

PARTITION COEFFICIENTS FOR FE, MG, TI AND K BETWEEN PLAGIOCLASE AND BASALT: IMPLICATIONS FOR ANORTHOSITES; W C Phinney NASA JSC, Houston TX 77058

The composition and fractionation trends of melts parental to calcic anorthosites have presented a longstanding problem on Earth and a more recent one on the Moon. Because plagioclase is commonly the only unaltered, original cumulate phase in anorthosites, parent melt compositions must be estimated by use of partition coefficients (D's) in conjunction with analyses of minor components in plagioclase. Because the very low values of Fe in plagioclase of lunar anorthosites when used with a D of .03 [1] predict an Fe content in the equilibrium melts that is anomalously low by a factor of 3, or more, one must question the accuracy of D and/or the interpretation of Fe analyses in lunar anorthosites [2]. Recent determinations of this D for terrestrial calcic anorthosites indicate a value of .04 [3]. Because Fe^{3+} is more readily accepted into the plagioclase structure than Fe^{2+} it is expected that D will vary with $f\text{O}_2$ and the value for terrestrial conditions should be higher than that for lunar conditions. In order to check the magnitude of the variation of D for Fe we undertook experimental studies to determine its value as a function of $f\text{O}_2$ for appropriate melt compositions.

Experiments conducted in 1 atm gas-mixing (CO-CO_2) furnaces using powdered matrices of moderately Fe-rich natural tholeiites as starting materials have shown that the first phase on the liquidus, at the $f\text{O}_2$ of the QFM buffer, is plagioclase, followed by cpx and/or olivine [4]. Plagioclase of composition An80-85 precipitates during the initial 5-10% crystallization from a liquidus temperature of $\sim 1215^\circ\text{C}$ down to $\sim 1175^\circ\text{C}$. Because the D for Fe may vary not only as a function of $f\text{O}_2$ but also as a function of temperature, melt composition, other coprecipitating phases, and, possibly, cooling rate, we conducted all of our experiments at the same temperature using the same tholeiitic basalt, BRN1B (Table 1), as starting material (it produces only An80-85 plagioclase for the first few tens of degrees below the liquidus). In order to thoroughly melt the starting material, samples were held for 4 hours at 1250°C which is well above the liquidus. The temperature was then dropped to 1000° for 12 hours to nucleate the plagioclase as well as other phases. The temperature was then raised to 1225° for 24 hours. This is about 10° above the liquidus and should melt most of the nuclei except possibly a few plagioclases. The few remaining plagioclase nuclei should grow to relatively large grains during the ensuing slow cooling of 1° per hour to the run temperature of 1180° ($\sim 10^\circ$ above the appearance of the next phase) where it is held for 4 days, or more, before being quenched. The $f\text{O}_2$ was controlled by mixtures of CO and CO_2 and monitored by zirconia cells using the method described by [5]. Control of $f\text{O}_2$ by this method at log values > -5.5 becomes very poor. Consequently, runs at log $f\text{O}_2 > -5$ were made with pure gases that did not require continual adjustment of flow from two sources. Two runs were made with a constant flow of pure CO_2 through the assembly (Fig.1). One was held at its final crystallization temperature of 1180° for 140 hours after reducing the number of nuclei at 1235° for 24 hours. In contrast, the other was held at 1180° for only 29 hours after reducing the number of nuclei at 1245° for 24 hours. The consistency of the D values after such different treatments is reassuring. Two runs were made with a constant flow of air through the assembly (Fig.1). Electron microprobe analyses of the resulting plagioclases and coexisting glasses were used to calculate the distribution coefficients. Only interiors of grains larger than $80\mu\text{m}$ were used for calculations of D to avoid interference effects. Because analyses of Ti, Mg and K were accomplished routinely, D's for these elements were also calculated.

The resulting coefficients for Ti, Mg and K are shown in Table 1 and for Fe in Fig.1. Plagioclase and glass are the only phases in the charges at log $f\text{O}_2 < -6$. At log values > -6 a series of Fe-rich spinels appear on the liquidus prior to formation of plagioclase. Volatilization of Na can be demonstrated during most of the runs. The starting material for all runs contained 1.90% Na_2O . Glasses resulting from initial melting of the charge at 1250° for 4 hours at log $f\text{O}_2$ of -9 and 5 hours at log $f\text{O}_2$ of -12 contained 1.67 and 1.48% Na_2O , respectively. Generally the final products of the charges which were initially melted at 1250° for 4 hours and run at intermediate $f\text{O}_2$ contain between 1.5 and 1.7% Na_2O in the glass and 2.2 to 2.3% in the plagioclase (An78.0-79.5) which makes up 10 to 15% of the charge by volume. Calculation of the total Na_2O in these runs equals 1.65 to 1.70%, i.e., 10-15% loss from the starting material. At low log $f\text{O}_2$, however, there is a greater loss of Na and an increase in the An values of plagioclase. Identical run lengths and temperatures at log $f\text{O}_2$ of 10^{-11} , or less, produce glasses with 1.0 to 1.1% Na_2O and plagioclases with 1.9 to 2.1% (An80.5-82.5). To evaluate the effects on D of cooling rate, runs were made at similar $f\text{O}_2$ (log=-7.6) at cooling rates of 0.1, 0.5, 1.0, 5.0 and 10 degrees per hour while maintaining all other run conditions at normal values. With the exception of the fastest cooling rate of 10° per hour all of the resulting D's for FeO_T were essentially identical at 0.065 to 0.067. The fastest cooling rate apparently excluded some Fe from the plagioclase and produced a D for FeO_T of 0.061. For TiO_2 there appears to be an effect from cooling rates. At 5 and 10° per hour the D is 0.033, at 1° per hour it is 0.030, and at 0.5 and 0.1° per hour it is 0.028. For MgO the D remains essentially the same for all

cooling rates, 0.042 to 0.044. For K_2O there may be a slight effect but not enough to be definitely outside the limits of experimental error, all values are between 0.204 and 0.211 except that for the slowest cooling rate which produces a value of 0.189.

At $\log fO_2 < -10$ the D for FeO_T remains nearly constant at about 0.030 as Fe^{2+} is essentially the only species of Fe present. At $\log fO_2$ of -9.5, as Fe^{3+} begins to form in appreciable amounts, D begins to increase slightly and reaches a value of about .04 at the QFM buffer. At higher fO_2 the D changes rapidly in a linear fashion from about 0.04 to 0.36 in air. At some higher value of fO_2 the melt should contain essentially all Fe as Fe^{3+} and the curve of Fig.1 should again become vertical at a nearly constant higher value of D but in our runs with air the melt still contains substantial amounts of Fe^{2+} . In runs conducted by [1] in Fe capsules, D was determined as 0.033, in good agreement with our values at low fO_2 . [3] found the average value of D for natural megacryst-matrix pairs in tholeiitic basalts to be 0.042 to 0.043, in good agreement with the experimental value of 0.044 at the QFM buffer which is a generally accepted fO_2 for tholeiitic basalts. [3] analyzed 17 calcic plagioclases from the BVL anorthosite for FeO_T by electron microprobe. For their average equilibrium melt to match the average value of 13.07% FeO_T for 13 coeval tholeiitic basalts requires a D of $\sim .04$ in good agreement with the value at the QFM buffer. The experimentally determined D 's for TiO_2 , MgO and K_2O were used with microprobe analyses of the 17 BVL plagioclases to predict concentrations in the equilibrium melts of the BVL plagioclases. For K_2O the predicted melts are in excellent agreement with the coeval basalts, for TiO_2 the experimental D produces melts that are low by a factor of 2, and for MgO the predicted melts are low by factors of 3 to 10. It has already been shown that the D for Ti may decrease with slower cooling which would bring the predicted value closer to the basalts. Apparently Mg is too mobile for predicting melts from plagioclase that was subjected to the greenschist metamorphism of the BVL anorthosite.

While lunar melts in equilibrium with initial anorthosite formation [6] are surely much lower in Na than terrestrial tholeiites, the other major components are not substantially different from the starting composition in this work. Thus, the pattern of variation for the D of Fe with fO_2 should be very similar to and in the same range of temperature as our experimental work. The question is whether the absolute values of D decrease by the necessary factors of 2 to 3 from the An80 plagioclase of the experiments to the An95-98 plagioclase of lunar anorthosites. In terrestrial basalts there is evidence for a small decrease of $\sim 15\%$ in the D for Fe as An-content increases over this range [2]. Furthermore, plagioclases in the An90's from lunar mare basalts display D 's for Fe in the vicinity of .03, in agreement with our experiments. Therefore, a different partition coefficient for Fe does not provide the explanation for low predicted FeO values in equilibrium melts for lunar anorthosites. Similar arguments and conclusions can be made for Mg whose content in plagioclase of lunar anorthosites predicts equilibrium melts that contain 4 to 10 times less MgO than expected. For Mg the variable of fO_2 should play no role and the maximum allowable variation in D is a factor of 2 [3]. Thus, the low contents of Fe and Mg in plagioclase of lunar anorthosite must result from a non-igneous process; probably redistribution of components as the anorthosites underwent recrystallization during high temperature metamorphism in the early lunar crust [2]. Such subsolidus reequilibration would render rather futile any attempts to utilize the Fe and Mg contents of plagioclase in lunar anorthosites for interpretation of igneous processes. The experimentally determined D 's for Ti and K would predict equilibrium melts for lunar anorthosites with 0.1 to 0.3% TiO_2 and 0.03 to 0.06% K_2O .

References: [1]Longhi et al (1976) Proc Lunar Sci Conf 7th, p1281-1300. [2]Phinney (1991) Proc Lunar Planet Sci Conf 21, in press. [3]Phinney & Morrison (1990) Geoch Cosmoch Acta, 54, p1639-1654. [4]Morrison et al (1985) Geol Assoc Can, Ann Mtg Prog Abstr, p103; Grant (1978) unpub MS thesis, Queens Univ, Kingston, Ont. [5]Williams & Mullins (1976) NASA TMX58167. [6]Longhi (1978) Proc Lunar Planet Sci Conf 9, p285-306; Warren & Wasson (1979) Proc Lunar Planet Sci Conf 10, p2051-2083.

	BRN1B	Avg D
SiO_2	49.79	
TiO_2	0.98	0.028 \pm 0.004 (30 runs)
Al_2O_3	15.29	
FeO_T	12.30	0.03 to 0.36
MnO	0.22	
MgO	6.63	0.043 \pm 0.003 (30 runs)
CaO	12.30	
Na_2O	1.89	
K_2O	0.29	0.20 \pm 0.02 (30 runs)

