RAMAN SPECTROSCOPIC STUDY OF QUARTZ IN LUNAR SOILS FROM APOLLO 14 AND 15 MISSIONS,

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Introduction: Silica minerals, SiO_2, are important rock-forming minerals. They are abundant in common rocks on Earth, such as granite, sandstone, chert, etc. However, silica minerals, especially quartz, are generally rare on the Moon. The commonly found silica polymorph in lunar basalt is cristobalite, which constitutes 5 vol % of some basalt [1]. Quartz is only found in a few granite-like (felsite) clasts [2], or some coarse grained lunar granites occurring in rare fragments. The largest lunar granite yet found, from Apollo 14 breccia 14321, weighs 1.8 g and contains 40 vol% quartz [3]. Although rare in the samples, the silica minerals are important indicators for the origin of some rocks and related geologic processes (e.g., red spots, domes) [4].

Laser Raman spectroscopy (LRS) has been proposed for lunar surface robotic exploration, for the purpose of definitive mineralogy, including mineral identification [5], mineral proportions [6], and major mineral chemistry [7-10]. Micro-Raman spectroscopy is by now a fairly routine technique for terrestrial mineralogy. The decrease of crystallinity in shocked minerals would induce variations in Raman spectral patterns and peak positions, and thus be useful for obtaining information on shock pressures for impact studies [12].

We have reported the finding of quartz grains in Apollo soil 14163 during a Raman point-count study of four endmember lunar soils [11]. Further analysis of the spectra led to the finding of quartz grains in Apollo sample 15273. In this abstract, we report the difference between the Raman spectra of six lunar quartz grains and the implied impact pressure.

Lunar soils and experiments: The sample 14163 was returned form the Fra Mauro region by Apollo 14 mission. It was collected at the end of EVA-1, northwest of the Lunar Module by scoop, and represents mixed material from the upper several cm of the regolith. The Fra Mauro formation is interpreted as the ejecta produced during the impact that formed the Imbrium basin. The Apollo 14163 samples are strongly enriched in KREEP-type material compared to the Apollo 11 and 12 soils [13]. This sample contains abundant impact-melt breccias and includes several unusual lunar lithologies such as alkali anorthosite, granite, and monzogabbro [14]. Sample 15723 was collected from station 6 on the Apennine Front by Apollo 15 mission [15]. The soils from that location consist of subequal amounts of rock types representing all three apices of the mixing triangle, i.e., the mixture of KREEP, mare, and feldspathic highland materials.

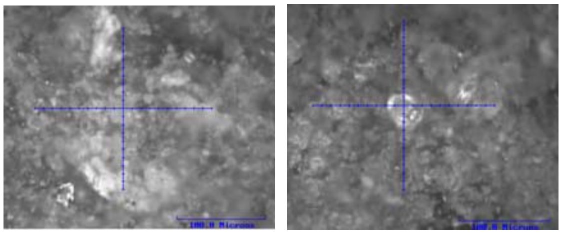
(a) (b)

Figure 1. Photos of (a) quartz and (b) cristobalite from Apollo 14163 and 15273, respectively.

LRS measurements were made by using a HoloLab 5000-532 nm KOSI Raman spectrometer with an automatic scanning stage. A Raman point-counting procedure [6] was applied over a n × m sampling grid with a step of ~100 μm. Manual adjustment of laser focus was made at each spot with a 6 μm laser beam diameter. Nearly 200 spectra were collected from each sample. The majority of the studied 14163 and 15723 lunar soil grains were less than 45 μm, measured from the images taken during Raman point counting.

Six Raman spectra of quartz were obtained from the two Apollo soil samples. Figure 1 shows a quartz grain (a) and a cristobalite grain (b), taken by a camera on the Raman spectrometer. The sizes of the six quartz grains are in the range of 40 to 10 μm.

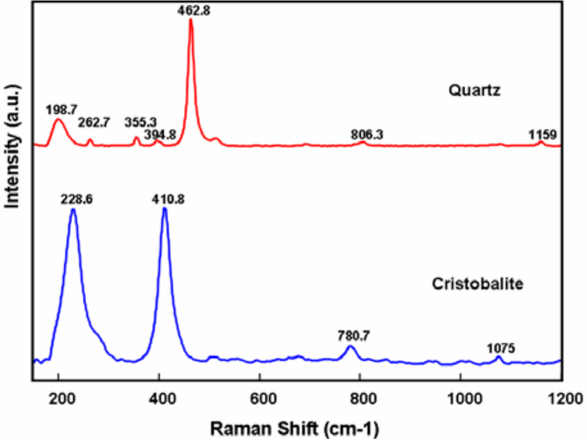

Figure 2. Raman spectra of quartz and cristobalite.

Results and Discussion: The Raman spectra of quartz and cristobalite are shown in Figure 2. The spectra can be divided into three regions, i.e., >1050 and 700–800 cm^{-1} (Si-O stretching modes), 350–500 cm^{-1} (O-Si-O bending modes), and <300 cm^{-1} (Si-O-Si bending and torsional/twisting modes) [16]. Cristobalite possess two predominant peaks at 410.8 and 228.6 cm^{-1}, whereas for lunar quartz they are at 462.8 and 198.7 cm^{-1}, respectively.

Our Raman point-count studies of 14163 and 15273 suggest that quartz takes 1.4 vol % of the overall mineral modes, and cristobalite takes 0.5 vol % for 15273 soil. Previous studies on the mineral modes of returned Apollo and Luna samples have generally suggested the rarity of quartz. A photographic grain-count study of lunar soils indicated less than 2 wt% silica (without distinguishing Qtz from other SiO_2) [17]. However, we studied the fine-grain portion of Apollo 14163 and 15273 samples (mainly in 10-20 µm size range), which is much smaller than the size range (20-500µm) used in previous optical grain-counting studies, and it was found the mineral modes in different grain size ranges of lunar soils are very different. Thus our studies reflect the fact that KREEP basalts and other late-stage, fractionated lunar rocks contain more quartz than other materials on the Moon..

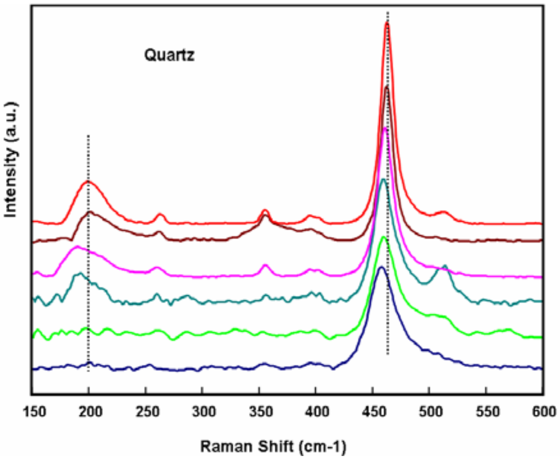

Figure 3. Six Raman spectra of quartz from Apollo 14163 and 15273, note the peak shifts and variations of ~460 and ~200 cm^{-1}.

Typical low temperature quartz has two sharp and intense peaks at 464 and 206 cm^{-1}. Among the six quartz spectra that we obtained from Apollo 14163 and 15273 samples, we find considerable peak position shifts shown in the Figure 3. Comparing with the terrestrial crystalline low temperature quartz, the major peaks of all six lunar quartz are shifted to lower peak positions with broadened peak widths. The change of Raman spectral features might be related to a distortion of the SiO_2 structural framework caused by shock-metamorphism [12]. There are many studies on pressure-induced Raman peak shifts for shocked quartz from terrestrial geologic settings, or from laboratory experiments. McMillan et al. [18] carried out a Raman spectroscopic study of crystalline quartz samples shocked to peak pressures of 31.4 GPa, which shifted the major Raman peak from 464 cm^{-1} of un-shocked quartz to 455 cm^{-1}. The largest Raman peak shift observed in our study of 14163 and 15723 soil samples is 457 cm^{-1}, suggesting the impact pressure experienced by these quartz grains are less than 31.4 GPa.

From nearly 400 Raman spectra taken from Apollo 14163 and 15273 samples, we didn't find any trace of the high pressure polymorphs of SiO_2, i.e., coesite and stishovite. Fiske et al. [19] did quantitative NMR studies on the shock loads on quartz and found that at very high shock pressures the shock temperatures can be high enough to permit a rapid transformation of four-coordinated silicon ($^{[4]}$Si) to six-coordinated $^{[6]}$Si, i.e., to form coesite and stishovite. Explanations for their absence in the lunar soils include the rarity of silica grains in the original target rocks and volatilization of silica during high-energy impact events in the high vacuum at the lunar surface [20].

Conclusions: Quartz is a rare but important mineral indicator for lunar crustal evolution and lunar surface processes. Its identification in Apollo 14163 and 15273 sample (≤45 µm grain size) and its characterization (pressure induced crystallinity change) demonstrate that the detection of trace mineral species can be achieved by Raman point-count procedures, which also provide major and minor mineral ID, mineral modes, and major mineral chemistry [11]. Planetary Raman spectroscopy is a crucial technology for characterization of surface materials and for *in-situ* resource utilization (ISRU) in future lunar exploration [21].

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