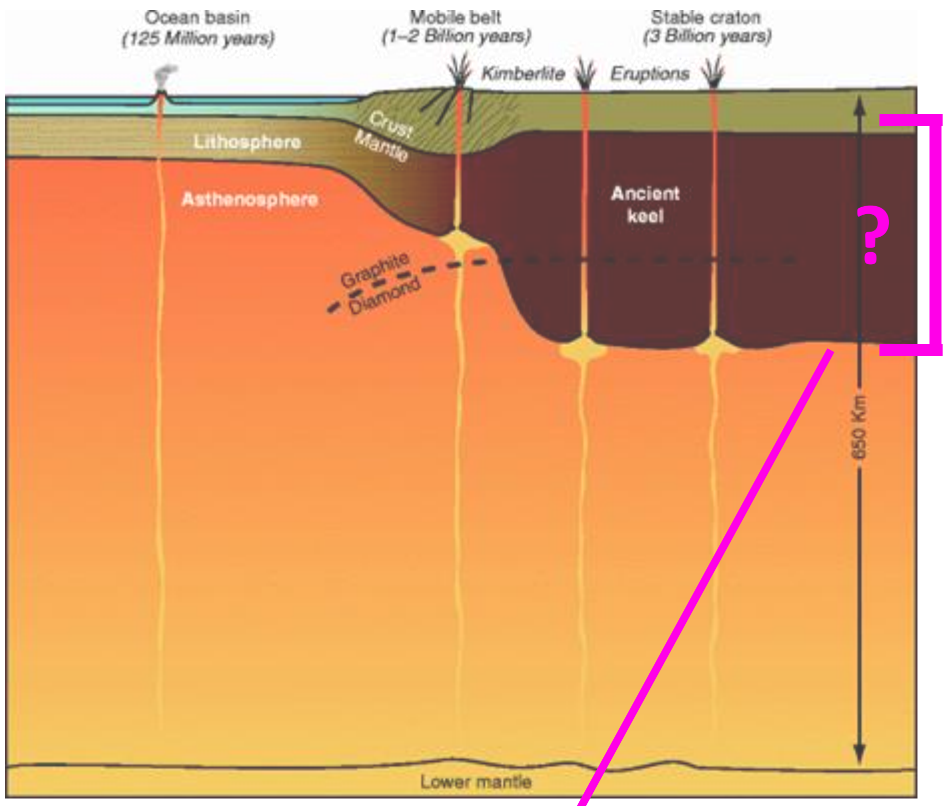
Mantle geothermometry: experimental evaluation and recalibration of Fe–Mg geothermometers for garnet-clinopyroxene and garnet-orthopyroxene in peridotite, pyroxenite and eclogite systems

Z. J. Sudholz[1] · D. H. Green[1,2] · G. M. Yaxley[1] · A. L. Jaques[1]

Geothermobarometry: Applications

Why is geothermobarometry so important and what are its uses?

- **Provides pressure and temperature constraints for samples derived from the lithospheric mantle**
- Can be used in conjunction with geochemical and isotopic data to study vertical changes in composition of the mantle
- Construct paleogeothermal gradients using pressure and temperature estimates for mantle xenoliths from volcanic eruptions (constrain the depth-to lithosphere asthenosphere boundary)

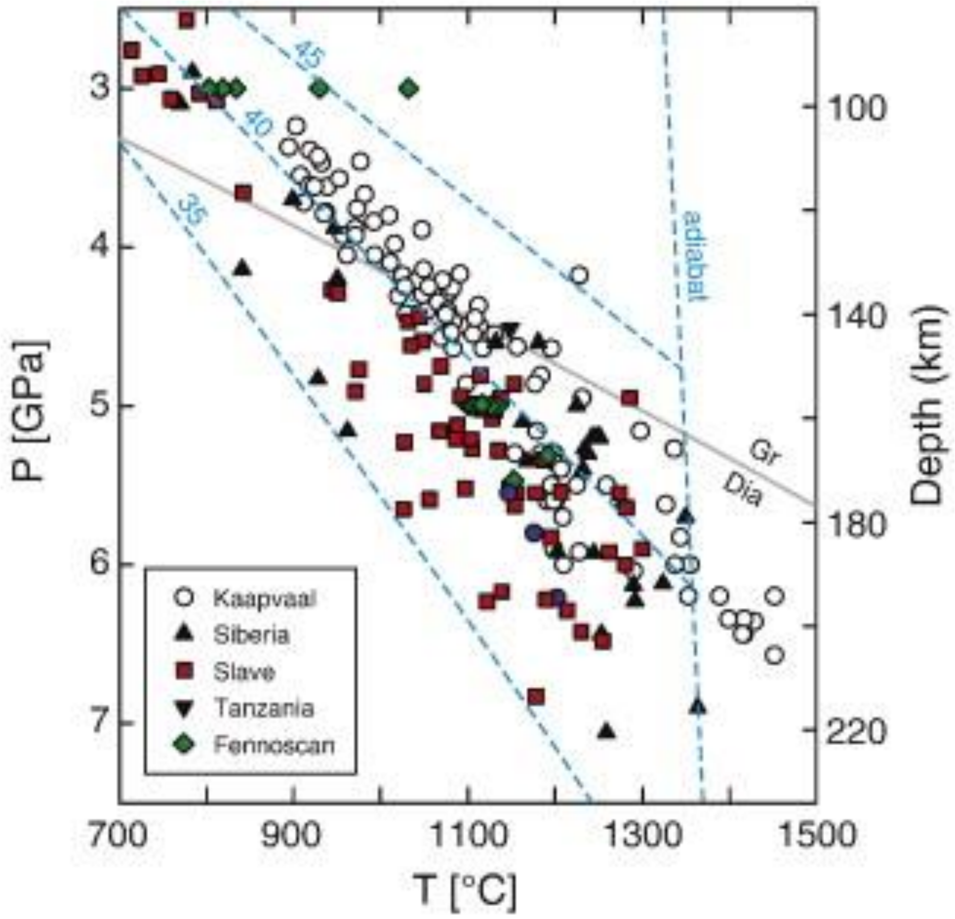


Geothermobarometry: Applications

Why is geothermobarometry so important and what are its uses?

Diamond Exploration:

- When kimberlites and related volcanic pipes travel through the mantle, they collect pieces of the surrounding mantle, which may include diamond
- The pieces of the entrained make up large portions of the pipe and may include mantle xenoliths or single-grain xenocrysts
- Geothermobarometer can be applied to these rocks and minerals to determine whether the volcanic pipe may have sampled the portion of the lithospheric mantle where diamond is stable!



Geothermobarometry pressure and temperature estimates of mantle xenoliths from various global kimberlites. After Stachel and Luth (2015)

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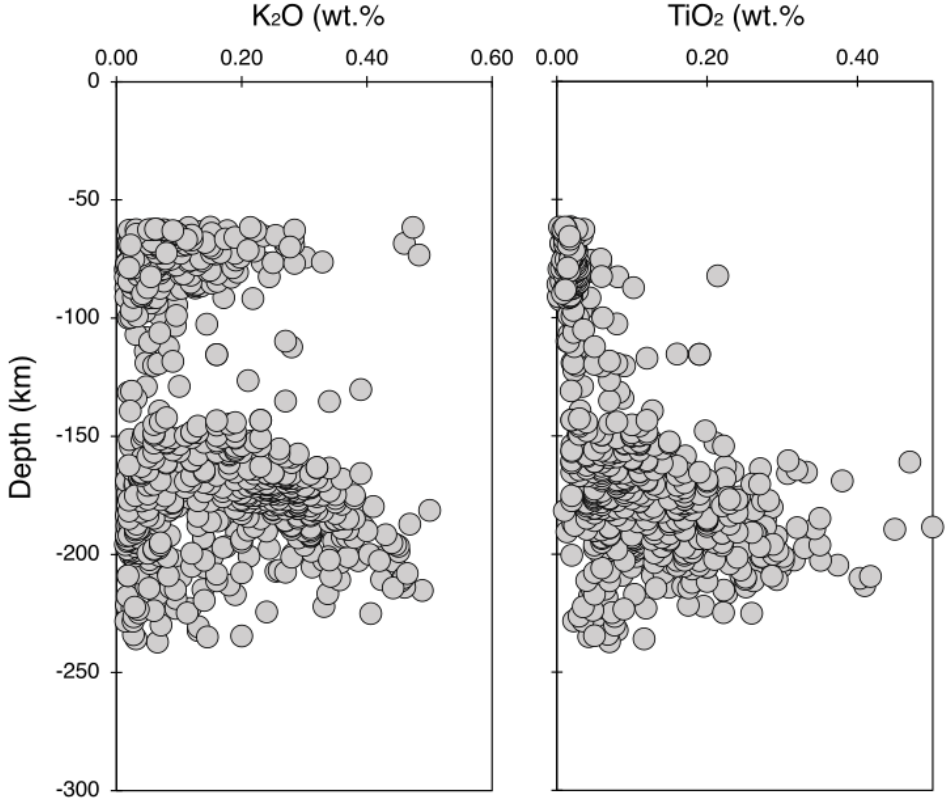

Variation in the concentration of TiO2 and K2O in clinopyroxene as a function of depth within the lithospheric mantle.

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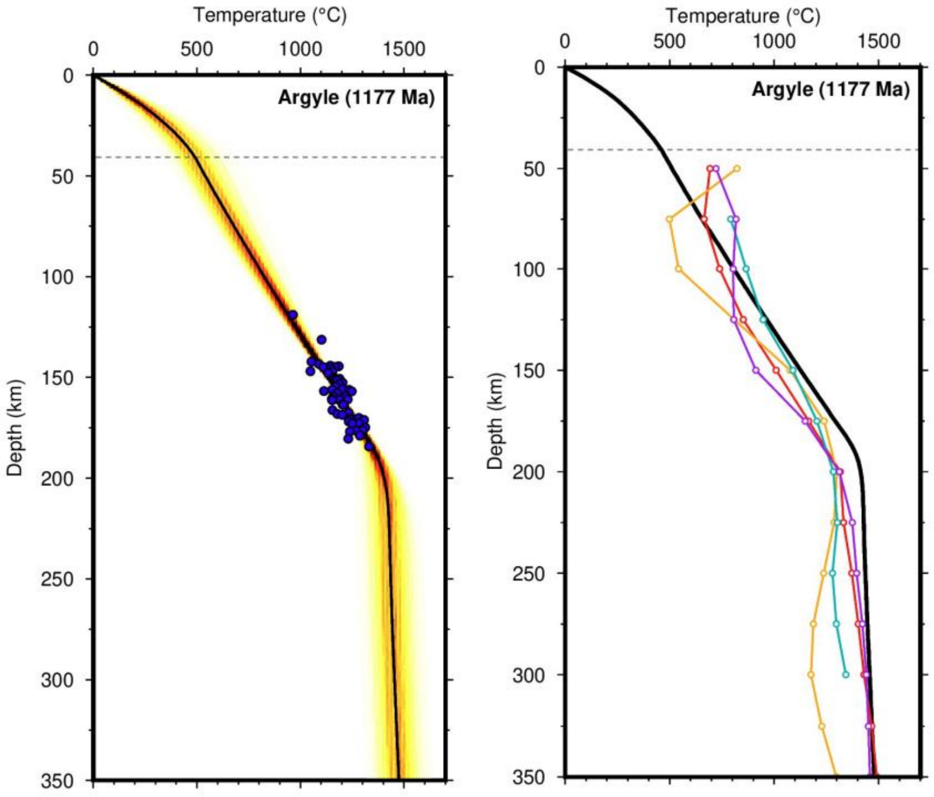

Representative geothermal gradient (yellow) fit to xenolith pressure-temperature estimates. After Hoggard et al. (2020)

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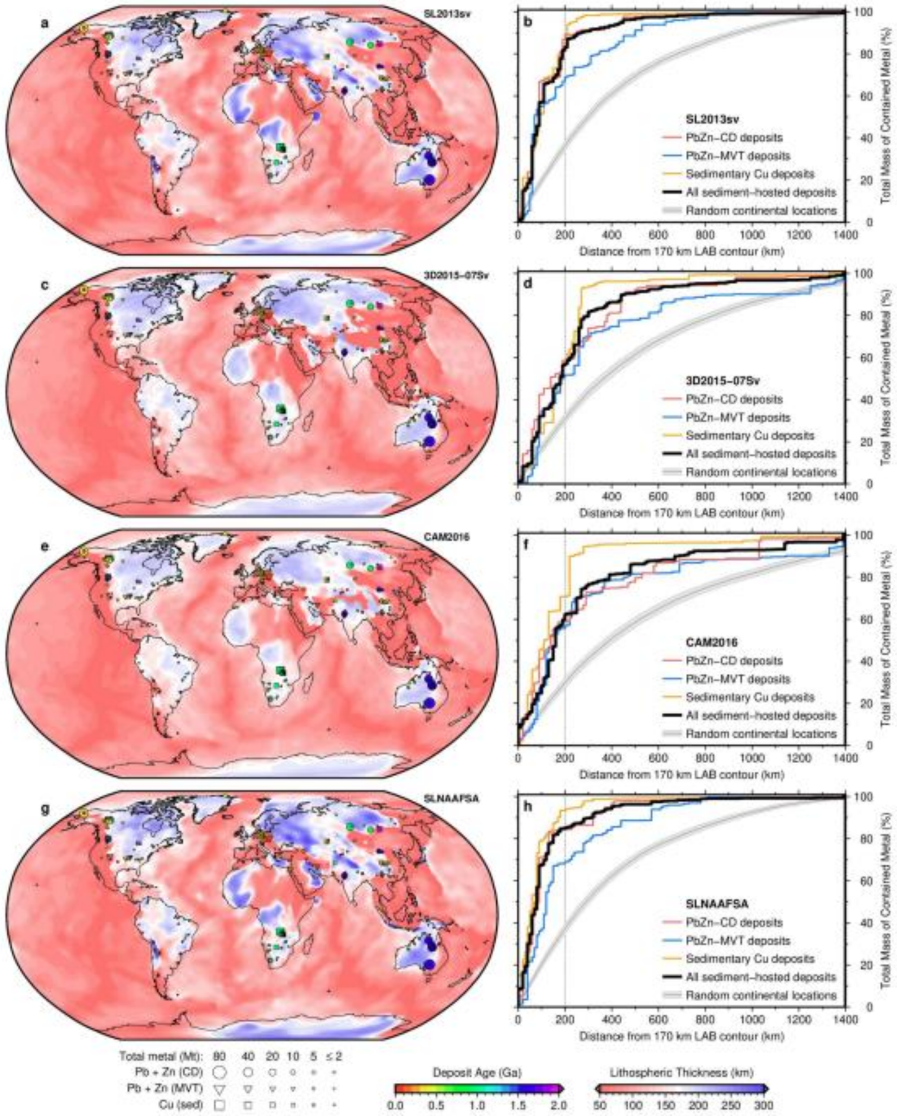


Hoggard et al. (2020)

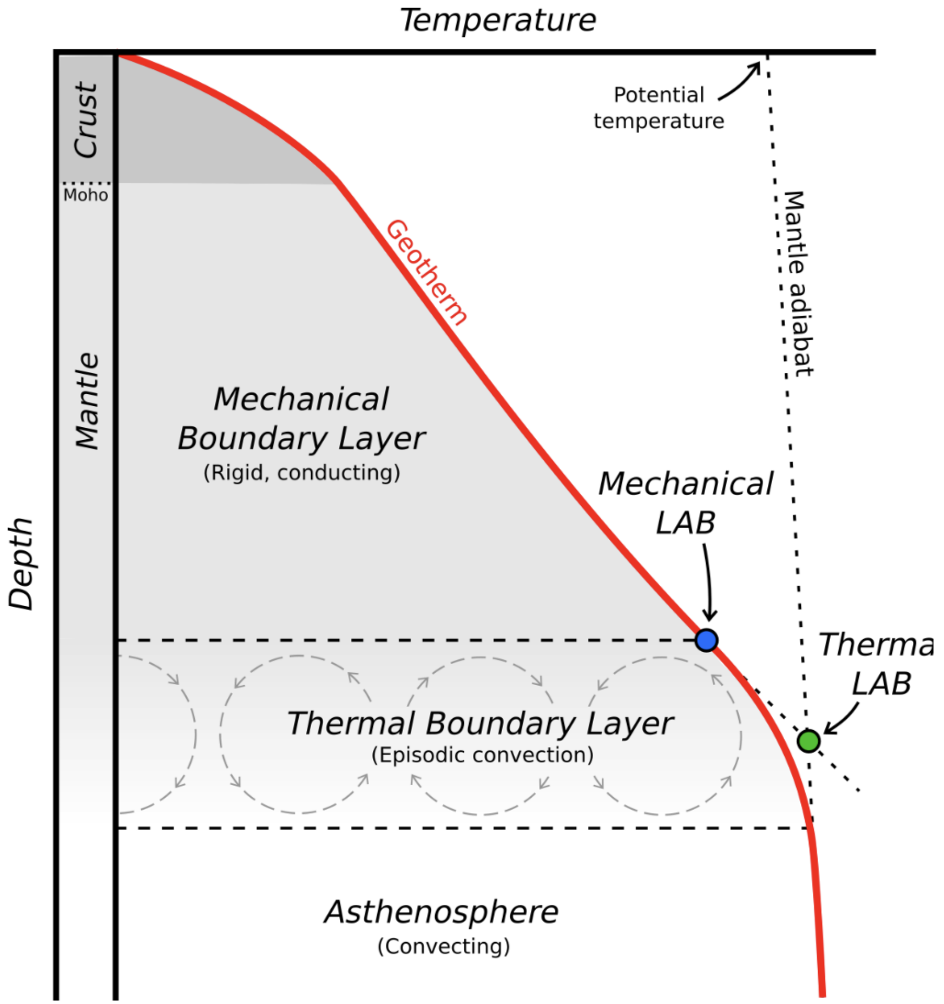
Geothermobarometry: Applications

Constructing a paleogeothermal gradient

The relationship between pressure and temperature within the lithospheric mantle defines a geothermal gradient

Geothermal gradients vary between different tectonic settings (i.e., cratons, active rifts and orogenic belts)

The intersection point between the geothermal gradient and the mantle adiabat defines the base of the lithosphere (lithosphere asthenosphere boundary; LAB)



After Hoggard et al. (pers. comms).

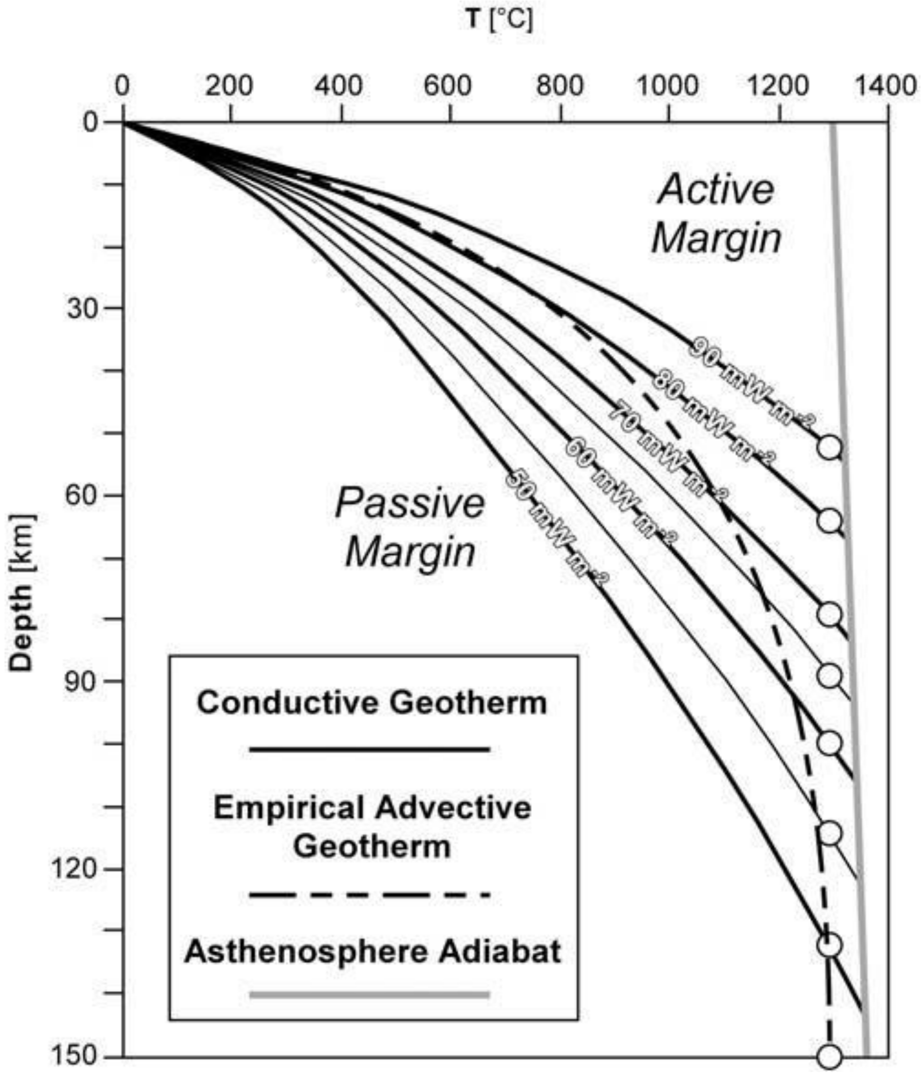
Geothermobarometry: Applications

Constructing a paleogeothermal gradient

We can estimate present-day geothermal gradients of the lithospheric mantle using numerous geophysical techniques

We can estimate **paleo-**geothermal gradients using geothermobarometry pressure and temperature estimates from mantle xenoliths hosted in volcanic rocks

Paleo-geotherms are useful for comparing spatial and temporal changes in the thickness of the lithosphere (delamination, thermal erosion)



Conductive geothermal gradients. After Moore and Wiltschko (2004)

Geothermobarometry: Applications

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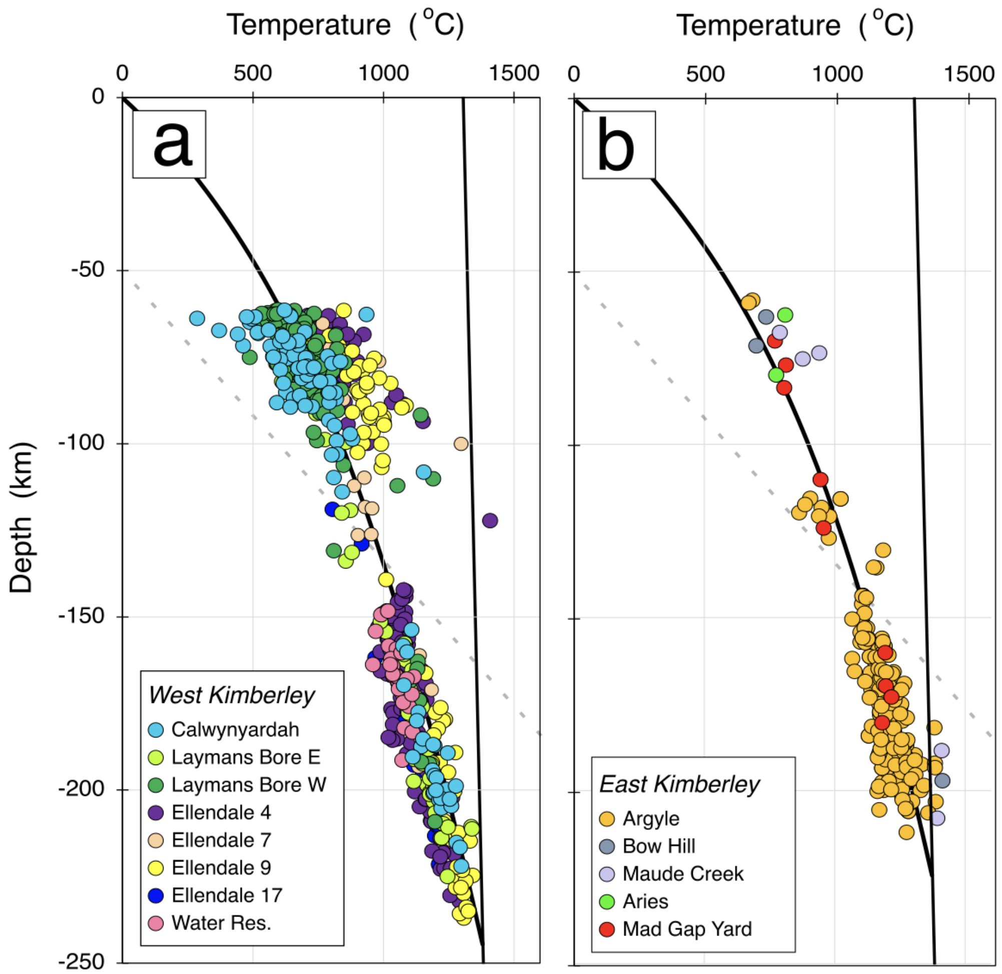

Paleo-geothermal gradient constructed from xenolith pressure and temperature estimates. Samples are from various kimberlites from NW Australia. After Sudholz et al. (2023)

Quick Summary

- Obtaining geochemical data is crucial for studying the lithospheric mantle
- Geochemical data may include Major and minor oxides (wt%), Trace elements (ppm), Isotopes
- There are two common analytical techniques used to obtain geochemical data: Electron probe microanalyzer (EPMA), Laser ablation ICPMS (LA-ICP-MS)
- Each techniques has various positive and negatives and requires different levels of sample preparation
- A common use of geochemical data for studying the lithospheric mantle is to obtain pressure and temperature estimates of rocks and minerals
- The chemical composition of minerals change because of chemical exchange reactions between different minerals
- These exchange reactions take places at different pressures and temperatures to maintain geochemical equilibrium
- There are many used of geothermobarometry PT estimates

Questions to think about..

- Geothermobarometers can sometimes return very erroneous pressure and temperature estimates, particularly for mantle xenoliths that have been geochemically modified by secondary melts and fluids. They may also be problematic for rocks and minerals that have been excessively oxidized. Why might this be?

- Most mantle-xenolith bearing volcanic rocks occur within cratons. LAB estimates from paleogeotherms made using these mantle xenoliths can be compared with present-day LAB estimates made from geophysical datasets, such as receiver functions and tomography. Why might it be expected that both techniques return similar estimates for the LAB? Conversely, why might they also be different?

Answers will be discussed in the following lecture