

PHASE RELATIONS IN THE Fe-Ti-Mg-O OXIDE SYSTEM AND HEMATITE STABILITY AT THE CONDITION OF VENUS' SURFACE M. Yu. Zolotov Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow

Activity-composition relations and miscibility gap of ilmenite-hematite-geikielite solid solution were estimated in the frame of Fe-Ti-Mg-O oxide system for the condition of Venus' surface. The existence of titanhematite-magnetite, titanhematite-rutile, ferrianiilmenite-rutile as well as magnetite-rutile or ferrianiilmenite-titanhematite assemblages is expected for the surface. Prediction of hematite stability as a Ti-, Mg-bearing solid solution is in accordance with the atmospheric redox potential and with the near-infrared spectral features of the surface. Magnetite-titanhematite assemblage could be considered as a buffer of atmospheric redox potential.

Iron and titanium oxides are minor but critical minerals in igneous rocks and their weathering products (1,2), and could be responsible for the low emissivity features of the Venus' surface (e.g. 3,4). Stability of end members of Fe-Ti oxides on the surface was investigated and reviewed in (5-7). While natural titanomagnetite usually also contains Al, Cr, Mn, and Mg; ilmenite usually contains Mg; hematite (formed as a result of silicates, titanomagnetite or ilmenite oxidation) contains Ti and Mg (2). The aim of that work is to evaluate the stability of solid solutions of Fe-Ti oxides at the conditions of Venus' surface.

The main end members which exist in the Fe-Ti-O system are: hematite, magnetite, ilmenite, ulvospinel, and rutile. Two main solid solution series: magnetite-ulvospinel and hematite-ilmenite exist in the system. The main assemblages which are expected for 700-800 K could be: magnetite-titanhematite, titanhematite-rutile, ilmenite-rutile, and rutile-magnetite or titanhematite-ferrianiilmenite (Fig. 1).

The magnetite-titanhematite phase assemblages, which form between magnetite and hematite solid solution are depended on the redox potential (e.g. 1,2). Therefore, the activity of solid phases - redox potential relations could be developed for the condition of Venus' surface (Fig. 2). The activity-composition relations and boundaries of miscibility gap for the ilmenite-hematite solid solution were calculated for the variable geikielite (MgTiO_3) content at 740 K on the basis of (8).

Activity of magnetite, which is suggested to be in equilibrium with rutile, titanhematite and ferrianiilmenite (compositions for the miscibility gap boundary), was calculated from equilibrium: $\text{Fe}_3\text{O}_4 + \text{TiO}_2 = \text{FeTiO}_3(\text{ss}) + \text{Fe}_2\text{O}_3(\text{ss})$ (see Fig. 1) for various geikielite content in hematite and ilmenite solid solutions at the TiO_2 activity given as unity. The magnetite activities obtained from that equilibrium are: 0.82 (at $x(\text{MgTiO}_3)=0$, $a(\text{ilm})=0.77$, $a(\text{hem})=0.63$); 0.73 (at $x(\text{MgTiO}_3)=0.15$, $a(\text{ilm})=0.67$, $a(\text{hem})=0.64$). The $\log(f(\text{O}_2))$ values at 740 K for the condition of magnetite-titanhematite equilibrium were calculated on the basis of hematite activity (for the boundary composition) and estimated magnetite activity: -21.66 and -21.43 (for 0 and 15 mol. % of MgTiO_3 in titanhematite respectively). These values of redox potential are suggested as lower limits for the stable existence of titanhematite on the surface.

The redox potential values for the of titanhematite-magnetite equilibrium were also estimated as a function of magnetite activity at the fixed composition of titanhematite on the boundary of the miscibility gap (Fig. 3). The $f(\text{O}_2)$ values for the magnetite-titanhematite equilibrium calculated as a function of hematite composition at fixed magnetite activities shown on Fig. 4.

Discussion. The redox potential estimated for the magnetite-titanhematite equilibrium appears to be in a good coincidence with Venus' $f(\text{O}_2)$ values, estimated on the basis of atmospheric chemistry (9). Titanhematite with variable composition should be stable at $\log(f(\text{O}_2)) = (-20.82)-(-21.66)$, as expected for the nearsurface atmosphere (see Fig. 4). That result is in agreement with the prediction of hematite existence made from near-infrared spectra of the Venus' surface (10). Magnetite ($a(\text{Mt})=0.6-0.7$ and more) - titanhematite ($a(\text{Hem})= 0.63-0.64$ and more) equilibrium could control atmospheric redox condition and composition (e.g. CO_2/CO ratio). That assemblage should form as a result of ilmenite, titanomagnetite and Fe^{2+} -silicates oxidation by $\text{CO}_2(\text{g})$ and/or $\text{H}_2\text{O}(\text{g})$.

Besides, taking into account the hematite and magnetite activities obtained from Fe-Ti-Mg-O system, phase diagrams in the Fe-S-O and Fe-S-O-C systems were developed at 740 K. The advanced position of

the pyrite-magnetite-hematite nonvariant point on these diagrams appears to be quite near to the $P(\text{O}_2, \text{CO}, \text{and } \text{COS})$ values, suggested for near-surface atmosphere of Venus (see 9).

The expected buffering of atmospheric redox potential by titanhematite-magnetite (+pyrite?) assemblage should be result of the previous physic-chemical evolution of coupled atmosphere-lithosphere system on Venus. At the present time that equilibrium is considered as a nonvariant point and future evolution (along with pyrite-hematite buffer) will begin only after totally magnetite oxidation in the near-surface soil/rock layer. At the present epoch the full and successful oxidation of magnetite seems to be limited by low rate of hydrogen escape as well as by the ability of relatively fresh basalts.

Acknowledgments. I thank Prof. R. Greeley for the scientific and organizational support. That research was supported by NASA grant No. NAGW-2102, Subgrant No. 93-102SG.

References. 1. Lindsley D.H. (1976) in Rev. in Mineralogy, Vol. 3, L61; 2. - (ed.) (1991) Rev. in Mineralogy, Vol. 25, 509p; 3. Garvin J.B. (1985) Abst. LPSC 16, 262; 4. Pettengill G.H. et al. (1988) JGR, 88, 14881; 5. Fegley B.J. and Treiman A.H. (1992) *Venus and Mars: Atmosphere, Ionosphere and Solar Wind Interaction*. AGU Chap. Comp., 7; 6. Fegley B.J. et al. (1992) Proc. LPSC 22, 3; 7. Zolotov M.Yu. and Volkov V.P. (1992) *Venus Geology, Geophysics and Geochemistry*, Ariz. Univ. Press, 177; 8. Ghiorso M.S. (1990) Contr. Miner. Petrol. 104, 645; 9. Zolotov M. Yu. this volume; 10. Pieters C. et al. (1986) Science 234, 1379;

Fig. 1. Expected phase assemblages in the system $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ at 740 K. **Fig. 2.** Redox potential ($\log(f(\text{O}_2))$, bar) for the hematite-magnetite equilibrium as a function of hematite and magnetite activity at 740 K. Horizontal lines show the boundaries of miscibility gap for the hematite-ilmenite-geikielite solid solution. Lower horizontal lines indicate the boundaries of miscibility gap at $x(\text{MgTiO}_3) = 0$, upper lines indicates these boundaries at $x(\text{MgTiO}_3) = 0.15$. **Fig. 3.** Redox potential for the hematite-magnetite equilibrium at the fixed activities of hematite as a function of magnetite activity at 740 K. The fixed activity of hematite is devoted to the boundary titanhematite composition in the hematite-ilmenite-geikielite solid solution. That hematite activity is estimated from miscibility gap boundaries and hematite activity-composition relations for the hematite-ilmenite-geikielite solid solution at $x(\text{MgTiO}_3)=0$ and 0.15. **Fig. 4.** Redox potential for the hematite-magnetite equilibrium as a function of hematite molar ratio in titanhematite (hematite solid solution) at 740 K. Fixed magnetite activities were obtained from $\text{Mt}+\text{Rut}=\text{Ilm}(\text{ss})+\text{Hem}(\text{ss})$ equilibrium.

