

ABUNDANCE AND ISOTOPIC COMPOSITION OF CARBON IN LUNAR ROCK 67016: SUGGESTIONS OF A CARBONATE-LIKE PHASE, Everett K. Gibson, Jr.<sup>1</sup> and Sherwood Chang<sup>2</sup> (<sup>1</sup>Geochemistry Branch, NASA Johnson Space Center, Houston, TX 77058; <sup>2</sup>Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035).

Characteristic of returned lunar samples from both the Apollo and Luna missions, as compared to terrestrial samples, is the virtual absence (except for ppm amounts) of volatile phases. However, despite the careful procedures used for contamination control during sample processing and examination, reports recur describing the presence of carbonates within a few lunar soils. Gay et al. (1) reported the presence of aragonite in Apollo 11 soil. Carter (2,3) presented microprobe and scanning electron microscope data to confirm the presence of calcite in Luna 20 soil and Apollo 16 soils. To date, to the best of our knowledge, there has not been any report of carbonate within a lunar rock. We believe that we have evidence which points strongly to the existence of a "carbonate-like phase" within lunar sample 67016.

Sample 67016 has been studied in detail by Warner et al. (4) and classified as a light-matrix breccia. The sample was collected at the rim crest of North Ray Crater and was probably excavated from depth during the North Ray cratering event (5). The sample is moderately coherent with several penetrative fractures. Our sample, 67016,88, was an interior piece but the exact location of the allocated sample with respect to the pre-existing fractures within the rock could not be determined.

A piece of sample 67016 contained 35  $\mu\text{gC/g}$  (6) and  $178 \pm 10 \mu\text{gS/g}$  (7). Total nitrogen abundances obtained in this study amounted to  $9 \mu\text{gN/g}$ . Gas release studies of 67016,88 using the procedures of Gibson and Moore (8) showed that  $\text{CO}_2$  was sharply released between 450-550°C (Figure 1). No previously examined lunar rock or breccia displayed a similar  $\text{CO}_2$  release profile. The low temperature  $\text{CO}_2$  evolution was identical to release profiles observed previously from terrestrial carbonates: calcite, magnesite, and siderite (9,10).  $\text{CO}_2$  is also evolved from the sample above 950°C. This high temperature  $\text{CO}_2$  is typical of that derived from lunar high grade breccias and results predominantly from pyrolysis of residual carbon; any  $\text{CO}_2$  which was trapped within the rock during brecciation may also be released at high temperatures.

Acid hydrolysis and vacuum pyrolysis as described in Chang et al. (11) were used to extract  $\text{CO}_2$  from the sample for abundance and isotopic analyses. For each experiment separate rock chips were crushed in a tool steel percussion mortar, then outgassed under vacuum ( $<10^{-4}$  torr) at 150°C for four hours to remove adsorbed terrestrial gases. No attempt was made to homogenize the samples. Pyrolysis data in Table 1 show that the bulk of the carbon is released as  $\text{CO}_2$  (42  $\mu\text{gC/g}$ ), 56% (23  $\mu\text{gC/g}$ ) of which is evolved below 550°C. This low temperature  $\text{CO}_2$  corresponds to that portion of the gas release profile (Figure 1) which is typical of carbonate decomposition. Comparable low temperature pyrolysis data are not yet available for other Apollo 16 rocks. However, by comparison the total amount of carbon released as  $\text{CO}_2$  by vacuum pyrolysis from 150-1200°C of five other Apollo 16 rocks ranges from 1 to 33  $\mu\text{gC/g}$  (12). Acid hydrolysis of a different chip of 67016,88 released 78  $\mu\text{gC/g}$  in the form of  $\text{CO}_2$ , an amount higher by a factor of two than previously observed in any other Apollo 16 rock (12) or rocks from other missions.

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The  $\delta^{13}\text{C}_{\text{PDB}}$  values for  $\text{CO}_2$  in Table 1 are all isotopically light and fall within or close to the range between -15 and -35 ‰ characteristic of total carbon in rocks obtained from other missions. In other Apollo 16 rocks,  $\text{CO}_2$  released by acid hydrolysis exhibited isotopic compositions ranging from -20.1 to -34.6 ‰ (12). On the other hand  $\text{CO}_2$  released by acid hydrolysis of Apollo 16 soils is isotopically heavy ranging from 9.8 to 15.2 ‰ (13). Values of  $\delta^{13}\text{C}_{\text{PDB}}$  in Table 1 fall outside the range of meteoritic carbonates (40 to 70 ‰) and for potential sources of  $\text{CO}_2$  contamination found in the laboratory where the analyses were performed. Furthermore,  $\delta^{18}\text{O}_{\text{SMOW}}$  of the  $\text{CO}_2$ , which ranges from -16 to -33 ‰, is much too light to be atmospheric  $\text{CO}_2$ , the likeliest source of terrestrial contamination, for which  $\delta^{18}\text{O}_{\text{SMOW}} = 40$  ‰.

Comparison of results obtained from different chips of 67016,88 by the gas release method (Figure 1), stepwise pyrolysis, and acid hydrolysis (Table 1) suggest that the total  $\text{CO}_2$  released by these methods comes from at least two sources, one of which appears to be "carbonate-like", and that the "carbonate-like" phase appears to be heterogeneous both in its distribution throughout the sample and in its isotopic composition. With the available data no firm conclusion can be drawn concerning the origin of this carbon-bearing phase. The collection site of 67016 at the crater rim crest suggests a possible origin within North Ray Crater, while the isotopic data are inconsistent with a meteoritic origin. It is also not clear whether this phase is unique to 67016,88. The evidence from acid hydrolysis and gas release studies of additional rocks from North Ray Crater and other Apollo 16 sites, which release  $\text{CO}_2$  (12, 14, 15), may reflect a widespread but not necessarily homogeneous distribution over the entire Apollo 16 site of rocks bearing a "carbonate-like phase". At the present time, optical and microprobe examination of thin sections of sample 67016 are being carried out in an attempt to further characterize this "carbonate-like phase".

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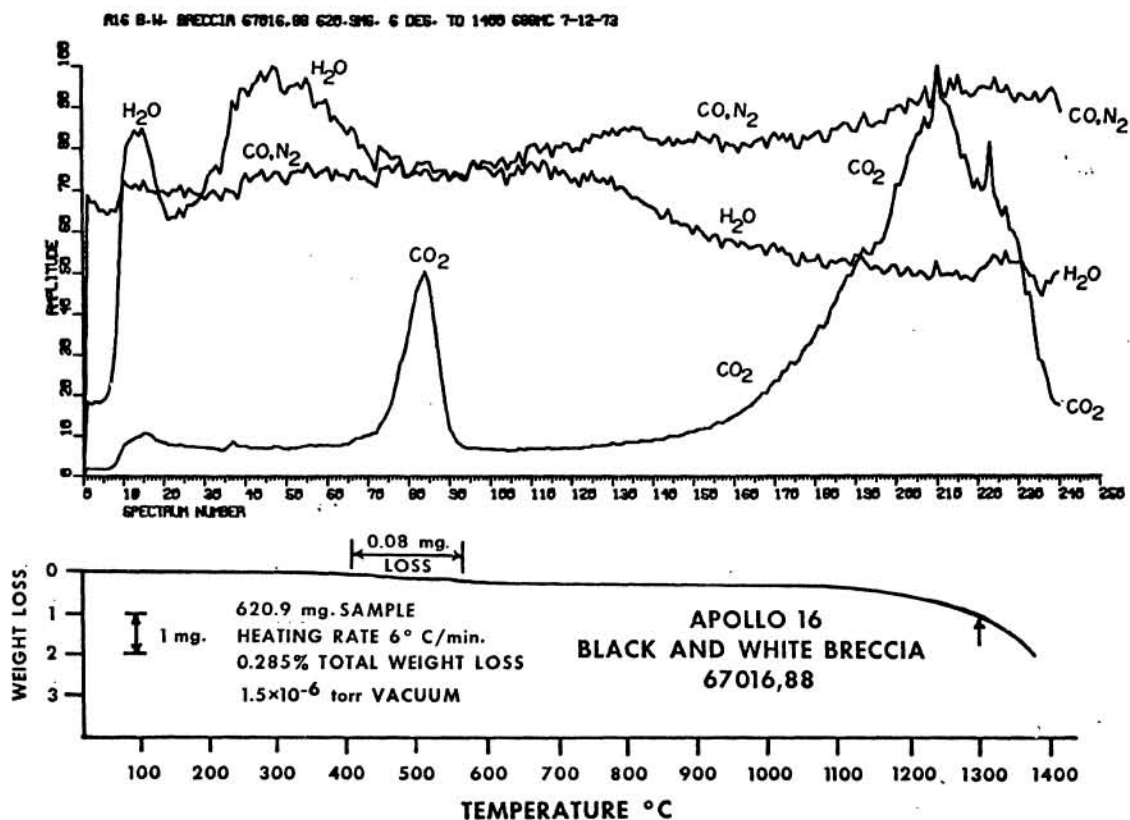


Figure 1. Gas release pattern for light-matrix breccia 67016,88. Note the carbon dioxide evolution between 450-550°C.

TABLE 1. Abundance and Isotopic Composition\* of Carbon in Lunar Breccia 67016,88

Sample Weight	Extraction Method	μgC/g as		$\delta^{13}\text{C}_{\text{PDB}}(\text{CO}_2)$	$\delta^{18}\text{O}_{\text{SMOW}}(\text{CO}_2)$
		CO	CO <sub>2</sub>		
0.414 gms	1. Acid Hydrolysis 6N H <sub>2</sub> SO <sub>4</sub> , 120°C 44 hours	0	78	-32.83	-16.57
0.484 gms	2. Vacuum Pyrolysis				
	a. 150-550°C	4	23	-12.53	-33.41
	b. 550-1200°C	6	18	-14.08	-31.03
	c. Combustion at 1200°C	-	1	-	-
Totals		10	42		

\* Isotopic measurements were kindly supplied by Dr. I. R. Kaplan.