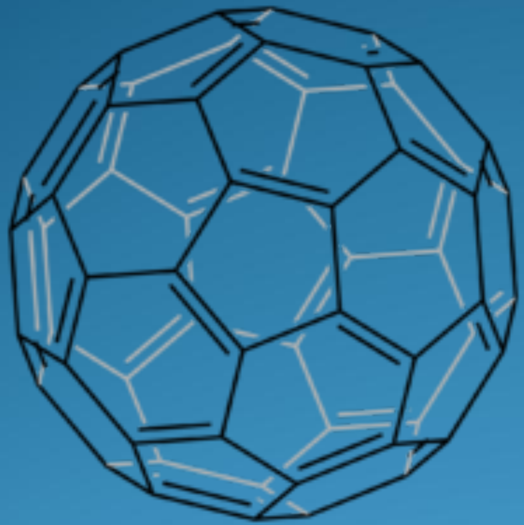
From Elemental Carbon to the Formation and Radiation Stability of Chiral Molecules



Various Products:
PAHs Oxyacids
Amino acids?

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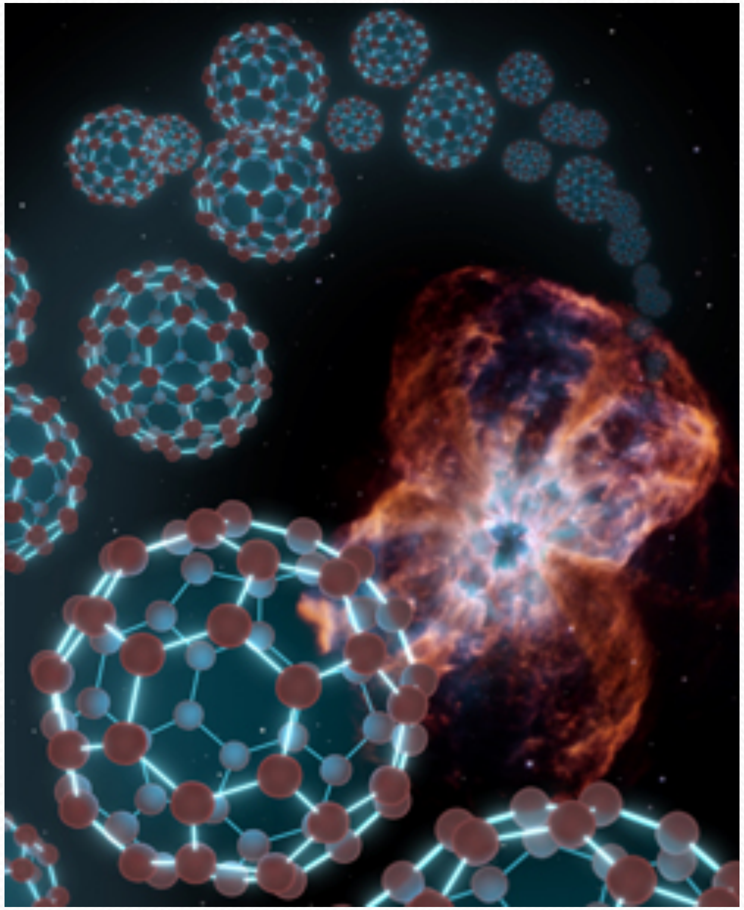
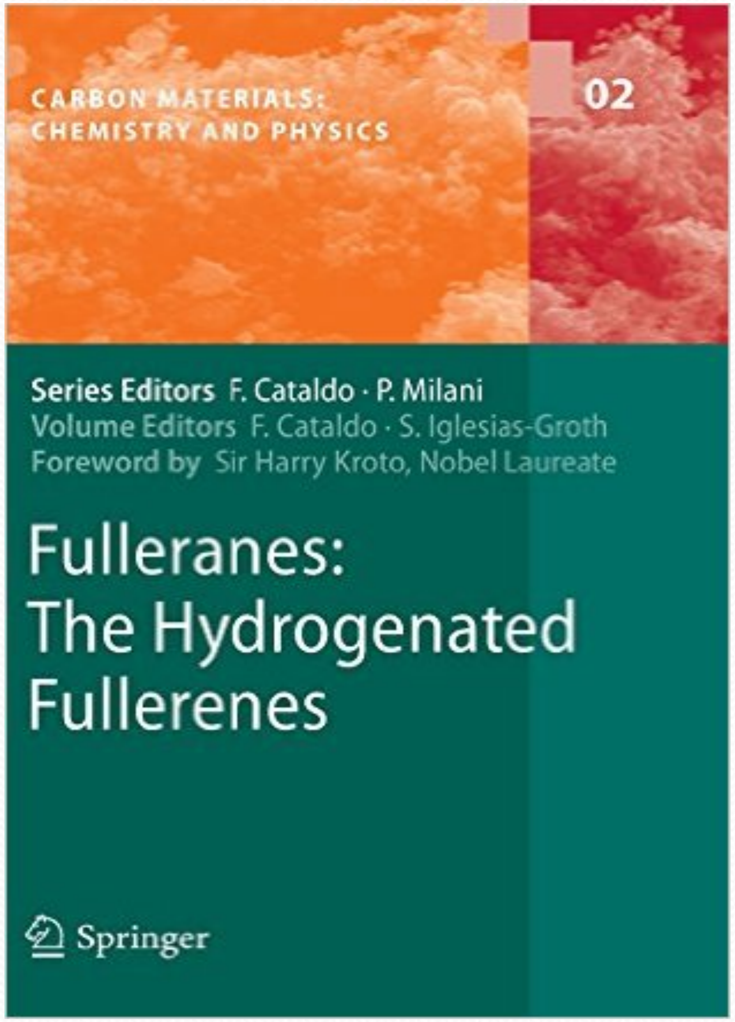
Carbon in space locked in the largest known molecule: C_{60}



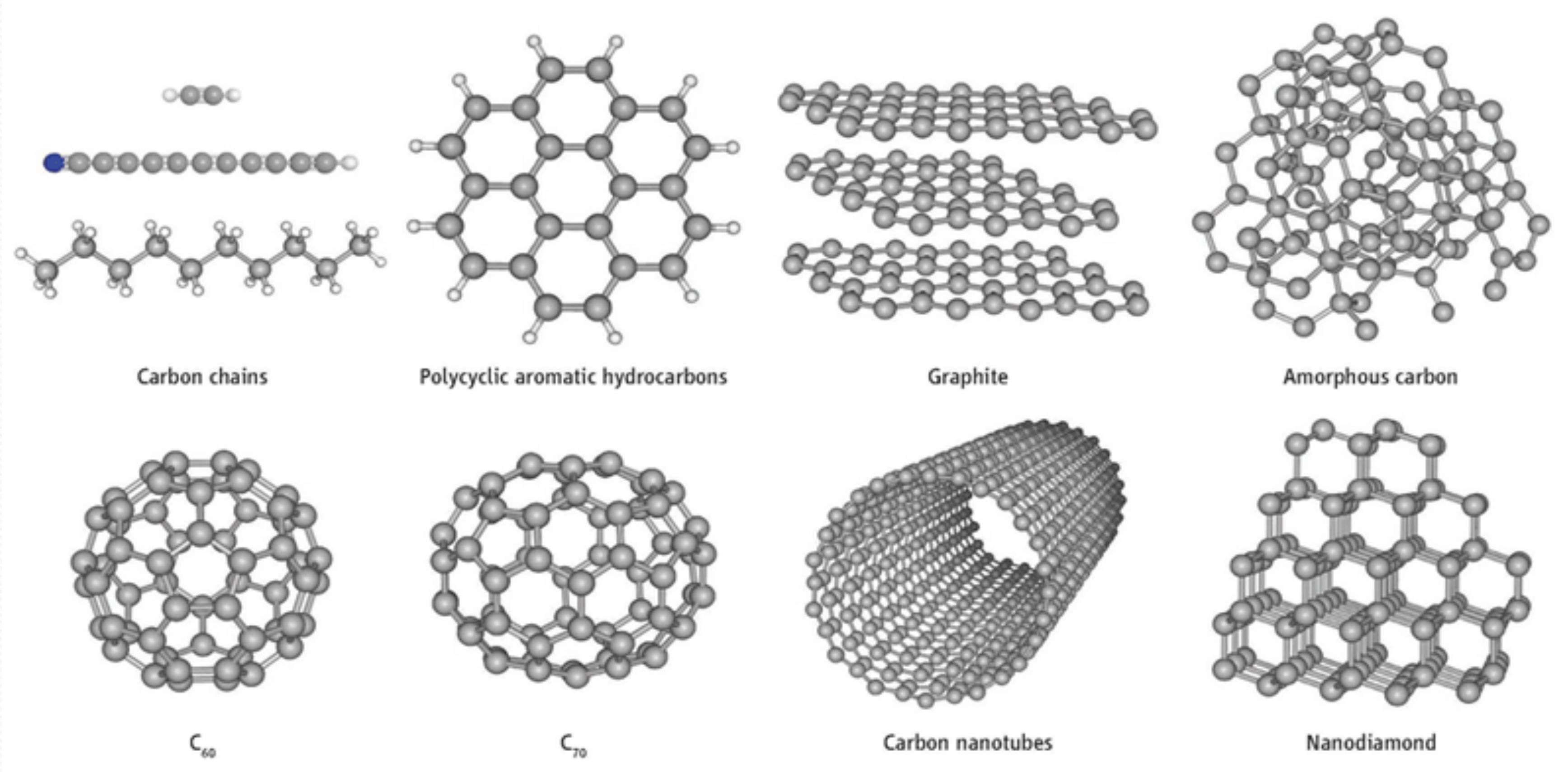
- Fullerene C_{60}
- The largest molecule known in space
- Detected for the first time by the orbiting telescope Spitzer in the infrared in 2010
- Circumstellar medium: young planetary nebulae like TC-1
- About >1% of total C is C_{60}
- Interstellar medium: reflection nebulae

Role of fullerenes in space



- Reaction of C_{60} with atomic hydrogen forming fullerAnes
- UV photolysis of fullerAnes leads to the formation of molecular hydrogen
- Radiolytic reactions of fullerenes embedded in ices: a way to make available locked C for further prebiotic reactions C_{60}.

Among C allotropes fullerenes are granted by higher reactivity



C_{60} radiolysis in H_2O & H_2O/NH_3

J Radioanal Nucl Chem (2013) 298:1073–1083 1079

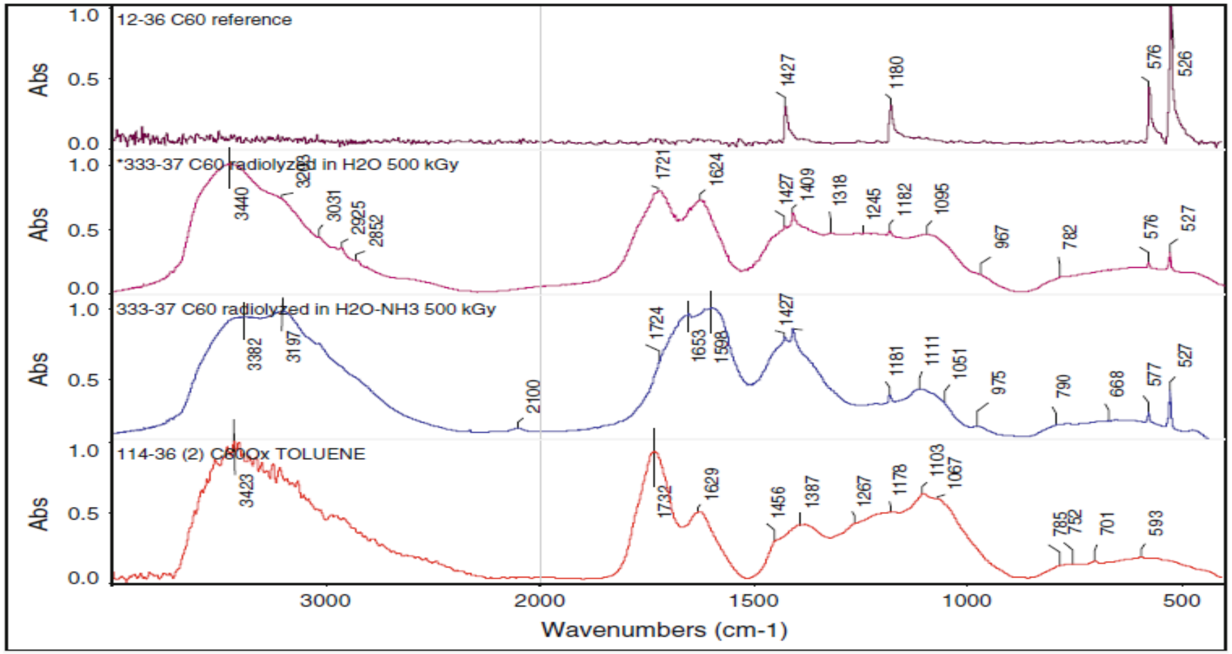


Fig. 3 Infrared spectra in KBr or CsI matrix of (from *top* to *bottom*): reference C_{60} fullerene; radiolysis product of C_{60} isolated from water ($RPC_{60}W$); radiolysis product of C_{60} isolated from aqueous ammonia ($RPC_{60}WA$); reference oxidized C_{60} prepared by ozonolysis in toluene [29, 30]

- Radiolysis at 500 kGy leads to water soluble products. Practically all C_{60} used was solubilized forming oxidized PAHs

C_{60} radiolysis in H_2O/CH_3OH & $/NH_3$

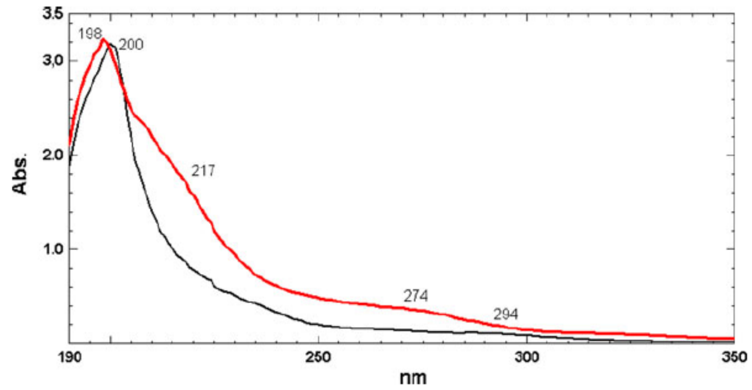
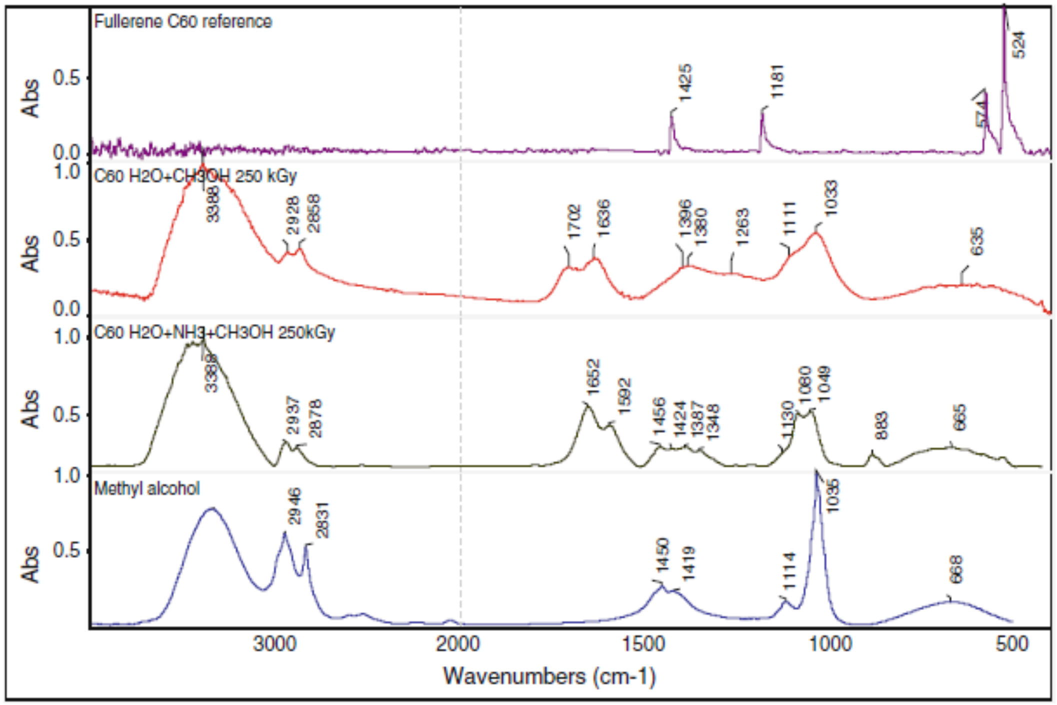


Fig. 2 Electronic absorption spectra of RPC$_{60}$WM (*red curve*) and RPC$_{60}$WAM (*black curve*) dissolved in water. (Color figure online)



C_{60} is completely insoluble in water and in methanol, after radiolysis 250 kGy, 64.8 % of the starting C_{60} was solubilized and 76.5 % in water/ammonia/methanol mixture

SUMMARY 1 –

C_{60} radiolysis in heterogeneous phase in H_2O/CH_3OH & /NH_3

- C_{60} Radiolysis at 500 kGy in water or water/ammonia → Complete solubilization formation of oxidized fragments of PAHs as detected also by HPLC.
- C_{60} Radiolysis at 250 kGy in water/methanol or water/methanol/ammonia → 65 to 76 % of the starting C_{60} solubilized with formation of oxidized fragments of PAHs as detected also by HPLC.
- No amino acids formation detected yet.

Radiation Chemistry and prebiotic molecules

Harold Urey Nobel Laureate 1934 –Chemistry-

- The Nobel laureate Harold C. Urey (1955, 1956) has calculated the amount of energy generated by the decay of radionuclides in comets, asteroids, meteorites and larger bodies of the solar system. Calculations confirmed in more recent times (Draganic et al. 1993).

- In a time scale of the age of the Solar System, i.e. 4.6×10^9 years, the total radiation produced by radionuclide decay **in bulk** comets, asteroids and larger bodies of the Solar System is **≈14 MGy**.

- Therefore, the **surface** of comets and asteroids is completely "burned" by an enormous radiation dose of **300 MGy** in 4.6×10^9 years due to the action of cosmic rays.

Let us focus on the radiation dose in bulk comets and asteroids

14 MGy in 4.6×10^9 year

or

3 MGy per billion year

Can these radiation doses be reached in the laboratory?

Can such work be done in a reasonable timescale?

The answer is: YES

- To do this we have used γ radiation from the decay of a ^{60}Co source.
- An emitter of monoenergetic photons at 1.17 and 1.33 MeV.
- The source emits also β particles at 0.314 MeV but they were not used in our experiments.
- **The irradiation was made to a total dose of 3.2 MGy (at a dose rate of 1.5 kGy/h) equivalent to 1.05×10^9 years**

Measurement of the extent of the radiolysis and the extent of radioracemization

- The amount % of residual sample after the solid state radiolysis $N\gamma$ was determined from the ratio of the melting enthalpy after the radiolysis at 3.2 MGy (ΔH_γ) and the enthalpy before radiolysis measured on the pristine sample (ΔH_o):

$$N_\gamma = 100\ [\Delta H_\gamma\ /\ \Delta H_o] \quad \rightarrow \quad \text{Radiolysis Resistance (higher better)}$$

- From the ratio of the specific optical rotation after radiolysis $[\alpha]\gamma$ and before radiolysis $[\alpha]_o$ the residual optical activity $R\gamma$ has been determined:

$$R_\gamma = 100\ [\alpha\ ]_\gamma\ /\ [\alpha]_o \quad \rightarrow \quad \text{Radioracemization Resistance (higher better)}$$

Radiolysis of proteinogenic and non-proteinogenic amino acids

- The analysis of Murchison meteorite 66 different types of amino acids.
- Only 8 of these 66 amino acids are proteinaceous amino acids used in the present terrestrial biochemistry in protein synthesis.
- The other 58 amino acids are somewhat "rare" or unusual or even "unknown" for the current terrestrial biochemistry and are used only by simple organisms like fungi and bacteria.
- **After radiolysis at 3.2 MGy of 20 proteinogenic amino acids we have radiolyzed also a selection of non-proteninogenic amino acids.**

Non-proteinogenic amino acids radiolyzed to 3.2 MGy [JRNC 295 (2013) 1235]

Scheme 1 Chemical structures of the amino acids radiolyzed in the present work

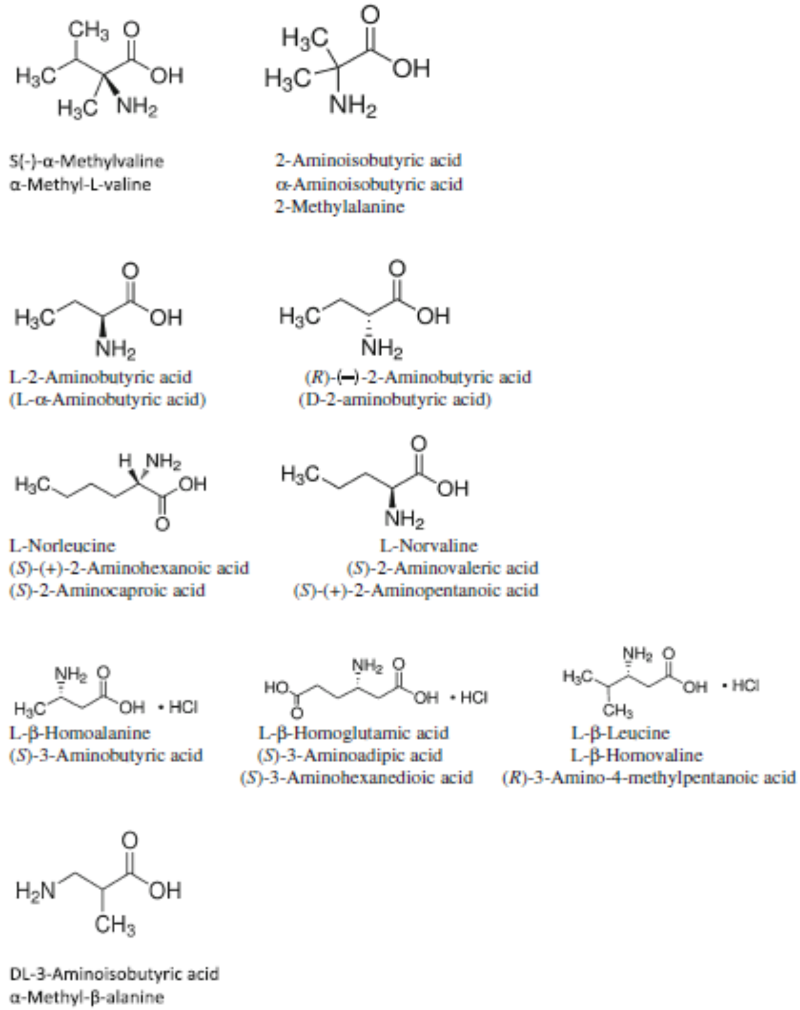


Table 1 Summary of results of the amino acids radiolyzed in vacuum

	Pristine $[\alpha]_D$ before	3.2 MGy vacuum $[\alpha]_D$ after	R_α (%)	R_γ (%)	Pristine $-\Delta H$ fus (J/g)	3.2 MGy vacuum $-\Delta H$ fus (J/g)	Pristine Melting point (°C)	3.2 MGy vacuum Melting point (°C)	N_γ (%)	Melting point shift (°C)	Notes after radiolysis
2-Aminoisobutyric acid	n.a.	n.a.	n.a.	n.a.	1,173.4	1,133.7	311.6	322.5	96.6	+10.9	Yellow color, aminic and fatty odor
S(−)-α-Methylvaline	−6.2	−5.5	88.7	92.8	850.9	595.2	306.1	298.8	69.9	−7.3	pale yellow color, pungent odor
L-2-Aminobutyric acid	18.5	11.9	64.3	73.7	954.2	408.1	297.3	271.3	42.8	−26.0	Yellow color, aminic and fatty odor
D-2-Aminobutyric acid	−19.6	−15.4	78.6	75.0	1,183.4	744.6	315.9	284.4	62.9	−31.5	dark yellow color, aminic and fatty odor
L-Norleucine	22.5	14.3	63.6	70.8	915.9	505.4	297.3	268.8	55.2	−28.5	light yellow color, weak aminic odor
L-Norvaline	21.1	17.1	81.0	84.0	995.4	616.3	318.9	284.4	61.9	−34.5	pale yellow color, distinctive aminic odor
L-β-Leucine HCl	30.4	22.6	74.3	79.9	138.9	74.2	176.3	159.8	53.4	−16.5	cream color color, sweet odor
L-β-Homoalanine HCl	20.9	17.6	84.2	86.4	61.2	44.6	49.5	49.9	72.9	0.4	Brown color, sweet odor
L-β-Homoglutamic acid HCl	19.5	17.8	91.3	93.4	180.2	134.8	190.8	182.1	74.8	−8.7	cream color
DL-3-Aminoisobutyric acid	n.a.	n.a.	n.a.	n.a.	208.6	166.6	181.2	179.1	79.9	−2.1	pale yellow color, aminic odor

Notes: $[\alpha]_D$ = specific optical rotation at the D line of Na; R_γ% and R_α% residual amount of amino acid after radiolysis as measured by ORD and by standard polarimetry see Eqs. 2 and 3 respectively; $-\Delta H$ fus: melting enthalpy; N_γ% residual amount of amino acid after radiolysis as measured by DSC, see Eq. 1; melting point shift occurred after 3.2 MGy radiolysis

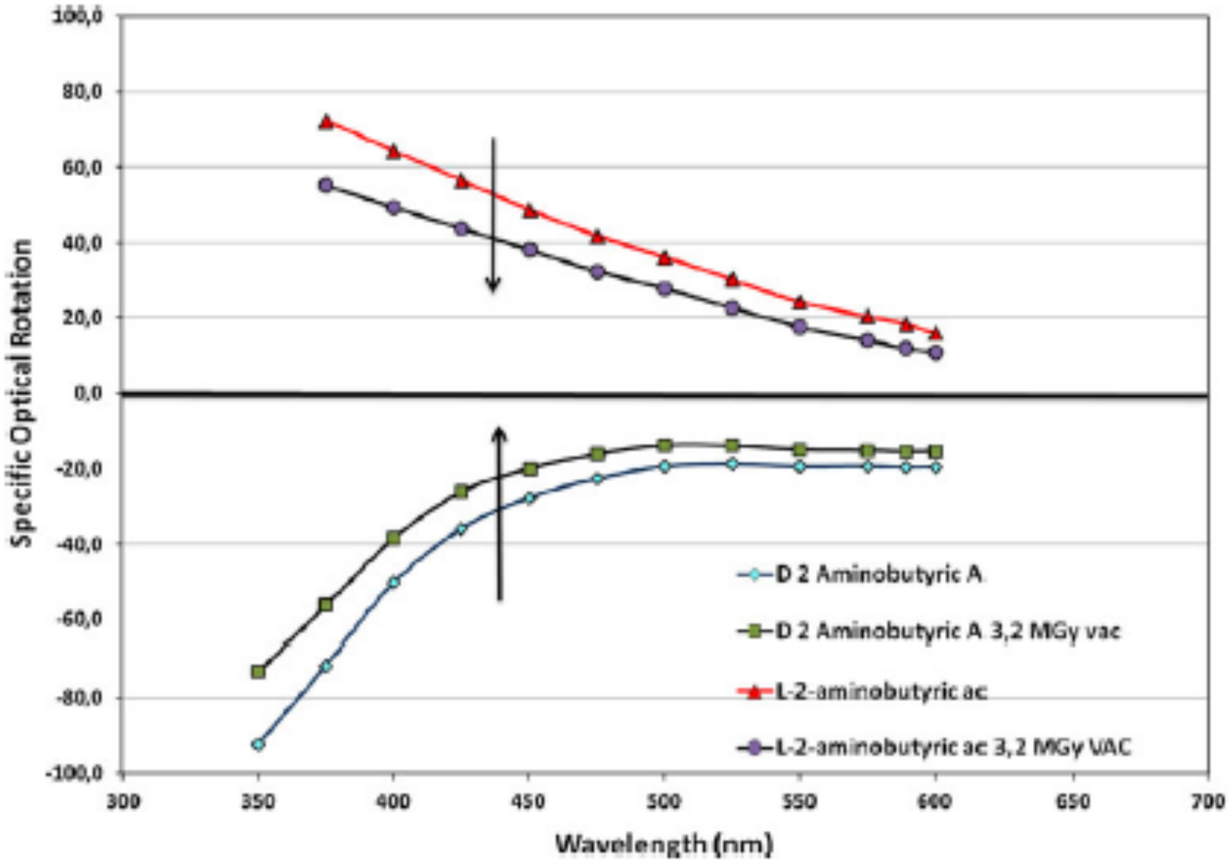
Comparison radiolysis/radioracemization resistance proteinogenic vs non-proteinogenic amino acids

Comparison of Ra% proteinogenic vs non-proteinogenic amino acids			
Proteinogenic amino acids	Ra%	**Non-Proteinogenic amino acids**	Ra%
L-tyrosine	98,9		
L-asparagine	97,6		
L-cystine	97,6		
L-histidine	96,3		
L-aspartic ac	94,2		
L-valine	94,0		
L- glutamic ac	92,7		
L-glutamine	91,6		
L-isoleucine	91,4	L-B-Homoglutamic ac HCl	91,3
L-proline	86,8	S(-)a-Methylvaline	88,7
L-methionine	82,6	L-B-Homoalanine HCl	84,2
L-leucine	82,6		
L-phenylalanine	82,5	L-Norvaline	81,0
L-arginine	75,3		
L-tryptophan	79,1	D-2-aminobutyric ac.	78,6
L-lysine	77,0		
L-alanine	75,8	L-B-Leucine HCl	74,3
L-cysteine	71,4		
L-serine	70,7		
L-threonine	62,8	L-3-aminobutyric ac.	64,3
		L-Norleucine	63,6

Some proteinogenic amino acids show higher radiolysis and radioracemization resistance than non-proteinogenic amino acids

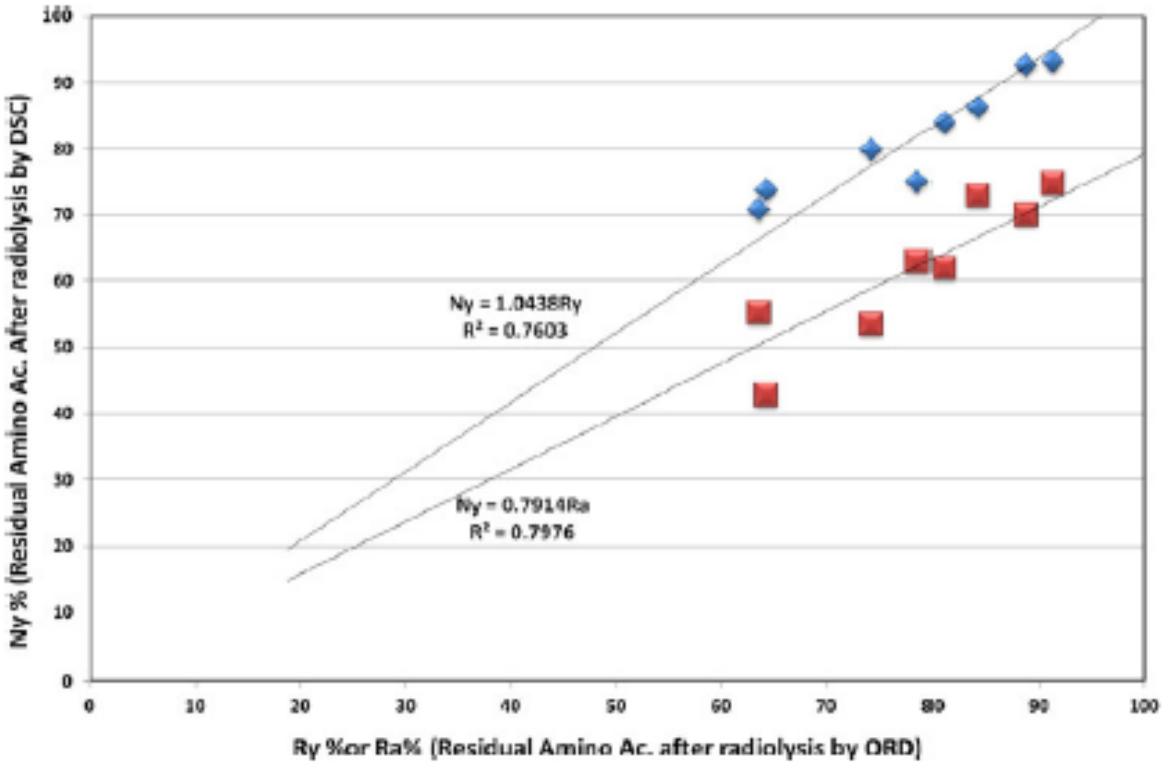
Example of radioracemization measured by ORD

Fig. 5 ORD spectra in HCl 1 M: top trace (*triangles*) L-2-aminobutyric acid; top trace (*circles*) L-2-aminobutyric radiolyzed at 3.2 MGy in vacuum, the *arrow* shows the shift of the ORD curve toward the abscissa axis due to radioracemization. Bottom trace (*diamonds*) D-2-aminobutyric acid; bottom trace (*squares*) D-2-aminobutyric radiolyzed at 3.2 MGy in vacuum, the *arrow* shows the shift of the ORD curve toward the abscissa axis due to radioracemization



Correlation between DSC and ORD data

Fig. 6 Correlation between the amount of residual amino acids after solid state radiolysis at 3.2 MGy. In ordinate is reported N_γ % i.e. the amount of residual amino acid measured by DSC and in abscissa are reported both R_γ % and R_α % respectively measured by ORD or by standard polarimetry at 589 nm. The *blue diamond* represent the R_γ % values and the *red squares* the R_α % values



Extrapolation to $4.6x10^9$ years

- The N_γ and R_γ values measured at 3.2 MGy of radiation dose correspond to $1.05x10^9$ years.
- Thus, the N_γ and R_γ values were extrapolated to $4.6x10^9$ years.

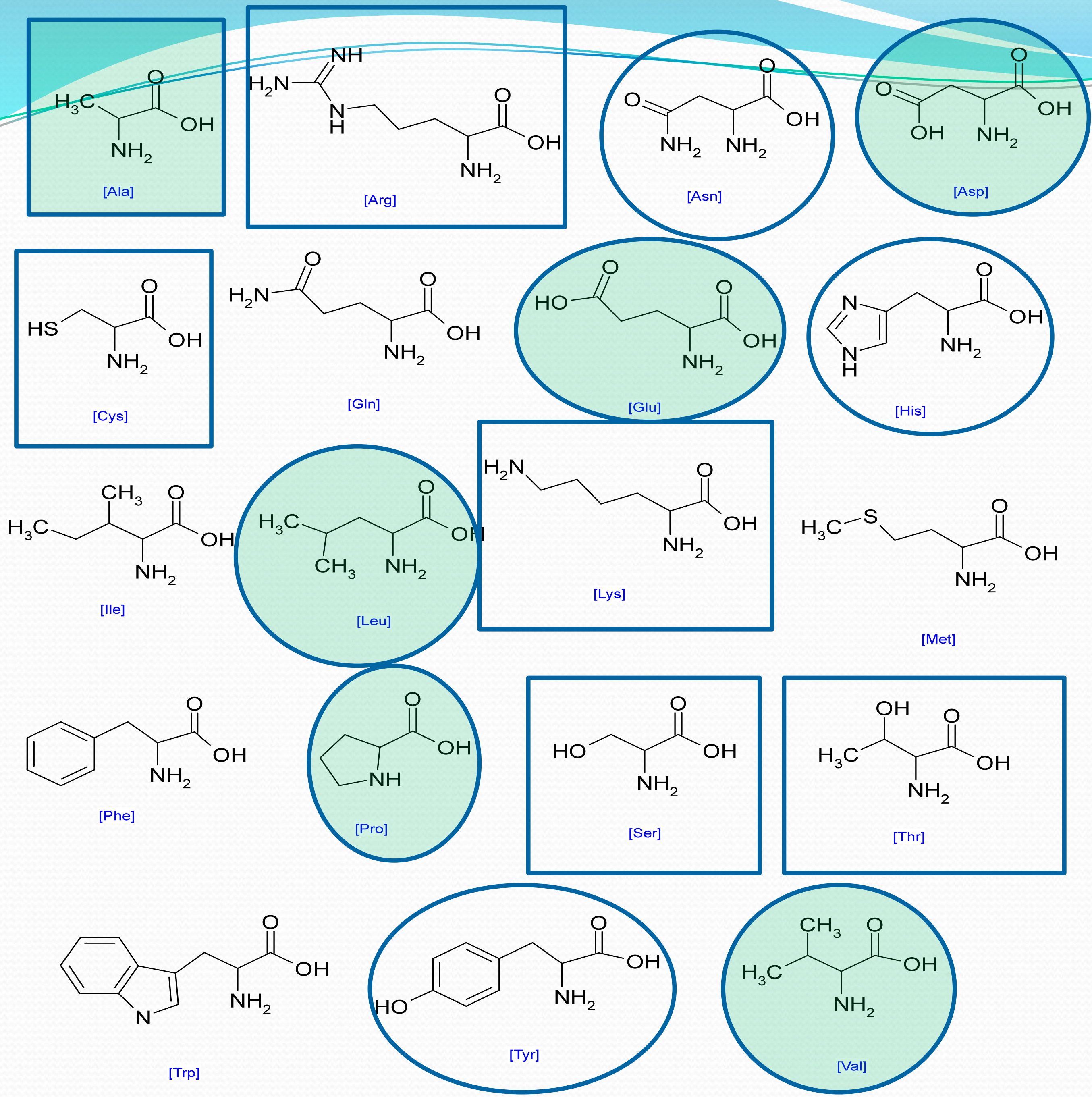
TABLE 1 - AMINO ACIDS ORDERED ACCORDING TO THE RADIORACEMIZATION RESISTANCE

Cataldo et al. MNRAS, in press, 2010

	R % after $1.05x10^9$ y	N % after $1.05x10^9$ y	R % after $4.6x10^9$ y	N % after $4.6x10^9$ y
l-threonine	62.8	66.6	13.1	16.9
l-serine	70.7	80.8	21.9	39.3
l-cysteine	71.4	63.5	22.9	13.7
l-arginine	75.3	56.6	28.9	8.3
l-alanine	75.8	68.8	29.7	19.5
l-lysine	77.0	54.6	31.9	7.1
l-tryptophan	79.1	92.2	35.8	70.1
l-phenylalanine	82.5	70.2	43.1	21.3
l-methionine	82.6	68.4	43.3	19.0
l-leucine	82.6	72.3	43.3	24.2
l-proline	86.8	83.5	53.8	45.4
l-isoleucine	91.4	70.5	67.5	21.7
l-glutamine	91.6	94.7	68.1	78.8
l-glutamic acid	92.7	84.5	71.8	47.8
l-valine	94.0	98.1	76.3	91.9
l-aspartic acid	94.2	95.5	77.0	81.7
l-histidine	96.3	83.4	84.8	45.2
l-asparagine	97.6	79.6	89.9	36.8
l-cystine	97.6	96.7	89.9	86.3
l-tyrosine	98.9	92.1	95.3	69.8

TABLE 2 - RADIORACEMIZATION AND RADIOLYSIS RATE CONSTANTS AND RELATIVE HALF LIFES (Cataldo et al. MNRAS, in press, 2010)

	k_{rac} ($\times 10^{-10}$ y^{-1})	k_{dsc} ($\times 10^{-10}$ y^{-1})	$\tau_{1/2rac}$ ($\times 10^{9}$ y)	$\tau_{1/2dsc}$ ($\times 10^{9}$ y)
l-threonine	4.43	3.87	1.57	1.79
l-serine	3.30	2.03	2.10	3.42
l-cysteine	3.21	4.32	2.16	1.60
l-arginine	2.70	5.42	2.57	1.28
l-alanine	2.64	3.56	2.63	1.95
l-lysine	2.49	5.76	2.79	1.20
l-tryptophan	2.23	0.773	3.11	8.97
l-phenylalanine	1.83	3.37	3.79	2.06
l-methionine	1.82	3.61	3.81	1.92
l-leucine	1.82	3.09	3.81	2.25
l-proline	1.35	1.72	5.15	4.04
l-isoleucine	0.856	3.33	8.10	2.08
l-glutamine	0.835	0.518	8.30	13.4
l-glutamic acid	0.721	1.60	9.61	4.33
l-valine	0.589	0.183	11.8	38.0
l-aspartic acid	0.569	0.438	12.2	15.8
l-histidine	0.359	1.73	19.3	4.01
l-asparagine	0.231	2.17	30.0	3.19
l-cystine	0.231	0.319	30.0	21.7
l-tyrosine	0.105	0.783	65.9	8.85



Amino acids and their stability to radiolysis.

Circle: most stable

Square: less stable

Green: found in meteorites

Validity of our Results

- The validity of our experimental approach can be confirmed by comparing the k_{dsc} results derived from calorimetric measurements with those of Kminek and Bada (2006) derived from HPLC measurements.

- Kminek and Bada (2006) have found the following radiolysis rate constants:

For **alanine** $k = 3.43x10^{-10}\ y^{-1}$ our result $k = 3.56x\ 10^{-10} y^{-1}$.

For **glutamic acid** $k = 5.26x10^{-10}\ y^{-1}$ our result $k = 1.60x\ 10^{-10}\ y^{-1}$

For **aspartic acid** $k = 4.78x10^{-10}$, our results $k = 0.44x10^{-10}\ y^{-1}$

CONCLUSIONS - 1

- The study shows that the amino acids are characterized by an **individual response to high energy radiation**.

- It is evident that all **amino acids studied can "survive" in relatively large amount to a radiation dose equivalent** to that administered by the radionuclide decay from the beginning of the history of the Solar System to the present.

- **Not only all the amino acids can survive to 14 MGy but also their enantiomeric enrichment can be partially preserved even after 14 MGy radiation dose.**

CONCLUSIONS-2

- Based on these results it is not at all a surprise that amino acids have been found in meteorites and in measureable enantiomeric excess.

- With the experimental data available we can even predict the concentration of the amino acids in comets and in asteroids at the beginning of the Solar System and also we can extrapolate to the original enantiomeric excess 4.6×10^9 years ago.