Phase Equilibria Study of Pseudobrookite Type Minerals

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INTRODUCTION

Minerals of the pseudobrookite-ferropseudobrookite solid solution series \((\text{Fe}_2\text{TiO}_5-\text{FeTi}_2\text{O}_5)\) do not seem to form in deep-seated plutonic rocks on the earth, but rather ilmenite and rutile are found. Pseudobrookite, however, is found in volcanic rocks, and the mineral armalcolite \(((\text{Fe},\text{Mg})\text{Ti}_2\text{O}_5)\) found in the Apollo 11 and subsequent lunar samples seems to be unique to the moon. In plutonic rocks on the earth ilmenite and rutile have been found with what appears to be an equilibrium liquidus texture, while on the moon armalcolite often appears to be the primary liquidus phase among Ti-oxides. This suggests that total pressure may be a factor in the formation of these minerals, and a knowledge of the phase relations in this system should yield information about the pressure under which a given magma crystallized.

Haggerty (1973) divided lunar armalcolites into three types based on chemistry. These are: Zr-free armalcolite characteristic of high titanium mare basalts, Cr-Zr-Ca armalcolite, and Zr-armalcolite, both of which are characteristic of the non-mare high-alumina basalts. This division, which was also observed by Steele (1974), indicates that zirconium may have an important role in the formation of armalcolite. It is therefore necessary to know the high pressure stability of armalcolite as a function of ZrO₂ content.
Hartzman and Lindsley (1973) found that armalcolite in equilibrium with metallic iron reacts below 1000°C to oxidize the iron and reduce some of the Ti$^{4+}$ to Ti$^{3+}$ according to the following reaction:

$$\text{Fe}^0 + 4\text{FeTi}_2\text{O}_5 = \text{Ti}_3\text{O}_5 + 5\text{FeTiO}_3$$

(in arm.)

It would therefore be interesting to know if there is any difference in the pressure stability between this reduced armalcolite and one in which all of the Ti is quadrivalent.

The objective of this study was to determine the pressure-temperature curve for the stability of armalcolite with and without ZrO$_2$ and also of armalcolite in equilibrium with metallic iron. In order to predict the behavior of armalcolite at high pressure, the difference in molar volumes was calculated for the probable armalcolite decomposition reaction. These are listed below:

$$2(\text{Fe}_{.5}\text{Mg}_{.5})\text{Ti}_2\text{O}_5 = 2\text{TiO}_2 + \text{MgTiO}_3 + \text{FeTiO}_3$$

112.6  37.6  30.9  31.7  $V = -12.4\text{cm}^3$

Since the ilmenite-rutile assemblage on the right has a smaller molar volume than the pseudobrookite type phase, the reaction should proceed to the right at high pressure.
SAMPLE PREPARATION

Mixtures of MgO, TiO$_2$, Fe$_2$O$_3$, and Fe$^0$ were prepared to make armalcolite according to the following reaction:

$$\frac{1}{6}Fe + \frac{1}{6}Fe_2O_3 + \frac{1}{3}MgO + 2TiO_2 = (Fe_{5}Mg_{5})Ti_2O_5$$

In the case of Zr-armalcolite, 4% and 10% by weight ZrO$_2$ was substituted for TiO$_2$, and a fourth composition was prepared with excess metallic iron. These mixtures were then ground in a mixer-mill for 30 minutes, after which time the mixtures appeared homogeneous at 10X magnification, and no white streaks of MgO or TiO$_2$ were observed.

Three of these mixtures (Zr-free, 4%, and 10% ZrO$_2$) were placed in silica glass capsules sealed at one end, and these capsules were placed in a larger SiO$_2$ glass capsule containing metallic iron at the bottom. The outer glass capsule was then evacuated and sealed. The Fe-rich material was prepared in the same manner but in a separate capsule. These silica tubes were suspended in a furnace at 1300$^\circ$C for ten days and then quenched. Each armalcolite composition was then reground for 30 minutes in the mechanical shaker, evacuated, and resealed, and placed in the furnace as before for seven more days. When this was quenched, the armalcolite appeared to be single phase when examined by X-ray diffraction, but optical examination revealed some birefringent TiO$_2$ (estimated to be about 1%) probably due to the presence of some Fe$^{3+}$. The ZrO$_2$
armalcolites also showed some unreacted ZrO$_2$, and the Fe-rich material produced a two phase starting material (armalcolite and ilmenite).

Semi-quantitative data from the energy dispersive detector on the scanning electron microscope indicate that the two starting compositions containing ZrO$_2$ contained approximately equal amounts of ZrO$_2$, on the order of 1 wt.%. This is consistent with the amount found in lunar armalcolites by Steele (1974) and may represent saturated armalcolite under these conditions. The remainder of the ZrO$_2$ weighed in was apparently lost to the silica glass capsules. Zircon (ZrSiO$_4$) was observed by X-ray diffraction of the glass after the runs; however, no zircon or other silicate was observed in the starting material.

EXPERIMENTAL TECHNIQUE

The pressure runs were made in a single-stage, piston-cylinder apparatus set up by Drs. Meyer and Weidner at Goddard Space Flight Center. The armalcolite samples were sealed in silver-palladium capsules which were then placed in crushable alumina between pyrophyllite plugs all within a graphite furnace and talc outer-sleeve. The Ag$_{60}$Pd$_{40}$ alloy was chosen for its ability to withstand the temperatures used without absorbing too
much iron from the sample. The runs were not buffered because it was felt that the small amount of air trapped in the capsule would not significantly change the composition of the sample. All runs were in the piston-out configuration, and the calibration of the press was done by Dr. Gene Ulmer against the melting point of gold. The apparatus was calibrated to ±5% pressure and ±8°C temperature, and when the temperature calibration was checked during this work, it was found to be ±6°C.

Three capsules each containing a sample of different composition were run at the same time in the press. These capsules were in an equilateral triangle configuration with their sides touching each other and all void space filled with crushable alumina as the pressure transmitting medium. This presumably allowed three compositions to be run under identical conditions, but to check this assumption three capsules containing the same composition material were run together at 1000°C and 5 kb. All produced a three phase assemblage in which the amounts of each phase were constant among the three charges as estimated from X-ray diffraction data.

The maximum drift during a run was 10°C and 0.2 Kb, and all runs were held for one hour at the temperature and pressure of interest. Reversed runs were held for one hour at a
pressure above the nearest phase boundary (still piston-out) and then dropped to the point of interest and held for one hour.

RESULTS

The results of this work are plotted in figures 1 and 2 in the form of a P-T plot. Figure 1 shows the 1-, 2-, and 3-phase stability regions of synthetic armalcolite with a 0.5 Fe/Fe+Mg ratio. The dashed curve is for the Zr-free material while the solid curve is for the material containing about 1% ZrO$_2$. The armalcolites produced by weighing in different amounts of ZrO$_2$ produced identical results in terms of the phases present, but this was expected after discovering that equal amounts of ZrO$_2$ were taken into the armalcolite.

The phases present were determined by X-ray diffraction, and a crude estimation of the amount of each phase was made from relative intensities in the X-ray pattern. While this is not very precise, it was used as a guide in placing the phase boundaries in figures 1 and 2. All two-phase regions were approached from lower pressure; i.e., arm. → ilm. + rut. All one-phase regions were approached from higher pressure; i.e., rut. + ilm. → arm., and the three-phase regions at 1000ºC were approached in both directions; i.e., arm. → rut. + ilm. + arm.
and rut. + ilm. → arm. + rut. + ilm. It was assumed that if equilibrium could be demonstrated by reversed runs at 1000°C, then equilibrium should also be attained at higher temperature.

It is apparent from figure 1 that ZrO₂ has the effect of destabilizing armalcolite at higher pressure; however, this effect is not great, and armalcolite containing approximately 1% ZrO₂ breaks down at about 1-2 kb lower pressure than Zr-free armalcolite. Figure 2 shows the stability of armalcolite prepared in equilibrium with metallic iron. No significant differences between this and the Zr-free armalcolite of figure 1 are apparent. This may be due to the limits of precision of the X-ray analysis used in this study, and possibly microprobe analysis of the resulting phases would uncover differences.

INTERPRETATION

Armalcolite has been interpreted as a primary liquidus phase in lunar rocks, and Akimoto et al. (1970) found that this liquidus is about 1200°C at 1 atm. sloping to about 1500°C at 40 kb. for one armalcolite bearing rock from Apollo 11. Figure 3 shows the P-T liquidus curve determined by Akimoto and its intersection with the extrapolation of my curves for synthetic armalcolite stability determined at lower temperature. This
indicates that rocks containing armalcolite of 0.5 Fe/Fe+Mg ratio must have crystallized in the region bounded by the whole rock liquidus and the curve separating the 3- and 2-phase regions, which corresponds to a maximum depth on the moon of about 350 km. Further, single-phase armalcolite not coexisting with ilmenite must have crystallized below the curve separating the 1- and 3-phase regions. Crystallization may, of course, have taken place at much lower pressures, and ilmenite plus rutile could be formed by reactions other than the breakdown of armalcolite, but these pressures should be the upper limit for the pressure at the time of crystallization of armalcolite-bearing lunar rocks.

Zirconium-bearing armalcolite consistently breaks down at lower pressure than Zr-free armalcolite. This effect is less than 1 kb. at 1200°C, and greater zirconia content would presumably increase this effect. This places an upper boundary on the pressure at the time of formation of the high-alumina non-mare basalts. This data is consistent with a derivation of these highly felspathic basalts from within the lunar crust; i.e., under less pressure than the more deeply derived mare basalts, although it certainly does not prove this interpretation.

Further study is necessary to determine the distribution
of Fe, Mg, Ti, and Zr in the armalcolite breakdown assemblage, and to see how armalcolite stability is influenced by variations in oxygen fugacity.
Figure 1: P-T stability for armalcolite \(((\text{Fe}_{0.5}\text{Mg}_{0.5})\text{Ti}_2\text{O}_5)\) and armalcolite containing about 1\% \text{ZrO}_2.

1 phase = arm.
2 phases = rut. + ilm.
3 phases = rut. + ilm. + arm.

Piston-cylinder apparatus in Ag_{60}Pd_{40} capsules.
$= Zr$-ARMALCOLITE

$= Zr$-FREE ARMALCOLITE

- $P$ (Kb)
- $T$ (°C)

- $2$ PHASES
- $3$ PHASES
- $1$ PHASE
Figure 2: P-T stability of armalcolite prepared in equilibrium with metallic iron. 2-phase starting material (arm. + ilm.)
Fe-RICH ARMALCOLITE

- 2 PHASES (RUT.+ILM)
- 3 PHASES (RUT.+ILM.+ARM.)
- 2 PHASES (ARM.+ILM.)

P (Kb) vs. T(°C)

Graph shows the relationship between pressure (P) and temperature (T) with different phases of Fe-RICH ARMALCOLITE.
Figure 3: Comparison of P-T stability of synthetic armalcolite \((\text{Fe}_{0.5}\text{Mg}_{0.5})\text{Ti}_2\text{O}_5\) with whole rock liquidus curve determined by Akimoto et al. (1970) for an armalcolite-containing Apollo 11 rock.
REFERENCES


Hartzman, M.J., and D.H. Lindsley (1973) The Armalcolite Join (FeTi_2O_5-MgTi_2O_5) with and without Excess Fe^0: Indirect Evidence for Ti^{3+} on the Moon. (abs.) GSA Abstracts with Programs, 653.