

The behavior of volatiles in mare basalts. An investigation of the mineralogy of linings in the vugs and vesicles in lunar basalt 12072. M. de Moor^{1,2,3}, C.K. Shearer^{2,3}, P.V. Burger², J.J. Papike^{2,3}, and P.P. Provencio². ¹OVSICORI-UNA, Heredia, Costa Rica, ²Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131 (cshearer@unm.edu), ³Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131

Introduction: Numerous studies over the last decade have illustrated the important role that H species and other volatiles play in lunar basalt petrogenesis and the evolution of the lunar mantle. [e.g. 1-3]. Characterizing the vapor-deposited mineralogy in vesicle and vugs from these basalts provides an alternative approach for understanding the composition and role of volatiles in lunar processes which is complimentary to previous investigations and may also be useful for understanding differences in volatiles between basalts and impact generated lithologies. Vesicles and vugs are produced during degassing and are common in several lithologies including mare basalt flows, impact melt sheets (e.g. impact melt breccias), and ejecta blankets (e.g. highly recrystallized breccias). In some of the mare basalts, vesicles represent >50% of the volume of a sample, with some as large as 5mm in diameter. Inter-connected, irregularly shaped vugs in basalts and impact lithologies can be >12mm along their long axis [4-6]. The mineralogy of these vesicle and vug wall minerals are highly variable [5-9] and have been described in varying degrees of detail. However, compositional data are limited on these minerals and there has never been a systematic comparison between the composition of melt- and vapor-deposited phases in lunar basalts. The mineralogy of vesicles from other extraterrestrial materials has not been explored extensively. The overarching objective of this study is to examine and characterize mineral assemblages in vesicles and vugs to deduce their origin (i.e. crystallization from melt or gas). Here we report on the initial results of this examination where we focus on olivine-bearing low-Ti mare basalt 12072.

Analytical approach: The analysis of vug minerals was accomplished with a combination of SEM-FIB, TEM/STEM/EFTEM, and EPMA. A FEI Quanta 3D Field Emission Gun FIB/SEM/EDS was used for the focused ion beam extraction of site-specific areas of the sample, scanning electron microscopy for imaging microtextures, and energy dispersive spectroscopy for identifying vug mineralogy. Large crystals of vug minerals (>100 μm) were extracted using tweezers after identification via SEM-FIB. EPMA were conducted using a JEOL JXA 8200 electron microprobe at UNM's Institute of Meteoritics and Department of Earth and Planetary Sciences.

SEM-FIB and EPMA imaging: Unprocessed vug walls were initially examined via SEM. Subsequent observation of sectioned portions of the vug walls, and

tweezer- and FIB-extracted mineral grains were conducted via SEM-FIB and EPMA.

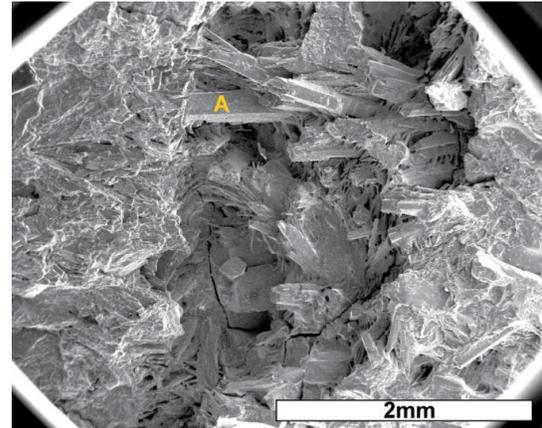


Figure 1. SEM-FIB examination of one of the vug walls in 12072. Most of the larger crystals growing into the vug from the wall are pyroxenes. This sample was mounted and sliced to intersect the vug (Fig. 2). The large pyroxene labeled "A" in the image was extracted and mounted (Fig. 3).

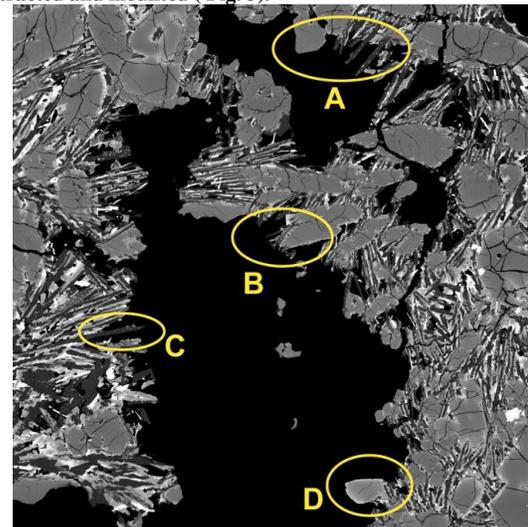


Figure 2. Compiled BSE image of polished mount of vug sample. Pyroxenes (A,B), plagioclase (A,B,C) and olivine (D) are observed to protrude from the vug walls into the vug, suggesting vapor-based deposition of these phases.

Initial SEM-FIB observations suggest that pyroxenes are the dominant silicate phase extending into the vug. Plagioclase needles and rare olivines also protrude into the vug. Nanometer-scale inclusions rich in P (likely phosphates) rim many of the silicate phases protruding into the vugs. Plagioclase needles exhibit an irregular distribution of Na which is not characteristic of magmatic plagioclase. Several of these textures suggest

that the silicates were either deposited from or reacted with a vapor.

Mineral Compositions: The compositions of pyroxenes that occur in the host basalt and extend into the vug (Fig. 1) are illustrated in Figure 4. Typically, clinopyroxenes that extend into the vugs exhibit Fe-rich rims ($Wo=10-20$ mol.%, $Fs=40-60$ mol.%, $En=30-50$ mol.%) compared to more Ca- and Mg-rich cores ($Wo=10-40$ mol.%, $Fs=20-40$ mol.%, $En=40-60$ mol.%) (Figs. 3 and 4). The large pyroxene extracted from the vug (Fig. 3) shows a similar range in compositions, including an Fe-rich rim, and irregular zoning of the core (Figs. 3 and 4). Micro-pyroxenes grown on plagioclase needles protruding into the vug are Fe-rich and have compositions similar to the rims of other pyroxenes but with slightly higher Ca content (Fig. 4). The pyroxene in the host basalt exhibits a broader compositional range including more extensive Fe enrichments (Fig. 4). Minor elements (TiO_2 , Cr_2O_3 , MnO , V_2O_5 , Na_2O) in vug pyroxenes and those crystallized from melt are very similar.

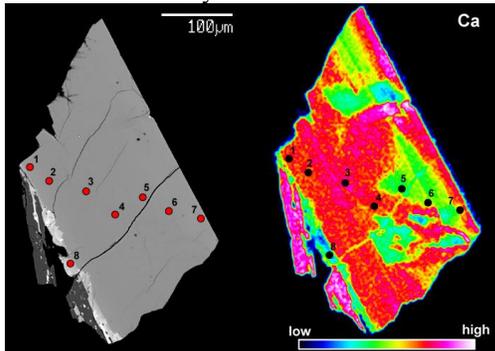


Figure 3. BSE image and Ca map of the vug pyroxene extracted from sample 12072 (labeled in Figure 1). Numbered dots indicate the locations of quantitative EPMA analyses shown in Figure 4.

Plagioclase needles protruding into the vugs range in composition between An_{93-88} and overlap with the range observed in plagioclase in the host basalt (An_{96-85}) [10].

Olivines in the host sample 12072 have a composition that ranges predominantly from Fo_{76-62} . These olivines will have Fe-rich rims with a composition that extends to Fo_{47} . An olivine crystal (D) protruding into the vug illustrated in Figure 2 exhibits Fe and P enrichment along the rim. However, the Mg# of this olivine overlaps with the range observed in the olivine from the host basalt.

Interpretation: This study represents the first systematic comparison between the composition of mineral phases in mare basalts and phases associated with vugs from the same basalt. The vug mineralogy has long been considered a product of vapor-phase crystallization [4-8]. However, it is interesting that phases thought to have precipitated from a “vapor” (based on strong textural evidence, see Figs. 1 and 2) have indistinguishable major and minor element compositions

from those precipitated from melt. We suggest two potential interpretations.

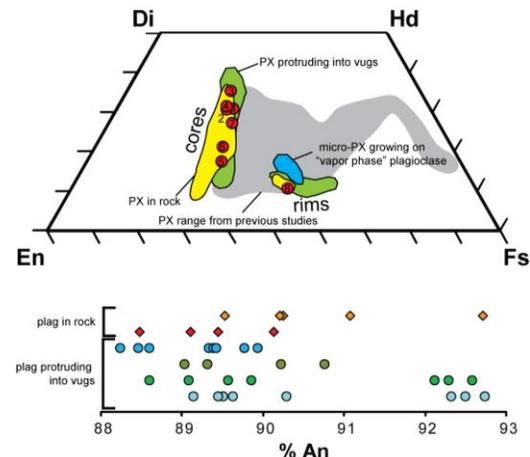


Figure 4. Pyroxene and plagioclase compositions comparing phases in the basalt to those interpreted to have precipitated from the vapor phase. “PX range from previous studies” from [10]

In a recent study, Zolenski et al. [11] examined the composition of phases precipitated from very high temperature ($>1000^{\circ}C$) volcanic gases at Erta Ale volcano. Minerals precipitated directly from the gas onto quartz glass tubing inserted into the fumarole included augite and plagioclase. Though no quantitative analyses of these phases were conducted, the compositions of gas condensates show that of the major rock-forming elements, Fe is one of the most enriched cations in high T volcanic gas (after Na and K), perhaps providing an explanation for the more Fe-rich compositions of some vapor phase pyroxenes and olivine in the lunar vugs. The mineral assemblage and texture of the vug deposits is consistent with precipitation from very high T magmatic gasses, in which the major elements are predominantly carried as silicate aerosols/melt droplets [11]. Alternatively, the major silicates may have crystallized extensively from a melt and only extended into the vug during its formation. In this case, the magmatic phases protruding into the vug may have reacted with the gas phase resulting in some of the micrometer to nanometer-scale mineral grains which rim the aforementioned protruding grains. Future study will examine the surfaces of the silicate phases extending into the vugs.

References: [1] Saal et al. (2008) *Nature*, 454(7201), 192-195. [2] McCubbin et al. (2010) *Proceedings of the National Academy of Sciences*, www.pnas.org/cgi/doi/10.1073/pnas.10066771107. [3] Hauri et al. (2011) *Science*, DOI: 10.1126/science.1204626. [4] Garvin et al., (1982) *Lunar Planet. Sci. XIII* 255-256. [5] Goldberg et al., (1976) *Proc. 7th Lunar Sci. Conf.* 1597-1613 [6] McKay et al., (1972) *Proc. Lunar Sci. Conf. 3rd*, 739-752. [7] Schmitt et al., (1970) *Proc. Apollo 11 Lunar Sci. Conf.* 1-54. [8] Skinner (1970) *Lunar Science III*, 710-711. [9] Papike et al., (1972) . In *The Apollo 15 Lunar Samples* (J.W. Chamberlain and C. Watkuns eds.) 144-145. [10] Neal et al., (1994) *Meteoritics* 29, 334-348. [11] Zelenski et al., (2013) *Chem Geol*, 357, 95-116.