Two major basalt types were recognized in numerous TiO$_2$-rich basalt samples collected from the Apollo 17 landing site: 1) plagioclase poikilitic ilmenite basalt and 2) olivine porphyritic ilmenite basalt. The two basalt types are characterized by two distinct paragenetic sequences involving armalcolite, ilmenite, and pyroxenes (1). Experimental phase relation studies under controlled f$_{O_2}$ and cooling rate indicate that the two crystallization sequences are indeed dependent on f$_{O_2}$ (6). Direct measurements of f$_{O_2}$ of two basalts belonging to the two basalt types revealed slightly different f$_{O_2}$ values for the two rocks (4). $^{39}$Ar-$^{40}$Ar age determination of several samples of the two TiO$_2$-rich basalt types indicate a distinct age difference of 80 m.y. (5). Olivine porphyritic ilmenite basalts are older than plagioclase poikilitic ilmenite basalts. These results are suggestive of various source regions for the two basalt types. The crystallization sequence in the early cooling history is identical in both types with chromian ulvöspinel on the liquidus followed by olivine and then armalcolite with falling temperature. In plagioclase poikilitic basalts armalcolite is followed by pyroxene ilmenite and plagioclase whereas in olivine porphyritic basalts armalcolite is followed by ilmenite, pyroxene, and plagioclase. Different values of f$_{O_2}$ during crystallization of the two basaltic liquids should not only influence the paragenetic sequence but also chemistry of the early crystallizing phases.

We have carried out a systematic chemical study of chromian ulvöspinel in various samples representing the two major basalt types with the electron microprobe (70017, 70035, 70215, 74242, 19). Our main aim was to investigate the influence of f$_{O_2}$ on 1) the chemistry of liquidus phases crystallized from liquids of almost the same composition but cooled at different f$_{O_2}$ 2) compositional zonational trends of ulvöspinel in the two basalt types. Chemistry of spinels in plagioclase poikilitic basalts (triangles) and olivine porphyritic basalts (circles) is shown in Fig.1. Our investigations indicate a bimodal distribution of spinel compositions in the two basalt types. Two distinct features distinguish chromian ulvöspinels in plagioclase poikilitic ilmenite basalts from their counterparts in olivine porphyritic ilmenite basalts: 1) Both initial FFM and TiO$_2$/TiO$_2$+$\text{Cr}_2\text{O}_3$+$\text{Al}_2\text{O}_3$ ratios in spinels in plagioclase poikilitic basalts are distinctly lower than the initial ratios of spinels in olivine porphyritic basalts. Initial FFM ratio of spinels in plagioclase poikilitic basalts vary between 0.79 and 0.90 whereas the initial ratios in spinels in olivine porphyritic basalts vary between 0.89 and 0.98 (Fig.1). TiO$_2$/TiO$_2$+$\text{Cr}_2\text{O}_3$+$\text{Al}_2\text{O}_3$ ratios for spinels in plagioclase poikilitic basalts range from 0.30 to 0.45 and for spinels in olivine porphyritic basalts from 0.40 to 0.57. 2) $\text{Cr}_2\text{O}_3$/($\text{Cr}_2\text{O}_3$+$\text{Al}_2\text{O}_3$) ratios for spinels in plagioclase poikilitic ilmenite basalts are lower than the ratios for counterparts in olivine porphyritic basalts. $\text{Cr}_2\text{O}_3$/($\text{Cr}_2\text{O}_3$+$\text{Al}_2\text{O}_3$) ratios for spinels in plagioclase poikilitic basalts vary between 0.62 and 0.78 whereas the ratio for spinels in olivine porphyritic basalts vary between 0.71 and 0.84. The distribution of the spinel compositions in both rock types (Fig.1 rectangular face of the spinel prism) would conceive a continuous trend with increasing
FFM and TiO₂/TiO₂+Cr₂O₃+Al₂O₃ ratios. However, this is not the case since plagioclase-poikilitic basalts are usually younger than olivine porphyritic basalts (5). We interpret the chemical bimodality as a strong evidence for crystallization of plagioclase-poikilitic basalts under more reducing conditions than olivine porphyritic basalts. The lower the oxygen fugacity the lower the FeO content of the cooling basaltic liquid will be due to precipitation of FeO metal from the liquid. This would decrease the FFM ratio of the cooling liquid and hence the FFM ratio of the crystallizing chromian ulvöspinel. Subsolidus reduction reactions of chromian ulvöspinel in plagioclase-poikilitic basalts are also much more pronounced and much more abundant than in olivine porphyritic basalts. These results are in excellent agreement with the experimental phase relation studies and measurements of fO₂ of two representative basalts of the two major types (4, 6).

El Goresy et al. (2) demonstrated that zoning in spinels is sensitive to compositional changes in the cooling basaltic liquid. Several olivine porphyritic basalts were found to contain numerous ulvöspinel grains with a gradational but reversed zoning showing increase of chromite from core to rim. Compositional variation trends in individual grains in sample 70215,159 were measured and the results are shown in Fig. 2. The variation trend is characterized by the following relationships: slight decrease in TiO₂/TiO₂+Cr₂O₃+Al₂O₃ (initial ratio 0.47, ratio at terminating stage 0.39), decrease in Cr₂O₃/Cr₂O₃+Al₂O₃ reversing at the terminating stage, increase in FFM ratio, and decrease in V₂O₃ content. This trend is indicative of simultaneous build-up of Cr₂O₃ and depletion in TiO₂. This trend is suggestive of first nucleation of ilmenite (TiO₂ depletion) and growth of spinel before pyroxene crystallization. An alternative mechanism for the enrichment of Cr₂O₃ may be the reaction between chromian ulvöspinel and armalcolite to ilmenite. This reaction will cause an enrichment of the melt in Cr₂O₃. Spinel layers precipitating after termination of this reaction will be higher in chromite molecule. This mechanism gained strong support through recent experimental investigations in the system FeO-Cr₂O₃-TiO₂ under controlled fO₂ (3). This reversed zoning is also characterized by a spectacular cationic Cr/Al substitutional trend. This trend is distinct from the trend observed in chromian ulvöspinels in TiO₂-poor basalts. In Ti-poor basalts the trend starts at a Cr:Al ratio of 3:1 and changes continuously to a ratio lower than 2:1 (2). In olivine porphyritic basalt 70215,159 the trend starts at a Cr:Al ratio of 2:1, reverses its direction towards higher Cr:Al ratio between 3:1 and 2:1 (Fig. 3). This sudden change towards higher Cr:Al ratio is indicative of change of that ratio in the cooling liquid. Perhaps, this signals the first precipitation of plagioclase before any nucleation of pyroxenes took place. This interpretation is in excellent agreement with the results of Usselman & Lofgren (6).

REFERENCES
APOLLO 17 TiO₂-RICH BASALTS......

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Fig. 1

Fig. 2

Fig. 3

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