

OXIDATION OF IRON IN MINERALS AND EVOLUTION OF THE ATMOSPHERE

Ignatiev V. D. The Institute of geology, Komi science centre, Russian Academy of Science, Syktyvkar, Russia

The magnitude of ratio of ferric/ferrous iron in early precambrian weathering profiles often is used to argue a high oxygen content in atmosphere of the Earth that time. However iron ions are oxidized not only in water solution but in minerals crystal structures as well. In a reducing environment the latter would be preserved in residuals. Analysis of mechanisms of weathering of minerals leads to conclusion that interior oxidation is controlled by pH of water solution. Oxidation of ilmenite is probably the most reliable example. Comparison of chemical composition of ilmenite from primary rocks, weathered rocks and placer deposits shows that there is close relation between H_2O^+ content and magnitudes of Fe/Ti and Fe^{3+}/Fe^{2+} ratios in weathered ilmenite. Proton exchange between water solution and ilmenite is described by the equation: $2 FeTiO_3 + H^+ = Fe_3^{3+}Ti_2O_5OH + Fe^{2+} + e^-$. In agree with the equation migrating of proton into crystal structure results in forming OH-ion. The nearest neighbouring Fe^{2+} is removed by electrostatic interaction with proton and the next neighbouring Fe^{2+} is oxidized by OH-ion. As crystal participates in electron exchange with water solution, than the free electron leave to interphase boundary. Finally an intermediate phase pseudorutile forms, which retain the anion lattice of ilmenite. In real ilmenite some Me^{2+} is substituted by Fe^{3+} with agree to rules: $Me^{2+} + Ti^{4+} = 2 Fe^{3+}$ and $3 Me^{2+} = 2 Fe^{3+} + \text{vacancy}$. Therefore the number of OH-ions in formula of pseudorutile may be less than 1. The example shows clearly that oxidation of iron in minerals is due to proton exchange and does not depend on oxygen fugacity of air. Both proton exchange and oxidation are solid state reactions. There are some restrictions to simple relation between proton exchange and oxidation. If there are two or more sorts of cations (weak Lewis acids), than iron ions would move to solution, if they occupy less energetically favourable positions in crystal structure. Such situation would be expected in olivines.