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A reexamination of amino acids in lunar soils: Implications for the survival of exogenous organic material during impact delivery

KAREN L. F. BRINTON and JEFFREY L. BADA

Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093-0212, USA

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Abstract—Using a sensitive high performance liquid chromatography technique, we have analyzed both the hot water extract and the acid hydrolyzed hot water extract of lunar soil collected during the Apollo 17 mission. Both free amino acids and those derived from acid labile precursors are present at a level of roughly 15 ppb. Based on the D/L amino acid ratios, the free alanine and aspartic acid observed in the hot water extract can be entirely attributed to terrestrial biogenic contamination. However, in the acid labile fraction, precursors which yield amino acids are apparently present in the lunar soil. The amino acid distribution suggests that the precursor is probably solar wind implanted HCN. We have evaluated our results with regard to the meteoritic input of intact organic compounds to the moon based on an upper limit of ≤0.3 ppb for α-aminoisobutyric acid, a non-protein amino acid which does not generally occur in terrestrial organisms and which is not a major amino acid produced from HCN, but which is a predominant amino acid in many carbonaceous chondrites. We find that the survival of exogenous organic compounds during lunar impact is ≤0.8%. This result represents an example of minimum organic impact survivability. This is an important first step toward a better understanding of similar processes on Earth and on Mars, and their possible contribution to the budget of prebiotic organic compounds on the primitive Earth.

1. INTRODUCTION

The Apollo missions provided geoscientists with a wealth of lunar material for study. Researchers were particularly interested in the search for organic compounds thought to be necessary for the origin of life on Earth. Between 1969 and 1976, intensive analyses of amino acids in lunar soils were carried out (Hamilton, 1965; Hare et al., 1970; Harada et al., 1971; Nagy et al., 1971; Gehrke et al., 1972; Hamilton and Nagy, 1972, 1975; Fox et al., 1973, 1976; Modzeleski et al., 1973). Compared to other biomolecules, the methods available for the determination of amino acids were relatively simple and sensitive (Hare et al., 1970; Harada et al., 1971; Nagy et al., 1971; Gehrke et al., 1972; Fox et al., 1973, 1976). Furthermore, the efficiency of an abiotic amino acid synthesis from likely prebiotic precursors had been demonstrated by Miller (1955) and Miller and Urey (1959). Many of the amino acids made during the Miller-Urey experiment have subsequently been found in carbonaceous chondrites (Kvenvolden et al., 1970; Wolman et al., 1972). Thus, the possibility that amino acids might be present in lunar soil was a tantalizing prospect for scientists studying the origin of life.

Several amino acid analyses were performed on both surface and subsurface lunar fines returned during the Apollo 11, 12, 14, 15, and 17 missions (Hare et al., 1970; Nagy et al., 1971; Harada et al., 1971; Gehrke et al., 1972; Fox et al., 1973, 1976; Modzeleski et al., 1973; Hamilton and Nagy, 1975). The most commonly used analytical technique was ion exchange chromatography (IEC), using ninhydrin as the post-column colorimetric derivatizing agent (Hare et al., 1970; Harada et al., 1971; Nagy et al., 1971; Fox et al., 1973, 1976). Another method used was gas chromatography coupled with a mass spectrometer (GC–MS), with N-trifluoroacetyl-*n*-butyl (TFA) ester amino acid derivatives (Gehrke et al., 1972). Together the two techniques provided independent and mostly concordant results. Nevertheless, these methods left open such questions as amino acid stereochemistry and the possible presence of α-dialkyl amino acids, both of which provide important evidence of exotic origin.

Amino acid analyses were performed both on hot water extracts (to determine free amino acids) and on acid hydrolyzed hot water extracts (to determine both free amino acids and those derived from acid labile precursors). A suite of amino acids was found, with amounts up to ~70 ppb in the hydrolyzate (Hare et al., 1970; Harada et al., 1971; Nagy et al., 1971; Gehrke et al., 1972; Fox et al., 1973, 1976; Modzeleski et al., 1973). The yield of amino acids increased by as much as 350% upon hydrolysis (Fox et al., 1976). The most abundant amino acid was glycine, followed by alanine, glutamic acid, aspartic acid, serine, threonine, and small amounts of other protein and non-protein amino acids. Hydrolyzates of samples collected at the surface may have been slightly enriched in amino acids compared to those from subsurface samples (Harada et al., 1971).

The amino acids and precursors in lunar soils could have several possible sources. Terrestrial contamination at some stage of collection, transport, and analysis may have occurred (Hamilton and Nagy, 1972, 1975). Also, the apparent amino acid enrichment of surface fines suggests that solar wind implantation of precursors may be an important process (Holland et al., 1972; Fox et al., 1976). A third possibility is that lunar amino acids come from meteoritic debris associated with impacts on the lunar surface. Carbonaceous chondrites are rich in organic compounds, including amino acids and their precursors (Cronin and Pizzarello, 1983). It has been estimated based on the Ir mass balance on the Moon that 1 to 4% of lunar soil consists of carbonaceous chondritic debris (Haskin and Warren, 1991).

The question of terrestrial contamination was addressed in several ways. The reagents used in all analytical procedures

were tested for purity, and parallel controls were run to correct for any contamination introduced during analysis. The amino acid content and distribution of other possible contamination sources, such as human fingerprints (Hamilton, 1965; Hamilton and Nagy, 1972, 1975) and an astronaut's glove (Hamilton and Nagy, 1972, 1975) were also evaluated. Rocket exhaust was simulated to determine if it produced significant amounts of abiotic amino acid precursors. It was found that a small, and perhaps insignificant amount of amino acids could have been derived from compounds present in rocket exhaust (Fox et al., 1976).

Although the evidence seems to suggest that the amino acids found in lunar soils could not be explained by contamination, the likelihood that some degree of contamination was introduced prior to analysis was not fully assessed. All known abiotic syntheses produce racemic amino acids, whereas modern terrestrial protein amino acids consist almost exclusively of the L-enantiomers (see Bada, 1995). Methods that permit the resolution of amino acid enantiomers can provide an index of terrestrial contamination. However, neither the IEC nor the GC–MS technique resolved the amino acid enantiomers, and thus whether contamination may have occurred remained uncertain.

The amino acids in carbonaceous chondrites in general (and the Murchison meteorite in particular) have undergone much study (see Kvenvolden et al., 1970; Cronin, 1976; Cronin and Pizzarello, 1983). Experiments in which both the extract and the hydrolyzate have been analyzed have shown that approximately 50% of the amino acids in the hydrolyzate are derived from acid labile precursors (Cronin, 1976). Therefore, meteorites contain a significantly higher percentage of free amino acids than do lunar soils.

The α-dialkyl amino acid α-aminoisobutyric acid (aib) is one of the most abundant amino acids present in Murchison, Murray, and several Antarctic meteorites (Cronin and Moore, 1971; Shimoyama et al., 1979, 1985; Cronin and Pizzarello, 1983; Cronin et al., 1988). In our calculations, we use the Murchison aib and amino acid values reported by Cronin and Pizzarello (1983) as representative of carbonaceous chondrites. In Murchison, amino acids and their acid-labile precursors constitute 1% of the total organic carbon. Aib comprises approximately 10% of the Murchison amino acids ($\sim$12 ppm), and therefore about 0.1% of the total organic carbon (Cronin and Pizzarello, 1983). In contrast, aib is extremely rare in the terrestrial environment. It exists biogenically only in a few fungal peptides (Mathew and Balaram, 1983; Brückner et al., 1989), and when found in geological environments it has been associated with extraterrestrial material (Zhao and Bada, 1989; Bada et al., 1995). Because of steric hindrance, the reactivity of α-dialkyl amino acids toward ninhydrin and TFA is considerably lower than that of protein amino acids. Thus, previous lunar soil analyses employed techniques poorly suited for the detection of one of the more abundant non-protein amino acids in carbonaceous meteorites.

Amino acids are an important indicator of both the level and the source of abiotic organic compounds on the Moon. Amino acid analysis of lunar soils can offer insight into the chemistry of amino acid precursors, as well as the process of exogenous organic delivery, both of which are important to our understanding of the origins of life on Earth. In order to further assess whether amino acids exist on the Moon, we analyzed both the hot water extract and the acid hydrolyzed hot water extract of lunar fine sample 78421, following the extraction and hydrolysis procedures of earlier researchers (Hamilton, 1965; Hare et al., 1970, 1971; Nagy et al., 1971; Gehrke et al., 1972; Hamilton and Nagy, 1972, 1975; Fox et al., 1973, 1976; Modzeleski et al., 1973). In order to detect aib, and to resolve the amino acid enantiomers, we used an analytical technique first reported by Aswad (1984), which employs *o*-phthaldialdehyde/N-acetyl L-cysteine (OPA/NAC) derivatization (Aswad, 1984; Zhao and Bada, 1989, 1995). Reverse phase high performance liquid chromatography (HPLC) was used to separate the diastereomeric derivatives (Zhao and Bada, 1989, 1995).

2. MATERIALS AND METHODS

All glassware was cleaned in Chromerge and annealed at 500°C for 3 h. Water was purified by double distillation, except where otherwise specified. Teflon cap liners were cleaned in Chromerge.

2.1. Lunar Soil Sample 78421

Soil sample 78421 was collected during the Apollo 17 mission from the Taurus-Littrow Valley on the lunar surface from the bottom of a trench dug 10 cm wide and 25 cm deep. The sample consists of medium-gray (N5) sieved fines less than 1 mm in diameter. It was stored in a clean plastic bag sealed in a metal canister. The sample was generously provided for this study by Professor James Arnold at the University of California, San Diego.

2.2. Preparation of the Unhydrolyzed Extract

1.0042 g of the lunar soil sample was added to a clean test tube along with 5 mL Milli-Q water and capped with a Teflon-lined plastic screw top. The tube was placed in a 100°C heating block for 24 h. After heating, the sample was centrifuged and the supernatant was transferred to another clean test tube. The pellet was resuspended in 2 mL Milli-Q water and centrifuged, and then the supernatant was added to the second tube. The extract was then evaporated to dryness under vacuum, leaving a white residue. This residue was redissolved in Milli-Q water, transferred to a 1.5 mL microcentrifuge tube in two 500 μL washes, and again evaporated to dryness. In order to remove any ammonia, the residue was twice dissolved in 50 μL 0.4 M borate buffer pH 9.5 and evaporated to dryness. A blank was prepared in the same way, minus the lunar soil.

2.3. Preparation of the Hydrolyzed Extract

1.1108 g of the lunar soil sample was added to a clean test tube along with 2 ml Milli-Q water, capped and placed in a 100°C heating block for 24 h. After heating, the sample was centrifuged and the supernatant was transferred and dried using the same procedure as for the unhydrolyzed extract. The extracted residue was redissolved in doubly distilled 6 N HCl, and the capped tube was placed in a 100°C heating block for 23 h. The hydrolyzed sample was then evaporated to dryness. The residue was transferred to a microcentrifuge tube and any ammonia removed using the same procedure as for the unhydrolyzed extract. A blank was prepared in the same way, minus the lunar soil.

2.4. Derivatization and HPLC Analysis

The residue of each sample and blank was redissolved in 20 μL water and derivatized with OPA/NAC for 15 min to enhance our ability to detect aib. The derivatives were then analyzed by reverse-phase HPLC using fluorescence detection. A standard amino acid solution was also analyzed. (For details of the derivatization and analysis, see Zhao and Bada, 1989, 1995.) With this technique, it is

possible to resolve the derivatized amino acid diastereomers by adjusting the elution gradient. In this experiment, the gradient was designed to resolve the aib derivative and the derivatized diastereomers of alanine.

3. RESULTS AND DISCUSSION

The results of the analyses are given in Table 1. Chromatograms of the hydrolyzate and the corresponding blank are shown in Fig. 1. We can infer that the peaks corresponding to aib, D-alanine, and D-aspartic acid represent indigenous lunar amino acids and their precursors. Although it is true that fungal (Mathew and Balaram, 1983; Brückner et al., 1989) and bacterial (see Chyba, 1990) sources of aib and D-amino acids exist, they are rare and would have had little opportunity to contaminate our sample. Unlike meteoritic samples which have all (with the exception of IDPs collected at high altitude) spent at least some amount of time exposed to terrestrial soil or ice prior to collection (for examples, see Kvenvolden et al., 1970; Cronin and Moore, 1971; Shimoyama et al., 1979, 1985; Maurette et al., 1991), the lunar soil was carefully collected and stored under clean conditions. Regarding the possibility of contamination with aib or D-amino acids during our analysis, none was present in our procedural blanks. Furthermore, one must consider that we observed the appearance of both D-aspartic acid and D-alanine upon hydrolysis with a concomitant increase in L-aspartic acid and L-alanine. The acid-labile precursors of the D-amino acids were therefore either racemic, or underwent extensive racemization during hydrolysis, which is inconsistent with the racemization observed during protein/peptide hydrolysis (Manning, 1970). Therefore, we feel justified in our assertion that these amino acids (or their precursors) are abiotic and truly indigenous to the soil of the Moon, and, furthermore, that the excess of the L-enantiomers represents terrestrial contamination. A study of the $\delta^{13}C$ and $\delta^{15}N$ of individual amino acid enantiomers in lunar samples could be useful in determining the level of terrestrial contaminants. The stable isotope ratios of meteoritic amino acids are distinguishable from terrestrial amino acids (see Epstein et al., 1987; Engel et al., 1990; Pizzarello et al., 1991, 1994), and solar wind implanted nitrogen in lunar soil possesses a unique isotopic signature (Kim et al., 1995). However, considering the trace quantities of amino acids found in lunar soils these measurements would be difficult.

The racemic nature of extraterrestrial amino acids has been challenged by Engel et al. (1990) and Engel and Nagy (1982, 1983), whose argument is based largely on the isotopic composition of the apparent L-amino acid excess in the Murchison meteorite. However, both the ubiquity of L-amino acids in the terrestrial environment and the observation that amino acids synthesized in abiotic simulation experiments are racemic indicate the difficulties inherent in this assertion (Miller, 1955; Bada et al., 1983; Bada, 1995). The scientific standards required to show that such an excess is in fact extraterrestrial are necessarily far more rigorous than those required to show that it is not. However, the results obtained by Engel and coworkers are interesting and warrant further study.

The free alanine and aspartic acid found in the hot water extract consisted entirely of the L-enantiomers, which is consistent with biogenic origin. The enantiomers of the remaining chiral amino acids observed were not resolved, and glycine, the most abundant amino acid, is achiral. Therefore, the biogenic component of these amino acids was not determined. A mixture of L-alanine and L-aspartic acid was also carried through the hot water/acid hydrolysis procedure used for the lunar soil sample. No significant racemization of either amino acid was detected ($D/L < 0.05$) and thus the D/L ratios of alanine and aspartic acid we found in the acid hydrolyzed lunar soil extract cannot be attributed to racemization during sample processing. Since we have reasoned that the excesses of L-alanine and L-aspartic acid in the hydrolyzate are terrestrial and the racemic component is not, we calculate that 30% of the alanine and 50% of the aspartic acid in the hydrolyzate is of abiotic origin and not due to terrestrial contamination. The aib concentration of ≤0.3 ppb is based solely on the presence of a peak with a retention time corresponding to that of an aib standard, and therefore represents a maximum value for aib.

Table 1. Amino acid contents (in ppb, blank corrected) in lunar soils. All identifications are based on chromatographic retention times only. Sample 78421 was analyzed in this study, while the 72501 results are reported by FOX et al. (1976). ND indicates that the amino acid was not detectable by the technique used.

	78421		72501	
	extract	hydrolyzate	extract	hydrolyzate
D-Aspartic acid*	≤0.05	0.4	ND	ND
L-Aspartic acid*	0.7	1.1	0.1†	0.7†
D,L-Serine	0.5	0.9	0.1	0.3
D,L-Glutamic acid	≤0.05	0.2	0.0	0.7
Glycine	3.5	10.6	1.7	7.1
D-Alanine	≤0.05	0.2	ND	ND
L-Alanine	1.1	1.2	0.3†	1.1†
Aib	≤0.3	≤0.2	ND	ND

*The identification of D- and L-aspartic acid in sample 78421 is tentative (see Figure 1).

†FOX et al. (1976) were unable to distinguish between enantiomers, so this value represents the combined concentration of the D- and L-enantiomers.

The distribution of amino acids in lunar soils differs significantly from that of the Murchison meteorite and other carbonaceous chondrites in which aib is an abundant constituent. Furthermore, the yield of amino acids upon hydrolysis of the extract increases 100% for carbonaceous chondrites (Cronin and Pizzarello, 1983) and >200% for sample 78421 (correcting for alanine and aspartic acid contamination; this represents a minimum value because some component of the remaining protein amino acids is almost certainly biogenic). Fox et al. (1976) observed a 350% increase upon hydrolysis.

The hot water extract of the Murchison meteorite contains a suite of free amino acids and their acid-labile precursors. Various studies suggest that the amino acids in carbonaceous chondrites such as Murchison were produced by a Strecker-type mechanism during aqueous alteration of the parent bodies (Peltzer et al., 1984; Cronin et al., 1993; Lerner et al., 1993). However, in the dry lunar environment an aqueous Strecker synthesis would not be feasible.

In lunar soil, solar wind implantation of prebiotic elements such as N and C has been suggested as a possible source of the amino acid precursors observed (Holland et al., 1972; Fox et al., 1976), and the species thought to responsible for some, if not all, of the observed amino acids is HCN. In Apollo 14 and 15 samples, 10 to 60 nmol/g HCN and DCN were detected by mass spectrometry (Holland et al., 1972). Fox et al. (1976) and Yuasa et al. (1984) investigated the chemistry of

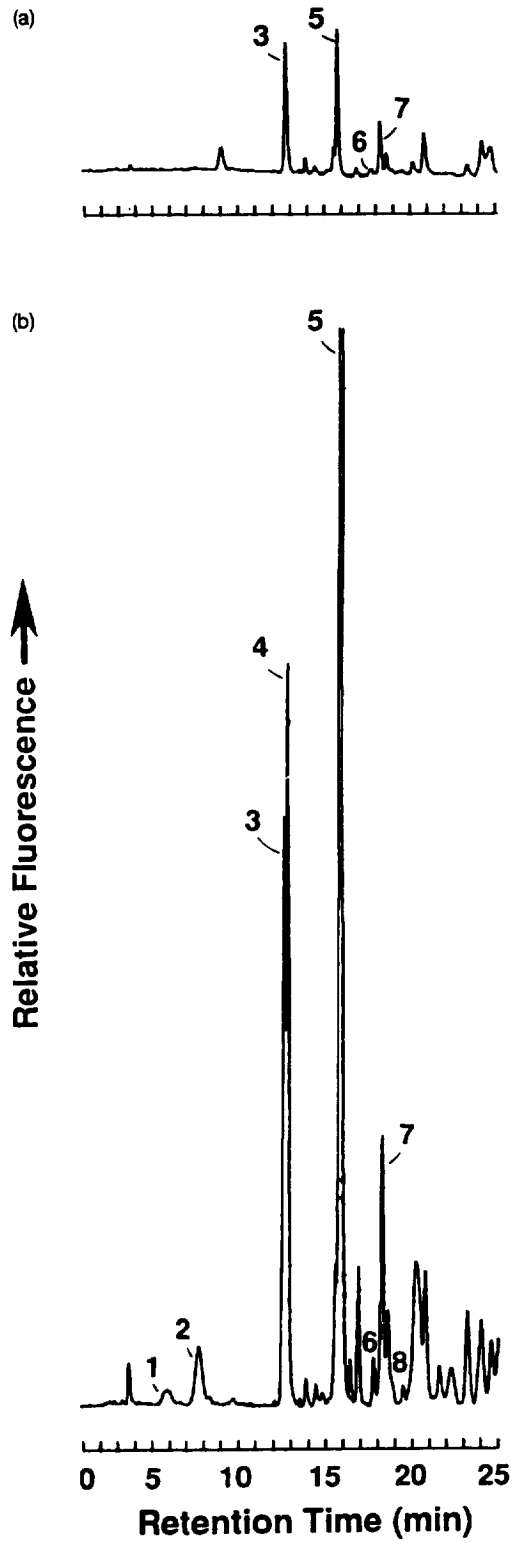

FIG. 1. HPLC chromatogram of the procedural blank (a) and lunar sample 78421 hydrolyzate (b). Both chromatograms were obtained after derivatization of the amino acid extracts with OPA/NAC for 15 min. The amino acids were identified and quantified by comparison with the retention times and peak areas of an amino acid standard (not shown). Peak assignments are as follows: D-aspartic acid (1), L-aspartic acid (2), D,L-serine (3), D,L-glutamic acid (4), glycine (5), D-alanine (6), L-alanine (7), aib (8). The retention times of D- and L-aspartic acid did not correspond exactly with those of an amino acid standard. Aspartic acid retention times commonly vary in samples which have not been desalted. Our sample size was so small that the risk of significant sample contamination resulting from the desalting protocol was too high, so we opted to omit the procedure. Therefore, peaks were tentatively identified as aspartic acid from their elution order relative to the other amino acids, and from their peak shape.

cyanide under the conditions of amino acid extraction and hydrolysis used for lunar material and have confirmed that the synthesis of amino acids from cyanide and its polymerization products does take place. Aqueous solutions of HCN, when heated to 100°C for several hours and subsequently acid-hydrolyzed, yield primarily glycine and smaller amounts of other amino acids. The large increase in glycine we observe upon hydrolysis is consistent with the suggestion that the precursor responsible for the amino acids in the hydrolyzate is HCN present in the lunar soil. In addition, the amino acid abundance roughly decreases with increasing carbon number, which is expected if cyanide polymerization reactions play a significant role in amino acid synthesis. It is reasonable to assume that the formation of amino acids took place during the extraction and hydrolysis of the lunar soil, but not before, as both the lunar surface and the conditions under which the lunar sample was stored were dry.

Meteoritic impacts are another interesting possible source of lunar amino acids, and similar processes on Earth have been suggested to be important with respect to the origin of terrestrial life. The cratering record of the Moon indicates that the terrestrial planets underwent a period of intense bombardment by meteorites and comets until approximately 4.0 Ga (see Chyba, 1990a). The possibility that these impactors may have delivered organic material to the early Earth has been raised (Chyba and Sagan, 1992). However, we lack conclusive evidence regarding the survivability of organic material during an impact event.

The survival and even the synthesis of meteoritic and cometary organic compounds upon impact are poorly understood, complicated by factors such as the density, scale height, and composition of the planetary atmosphere. Calculations have shown that the atmosphere should provide some cushioning effect for an impactor (Chyba et al., 1990), thus increasing the probability that more of its organic compounds will survive to reach the planetary surface, but there is as yet no empirical evidence to support theoretical claims. The situation is much simpler on the Moon, as it has virtually no atmosphere to slow impacting objects. Thus, lunar soils represent a "worst case" scenario for the survival of exogenous organic compounds and are an excellent starting point for the evaluation of current theories of impact survivability.

While Yuasa et al. (1984) demonstrated that cyanide polymerization in a 0.2 M cyanide solution can yield small quantities of aib, we observed no increase in aib upon hydrolysis. The amino acid distribution resulting from cyanide hydrolysis is highly dependent on the cyanide concentration (Yuasa et al., 1984). In lunar soil, 10 to 60 nmol/g cyanide have been detected (Holland et al., 1972), so that the aqueous cyanide concentration during our extraction procedure was probably under 30 μM. The negligible production of aib in our exper-

Table 2. Predicted maximum aib content of lunar soils.

Estimated from long-term accumulation of IDP's	
Annual flux of intact organic compounds from IDP's to the Earth (ANDERS, 1989)	$3x10^8$ g/yr
Gravitational cross section of the moon relative to that of the Earth (CHYBA, 1990a)	4.2%
Annual flux of intact organic compounds to the lunar surface	$1x10^7$ g/yr
Aib content of IDP organic material (calculated from CRONIN and PIZZARELLO, 1983)	0.1%
Annual aib flux to the lunar surface	$1x10^4$ g/yr
Amount of lunar surface containing aib assuming IDP organic accumulation only in the upper 10m (HÖRZ et al., 1991)	$1x10^{21}$ g
Accumulation period with no subsequent destruction (TAYLOR et al., 1991)	$4x10^9$ yr
Aib content of lunar soils from IDP organic material, assuming 100% survival	$4x10^{-6}$ g/g
Estimated from carbonaceous chondritic debris	
Carbonaceous chondritic component of lunar soils (HASKIN and WARREN, 1991)	1-4%
Aib content of carbonaceous chondritic material assuming a Murchison composition (CRONIN and PIZZARELLO, 1983)	$1x10^{-5}$ g/g
Predicted aib content of lunar soils from carbonaceous chondritic material, assuming 100% survival	$1\text{-}2x10^{-7}$ g/g

iment is consistent with such a low concentration of HCN. Therefore, we can assume that the aib measured in sample 78421 is entirely due to meteoritic sources. We can estimate the maximum value of aib from exogenous sources expected to be present in lunar soils by evaluating both the flux of carbonaceous material to the Moon and the aib content of that material. The figures involved in this calculation are given in Table 2. Using the value of 12 ppm (hydrolyzed) for aib in the Murchison meteorite (Cronin and Pizzarello, 1983), an annual aib flux of 10^4 g/y to the lunar surface (see Table 2 for how this value was calculated), and a lunar surface mixing depth of 10 m, we have estimated that the aib content of lunar soil should be 40 ppb, assuming 100% survivability. [Because some carbonaceous chondrites have been reported to have higher amounts of aib than Murchison (see Shimoyama et al., 1985), the maximum aib content of lunar soil could be even higher than this estimate.] We obtain a similar value (see Table 2), to within an order of magnitude, from the actual measurements of the carbonaceous chondritic debris in lunar soil. Since our results show the actual aib content of lunar soil to be $\leq$0.3 ppb, we calculate the impact survivability of aib on the lunar surface to be $\leq$0.8% (see Table 2). This is likely an overestimate, since the measured value of aib represents an upper limit, and we have assumed that little, if any, aib is produced from the hydrolysis of solar wind implanted cyanide.

4. CONCLUSIONS

Studies of amino acids on the Moon are important in evaluating whether organic compounds required for the origin of life on Earth may have been supplied from extraterrestrial sources (Chyba and Sagan, 1992). The results of our Apollo 17 analyses confirm our expectation of low survival of organic compounds during impact delivery on the Moon, where there is no atmosphere to cushion infalling bodies. Unfortunately, because the Earth is so "contaminated" with biogenic amino acids, it is difficult to evaluate the importance of exogenous delivery of organic material to the Earth. The eventual analyses of amino acids on other planetary bodies such as Mars (which is hopefully still free of terrestrial amino acids) should enable us to better evaluate the efficiency of impact delivery of organic compounds and the role of this process in the origin of life.

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