Icarus **145**, 272–281 (2000)
doi:10.1006/icar.1999.6328, available online at http://www.idealibrary.com on IDEAL®

Racemization of Meteoritic Amino Acids

Barbara A. Cohen

Department of Planetary Sciences, University of Arizona, Tucson, Arizona 85721
E-mail: bcohen@lpl.arizona.edu

and

Christopher F. Chyba

SETI Institute, Mountain View, California 94043, and the Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305

Received July 20, 1998; revised November 10, 1999

Meteorites may have contributed amino acids to the prebiotic Earth, affecting the global ratio of right-handed to left-handed (D/L) molecules. We calculate D/L ratios for seven biological, α-hydrogen, protein amino acids over a variety of plausible parent body thermal histories, based on meteorite evidence and asteroid modeling. We show that amino acids in meteorites do not necessarily undergo complete racemization by the time they are recovered on Earth. If the mechanism of amino acid formation imposes some enantiomeric preference on the amino acids, a chiral signature can be retained through the entire history of the meteorite. Original enantiomeric excesses in meteorites such as Murchison, which have undergone apparently short and cool alteration scenarios, should have persisted to the present time. Of the seven amino acids for which relevant data are available, we expect glutamic acid, isoleucine, and valine, respectively, to be the most likely to retain an initial enantiomeric excess, and phenylalanine, aspartic acid, and alanine the least. Were the D/L ratio initially identical in each amino acid, final D/L ratios could be used to constrain the initial ratio and the thermal history experienced by the whole suite. © 2000 Academic Press

Key Words: **exobiology; meteorites; organic chemistry; prebiotic chemistry; prebiotic environments.**

INTRODUCTION

Amino acids are the building blocks of proteins, among the most biologically critical molecules. The majority of amino acids used by living organisms are left-handed (laevorotatory, or L-enantiomers) rather than right-handed (dextrorotatory, or D-enantiomers) (Fig. 1). The questions of why and how life chose to use only L-enantiomers has been considered by many workers, from both a biophysical (e.g., Jacques *et al*. 1981, Mason 1991, Cline 1996) and a planetary (e.g., Chyba 1990, 1997) standpoint.

Biology's choice between L- and D-enantiomers may have been random; that is, either the L or the D molecules would have worked equally well. However, an intriguing idea is that an enhanced L/D ratio in the prebiotic Earth might have pushed the first biota to prefer left-handed molecules. L enhancement could occur either by some process on Earth or by delivery of chirally enhanced extraterrestrial organic material, possibly by way of meteorites or comets (e.g., Chyba and Sagan 1992, Pierazzo and Chyba 1999). Amino acids have been found in CM-type carbonaceous chondrites (Kvenvolden *et al*. 1970), thought to come from asteroids. The amino acids in meteorites could be created in solution from less complex molecules during a liquid water phase on the asteroid (Peltzer *et al*. 1984); however, a mechanism for chiral enhancement during the Strecker synthesis is unknown. Bonner (1991) reviews the idea that that amino acids produced in the interstellar medium (ISM) could be nonracemic (D/L $\neq 1$) due to physical processes such as parity violation, β-particle bombardment, or exposure to circularly polarized light. If a nonracemic mixture of amino acids were incorporated into an asteroidal parent body, the chiral signature might be transmitted to Earth through meteorite delivery. However, racemization (the process by which enantiomers are naturally converted from one handedness to the other) may take place on the parent body and erase any initial chiral signature.

This paper investigates whether meteoritic amino acids can retain an initial chiral signature throughout their lifetime. Many amino acids are quite resistant to racemization, and so are not considered here (Cronin and Pizzarello 1997). The class of amino acids we consider are α-hydrogen amino acids, which are the amino acids used in terrestrial biology, having the capacity to racemize rapidly compared to the age of the Solar System. Meteoritic amino acids will experience a range of circumstances during their lifetimes: incorporation into the Solar System or formation *in situ*, residence on an asteroidal parent body (possibly including aqueous alteration processes), and delivery to Earth. During these times, the amino acids are subjected to conditions varying in temperature, pH, material state, etc. We investigate

0019-1035/00 $35.00
Copyright © 2000 by Academic Press
All rights of reproduction in any form reserved.

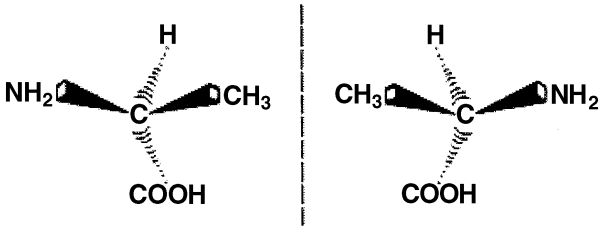

FIG. 1. The left-handed (L) and right-handed (D) forms of alanine. Both molecules are chemically identical but their structure is related by a mirror plane (dashed line). Reprinted from Chyba 1997, *Nature* **389**, p. 234. Copyright 1997, MacMillan Magazines Ltd.

how much amino acid racemization takes place during some possible histories for a variety of α-hydrogen amino acids.

PARENT BODY THERMAL HISTORY

To obtain bounds on the history experienced by meteoritic amino acids, we consider amino acid formation, residence on an asteroid, and delivery to Earth.

Formation. There are two main ways, it is thought, by which amino acids make their way into meteorite parent bodies. The first is through the Strecker synthetic process in liquid water (Peltzer *et al.* 1984) on the parent body itself. This process requires HCN, which has a limited *e*-folding half-life (0.37-life, or the time in which the concentration decreases to $1/e$ of its initial value) in liquid water at 273 K of $\sim 10^4$ years (Peltzer *et al.* 1984). Thus, the amino acids would have been formed within $\sim 10^4$ years within the parent body. After 10^4 years, the synthesis would be over (barring some source of HCN), but liquid water might persist.

The second method is incorporation of amino acids into the parent body through accretion of previously synthesized molecules from the interstellar medium (ISM). Spectroscopic observation of grains in the ISM (Pendleton *et al.* 1994) reveals features attributable to the C–H stretch in organic material. Flores *et al.* (1977) and Norden (1977) showed experimentally that amino acids could have an enantiomeric excess imposed by selective destruction by circularly polarized ultraviolet radiation, such as that from the poles of a neutron star (Bonner 1991) or an active star-forming region (Bailey *et al.* 1998). The conditions for creating such excesses are not uncommon, and chiral excesses of up to a few percent may be created. It is not known whether or to what degree the molecular cloud that collapsed to form our solar nebula experienced these conditions. However, ample evidence exists for incorporation of supernova ejecta into meteorites (Zinner 1998); consequently, exposure of this material to circularly polarized radiation from a neutron star, the supernova residuum, might be inferred. Much work has gone into finding other mechanisms that impose chiral excesses on molecules (see Bonner (1991) or Cline (1996) for reviews), but none has as large an effect as the circularly polarized light source on ISM molecules.

Accretion. If the ISM origin of organic material is chosen, then location and accretion of the parent body becomes important. The maximum temperatures seen by material in the center plane of the solar nebula at 3 AU can be considerable (>1500 K) (Cassen 1994). Any amino acids in this region would be destroyed at such temperatures (Rodante 1992). However, temperatures at larger radial distances and at the disk edges would have been considerably lower. It is possible that radial mixing and disk settling would provide an influx of organic material that had been kept at low temperatures and that this material would have been incorporated as the asteroid accreted (at lower nebular temperatures). Even if all the potential energy of material accreting onto a 100-km body were converted to heat, the rise in temperature (assuming a density of 2500 kg m^{-3} and a material heat capacity of 30 J mol^{-1} K^{-1}) is no greater than 50 K. Chirality imposed onto ISM amino acids could be retained as the amino acids are incorporated into an asteroidal body in the inner Solar System and would almost certainly be preserved during accretion into small bodies at the Solar System edge.

Aqueous alteration. In situ aqueous alteration was an important process on carbonaceous chondrite parent bodies (Bunch and Chang 1980, Zolensky and McSween 1988). There are a variety of constraints on the temperature and duration of aqueous alteration. There is little evidence of high-temperature postaccretional thermal processing in CM-type carbonaceous meteorites; the aqueous system that produced the alteration in CM chondrites was probably at temperatures less than about 300 K (DuFresne and Anders 1962, Clayton and Mayeda 1984, Zolensky and Browning 1994). The time scales suggested for the duration of liquid water are quite variable, but generally, the observed alteration is thought to be able to occur within 10^2–10^4 years (Zolensky and McSween 1988). This is in agreement with Lerner's (1995) argument that the deuterium/hydrogen ratio in Murchison and Allende amino acids, which are deuterium-enriched, would have equilibrated with deuterium-depleted asteroidal water over time scales longer than $\sim 10^3$ years. Considerations of asteroid environments (Scott *et al.* 1989) and modeling of asteroidal parent bodies (Grimm and McSween 1989, Zolensky *et al.* 1989) show as well that these low-temperature, short-duration aqueous scenarios are reasonable.

If the amino acids were already present on the parent body, then water would have brought them into solution. If the amino acids were not already present, they presumably formed in solution via Strecker synthesis (Peltzer *et al.* 1984) or other synthetic mechanisms such as polymerization of HCN (Lerner *et al.* 1993), although these processes would not be expected to have produced an initial enantiomeric excess. The time scale for amino acid synthesis, based on HCN thermal decomposition lifetimes, was probably less than $\sim 10^4$ years (Peltzer *et al.* 1984). Aqueous extracts of CM chondrites contain free amino acids along with compounds that yield amino acids on acid hydrolysis (Cronin *et al.* 1980); about 30% of the total amino acid content is in the form of free amino acids (Cronin 1976). We model here only the simplest case, racemization of free amino

acids. Racemization of amino acids in proteins or other precursor molecules to subsequently extracted amino acids might also occur.

Racemization is especially rapid in solution, as compared to the dry state (Schroeder 1974, Bada *et al.* 1994), and the solution phase will prove to be dominant in determining final D/L ratios, so the choice of duration and temperature of the aqueous system is critical. To bracket the racemization scenarios, liquid water phases at 273 and 298 K for lifetimes of 10^3 and 10^4 years each were considered. These temperatures and times are based on the meteorite observational and modeling considerations discussed above. Other regions of the parent body, not sampled by the meteorites currently available to us, may have experienced very different aqueous alteration histories and therefore, different levels of racemization. We assume that all types of chiral amino acids have the same initial chiral signature. We considered a variety of initial D/L ratios, from 0.01 to 0.99.

Residence on the parent body. After cooling from the initial warm temperatures during the liquid-water phase, asteroidal material spends its lifetime ($\sim 4.5 \times 10^9$ years) at solar equilibrium (about 155 K at 3 AU, assuming an albedo of $\sim$0.1) and is geologically inactive. Collisions may have significantly heated parts of the parent body, but the high temperatures associated with collisional heating would have destroyed amino acids altogether (Rodante 1992). Collisional heating might also have served to temporarily melt ice near the site of the impact, allowing localized aqueous alteration to occur, but this effect is neglected here.

Transit to Earth. At some point, material from the parent body escapes and enters a new orbit which eventually intersects that of Earth. The effective temperature of the meteoroid at 1 AU is 270 K. We consider elevated temperatures for 10^6 years (the Murchison cosmic ray exposure age (Caffee *et al.* 1988)), even though this is an upper limit on the length of time the meteoroid spent in near-Earth orbit. However, the meteoroid is dry throughout this time, and we will show later that in a dry environment, amino acid racemization is negligible at temperatures $\leq$270 K.

Residence on Earth. After a meteorite lands on Earth, it may be picked up immediately (as was the case with Murchison), or it may not be found for some time. The lifetime of a rock on Earth's surface can be quite variable, depending on environment and composition. In the dry Antarctic, racemization of indigenous meteoritic material will be quite slow, and Shimoyama *et al.* (1985) have shown that terrestrial contamination is not an issue for some meteorites. On the other hand, if a meteorite lands in a temperate zone and is not found, aqueous alteration and contamination is likely to occur and overprint the indigenous meteoritic signature. Racemization due to terrestrial weathering is not considered here.

Table I is a summary of the different steps in the thermal history models used in this paper, with the temperature and time scale for each.

TABLE I
Phases Used to Construct Model Parent Body Thermal Histories

Phase	Temperature (K)	Time (years)
ISM	4	$\sim 10^8$
Accretion and liquid water	273 or 298	10^2–10^4
Residence in asteroid belt	155	$\sim 4.5 \times 10^9$
Transit to Earth	270	10^6

RATE CONSTANT CALCULATIONS

The amino acids considered in this paper are called α-hydrogen amino acids, because they have a lone hydrogen atom (the α-hydrogen) attached to the carbon atom adjacent to the amino and carboxyl groups. Racemization occurs when an H_2O or OH^- molecule or another base abstracts the α-hydrogen atom. The three remaining functional groups rearrange, giving a planar molecular ion, and a hydrogen ion can then bond on either side of the plane with equal likelihood. Thus, over time, hydrogen groups detach and reattach, bringing the amino acid mixture toward enantiomeric equilibrium.

Racemization in natural systems has been extensively studied for its applications to geological dating (see reviews by Bada 1991 and 1985a). The complete derivation of equations in this section was first presented in Bada and Schroeder (1972).

The racemization process interconverts enantiomers via a reversible first-order reaction,

$$\text{L-amino acid} \underset{k_D}{\overset{k_L}{\rightleftharpoons}} \text{D-amino acid}, \tag{1}$$

where k_L and k_D are the first-order rate constants for the forward and backward reactions, respectively. The equilibrium rate constant K_{eq} is the ratio of the backward to forward reaction constants k_D/k_L, but its inverse K' ($1/K_{eq} \equiv K'$) is often used for convenience. For amino acids with a single center of symmetry, as is the case for most in this study, $K_{eq} = 1$. However, isoleucine has two centers of symmetry and has $K_{eq} = 1.3$ at pH 7.6 (Bada 1985b).

The ratio of enantiomers, that is, the D/L ratio, follows an exponential kinetic rate equation,

$$\ln\left\{\frac{1+\frac{D}{L}}{1-K'\frac{D}{L}}\right\}_t - \ln\left\{\frac{1+\frac{D}{L}}{1-K'\frac{D}{L}}\right\}_0 = (1+K')k_L t, \tag{2}$$

for all but isoleucine, $k_L = k_D$ and $K' = k_L/k_D = 1$. For isoleucine, k_L was calculated explicitly using $1/K' = 1.3$, and then $k_L \equiv k$ in further calculations.

The solution to Eq. (2) involves four variables: the D/L ratio, time, the rate constant $k_L = k$, and temperature. The rate constant is a measure of how fast the racemization reaction takes place. It follows an Arrhenius relationship: $k(T) = A\exp[-E/RT]$,

TABLE II
Amino Acid Racemization Rate Constants Derived from Fig. 2

Amino acid	Rate constant k (s^{-1})
Alanine, wet	exp[24.91–15863/T]
Alanine, dry	exp[21.59–15493/T]
Aspartic acid, wet	exp[23.34–14725/T]
Aspartic acid, dry	exp[22.45–15493/T]
Glutamic acid	exp[22.56–15675/T]
Isoleucine, wet	exp[27.24–16913/T]
Isoleucine, dry	exp[20.49–15493/T]
Leucine	exp[24.30–15750/T]
Phenylalanine	exp[19.82–13440/T]
Valine	exp[23.61–15754/T]

where k is the rate constant in s^{-1}, A the frequency factor in s^{-1}, E the activation energy in J mol^{-1}, R the gas constant in J mol^{-1} K^{-1}, and T the absolute temperature. The rate constant is not a true constant. It is primarily a function of temperature but also varies with the state of the amino acid: in solution or dry. In solution, k varies with pH and ionic strength as well. A literature search was conducted to determine rate constants at varied temperatures, pH, and states. Data were obtained for seven different amino acids: alanine, aspartic acid, glutamic acid, isoleucine, leucine, phenylalanine, and valine.

To determine rate constants, previously published values of k or $\ln k$ at a given temperature were used, or k was calculated from amino acid racemization half-lives. After obtaining rate constants at a variety of conditions, $\ln k$ may be graphed vs $1000/T$ taking advantage of the linear relationship $\ln k = E/RT + \ln A$. The resulting graphs are shown in Fig. 2. A least-squares fit to the data was employed to construct a relationship between k and T. The racemization rates for each amino acid as a function of temperature derived from these graphs are shown in Table II. For T in K, these coefficients yield k in s^{-1}.

For all seven amino acids, data were found for free amino acids in solution. In all cases, pH was buffered in the range 7–7.6, and total ionic strength varied from 0.01 to 0.5 M. For isoleucine, two lines were fit, one through only the solution data and another through the dry values of Schroeder (1974). Dry data for alanine and aspartic acid were obtained following Bada and McDonald (1995), multiplying the isoleucine dry data by 3 for alanine, and 7 for aspartic acid. Wonnacott (1979) demonstrated that the effect of ionic strength is not important in the racemization of alanine, and so we do not consider ionic strength differences to be significant in our calculations. Bada (1972) and Shou (1979) show that racemization rates for α-hydrogen amino acids are not strongly affected by pH in the range pH 7–12. The range pH 7–12 is the pH range modeled by Zolensky *et al.* (1989) of the aqueous phase on an asteroidal parent body, so we did not consider the effects of pH any further. Our absolute racemization rates are consistent with the relative racemization rates in Smith and Evans (1980) and Smith and Reddy (1989).

D/L RATIO MODELING

After finding k, there are only two unknowns in Eq. (2): D/L ratio and time. Two methods of solution both yield useful results: choosing a time interval gives the racemization extent after that interval, and choosing a fixed D/L ratio of 0.5 gives the racemization half-life.

Forward modeling involves choosing a time interval, constructing a temperature–time history, setting $K' = 1$ (or 1.3 for isoleucine), choosing an initial D/L ratio, and solving Eq. (2) for the D/L ratio at time t,

$$\left(\frac{\mathrm{D}}{\mathrm{L}}\right)_t = \frac{e^{2kt} R_0 - 1}{e^{2kt} R_0 + 1}, \tag{3}$$

where $R_0 = [(1 + \mathrm{D/L})/(1 - \mathrm{D/L})]_0$. The D/L ratio was determined after each time step in hypothetical thermal models based on the steps described in Table I, using the result from each time step to determine R_0 for the next time step in Eq. (3). A typical time–temperature history consisted of 550 time steps spaced logarithmically from $t = 1$ year to $t = 4.5 \times 10^9$ years.

We chose a range of initial D/L ratios to model, but our conclusions do not depend strongly on the initial ratio. For amino acids with an initial D/L ratio of 0.9 (approximately the excess Cronin and Pizzarello (1997) report in racemization-resistant amino acids), the extent of racemization depends strongly on the choice of temperature and duration of the liquid water phase (Figs. 3a and 3b). Over time scales of 10^3–10^4 years, a few amino acids can experience a wide range of final ratios, while others are extremely slow to racemize. This range of final ratios may be observable in the final product. If the initial enrichment were great, the final signature would be very different from the original. However, for smaller enrichments, the final D/L ratio may be close to the initial excess. Modeling a dry environment shows that racemization does not take place at all when the temperature of the asteroid is 155 K and is negligible for $\sim 10^6$ years when the temperature is 270 K (Fig. 3c).

This process can instead be worked backward, beginning at time $t =$ now with some D/L ratio and determining the initial ratio. However, this backward process does not work if the D/L ratio at time $t =$ now is already 1, because D/L in Eq. (3) can only asymptotically approach 1. The exponential form also means that for a final D/L ratio (at time $t =$ now) greater than 0.99, it takes longer than the age of the Solar System back in time for the D/L ratio to deviate significantly from its original value.

Cronin and Pizzarello (1997) found L-enantiomeric excesses in Murchison amino acids which are resistant to racemization (α-methyl amino acids), but a racemic mixture (to within 1% accuracy (Cronin and Pizzarello 1997)) in the α-hydrogen amino acids investigated. Engel and Macko (1997) reported L-enantiomeric excesses in the α-hydrogen amino acids alanine (D/L = 0.5) and glutamic acid (D/L = 0.3). Backward modeling these excesses (Fig. 4) shows that the initial D/L ratio of alanine is strongly dependent on the conditions of aqueous alteration. A current alanine D/L ratio of 0.5 implies that the original D/L ratio

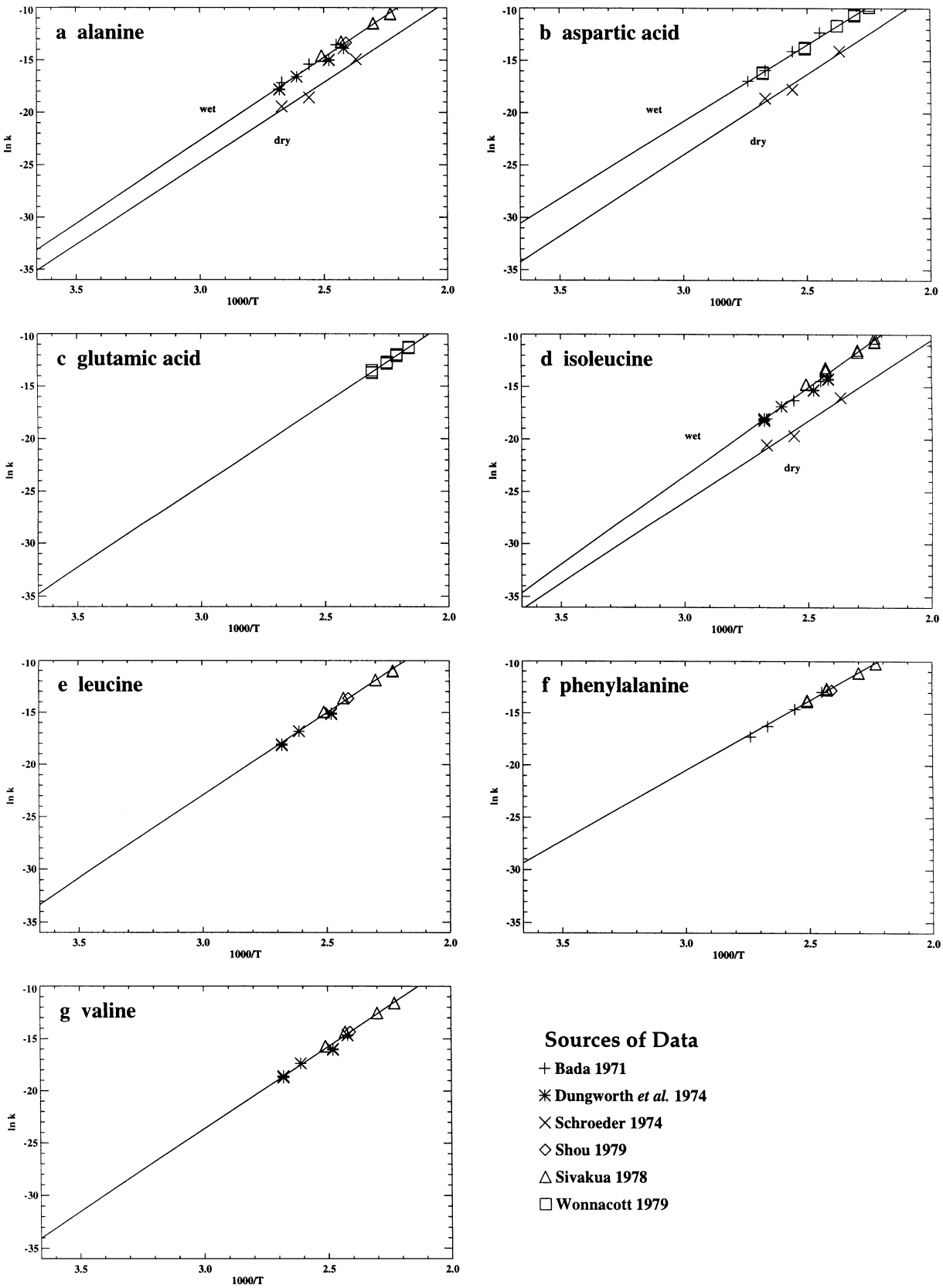

FIG. 2. Data used to determine racemization rate k. The black line is a least-squares linear fit to the data for each amino acid. The data used for each specific line fit are discussed in the text. (a) Alanine, (b) aspartic acid, (c) glutamic acid, (d) isoleucine, (e) leucine, (f) phenylalanine, (g) valine.

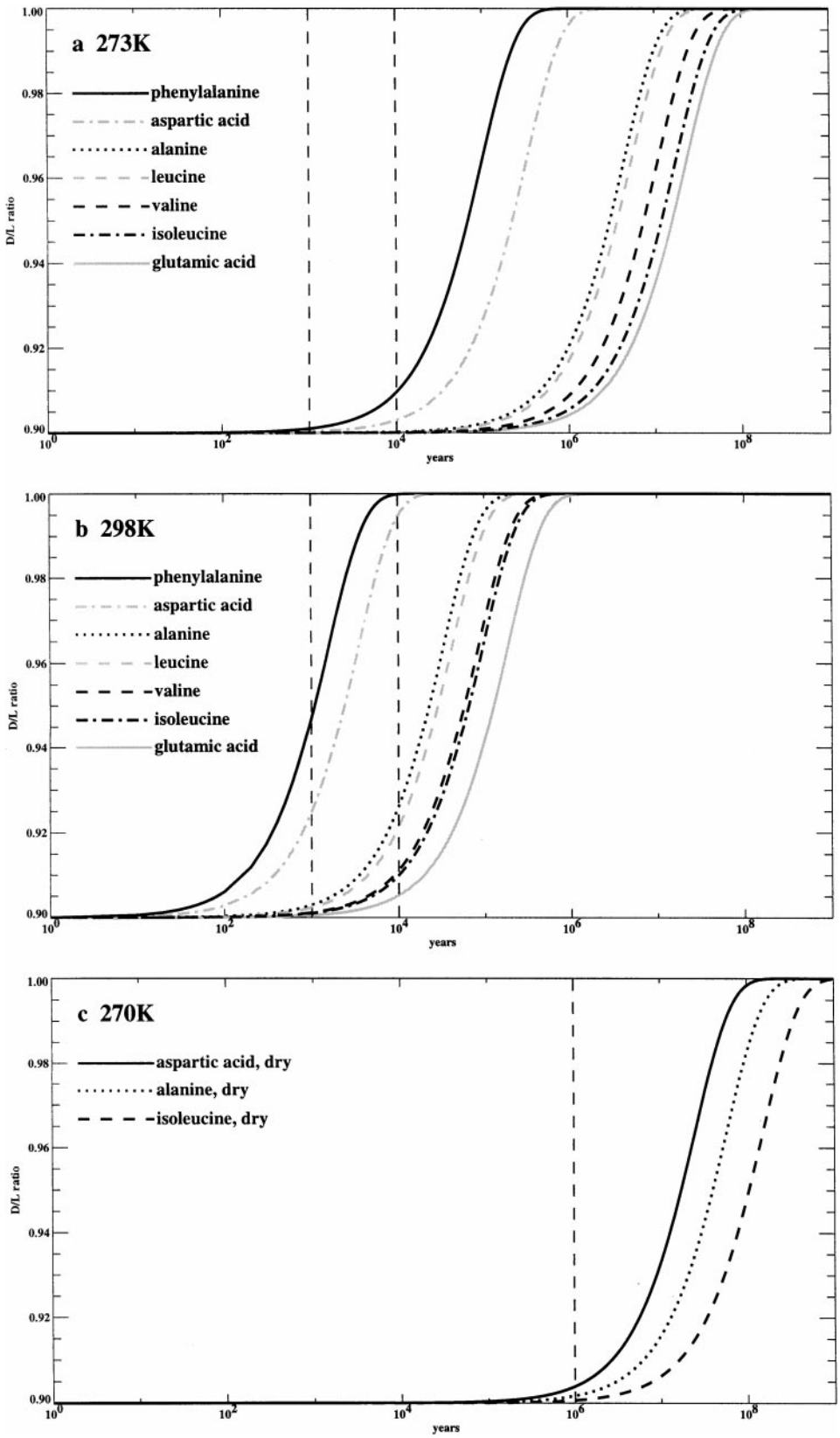

FIG. 3. D/L ratio forward modeling in solution, beginning at time $t = 0$. The D/L ratio was determined after each time step in the thermal model described in Table I, using the result from each time step as the initial ratio for the next in Eq. (2). A typical temperature–time history consisted of 550 time steps spaced logarithmically until 4.5 Ga. (a) 273 K, free amino acids in solution, (b) 298 K, free amino acids in solution, (c) 270 K, dry conditions.

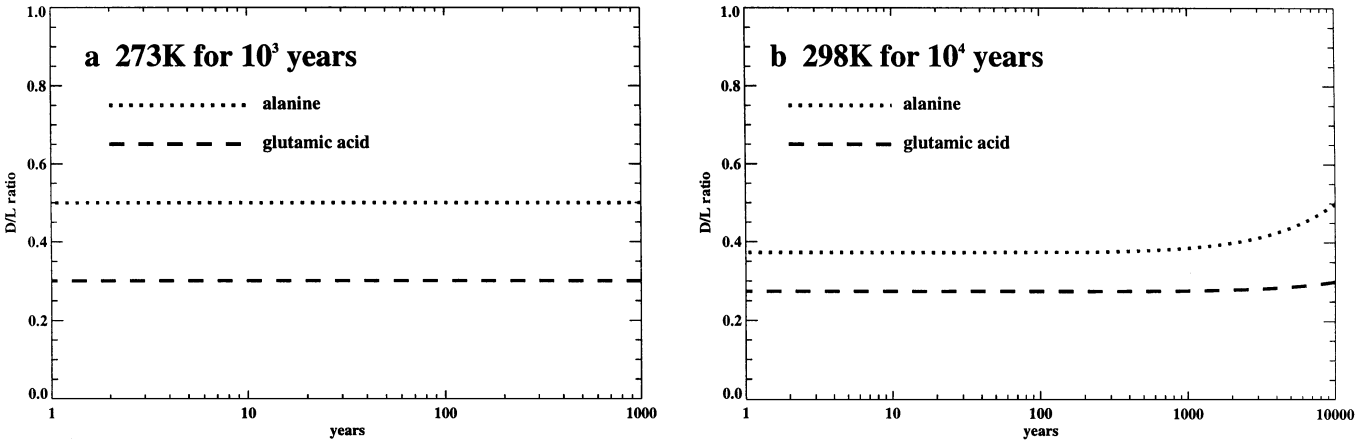

FIG. 4. D/L ratio backward modeling for glutamic acid and alanine in solution to produce the D/L ratios reported by Engel and Macko (1997) (alanine D/L = 0.5 and glutamic acid D/L = 0.3). The model inputs are the same as for Fig. 3, but were run backward and allowed to proceed only for a specific length of time. (a) 273 K water for 10^3 years. (b) 298 K water for 10^4 years.

could have ranged from 0.5 to ~0.35. In the case of glutamic acid, the initial ratio was likely identical to its current value, a result that holds true almost independently of aqueous alteration conditions. This makes glutamic acid an especially good target of D/L determination experiments in meteorites. We note that the Engel and Macko (1997) results may be in error (Pizzarello and Cronin 1998), but we consider them here for illustrative purposes.

Half-lives. Racemization half-life as used in this paper is the time it takes for the D/L ratio to reach 0.5 of its initial value. Setting the D/L ratio to 0.5 in Eq. (2) and solving for $t_{1/2}$ gives $t_{1/2} = (\ln 3)/2k$. Figure 5a plots the half-lives of the amino acids in solution as a function of temperature. At temperatures of interest (150–300 K), the half-lives for this group of α-hydrogen amino acids varies over approximately five orders of magnitude. This emphasizes the importance of constraining the temperature and duration of each environment to which the amino acids are exposed.

DISCUSSION

Both the half-life calculations and the thermal model evolution shed light on the behavior of meteoritic amino acids. Here we discuss a number of important issues.

For the bulk of their lifetime before we find them, extraterrestrial amino acids experience cold temperatures and dry conditions that prevent racemization from taking place at all. However, elevated temperatures for even relatively short durations can serve to begin (and often complete) the racemization reaction in solution. All seven amino acids considered here, if beginning with an initial D/L ratio of 0.9, would reach a D/L ratio of $\geq$0.99 in 10^6 years if dissolved into a 298 K solution (Fig. 3b). This amount of racemization requires 10^7 years or more for five of the seven amino acids in solutions at 273 K. Figure 5b shows the 0.99-life, or the time for 99% of the initial D–L mixture to racemize, as a function of temperature in aqueous solution. The 0.99-life can be considered "total racemization" as current laboratory chirality measurements have errors on the order of 1% (Cronin and Pizzarello 1997).

The racemization process during the aqueous alteration phase is extremely sensitive to the assumed time scales and temperatures. Most of the amino acids experience a degree of racemization during aqueous alteration. However, some amino acids show a relatively slow rate of racemization. Glutamic acid and isoleucine can retain a D/L $\neq 1$ for 10^8 years in a 273 K solution. The aqueous alteration phase is the dominant environment in which racemization takes place on the parent body.

Bada and McDonald (1995) have pointed out the large difference in rate of racemization between amino acids in wet vs dry environments. The noticeable difference between the dry rate constant and the solution rate constant for isoleucine, aspartic acid, and alanine implies that rate constants are state-dependent for other amino acids as well. Racemization is extremely slow when the asteroid is dry, in agreement with the noted retardation of racemization in other anhydrous environments, such as amber (Bada *et al.* 1994). The cold (155 K), dry conditions experienced by the asteroid for most of its lifetime prohibit any racemization from taking place at all. The warmer (270 K), but still dry, conditions in near-Earth orbit can delay racemization for ~10^6 years, typical of C2 meteorite cosmic ray exposure ages (Caffee and Nishiizumi 1997).

A common method of extracting amino acids in laboratory settings is by crushing the meteorite and extracting free amino acids with hot water. This method is analogous to the parent-body scenario we envision. Therefore, the amino acids extracted with only water in the laboratory would be the same amino acids that underwent the aqueous alteration phase on the parent body. Another common laboratory practice is to add acid to the hot-water extract (acid hydrolysis). This step breaks some related compounds (such as pyroglutamic acid) into amino acids (Cooper and Cronin 1995), therefore creating a higher concentration of amino acids for analysis. Acid hydrolysis is not expected to

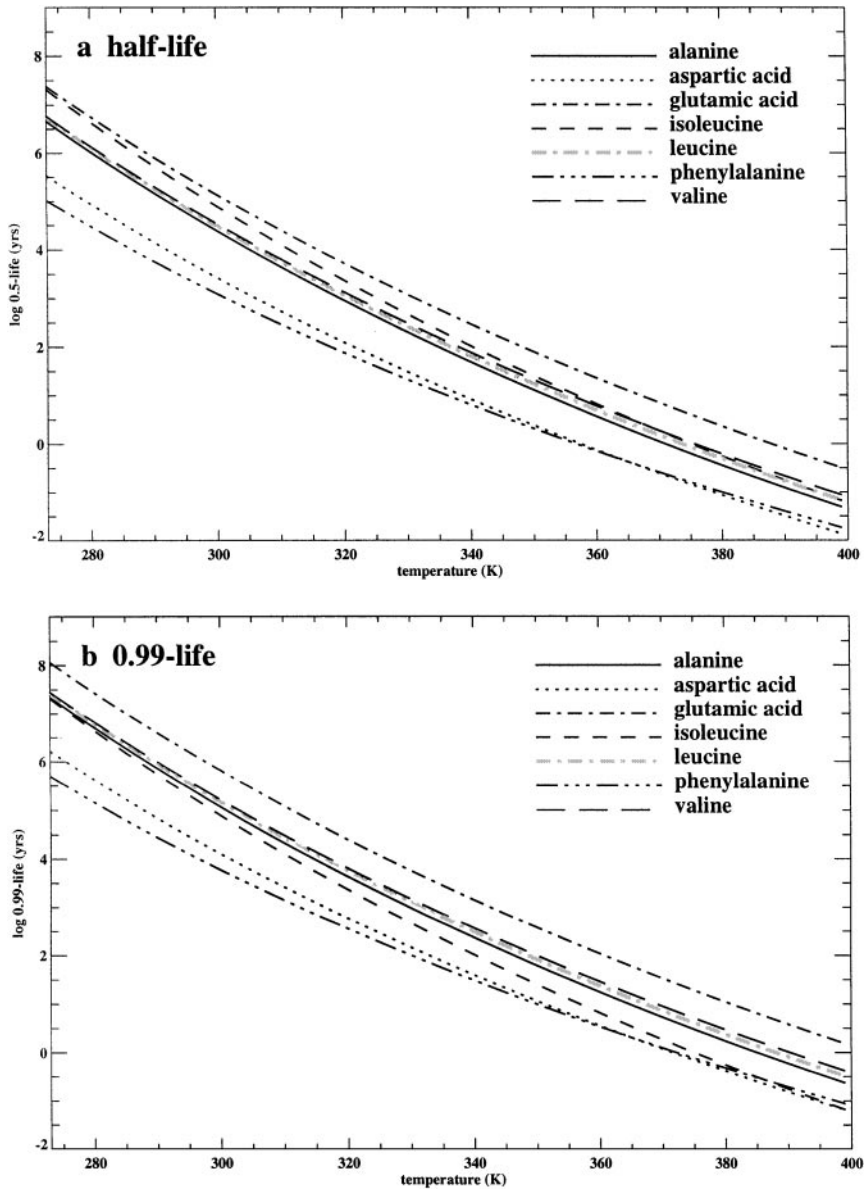

FIG. 5. (a) Half-lives and (b) 0.99-lives in years versus temperature in K for the amino acids described in this paper. Over the temperatures of interest (150–300 K), the half-lives vary by about 5 orders of magnitude.

occur in the basic waters of the parent body fluids, and therefore it is expected that amino acids will racemize to an extent independent of the state of their acid-labile precursors. However, to use the suite of α-hydrogen amino acids as indicators of parent-body conditions as described here, only the unhydrolyzed extract of the meteorite can be useful.

Glutamic acid, in particular, exists in meteorite extract largely as pyroglutamic acid. Analyses of hydrolyzed extracts report up to an order of magnitude more glutamic acid after acid hydrolysis than in the neutral water extract (20 nmol/g vs 2 nmol/g (Shock and Schulte 1990)), an effect that is explained by breakdown of pyroglutamic acid or other complex molecules in acid (Cooper and Cronin 1995). The reaction between pyroglutamic acid and glutamic acid in neutral or slightly basic solutions favors formation of pyroglutamic acid (Wilson and Cannan 1937). Thus, since free glutamic acid is found in unhydrolyzed extract, we may argue that it is almost certainly original glutamic acid and not derived from a related compound. Further, the unhydrolyzed parent body solution most likely contained free glutamic acid as well.

CONCLUSIONS

We have shown that amino acids in meteorites do not necessarily undergo complete racemization by the time they are recovered on Earth. If the mechanism of amino acid formation imposes some enantiomeric preference on the amino acids, the

chiral signature can be retained through the entire history of the meteorite. In particular, original enantiomeric excesses in meteorites such as Murchison, which have undergone presumably short and cool alteration scenarios, should have persisted to the present time. If the conditions of the meteorite's residence on Earth can be determined, then the thermal history of the amino acids will provide insight into the conditions on the meteorite parent body. The α-hydrogen amino acids are a potentially enormous source of information, but of course extreme care must be taken while studying them to rule out terrestrial contamination.

A separation effect is shown to occur for some likely aqueous alteration scenarios. Because each amino acid racemizes at a different rate, some can be racemized completely while under the same conditions, others are unaffected. If the meteorite parent body experienced only a short wet period, we should expect to be able to observe that this suite of amino acids has differing D/L ratios, with phenylalanine the most racemic and glutamic acid the least racemic amino acids in the suite examined (Fig. 3). If a mechanism for imposing chirality on the α-hydrogen amino acids creates D/L ratios that are initially identical in each amino acid, then the final D/L ratios of each amino acid can be used to constrain the thermal history experienced by the entire suite.

An absence of enantiomeric excesses in meteoritic amino acids could mean one of two things: either (a) no chiral excess ever existed, or (b) the meteorite experienced a combination of temperature–time–fluid conditions that allowed the free amino acids to completely racemize. If scenario (a) could be ruled out by the presence of chiral excesses in other types of amino acids (such as those studied by Cronin and Pizzarello (1997)), then limits on the meteorite's thermal history could be inferred by this suite of amino acids as well.

Since all asteroids do not necessarily undergo the same thermal history, and since thermal histories may vary within the same parent body, a variety of D/L ratios may be expected between meteorites, even if the initial organic material began with identical D/L ratios. Furthermore, the degree of racemization is sensitive to a number of parameters that are not always easy to constrain, largely the temperature and duration of a solution phase.

The final D/L ratio of amino acids in a meteorite does not necessarily give unambiguous information about the path that produced it. However, this work does imply that delivery to Earth of extraterrestrial organic material with a predetermined handedness is possible and that this initial chirality may be determinable.

ACKNOWLEDGMENTS

Special thanks to Robert Coker for programming assistance. We thank Sherwood Chang, George Cooper, Gene McDonald, and Sandra Pizzarello for their comments and suggestions. We also thank Jeffrey Bada and an anonymous reviewer for their constructive reviews. B.A.C. is supported with a NASA Space Grant fellowship. C.F.C. acknowledges support from a Presidential Early Career Award for Scientists and Engineers and the NASA Exobiology Program. This research has made use of NASA's Astrophysics Data System Abstract Service.

REFERENCES

Bada, J. L. 1971. Kinetics of the nonbiological decomposition and racemization of amino acids in natural waters. *Adv. Chem. Ser.* **106**, 309–331.

Bada, J. L. 1972. Kinetics of racemization of amino acids as a function of pH. *J. Am. Chem. Soc.* **94**, 1371–1373.

Bada, J. L. 1985a. Amino acid racemization dating of fossil bones. *Annu. Rev. Earth Planet. Sci.* **13**, 241–268.

Bada, J. L. 1985b. Racemization of amino acids. In *Chemistry and Biochemistry of the Amino Acids* (G. C. Barrett, Ed.), pp. 399–414. Chapman and Hall, London.

Bada J. L. 1991. Amino acid cosmogeochemistry. *Phil. Trans. R. Soc. London B* **333**, 349–358.

Bada, J. L., and G. D. McDonald 1995. Amino acid racemization on Mars: Implications for the preservation of biomolecules from an extinct martian biota. *Icarus* **114**, 139–143.

Bada, J. L., and R. A. Schroeder 1972. Racemization of isoleucine in calcareous marine sediments: Kinetics and mechanism. *Earth Planet. Sci. Lett.* **15**, 1–11.

Bada, J. L., X. S. Wang, H. N. Poinar, S. Paabo, and G. O. Poinar 1994. Amino acid racemization in amber-entombed insects: Implications for DNA preservation. *Geochim. Cosmochim. Acta* **58**, 3131–3135.

Bailey, J., A. Chrysostomou, J. H. Hough, T. M. Gledhill, A. McCall, S. Clark, F. Menard, and M. Tamura 1998. Circular polarization in star-formation regions: Implications for biomolecular homochirality. *Science* **281**, 672–674.

Bonner, W. A. 1991. The origin and amplification of biomolecular chirality. *Origins Life Evol. Biosphere* **21**, 59–111.

Bunch, T. E., and S. Chang 1980. Carbonaceous Chondrites. II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.

Caffee, M. W., and K. Nishiizumi 1997. Exposure ages of carbonaceous chondrites. II. *Meteoritics Planet. Sci.* **32**, A26.

Caffee, M. W., J. N. Goswami, C. M. Hohenberg, K. Marti, and R. C. Reedy 1988. Irradiation records in meteorites. In *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, Eds.), pp. 205–245. Univ. of Arizona Press, Tucson.

Cassen, P. 1994. Utilitarian models of the solar nebula. *Icarus* **112**, 405–429.

Chyba, C. F. 1990. Extraterrestrial amino acids and terrestrial life. *Nature* **348**, 113–114.

Chyba, C. F. 1997. A left-handed Solar System? *Nature* **389**, 234–235.

Chyba, C. F., and C. Sagan 1992. Endogeneous production, exogeneous delivery, and impact-shock synthesis of organic molecules: An inventory for the origins of life. *Nature* **355**, 125–132.

Clayton, R. N., and T. K. Mayeda 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67**, 151–161.

Cline, D. B. 1996. On the determination of the physical origin of homochirality in life. In *Chemical Evolution: Physics of the Origin and Evolution of Life* (J. Chela-Flores and F. Raulin, Eds.), pp. 251–267. Kluwer Academic, The Netherlands.

Cooper, G. W., and J. R. Cronin 1995. Linear and cyclic aliphatic carboxamides of the Murchison meteorite: Hydrolyzable derivatives of amino acids and other carboxylic acids. *Geochim. Cosmochim. Acta* **59**, 1003–1015.

Cronin, J. R. 1976. Acid-labile amino acid precursors in the Murchison meteorite. 1. Chromatographic Fractionation. *Origins Life* **7**, 337–342.

Cronin, J. R., and S. Pizzarello 1997. Enantiomeric excesses in meteoric amino acids. *Science* **275**, 951–952.

Cronin, J. R., W. E. Gandy, and S. Pizzarello (1980). Amino acids of the Murchison meteorite. In *Biogeochemistry of Amino Acids* (P. E. Hare, T. C. Hoering, and K. King, Jr., Eds.), pp. 145–168. Wiley, New York.

DuFresne, E. R., and E. Anders 1962. On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26**, 1085–1114.

Dungworth, G., N. J. Vincken, and A. W. Schwartz 1974. Racemization of aliphatic amino acids in fossil collagen of Pleistocene, Pliocene, and Miocene ages. In *Advances in Organic Chemistry* (B. Tissot and F. Bienner, Eds.), pp. 689–700. Editions Technip, Paris.

Engel, M. H., and S. A. Macko 1997. Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite. *Nature* **389**, 265–268.

Flores, J. J., W. A. Bonner, and G. A. Massey 1977. Asymmetric photolysis of (RS)-leucine with circularly polarized ultraviolet light. *J. Am. Chem. Soc.* **99**, 3622–3624.

Grimm, R. E., and H. Y. McSween, Jr. 1989. Water and the thermal evolution of carbonaceous chondrite parent bodies. *Icarus* **82**, 244–280.

Jacques, J., A. Collet, and S.H. Wilen 1981. *Enantiomers, Racemates, and Resolutions.* Wiley, New York.

Kvenvolden, K., J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. R. Kaplan, and C. Moore 1970. Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* **228**, 923–926.

Lerner, N. R. 1995. Influence of Murchison or Allende minerals on hydrogen–deuterium exchange of amino acids. *Geochim. Cosmochim. Acta* **59**, 1623–1631.

Lerner, N. R., E. Peterson, and S. Chang 1993. The Strecker synthesis as a source of amino acids in carbonaceous chondrites: Deuterium retention during synthesis. *Geochim. Cosmochim. Acta* **57**, 4713–4723.

Mason, S. F. 1991. Origins of the handedness of biological molecules. In *Biological Symmetry and Handedness*, Ciba Foundation Symposium 162, pp. 3–15. Wiley, Chichester.

Norden, B. 1977. Was photoresolution of amino acids the origin of optical activity in life? *Nature* **266**, 567–568.

Peltzer, E. T., J. L. Bada, G. Schlesinger, and S. L. Miller 1984. The chemical conditions on the parent body of the Murchison meteorite: Some conclusions based on amino, hydroxy and dicarbolic acids. *Adv. Space Res.* **4**, 69–74.

Pendleton, Y. J., S. A. Sandford, L. J. Allamandola, A. G. G. M. Tielens, and K. Sellgren 1994. Near-infrared absorption spectroscopy of interstellar hydrocarbon grains. *Astrophys. J.* **437**, 683–696.

Pierazzo, E., and C. F. Chyba 1999. Amino acid survival in large cometary impacts. *Meteoritics Planet. Sci.* **34**, 909–918.

Pizzarello, S., and J. R. Cronin 1998. Alanine enantiomers in the Murchison meteorite. *Nature* **394**, 236.

Rodante, F. 1992. Thermodynamics and kinetics of decomposition processes for standard α-amino acids and some of their dipeptides in the solid state. *Thermochim. Acta* **200**, 47–60.

Schroeder, R. A. 1974. *Kinetics, Mechanism, and Geochemical Application of Amino Acid Racemization in Various Fossils*. Ph.D. thesis, University of California at San Diego, San Diego, CA.

Scott, E. R. D., G. J. Taylor, H. E. Newsom, F. Herbert, M. Zolensky, and J. F. Kerridge 1989. Chemical, thermal, and impact processing of asteroids. In *Asteroids II* (R. P. Binzel, T. Gehrels, and M. S. Matthews, Eds.), pp. 701–739. Univ. of Arizona Press, Tucson.

Shimoyama, A., K. Harada, and K. Yanai 1985. Amino acids from the Yamato-791198 carbonaceous chondrite from Antarctica. *Chem. Lett.* **1985**, 1183–1186.

Shock, E. L., and M. D. Schulte 1990. Summary and implications of reported amino acid concentrations in the Murchison meteorite. *Geochim. Cosmochim. Acta* **54**, 3159–3173.

Shou, M. Y. 1979. *Kinetics and Mechanisms of Several Amino Acid Diagenetic Reactions in Aqueous Solutions and in Fossils*. Ph.D. thesis, Scripps Institution of Oceanography, University of California at San Diego, San Diego, CA.

Sivakua, T. 1978. *Structural Effects on the Kinetics and Mechanism of the Racemization of Arylglycines*. Ph.D. thesis, Utah State University, Logan, UT.

Smith, G. G., and R. C. Evans 1980. The effects of structure and conditions on the rate of racemization of free and bound amino acids. In *Biogeochemistry of Amino Acids* (P. E. Hare, T. C. Hoering, and K. King Jr., Eds.), pp. 257–282. Wiley, New York.

Smith, G. G., and G. V. Reddy 1989. Effect of the side chain on the racemization of amino acids in aqueous solution. *J. Org. Chem.* **54**, 4529–4535.

Wilson, H., and R. K. Cannan 1937. The glutamic acid–pyrrolidonecarboxylic acid system. *J. Biol. Chem.* **119**, 309–331.

Wonnacott, D. M. 1979. *The Application of Gas Chromatography to the Resolution of Enantiomeric Mixtures of Amino Acids. Factors Affecting the Racemization of Amino Acids.* Ph.D. thesis, Utah State University, Logan, UT.

Zinner, E. 1998. Stellar nucleosynthesis and the isotopic composition of presolar grains from primitive meteorites. *Annu. Rev. Earth Planet. Sci.* **26**, 147–188.

Zolensky, M., and H. Y. McSween 1988. Aqueous alteration. In *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, Ed.), pp. 114–143. Univ. of Arizona Press, Tucson.

Zolensky, M. E., W. L. Bourcier, and J. L. Gooding 1989. Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulations. *Icarus* **78**, 411–425.

Zolensky, M. E., and L. B. Browning 1994. CM chondrites exhibit the complete petrologic range from type 2 to 1. *Meteoritics* **29**, 556.