

Amino acid composition, petrology, geochemistry, ^{14}C terrestrial age and oxygen isotopes of the Shişr 033 CR chondrite

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Abstract—We have analyzed Shişr 033, a CR chondrite from the Omani desert, using several different analytical techniques designed to study the degree of terrestrial alteration of this meteorite and also its petrologic classification. Bulk chemical analyses (including organic carbon and mean total H_2O content) are consistent with a CR classification. Additionally, oxygen isotope analysis on a bulk sample indicates that Shişr 033 is of type CR2. Amino acid analysis using liquid chromatography with UV fluorescence detection (HPLC-FD) and liquid chromatography-time of flight-mass spectrometry (LC-ToF-MS) show that the absolute and the relative amino acid content of Shişr 033 is distinct from other carbonaceous chondrites. Oxygen isotope analysis of a phyllosilicate-rich dark inclusion shows that this inclusion is closer to CV3 or CO3 chondrites. The effects of terrestrial weathering in Shişr 033 are evident from the dark inclusion carbon isotopic data, bulk chemistry (through the elevated concentrations of Sr and Ba), and amino acid data, which suggests extensive amino acid contamination of the meteorite from the fall site soil. Nevertheless, Shişr 033 contains a small fraction of indigenous components, as indicated by the presence of the extraterrestrial amino acid α -aminoisobutyric acid (AIB) that was not detected in the Shişr soils. Finally, the terrestrial age of Shişr 033 was determined and is discussed in the context of high levels of contamination.

INTRODUCTION

Hot deserts (including Australia, western USA, North Africa, and the Arabian Peninsula) have become a source of an increasing number of meteorite finds in the past years (Jull et al. 1990; Ash and Pillinger 1995 and references given; Bischoff and Geiger 1995; Al-Kathiri et al. 2005). The meteorites collected in these arid areas suffer physical and chemical alterations, i.e., weathering. These terrestrial alteration effects were studied previously by other authors, and several different techniques were used to quantify the weathering degree. For example, the degree of oxidation in meteorites, as well as changes in the isotopic and chemical compositions, were determined using, among other

techniques, ^{57}Fe Mössbauer spectroscopy, atomic emission spectrometry (ICP-AES), stepped combustion analysis, evolved gas analysis, X-ray fluorescence spectroscopy (XRF), electron probe analysis (EPMA), backscattered electron spectrometry (BSE), and mass spectrometry (ICP-MS) (Ash and Pillinger 1995; Bland et al. 1996a, 1996b, 1998a, 1998b; Franchi et al. 1996; Gillet et al. 2005; Lee and Bland 2004; Stelzner and Heide 1996; Stelzner et al. 1999).

In this study, an interdisciplinary team of researchers analyzed the Shişr 033 meteorite. Shişr 033 is the first CR carbonaceous chondrite to be recovered from the Omani desert (in October 2002). A unique feature of Shişr 033 is the presence of millimeter-sized dark inclusions that were thought to be similar to CI-type carbonaceous chondrites (Russell

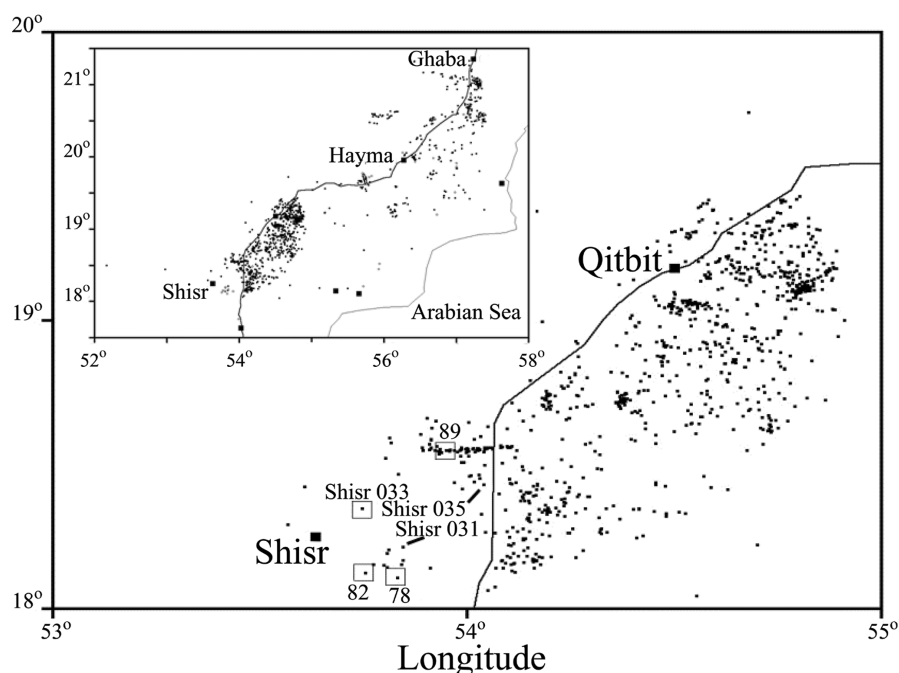


Fig. 1. Map showing the fall site of Shişr 031, Shişr 033, and Shişr 035 meteorites and the places where the soil samples were collected, here named 78, 82, and 89. The inset shows the map of part of Oman, bordered by the Arabian Sea. One degree is about 111 km.

et al. 2004). The goals of this study were to investigate how terrestrial alteration has changed the organic, chemical, mineralogical, and isotopic composition of the meteorite as well as the dark CI-like inclusions. Hence, major and trace elements, iron, and volatiles abundances were obtained for the Shişr 033 meteorite. In addition, amino acid abundances of Shişr 033 were measured and compared to 1) CM- and CI-type carbonaceous chondrites, 2) two ordinary chondrites collected in the same area, and 3) desert soil samples collected on the proximities of the meteorite fall site location. We have also investigated the oxygen and carbon isotopes of Shişr 033 and compared these values to other meteorite classes. Finally, we have also determined the terrestrial ages of Shişr 033 and of the two ordinary chondrites collected in the Omani desert and have investigated their relationship to the extent of terrestrial contamination.

MATERIALS AND METHODS

Samples and Sample Preparation

Shişr 033 (a CR chondrite), Shişr 031, and Shişr 035 (both L6 chondrites), and three soil samples (named 78, 82, and 89) were collected in Oman (Fig. 1) by a joint meteorite search program (Al-Kathiri et al. 2005). Shişr 033 consists of 65 fragments with a total mass of 1098 g recovered from an area of a few square meters. A large Shişr 033 meteorite fragment (249.9 g) was selected for analysis and interior material was obtained by removing the surface. The interior fragment was then crushed, followed by removal of metal

nodules and chondrules, hand-picked using flamed tweezers, to enrich the phyllosilicate-rich material. This enriched material (fines fraction) was homogenized into powder (4.86 g) and used for the amino acids and oxygen isotopes analysis. Individual phyllosilicate-rich dark inclusions were selected for oxygen and carbon isotope analysis, as well as individual chondrules picked from the coarse material for the oxygen isotope analysis. A large piece of Murchison meteorite (6.294 g, USNM 6650) was provided by the Smithsonian National Museum of Natural History, Washington, D.C., USA. Orgueil meteorite (7.76 g) was provided by the Musée National d'Histoire Naturelle, Paris, France. The Murchison, Orgueil, Shişr 031, and Shişr 035 meteorites, together with the three soil samples (78, 82, and 89) were separately ground and homogenized into powder using a ceramic mortar and pestle in a glovebox containing argon. They were stored in sterilized glass vials before being analyzed. A serpentine (hydrated magnesium silicate) sample, provided by the Natural History Museum, Bern, Switzerland, was crushed into powder in the same glove box, heated to 500 °C for 3 hr prior to analysis, subjected to the same processing procedure as the meteorites and soil samples and used as a procedural blank.

Powdered aliquots of Tiffa 001 (an H5 with weathering degree W2), and Grein 003 (an H6 with weathering degree W1), collected in the Tenere region of Niger, were used in our study (for the oxygen isotope analysis) to test the efficiency of the ethanolamine-thioglycollate washing method (Cornish and Doyle 1984) in removing terrestrial weathering products and their effects on the indigenous oxygen isotopic composition of the meteorite samples.

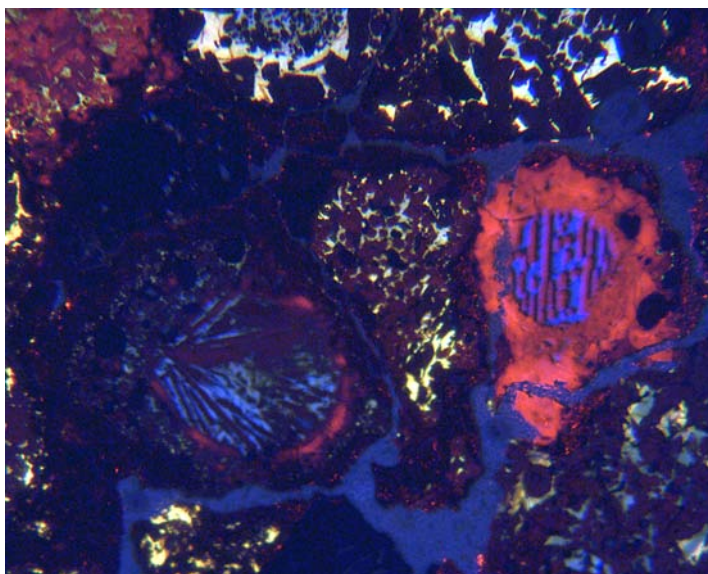


Fig. 2. Cathodoluminescence (CL) image of a polished thin section of Shişr 033 showing the unequilibrated nature expressed by coexisting yellow, red, greenish and blue CL colors of chondrule minerals and glass. Field of view is 3.8 mm.

Chemicals, Reagents and Tools

Amino acid standards (except D- and L-isovaline), sodium acetate trihydrate, sodium borate decahydrate, HPLC-grade water, *o*-phthaldialdehyde (OPA), and N-acetyl-L-cysteine (NAC) were purchased from Sigma-Aldrich. Ammonium hydroxide (28–30 wt%), and D- and L-isovaline standards were purchased from Acros Organics. Methanol (absolute HPLC) was acquired from Biosolve Ltd., sodium hydroxide and hydrochloric acid (37%) from Boom, and AG 50W-X8 cation exchange resin (100–200 mesh) from Bio-Rad. All tools, glassware, and ceramics used in the amino acid analysis were sterilized by annealing in aluminum foil at 500 °C for 3 hr. All tips and Eppendorf tubes used in the same analysis were supplied sterilized from Sigma-Aldrich.

Petrology and Chemistry Analysis

The petrology of Shişr 033 was investigated using a polished thin section of 5.9 cm² surface with transmitted and reflected light microscopy. Mineral compositions were determined using a Cameca SX-50 microprobe equipped with wavelength-dispersive spectrometers using natural and synthetic mineral standards and beam conditions of 15 kV and 20 nA. Data were corrected using the PAP procedure (Pouchou and Pichoir 1994). Cathodoluminescence (CL) images (Fig. 2) were obtained using a high-sensitivity CL microscope (Ramseyer et al. 1989) equipped with a computer-controlled digital camera system (ColorView 12 run under analysis FIVE image analysis program). Beam conditions applied were 0.2–0.4 µA/mm² and 25 keV. Iron hydroxides were removed from certain sample fractions for

oxygen isotope (see the Oxygen and Carbon Analysis section) and iron analyses using ethanolamine thioglycollate in solution with an equal volume of isopropanol to reduce viscosity and prevent precipitation of Fe-complexes. Samples were leached until the production of the red iron complex ceased, which indicated that all iron hydroxides were dissolved, and then washed in deionized water. This treatment removes iron oxides, hydroxides, and metallic iron, but not silicate-bound iron.

The bulk chemistry analysis was performed by lithium metaborate/tetraborate fusion and a combination of inductively coupled plasma–optical emission spectroscopy (ICP-OES, for major elements reported in wt%) and inductively coupled plasma–mass spectrometry (ICP-MS, for trace elements reported as ppm; analysis code 4 lithoresearch). Bulk iron was determined using ICP-OES, and the total carbon and CO₂ were determined by combustion/infrared detection using oxygen and an inert gas, respectively. The organic carbon is obtained by difference.

Amino Acid Extraction Procedure, HPLC-FD, and LC-ToF-MS Analysis

Approximately 100 mg each of Shişr 033, Shişr 031, Shişr 035, Murchison, and Orgueil meteorites, together with Shişr landing site soil samples (named 78, 82, and 89) and a serpentine control blank were analyzed using the established procedure for extracting, separating, and analyzing amino acids in meteorites (Zhao and Bada 1995; Botta et al. 2002; Glavin et al. 2006). Each of these powdered samples was flame-sealed inside a test tube (20 × 150 mm) together with 1 ml of HPLC water and heated for 24 hr in a heating block (temperature set at 100 °C). After the hot water extraction, the

test tubes were rinsed with HPLC water, cracked open, and centrifuged. One of two equal parts of the water supernatants was then transferred to a smaller tube (10 × 75 mm), dried under vacuum, flame-sealed inside a test tube (20 × 150 mm) containing 1 ml of 6 N HCl, and subjected to acid vapor hydrolysis for 3 hr at 150 °C. The test tubes were then rinsed with HPLC water and cracked open; the small tubes were removed and dried under vacuum. The hydrolyzed extracts were brought up in 3 ml of HPLC water, desalted on a cation exchange resin, and the amino acids eluted from the resin with 5 ml of 2 M ammonium hydroxide. These eluates were dried under vacuum, and derivatized (Zhao and Bada 1995) with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) separately first at the Leiden Institute of Chemistry and then at NASA Goddard. At the Leiden Institute of Chemistry, the dried ammonium hydroxide eluates were brought up in 100 µl HPLC water, and 10 µl aliquots were added to 10 µl of 0.1 M sodium borate buffer in Eppendorf vials. These were dried under vacuum to remove any residual ammonia, brought up in 20 µl of sodium borate buffer, and then derivatized with 5 µl of OPA/NAC. The derivatization was quenched after 1 or 15 min by adding 475 µl of 50 mM sodium acetate buffer (mobile phase). At NASA Goddard, the same extracts were derivatized using the same procedure and then quenched after 1 or 15 min with 75 µl of 0.1 M hydrazine hydrate. OPA/NAC amino acid derivatives were analyzed by HPLC-FD at the Leiden Institute of Chemistry and by simultaneous HPLC-FD and ToF-MS at NASA Goddard. HPLC-FD analysis was carried out in a C18 reverse phase (250 × 4.6 mm) Synergi 4µ Hydro-RP 80A column (from Phenomenex), flow rate 1 ml/min, and UV fluorescence detection on a Shimadzu RF-10AXL (excitation wavelength at 340 nm and emission at 450 nm). The conditions for amino acid separations for the mobile phase at 25 °C were as follows: Buffer A was 50 mM sodium acetate, containing 4% methanol (v/v); buffer B was methanol. The gradient used was 0 to 4 min, 0% buffer B; 4 to 5 min, 0 to 20% buffer B; 5 to 10 min, 20% buffer B; 10 to 17 min, 20 to 30% buffer B; 17 to 27 min, 30 to 50% buffer B; 27 to 37 min, 60% buffer B; 37 to 49 min, 60% buffer B; 49 to 50 min, 60 to 0% buffer B; 50 to 60 min, 0% buffer B. Amino acids were identified by comparison of retention time with known standards. LC-ToF-MS analyses were carried out according to the procedures described by Glavin et al. (2006). In all analyses, the amino acid abundances (part per billion by weight) in the samples were calculated by comparing the integrated peak area, corrected for the abundances in the serpentine blank sample, with the integrated peak area of known amino acid standards.

Oxygen and Carbon Analysis

Oxygen isotope analyses were performed on four samples of the Shişr 033 meteorite: a whole rock sample

(WR), a whole rock sample washed in ethanolamine thioglycollate (washed WR), a composite of hand-picked chondrules, and a hand-picked phyllosilicate-rich inclusion (D). In addition, powdered aliquots of the Tiffa 001 meteorite and the Grein 003 meteorite were washed in ethanolamine thioglycollate (see the Petrology and Chemistry Analysis section for more details) until the solution barely changed color, rinsed first in water, then in isopropanol, and dried before analysis.

Oxygen isotopic analysis was done by laser fluorination. Samples of 1 to 2 mg of powdered material were heated with a CO₂ laser (10.6 µm) in the presence of approximately 200 torr of BrF₅. The oxygen gas liberated was purified cryogenically and chemically before analysis on a PRISM III (VG Micromass, UK) dual inlet mass spectrometer. Analytical precision is ±0.08‰ for δ¹⁸O and ±0.04‰ for δ¹⁷O. Details of the method are given by Miller et al. (1999).

Carbon isotope measurements were performed on the phyllosilicate-rich dark inclusion (D). A sample of 0.423 mg of crushed material was step combusted in 50 °C and 100 °C increments, the gas at each heating step purified, and the abundance and isotopic composition of carbon (as CO₂) measured using a modified SIRA 24 (VG Micromass, UK) redesigned to operate in static vacuum mode. The system is readily capable of analyzing less than 1 nmole of carbon with a precision of approximately ±1‰ for δ¹³C. Details of the analytical technique are given by Wright and Pillinger (1989).

Terrestrial Age Analysis

The terrestrial ages of the Shişr 033, Shişr 031, and Shişr 035 meteorites (see Table 10 for the samples mass) were determined by accelerator mass spectrometry (AMS) of cosmic ray-produced ¹⁴C. Untreated and acid-etched (used to remove any weathering products) samples, as well as a sample of Shişr 033 treated both by acid etching and with ethanolamine thioglycollate (used to remove iron hydroxides as discussed earlier) were measured. Additional sample treatment included preheating to 500 °C in air to remove terrestrial organic contaminants followed by fusion of the sample with iron using RF furnace heating in oxygen to produce CO₂. Further sample preparation, ¹⁴C extraction and AMS measurement procedures are described elsewhere (Jull et al. 1989, 1990, 1993, 1998).

RESULTS AND DISCUSSION

Petrology

Shişr 033 was classified as a CR chondrite (Russell et al. 2004) based on the reduced character of silicates (olivine with Fa_{2-7.9} by electron microprobe; Fe-poor pyroxene, Fs_{1.2-12.1}) and the presence of phyllosilicate-rich inclusions.

Representative olivine and pyroxene analyses performed in this study are listed in Table 1. A low metamorphic grade (3 or lower) is supported by cathodoluminescence images (Fig. 2) showing a heterogeneous and unequilibrated texture. This is spectacularly expressed by the bright yellow, red, greenish, and blue chondrule minerals and glass under the cathode. Many chondrules show abrupt or gradual color zoning. The luminescence activity of enstatite and forsterite is caused by traces of Cr and Mn (e.g., Steele et al. 1990). At higher metamorphic grades, the cathode luminescence colors are suppressed by the higher iron contents in forsterite and enstatite. The average chondrule size of the PO, POP, PP, BO, and RP chondrules is 1.0 mm and the matrix/chondrule + aggregate ratio is 0.53. Large metal grains and metal-rich PO chondrules are common.

Shişr 033 contains <10 vol% dark, soft inclusions up to 5 mm in size that were originally classified as CI (Russell et al. 2004). These inclusions show the presence of smectitic (possible smectite-chlorite mixed-layer clay minerals) phyllosilicates in XRD-patterns (peak at ~15 Å). In polished thin sections, laths of pyrrhotite up to 60 µm in length and micrometer-sized magnetite forming framboids of 5–10 µm in diameter are the major coarse phases in a fine-grained matrix rich in phyllosilicates, bearing a similarity to CI matrix rather than to CM and CO matrices. These phyllosilicate-rich inclusions clearly correspond to the dark inclusions (DI) in CRs described by Weisberg et al. (1993), both in terms of mineralogy and mode of occurrence. According to Weisberg et al. (1993), the DI are essentially identical to the matrix of CR in mineralogy and composition. The average composition (Table 8 in Weisberg et al. 1993) is close to CI (except for K and S).

The meteorite shows minor weathering of the metal (W2), but this is based only on limited alteration of metallic iron. However, iron hydroxides released during weathering impregnate the meteorite, including the dark inclusions, giving the meteorite a generally yellow-brown rusty appearance.

Chemistry

Bulk chemistry data were obtained on two bulk samples (from which some large metal nuggets were excluded due to grinding problems) and on the fraction of fines used for amino acid analysis (Table 2). Data for volatiles (C, CO₂, and H₂O) are presented in Table 3. Data obtained on Shişr 033 are compared with CR analyses discussed in Bischoff et al. (1993). Shişr 033 has a bulk composition very similar to the averaged CR chondrites (Table 2). The slightly lower iron content might be due to the exclusion of some large metal nuggets. Compared with bulk analyses, the fines fraction of Shişr 033 used for amino acid analysis is slightly enriched in iron and volatiles, including organic carbon, and is slightly depleted in Mg, but is close in composition to the bulk meteorite. Iron enrichment is probably due to a higher iron

Table 1. Representative microprobe analyses of the Shişr 033 silicates.

Mineral	Olivine			Pyroxene		
SiO ₂ (wt%)	42.27	42.13	41.55	56.35	56.42	57.63
TiO ₂	b.d.	b.d.	b.d.	0.16	0.11	0.10
Al ₂ O ₃	0.02	0.11	0.01	2.94	0.94	0.82
Cr ₂ O ₃	0.59	0.89	0.74	0.76	0.89	0.81
FeO	2.60	2.41	6.82	4.09	4.58	3.45
MnO	0.26	0.24	0.99	0.48	0.47	0.14
NiO	0.04	0.05	b.d.	0.04	0.22	0.20
MgO	54.70	54.90	50.60	33.51	35.64	37.04
CaO	0.19	0.21	0.26	1.68	0.62	0.55
Na ₂ O	b.d.	b.d.	b.d.	0.16	b.d.	0.04
K ₂ O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	100.68	100.94	101.15	100.19	100.12	100.98
Si (a.f.u.)	0.999	0.993	1.000	1.935	1.937	1.948
Ti	—	—	—	0.004	0.003	0.002
Al	0.001	0.003	0.004	0.119	0.039	0.039
Cr	0.011	0.017	0.014	0.021	0.024	0.022
Fe	0.051	0.047	0.138	0.118	0.132	0.098
Mn	0.005	0.005	0.020	0.014	0.014	0.018
Ni	0.001	0.001	—	0.001	0.006	0.006
Mg	1.927	1.928	1.816	1.715	1.824	1.791
Ca	0.005	0.005	0.007	0.062	0.023	0.020
Na	—	—	—	0.011	—	0.002
K	—	—	—	—	—	—
Fa/Fs	0.026	0.024	0.069	0.062	0.038	0.025
Wo/Or				0.034	0.012	0.010

a.f.u. = atoms per formula unit.

b.d. = below detection.

content of dark inclusions combined with iron hydroxide accumulation from altered iron metal preferentially enriched in the fine-grained fraction. As evidenced from total iron data of ethanolamine thioglycollate-leached samples (Table 3), about 70% of iron is easily leached and thus present in oxide or metallic form. The silicate fraction contains 6.1 to 6.7 wt% iron, which is consistent with mineral analyses by electron microprobe (Table 1). Rare earth elements (REE) are present at typical chondritic concentrations (Anders and Grevesse 1989) with no significant evidence of fractionation. Repeat analyses on different subsamples indicate an organic carbon content in the bulk meteorite of 0.29% ± 0.03%, which is lower than in Renazzo, Al Rais, Elephant Moraine 87770 and Yamato-790112, but is similar to CRs from the Sahara (Bischoff et al. 1993). Assuming that most of the organic carbon is concentrated in fine-grained dark inclusions that represent <10% of the rock, a concentration of several wt% carbon is required in these inclusions. The mean total H₂O content of Shişr 033 is 6.07% (Table 3), which is similar to Renazzo (5.67 wt%) and Al Rais (8.49 wt%) (Weisberg et al. 1993). Bulk chemical analyses are therefore consistent with the CR classification of Shişr 033 (see the Petrology section). An unknown fraction of H₂O in the fines (Table 3) is likely due to terrestrial weathering (mainly in iron hydroxides). Furthermore, the effects of terrestrial weathering are seen in the elevated concentrations of Sr and Ba (Table 2).

Table 2. Chemical composition of the CR-type carbonaceous chondrite Shişr 033 (in two bulk samples and in fines) as measured by ICP-OES (major elements; reported in wt%) and ICP-MS (trace elements; reported in ppm). For comparison, literature CR-type carbonaceous chondrite bulk data are shown.

Elements	Shişr 033			Renazzo ^b	Al Rais ^b	Average CR ^c
	Bulk	Bulk	Fines ^a			
Si (wt%)	15.79	15.67	15.53	15.81	14.14	
Ti	0.06	0.06	0.06	0.11	0.05	
Al	1.21	1.17	1.08	1.25	1.04	1.18
Fe	21.47	21.66	23.67	24.93	23.78	23.58
Mn	0.16	0.16	0.16	0.18	0.18	0.17
Mg	13.86	13.82	12.10	14.33	12.78	13.21
Ca	1.55	1.51	1.50	1.27	1.43	1.29
Na	0.15	0.15	0.18	0.41	0.46	0.33
K	<0.008	0.02	<0.008	0.03	0.03	0.03
P	0.08	0.08	0.09	0.12	0.12	
LOI ^d	6.46	6.22	7.61	7.17	11.17	
V (ppm)	81	71	70	78	70	72
Cr	3970	3430	3410	3740	3250	3558
Co	627	548	629	680	616	650
Ni	>10,000	>10,000	>10,000	13,600	12,600	13,591
Cu	96	78	108			80
Zn	79	66	88	94	162	106
Ga	4.85	4.37	5.55	5.2	6.80	5.4
Ge	9.26	7.61	10.84			
As	<5	<5	<5	2.93	1.47	1.6
Rb	1.46	1.59	1.76			
Sr	148	129	162			
Y	2.69	2.25	2.23			
Zr	11.33	7.73	7.28			
Nb	0.75	0.59	0.59			
Mo	<2	<2	<2			
Ag	<0.5	<0.5	<0.5			
In	<0.1	<0.1	<0.1			
Sn	1.87	1.31	1.63			
Sb	<0.2	<0.2	<0.2	0.072	0.098	0.08
Cs	<0.1	0.11	0.11			
Ba	9.74	6.57	11.25			
La	0.43	0.38		0.319	0.3	0.31
Ce	1.18	1.04				0.89
Pr			0.19			
Nd			0.81			0.5
Sm	0.24	0.25	0.20	0.2	0.186	0.212
Eu	0.09	0.08	0.09	0.079	0.074	0.081
Gd	0.36	0.37	0.26			
Tb	0.11	0.10	0.05			0.05
Dy	0.68	0.66	0.34			0.32
Ho	0.08	0.08	0.07			0.1
Er	0.24	0.22	0.21			
Tm	0.04	0.04	0.04			
Yb	0.23	0.23	0.23	0.223	0.211	0.227
Lu	0.03	0.03	0.03	0.033	0.03	0.033
Hf	0.20	0.19	0.16			0.18
Ta	0.04	0.02	0.03			0.045
Tl	<0.05	0.06	<0.05			
Pb	<5	<5	<5			
Bi	<0.1	<0.1	<0.1			
Th	0.11	0.08	0.25			
U	0.04	0.04	0.08			

^aSame fraction as used for amino acid analysis.

^bWeisberg et al. (1993); Kallemeyn and Wasson (1982).

^cFrom Bischoff et al. (1993).

^dLoss on ignition.

Table 3. Percentage of iron and volatiles in different subsamples of the CR type carbonaceous chondrite Shişr 033 (bulk samples and fines) as measured by ICP-OES and by combustion/infrared detection.

Sample	C total	CO ₂	C organic	H ₂ O ⁻	H ₂ O ⁺	Fe total
Bulk	0.31	0.20	0.25	1.53	4.56	21.47
Bulk	0.31	<0.01	0.30	1.60	4.46	21.66
Bulk	0.32	<0.01	0.32	1.29	4.88	21.02
Bulk	0.30	<0.01	0.30	1.40	4.52	21.72
Mean bulk	0.31	<0.01	0.29	1.46	4.61	21.47
Bulk ETG-leached ^a						6.69
Bulk ETG-leached ^a						6.09
Fines ^b	0.34	<0.01	0.34	n.a.	n.a.	23.67

^aEthanolamine thioglycollate leach; it removes iron hydroxides.

^bFraction used for amino acid analysis.

n.a. = not analyzed.

Amino Acid Composition and Terrestrial Contamination

We have analyzed the amino acid composition of the desert meteorite CR Shişr 033. Figure 3 shows a typical HPLC-FD chromatogram of the acid hydrolyzed hot-water extracts of the Shişr 033, Orgueil, and Murchison meteorites, as well as a serpentine blank. The corresponding amino acid abundances are displayed in Table 4. The most abundant amino acids present in the Shişr 033 meteorite extract include L-alanine (738 ppb), L-glutamic acid (687 ppb), glycine (548 ppb) and L-aspartic acid (315 ppb). The abundances of amino acids in the Shişr 033 meteorite were independently verified by LC-ToF-MS. Figure 4 displays a typical HPLC-FD chromatogram of the Shişr 033, Shişr 031, and Shişr 035 meteorites, as well as soil sample 78 and a serpentine blank. Figure 5 displays both HPLC-FD and ToF-MS chromatograms of the Shişr 033 meteorite acid hydrolyzed hot-water extract. All the corresponding amino acid abundances are shown in Table 5. In accordance with the HPLC-FD data, the most abundant amino acids in Shişr 033 determined by LC-ToF-MS are L-glutamic acid (489 ppb), glycine (417 ppb), L-alanine (330 ppb), and L-aspartic acid (189 ppb). A comparison of the Shişr 033 amino acid content determined by HPLC-FD (Table 4) and by LC-ToF-MS (Table 5) shows that the abundances generally agree within the experiment uncertainties. However, for L-glutamic acid, β -alanine, and L-alanine, the abundances measured by LC-ToF-MS are lower than by HPLC-FD. The difference may be explained due to the fact that amino acid identification by HPLC-FD is based only on retention time comparison, while identification by LC-ToF-MS is also based on the exact molecular mass of the eluting compounds. Therefore, it cannot be excluded that there could be a small fraction of co-eluting compounds contributing to the fluorescence signal intensity in HPLC-FD analyses. In any case, this will not change the overall amino acid distribution in the Shişr 033 meteorite. Amino acid distribution provides important clues

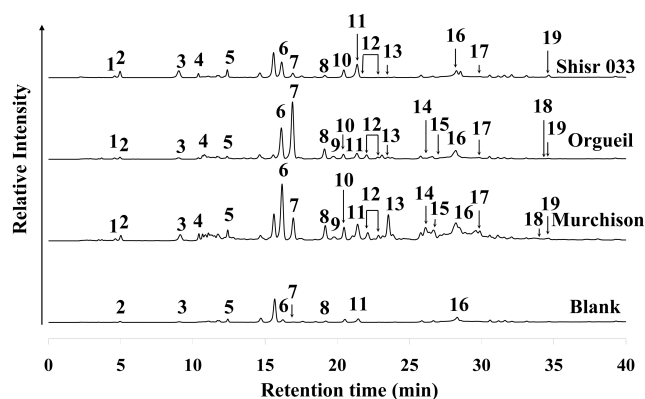


Fig. 3. The 0 to 40 min region (no peaks were observed outside this region) of the HPLC-FD chromatograms. OPA/NAC derivatization of amino acids in the 6M HCl-hydrolyzed hot-water extracts from the CM2 carbonaceous chondrite Murchison, the CI1 Orgueil, the CR Shişr 033, and the serpentine blank. The peaks were identified by comparison of the retention time to those in the amino acid standard run on the same day: 1 = D-aspartic acid; 2 = L-aspartic acid; 3 = L-glutamic acid; 4 = D-glutamic acid; 5 = D, L-serine; 6 = glycine; 7 = β -alanine; 8 = γ -amino-*n*-butyric acid (γ -ABA); 9 = D,L- β -aminoisobutyric acid (D, L- β -AIB); 10 = D-alanine; 11 = L-alanine; 12 = D, L- β -amino-*n*-butyric acid (D, L- β -ABA); 13 = α -aminoisobutyric acid (α -AIB); 14 = D-isovaline; 15 = L-isovaline; 16 = L-valine; 17 = D-valine; 18 = D-leucine; 19 = L-leucine.

about the degree of terrestrial contamination and therefore the degree of weathering suffered by the meteorite. There are three ways to evaluate the source of amino acids present in carbonaceous chondrites (see Botta and Bada 2002): 1) determination of the D/L enantiomeric ratios for chiral amino acids, with a racemic ratio (D/L \sim 1) indicating an abiotic synthetic origin, 2) detection of amino acids in the meteorite extract that are unusual in the terrestrial environment, including α -aminoisobutyric acid (α -AIB) and isovaline, and 3) measurement of compound-specific stable isotope ratios of hydrogen, carbon, and/or nitrogen. In the present study, the abundance of amino acids extracted from the available 100 mg sample of Shişr 033 is below the detection limit of current state-of-the-art gas chromatography isotope ratio mass spectrometers, preventing the use of this method. With regard to (1), our amino acid data show that L-amino acids are significantly more abundant than D-amino acids in Shişr 033 (Tables 4 and 5), clearly indicating the presence of terrestrial contamination in these samples. Additionally, we calculated the amino acid enantiomeric ratios (Table 6) in the Shişr 033 for four protein amino acids (aspartic acid, glutamic acid, alanine, and valine). The D/L ratio values obtained by HPLC-FD and LC-ToF-MS agree with each other within the experimental error. All values were found to be smaller than 0.4, which is an indication of a high terrestrial contamination level. The only exception is the D/L alanine ratio of 0.83 ± 0.15 , obtained by LC-ToF-MS, and therefore we cannot exclude the presence of extraterrestrial components in this meteorite. The D/L alanine ratios in the soil samples (Tables 5

Table 4. Summary of the average total amino acid abundances (in ppb) in the 6M HCl acid hydrolyzed hot-water extracts of the CM2 carbonaceous chondrite Murchison, CI1 carbonaceous chondrite Orgueil, and CR-type carbonaceous chondrite Shiřr 033 as measured by HPLC-FD^a.

Amino acid	Murchison CM2	Orgueil CI1	Shiřr 033 CR
D-aspartic acid	98 ± 5	83 ± 9	86 ± 1
L-aspartic acid	182 ± 10	101 ± 22	315 ± 32
D-glutamic acid	292 ± 20	45 ± 8	164 ± 15
L-glutamic acid	479 ± 34	111 ± 19	687 ± 40
D,L-serine ^b	271 ± 63	386 ± 100	266 ± 97
Glycine	1429 ± 66	1040 ± 191	548 ± 123
β-alanine	1007 ± 73	2784 ± 212	173 ± 7
γ-ABA	647 ± 76	410 ± 40	42 ± 3
D-alanine	617 ± 21	220 ± 40	290 ± 11
L-alanine	708 ± 96	286 ± 42	738 ± 53
DL-β-ABA ^c	529 ± 11	399 ± 17	<10 ± 2 ^d
DL-β-AIB ^c	353 ± 19	218 ± 20	<2 ± 1 ^d
α-AIB	1923 ± 275	73 ± 23	34 ± 5
D-isovaline	2493 ± 513	52 ± 33	<6 ± 2 ^d
L-isovaline	2297 ± 316	74 ± 27	<6 ± 1 ^d
D-valine	395 ± 42	80 ± 4	20 ± 16
L-valine	737 ± 205	346 ± 61	209 ± 49
D-leucine	110 ± 30	17 ± 5	<15 ± 5 ^d
L-leucine	104 ± 10	72 ± 31	199 ± 25
Total	14700	6800	3800

^aQuantification of the amino acids included background level correction using a serpentine blank. The associated errors are based on the standard deviation of the average value between three and four separate measurements (N) with a standard error, $\delta x = \sigma_x \times N^{-1/2}$.

^bEnantiomers could not be separated under the chromatographic conditions.

^cOptically pure standard not available for enantiomeric identification.

^dThese concentrations were very similar to blank levels and therefore were considered to be maximum values.

and 6) range from 0.29 to 0.45, with D-alanine probably coming from the racemization of microbial detritus in the soil. If the alanine present in the Shiřr 033 meteorite was all due to contamination, then its D/L ratio would be expected to fall within the same range. Clearly, the D/L alanine ratio of 0.83 ± 0.15 in Shiřr 033 is significantly higher and can best be explained by an initial D/L alanine ratio in the Shiřr 033 meteorite of ~1 and a subsequent L-alanine contamination of the meteorite after its fall to Earth, leading to the lower ratio observed today in the meteorite. Finally, with regards to (2), a small quantity of α-AIB was detected in Shiřr 033 both by HPLC-FD (34 ± 5 ppb; Table 4) and LC-ToF-MS (38 ± 3 ppb; Table 5). However, no isovaline or β-amino-*n*-butyric acid were detected (both at the same level as the detection limit; Tables 4 and 5). As a terrestrial contamination control, we also analyzed the amino acid content of two L6 chondrites (Shiřr 031 and Shiřr 035) collected in the same area as the Shiřr 033 meteorite (Fig. 1). Those meteorites are not expected to contain any indigenous amino acid, as they were

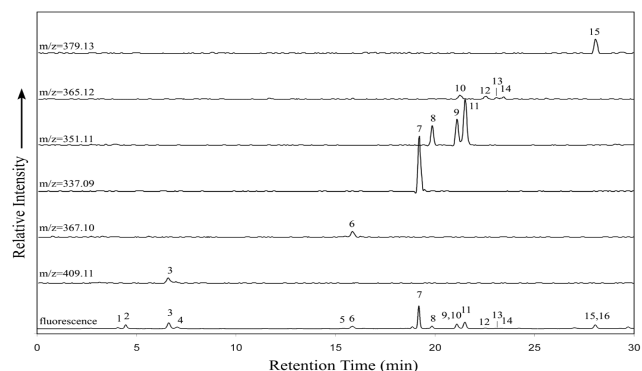


Fig. 5. The 0 to 30 min region of the HPLC-FD and ToF-MS chromatograms of the Shiřr 033 meteorite acid-hydrolyzed water extract. The peaks were identified by comparison of the retention time and exact molecular mass to those in the amino acid standard run on the same day. 1 = D-aspartic acid; 2 = L-aspartic acid; 3 = L-glutamic acid; 4 = D-glutamic acid; 5 = D-serine; 6 = L-serine; 7 = glycine; 8 = β-alanine; 9 = D-alanine; 10 = γ-amino-*n*-butyric acid (γ-ABA); 11 = L-alanine; 12 = D-β-amino-*n*-butyric acid (D-β-ABA); 13 = α+β-aminoisobutyric acid (AIB); 14 = L-β-amino-*n*-butyric acid (L-β-ABA); 15 = L-valine; 16 = ε-amino-*n*-caproic acid (EACA). Aspartic acid (peaks 1–2) could not be identified by exact mass due to poor ionization of this compound during the analysis.

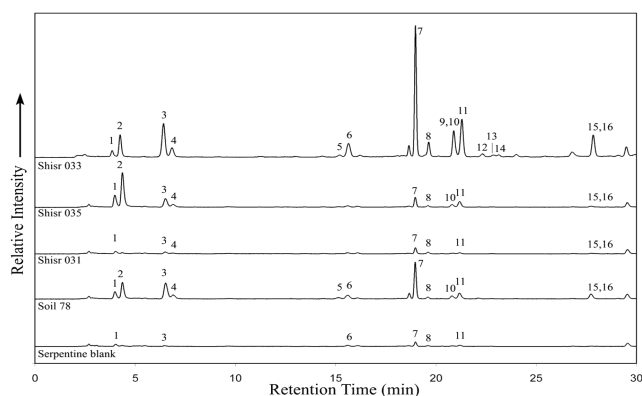


Fig. 4. The 0 to 30 min region of the HPLC-FD chromatograms from the NASA Goddard analyzes. OPA/NAC derivatization of amino acids in the 6M HCl-hydrolyzed hot-water extracts from the Shiřr 033, Shiřr 031, and Shiřr 035 meteorites, soil sample (78), and serpentine blank. The peaks were identified by comparison of the retention time and exact molecular mass to those in the amino acid standard run on the same day: 1 = D-aspartic acid; 2 = L-aspartic acid; 3 = L-glutamic acid; 4 = D-glutamic acid; 5 = D-serine; 6 = L-serine; 7 = glycine; 8 = β-alanine; 9 = D-alanine; 10 = γ-amino-*n*-butyric acid (γ-ABA); 11 = L-alanine; 12 = D-β-amino-*n*-butyric acid (D-β-ABA); 13 = α+β-aminoisobutyric acid (AIB); 14 = L-β-amino-*n*-butyric acid (L-β-ABA); 15 = L-valine; 16 = ε-amino-*n*-caproic acid (EACA).

heated to >800 °C in the parent body (Slater-Reynolds and McSween 2005 and references therein), and therefore all amino acids observed will be due to terrestrial contamination from the meteorite fall site. Table 5 shows the amino acid abundances in the acid hydrolyzed hot-water extracts of Shiřr

Table 5. Summary of the average total amino acid abundances (serpentine blank corrected) in the 6M HCl acid hydrolyzed hot-water extracts of the CR type carbonaceous chondrite Shişr 033, L6 ordinary chondrites Shişr 031 and Shişr 035, and three soil samples collected in the Omani desert^a as measured by LC-ToF-MS^b.

Amino acid	CR chondrite	L chondrites		Soil samples		
	Shişr 033	Shişr 031	Shişr 035	78	82	89
D-aspartic acid	57 ± 5	<5	126 ± 38	68 ± 2	20 ± 1	<10
L-aspartic acid	189 ± 23	<3	398 ± 100	232 ± 53	36 ± 1	17 ± 1
D-glutamic acid	124 ± 7	6 ± 1	50 ± 11	61 ± 3	24 ± 2	14 ± 1
L-glutamic acid	489 ± 34	16 ± 2	156 ± 38	271 ± 5	81 ± 1	38 ± 2
D-serine	32 ± 11	<4	<4	18 ± 2	<4	<3
L-serine	140 ± 34	<4	<4	69 ± 16	<4	<2
Glycine	417 ± 55	24 ± 11	41 ± 13	183 ± 36	4 ± 2	7 ± 1
β-alanine	62 ± 10	9 ± 2	8 ± 2	9 ± 3	2 ± 1	3 ± 1
γ-amino- <i>n</i> -butyric acid (γ-ABA)	49 ± 23	<2	<2	<2	<2	<2
D-alanine	274 ± 14	<2	28 ± 11	23 ± 7	5 ± 2	<2
L-alanine	330 ± 59	<3	49 ± 12	51 ± 11	17 ± 1	2 ± 2
D-β-amino- <i>n</i> -butyric acid (D-β-ABA)	<6	<2	<2	<2	<3	<3
L-β-amino- <i>n</i> -butyric acid (L-β-ABA)	<4	<2	<2	<2	<3	<3
α+β-aminoisobutyric acid (AIB) ^c	23	<4	<4	<4	<5	<6
D,L-α-amino- <i>n</i> -butyric acid (α-ABA) ^c	<5	<2	<2	<2	<2	<2
D-isovaline	<3	<3	<3	<2	<2	<2
L-isovaline	<5	<6	<6	<3	<4	<4
ε-amino- <i>n</i> -caproic acid (EACA)	<3	<4	<4	<4	<5	<5
D-valine	8 ± 3	<2	<2	<2	<3	<3
L-valine	174 ± 19	2 ± 1	11 ± 3	53 ± 16	13 ± 2	7 ± 2
Total	2300	60	870	1040	200	90

^aSee Fig. 1 for exact location of sample collection.

^bAll values are reported in ppb on a bulk sample basis. The associated errors are based on the standard deviation of the average value between two and four separate measurements (*N*) with a standard error, $\delta x = \sigma_x \times N^{-1/2}$.

^cEnantiomers could not be separated under the chromatographic conditions.

031 and Shişr 035 meteorites measured by LC-ToF-MS. In the case of Shişr 031, glycine and glutamic acid are the most abundant amino acids with concentrations of 24 and 6 ppb, respectively. All other amino acids are present at even lower abundance or are below the limit of detection. In the case of the Shişr 035 meteorite, the degree of terrestrial contamination is higher than for Shişr 031, containing aspartic acid (398 ppb for the L-enantiomer and 126 ppb for the D-enantiomer), glutamic acid (156 ppb for the L-enantiomer and 50 ppb for the D-enantiomer), alanine (49 ppb for the L-enantiomer and 28 ppb for the D-enantiomer), and glycine (41 ppb) as the most abundant amino acids. All these amino acids are typical components of bacteria (e.g., Howe et al. 1965). Comparison of the amino acid content of the L6 chondrites to the amino acid content of the CR Shişr 033 can help determine which amino acids may be in part (or totally) due to terrestrial contamination. Since glutamic acid and glycine were detected in both ordinary chondrites, it can be concluded that at least a fraction of their abundances in Shişr 033 is due to terrestrial contamination. It is also interesting to note the very low content of ε-amino-*n*-caproic acid (EACA). This amino acid is a contaminant derived from nylon bags frequently used to store meteorite samples (Glavin et al. 2006). Since all the meteorites analyzed in our study were collected in aluminum foil and

polypropylene bags, it is not surprising that no EACA has been detected.

In an attempt to understand why the amino acid contamination is not uniform in the two ordinary chondrites studied, we have analyzed Omani desert soils from three different locations (Fig. 1) using LC-ToF-MS. Figure 4 displays a typical HPLC-FD chromatogram of the soil 78 acid-hydrolyzed hot-water extract as well as a serpentine blank, with the amino acid content of all three soil samples compiled in Table 5. In contrast to previous analysis, which showed that the chemical composition of the Omani desert soil is uniform (Al-Kathiri et al. 2005), our data show that the amino acid distribution is not uniform in these three soils. The total amino acid abundances measured in these samples are 1040 ppb, 200 ppb, and 90 ppb for soils 78, 82, and 89, respectively. Despite these quantitative differences, there is some qualitative agreement, as the most abundant amino acids in all soils are the L-amino acids and glycine. Non-protein amino acids (including α-AIB) are absent in the soil, which indicates that there was no leaching of amino acids from any meteorite present in the surroundings into the soil. Comparison of the protein amino acid enantiomeric ratios (Table 6) of Shişr 033 to those of the soil shows agreement within the experimental error. Furthermore, the ratios are smaller than 0.4, indicating that, with the exception of a small

Table 6. Amino acid enantiomeric ratios in the CR carbonaceous chondrite Shiřr 033 and in the soil sample 78, collected in the Omani desert.

Amino acid	Enantiomeric ratio (D/L) ^a		
	Shiřr 033 ^b	Shiřr 033 ^c	Soil 78 ^b
Aspartic acid	0.27 ± 0.03	0.30 ± 0.05	0.29 ± 0.07
Glutamic acid	0.24 ± 0.03	0.25 ± 0.02	0.22 ± 0.01
Alanine	0.39 ± 0.03	0.83 ± 0.15	0.45 ± 0.17
Valine	0.10 ± 0.08	0.05 ± 0.02	< 0.04

^aThe uncertainties are based on the absolute errors shown respectively in Table 4 and Table 5, and are obtained by standard propagation calculation.

^bD/L ratios calculated from the concentrations reported in Table 4, measured by HPLC-FD.

^cD/L ratios calculated from the concentrations reported in Table 5, measured by LC-ToF-MS. Soil selected due to the higher total amino acid abundance.

Table 7. Relative amino acid abundances (glycine = 1) of several carbonaceous chondrites^a.

AA/glycine	CM2 Murchison	CM1 Orgueil	CR Shiřr 033	CR ^b Renazzo
β-alanine	0.71	2.68	0.32	0.25
D-alanine	0.43	0.21	0.53	<0.04
α-AIB	1.35	0.07	0.06	<0.08
γ-ABA	0.45	0.39	0.08	1.25

^aRelative amino acid abundances calculated from the absolute amino acid concentrations reported in Table 4, measured in this study by HPLC-FD, for the CM2 Murchison, the CM1 Orgueil, and the CR Shiřr 033 meteorites.

^bThe data for the Renazzo meteorite was calculated from previous analyses (Botta et al. 2002). In case only upper limits of the absolute concentrations were measured, upper limits for the relative concentrations were calculated.

Table 8. Oxygen isotopic composition of the Shiřr 033 meteorite (whole rock, chondrules, and dark clast) measured by laser fluorination.

Sample	Sample type	δ ¹⁷ O (‰)	δ ¹⁸ O (‰)	Δ ¹⁷ O
B	Whole rock	-0.59	2.29	-1.78
B	Whole rock	-0.70	2.21	-1.85
B2	Washed whole rock ^a	-2.33	0.14	-2.40
H	Chondrules	-1.55	1.20	-2.17
H	Chondrules	-1.45	1.41	-2.18
D	Dark clast	-4.59	-1.22	-3.96

^aTreated with ethanolamine thioglycollate.

extraterrestrial component (see above), most of the amino acids in the Shiřr 033 meteorite are terrestrial in origin. Possible reasons for the higher contamination in Shiřr 033 than in the two ordinary chondrites will be discussed in the Terrestrial Ages and Their Relationship to the Extent of Terrestrial Contamination section.

Shiřr 033 Amino Acid Composition and Comparison to Other Carbonaceous Chondrites

The typical HPLC-FD chromatograms of the acid-hydrolyzed hot-water extracts of the Shiřr 033, Orgueil, and Murchison meteorites and a serpentine blank are shown in

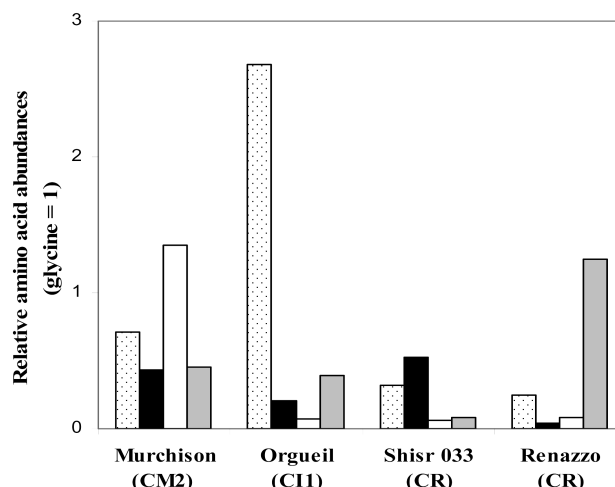


Fig. 6. A comparison of the relative amino acid abundances (glycine = 1) of β-alanine (dots), D-alanine (black), α-aminoisobutyric acid (white), and γ-amino-n-butyric acid (gray) in the acid-hydrolyzed hot-water extract of different carbonaceous chondrites. The relative amino acid abundances were calculated from the absolute amino acid concentrations reported in Table 4, measured in this study by HPLC-FD, for the CM2 Murchison, the CI1 Orgueil, and the CR Shiřr 033 meteorites. The data for the Renazzo meteorite was calculated from previous analyses (Botta et al. 2002). In the case of D-alanine and α-aminoisobutyric acid present in the Renazzo meteorite, only upper limits of the absolute concentrations were measured and therefore only upper limits for the relative concentrations were calculated.

Fig. 3, with the corresponding amino acid abundances shown in Table 4. The Shiřr 033 meteorite was compared to these two other carbonaceous chondrites because Murchison is a well-studied sample (and therefore can be used as a reference to confirm accurate measurements) and Orgueil is a CI1 type, which allows the amino acid composition to be compared to that of the alleged CI inclusion present in Shiřr 033 (Russell et al. 2004). We also compared Shiřr 033 to literature data of the CR chondrite Renazzo (Botta et al. 2002). The most abundant amino acids in Murchison are D- and L-isovaline (with 2493 and 2297 ppb, respectively), followed by α-AIB (with 1923 ppb). Glycine, β-alanine, and D- and L-alanine are also present (Table 4). In the case of Orgueil, the most abundant amino acids are β-alanine (2784 ppb) and glycine (1040 ppb), with very low levels of isovaline and α-AIB (Table 4). All these values agree with analyses performed previously by other authors (Ehrenfreund et al. 2001; Botta et al. 2002). The Renazzo amino acid content (Botta et al. 2002) includes γ-ABA (1092 ppb), glycine (875 ppb), L-glutamic acid (856 ppb) and D,L-β-amino-n-butyric acid (534 ppb). Comparison of the absolute amino acid content of the CM2 Murchison, the CI1 Orgueil, and the CR Renazzo shows a distinct absolute amino acid distribution for Shiřr 033 meteorite. In fact, Shiřr 033 has a lower total amino acid content (3800 ppb) than any of these other carbonaceous chondrites. We also compared the relative amino acid content (glycine = 1) of Shiřr 033 to the relative amino acid content of

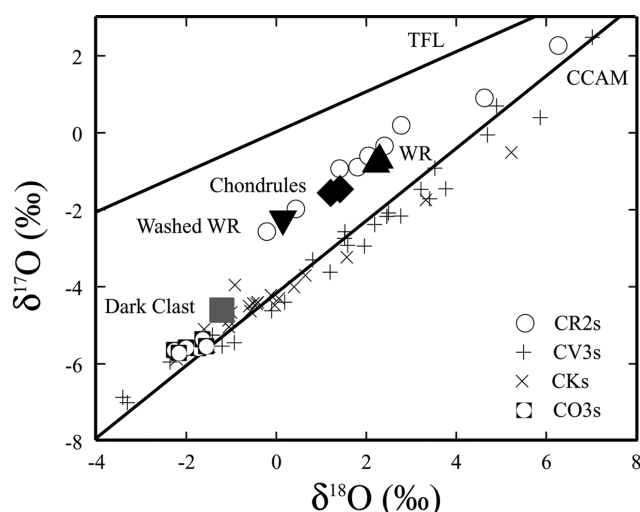


Fig. 7. Oxygen isotopic composition of Shişr 033 and other carbonaceous chondrite groups. Filled symbols for Shişr 033: whole rock sample (WR ▲); composite of chondrules (chondrules ◆); whole rock sample washed in ethanolamine thioglycollate (washed WR ▼); hand picked phyllosilicate rich dark clast inclusion (Dark Clast ■). The terrestrial fractionation line (TFL) and the carbonaceous chondrite anhydrous mineral (CCAM) line are shown for reference. CR2, CV3, and CK data from Clayton and Mayeda (1999); CO3 data from Greenwood and Franchi (2004).

other carbonaceous chondrites (Table 7; Fig. 6). If CI-type inclusions were present in Shişr 033, as suggested in the initial description (Russell et al. 2004), a high relative abundance of β -alanine, similar to the CI Orgueil, can be expected (Table 7; Fig. 6). However, as illustrated in Fig. 6, the relative amino acid distribution of Shişr 033 is dissimilar to the distribution of the CM and CI meteorites analyzed. Shişr 033 has relative β -alanine and α -AIB abundances (0.32 and 0.06, respectively) similar to the ones in the CR chondrite Renazzo (0.25 and <0.08, respectively), but all other relative amino acid abundances are significantly different (Table 7). Our data suggests that the fraction of fines of Shişr 033 analyzed in our study does not correspond neither to a typical CI type nor to the CR Renazzo, which is the only CR analyzed for amino acids so far.

Oxygen and Carbon Isotopes

The oxygen isotopic composition of the whole rock and components in Shişr 033 are shown in Table 8 and plotted in Fig. 7. The whole rock samples (WR and washed WR) and the chondrule composite all have oxygen isotopic signatures indistinguishable from other CR2 meteorites. The oxygen isotopic composition of whole rock samples of CR2s fall along a mixing line of slope 0.7, with anhydrous silicates primarily at the ^{16}O -rich end and hydrous matrix and dark inclusions at the ^{16}O -poor end of the mixing line (Weisberg et al. 1993). The unwashed whole rock sample (WR) plots approximately midway along the mixing line suggesting that the oxygen isotopic composition is a mixture of anhydrous and

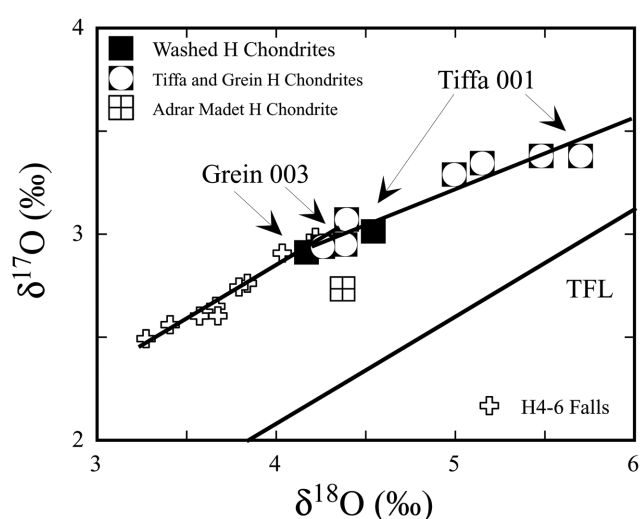


Fig. 8. Oxygen isotopic composition of weathered and washed H chondrites from Tenere, Niger. It illustrates the efficiency of the ethanolamine thioglycollate wash method at removing terrestrial weathering products from anhydrous silicates without affecting the indigenous oxygen isotopic composition.

phyllosilicate material from either end of the mixing line. However, it is not clear what the influence of terrestrial weathering (grade W2), in the form of metal oxidation and iron hydroxide staining is. The sample washed in ethanolamine thioglycollate, which largely removed the iron hydroxides, has an oxygen isotopic composition at the ^{16}O -rich end of the CR2 mixing line, where CR2s are dominated by anhydrous phase, such as LEW 85332, a meteorite that shows no evidence of aqueous alteration (Clayton and Mayeda 1999).

The efficiency and effects of the ethanolamine thioglycollate wash on the samples, in terms of oxygen isotopic measurements, has been assessed using a suite of variable weathered H chondrites collected in the Tenere region of Niger (Schultz et al. 1998), which is a hot desert area with latitudes similar to Oman. Unwashed samples collected from the Tiffa and Grein areas fall along a common mixing line between typical H chondrite values and a point on the terrestrial fractionation line with $\delta^{18}\text{O} \approx 8\text{‰}$ (Fig. 8). The oxygen isotopic composition of the ethanolamine thioglycollate washed samples, in the case of the lightly weathered Grein 003, is now indistinguishable from typical H chondrite falls, while the heavily weathered Tiffa 001 is now much closer to that of the H chondrite falls, although it would appear that some weathering persists. The equilibrated H chondrites used in this study contain only well-crystallized ferro-magnesian silicates and some feldspathic phases, but results show that the ethanolamine thioglycollate wash method is extremely efficient at removing alteration phases from anhydrous silicates without noticeably affecting the bulk properties in terms of oxygen isotopic signature. Shişr 033 contains abundant (see the Petrology section) indigenous phyllosilicate-rich material, and therefore it is unlikely that the pre-atmospheric entry whole rock oxygen isotopic

Table 9. Stepped combustion data from a phyllosilicate-rich dark inclusion D, which contains 2.88 wt% carbon.

Temperature (°C)	C yield (ng)	$\delta^{13}\text{C}$ (‰)
50	7.1	-24.2
100	21.1	-31.8
150	71.2	-33.5
200	199.2	-30.1
250	471.2	-26.8
300	398.0	-21.3
350	239.2	-19.3
400	188.0	-15.0
450	160.9	-11.4
500	360.6	-8.2
550	1300.1	-6.6
600	3693.9	-7.8
650	3796.0	-7.6
700	760.7	-7.8
800	150.5	-7.6
900	177.9	-8.0
1000	80.6	-10.0
1100	20.5	-11.9
1200	18.5	-18.3
1300	20.3	-26.1
1400	41.0	-20.5

composition would plot at the anhydrous end of the CR2 mixing line. In addition, it is likely that the ethanolamine thioglycollate washing did not discriminate between asteroidal and terrestrial alteration products. That said, it is interesting to note that the hot-desert weathering in the Tenere samples has a $\delta^{18}\text{O}$ of $\approx 8\%$, although it should also be noted that the $\delta^{18}\text{O}$ of the weathering products does appear to vary as indicated by the distinct isotopic composition of the heavily weathered H5-6 from Adrar Madet (Fig. 8). Assuming a $\delta^{18}\text{O}$ value of $\approx 8\%$ for the Oman weathering products, then any mixing line between CR2 and terrestrial weathering would be unresolvable from the indigenous CR2 mixing line. It is not unreasonable to assume a $\delta^{18}\text{O}$ value of $\approx 8\%$, given that Oman local rain water has $\delta^{18}\text{O}$ values between -4.3 and $+1.4\%$ VSMOW (Waber 2006), based on rain water samples collected near Haima during the meteorite search project in 2005. Additionally, $\delta^{18}\text{O}$ values of monsoon precipitation given by Fleitmann et al. (2004) range between -0.3 and 1.0% (VSMOW).

The oxygen isotopic composition of the phyllosilicate-rich, dark inclusion (sensu Weisberg et al. 1993; sample D) is not consistent with typical CR2 matrix or dark inclusions found in CR2s (Fig. 7), but instead falls in the range of typical CV3 or CK carbonaceous chondrites (Clayton and Mayeda 1999), and close to those of CO3s (Greenwood and Franchi 2004). These results are in contrast with the reports of Sephton et al. (2006a, 2006b) and Watt et al. (2006), who argue against transport and incorporation of dark inclusions into a matrix. In that regard, it would be interesting to further analyze the dark inclusions measured in this work.

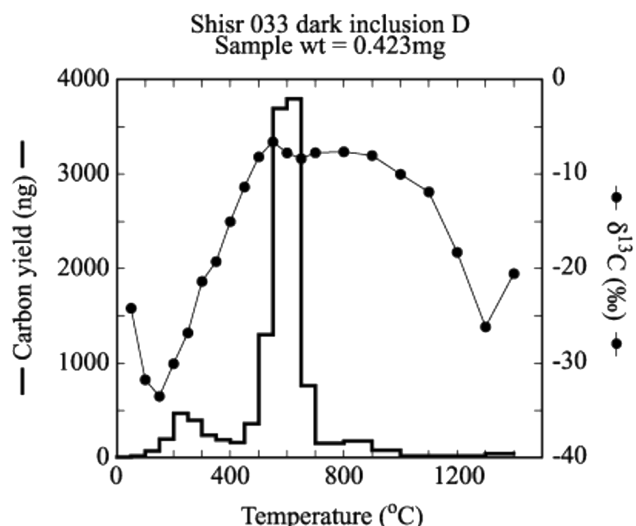


Fig. 9. Stepped combustion profile of a dark inclusion (D), showing yield (bold histogram plot) and isotopic composition (point/line plot) with increasing temperature. Organics are oxidized between 200 and 500 °C, while carbonates generally decompose between 500 and 700 °C.

The nature of the carbon present in the phyllosilicate-rich dark inclusion D was investigated by stepped combustion, with the results shown in Table 9 and Fig. 9. The carbon inventory is dominated by a large release (2.3 wt% C), in the range of 550–650 °C, which is typical of carbonates (Wright and Pillinger 1989). The $\delta^{13}\text{C}$ of this component is around -8% , much less than typical values ($\delta^{13}\text{C}$ of 30 – 65%) for carbonates in carbonaceous chondrites (Grady et al. 1988). Given that the local carbonate deposits found in the desert regions of Oman where Shişr 033 was collected have a $\delta^{13}\text{C}$ value of -5.31 to -9.07% (unpublished data, University of Bern) it is likely that the carbonates in Shişr 033 are remobilized terrestrial carbonates. At lower temperatures (150–350 °C), there is evidence of a smaller release of organic carbon (0.4 wt% C), with $\delta^{13}\text{C}$ values ranging from -34 to -19% . The majority of this carbon appears to be terrestrial contamination, which typically has a $\delta^{13}\text{C}$ value of -35 to -25% , and is quite distinct from indigenous organic carbon found in carbonaceous chondrites with $\delta^{13}\text{C}$ values of -18 to -10% (e.g., Botta and Bada 2002). It may be that the small amount of carbon above 300 °C is largely indigenous as the isotopic composition approaches that expected from meteoritic macromolecule. However, this component is only present at the level of no more than 0.2 wt% C, assuming some overlap with the carbonate peak.

Terrestrial Ages and Their Relationship to the Extent of Terrestrial Contamination

The terrestrial age of the carbonaceous chondrite Shişr 033 and the ordinary chondrites Shişr 031 and Shişr 035 are summarized in Table 10. The expected ^{14}C saturation value

Table 10. Terrestrial age of the carbonaceous chondrite Shişr 033, the L6 ordinary chondrites Shişr 031 and Shişr 035 as measured by AMS.

	Shişr 031	Shişr 033 (A)	Shişr 033 (B)	Shişr 033 (C)	Shişr 035
Type	L6	CR (bulk slices)	CR (bulk ground)	CR (bulk ground)	L6
Weight (g)	0.390	0.269	0.081	0.113	0.154
Chemical treatment	Acid etch	Acid etch	Acid etch	Acid etch	Acid etch
Fm	0.5439	1.0189	0.8992	1.9680	0.0530
Error	0.0056	0.0095	0.0063	0.0180	0.0013
CO ₂ (cc)	0.59	0.78	0.57	0.33	0.17
Diluted (cc)	0.59	0.78	0.57	0.33	2.117
¹⁴ C atoms	7.994×10^6	2.164×10^7	1.352×10^7	1.746×10^7	1.982×10^6
¹⁴ C/weight (g)	2.050×10^7	8.046×10^7	1.668×10^8	1.542×10^8	1.284×10^7
Bulk ¹⁴ C (dpm/kg)	4.72	18.52	38.38	35.49	2.95
Error (dpm/kg)	0.18	0.31	0.89	0.69	0.45
Saturated activity ^a	51.1	51.1	51.1	51.1	51.1
¹⁴ C age (kyr)	19.7	8.4	2.4	3.0	23.6
Error (kyr)	1.3	1.3	1.3	1.3	1.8
Bulk ¹⁰ Be (dpm/kg)	11.70	16.04			15.95
Error (dpm/kg)	0.23	0.34			0.28
¹⁴ C/ ¹⁰ Be	0.40	1.15			0.18
¹⁴ C/ ¹⁰ Be age (kyr)	15.0	6.4			21.4
Error (kyr)	0.4	0.2			1.3

^aWhen class is not known, ¹⁴C saturated activity of L chondrites (51.1 dpm/kg) was used.

was approximated by using the value for L chondrites (51.1 dpm/kg) for subsamples A, B, and C. For Shişr 033, a ¹⁴C/¹⁰Be terrestrial age of 6.4 ± 0.2 kyr was obtained, which is much younger than those of the two L6 chondrites Shişr 031 (15.0 ± 0.4 kyr) and Shişr 035 (21.4 ± 1.3 kyr). The relatively low terrestrial age of Shişr 033 of a few thousand years is consistent with the low degree of weathering (W2) of the iron metal in this meteorite. In that sense, the first thought would be that the older age of the other two ordinary chondrites would lead to a higher degree of terrestrial contamination of those samples compared to Shişr 033. However, as our amino acid analysis shows, the Shişr 033 meteorite has a higher contamination degree than Shişr 031 and Shişr 035 (see the Amino Acid Composition and Terrestrial Contamination section). Three possibilities can be invoked to explain this. The first is the fact that the meteorites landed in different locations (Fig. 1), exposing them to different local terrestrial environments (see the Amino Acid Composition section). The second possibility is the difference in porosity between the CR Shişr 033 and in the ordinary chondrites, as carbonaceous chondrites have, on average, a higher porosity (ranging from 24% to 35%) than L6 chondrites (ranging from 0% to 10%) (Consolmagno and Britt 1998). Although Oman is a desert, there is occasional precipitation (Sanlaville 1992; Al-Kathiri et al. 2005), including monsoons, during which soil material can be percolated through the meteorites. A higher porosity, and therefore a higher internal surface, probably increases the changes for absorption of organic material from the soil. The third possibility is the difference in the oxidation state of iron present in the meteorites studied. The significantly higher abundance of metallic iron in Shişr 033 (see the Petrology and

Chemistry sections) may serve as a nutrient for iron-oxidizing micro-organisms that colonize the meteorite, leading to higher amino acid contamination degree in the CR meteorite. This colonialization is less likely in the L6 chondrites due to their higher content of oxidized iron.

CONCLUSIONS

We have performed for the first time a multidisciplinary study of the Shişr 033 meteorite, which was collected in the Omani desert. The initial classification as a CR chondrite is confirmed by bulk chemical analyses as well as oxygen isotopes, these latter showing that Shişr 033 falls into the CR2 group. Based on oxygen isotopes, dark inclusions hosting organic material are more closely related to CV3-CO3 chondrites than CR2 bulk material. Amino acid analysis shows no evidence for CI- or CM-like material in these inclusions.

Amino acid and carbon isotopic data indicate high terrestrial contamination in Shişr 033. Both the Shişr 033 meteorite and the Oman soil samples show that L-amino acids and glycine were the most abundant amino acids. Additionally, Shişr 033 D/L proteic amino acid ratios are generally smaller than 0.4 and are in agreement with the D/L amino acid ratios of the Omani desert soils. Carbon isotope analysis of a Shişr 033 dark inclusion revealed high carbonate contents, with a $\delta^{13}\text{C}$ value of -8‰ (falling within the range of typical terrestrial carbonates of the Omani desert), and a low organic carbon content, with $\delta^{13}\text{C}$ values ranging from -34 to -19‰ . However, the presence of a small fraction of indigenous extraterrestrial organic compounds in Shişr 033 cannot be excluded because the extraterrestrial

amino acid α -AIB was preserved in this meteorite over thousands of years. Sh  r 033 was found to have a terrestrial age of 6.4 ± 0.2 kyr, which is consistent with the low weathering of its metal. Differences in the amino acid contamination content between Sh  r 033 and two ordinary chondrites (Sh  r 031 and Sh  r 035) also collected in the Omani desert can be explained by differences in the composition of their fall sites, in the porosity of these meteorites, in the abundances of metallic iron, or a combination of these effects. This study supports previous observations that meteorites collected in hot deserts suffer significant terrestrial alteration and contamination during their residence time.

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