Accessory (silicates) and Oxide Minerals

Common accessory and metal oxide species are often valuable ore minerals or important phases for petrographic interpretation.

**An accessory mineral**

<1 % of a rock by volume

**An ore mineral**

The occurrence of a mineral in quantities sufficient for economic exploitation.

The most important rock-forming accessory and oxides include titanite (sphene), the spinel group, rutile, ilmenite, and zircon.

Accessory phase silicates are typified by small grain size, high relief, high birefringence.

Oxide minerals are typically opaque – implications for *transmitted* light microscopy?
Titanite (sphene) – CaTi[SiO$_4$](O,OH,F)

A nesosilicate where the dominant structural unit are corner-sharing TiO$_6$ octahedra.

What is special about the Ca coordination?
Sphene is monoclinic, +ve, with a $2V = 27^\circ$.

Pale pinkish-brown to dark brown with 4th order birefringence.

It has a very distinctive form, particularly in thin section, and is a common accessory phase in many magmatic rocks. It will also form large crystals under correct metamorphic terranes.

Its occurrence in alkaline (syenites ± nepheline) can be of economic value.
Zircon – (Zr[SiO$_4$])

An orthosilicate, which is very special in the mineral world, because of its textural, chemical and isotopic complexity.

It is also extremely stable: both physically and chemically.

Zircon growth requires the local geological (chemical) system to be saturated with Zr and SiO$_2$. 
Zircon stability – a key to the past

These very small crystals contain very small concentrations of $^{238}\text{U}$ and $^{235}\text{U}$.

The elements are radiogeneic and decay to $^{206}\text{Pb}$ and $^{207}\text{Pb}$ respectively.

It is possible to measure the ratios of these elements in a zircon against a known standard (normally man-made $^{205}\text{Pb}$). Then we can use the very well constrained half-lives and decay constants of $^{238}\text{U}$ and $^{235}\text{U}$, to calculate the age of that grain.
The great stability of zircon means that after the $^{238}$U and $^{235}$U are enclosed in the structure, an internal “clock” is started and if often not stopped until a geologist wants it stopped.

The technique is robust from shortly after Earth’s formation (4.5 Ga) until “recently”.

The diagram shows the distribution of zircon ages from different locations around the world, with ages ranging from ~4.1 Ga to 10-25 Ma.
Zircon is tetragonal (+ ve) and grows in many different forms.

High relief, high birefringence, and where enclosed in phyllosilicates, may give rise to radiation halos.

Under correct conditions it will form perfect euhedral bipyramids.
Spinel Group \((\text{AB}_2\text{O}_4)\)

The spinel group minerals consist of 6 end-members, with variable occupancy of the A- and B-sites.

Spinel, \((\text{MgAl}_2\text{O}_4)\) and hercynite, \((\text{FeAl}_2\text{O}_4)\) make up the simplest solid-solution. Other variations in this series include Zn and Mn end-members.

An alternative substitution occurs at the B-site with \(\text{Fe}^{3+}\) replacing \(\text{Al}\).

The most common form being magnetite \((\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4)\).

There is also a \(\text{Cr}^{3+}\) substitution.
Ilmenite (FeTiO$_3$)

Ilmenite has a hexagonal structure comparable to corundum (Al$_2$O$_3$).

It is fairly ubiquitous in many igneous and metamorphic rocks, occurring as an accessory phase, or in veins or stratiform layers, where it can occur as economic deposits.

Compositionally, it will partake in solid-solution with hematite (Fe$_2$O$_3$).

While nice crystals are not uncommon, most ores are dark grey and non-descript, while grains in thin section are opaque.
Reflected Light Microscopy

This is a technique which is applicable to opaque minerals and uses a set of observations remarkably similar to those made during transmitted light work.

Colour – Simple observation, or by comparison with knowns.

Reflectivity – The amount of light reflected back to photocell.

Hardness – Microhardness indentation or pseudo-Becke line.

Texture – Cleavage textures, orthogonal vs oblique and pitting.

Bireflectance – a property akin to pleochroism; mineral changes colour on rotation.

Anisotropy – a property akin to birefringence in cross polarised light.
Ilmenite to rutile

While ilmenite is fairly common in most greenschist, amphibolite and even granulite facies rocks, it is far less common at pressures above ~11 kbar.

At these pressures it is typically converted to rutile (TiO$_2$)

- **Rutile** (tetragonal + ve)
  - Share edges are parallel
- **Anatase** (tetragonal - ve)
  - Shared edges are perpendicular
- **Brookite** (orthorhombic + ve)
Optical properties of ilmenite are difficult to determine in transmitted light. Possible indicators are a faint purple tinge when viewed with intense light.

Rutile, on the other hand, has a characteristic deep red-brown colour, extreme birefringence and high relief.

TiO₂ is a valuable ore, but its limited paragenesis make economic deposits unviable. Instead, large ilmenite deposits are exploited. This has an added bonus of high purity Fe-ore byproducts.

Ti is used in paints, plastics and paper, most commonly as a pigment.
Other important, but uncommon oxides.

- \( \text{Fe}_2\text{O}_3 \) - Hematite
- \( \text{SnO}_2 \) - Cassiterite
- \( \text{FeCr}_2\text{O}_4 \) - Chromite
- \( \text{Al}_2\text{O}_3 \) - Corundum
Hydroxide Minerals

There are two important hydroxide minerals that you should be aware of.

Brucite (Mg[OH]₂), because of its potential role in CO₂ sequestration and the fact that it defines the octahedrally coordinated site in the trioctahedral phyllosilicates.

Gibbsite (Al[OH]₂), because it defines the octahedrally coordinated site in the dioctahedral phyllosilicates, and it is the world's foremost source of Al metal.
Sulphides and Sulphates

Important minerals in ore-deposit geology and their occurrence is controlled, primarily, by the REDOX conditions of the local geological system.

Reduction may be simply defined as the gain of an electron, while oxidation is the loss of an electron. Often they occur together, "linked", in what are referred to as reduction/oxidation (REDOX) reactions.
Anoxic environments - sulphides

The biggest generator of sulphide minerals are black smokers.

The primary component of such smokers is pyrite (FeS$_2$) which accumulates in stratiform deposits that may result in Mississippi Valley Type economic deposits.
Pyrite, while sometimes occurring in large economic deposits is a common accessory mineral in many igneous, sedimentary and metamorphic rocks.

It has a high metallic lustre, is often yellow/gold in colour, high density (5.1), and a dark streak. Its structure is closely related to NaCl.

Pyrite is a common mineral in fossils, using components in the immediate environment to replace the skeletal structure of dead organisms.
Other Sulphide Minerals

Commonly occurring together are sphalerite (ZnS) and Galena (PbS)

These two minerals are the principle ore minerals for both metals and also form economic deposits of the Mississippi Valley type. The mining operations will also look to recover significant Cu, Ag, Sb and Bi.

Observable properties not dissimilar, but PbS is much heavier!

Zn is the 4th most common metal in use. Pb, perhaps has more former uses than present uses, but is still important.
Sulphates – hydrous or anhydrous

100’s of species known, two are rock-forming, and only four will be commonly found in rock-forming strata.

Anhydrite – CaSO₄
Celestite – SrSO₄
Gypsum – CaSO₄.2H₂O

Evaporite Deposits

Baryte (Barite) – BaSO₄ is a primary constituent of white smokers.