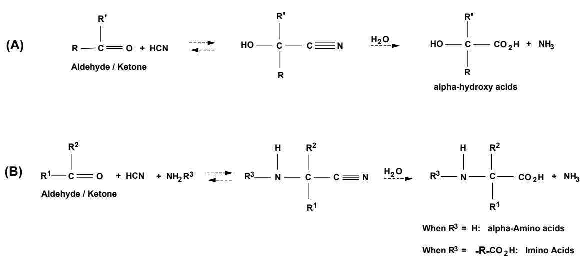
IMINO ACIDS IN THE MURCHISON METEORITE: EVIDENCE OF STRECKER REACTIONS.
N. R. Lerner and G. W. Cooper. Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035 USA. gcooper@mail.arc.nasa.gov.

Introduction: Both α-amino acids and α-hydroxy acids occur in aqueous extracts of the Murchison carbonaceous meteorite. The Strecker-cyanohydrin reaction, the reaction of carbonyl compounds, cyanide, and ammonia to produce amino and hydroxy acids, has been proposed as a source of such organic acids in meteorites [1]. Such syntheses are consistent with the suggestion [2] that interstellar precursors of meteoritic organic compounds accreted on the meteorite parent body together with other ices [3]. Subsequent internal heating of the parent body melted these ices and led to the formation of larger compounds in synthetic reactions during aqueous alteration, which probably occurred at temperatures between 273K and 298K [4]. In the laboratory, imino acids are observed as important by-products of the Strecker synthesis (scheme-B). When $R^3 = CR_XR_YCO_2H$, $C\,R_XR_YCONH_2$ or CR_XR_YCN, i.e., when NH_2R^3 is an amino acid, an amino acid amide, or an amino acid nitrile, imino acids are formed [5].



In Murchison, the detection of possible precursor carbonyl compounds [6] and ammonia [7] supports the conjecture that the Strecker synthesis led to the more familiar alpha-hydroxy and alpha-amino acids in meteorites. In fact, one imino acid (iminopropionacetic) has been reported in Murchison and its chiral distribution analyzed [8]. We report here on the presence in Murchison of an extensive suite of imino acids whose distribution appears to parallel those of indigenous amino acids in carbonaceous meteorites.

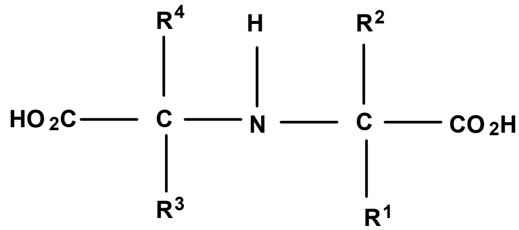
We examined aqueous extracts of Murchison. The procedures used to extract, isolate (including ion exchange chromatography), and dry the amino acids from Murchison was described previously [9]. The extracts were derivatized and analyzed by gas chromatography-mass spectrometry (GC-MS) and high-pressure liquid chromatography (HPLC). GC-MS derivatives were the t-butyldimethylsilyl (TBDMS) and triflouracetyl isopropyl esters (TFA-ISP) [10]. An aliquot of the ammonium hydroxide eluent from ion exchange was separated into fractions by reversed phase HPLC. The chromatograph used was a Beckman Model 126 with a Beckman Model168 diode array detector. Samples were applied to a 25 cm x 4.6 mm Inertsil ODS3 reversed phase column. The column was eluted at room temperature with 0.5 ml/min. of 0.1% aqueous trifluoroacetic acid solution. Imino acetic acid standards were produced from the reaction of aqueous solutions of the appropriate carbonyl compounds, ammonia, and hydrogen cyanide and/or the reactions of solutions of the corresponding amino acid with formaldehyde and hydrogen cyanide.

Analyses of aqueous extracts from the Murchison meteorite revealed a suite of imino acids (Table 1). With the exception of a possible 7-carbon isomer (iminioisobutyriopropionic), all of the 4-carbon to 7-carbon (C4-C7) α-imino acids were identified. Imino acids can be found in nature in marine invertebrates, however, they are not common biological contaminants [11]. In addition, their distribution in Murchison is similar to that of other known indigenous (abiotic) meteoritic compounds; for each carbon number through C7 all possible isomers are present (with the above exception) and abundances generally decrease with increasing carbon number. As mentioned, the α-imino acids are known by-products of the Strecker synthesis. The observation of these relatively unusual compounds in the Murchison meteorite is strongly suggestive that the Strecker synthesis made some contribution to the formation of extraterrestrial amino acids.

EVIDENCE OF STRECKER REACTIONS: N. R. Lerner and G. W. Cooper

Table 1

Meteoritic Imino Acids: C4 Through C7



Imino acid	R^1	R^2	R^3	R^4
<u>C4 Imino Acid</u>				
Iminodiacetic (IDA)	H	H	H	H
<u>C5 Imino Acid</u>				
Iminopropionicacetic (IPA)	H	H	H	CH_3
<u>C6 Imino Acids</u>				
Iminobutyricacetic (IBA)	H	H	H	CH_2 CH_3
Iminoisobutyricacetic (IIBA)	H	H	CH_3	CH_3
Iminodipropionic (IDP)	H	CH_3	H	CH_3
<u>C7 Imino Acids</u>				
Iminopentanoacetic (IP'A)	H	H	H	$(CH_2)_2$ CH_3
Imino β-methylbutyricacetic (IBMBA)	H	H	H	$CH(CH_3)_2$
Imino α-methylbytyricacetic (IAMBA)	H	H	CH_3	CH_2 CH_3
Iminobutyriopropionic (IBP)	H	CH_3	H	CH_2 CH_3
Iminioisobutyriopropionic (IIBP)	H	CH_3	CH_3	CH_3

References: [1] Peltzer E. T. and Bada J. L. (1978) *Nature 272*, 443-444. [2] Cronin J. R. et al. (1988) Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets. In *Meteorites and the Early Solar System* (ed. J.F. Kerridge and M.S. Mathews), pp. 819-857 Univ. Arizona Press. [3] Bunch T.E. and Chang S. (1980) *Geochim. Cosmochim. Acta, 44,* 1543-1577. [4] Clayton R.N. and Mayeda T.K. (1984) *Earth Planet. Sci. Lett., 67*, 151-161. [5] Chadha M.S. et al. (1971) *Biorg. Chem., 1*, 269-274; Lerner N.R. et al. (1993) *Geochim. Cosmochim. Acta*, *57,* 4713-4723. [6] Jungclaus G. A. et al. (1976) *Meteoritics, 11,* 231-237. [7] Kung C. C. and Clayton R. N. (1978) *Earth and Planet. Sci. Lett., 38*, 421-435; Pizzarello et al. (1994) *Geochim. Cosmochim. Acta, 58,* 5579-5587. [8] Pizzarello S. and Cooper G.W. (2001) *MAPS, 36*, 897-909. [9] Cooper G. W. and Cronin J.R. (1995) *Geochim . Acta, 59*, 1001-1015. [10] Lerner N.R. (1995) *Geochim. Cosmochim. Acta, 59*, 1623-1631. [11] Greenstein and Winitz (1961