

Chapter 5: Magmatic processes of ore formation

Abigail Barker

Sulphides and iron oxides are minor constituents of magmatic systems, typically they occur as accessory minerals in silicate dominated systems. However, magmatic sulphide deposits concentrate nickel-copper sulphides, PGE sulphide minerals, and chromite. Additionally magmatic processes potentially play important roles in the formation of iron-apatite ores. Below the processes and conditions of magmatic sulphide and iron oxide ore formation are described.

Goals:

After reading this chapter you should be able to:

- Describe the conditions of Ni-Cu-sulphide and Iron oxide crystallisation.
- Evaluate the conditions that lead to sulphur saturation and sulphide precipitation.
- Describe the processes of immiscibility between FeO, SiO₂ and S liquids and the formation of iron oxide and Ni-Cu-sulphide ores.

5.1 Formation of magmatic Ni-Cu sulphides

Magmatic Ni-Cu sulphide deposits are found in a variety of settings from Continental Flood Basalt Provinces (CFB), to rifts, komatiites, greenstone belts, ultramafic intrusions through to meteorite impact craters (Eckstrand & Hulbert, 2007).

In order to understand the conditions and processes of formation of Ni-Cu sulphide mineralisation, we will review the sulphide mineral assemblages that occur along with experimental phase equilibria.

*Layered intrusion
Bushveld, South Africa
Chromite,
Pyrrhotite, pentlandite,
chalcopyrite, troilite,
magnetite,
PGE*

The majority of Ni-Cu sulphide deposits irrespective of setting exhibit pyrrhotite and pentlandites, with common appearance of chalcopyrite, pyrite, bornite, and occasional cubanite and mooihoeite. Magnetite and chromite can also be found co-existing with these sulphides, plus arsenic bearing sulphides as well as rare PGE minerals (Eckstrand & Hulbert, 2007).

5.2 Insights from sulphide phase equilibria

Fe-S phase equilibria shows that pyrrhotite crystallises $\leq 1192^\circ\text{C}$, extending into monosulphide solid solution (mss) in the Ni-S system (Figures 5.01 and 5.02; Fleet, 2006). At comparable temperatures in the Ni-S system in order of increasing sulphur content pentlandite ($\text{Ni}_{3-x}\text{S}_2$), Ni_{1-x}S (mss) and vaesite (NiS_2) occur (Figure 5.02; Sack & Ebel, 2006). Pentlandite begins to crystallise at 1022°C , and at $>850^\circ\text{C}$ has Ni contents of 47-60 at%, extending to Ni-rich contents (<100 at%) as temperature decreases to 725°C (Figure 5.02).

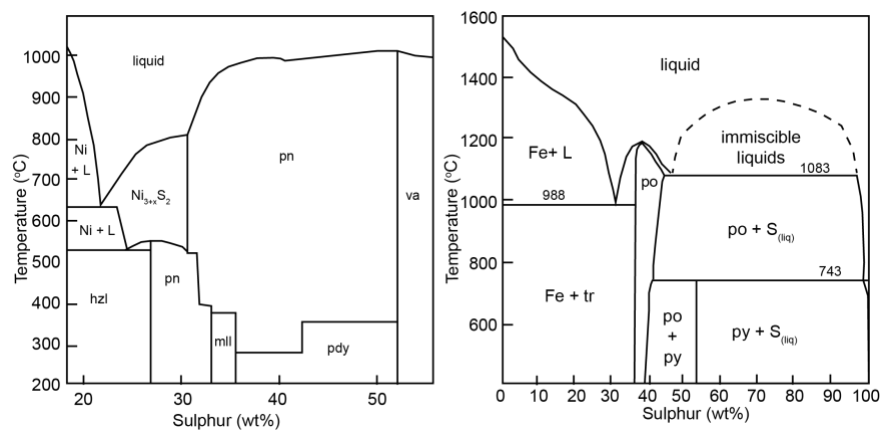


Figure 5.01 Ni-S and Fe-S phase diagrams at temperatures of 200-1100°C and 400-1600°C respectively. Modified from Fleet (2006).

The Fe_{1-x}S deficiency of pyrrhotite, can vary between $x=0.00$ and 0.19 , with pure stoichiometric pyrrhotite (troilite) occurring with iron below 988°C and sulphur and iron liquids $>988^\circ\text{C}$ (Fleet, 2006). The extent of the deficiency is influenced by temperature and sulphur fugacity, decreasing deficiency occurs at higher temperature, or as sulphur fugacity increases; one log unit is accompanied by a change in deficiency of approximately 0.02 at% (Figure 5.03; Fleet, 2006).

*Flying Fox deposit
Western Australia
Komatiite hosted
pyrrhotite, pentlandite,
magnetite, pyrite, chalcopyrite*

hzl – hazelwoodite
mll – millerite
L – liquid
mss – monosulphide solid solution
pdy - polydymite
pn – pentlandite
po – pyrrhotite
py – pyrite
tr – troilite
va - vaesite

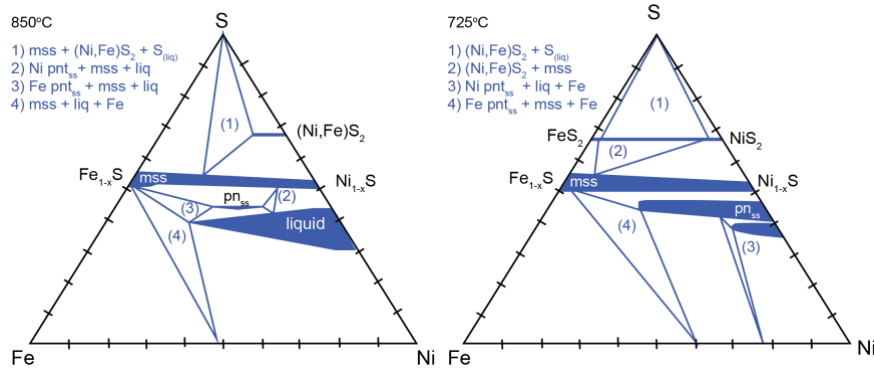
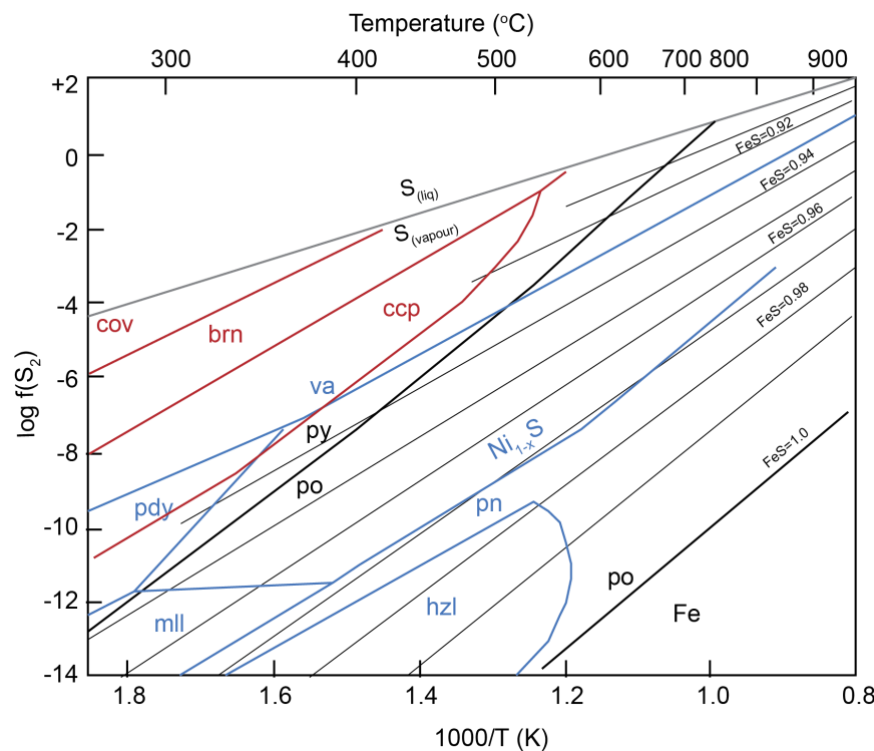


Figure 5.02 Ternary phase diagrams for the Ni-Fe-S system at 850°C and 725°C. Modified from Fleet (2006).

liq - liquid
 pn/pnt - pentlandite
 ss – solid solution

The vaesite field expands from 10-19 at% to >70 at% Ni as temperature decreases from 850 to 725°C forming a solid solution with pyrite below 742°C (Figure 5.02). In the Cu-S part of the system only chalcocite and bornite solid solution are present at high temperatures (ca. 1000°C), in addition to the Fe and Ni sulphides (Figure 5.04).



brn – bornite
 ccp – chalcopyrite
 cov - covelite

Fig 5.03 Variations in sulphur fugacity with temperature in sulphide systems. Modified from Fleet (2006).

At lower temperatures pyrite forms (<742°C), and by 700°C intermediate solid solution (iss) joins the phase assemblage, with chalcopyrite appearing at 557°C and at even lower temperatures cubanite and mooihokite can occur (Figures 3.01, 3.02, 3.04). The occurrence of pyrite, chalcopyrite, bornite and cubanite are all

controlled by the sulphur fugacity of the system in addition to the composition (Figure 5.03). Increasing fugacity stabilises chalcopyrite, bornite and pyrite at the expense of pyrrhotite and cubanite. Magnetite occurrence with pyrrhotite is possible at very low sulphur fugacities.

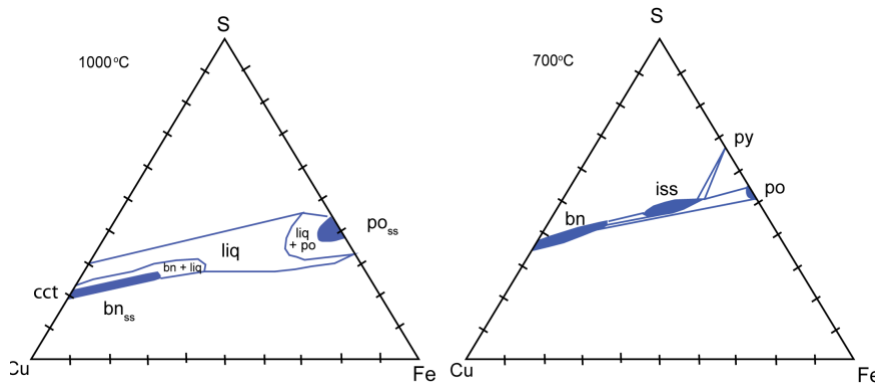


Figure 5.04 Cu-Fe-S phase diagrams at 1000°C and 700°C. Modified from Fleet (2006).

These phase relations suggest that the high temperature phases pyrrhotite, pentlandite, mss and vaesite are the primary magmatic mineral assemblages. The appearance of pyrite, chalcopyrite, bornite, then cubanite and mooihoekite at lower temperatures suggest exsolution and diffusion processes can occur as the system cools slowly allowing equilibration at lower temperature and also potentially fluid influenced alteration processes.

An example of a komatiite hosted deposit is the Flying Fox Ni-Cu-PGE deposit in Western Australia. The sulphide assemblage is pyrrhotite, pentlandite, pyrite, chalcopyrite and magnetite (Collins et al., 2012). The samples cluster at 30-35 at% Ni (Figure 5.05A) and extend from pyrrhotite-pentlandite (mss) up to pyrite. The trend to pyrite displays increasing iron and sulphur suggesting that pyrite formed due to post-magmatic addition of sulphur (Figure 5.05B; Collins et al., 2012).

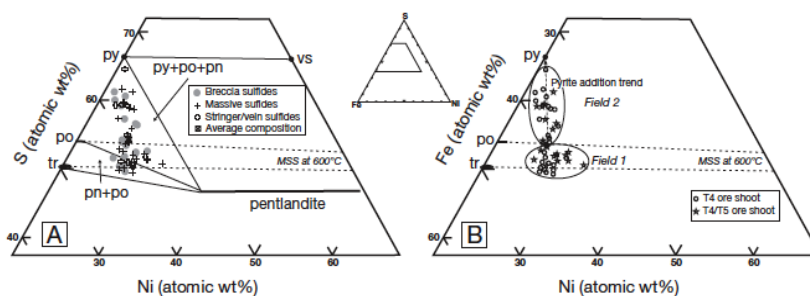


Figure 5.05 Ni-Fe-S systematics of the Flying Fox Deposit (Collins et al., 2012).

cct – chalcocite
iss – intermediate solid solution

*Flying Fox deposit
Western Australia
Komatiite hosted
pyrrhotite, pentlandite,
magnetite, pyrite, chalcopyrite*

5.3 The behaviour of sulphur in magma

Magmas are associated with volatiles, of which sulphur forms a significant proportion. Volatile sulphur is most likely dissolved in silicate melt as S_2 (Philpott, 1990). Solubility refers to the amount of a substance that can be dissolved in a liquid, in this case we are interested in how much S_2 can be hosted by a silicate melt. Once solubility is reached excess sulphur will begin to crystallise as sulphides. The solubility of sulphur is a function of the oxygen and sulphur fugacities, temperature, as well as the iron and silica content of the melt.

The sulphur dissolved in the magma will under some circumstances form a sulphide melt. Sulphur immiscibility occurs when the dissolved sulphur separates from the silicate melt; like mayonaise, where droplets of oil are suspended in egg white. Under conditions of sulphur immiscibility the sulphur will segregate from the silicate melt into droplets of sulphide liquid (Figure 5.06, Philpott, 1990).

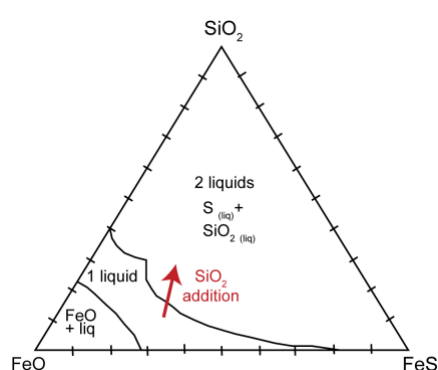


Figure 5.06 $FeO-FeS-SiO_2$ phase diagram showing the single phase field and two phase fields where silicate and sulphide liquids separate on addition of silica. Modified from Philpott, (1990).

Initially sulphur solubility decreases with increasing oxygen fugacity, such that a primitive magma will have decreasing sulphur solubility as it differentiates. In a system with higher oxygen fugacity such as an andesitic magma the sulphur solubility will increase as oxygen fugacity increases (Philpott, 1990).

Sulphur solubility is however also influenced by FeO content, such that increasing oxygen fugacity will decrease the FeS activity of the melt and therefore the sulphur solubility. Additionally crystallisation of iron oxides or iron silicates such as olivine (fayalite), will decrease the activity of FeO and the sulphur solubility of the magma (Philpott, 1990). Addition of silica will also decrease the sulphur solubility by changing the ratio of octahedral and tetrahedral sites in the magma (Figure 5.06; Lightfoot and Hawkesworth, 1997).

Detailed phase petrology shows that there is an important two liquid field in the FeO-FeS-SiO₂ system. When a melt meets this field it will separate into two liquids thus it is called immiscible (Figure 5.06). For example a melt with composition 65% FeO and 10% SiO₂ will crystallise olivine ((Fe, Mg)SiO₄) and the melt composition will move towards the SiO₂ apex until the melt composition meets the two liquid field. At this point the sulphide melt will separate from the silicate melt (Philpott, 1990). Once formed, the two liquids will develop separately, and the sulphide liquid will scavenge Ni, Cu and PGE from the silicate melts, due to high partition co-efficients of these elements in sulphide melt. Nickel contents of sulphide melts will depend on how much silicate crystallisation has already extracted Ni into olivine. In more oxidising conditions applicable to ultramafic and mafic magmas magnetite and pyrrhotite are crystallising phases.

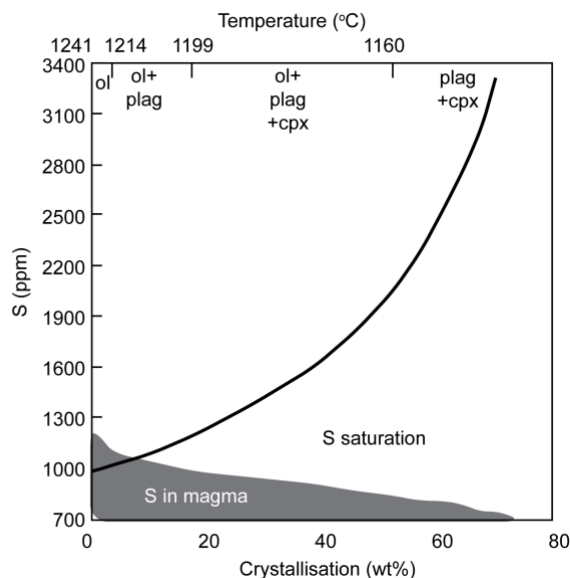


Figure 5.07 Solubility of sulphur with sulphur composition, temperature and degree of crystallisation. Fractional crystallisation decreases sulphur solubility and promotes saturation of the melt in sulphur leading to sulphide liquid immiscibility and sulphide precipitation. Source: Li and Ripley (2005).

The process of crystallisation serves to add silica, as well as increase the FeO content of the system, decreasing the sulphur solubility (Philpott, 1990; Lightfoot and Hawkesworth, 1997). Therefore fractional crystallisation helps to decrease the sulphur solubility and promote sulphide immiscibility and sulphide crystallisation (Figure 5.07; Li and Ripley, 2005). Moreover adding silica in the form of assimilation of silica rich crustal material will also decrease the sulphur solubility and cause sulphur immiscibility, moving the composition from the single phase field across the immiscibility gap

into the two phase field (Figure 5.06; Lightfoot and Hawkesworth, 1997).

It is thought that the immiscible sulphide melts in a silicate magma can continue to be supplied by as new magmas recharge and equilibrate with the two phase silicate and sulphide magmas (Lightfoot & Hawkesworth, 1997).

hem - hematite
ilm - ilmenite
mgt - magnetite
Ti mgt - titanomagnetite
usp - ulvöspinel
ss – solid solution

5.4 Iron oxide magmatic deposits

In magmatic systems iron oxides naturally occur in small quantities, for example in mafic magmas a few percent of ilmenite and titanomagnetite can crystallise. However, iron oxide often with apatite can form large high grade deposits, where the role of immiscible iron oxide melts are potentially significant.

5.5 Insights from iron oxide phase equilibria

Magmatic temperatures of 800-1200°C have relatively low oxygen fugacity conditions starting at FMQ conditions and increasing oxygen fugacity with differentiation (Figure 2.6). Typical iron oxide assemblages are ilmenite and titanomagnetite, where ilmenite-hematite and ulvöspinel-magnetite solid solutions occur above 800°C and 600°C respectively (Figure 5.08; Lindsley, 1991). At compositions between the solid solutions, both solid solutions can be present and thus co-existing ilmenite-magnetite pairs can crystallise (Figure 5.08). The compositions of co-existing ilmenite-magnetite pairs are controlled by the oxygen fugacity and temperature (Figure 5.09). Typically a high X_{ilm} (proxy for Ti content in ilmenite-hematite solid solution), composition is paired with a lower X_{Usp} (proxy for Ti content in titanomagnetite solid solution), e.g. X_{ilm} 0.94 and X_{Usp} 0.80 at $-15 \log fO_2$ and 900°C (Lindsley, 1991). With decreasing temperature and increasing fO_2 the compositions both become more iron rich. For instance, at increasing fO_2 from -15 to $-11 \log$ units and 950-900°C the X_{ilm} changes from 0.94 to 0.80 and X_{Usp} from 0.80 to 0.40 (Figure 5.09).

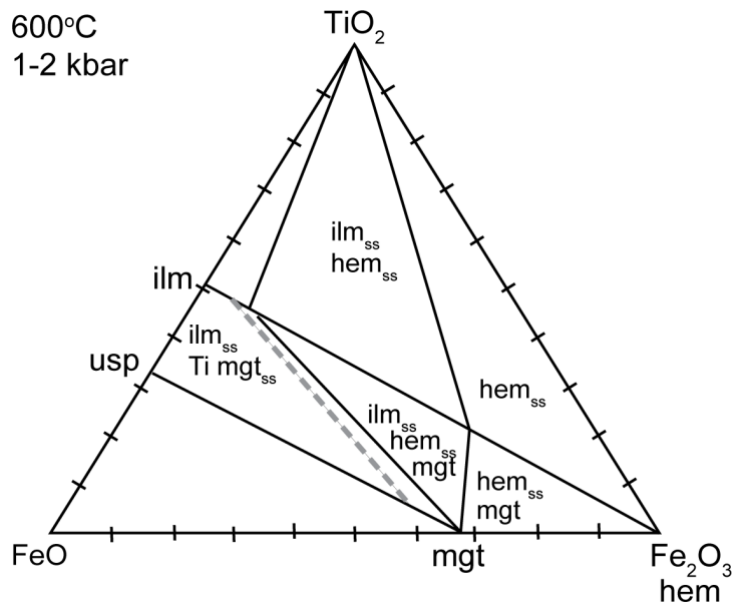


Figure 5.08 FeO-Fe₂O₃-TiO₂ phase diagram at 600°C. Source Lindsley (1991).

Likewise at nearly uniform fO_2 of -14 to -15 log units with a temperature change from 900°C to 800°C X_{ilm} changes from 0.94 to 0.90 and X_{Usp} from 0.80 to 0.30 (Lindsley, 1991).

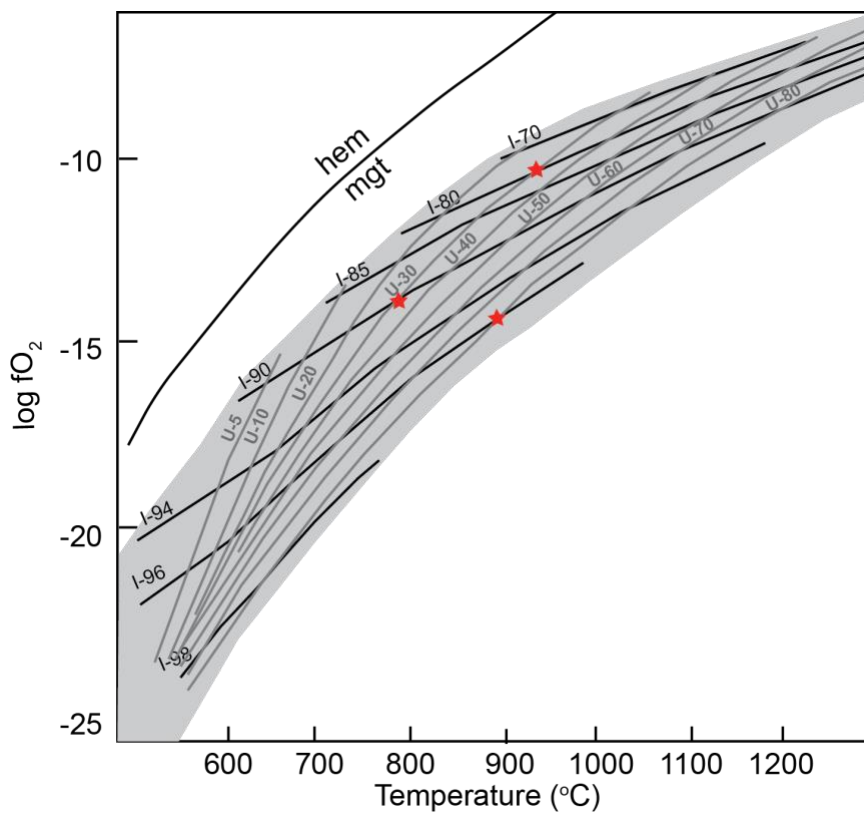


Figure 5.09 Variations in composition of iron oxide pairs with oxygen fugacity and temperature. Source Lindsley (1991).

At lower temperatures as the magmatic system cools, immiscibility gaps appear producing two phase systems, and associated exsolution. Figure 5.10 shows the titanomagnetite solid solution, and in red a bulk composition of 0.45 X_{Ti} which would exsolve ulvöspinel ($X_{Ti}=0.82$ at 500°C) from magnetite ($X_{Ti}=0.45$). Depicted in blue is a bulk composition of 0.9 X_{Ti} , which would exsolve magnetite ($X_{Ti}=0.25$ at 320°C) from ulvöspinel ($X_{Ti}=0.90$). For example at the Khibiny pluton, Russia, titanomagnetite has ulvöspinel exsolution lamellae. The titanomagnetites have compositions of $X_{Ti}=0.5-0.8$ and ulvöspinel exsolution lamellae have compositions of $X_{Ti}=0.0-0.5$ (Ivanyuk et al., 2012).

Similar processes form exsolution of ilmenite in magnetite and vice versa. Below 800°C the ilmenite-hematite solid solution splits into two fields one each for ilmenite solid solution and hematite solid solution, therefore the bulk composition of the system then controls the occurrence of ilmenite and/or hematite.

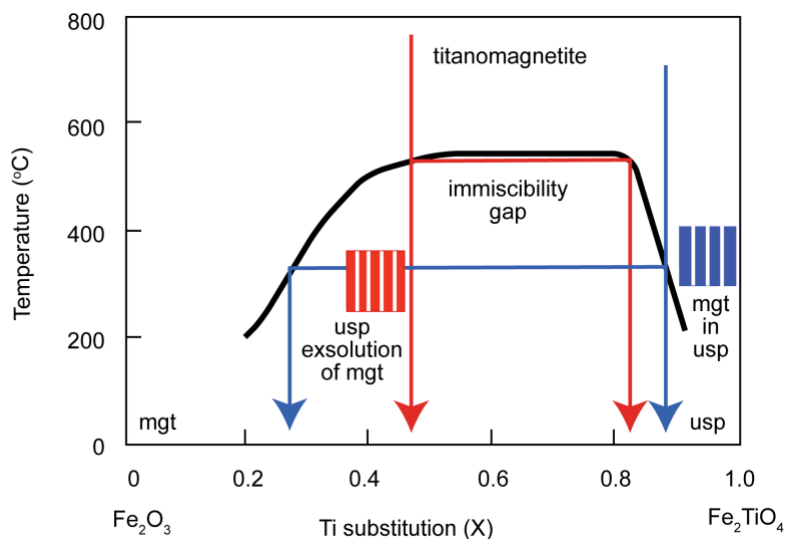


Figure 5.10 Binary phase diagram for titanomagnetite solid solution. At approximately 550°C a miscibility gap forms and titanomagnetite separates into two phases; magnetite and ulvöspinel. The miscibility gap leads to exsolution of one phase from the other.

5.6 Formation of iron oxide magma

Little is known about the immiscibility of iron oxide melts in silicate melt systems. But presumably solubility and immiscibility work similarly to sulphide-silicate systems, with perhaps rarer occurrence of iron oxide immiscibility but when it does occur it forms greater amounts of iron oxide reflecting the higher iron content available in silicate melts.

Recent work employing oxygen isotopes on iron-apatite ores, suggests that magmatic processes are dominant, with minor roles envisaged for magmatic fluids and hydrothermal processes (Jonsson et al., 2013).

Grängesberg, Sweden
Iron-apatite deposit
Magnetite, apatite, minor hematite

Study Questions

- 1) Analyse the evolution of a liquid in the Fe-S binary phase system with 70 at% S. What primary minerals do you expect? What minerals will form as the system cools? What processes are reflected during cooling of the system?
- 2) Given an assemblage of pyrrhotite-pendlandite-chalcopyrite-pyrite, evaluate the conditions of formation and evolution of the assemblage.
- 3) Describe the processes that modify the sulphur saturation and sulphur concentration of a magmatic system. Evaluate the conditions under which you expect sulphide crystallisation?

Sources and Further reading

Collins et al., (2012). Postmagmatic variability in ore composition and mineralogy in the T4 and T5 ore shoot at the high-grade Flying Fox Ni-Cu-PGE deposit, Yilgarn craton, Western Australia. *Economic geology* 107, 859-879.

Eckstrand, O.R., and Hulbert, L.J., (2007). Magmatic Nickel-Copper-Platinum Group Element deposits. in Goodfellow, W.D., ed., *Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods*: Geological Association of Canada, Mineral Deposits Division, Special Publication No. 5, p. 205-222.

Fleet, M.E., (2006) Phase Equilibria at High Temperatures In: Editor Vaughan, D.J., *Sulfide mineralogy and geochemistry MSA Reviews in Mineralogy Volume 61*, p 365-420, ISBN 0-939950-73-1

Lindsley D.H., (1991) Experimental Studies of Oxide Minerals In: editor: Lindsley D.H., Oxide Minerals: petrologic and magnetic significance, MSA Reviews in Mineralogy Volume 25, p 69-106 ISBN 0-939950-03-0.

Ivanyuk et al., (2012). Ulvospinel from xenoliths of contact-altered volcanic and volcanosedimentary rocks in nepheline syenites of the Khibiny and Lovozero Plutons. *Geology of Ore Deposits*, 2012, Vol. 54, No. 7, pp. 575–579.

Jonsson et al., (2013). Magmatic origin of giant ‘Kiruan-type’ apatite-iron-oxide ores in Central Sweden. *Scientific Reports* 3: 1644 DOI: 10.1038/srep01644.

Lundh, J., (2014) A litho-geochemical study of Northern Sweden and the Kiruna and Malmberget iron-apatite ore deposits. MSc thesis, Uppsala University ISSN 1650-6553 Nr. 289.
<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-227039>

Li, C., Ripley, E.M., (2005). Empirical equations to predict the sulfur content of mafic magmas at sulfide saturation and application to magmatic sulfide deposits. *Mineralium Deposita* 40: 218-230, doi: 10.1007/s00126-005-0478-8.

Lightfoot, P.C., Hawkesworth, C.J., (1997). Flood basalts and magmatic Ni, Cu, PGE sulphide mineralisation: Comparative geochemistry of the Noril'sk (Siberian Traps) and West Greenland sequences. In: eds Mahoney, J.J., Collin, M.F., Large Igneous Provinces, Continental, oceanic and planetary flood volcanism. *Geophysical Monography* 100. American Geophysical Union.

Philpott, A.R., (1990). Principles of Igneous and Metamorphic Petrology. Prentice Hall.

Sack, R.O., and Ebel, D.S., (2006). Thermochemistry of Sulfide Mineral Solutions In: Editor Vaughan, D.J., Sulfide mineralogy and geochemistry MSA Reviews in Mineralogy Volume 61, p 365-420, ISBN 0-939950-73-1

Weis, F., (2011). Oxygen Isotope Signatures of the Apatite-Iron Oxide Ore at Grängesberg. BSc thesis, Uppsala University.
<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-173031>

Weis, F., (2013). Oxygen and iron isotope systematics of the Grängesberg Mining District (GMD), Central Sweden. MSc thesis, Uppsala University, ISSN 1650-6553 Nr. 251.

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-192216>

Tulane: review of phase equilibria

<http://www.tulane.edu/~sanelson/eens212/#Lecture%20Notes>