THE EXPERIMENTAL MODELING OF AIR OXIDATION ILMENITE

D.A.Khramov, M.A.Glazkova, V.S.Rusakov, V.S.Urusov

(Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia)
khramov@geokhi.ru; phone: (095) 939-70-53

The study of ilmenite ($FeTiO_3$) - **I** oxidation mechanism causes an essential interest as from a standpoint of understanding the minerals evolution processes as from inorganic materials positions. It is the experimental modeling of similar processes at the controlled **(T, P, f_{O2})** – conditions to allow reconstructing the history of mineral formation and their ensuing transformations.

In this work the structural and phase mechanisms of air oxidation (T = 400 – 950^0 C) stoichiometrical samples of **I** and **F** with titanium deficiency ($Fe^{3+}_{0.16}Fe^{2+}_{0.86}Ti^{4+}_{0.88}O_3$) were studied by ^{57}Fe Mössbauer spectroscopy (MS) and X-ray. The samples were synthesized at temperature T = 1150^{0}C, which is characteristic of the igneous processes running. It is determined, that the process of oxidation of **I** and **F** under T = 400-600^0 C is realized by two parallel ways: 1) the transition of Fe^{2+} ions to the Fe^{3+} in the mineral structure; 2) the formation of hematite (α-Fe_2O_3) in amounts $\approx$ 8% (400^0 C) and $\approx$22% (600^0 C). The following schemes of local charge compensation are the most probable: $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+}(Fe) + Fe^{3+}(Ti)$; $3Fe^{2+} \rightarrow 2Fe^{3+}(Fe) + V (Fe)$. At the temperature of oxidation T = 700° C the **I** structure is completely destroyed while hematite and $Fe_2Ti_2O_7$ (landauite) phases are forming. The further increasing of the oxidation temperature (800-950° C) does not lead to other phases formed in the system. At T > 1150° C pseudobrookite (Fe_2TiO_5) is formed.

The oxidation degrees of **I** and **F** k = (Fe^{3+} /(Fe^{3+} + Fe^{2+})) are monotonously increased with the oxidation temperature rise and they have one and the same value in within the accuracy of fitting for **I** and **F** in the structure destroy range (600-700^0 C) and equal to 29-30(2)%. The concentration of $Fe^{2+}_{ptet.}$ ions with «pseudotetrahedral» coordination is decreased from 20% to 17% for **I** and increased from 3% to 8% - for **F** in dependence on k value.

In the **I** and **F** structure the isomer shift values for $Fe^{2+}_{ptet.}$ ions show that they don't practically depend on k and are significantly differed for **I** and **F**: 0.85 mm/s - (**I**) and 0.96 mm/s - (**F**). The isomer shifts are given relative to metal iron. These differences is indicative to essentially various character of the $Fe^{2+}_{ptet.}O_6$ octahedrons distortions in the **I** and **F** structure (Fig. 1,2).

Table

The products of ilmenite and ferriilmenite oxidation

| Initial samples synthesized at T = 1150^{0}C	The samples oxidized on air			
Ilmenite ($FeTiO_3$)	(Ferriilmenite) (Hematite α-Fe_2O_3)	Region of dest-ruction	(Landauite $Fe_2Ti_2O_7$) (Hematite α-Fe_2O_3)	(Pseudobrookite Fe_2TiO_5)
Ferriilmenite ($Fe^{3+}_{0.16}Fe^{2+}_{0.86}Ti^{4+}_{0.88}O_3$)	(Ferriilmenite) (Hematite α-Fe_2O_3)	Region of dest-ruction	(Landauite $Fe_2Ti_2O_7$) (Hematite α-Fe_2O_3)	(Pseudobrookite Fe_2TiO_5)
	400	600 700	950	1300 T^{o}C

δ, mm/s
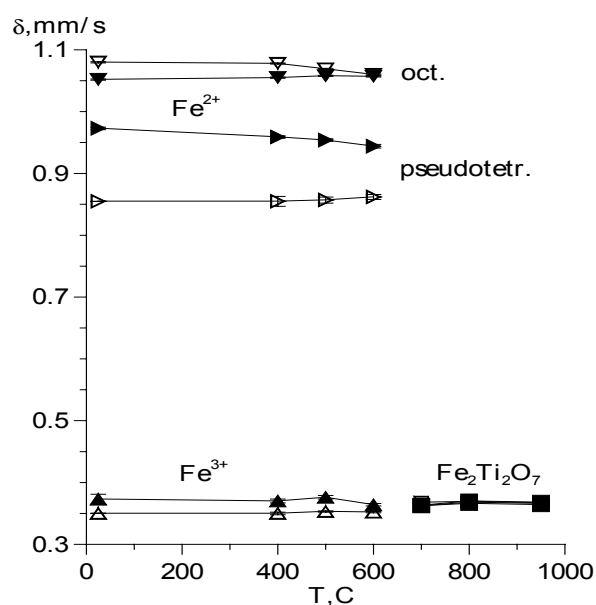
Fig.1. The isomer shifts (relative α-Fe) Fe^{2+}, Fe^{3+}- atoms in ilmenite (Δ), ferriilmenite ($\blacktriangle$) and landauite ($Fe_2Ti_2O_7$).
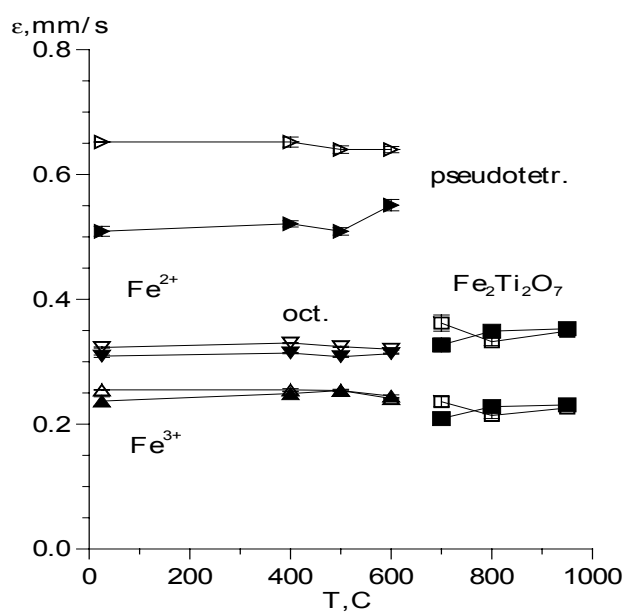
ε, mm/s

Fig.2. Quadrupole splitting (QS = 2ε) Fe^{2+}, Fe^{3+}- atoms in ilmenite (Δ), ferriilmenite ($\blacktriangle$) and landauite ($Fe_2Ti_2O_7$).