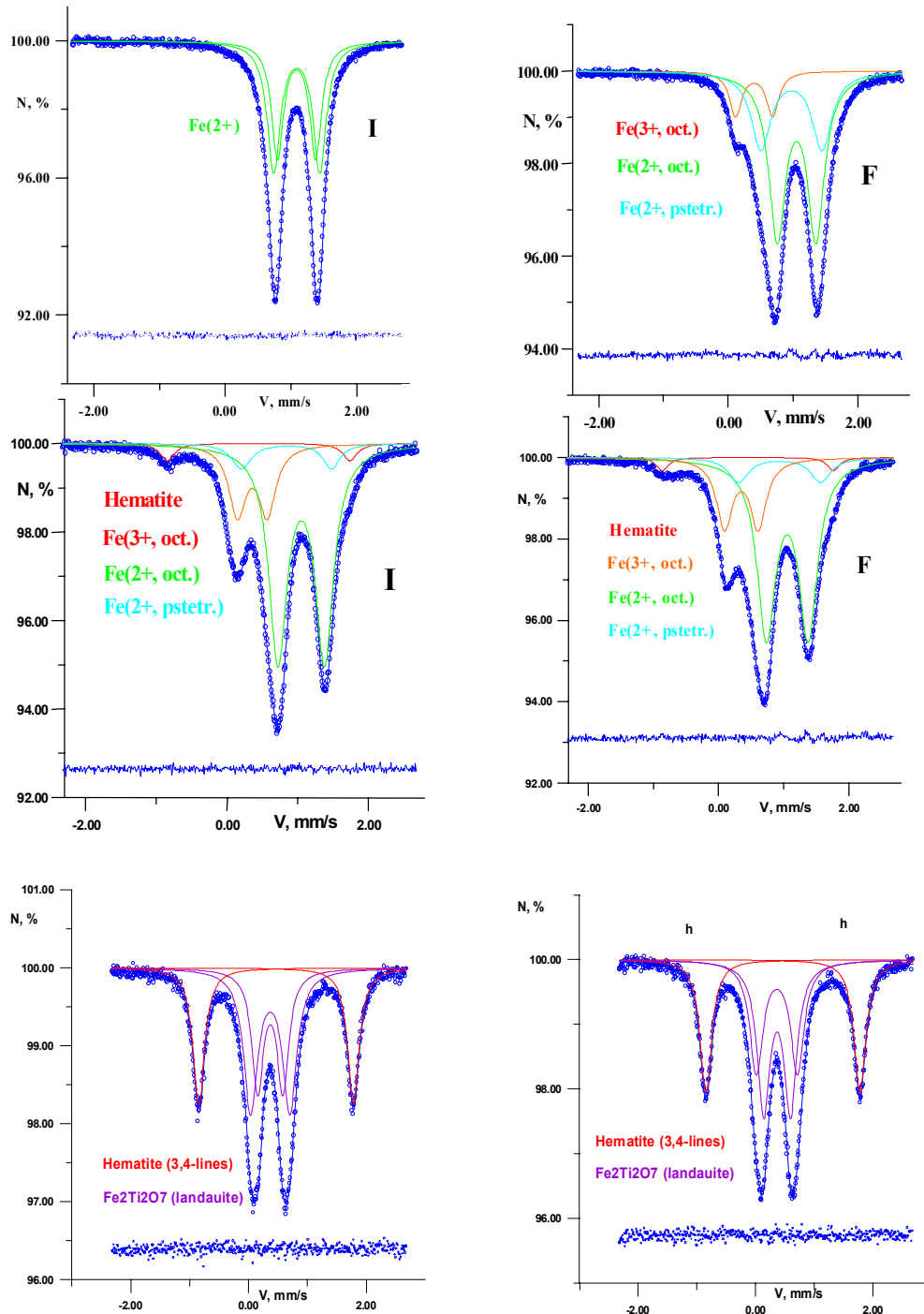


¹Khramov D.A., ²Rusakov V.S., ¹Glazkova M.A., ¹Urusov V.S. Experimental modeling of ilmenite oxidation on air.

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A study of the mechanism of ilmenite (FeTiO_3) – *I* oxidation is interesting both for understanding of the evolution of rock-forming minerals and for inorganic material sciences. An experimental modeling of such processes at controlled T, P, f_{O_2} – conditions allows reconstruction of a formation and subsequent changing of rock-forming minerals. Besides, partially oxidized (~20 % Fe^{3+}) ilmenites (ferroilmenites – *F*) are considered as new perspective magnetic materials, i.e. concentrated spin glasses (SG). The parameters of the transition into the SG state are mostly determined by peculiarities of the nearest order in the system.



In the present study, structural and phase mechanisms of oxidation on air ($T = 400-950^{\circ}\text{C}$) of samples of stoichiometric **I** (FeTiO_3) ilmenite and **F** with deficiency of Ti ($\text{Fe}^{3+}_{0.16} \text{Fe}^{2+}_{0.86} \text{Ti}^{4+}_{0.88}\text{O}_3$) are investigated by the Mössbauer spectroscopy (MS) on ^{57}Fe nuclei and x-ray diffraction (XRD). The samples were synthesized at temperature 1150°C , which is characteristic for magmatic processes and conditions of production of SG of the given type.

It is found, that the process of oxidation of **I** and **F** at $400-600^{\circ}\text{C}$ proceeds by two parallel ways: 1) transition of some portion of Fe^{2+} ions to Fe^{3+} in the **I** and **F** structures; 2) separation of $\sim 8\%$ (400°C) and 22% (600°C) of hematite and TiO_2 . The most possible schemes of the local charge compensation are the following: $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+}_{\text{Fe}} + \text{Fe}^{3+}_{\text{Ti}}$ and $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{V}_{\text{Fe}}$. In the temperature interval $600-700^{\circ}\text{C}$, **I** and **F** are completely destroyed with the formation of hematite, rutile, and landauite ($\text{Fe}_2\text{Ti}_2\text{O}_7$) [1].

A degree of oxidation $k = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ monotonously increases with temperature and, within the analytical error, at 600°C is $29-30(2)\%$ both for **I** and **F**. A comparison of values of isomer shifts for the portion of Fe^{2+} ions in **I** and **F** shows that they practically do not depend on k , but differ for **I** and **F**: 0.85 mm/sec for **I** and 0.96 mm/sec for **F**. The shifts are shown with respect to metallic iron. Such shifts are characteristic for bivalent iron ions in the tetrahedral coordination of oxygens. As it is found earlier [2], it is related to the local distortions of ilmenite structure near Fe^{2+} ions. As a result, two oxygen ions in the neighbor octahedron FeO_6 are displaced from the equilibrium state. That allows to consider this coordination as “pseudo-tetrahedral”.

References:

1. A.M. Portnov, L.E. Nikolaeva, T.N. Stolyarova. Dokl. Acad. Sci. SSSR (1966). V.166, N 6.
2. M.A. Glazkova, D.A. Khramov, A.M. Bychkov, V.S. Urusov. (1997). Distortions of the tin-containing ilmenite structure at different oxidation states.//Experiment in Geosciences V.6, N 2, pp. 54-55.