SILICA POLYMORPHS IN LUNAR GRANITE. Stephen. M. Seddio, Alian Wang, Randy L. Korotev, Bradley L. Jolliff. Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri 63130 (sseddio@levee.wustl.edu).

Introduction: Lunar granite and felsite samples largely consist of granophyric intergrowths of silica and K-feldspar. The identification of the silica polymorph present in the granophyre can clarify the petrogenesis of the lunar granites. Robinson and Taylor [1] noted that if lunar granite crystallized at depth (~10 km [2]), where the conditions would be favorable for large-scale silicate-liquid immiscibility, the silica phase should have cooled slowly enough for quartz to form. Alternatively, if silicic lava were to erupt volcanically (~0 bar), the silica polymorph should occur as a high-temperature phase (tridymite, 870-1470°C, or cristobalite, 1470-1705°C; [3,4,5]).

Quick et al. [6] optically identified quartz and tridymite in granitic breccia 12013. Robinson and Taylor [1] identified quartz as the silica polymorph in 19 granitic lunar samples using laser-Raman spectroscopy (LRS). Seddio et al. [7] identified quartz as the silica polymorph in granitic fragment 12032,366-19. Here, we identify the silica polymorphs present in 5 recently characterized Apollo 12 granitic fragments using LRS imaging and interpret the LRS data in conjunction with the textures of the analyzed silica polymorphs.

Methods: We identified the silica polymorphs that occur in Apollo 12 granitic fragments 12001,909-14, 12023,147-10, 12032,367-16, 12033,634-30, and 12033,634-34 [7] by LRS analysis using an inVia® Raman System (Renishaw). We obtained the LRS data using in both spot analysis mode and Streamline™ imaging mode. The 532-nm line of a diode-pumped solid-state laser was used as the excitation source. Analyses were done using a 50× long-working-distance objective (NA=0.5), which condenses the laser beam into a spot of 1 μm diameter on the sample in spot analysis mode or into an elliptical spot of 1 μm × 30 μm for the Streamline™ imaging mode. The objective also collects back-scattered Raman photons from the sample which were sent to a Raman spectrometer through a width-adjustable slit. A 2400 line/mm holographic grating disperses the collected Raman photons into a Raman Stokes shift range of 50 to 1300 cm^{-1} for this study, with a spectral resolution of ~1 cm^{-1}. Back-scattered electron (BSE) images were made using a JEOL 8200 electron probe.

Results: Raman spectra from the analyzed samples are shown in Fig. 1. Granitic breccia 12001,909-14 contains quartz where the silica has a hackle fracture pattern and silica glass where the silica is not fractured. Sample 12032,367-16, a granitic breccia, contains cristobalite; and although the sample is heavily fractured, the cristobalite is not. Granitic fragments 12023,147-10, 12033,634-30, and 12033,634-33 contain quartz with hackle fracture patterns.

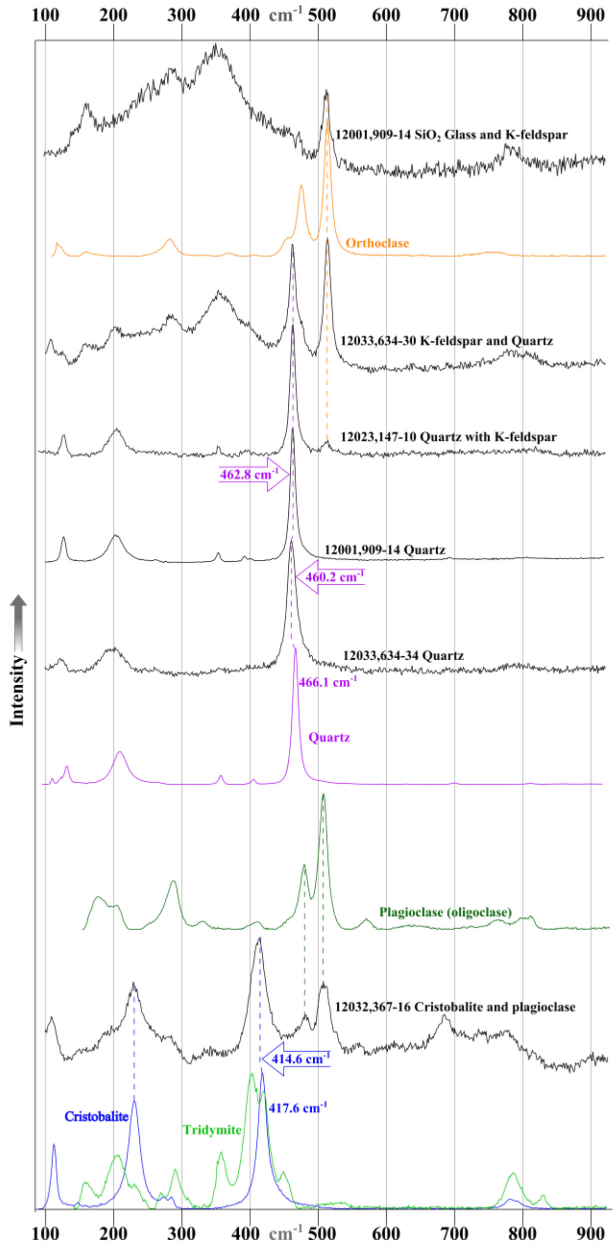

Fig. 1. Raman spectra of silica phases identified in this study (black spectra) have been baseline-subtracted and normalized for clarity. Standard spectra from RRUFF Database [8] of orthoclase (orange), quartz (purple), plagioclase (dark green), cristobalite (blue), and tridymite (green). Arrows indicate where band is slightly shifted from ideal position presumably indicating that the crystal is stressed.

Discussion: The silica polymorphs quartz, cristobalite, and tridymite have been identified in granitic lunar lithologies [1,2,3]. Typically, the silica polymorph intergrown with K-feldspar in lunar granite is quartz that

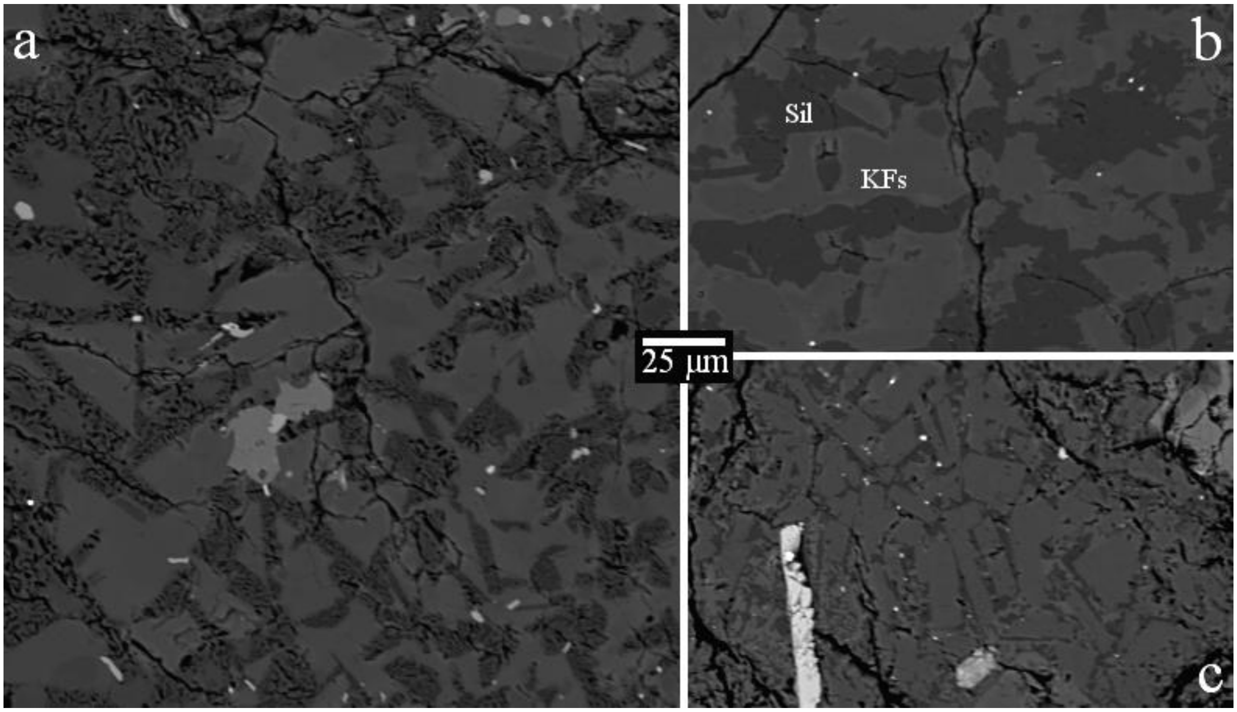

Fig. 2. BSE images of granophyric intergrowths of silica and feldspar in lunar granite. Contrast of images has been enhanced so that similar phases have similar brightness in all images. **a.** Quartz with a hackle fracture pattern and K-feldspar intergrown in 12001,909-14. This hackle fracture pattern is typical of silica in lunar granite identified as quartz. **b.** Silica glass and K-feldspar intergrown in 12001,909-14. **c.** Cristobalite intergrown with K-feldspar and plagioclase (two feldspars identified by LRS).

occurs with a hackle fracture pattern. For occurrences in which a silica polymorph with a hackle fracture pattern has been analyzed by LRS, all have been identified as quartz. Cristobalite and silica glass do not occur with a fracture pattern. Tridymite has only been reported in granitic breccia 12013 (optically identified by [6]).

The hackle fracture pattern of quartz in lunar samples is attributed to inversion from cristobalite (density: 2.33 g/cm^3 [9]) or tridymite (density: 2.18 g/cm^3 [10]) to quartz (density: 2.65 g/cm^3 [11]) [2, 8]. Inverting from a less to a more dense phase would produce isotropic tensional stress within the quartz, causing it to fracture (i.e., the hackle pattern). Jolliff et al. [12] refer to quartz with the hackle fracture pattern as "relict cristobalite."

Robinson et al. [1] suggest that the presence of quartz in lunar granite likely indicates that it crystallized at depth, allowing it to cool slowly forming quartz. However, because the majority of lunar granite samples have "relict cristobalite," it is more likely that quartz-bearing lunar granite cooled rapidly, preserving cristobalite as the silica polymorph. Furthermore, the small (<1 mm) crystal sizes that typically occur in lunar granites indicate rapid crystallization (samples 12034,634-34 and 15405,12 are exceptions with grain sizes > 1 mm).

The absence of cristobalite or tridymite in ancient terrestrial samples (relative to ancient lunar samples) has been ascribed to inversion accelerated by the presence of H_2O acting as a catalyst [2]. Perhaps the inversion from cristobalite or tridymite to quartz occurred in lunar granite because H_2O became concentrated in the late stages of fractional crystallization and then degassed.

Conclusions: The silica polymorph contained in lunar granite is most frequently quartz. However, the quartz typically has a hackle fracture pattern indicating that it inverted from a high temperature phase (cristobalite or tridymite). The preservation of high-temperature silica polymorphs (before inversion at some point later) and the fine-grained textures of most granitic lunar samples indicate that that the samples experienced relatively rapid cooling (e.g., rhyolitic volcanism).

The larger crystal structure of cristobalite and tridymite (relative to quartz) allow for higher concentrations of cations other than Si. In the future we will conduct an EPMA study of the silica polymorphs in lunar granite to explore the extent to which this is true.

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References: [1] Robinson and Taylor (2011) *LPSC42*, Abstract #1257. [2] Charles et al. (1971) *PLSC2*, 645-664. [3] Hollerman and Wyberg (1985) ISBN 3-11-007511-3. [4] Wenk and Bulakh (2003) ISBN 0-521-52958-1. [5] Rykart (1995) ISBN 3-7225-6204-X. [6] Quick et al. (1981) *PLPSC12*, 173-184. [7] Seddio et al. (2012) *Am. Min.*, submitted. [8] Downs (2006) *Prog. Abs. 19th Gen. Mtg. Int'l. Min. Assc*. O03-13. [9] Schmahl et al. (1992) *Z. Kristallogr.*, 201, 125-145. [10] Kihara (1978) *Z. Kristallogr.*, 148, 237-253. [11] Will et al. (1988) *J. Appl. Cryst.*, 21, 182-191. [12] Jolliff (1991) *PLPSC21*, 101-118.