FLUORAPATITE NEEDLE MATS ON VESICLE WALLS IN APOLLO 15556 FROM FINAL-STAGE WATER-RICH LIQUIDS.

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Introduction: Apollo vesicular basalts are direct evidence of lunar magmatic volatiles. We examined vesicle walls in one such basalt, 15556, and have found interesting minerals on the vesicle walls. Discovery of copper sulfide ($Cu_{2-x}S$) was previously presented ([1] & paper in review). Here, we report interesting morphology and texture of apatite on the same vesicles where copper sulfide was discovered. Our manuscript of this finding is under review.

Methods: Pristine chips of Apollo 15556 were directly characterized using a ZEISS 1550VP field emission scanning electron microscope (FE-SEM). Samples were minimally processed with only carbon coating. The elemental compositions of minerals on vesicle walls were analyzed with an Oxford X-Max 80 mm^2 SDD Energy Dispersive Spectrometer (EDS) system attached to the SEM and quantified with an XPP correction procedure calibrated using Oxford factory internal standards.

To compare with apatite inside rock matrix, we characterized the petrographic context in polished sections (30 and 33) using the SEM and measured the chemistry of apatite using a field emission electron probe microanalyzer JEOL JXA-iHP200F.

Results: *Fluorapatite needles on vesicle walls:* We observed two occurrences of apatite needle mats on vesicle walls among four chips examined. These needle mats form linings extending from walls of holes in vesicle walls onto the vesicle walls. Long axes of these needles are aligned in patterns, suggesting flow around the hole (Figs. 1-3). The length of needles ranges from 2 to 26 µm and the width ranges from 0.3 to 3.2 µm. Most grains display large aspect ratios (length/width) of 8-21, whereas a few small ones are more equant of aspect ratios of 2-7. Apatite needles on the vesicle walls in both occurrences are free of any silicate glass or minerals, although the occurrence in Fig. 1 contains interstitial glass before the needles exist the hole, whereas the other occurrence contains ilmenite and zirconolite. SEM-EDS measurements suggest that these needles are fluorapatite.

Needle mats are not easily preserved in polished sections. We located a few occurrences in the polished sections and measured their chemistry. The best example in polished section shows fluorapatite just beneath vesicle walls intergrows with glass, silicate and oxide minerals (Fig. 4).

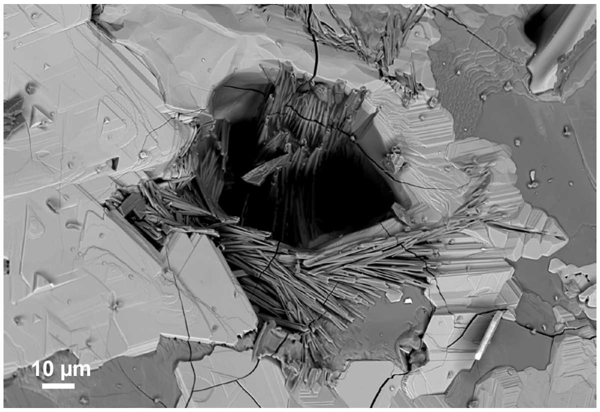

Fig. 1. BSE image showing apatite needle mat in a hole on a vesicle wall in Apollo 15556 Chip C3.

Fig. 2. Apatite needles inside the hole from Fig. 1 are embedded in Si-rich glass.

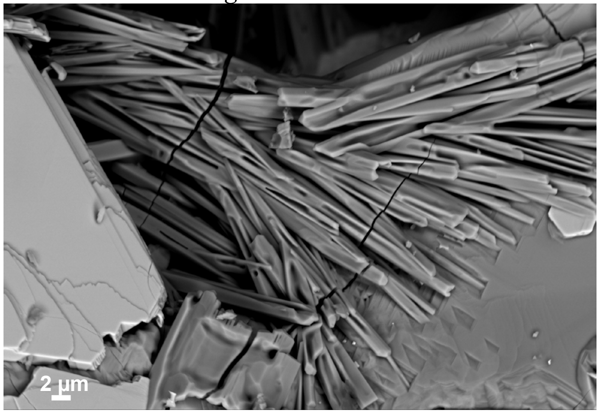

Fig. 3. Apatite needles on the vesicle wall in Fig. 1 are free of silicates.

Fluorapatite in the rock matrix: Fluorapatite in the rock matrix occurs in mesostasis regions. Some mesostasis regions show no clear association with vesicles (named “Rock Fap”). Some grains occur in mesostasis with small vesicles but whether they are linked to the larger round vesicles in the third dimension is unknown from the thin sections. These grains are named "Wall Fap?".

Fluorapatite Chemistry: Fluorapatite, regardless of its petrographic location, contains very low Cl contents. Fluorapatite needles on/near vesicle walls are more enriched in REE and depleted in F than those larger grains in mesostasis (Fig. 5). This indicates fluorapatite on/near vesicle wall is enriched in OH, to make up the anion charge balance. There are some overlaps in composition between fluorapatite near vesicles and those in mesostasis. Overall, the chemical variation of fluorapatite suggests a progressive enrichment of incompatible elements (REEs) and OH in the late stage melt by crystallization.

Discussion: Fluorapatite needle mats have never been reported previously in lunar samples. In previous studies of vug or vesicle walls, McKay et al. [2] observed individual, free-standing, euhedral, Cl-rich apatite grains in Apollo 14 breccias, which are more stubby and much larger (width of 12 µm and length up to ~50 µm) than those observed in 15556. McKay et al. [2] proposed these free-standing apatite grains were deposited by vapor.

However, vapor deposit cannot explain the texture and petrological association of fluorapatite needle mats in Apollo 15556. These needle mats coat the surface of vesicles and extend into the rock matrix beneath the vesicles. Beneath the vesicle wall, fluorapatite needles are either fully embedded in silicate glass (Fig. 1) or minerals (Fig. 4). The µm-sized zirconolite and ilmenite grains interstitial to fluorapatite needles are also unlikely to be deposited by vapor since Zr and Ti are refractory and non-volatile elements.

The 3D arrangement of fluorapatite needles indicates they were aligned by flowing melts or liquids. Considering lower pressure in vesicles, the melt/liquid likely flowed from inside the rock to the vesicle. The initial liquid is silicate melt based on the petrographic context beneath vesicle walls (Figs. 1&4). The silicate and mineral free nature and the high OH contents for fluorapatite needles on the vesicle wall indicate the final liquid/melt was silicate-poor and water-rich. Apatite needles, often with a hollow center, are products of non-equilibrium crystallization [3]. Collectively, we propose the fluorapatite needle mats on vesicle walls in Apollo 15556 formed by rapid precipitation in evolving melt from water-bearing silicate melt to silicate-poor water-rich liquid.

Experiments show needles formed without a water vapor phase are much elongated (length/width >20) that those with water vapor present (length/width >10) [3]. Aspect ratios of apatite needles in Apollo 15556 are generally <20, suggesting the final liquid possibly coexisted with a vapor phase if previous experiments [3] for terrestrial conditions apply. Nonetheless, the needle shapes and hollow centers are signs of non-equilibrium growth of apatite.

Vesicular basalt 15556 is located near the top of a lava flow [4] and likely exposed to the vacuum in the space at the late stage of the solidification [1]. When the late-stage liquid formed near the vesicles, they were pulled to the vesicle while apatite quickly grows from the cooling melt. Along its flow toward the vesicle wall, most silicates would have formed leaving the final liquid water-rich and silicate-poor as evidenced by nearly pure apatite needle mats on vesicle wall. The rare occurrence of these needle mats on vesicle walls indicates the water-rich final liquid is localized to places where mesostasis is in the proximity of vesicles.

References: [1] Liu, Y. et al. (2023) *86th MetSoc,* 6029. [2] McKay, D. S. et al. (1972) *PLSC, 3,* 739-752. [3] Wyllie, P. J. et al. (1962) *J. Petro.*, *3*, 238-243. [4] Gawronska, A.J. et al. (2021) *Icarus*, 388, 115216.

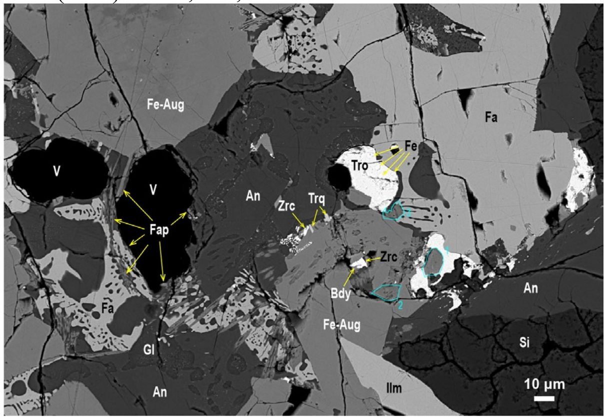

Fig. 4. *Arrangement of fluorapatite (Fap) in polished section 15556, 33 around vehicles (V), resembling the needle mats on vesicle walls. Phases: anorthite (An), baddeleyite (Bdy), fayalite (Fa), Fe-augite (Fe-Aug), Fe-metal (Fe), ilmenite (Ilm), K-Ba-rich glass (Gl), troilite (Tro), zirconolite (Zrc), tranquillityite (Trq), and a silica phase (Si).*

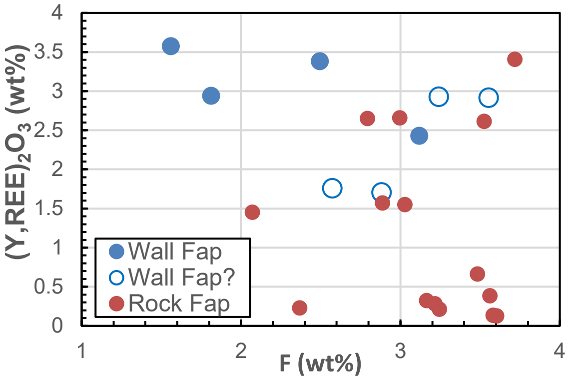

Fig. 5. Compositional difference between fluorapatite (Fap) on the wall and those in the rock matrix. Y-axis is the total abundances of Y_2O_3 and REE_2O_3 in wt%.