THE CHROMIUM CONCENTRATION OF ILMENITE AND ITS POSSIBLE APPLICATION AS A LUNAR THERMOMETER. B. Knecht, B. Simons & E. Woermann, Institut für Kristallographie der RWTH Aachen, and A. El Goresy, Max Planck Institut für Kernphysik, Heidelberg, Germany.

Ilmenite is one of the major opaque minerals in lunar basalts. Its composition corresponds essentially to FeTiO₃, with various amounts of the components MgTiO₃, TiO₂, Al₂O₃ and Cr₂O₃. Fe₂O₃ is virtually absent in the highly reduced basaltic matrix containing metallic iron as a frequent accessory mineral. While at high temperatures FeTiO₃ and MgTiO₃ are miscible over the whole compositional range, the solubilities of TiO₂, Al₂O₃ and Cr₂O₃ in the ilmenite phase are restricted to low concentrations. Here the temperature dependence of the chromium solubility is investigated with the aim to provide a possible new lunar thermometer. The theoretical model offered is also valid for ilmenite - Al₂O₃ solid solutions.

Subsolidus phase relations in the systems MgO-Cr₂O₃-TiO₂, MgO-Al₂O₃-TiO₂ and FeO-Al₂O₃-TiO₂ have been investigated (3, 4) at the 1300°C-isotherm. In each system the ilmenite phase has a limited solid solution range. Additions of Cr₂O₃ or Al₂O₃ in excess of the solubility limits lead to (sp+ilm+ps)-assemblages. The same general pattern is again observed here for the presently investigated system FeO-Cr₂O₃-TiO₂ (fig. 1).

Lindsay et al. (2) presented in their fig. 6 a schematic T-fO₂-diagram of the system Fe-Ti-O which is confirmed by experimental investigations of this system in equilibrium with metallic iron (5) (fig. 2). From these diagrams it appears that the stability field of ilmenite is narrowing towards higher temperatures. An intersection of lines (1) and (3) in fig. 2 would result in an isobarical invariant point (sp+ilm+ps+FeO), indicating an upper stability limit of ilmenite, which must be located, however, above its melting point at 1395°C. This hypothetical intersecting point M is constructed schematically in figure 3.

Upon addition of a further component - e.g. Cr₂O₃ - the invariant point M will be converted to a monovariant line M-N (sp+ilm+ps+FeO). This phase assemblage has been shown above to be common for the Al- and Cr-bearing systems quoted. The monovariant line is thus sloping from above 1395°C in the
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Figure 2.
Stability of the iron-titanium oxide phases in equilibrium with metallic iron in the system Fe-Ti-O. 
\[ \Delta G^0 \text{ (KJ.mol}^{-1}\text{)} = -2.303 \text{RT log } f_{O_2} \]
circles: e.m.f.-measurements; squares: equilibrium runs in H$_2$/CO$_2$ gas mixtures.

Fe-Ti-O system to 1150°C and below in the Fe-Ti-Cr-O system.
The simultaneous shift along the $\Delta G^0$- or the log $f_{O_2}$-parameter can be deduced from a comparison of the relative stabilities of the end member components of the corresponding spinel series. From fig. 4 it is evident that chromite has a higher stability compared with ulvite, i.e. it decomposes at a lower oxygen fugacity. Increasing chromium activities in the continuous chromite-ulfite series will thus result in increasing stabilities of the spinel phase. Thus corresponding equilibrium phase assemblage (sp+ilm+ps+FeO$^0$) will be shifted to lower oxygen fugacities with increasing chromium concentrations.

With these informations on the line M-N with respect to the T- and fO$_2$-parameters it has been constructed schematically in figure 3. It is located quantitatively by determining the oxygen fugacity of the (sp+ilm+ps+FeO$^0$)-assemblage as a function of temperature by e.m.f.-measurements in fig. 4.

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Figure 4.
\[ \Delta G^0/T \text{ curves for the reactions } \text{ulvite} + \text{ilmenite} + \text{iron and chromite} + \text{eskolaite} + \text{iron. } N-N = \text{monovariant curve (sp+ilm+ps+FeO)} \] as determined from e.m.f.-measurements.

Accordingly high temperature (sp+ps+FeO)-phase assemblages will, upon cooling, finally hit the (sp+ilm+ps+FeO) monovariant line. The resulting reaction sp+ps=ilm is common in lunar samples. Upon further cooling the equilibrium oxygen fugacity will decrease and all three oxide phases involved will gradually be enriched in Cr\textsubscript{2}O\textsubscript{3}, i.e. the three phase triangle in fig. I will move away from the FeO-TiO\textsubscript{2} boundary line, while ilmenite is growing at the expense of the spinel- and the pseudobrookite phase. A negative temperature coefficient for the solubility must also - for analogous reasons - be valid for incorporation of Al in the ilmenite phase. While the general trend in lunar basaltic magmas leads to an enrichment of Ti with simultaneous decrease in Cr in the crystalline phases (e.g. increase in ulvite-, decrease in chrome-component in spinel), this trend is reversed as soon as ilmenite is formed as a solid state reaction product of spinel and a pseudobrookite phase. This reversal has been observed in natural lunar samples (1, 6).

In equilibrium with metallic iron the pseudobrookite phase in the system Fe-Ti-O decomposes at 1068° C to ilmenite + rutile. Upon addition of Cr\textsubscript{2}O\textsubscript{3} this stability limit is shifted to 1031° C. The resulting equilibrium point (sp+ilm+ps+rt+FeO) terminates the line M-N. Below 1031° C ilmenite is in equilibrium with spinel+rutile+metallic iron.

REFERENCES