OBservations on titanium in lunar oxides and silicates.
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We have evaluated thermodynamic functions of mineral assemblages of lunar rocks, to describe quantitatively the variation of (a) silica activity, (b) temperature of crystallization, and (c) oxygen fugacity. These functions point out some of the differences between lunar and terrestrial environments.

I. Silica activity. Some mare basalts such as 70215 and 74275 have phenocrysts of a titanium-rich pyroxene. Titanium/aluminum ratios of these pyroxenes indicate that the titanium is probably in the pyroxene molecule CaAl$_2$TiO$_6$. The following reaction involving this pyroxene is appropriate for mare basalts.

$$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{FeTiO}_3 = \text{CaAl}_2\text{TiO}_6 + \frac{1}{2}\text{Fe}_2\text{SiO}_4 + \frac{3}{2}\text{SiO}_2 (\text{liquid})$$

The above reaction apparently takes place in rocks like 70215 since plagioclase (-An90) does not appear in substantial amounts until the pyroxene has differentiated from titanaugite to augite. Figure 1 shows the silica activity curves for (1) the pure reaction, (2) the reaction at Fo80, An90, Ti-pyroxene 20, and ilmenite. Ranges of silica activities for terrestrial tholeiite and alkali-olivine basalts and their differentiates are also shown. The initial phases to crystallize from the lunar magma are either oxides or olivine and Ti-pyroxene. However, the residuum contains abundant free silica and therefore the final silica activity of the magma must near unity. Curve #3 shows the approximate path of silica activity during crystallization of mare basalt 70215. The path is in marked contrast to terrestrial basalts where silica activities either remain relatively constant or decrease with differentiation.

II. Silicate-Ilmenite Geothermometer. The variation of the equilibrium constant with temperature for the reaction FeSiO$_3$ + MgTiO$_3$ = FeTiO$_3$ + MgSiO$_3$ has been evaluated. This function indicates that the Mg content of ilmenites and pyroxenes is related to the temperature of equilibration. Figure 2 is a graph of log K vs. T for the reaction. At this stage, the reaction appears to be accurate to ±75°C for pyroxenes containing up to about 60 mole % FeSiO$_3$. Similar curves for olivine and clinopyroxene with ilmenite have been derived. An equilibration temperature of approximately 1000°C is indicated for complexly intergrown ilmenite and orthopyroxene in lunar breccia 60016. In addition, data points for terrestrial orthopyroxenes and ilmenites in which the temperatures are derived by the Buddington-Lindsley geothermometer are shown.

III. Oxygen Fugacities. Much has been made of the apparent late stage reduction of lunar oxides (1,2,3,4) to explain the existence of assemblages such as armalcolite-ilmenite-rutile-iron. However, such assemblages may be due to the isochemical exsolution of iron and rutile from oxide phases which contain trivalent titanium. The reaction would be of the form

$$\text{Fe}^{+2} + 2\text{Ti}^{+3} \rightleftharpoons \text{Fe}^0 + 2\text{Ti}^{+4}$$

An example of this reaction for an ilmenite containing trivalent titanium as Ti$_2$O$_3$ is

$$[\text{FeTiO}_3 + \text{Ti}_2\text{O}_3] \rightleftharpoons \text{Fe}^0 + 3\text{TiO}_2$$

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and for an armalcolite phase represented by ferropseudobrookite

\[ [\text{FeTi}_2\text{O}_5 + \text{Ti}_3\text{O}_5] \text{ ss} \pm \text{Fe}^++5\text{TiO}_2 \]  

Lunar ilmenites are nearly stoichiometric, but analyses commonly contain a small amount of "excess" titanium. Armalcolite generally contains a considerable excess of TiO$_2$ beyond that necessary to make M($^+2$)Ti$_2$O$_5$ or M($^+3$)$_2$TiO$_5$ compounds.

The studies of Webster and Bright (4) and Yoshida and Takei (5,6) have shown that little solubility of TiO$_2$ can exist in ilmenite (orthorhombic) phases. However, the data of Webster and Bright (4) indicate a ferropseudobrookite phase in equilibrium with a stoichiometric ilmenite must contain some Ti$_3$O$_5$. Figure 3 is a diagram of the FeO-TiO$_2$O$_2$ partial system at 1200$^\circ$C derived from the data of the above authors. Approximate values of $\log f_{\text{O}_2}$ for pertinent assemblages are given. At slightly reduced $f_{\text{O}_2}$ values the oxides contain some Ti$^+(+3)$ and are in equilibrium with metallic iron. This data is in good agreement with the melting experiments of Kesson (7) and others that indicate that mare basalts are saturated or very nearly so with iron. A thermodynamic analysis of reaction 3a indicates that a 1200$^\circ$C an equilibrium ilmenite in the assemblage $\text{Fe}^++\text{FeTi}_3\text{O}_5$ ss $+ \text{Fe}_2\text{TiO}_5$ ss should contain 2% to 4% Ti$_2$O$_3$. If this is so then the "reduced" (Fe bearing) assemblage may be produced as is shown in figure 4.

A sample of composition (x) in fig. 4a is initially a 2 phase assemblage of ilmenite and ferropseudobrookite solid solutions, both of which contain some Ti(+3). With a decrease in temperature to $T_1$, accompanied by a decrease in the solubility of Ti(+3) in the oxides, metallic iron exsolves by reaction 3. At a still lower temperature the armalcolite type phase is no longer stable and at least in part breaks down to magnesian ilmenite + rutile (fig. 4b). In the Fe-Ti-O system this takes place at about 1140$^\circ$C (8).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

DATA FROM CARMICHAEL (9)

COMPLEX ILMENITE-PYROXENE INTERGROWTHS

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