Taking Off the Potassium Coat: A New Hypothesis for VHK Petrogenesis.

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Introduction: Among the polymict breccias returned from the Fra Mauro region by the Apollo 14 mission was a new basalt type, very high potassium (VHK) basalt, which was first described in 1985 [1] although its existence was noted 5 years earlier [2]. Six VHK mare basalts, samples were found to be nearly identical to Apollo 14 high-Al (HA) basalts with the exception of elevated abundances of K2O (>0.5 wt%), K2O/Na2O >1, and K/Na ratios between 500 and 1300 [1].

The enrichment of K that distinguishes the VHKs from other mare basalts has proved difficult in constructing a petrogenetic model and identifying the source of the enrichment. Using whole rock data, Shervais et al. [1] hypothesized the formation of VHK basalts through the variable lunar granite assimilation by a HA mare basaltic magma. The variations in texture between the samples was attributed to different cooling rates within a single lava flow. Goodrich et al. [3] discovered 2 VHK basalts in breccia 14304 with notably lower K/Na ratios of between 580 and 700, suggesting a transitional composition between VHK and Apollo 14 HA basalts. The lower K abundances along with the coincidence of breccia 14305 and 14304 having been collected in the same weigh bag suggested that all of the VHK samples were part of the same flow and variations among compositions were due to modal heterogeneity. An additional hypothesis for the formation of VHK basalts through the partial melting of a HA basalt source that was metasomatized and enriched in K, Rb, and Ba was also proposed [3].

With the discovery of 5 samples in breccia 14303, Neal et al. [4] used whole rock data to construct an assimilation and fractional crystallization (AFC) model that encompassed all known VHK samples. The model posited that a primitive HA basalt magma variably assimilated lunar granite while crystallizing the minerals in the sequence defined by petrography [4]. Samples from breccia 14304 are from a more evolved HA basalt magma with KREEP assimilation replacing granite in the AFC process. With two different sources now needed for VHK generation, VHKs were now linked to at least two distinct lava flows [4].

In a second study, Neal et al. [5,6] analyzed an additional 7 VHKs from breccias 14303 and 14304 and identified the K rich glass as having the composition of the residual magma, however an external source of K was needed to generate the high K abundances present in the glass as it could not be produced by fractional crystallization alone. VHK basalts were generated by at least 3 separate parental HA basalts assimilating granite, however variable granite assimilant compositions were needed. Three basalt flows at the Apollo 14 site were necessary to accommodate the modeling parameters.

After a respite in research on the petrogenesis of VHK basalts for 25 years, we are revisiting VHK samples with new analytical techniques. Elemental maps measured by electron probe microanalysis (EPMA) are used to provide additional clues into the distribution of K within the samples. Major element and trace element abundances in plagioclase are measured using EPMA and Laser Ablation ICP-MS (LA-ICP-MS), respectively. Here we present a new hypothesis for the enrichment of K in otherwise HA basalts.

Figure 1. Elemental map of VHK 14304,177. Pink=Ti, white=Al, yellow=Ca, cyan=K, blue=Si, green=Mg, and red=Fe. Apatite grains are shown in yellow and K rich glass in cyan. Scale bar is equivalent to 1mm. Color composite was created using ImageJ macro for Mineral False Color Maps [7].

Samples and Methods: Seven samples from breccia 14304 and 1 sample from breccia 14305 are investigated for this study. The VHK basalts range from granulated to coarse grained. Euhedral to subhedral plagioclase crystals from 0.25 to 1mm long are co-
mon in predominantly ophitic to subophitic texture. Olivine is either not present or present as cores to pyroxene crystals and as individual grains. Interstitial K-rich glass is found in varying abundance between the samples. K-felspar is an interstitial phase.

Major element analyses, backscatter electron (BSE) images and elemental maps were collected on a JEOL JXA-8200 electron microprobe at Washington University in St. Louis. Analyses were collected using a 3 μm beam, accelerating voltage of 15 kV and a probe current of ~25 nA. Trace element compositions of plagioclase crystals were collected using a New Wave UP-213 UV laser ablation system with a ThermoFinnigan Element 2 high-resolution magnetic sector ICP-MS at the University of Notre Dame. A laser frequency of 4 Hz, pulse energy of 0.07 mJ/pulse, and a spot size of 30 microns in diameter were used. Calcium measured by EPMA was used as an internal standard for each LA-ICP-MS spot analysis. The NIST 612 glass was used as an external calibration standard. Data was exported in ASCII format for reduction by Glitter® software. All laser ablation analyses were collected using time-resolved mode and during data reduction the background and data signals were selected visually to ensure that the best signals were measured. Detection limits were better then 0.2 ppm for La, Ce, Rb, Nb, Eu, Tb, Dy, and better then 0.3 ppm for Sm, Gd, and Ba. Sr and Nd had detection limits of 0.9 and 0.5 ppm respectively. Partition coefficients were used to calculate equilibrium liquid compositions in order to trace the evolution of the remaining liquid as the VHK basalts crystallized. They were calculated using plagioclase compositions of individual spot analysis collected with EPMA and using the method of Hui et al. [8].

**Results:** Element maps of VHK samples show a heterogenous distribution of K-rich phases that are interstitial of K enrichment among the samples (Fig. 1). K-rich overgrowths on plagioclase is most commonly seen while large K-rich interstitial areas are less common. Sample 14304, 177 shows interstitial K-rich areas and vein like structures running through pyroxene, plagioclase and apatite grains. In samples with attached fine grained breccia matrix, K is abundant in the matrix.

Plagioclase ranges in composition from An₈₁ to An₆₉, average of An₉₀.₃ and K-feldspar ranges from Or₇₅ to Or₉₃ with an average of Or₅₆. Zoning within plagioclase is not apparent in BSE images. EPMA point analyses support this observation. Olivine Fo composition ranges from Fo₄₆ to Fo₇₁ averaging Fo₆₀. Zoned olivines are rare. Apatite grains are present in 14304, 177 as shown in Figure 1. Equilibrium liquids of plagioclase crystals from VHK 14303, 245 were calculated using partition coefficients and the trace element concentrations of the plagioclases. Plagioclase equilibrium liquids calculated from sample 14303, 245 show similar enrichment of Sr vs La/Ce as HA group C basalts (figure 2).

**Discussion:** The previous model for VHK basalt petrogenesis was devised using whole rock data. Whole rock compositions represent an average of all the processes that have affected the rocks. The was the different phases relate to each other, as well as compositional zonations, give important petrogenetic clues that are lost in whole rock data. The quenched texture and varied distribution of K-rich areas suggests K enrichment was a secondary process unrelated to basalt petrogenesis. Here we hypothesize that the enrichment of K in otherwise HA basalts was impact generated. Given the textural relationship of the K-rich glass to the basaltic phases and the breccia matrix suggests it infiltrated the clasts after inclusion in the breccia. We suggest that after breccia formation it was covered in a hot impact melt sheet that melted the low melting point components, such as granite, also present in Apollo 14 breccias [9]. The k-rich impact melt infiltrated HA basalt clasts, preserving the basaltic texture, but altering the whole-rock chemistry. Without detailed textural and mineralogic studies, this evidence would not be available for interpretation


![Figure 2. Calculated Sr and La/Ce concentrations of melts equilibrated in plagioclase grains in VHK sample 14303, 245 (red circles) compared to plagioclase equilibrium liquids from HA Group A (blue triangles), Group B (green triangles), and Group C (purple triangles) basalts. HA data from Hui et al. [8]](image)