

Chapter 2: Oxide Mineralogy

Abigail Barker

The oxide minerals are minerals where metal cations bond with oxygen instead of silica or sulphur. The most common and important oxide minerals in ore mineralogy are the Fe-Ti-oxides, where Fe and Ti are the main metals. However, Cr and Sn form the oxides chromite and cassiterite respectively, which are important resources for chromium and tin.

The oxides find their primary economic significance in the most important source of iron. Furthermore the oxide chromite is the only commercial source of chromium and cassiterite an important source of tin; they are both used as alloys and tin is used in electronics. Another noteworthy oxide is uraninite, the crucial uranium host, required for nuclear energy production.

The oxide minerals are classified by their metal:oxygen (X:O) ratio, commonly forming X_2O (2:1), X_2O_3 (2:3) and XO (1:1) complexes. Multiple oxide minerals have two metal sites e.g. XY_2O_4 , such as magnetite Fe_3O_4 , where X hosts Fe^{3+} and Y hosts Fe^{3+} and Fe^{2+} . We will focus on the Fe-Ti-oxides and spare a little space for chromite and cassiterite.

Goals:

After reading this chapter you should be able to:

- Describe the mineral structures of common oxide ore minerals.
- Relate oxide minerals to one another by substitutions leading to solid solution.

2.1 Fe-Ti-oxides

The relationships between minerals containing Fe, Ti and oxygen can be represented by the Fe-Ti-O ternary system (Fig 2.01). The apex is TiO_2 (rutile), the left hand corner FeO , i.e. Fe^{2+} and the right hand corner Fe_2O_3 , i.e. Fe^{3+} , hematite. The main Fe-Ti oxides are: 1) **Magnetite Fe_3O_4** forming a **titanomagnetite** series with increasing Ti to the endmember **ulvöspinel Fe_2TiO_4** . 2) **Hematite Fe_2O_3** forming a series with **ilmenite FeTiO_3** as Ti is progressively substituted into the mineral structure.

These two groups reflect the two main mineral structures occurring as Fe-Ti oxides, namely the spinel and hematite groups.

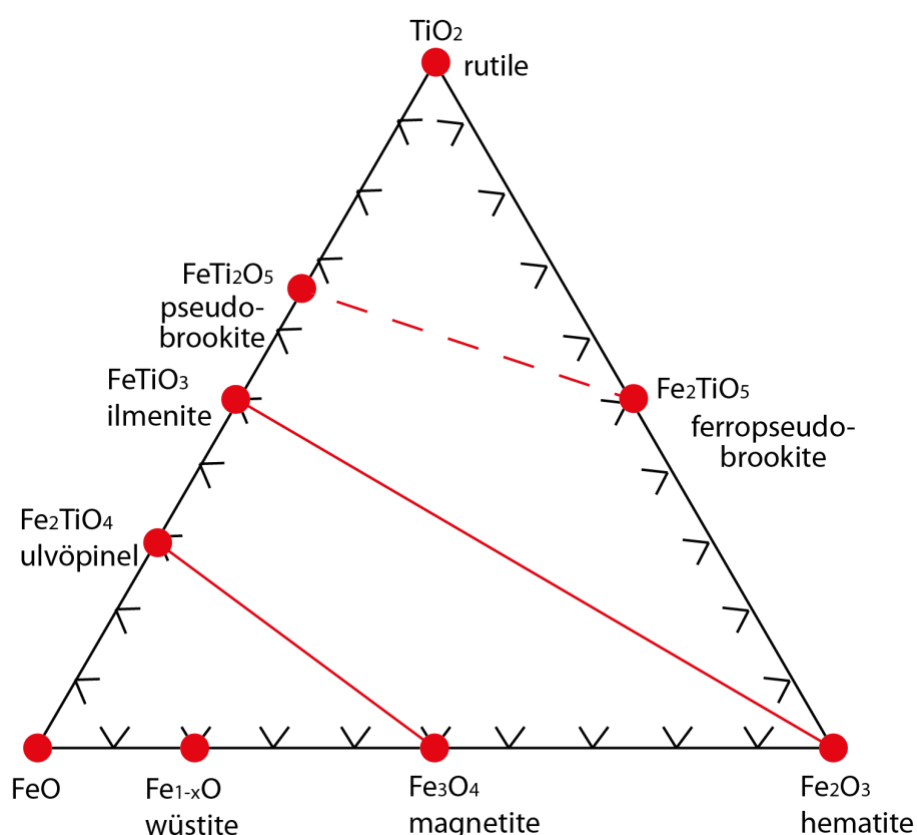


Figure 2.01 Ternary diagram of the Fe-Ti-O system.

The Fe and Ti endmembers are connected by solid solutions, where cation substitution allows mixing between different elements in a mineral site. Such substitution can be homovalent, i.e. the cations have the same valency and therefore comparable size and ionic radius or heterovalent where different valencies are balanced across the mineral structure. Heterovalent substitutions can be between the same element e.g. Fe^{2+} and Fe^{3+} or different elements e.g. Fe^{3+} and Ti^{4+} . A balance is achieved via cation valencies or the occurrence of vacancies, defects or interstitial sites.

The spinel structure

The spinel structure has oxygens arranged in a cubic close packed (ccp) arrangement like the NaCl structure (Box 1.2). The cation sites are denoted X and Y, where X is in tetrahedral co-ordination and Y is in octahedral co-ordination. Order is attained by separating the octahedral and tetrahedral sites into different layers. Typically $\frac{1}{4}$ of the tetrahedral sites (X) and $\frac{1}{2}$ of the octahedral sites (Y) will be filled with anions leading to the formula XY_2O_3 (Fig 2.02).

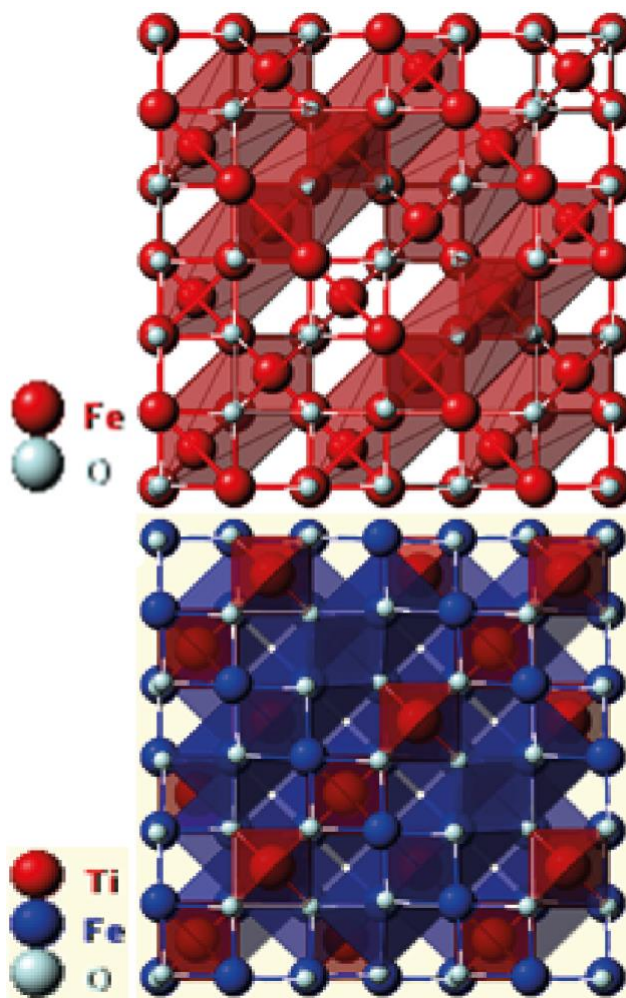


Figure 2.02 Mineral structure of magnetite (top) and ulvöspinel (bottom). Magnetite follows the inverse spinel structure with Fe^{2+} in the octahedral sites and Fe^{3+} shared between octahedral and tetrahedral sites. Ulvöspinel is similar with Ti^{4+} in the octahedral site and Fe^{2+} occurring in both the octahedral and tetrahedral sites. Source: Webmineral

Commonly two different cations are involved representing two different valencies, in a 2:1 ratio. In a normal spinel there will be one type of cation in each site, i.e. 16 matching octahedral cations and 8 of another type in the tetrahedral sites. In “inverse spinels” 8 of the

Interstitial sites
Spaces in the mineral
structure



16 octahedrally co-ordinated cations are different to the other 8 e.g. ulvöspinel Fe_2TiO_4 is an inverse spinel with $X = 8\text{Fe}^{2+}$ and $Y = 8\text{Fe}^{2+}$ and 8Ti^{4+} and similarly **magnetite** Fe_3O_4 has $X = 8\text{Fe}^{3+}$ and $Y = 8\text{Fe}^{2+}$ and 8Fe^{3+} (Fig 2.02). The cations Fe^{2+} , Fe^{3+} and Ti^{4+} in the octahedral site interchange with each other allowing a solid solution series to form between ulvöspinel and magnetite, referred to as the titanomagnetites (Fig 2.01).

Ulvöspinel accommodates Fe^{2+} and Ti^{4+} randomly in the octahedral site. Larger cations such as Ti^{4+} fit into the mineral structure by distorting the structure, this results in greater distances between bonding oxygens, larger tetrahedral and smaller octahedral sites.

Titanomagnetites are rarely pure but commonly substitute Mg^{2+} and Mn^{2+} for Fe^{2+} and Al^{3+} , Cr^{3+} , Mn^{3+} and Ti^{4+} for Fe^{3+} .

The hematite group

The hematite group minerals have the formula M_2O_3 , with **hematite** Fe_2O_3 as the type example. They are constructed around a hexagonal closed packing (hcp) structure of oxygens with cations in octahedral co-ordination (Fig 2.03). This would lead to a 1:1 ratio of M:O if each oxygen in hcp was octahedrally co-ordinating a cation. However only 2/3 of the cation sites are filled meaning that 1/3 of the octahedral sites are empty, with no central cation. This also serves to help balance the charges between Fe^{3+} and O^{2-} . The vacancies mean that each oxygen atom is shared by four octahedra.

Ilmenite FeTiO_3 is a superstructure of hematite forming by solid solution substitution of Fe^{3+} for Ti^{4+} and Fe^{2+} to ultimately produce $\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$ (ilmenite). Fe and Ti are positioned in alternating layers and the anions respond to the charge differences by moving away from the larger Ti^{4+} cations towards the smaller Fe^{2+} cations (Fig 2.03).

Solid solution (SS)

Cation substitution allows mixing between different elements in a mineral site

Magnetite Fe_3O_4

Igneous, sedimentary and metamorphic rocks
BIF, Fe-skarn, IOCG

Hematite Fe_2O_3

Sedimentary ores, BIF
Most important iron ore mineral.

Superstructure

A related mineral structure, where differences in cations, or cation-vacancy ordering modify the mineral

Ilmenite FeTiO_3

Source of Ti in intrusions and placers.

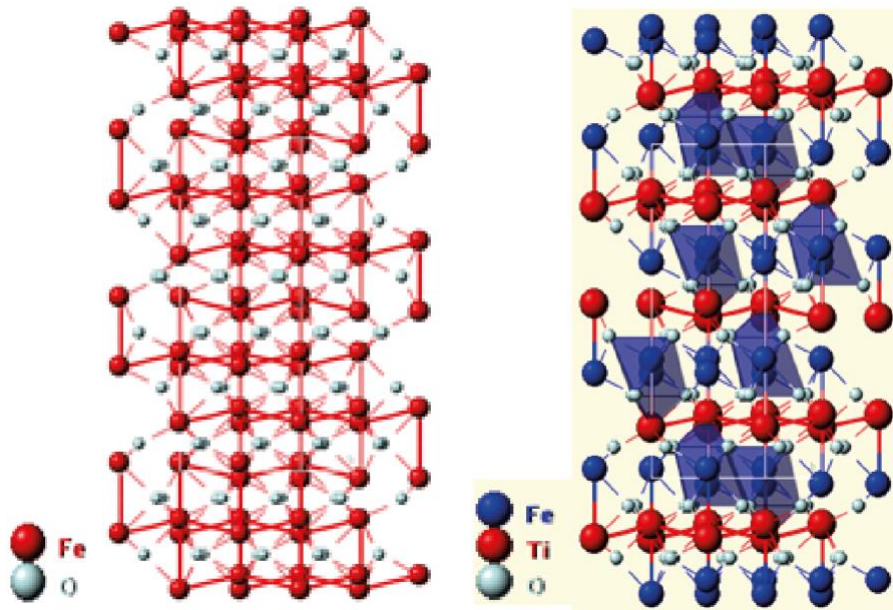


Figure 2.03 Mineral structures for hematite (left) and ilmenite (right). Sources: Webmineral

2.2 Chromite

Chromite, FeCr_2O_4 , follows a normal spinel structure with Fe^{2+} in the tetrahedral sites and Cr^{3+} in the octahedral sites (Fig 2.04). Chromite shares a solid solution with magnesiochromite (MgCr_2O_4) and other common substitutions include Al^{3+} and Fe^{3+} for Cr^{3+} in the octahedral site.

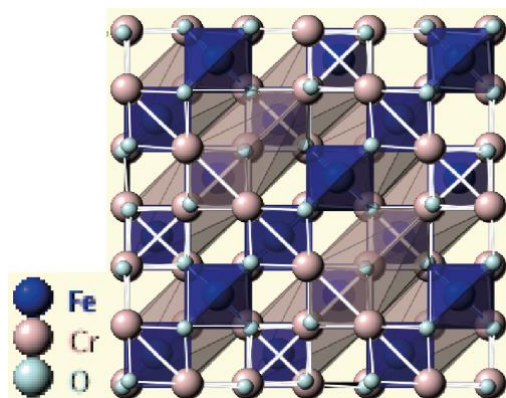


Figure 2.04 The mineral structure of chromite. Source: Webmineral



Chromite FeCr_2O_4
*Ultramafic/mafic
 layered intrusions.*



2.3 Cassiterite

Cassiterite, SnO_2 , is the most important host of tin. It follows the TiO_2 structure of rutile with hexagonal closed packing (hcp) and cations in octahedral co-ordination (Fig 2.05). Only 50% of the octahedral sites are filled by cations and the charge balance causes the oxygens to repel the cations producing a distorted hexagonal close packing (hcp) structure with tetragonal symmetry. The distortion results in undulating layers of oxygens.

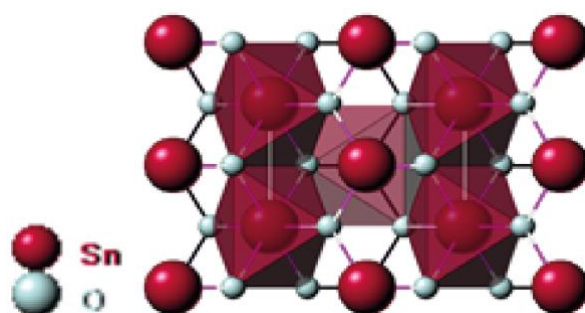


Figure 2.05 The mineral structure of Cassiterite. Source: Webmineral

2.4 Oxygen fugacity

Oxygen fugacity ($f\text{O}_2$) is a variable that describes the expected valence state of iron (Fe^0 , Fe^{2+} , Fe^{3+}) in a silicate or oxide mineral. It is a proxy for oxidation state, as oxidation increases from Fe^0 to Fe^{3+} and oxygen fugacity can be considered to be similar to the activity of oxygen in the system.

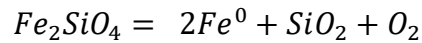
At the lowest oxygen fugacity, iron is found in the native state (Fe^0), typically in the Earth's core or in meteorites. Increasing oxygen fugacity allows iron to be incorporated into silicates like olivine as FeO , i.e. Fe^{2+} . Higher oxygen fugacity leads to the formation of magnetite (Fe_3O_4), with iron coexisting in Fe^{2+} and Fe^{3+} states. At the highest oxygen fugacity iron is found in hematite Fe_2O_3 , with all iron in a Fe^{3+} state (Fig 2.06).

These changes in oxidation state can be represented by mineral reactions referred to as buffers. In order of increasing oxygen fugacity, with the more oxidised species listed on the left:

Cassiterite SnO_2
Porphyry tin deposits.

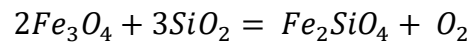


QIF (Quartz-Iron-Fayalite)



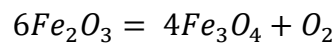
fayalite iron + quartz

FMQ (Fayalite-Magnetite-Quartz)



magnetite + quartz fayalite

MH (Magnetite-Hematite)



hematite magnetite

This sequence of reactions is typically portrayed with fO_2 log units and temperature (Fig 2.06). The buffers have a similar shape and are therefore parallel to each other and offset to higher fO_2 for increasing oxidation.

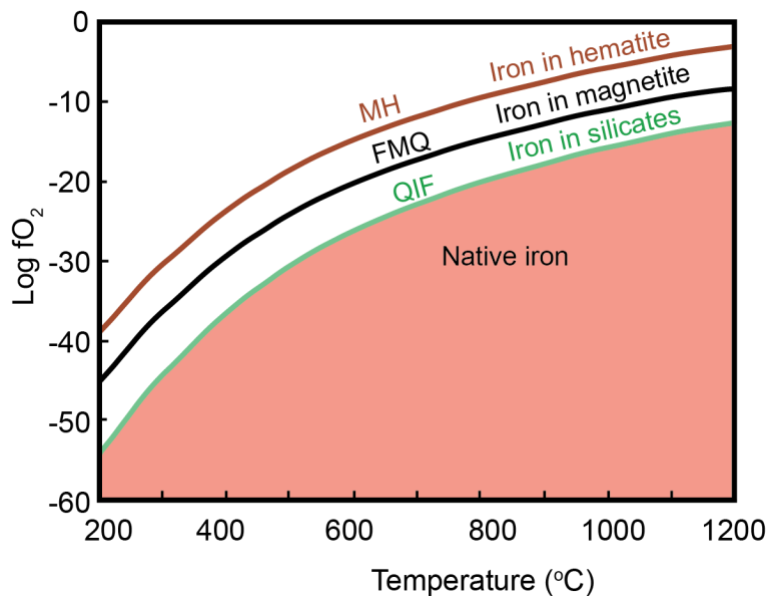


Figure 2.06 Variations in oxygen fugacity with temperature.
Modified after Frost, 1991

Oxygen fugacity is a variable that describes the state iron will occur in, and is therefore associated with mineral stability. The composition of the system also plays a role in mineral stability, for instance Mg and Ti content influences the stability of silicates, magnetite and ilmenite. Substitution of Mg for Fe^{2+} in silicates allows them to remain stable to higher oxygen fugacity, even into the presence of hematite. On the other hand, coupled Ti^{4+} and Fe^{2+} substitution for Fe^{3+} in magnetite and hematite stabilises the oxides titanomagnetite and ilmenite preferentially to the silicates.

Igneous rocks tend to equilibrate within a few log units of the FMQ buffer, with mafic rocks 2 log units below FMQ and felsic rocks extending 1 to 2 log units above FMQ.

Study Questions

- 1) Where do Fe^{2+} , Fe^{3+} and Ti^{4+} sit in the titanomagnetite endmember ulvöspinel?
- 2) Sketch the basic structure of hematite, noting the vacancies. Where does Ti substitution occur to form ilmenite?
- 3) What solid solution does chromite form? What is the substitution involved?
- 4) Indicate on a sketch where the empty octahedral sites, leading to undulating oxygen layers, occur in cassiterite.
- 5) Why are ilmenite and magnetite stable together?

Sources and Further reading

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Webmineral: Credit is due to www.webmineral.com for illustrations of mineral structures.