It is now a well known fact that most lunar samples are depleted in their volatile components as compared to terrestrial samples. However, despite the careful procedures used for contamination control during sample processing and examination there are recurring reports of volatile components in selected lunar samples. The Apollo 16 highland site has produced the widest variety of volatile components found in lunar soils and breccias. The "volatile-rich" soil 61221 which contained unusual gases (HCl, CO₂, H₂O, etc.) is an example (1). "Rusty-rock" 66095 contained lawrencite (FeCl₂) and its alteration product FeO(OH) (akaganeite) (2) along with sulfate minerals (3). Gibson and Chang (4) noted the existence of a possible carbonate phase in Lunar rock 67016. They concluded, on the basis of gas release information, carbon abundances obtained from vacuum pyrolysis and acid hydrolysis along with the corresponding isotopic data, that the possible carbonate phases in 67016 were lunar in origin and not the products of terrestrial alteration and contamination. Carter (5,6) presented microprobe and scanning electron microscope data to confirm the presence of calcite in Apollo 16 soils and in Luna 20 soil.

This is a report on the gas release profiles of four additional Apollo 16 rocks which contain possible carbonate phases: [1] 61016,143 and [2] 64435,45 and 54 are black and white rocks which are a mixture of cataclasite anorthosite and crystalline polymict breccia (7), [3] 66095,40 ("rusty-rock") is a crystalline polymict breccia (7), and [4] 67016,38 is a vitric or light matrix breccia (7). All of these samples were studied using the gas release procedures of Gibson and Moore (8). Each sample was heated at a rate of 6°C/minute and the evolved gases were measured using a computer controlled quadrupole mass spectrometer. Each of the four lunar rocks studied released CO₂ in the temperature interval 400-500°C. The low temperature CO₂ evolution was identical to release profiles observed previously for the terrestrial carbonates calcite, magnesite and siderite (9). CO₂ was also evolved from the samples above 950°C. This high temperature CO₂ is typical of that derived from high grade lunar breccias and results predominantly from pyrolysis of residual carbon. Any CO₂ which was trapped within the rock during lithification may also be released at high temperatures.

61016,143 evolved the least amount of CO₂ of the four samples. However, the temperature for the CO₂ evolution was typical of other Apollo 16 rocks. The sample is depleted of volatiles with the exception of the water released below 300°C which is characteristic of either adsorbed or solar wind derived water (Figure 1).

64435,54 was a sample of the gray matrix of 64435 which contained abundant CO₂, released between 400-500°C, typical of carbonate phases (Figure 2). In addition sample 64435,54 had considerable adsorbed water and other low temperature gases (CO₂ and H₂O) which were evolved below 300°C. The cataclastic anorthosite "clast" 64435,45 does not contain the possible carbonate phases (Fig. 3) whereas the brecciated gray portion of the rock (64435,54)
APOLLO 16 SAMPLES WITH CARBONATE-LIKE PHASES

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contains the carbonate-like phases (Figure 2).

66095,40 ("rusty-rock") contains appreciable amounts of the low temperature hydrate phase (FeOOH) (2) along with possible sulfate phases (3) and chlorides. Sample 66095,40 contains the hydrates as evidenced by the large quantity of H2O evolved between 100-200°C (Figure 4). This water is from the decomposition of hydrated iron oxides (FeOOH) between 125-175°C. Evidence for carbonate phases is seen from the CO2 evolution (Figure 4) below 500°C. No sulfate phases are present in sample 66095,40. SO2 would have been released in the temperature interval 300-500°C should a sulfate have been present in the sample. SO2 was evolved above 800°C, as a reaction product of troilite with the silicate matrix at elevated temperatures.

67016,88 has previously been studied by Gibson and Chang (4). The CO2 evolved in the temperature range 400-550°C (Figure 5) is isotopically too light to be atmospheric. The possible carbonate phase in 67016 appears to be heterogeneous both in its distribution throughout the sample and in its isotopic composition (4).

It is suggested that the CO2 evolved from the Apollo 16 polymict breccias in the 400-550°C temperature interval originates from carbonates which are secondary alteration products. Each Apollo 16 sample with the possible carbonate phases has been brecciated and at one time resided in the regolith. The large number of clasts or relict clasts also suggest that the samples were derived from a regolith-like environment and have subsequently been subjected to metamorphic processes. The regolith has been exposed to the solar wind. Upon heating regolith materials containing solar wind derived carbon, CO gas is released at temperatures above 700°C (10). The gas phase (CO) could be retained in an enclosed vug or cavity and upon cooling CO2 would form because of the shift in the chemical equilibrium established in the gas phases trapped in the enclosed space. Subsequent reaction of the CO2 with a metallic iron grain or with an iron rich glass could form carbonate. The resulting carbonates would explain the low temperature (400°-550°C) release of CO2 reported on in this work.

References
Note: The gas release profiles vs. temperature have been normalized to 100% amplitude in the region of greatest abundance. Arrow on the weight loss curve represents the initial melting of the sample.