

4.0 GEOCHEMISTRY OF IRON-TITANIUM OXIDES

This chapter presents a brief introduction to the geochemistry of the iron-titanium oxides. The scope is strictly limited to those aspects that directly affect the sample preparation procedures used in this study. Readers wishing a detailed introduction are referred to Nagata [1961], Stacey and Banerjee [1974], O'Reilly [1984] and Lindsley [1991].

4.1 Titanomagnetite geochemistry

4.1.1 FeO - Fe₂O₃ - TiO₂ phase diagram

The majority of the minerals of interest in rock magnetism are oxides of iron and titanium [Nagata, 1961]. The iron-titanium oxides of interest form a ternary system with FeO, Fe₂O₃, and TiO₂ as the end-members (figure 2). The most interesting minerals in this system are wüstite (Fe_{1-x}O), magnetite (Fe₃O₄), hematite (Fe₂O₃), maghemite (Fe₂O₃), pseudobrookite (Fe₂TiO₅), ferropseudobrookite (FeTi₂O₅), ilmenite (FeTiO₃), and ulvöspinel (Fe₂TiO₄). There are three fundamental solid-solution series in this system: the magnetite-ulvöspinel series (titanomagnetites) with an inverse spinel structure, the rhombohedral hematite-ilmenite series (titanohematites), and the orthorhombic pseudobrookite-ferropseudobrookite series. Of these, the titanomagnetites are the most important, particularly in igneous rocks [Nagata, 1961].

Titanomagnetites can be oxidized or reduced by a variety of processes (figure 3). Most naturally-occurring titanomagnetites are slightly oxidized towards the titanohematite line. The oxidation state affects the magnetic properties of titanomagnetite (figures 3 and 4), so it is important to keep chemical changes from occurring during and between magnetic experiments.

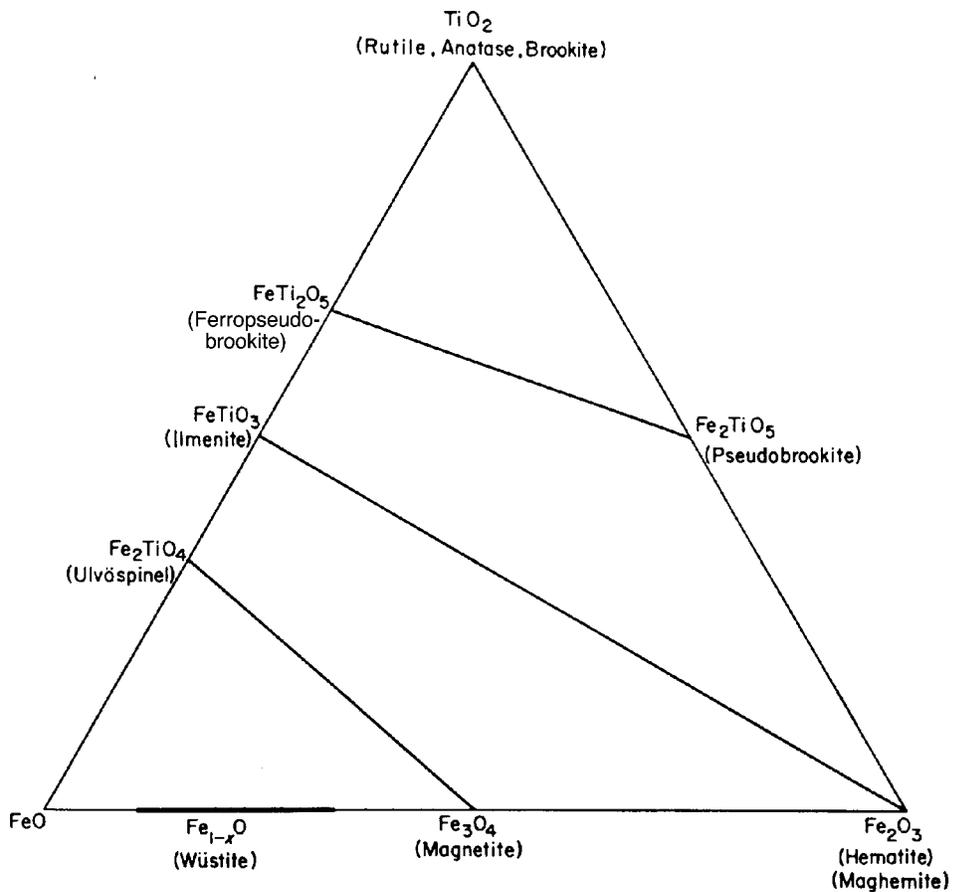


FIG. 1. Phases in the system FeO-Fe₂O₃-TiO₂, showing the major solid solution series magnetite-ulvöspinel, hematite-ilmenite, and pseudobrookite-FeTi₂O₅. Mole per cent.

Figure 2 The FeO-Fe₂O₃-TiO₂ ternary system. Adapted from Buddington and Lindsley [1964].

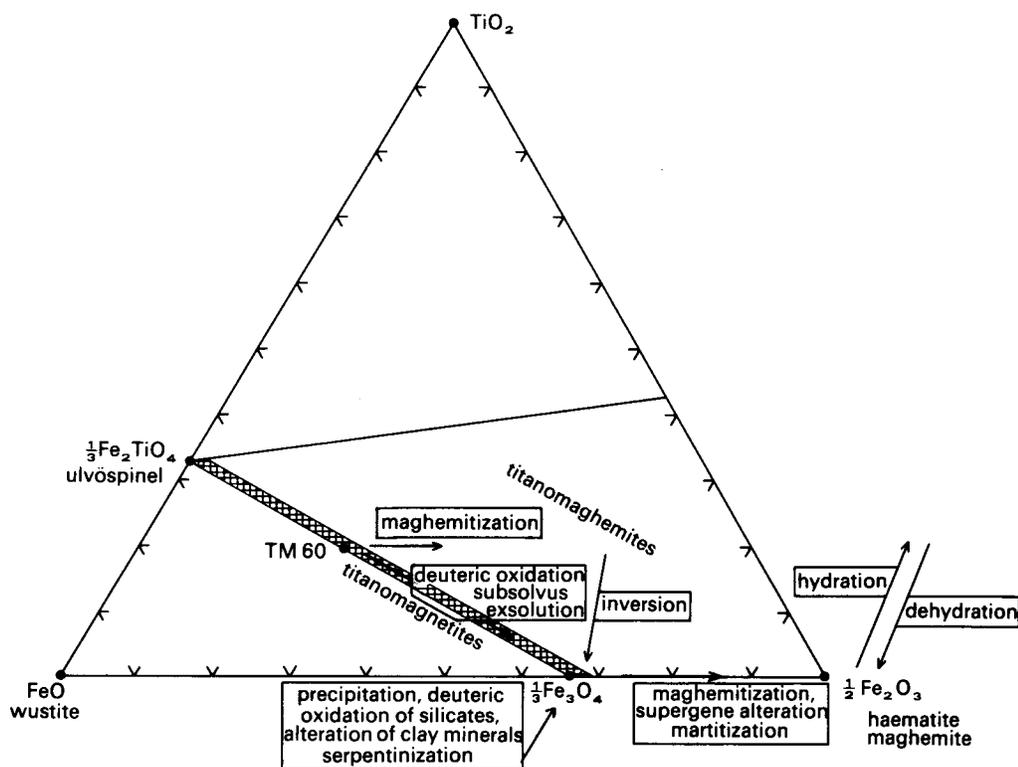


Figure 2.1 The FeO-TiO₂-Fe₂O₃ ternary diagram of rock magnetism. Points in the triangle correspond to oxide compounds or mixtures of compounds containing Fe²⁺, Fe³⁺ and Ti⁴⁺. The point TM60 represents the idealized titanomagnetite with composition Fe_{2.4}Ti_{0.6}O₄ and on the diagram are indicated some of the paths which may be followed by the magnetic mineral fraction of crustal rocks in the course of geological history.

Figure 3 Alteration in the FeO-Fe₂O₃-TiO₂ ternary system. From O'Reilly [1984].

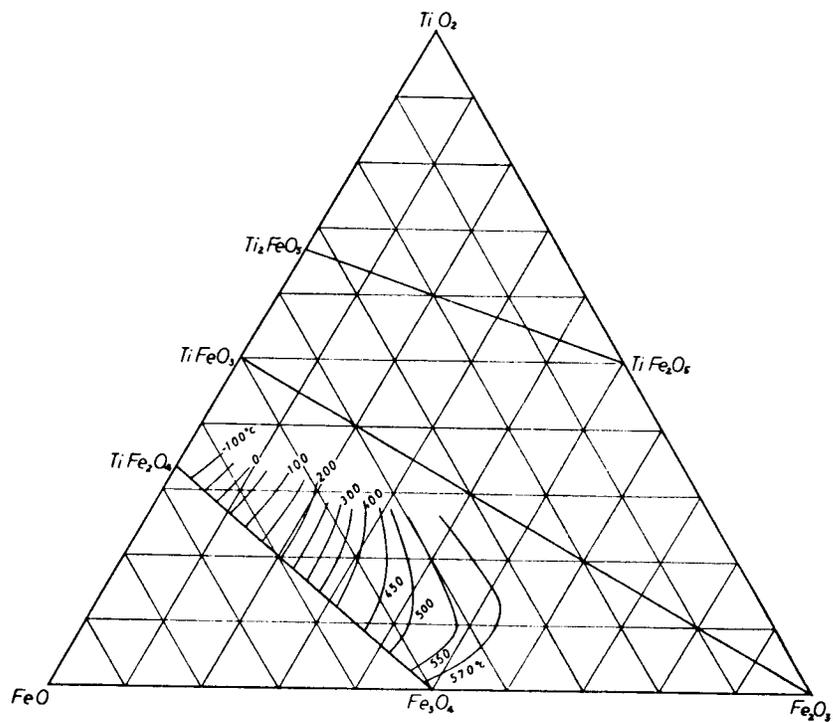


Fig. 7 Lines of equal Curie temperature of the generalized titanomagnetite in a $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system.

Figure 4 Effect of oxidation on titanomagnetite Curie temperature [Akimoto, 1957].

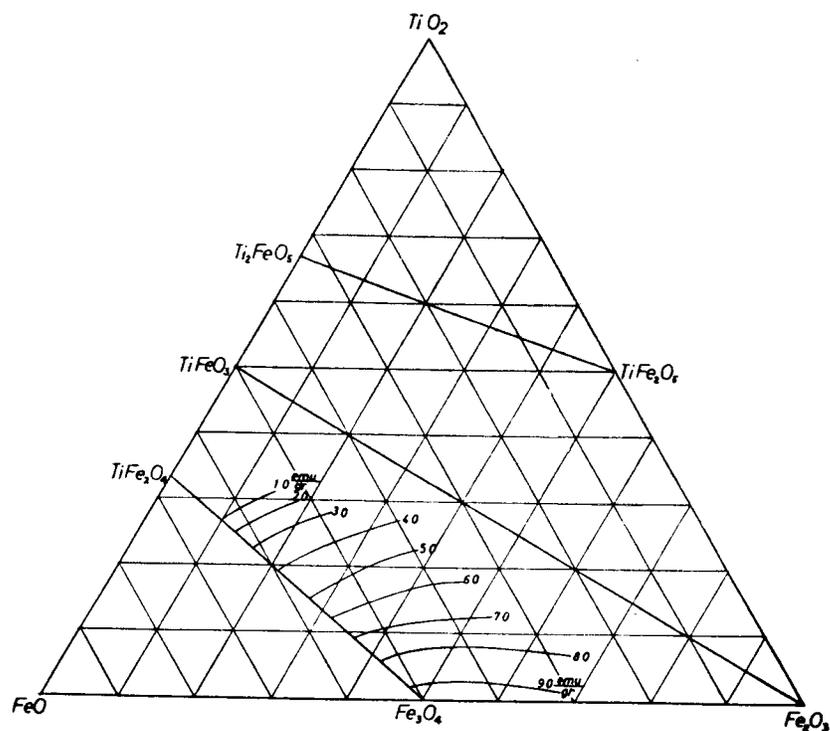


Fig. 8 Lines of equal saturation moment at the room temperature of the generalized titanomagnetite in a $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ system.

Figure 5 Effect of oxidation on titanomagnetite saturation moment [Akimoto, 1957].

The Curie temperature of the titanomagnetites decreases as the ulvöspinel content increases (figure 6). This suggests that working with an intermediate titanomagnetite might be preferred, because the lower temperatures involved would be less likely to cause chemical alterations in the sample. For example, $\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$ has a Curie temperature of only about 200 °C. The saturation moment also decrease as the Ti content increases (figure 7). A lower saturation moment is desirable because would reduce the interaction between grains.

Unfortunately, there are difficulties with this approach. Magnetite and ulvöspinel do not form a solid solution at room temperature. Upon cooling, intermediate titanomagnetites exsolve into two spinel phases. Since the ulvöspinel content affects the magnetic properties, partial exsolution could introduce uncontrolled variations in the samples. The easiest means to avoid these changes is to use magnetite instead of titanomagnetite for the experiments. Of course, magnetite itself is an important magnetic mineral, so the results of the experiments should be widely applicable.

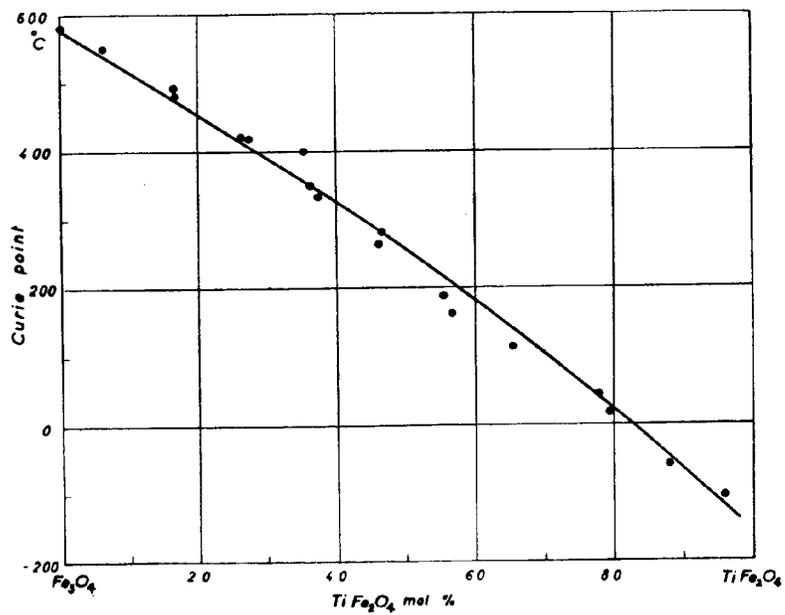


Figure 6 Effect of ulvöspinel content on titanomagnetite Curie temperatures [Akimoto, 1957].

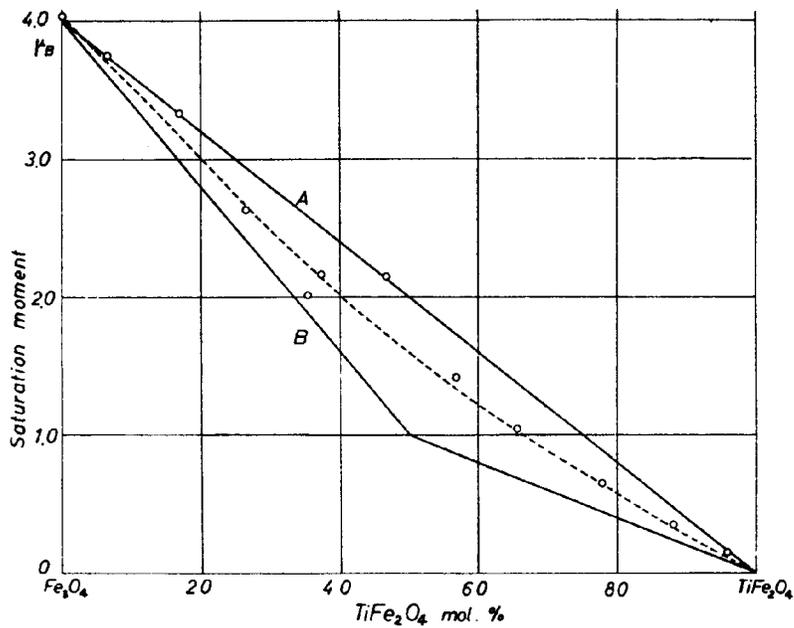


Fig. 5 Estimated saturation moment at 0°K vs. composition for $TiFe_2O_4-Fe_3O_4$ solid solution series.
 A: theoretical value for Akimoto's model.
 B: theoretical value for Néel-Chevallier's model.

Figure 7 Effect of ulvöspinel content on titanomagnetite saturation moment [Akimoto, 1957].

4.1.2 Stability fields

Titanomagnetites are not in chemical equilibrium with air at room temperature or at temperatures of interest in this work (figure 8), so some form of oxygen fugacity control is necessary for their synthesis and study. The equilibrium ferric/ferrous ratio in silicate melts is controlled by temperature, oxygen fugacity, and composition, particularly alkali content [Carmichael and Nichols, 1967]. Unfortunately, no data exists for the melts used in this work [Worm and Markert, 1987]. Spencer and Lindsley [1981] provide a temperature-fugacity diagram for coexisting titanomagnetite-titanohematite pairs (figure 9) that, although not strictly applicable to this work, has proven adequate for selecting oxygen fugacities to synthesize titanomagnetites. Dr. Worm [personal communication] has found the same diagram useful for synthesizing titanomagnetites as well. Figures 9 and 10 shows the equilibrium oxygen isobars for the FeO - Fe₂O₃ - TiO₂ system at 1200 °C, and may prove useful for synthesizing titanomagnetites in future studies.

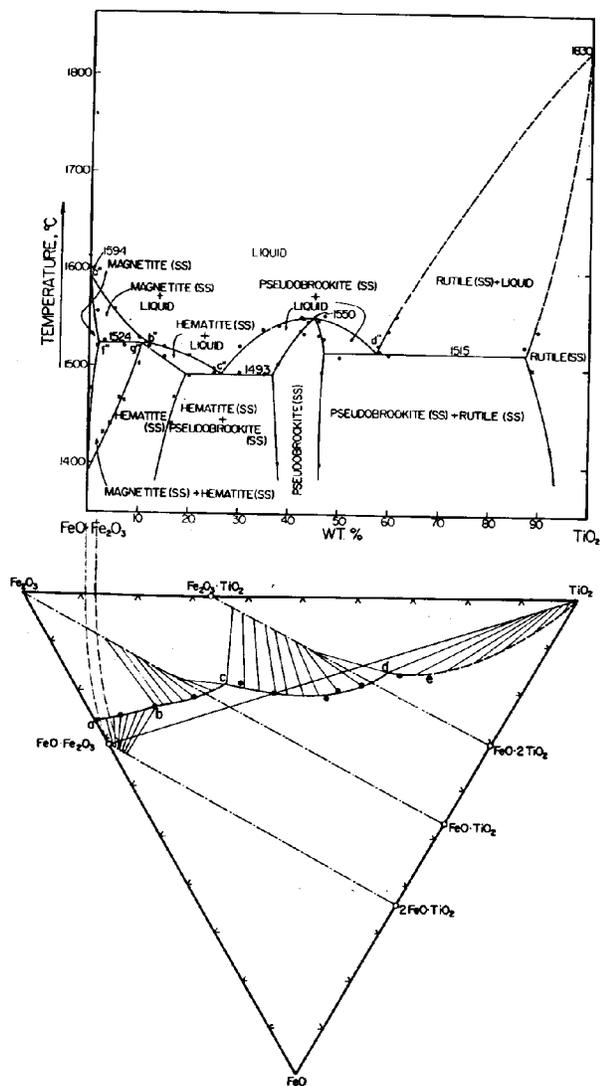


Figure 8 Phase relations for the FeO - Fe₂O₃ -TiO₂ system in air.
[MacChesney and Muan, 1959].

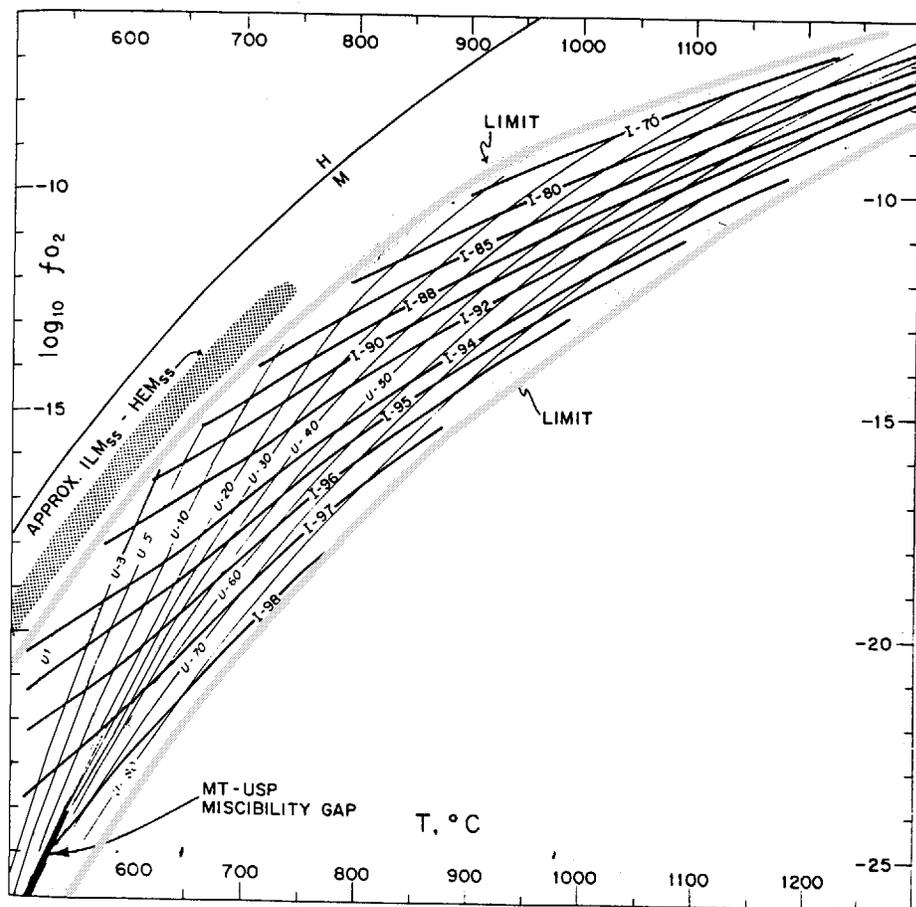


Fig. 4. T - f_{O_2} grid for coexisting Mt_{ss} - Ilm_{ss} pairs, based on the solution model. The stippled fields are our estimates of the limits of the model. The Mt - Usp miscibility gap is that calculated by the model for the three-phase assemblage $Mt_{ss} + Usp_{ss} + Ilm_{ss}$. The Ilm - Hem miscibility gap (labeled "Approx. ILM_{ss} - HEM_{ss} ") is our best guess from experimental data—it is *not* calculated.

Figure 9 T - f_{O_2} for coexisting magnetite-ilmenite solid solution pairs. [Spencer and Lindsley, 1981]

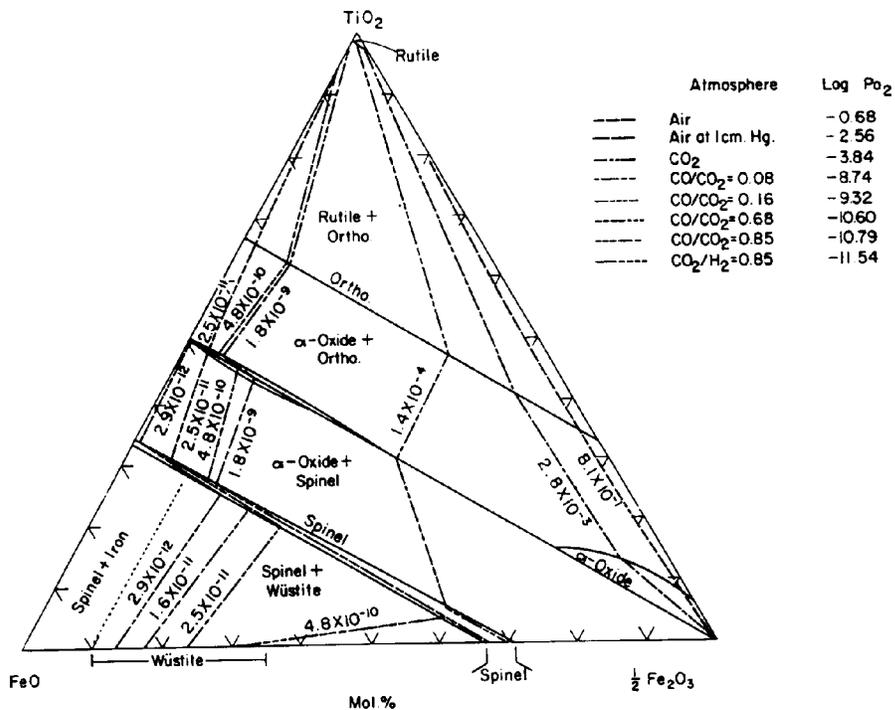


FIG. 91.—System FeO-Fe₂O₃-TiO₂ at 1200°C and showing oxygen isobars. Ortho. = orthorhombic oxide. A. H. Webster and N. F. H. Bright, *J. Am. Ceram. Soc.*, **44** [3] 115 (1961).

Figure 10 Oxygen isobars in the FeO - Fe₂O₃ -TiO₂ system. [Levin, et al, 1964]

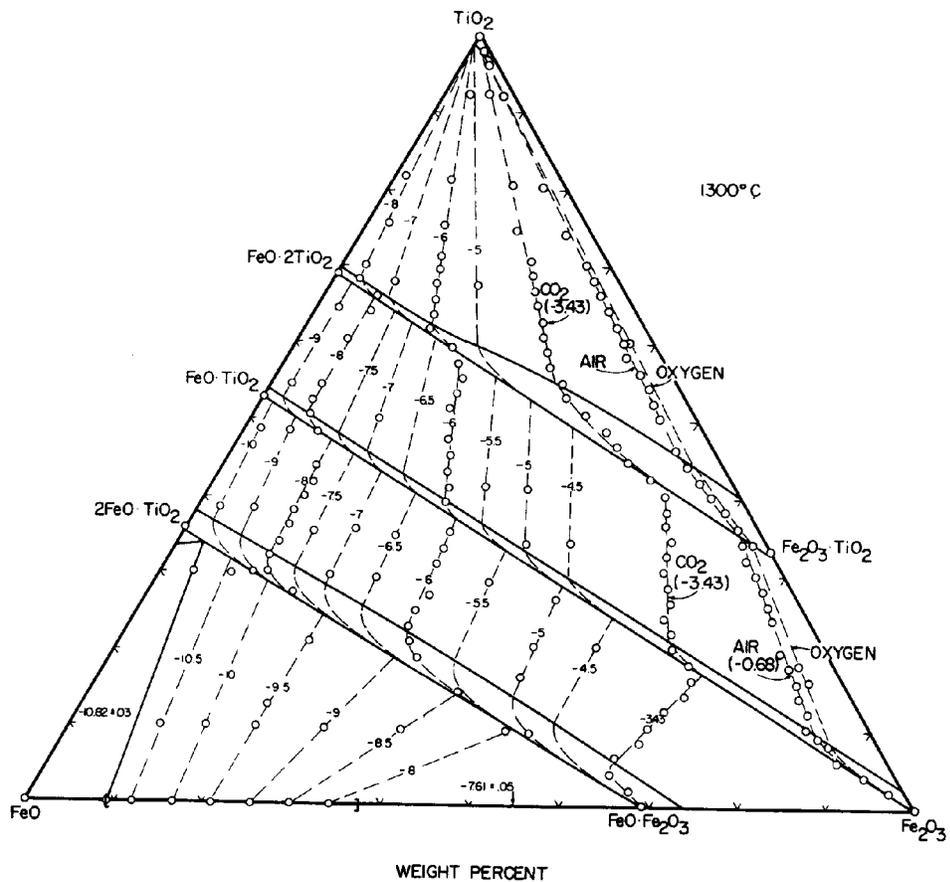


Figure 11 Oxygen isobars in the FeO - Fe₂O₃ -TiO₂ system. [Taylor, 1961]

4.2 Titanomagnetite crystallography

It is well-known that the titanomagnetite solid-solution series has an inverse spinel structure at all temperatures of interest in this study. The unit cell of magnetite consists of eight Fe_3O_4 subunits, occurring as $\text{Fe}_8^{++}(\text{Fe}_8^{+}\text{Fe}_8^{++})\text{O}_{32}$. Figure 12 shows one-eighth of the unit cell. The magnetic moments of the Fe in the 8a sites and 16b sites are in opposite directions, making magnetite ferrimagnetic.

The titanomagnetite solid solution series is formed by the substitution $2\text{Fe}^{+++} \rightarrow \text{Fe}^{++} + \text{Ti}^{+++}$. An increase in the Ti content results in an increase in the cell lattice parameter (figure 13). This can be used to estimate the composition of titanomagnetites. One must guard against oxidation, which changes the cell lattice parameter (figure 14).

There is some evidence that annealing changes the ordering of the Fe and Ti atoms. All samples used in this study were annealed by repeated cycling between room temperature and 600 °C before the magnetic experiments were performed.

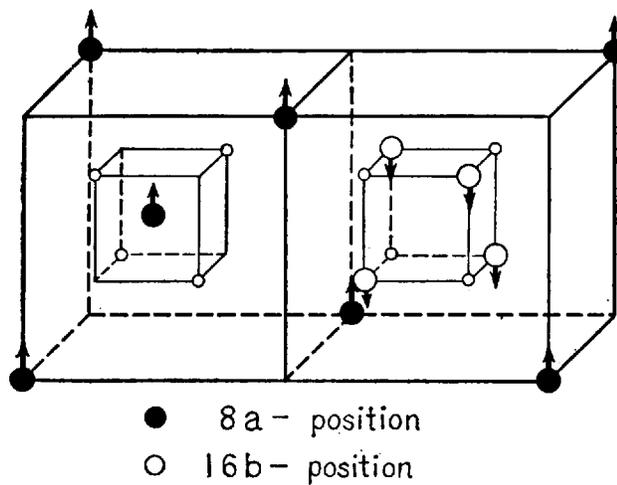


Fig. 1-23 Inverse spinel structure, (magnetite).
The arrows indicate the spin magnetic moment.

Figure 12 One-eighth of the magnetite unit cell. [Nagata, 1961]

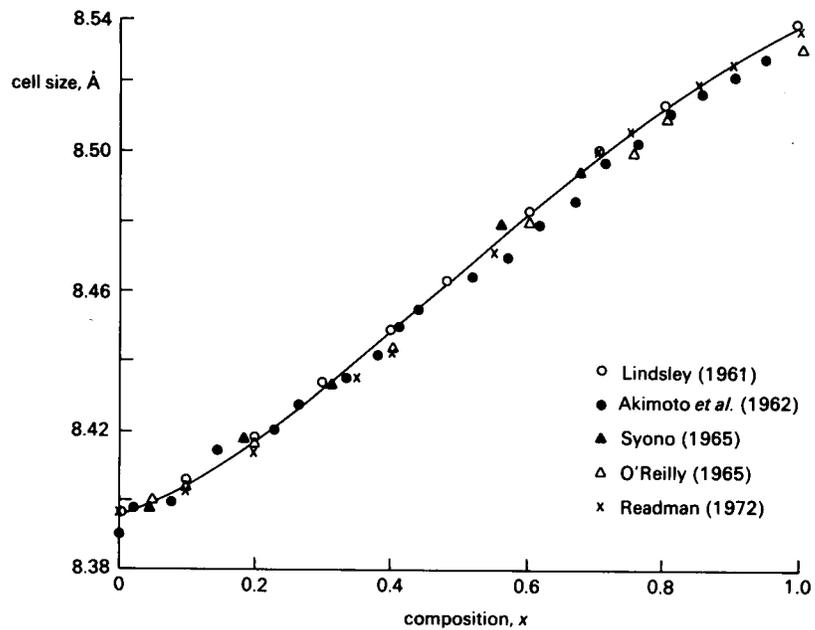


Figure 2.4 The unit cell parameter (Å) of synthetic titanomagnetites as determined by a number of investigators. Variations are probably due to variations in high temperature non-stoichiometry, lower values indicating greater degrees of non-stoichiometry.

Figure 13 Effect of ulvöspinel content on the magnetite cell lattice parameter. [O'Reilly, 1984]

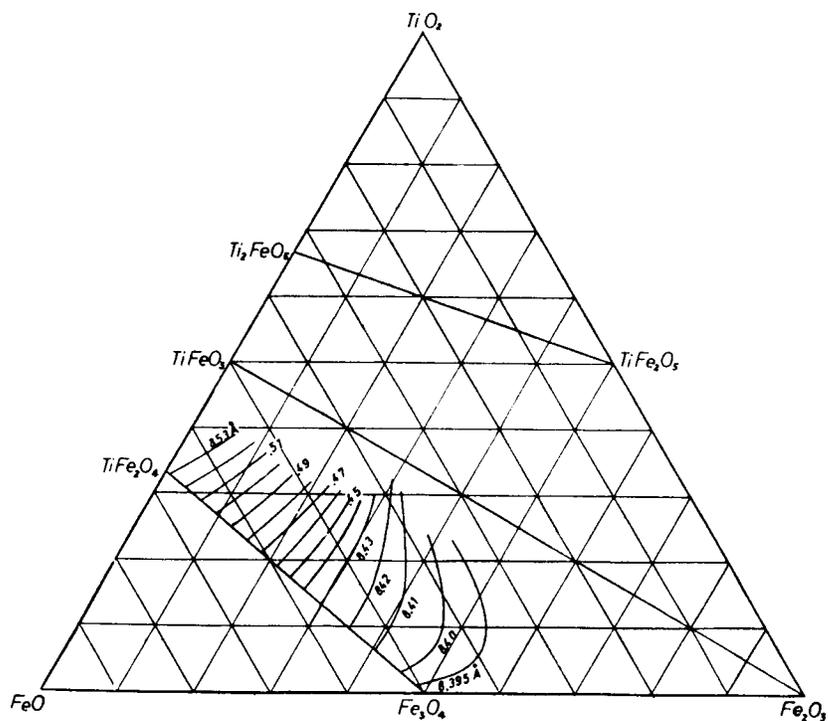


Fig. 6 Lines of equal lattice parameter of the generalized titanomagnetite in a FeO-Fe₂O₃-TiO₂ system.

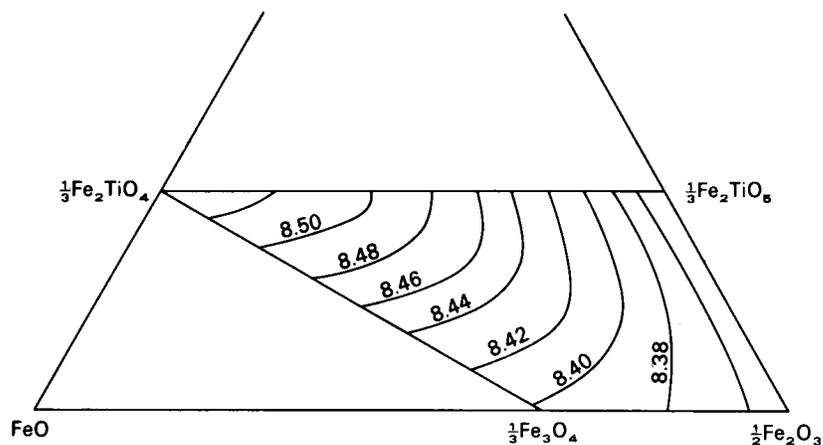


Figure 2.6 The unit cell parameter (Å) for titanomaghemites synthesized by the addition of oxygen mechanism (O'Reilly and Readman, 1971). Cell edge is not very sensitive to cation distribution and it is probable that no great differences would result from maghemitization by the alternative mechanisms.

Figure 14 Variation in the magnetite lattice parameter with ulvöspinel content and oxidation. Top: Akimoto [1957]. Bottom: O'Reilly [1984]

4.3 Effects of impurities

Iron and Titanium are not the only cations that can be incorporated into the spinel structure. Cations that can affect the magnetic properties of titanomagnetites include Cu^{++} , Ni^{++} , Co^{++} , Mg^{++} , Mn^{++} , Mn^{+++} , Mn^{++++} , Al^{+++} , Cr^{+++} , and V^{+++} . Of these, the manganese cations are the most troublesome, and must be avoided completely. Hausmannite (Mn_3O_4) forms a magnetic solid solution series with magnetite; indeed, the Mn_3O_4 - Fe_3O_4 series may be ranked second in importance to the FeO - Fe_2O_3 - TiO_2 system (Nagata [1961]).

Nagata [1961] summarizes the effects of Cu^{++} , Ni^{++} , Co^{++} , Mg^{++} , Al^{+++} , Cr^{+++} , and V^{+++} . The effects of Mg^{++} and Al^{+++} , which are often present to a few percent in natural magnetites, are discussed by Richards, et al [1973]. The effects of Al^{+++} are also discussed by Özdemer and O'Reilly [1978].

Calcium and silicon are often reported in magnetite analyses. The latter is almost certainly due to silicate contamination (Richards, et al [1973]). It seems impossible to eliminate Ca and Si from the glass-ceramic process; indeed, their presence in the glass melts used in high concentrations may result in their saturation within the magnetite structure, and is certainly consistent with the high Ca and Si concentrations in many igneous rocks.