
Introduction: A number of recent studies have been directed at determining the petrogenetic relationship of KREEP-rich lunar lithologies, such as lunar granites and quartz monzodiorite (QMD), to one another and to some original "ur"KREEP [1,2,3,4]. It has been proposed that KREEP or urKREEP is the residuum formed by extreme fractionation of the lunar magma ocean, but pristine KREEP basalts such as 15386 have an mg* which is apparently much too high for such a residual melt [5]. Emphasizing this point, Warren [3] has suggested that the more evolved QMD may be used to represent urKREEP. However, the petrogenesis of QMD is not well known; previous work indicated that fractionation of a KREEP basalt composition at 1 atm produces a QMD residual melt composition just before becoming immiscible [6], but it is not known if this same process occurred at depth. It is generally accepted that immiscibility was involved in the genesis of lunar granites in the near-surface environment; it has not been established whether immiscibility is stable at the base of the lunar crust (3 kbar). Two recent discoveries bear on the general problem: 1) the ages of lunar granites have been shown to extend from 4.4 to 3.9 Ga [7], and 2) modeling indicates that crystal cumulates of the lunar magma ocean would have overturned on a short time scale tending to mitigate against the strong decrease in the mg* of the late stage cumulates [8]. These developments give additional potential importance to magmas such as the A15 KREEP basalt, 15386. Accordingly, experiments have been done at 3 kbar in order to determine what melt compositions are produced by fractionation A15 KREEP at the base of the lunar crust in contrast to those produced at the surface. Are QMD-like compositions produced by fractional crystallization at the base of the crust, and can immiscibility occur at this depth?

Methods: Experiments on the 15386 composition were initially done at 1 atm using an oxide powder prepared and pre-reduced to an fo2 equal to the M-W buffer [9]. Using Mo foil as a container to prevent sample oxidation inside sealed silica glass tubes, crystallization and melting experiments were performed to determine the phase equilibria and residual liquid compositions produced by fractionation of KREEP basalt at near-surface (~1 atm) conditions. The charge was suspended in a furnace and held at near liquidus temperature (1180-1200°C) for several hours to fuse the powder, dropped at ~3°C/hr to the experimental temperature, held for 48-230 hours (longer for lower T), then removed and quenched in water. Experiments were conducted over a temperature range from 1185°C (super-liquidus) to 1026°C (near-solidus), and were controlled to ±1-2°C. The 3 Kb experiments used chips of sample from 1 atm experiments at different temperature depending on the desired crystallinity of the starting material. These chips were run in Pt tubes surrounded by graphite to prevent Fe-loss to the container and to maintain the pre-set low oxidation state of the sample. The 3 kb experiments were performed using an internally heated pressure vessel, with Ar gas as the pressure medium. Since these experiments began with partially to strongly crystallized samples approximating the crystallinity of the equilibrium 3 kb state, they were put in directly at the final temperature and were run for times ranging from 4 hours at 1200 °C to 4 days at 1040 °C. The samples were then sectioned and examined by optical microscope and electron microprobe to determine the phases present and their composition.

Results: The 1 Atm liquidus temperature of 15386 basalt is tightly constrained by experiments run at 1180°, and 1175°C, both of which yield glass only. At 1172°C, immediately below the liquidus, the melt (mg*=55) is apparently multisaturated, containing crystals of low-Ca pyroxene (En65Fs24Wo8), plagioclase (An59-77) and olivine (Fo79-80); the olivine is in reaction relationship with the pyroxene. At 1140°C, with ~11% crystallization, the only crystals in contact with the melt are px+plag, though a core of olivine is present in one pyroxene. From 1140° to 1080°C, the phases present are low-Ca px+plag+glass, and melt mg* drops from 47 to 34. Ilmenite saturation is reached at 1064°C, when the melt is 55-60% crystallized (although a few minute ilmenite crystals occur in a couple of the higher temperature experiments, they appear to be quench crystals). With further crystallization beyond ilmenite saturation, Ti and Fe contents in the residual melt start to decrease. At 1039°C, with approximately 70% crystallization and mg*=19, the melt becomes immiscible, separating into high-FeO and high-SiO2 compositions [1,10]. The 1039°C charge contains large (up to 100μm), euhedral tridymite crystals, in addition to px+plag+il+liquids. An experiment at 1026°C produced the same phases, plus a phosphate. The maﬁc glass in these low temperature experiments showed signiﬁcant compositional variation; presumably this is due to observed incomplete immiscible melt separation, but it may also be indicate poor communication between melt pools in these crystal-choked charges.
Results from crystallization and melting experiments carried out at 3 kbar pressure (equivalent to conditions at the base of the lunar crust) indicate some interesting differences compared to the low pressure data. The same general sequence of phases crystallize at 3 kbar and 1 atm: first plag+Io-Ca px, joined by ilmenite, tridymite and whitlockite as crystallization proceeds. The olivine field is not encountered by this composition at 3 kbar. Another difference is that a Ca-rich pyroxene crystallizes at 1150 °C in the 3 kbar experiments and is not present at 1 atm. The 3 kbar liquid line of descent defined by 8 experiments in the range 1200 to 1040 °C, is characterized by nearly constant FeO, CaO and SiO2, and a decreasing MgO (5.0 to <1 wt %). TiO2 increases from 2.3 to 5.6 wt % at 1125 °C where ilmenite becomes stable. At this point TiO2, and to a lesser extent FeO, begin to decrease in the residual melt with additional crystallization, and SiO2 begins to increase slightly from about 51-52 wt%. Tridymite begins to crystallize at 1100 °C, and whitlockite is present at 1075 °C. This combination of crystallizing phases yield a melt with 54 wt% SiO2 at 1080°C, 56 wt% at 1060, and 68 wt% at 1040°C. Silicate liquid immiscibility is not encountered in any of these experiments. Further, immiscible melts disappeared from a 1039°C, 1 atm sample when it was subjected to 3 kbar and 1060°C even though 30 % melt remained and a silica polymorph is still stable. An experiment on a sample of 15386 with the mg* reduced from 56 to 40 resulted in significantly lower liquidus temperatures, however, and immiscibility is present in this 3 kbar experiment at 1040 °C.

Discussion and Conclusions: The presence of olivine on the low pressure liquidus of the 15386 composition, followed closely by low-Ca pyroxene (in reaction) and plagioclase indicates that olivine could have been present in the source region. At near-surface conditions, our experiments demonstrate that fractionation of 15386-type KREEP basalt follows the path: (1) initial olivine crystallization, (2) crystallization of low-Ca pyroxene+plagioclase (and reacting out of olivine) producing FeO-enriched residual melts with little SiO2 build-up, (3) ilmenite crystallization at ~1064°C, resulting in moderate SiO2 enrichment, and (4) liquid immiscibility producing FeO-rich basaltic and granitic melts at T<1040°C. At base-of-the-crust pressure (3 kbar), the 15386 melt follows a similar crystal fractionation path. However, while px+plag+il crystallization produce a range of QMD-like, silica-bearing melts at 1060°C, and even a granitic-like melt at 1040, there is no liquid immiscibility. The increased pressure apparently increases the solidus temperature far more than it raises the critical point of the miscibility gap. An experiment on a more FeO-rich A15 KREEP basalt composition (mg* = 40) indicates that silicate liquid immiscibility is stable at 3 kbar; residual melts of 15386 KREEP simply crystallize by the miscibility gap before reaching a sufficiently low temperature while otherwise equivalent residual melts with a lower mg* do become immiscible.

The above experiments have shown that within the range of pressures of the lunar crust, a liquid of KREEP basalt composition will evolve through crystallization to form QMD and granite. At low pressures the granites form by silicate liquid immiscibility; at 3 kbar they may form by continuous fractional crystallization. Thus, KREEP basalt can satisfy this fundamental constraint for an ur-KREEP. KREEP basalt is generally considered a derivative of ur-KREEP, however, because the relatively high mg* characterizing these basalts is incompatible with calculations which suggest urKREEP was close to mg* = 0 [3,4]. However, the recent models of overturn in the cooling lunar magmasphere due to gravitational instability [11] may provide the means for increasing the mg* of ur-KREEP through interaction with more Mg-rich materials brought up from depth. Model ages for KREEP-rich lithologies indicate that KREEP lithologies, including lunar granites and KREEP basalts, may have existed as early as 4.3 Ga [12,13], constraining these processes to a time early in lunar history. This is consistent with crystallization ages of lunar granites which range from 4.4 to 3.9 Ga [7].