

# Radiation-induced racemization and amplification of chirality: implications for comets and meteorites\*

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**Abstract:** The action of high-energy radiation on prebiotic chiral molecules plays against the preservation of chirality. Chiral molecules incorporated in comets and meteorites are bombarded for billions of years by cosmic rays and by the high-energy radiation due to the decay of naturally occurring radionuclides. The action of cosmic rays on the surface of comets and meteorites causes the complete radiation processing of the surface of these bodies, but at depths of 20 m or so the cosmic rays are completely shielded and the radiation should derive only from the decay of radionuclides. In  $4.6 \times 10^9$  yr the radiation dose supplied by the radionuclide decay to the organic molecules present inside the cometary or meteoritic body is equivalent to 14 000 kGy. Our studies on the radiolysis of a series of naturally occurring chiral molecules, the terpenes, have shown that although all undergo the radoracemization reaction, the extent of radoracemization is such that a significant fraction of chiral excess and chiral molecules can survive a radiation dose equivalent to 14 000 kGy. A unique exception is represented by the terpene  $\beta$ -(-)-pinene which, instead of the expected radoracemization reaction, undergoes a radiation-induced polymerization. The resulting poly- $\beta$ -pinene, having an highly ordered supramolecular structure, displays an optical activity which is 1.7 times higher than the starting monomer. Thus, in this specific case, the optical activity is not reduced but enhanced by the action of radiation and remains locked into a polymer which displays a considerable radiation resistance and may act as a chiral template and as a chiral surface for prebiotic chemistry.

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## Introduction

The biochemistry of the biological world is based on molecules and macromolecules having one or more centres of asymmetry; these molecules are called chiral molecules. Thus, life is strictly linked to the chirality of the molecules and macromolecules. No life can be conceived without chirality because all the complex chemistry and biochemistry, i.e. high selectivity in chemical reactions in living organisms, which are the basis of life would be impossible (Cataldo & Keheyen 2003a,b; Cataldo *et al.* 2005; Cataldo *et al.* 2007a).

A central problem in the research for the origin of life is the origin of chirality. Phenomena such as the action of circularly polarized light on a racemic mixture of prebiotic molecules have been pointed out as the spontaneous source of chiral excess in an abiotic world (Bailey *et al.* 1998; Lucas *et al.*

2005). Although the action of circularly polarized light seems to be the most plausible source of chirality, a certain number of other possible sources of chirality have been proposed (see Podlech 2001; Cataldo *et al.* 2005). Some authors have proposed that the chiral molecules are formed in the interstellar medium, in the molecular clouds, and then they are incorporated into primitive bodies such as comets and meteorites (Kwok 2004). Others are convinced that most of the prebiotic molecules are likely to have been formed in the Solar nebula itself and are then incorporated in meteorites (Pizzarello *et al.* 2003). Aqueous alteration processes and interactions with meteorite minerals may lead to the formation of heterocycles and amino acids (Hazen *et al.* 2001). A clear experimental fact is represented by the presence of amino acids in chiral excess in certain meteorites (Pizzarello & Cronin 2000; Pizzarello 2004). Some of the amino acids found in meteorites are unusual in the Earth biosphere and this fact strongly supports their extraterrestrial origin and excludes the possibility of terrestrial contamination (Cronin & Pizzarello 2000).

The most commonly accepted scenario involves the delivery of the prebiotic molecules in chiral excess to the Earth

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through comets and meteorites and the necessity of chiral amplification mechanisms on the Earth which are able to expand the limited enantiomeric excesses usually observed in meteorites. A series of chiral amplification mechanisms has been advocated (Podlech 2001; Blackmond 2004; Cataldo *et al.* 2005; Breslow & Levine 2006).

However, there is a well-known phenomenon which plays against the preservation of chirality: the racemization reaction. Racemization on the Earth can occur because of the action of heat, the catalysis of metal ions, the action of the Sun's rays and the natural background radiation. The same phenomena, with different weighting, also causes racemization in space. In fact in space the predominant phenomena which plays against the preservation of chirality of asymmetric molecules are the photoracemization and the radio-racemization reactions, although thermal and water-driven racemization may also be effective (Cohen & Chyba 2000).

The photolysis and the radiolysis of chiral molecules caused by UV light or by high-energy radiation and by cosmic rays in general causes a reduction in the optical activity. Apparent and true photo- and radoracemization must be distinguished (Cataldo *et al.* 2004; Cataldo *et al.* 2005).

Here we present our data on the radoracemization of model molecules with the action of  $\gamma$  radiation, and we show that the radoracemization phenomenon, although general and irreversible, in a special case leads to the amplification of chirality.

### An inventory of the total radiation dose received by organic molecules in comets and meteorites

Prebiotic organic molecules formed in the Solar nebula are incorporated in comets and meteorites. In general, it is assumed that these bodies (or some of them) do not undergo significant thermal processing, and, because they are so distant from the Sun, receive only a very small amount of UV radiation. Therefore, the organic matter locked in cometary bodies remains in its primitive state. The processing occurs because of the action of cosmic rays and the decay of the radionuclides naturally occurring in the mineral rocks of the body.

It has been calculated by Draganic *et al.* (1993) that in  $4.6 \times 10^9$  yr the total amounts of cosmic rays (mainly protons and  $\alpha$  particles) which bombard the first few centimetres of the surface of these bodies are equivalent in total to a radiation dose of 300 000 kGy ( $1 \text{ Gy} = 1 \text{ J g}^{-1}$ ). However, at depths greater than 20 m from the surface there is sufficient shielding that the radiation dose is reduced to only 300 kGy. Further towards the core of the body the radiation dose reduces further. Thus, at high depths the radiolysis due to cosmic rays becomes negligible and the unique source of radiation is the result of the decay of radionuclides which have survived the process of the accretion of the pre-Solar nebula. To calculate the absorbed dose resulting from the embedded radionuclides it is sufficient to consider only the main contributor isotopes:  $\text{Be}^{10}$ ,  $\text{K}^{40}$ ,  $\text{I}^{129}$ ,  $\text{Th}^{232}$ ,  $\text{U}^{235}$ ,  $\text{U}^{238}$ ,  $\text{Np}^{237}$ ,  $\text{Pu}^{244}$  and  $\text{Cm}^{247}$  (Prialdnik *et al.* 1987; Prialdnik & Podolak 1995).

These nine radioisotopes deliver a total dose of 2800 kGy in  $4.6 \times 10^6$  yr of the comet's life (Draganic *et al.* 1993). To this list the shorter-lived  $\text{Al}^{26}$ , whose half-life is  $7 \times 10^5$  yr, should also be considered (Prialdnik & Bar-Nun 1990). The contribution derived from the decay of  $\text{Al}^{26}$  in  $4.6 \times 10^9$  yr is 11 000 kGy (Draganic *et al.* 1993) so that is largely the main contributor.

The total radiation dose emitted by the main radionuclides in  $4.6 \times 10^9$  yr reaches approximately 14 000 kGy; in the depth it is almost the unique source of high-energy radiation which can process the prebiotic molecules. On the comet's surface and through the first few metres of the surface layer the amount of total dose received is the sum of cosmic ray dose plus radionuclide decay, approximately 314 000 kGy. Owing to this very high radiation dose it is assumed that the first cometary layer is completely radiation-processed. Instead it has been calculated that the core of a comet essentially made of water ice may even reach a liquid state owing to the radiogenic heat, meaning that a comet having a cross section of 20 km is expected to have a liquid core with a radius of 7 km (Draganic *et al.* 1993; Prialdnik & Podolak 1995). In these conditions many radiation-induced chemical reactions may occur but only part of the 14 000 kGy will be utilized for the processing of the primitive organic molecules present in comets so it is expected that only 15% of the original organic material is changed into other products in the core (Draganic *et al.* 1993).

### The radoracemization of model chiral molecules

Based on the above calculations it is not a surprise that Pizzarello (2004), Pizzarello & Cronin (2000) and Cronin & Pizzarello (2000) have found a series of amino acids and other organic molecules in enantiomeric excess from extracts derived from the Murchison and Murray meteorites. The radiation dose was not sufficient to cause complete radiolysis, and hence radoracemization, of the starting chiral molecules. In particular, the amino acid isovaline was found in 8.4% levo enantiomeric excess in the Murchison meteorite. This means that the original enantiomeric excess at the time of the formation of the Solar System was much higher. The same applies for the original concentration of the scalemic mixture of isovaline  $4.6 \times 10^9$  years ago.

Using a series of natural molecules, the terpenes (see Fig. 1) as model compounds we have performed a series of radiolysis and radoracemization experiments using different levels of radiation doses from a  $\text{Co}^{60}$  source which emits  $\gamma$  photons having energies of 1.33 and 1.17 MeV (Cataldo *et al.* 2004; Cataldo & Keheyran 2006; Cataldo 2007; Cataldo *et al.* 2007a,b).

The racemization can be followed polarimetrically and a distinction between true and apparent racemization has been explained (Cataldo *et al.* 2004). True racemization is when a given chiral molecule passes through an excited state and then decays into its enantiomer until an equimolar mixture of the two enantiomers is obtained. This implies that the centre of asymmetry in the molecule is involved in the excited

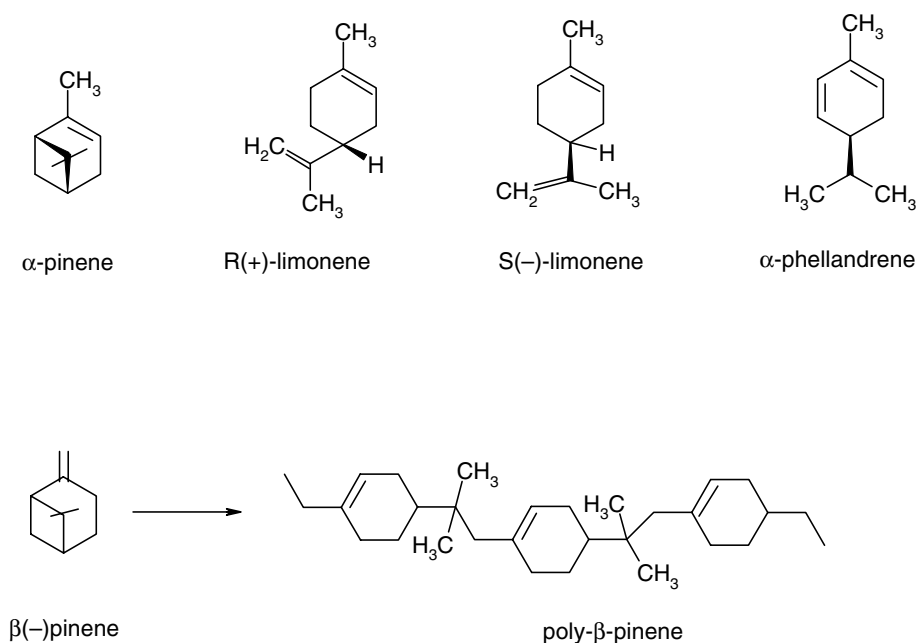


Fig. 1. Chemical structures of the terpenes employed in the radiolysis experiments.

state and undergoes an inversion. The apparent racemization is due to the fragmentation of the molecule as a consequence of its radiolysis; the centre of asymmetry is lost and the associated optical activity drops to zero. In general, the radiation-induced racemization of chiral molecules involves mainly the apparent racemization, and the optical activity drops gradually to zero (as function of the radiation dose) because of the decomposition of the original molecule.

Figure 2 shows the results of our radiolysis experiments on a series of chiral natural terpenes, two limonene enantiomers and  $\alpha$ -phellandrene (Cataldo *et al.* 2004). The two limonene samples were characterized by a relatively high optical purity (enantiomeric excess nearly 100 %) and the radiation treatment has caused a reduction of the original optical activity of  $-4.3\%$  for the R(+) enantiomer and  $-7.6\%$  for the S(-) enantiomer. The changes in optical activity are slightly more significant for the less pure  $\alpha$ -phellandrene.

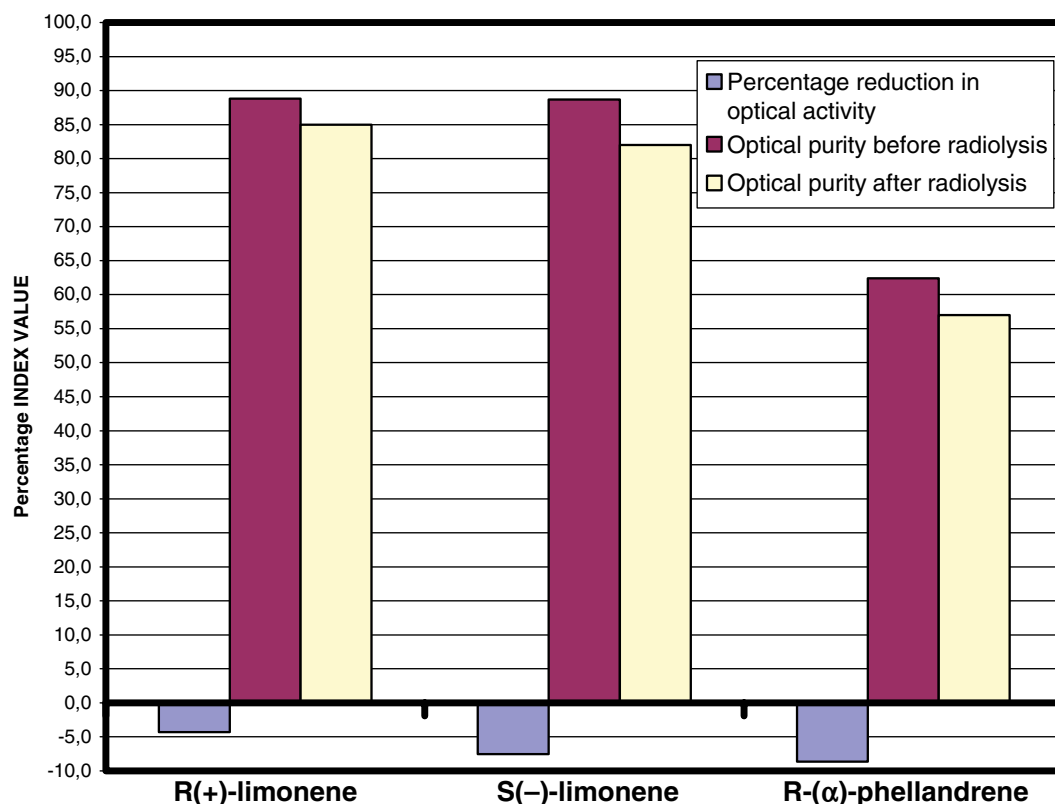
The radiation dose deposited by cosmic rays in  $4.6 \times 10^9$  yr at depths greater than 20 m in a comet is just 300 kGy and our experiments demonstrate that such a radiation dose is not at all sufficient to destroy chirality eventually present in the cometary body or meteorite. It is possible to add that a dose of 300 kGy will also have only a limited racemizing effect.

In the previous section we have shown that the radiation dose from the decay of the radionuclides in the bulk of the comet is equivalent to 14 000 kGy (in  $4.6 \times 10^9$  yr), which is about 47 times the radiation deposited by the cosmic rays at a depth of 20 m. Based on the data of our experiment and assuming that the optical purity will decay at a rate of 5 % every 300 kGy of radiation, it is possible to show that even a dose of 14 000 kGy is insufficient to destroy all the original chirality. For instance, a simple calculation shows that if we start from 95 % optical purity after a radiation dose of 14 000 kGy it will be reduced to 8.5 %, and starting from

a more realistic 15 % original optical purity the calculation shows that a residual enantiomeric excess of 1.3 % should be expected after a 14 000 kGy radiation dose. Based on these considerations it is not a surprise that amino acids with enantiomeric excess as high as approximately 10 % in the case of isovaline have been found in the Murchison meteorite (Cronin & Pizzarello 2000; Pizzarello & Cronin 2000), although in general the enantiomeric excess for all other amino acids is limited to a few percent or less. Particularly fascinating is the observation that all amino acids, which were found in the meteorite at ppm concentration levels (Kvenvolden *et al.* 2000), were in enantiomeric excess in the l-form, the same preferred enantiomeric form employed by the life biochemistry on Earth.

The possibility of terrestrial contamination of the amino acids extracted from meteorites has been excluded because the common  $\alpha$ -amino acids are accompanied by the  $\alpha$ -methyl-amino acids which are unusual for terrestrial biochemistry and must be of extraterrestrial origin (Pizzarello & Cronin 2000; Cronin & Pizzarello 2000). Furthermore, the common  $\alpha$ -amino acids racemize quite easily by the action of metal ions and heat; this is not the case for  $\alpha$ -methyl-amino acids whose racemization should be due almost exclusively to the radiolysis. Cronin & Pizzarello (2000) have shown that the enantiomeric excess found in meteorite extracts is a maximum just for the  $\alpha$ -methyl-amino acids and a minimum or negligible for the common  $\alpha$ -amino acids. Other observations and experiments from Kvenvolden *et al.* (2000) have excluded definitively the risk of contamination in the analysis of the meteorite's chiral excess. Thus, the chiral excess recorded was truly genuine.

Our further work on the radiolysis of chiral terpenes has involved  $\alpha$ (-)-pinene,  $\alpha$ (+)-pinene and  $\beta$ (-)-pinene (Cataldo & Keheyan 2006; Cataldo 2007; Cataldo *et al.*



**Fig. 2.** Reduction in optical purity after the absorption of a radiation dose of 317 kGy. For R(+)-limonene the optical purity before radiolysis was 88.8 % and this was reduced to 85.0 % with a reduction in optical activity of -4.3 %. The optical purity of the enantiomer S(-)-limonene was reduced by -7.6 %. Phellandrene was characterized by a relatively low starting optical purity and the radiolysis causes its reduction of -8.7 %.

2007a,c). Figure 3 shows a summary of our results on the crude radiolysed samples. While both  $\alpha$ -pinene enantiomers show a reduction in their optical activity after the administration of a  $\gamma$  radiation dose of 600 kGy, so that their optical purity is reduced from -3 % to -3.5 %, the  $\beta$ -(-)-pinene sample shows an unexpected increase in its optical activity which will be discussed in the next section.

Earlier work dedicated to  $\alpha$ -(+)-pinene radiolysis (Bathes *et al.* 1962) was conducted at approximately the same dose rate used in our work (Cataldo 2007). However Bathes *et al.* (1962) followed the radoracemization of  $\alpha$ -(+)-pinene to a total dose of 8100 kGy, which is about 57 % of the 14000 kGy radiation dose due to radionuclide decay in comets and 13.5 times the maximum radiation dose administered to our samples. In Fig. 4 we compare the earlier radoracemization data of  $\alpha$ -(+)-pinene derived from Bathes *et al.* (1962) with the radoracemization results obtained from our work (Cataldo 2007) for a much lower radiation dose. It is possible to observe in both cases a linear trend in the reduction of the specific optical rotation as a function of the radiation dose. The two lines run parallel with almost the same slope, which suggests a value of approximately  $2.5 \times 10^{-3} [\alpha]_D \text{ kGy}^{-1}$ . Thus, our results are in good agreement with earlier data on  $\alpha$ -(+)-pinene radoracemization. The intercept differences of the two curves are linked to the initial optical purity of the samples employed, i.e. our sample

was more pure than that of Bathes *et al.* (1962). In any case, the experiment of Bathes *et al.* (1962) has demonstrated that the optical activity can survive a massive dose of radiation. Using the equation derived from the graphs in Fig. 4,

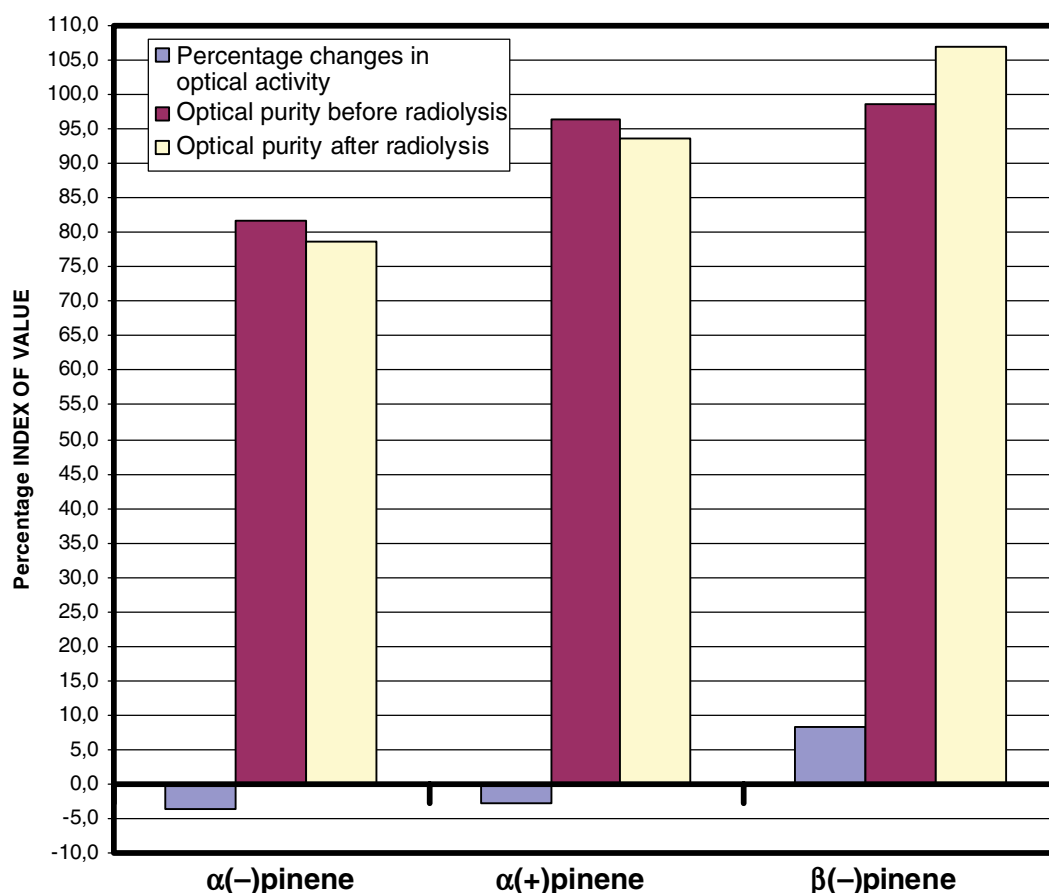
$$[\alpha]_D = -0.0026 R_d + 49.2$$

where the specific optical rotation  $[\alpha]_D$  depends on the radiation dose  $R_d$  in kGy, it is possible to calculate that at 14000 kGy about 26 % of the original optical activity should have been preserved even after  $4.6 \times 10^9$  yr.

### The anomalous behaviour of $\beta$ -pinene: it radiopolymerizes into a polymer having higher optical activity than the starting monomer

All our experiments on the radoracemization of chiral molecules have shown the inevitable tendency towards a reduction in optical activity in line with earlier works (Bathes *et al.* 1962).

However, the behaviour of  $\beta$ -(-)-pinene is markedly in countertendency and may represent an exception. In fact Fig. 3 has shown an increase in the optical activity after the absorption of 600 kGy of  $\gamma$  quanta. Fractionation of the crude radiolysed  $\beta$ -(-)-pinene mixture has permitted us to isolate a solid resin and an oligomeric product both showing a significantly higher optical activity than the starting

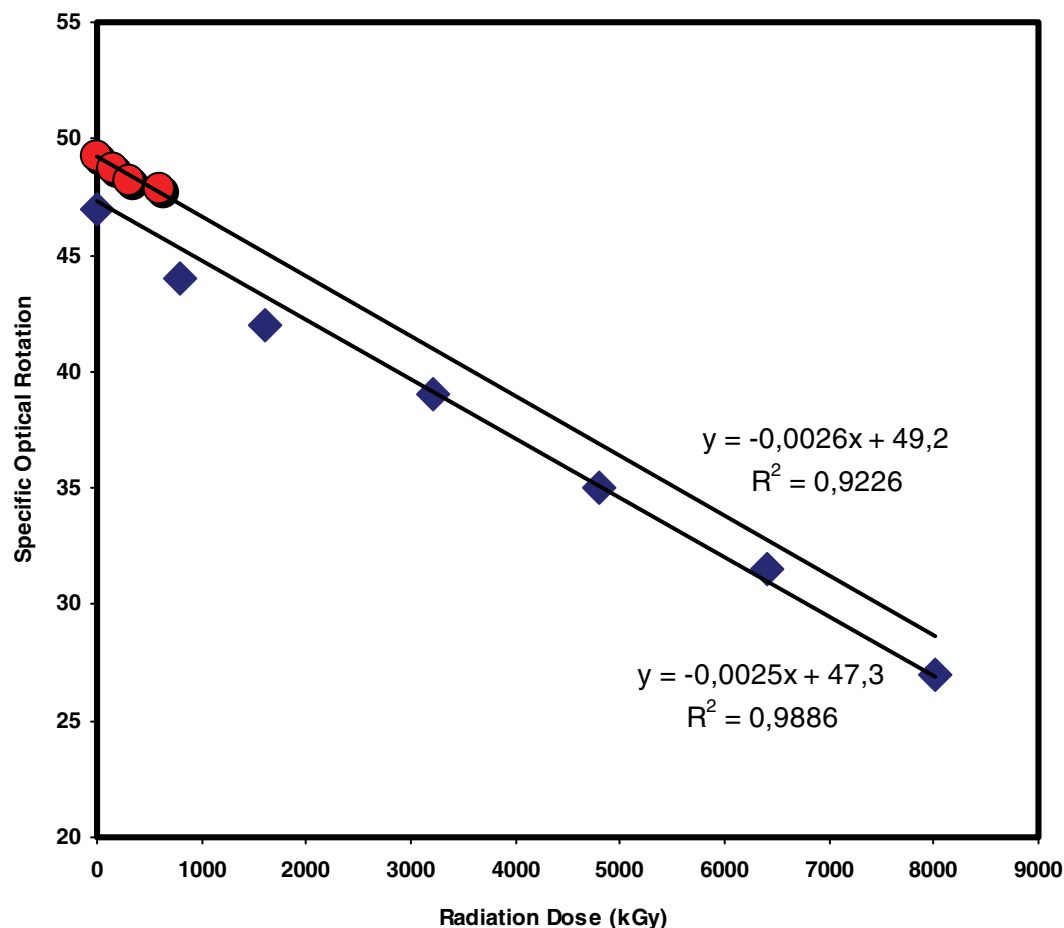


**Fig. 3.** Change in the optical purity of the two  $\alpha$ -pinene enantiomers after a radiation dose of 600 kGy. The optical purity of the  $\alpha(-)$ -pinene was reduced by  $-3.7\%$  while for the optical antipode  $\alpha(+)$ -pinene the optical purity was reduced by  $-2.7\%$ .  $\beta(-)$ -pinene shows an anomalous and unique behaviour, the optical activity is increased after radiation treatment by  $+8.4\%$ .

monomer (Cataldo & Keheyán 2006; Cataldo *et al.* 2007a,c). Figure 5 illustrates with index data that, taking as 100 the specific optical rotation of the starting monomer,  $\beta(-)$ -pinene in toluene, the resulting poly- $\beta$ -pinene isolated after the radiation polymerization of the monomer shows an increased specific optical rotation which is 1.7 times the value of the starting monomer. This fact was completely unexpected since a reduction in optical activity is the general rule following the radoracemization phenomenon. In the special case of the  $\beta(-)$ -pinene monomer the radiation causes its polymerization instead of its degradation and the resulting polymer has a sufficiently high structural order that it amplifies the chirality of the single monomeric unit. There are many experimental facts supporting the model of the higher structural order of the resulting radiopolymers which justify the amplification of chirality. Figure 6 shows the differences in the infrared spectra from a chemically produced poly- $\beta$ -pinene, which has a very low optical activity (see also Fig. 5), with the spectra of three poly- $\beta$ -pinene radiopolymers obtained at different radiation doses and having high optical activity. Without entering into the detail of the band assignment of the infrared spectra, which has been discussed elsewhere (Cataldo & Keheyán 2006), at first glance from Fig. 6

it is possible to observe that the absorption bands of the chemically produced poly- $\beta$ -pinene (the spectrum at the top of Fig. 6) are poorly resolved. In contrast, the infrared spectra of poly- $\beta$ -pinene radiopolymers having high optical activity are rich in very well resolved absorption bands. Thus, the relation between chemical structure regularity with optical activity and with infrared spectral resolution is demonstrated.

A similar situation can be also observed in the case of the solid-state  $C^{13}$ -NMR spectra shown in Fig. 7 where again the higher optical activity is associated with a series of much better resolved NMR signals. The details of the NMR spectra will be discussed in a separate paper (Cataldo *et al.* 2007b). Furthermore, the poly- $\beta$ -pinene radiopolymer has a completely different thermal behaviour than the chemically prepared poly- $\beta$ -pinene, with a much higher softening point and hence a higher molecular weight (Cataldo *et al.* 2007c). Particularly interesting is the fact that the optical activity of a poly- $\beta$ -pinene obtained on a stereospecific Ziegler–Natta catalyst, thus having a highly ordered structure, is quite comparable with the optical activity recorded on the poly- $\beta$ -pinene radiopolymer (see Fig. 5). Also this fact supports the idea that the radiopolymer has an ordered



**Fig. 4.** Radioracemization of  $\alpha$ -(+)-pinene as reported in previous work by Bathes *et al.* (1962) (diamonds) and as found in Cataldo (2007) (circles). Despite the different total radiation dose used and the different starting optical purity the two trend lines run parallel, showing the same slope of approximately  $2.5 \times 10^{-3} [\alpha]_D \text{ kGy}^{-1}$ .

supramolecular structure which justifies its higher optical activity.

Another feature of the poly- $\beta$ -pinene radiopolymer is the fact that its optical activity is independent from the radiation dose administered to the sample (see Fig. 5). This means that once the  $\beta$ -pinene monomer undergoes the radiation-induced polymerization, its optical activity is amplified 1.7 times and then remains locked into a polymeric structure which is radiation-resistant and which is able to preserve its optical activity at any radiation level (Cataldo *et al.* 2007b).

## Experimental section

### Materials and equipment

$\beta$ -(-)-pinene,  $\alpha$ -(-)-pinene, limonene enantiomers and  $\alpha$ -phellandrene were obtained from Fluka (Switzerland) or Aldrich (USA) and used without further purification. The  $\beta$ -(-)-pinene used in this work was greater than 99.0% pure (by GC as sum of enantiomers). The specific optical rotation was checked before irradiation and was found to be  $[\alpha]_D = -21.3$  (neat using  $d = 0.871 \text{ g ml}^{-1}$ ).

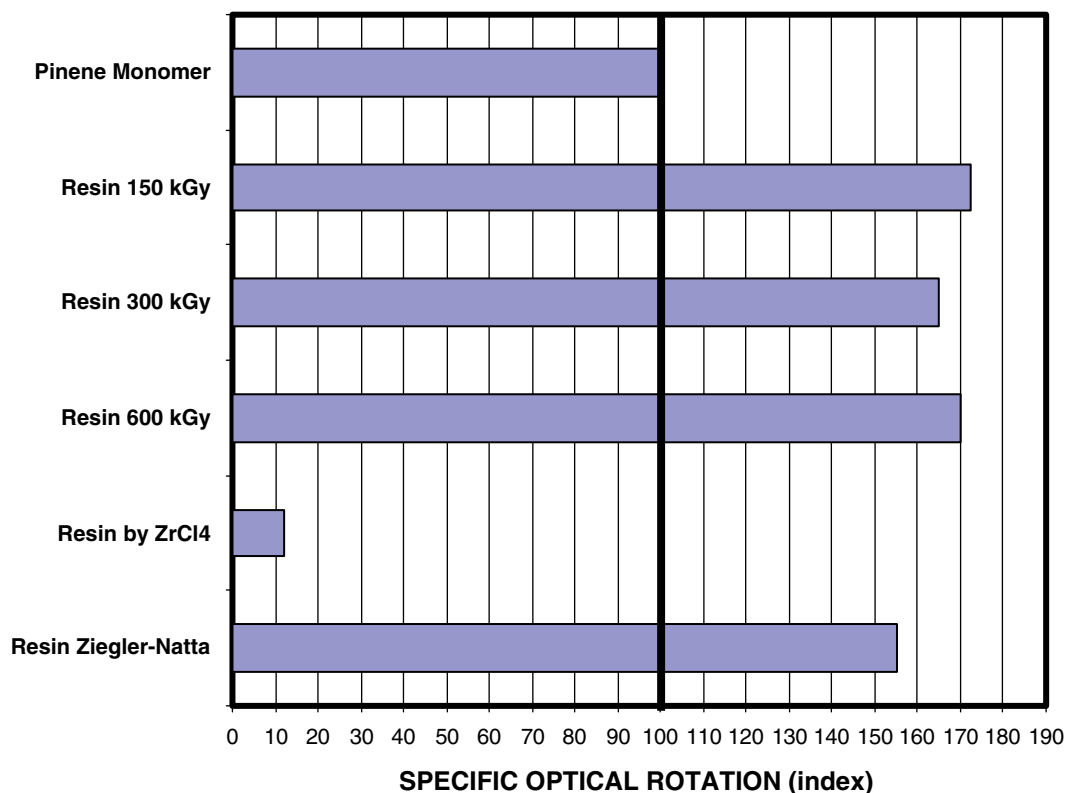
Fourier transform infrared (FT-IR) spectra of the resulting solid poly- $\beta$ -pinene polymers were recorded on solid samples

embedded in KBr pellets in transmittance mode or on an ZnSe plate on an ATR accessory in reflection mode. Use was made of an FT-IR spectrometer from the Nicolet Thermo-Electron Corporation.

The polarimetric measurements were made on an Optika polarimeter model Pol 1 using the D sodium line at 589.3 nm. The specific optical rotation was measured on the liquid terpene samples before and after the irradiation at any prefixed total radiation dose. If the irradiation led to the formation of a solid polymer, for instance as in the case of  $\beta$ -(-)-pinene, the solid polymer was separated from the unreacted monomer and its optical activity was measured after dissolution in toluene. The Biot law was applied to determine the specific optical rotation (Cataldo *et al.* 2004).

Solid-state  $^{13}\text{C}$ -MAS NMR spectra on the poly- $\beta$ -pinene samples were performed at 50.13 MHz on a Bruker ASX-200 spectrometer. The spin rate was 8 kHz; the  $\pi/2$  pulse width was 3.5  $\mu\text{s}$ ; 4000 scans were acquired for each spectrum. The cross-polarization was performed applying the variable spin-lock sequence RAMP-CP-MAS, the RAMP was applied on the  $^1\text{H}$  channel, and, during the contact time  $\tau = 1 \text{ ms}$ , the amplitude of the RAMP increased from 50 to 100% of its maximum value.





**Fig. 5.** The specific optical rotation values are plotted as index values. We take the  $[\alpha]_D$  value of pure, non-radiolysed  $\beta$ -pinene monomer in toluene as 100: the  $[\alpha]_D$  values of poly( $\beta$ -pinene) resins obtained by radiation-induced polymerization reach the index value of 170, which is even higher than the 155 value reached by the poly( $\beta$ -pinene) resin obtained on a Ziegler–Natta stereospecific catalyst. The index value of  $[\alpha]_D$  of the resin produced from  $\beta$ -pinene by cationic polymerization is only 1/10 of the value of the monomer and about 1/17 of the value of poly( $\beta$ -pinene) resins prepared by radiation-induced polymerization.

Spectra were acquired using 1024 data points in the time domain, zero filled and Fourier transformed. The chemical shift was externally referred to tetramethylsilane. Samples were packed into 4 mm zirconia rotors, and sealed with Kel-F caps.

#### *Irradiation experiments of $\beta$ -(–)-pinene or other chiral substrates: a general procedure*

In this section we report a typical procedure for the irradiation experiments with  $\gamma$  radiation. Further details can be found in previous works (Cataldo & Keheyan 2006; Cataldo *et al.* 2007a,b).

The terpenes mentioned in this work were irradiated in screw cap vials or in sealed glass vials under vacuum. In general, simple screw cap vials having a volume of 28 ml were used. The vials were completely filled with the selected chiral terpene, tightly closed with the screw cap and irradiated. When irradiation was conducted in a high vacuum, thick-walled glass vials were charged with 18 ml of appropriate substrate and sealed in a high-vacuum line after repeated cycles of a degassing procedure.

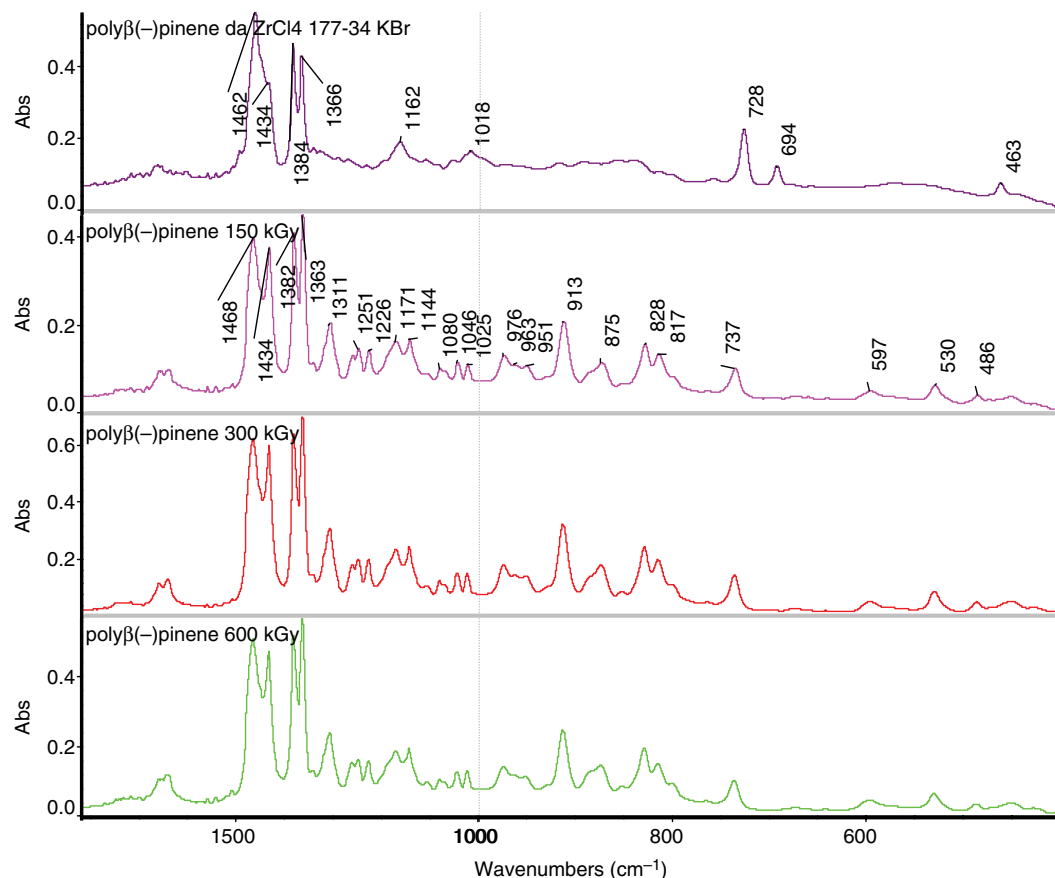
The irradiation was simply performed by placing the vials at room temperature inside a  $^{60}\text{Co}$   $\gamma$ -cell from Atomic Energy of Canada Limited (Mississauga, ON) as a  $\gamma$ -radiation source. The  $\gamma$  cell used was working at a radiation dose rate

of  $2.2 \text{ kGy h}^{-1}$ . Thus, to reach a total dose of 100 kGy the vial was left in the  $\gamma$  cell for  $100/2.2 = 45.5 \text{ h}$ . For 1000 kGy the irradiation time was about 19 days.

After the radiation treatment the vials were opened. In all cases they were found under pressure because of the radiolysis gases accumulated. The content of the vials was used for spectroscopic and polarimetric measurements. Wherever possible, solvent fractionation of the products was adopted to permit their separation (Cataldo & Keheyan 2006; Cataldo 2007).

The irradiated  $\beta$ -(–)-pinene samples presented a solid phase (a white solid precipitate) and a liquid phase. The solid phase (consisting in poly- $\beta$ -pinene) was recovered by filter paper ‘Rapida A’, washed with methanol and left to dry in a desiccator under reduced pressure. The solid polymer yield was determined gravimetrically. The crude liquid phase was studied polarimetrically, by electronic absorption spectroscopy and by FT-IR spectroscopy.

When the  $\beta$ -pinene irradiation was conducted in a vacuum the yield of solid poly- $\beta$ -pinene resin over the starting monomer was 0.42% by weight at 100 kGy. At 200 kGy the yield reached 1.4% and at 400 kGy was approximately 6.0%  $[\alpha]_D = -48.1$  (toluene  $c = 1.3$ ). Finally, at 943 kGy the yield of solid poly- $\beta$ -pinene was 37.2%  $[\alpha]_D = -50.3$  (toluene  $c = 1.3$ ). The specific optical rotation was measured



**Fig. 6.** FT-IR spectra of various poly- $\beta$ -pinenes. The first spectrum at the top of the figure is from a poly- $\beta$ -pinene obtained by cationic polymerization having a very low residual optical activity. The spectrum is characterized by poorly resolved absorption bands. The other three spectra from top to bottom are from three poly- $\beta$ -pinenes obtained by radiation-induced polymerization at 150, 300 and 600 kGy, respectively. These polymers have an enhanced optical activity in comparison with the starting monomer and show very well defined infrared spectral bands suggesting a very highly ordered structure, which instead is lacking in the case of the polymer prepared by cationic polymerization.

only on the toluene soluble fraction of the poly- $\beta$ -pinene resin.

## Conclusions

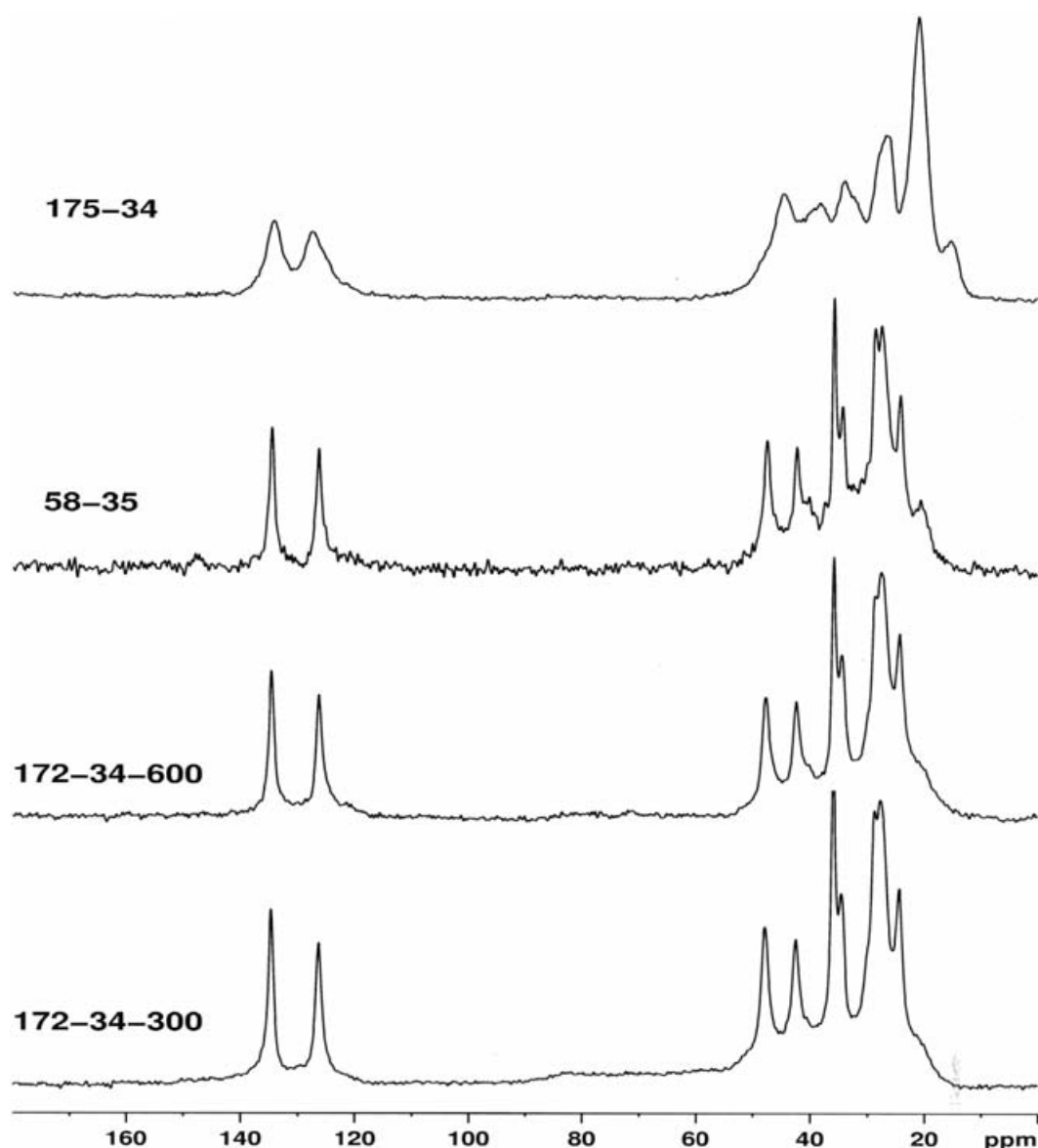
It is still not clear how molecules in chiral excess present in comets and meteorites have been formed by abiotic processes in space. In any case, high-energy radiation under the form of cosmic rays and radionuclide decay plays against the preservation of chirality. Although the cosmic rays cause the complete radiation processing of the surface of comets and meteorites in  $4.6 \times 10^9$  yr, their influence at a depth of 20 m is already negligible. At such depths only the radiation from radionuclide decay is the real player against the preservation of the chiral excess inside comets and meteorites. Draganic *et al.* (1993) have reported that the total radiation dose from radionuclide decay is equivalent to 14 000 kGy in  $4.6 \times 10^9$  yr.

Our studies on the action of radiation on a series of chiral terpenes with a radiation dose of up to 600 kGy have shown that the extent of radoracemization is not so dramatic and that the extrapolation to 14 000 kGy shows

that a significant fraction of the irradiated chiral molecules can survive such a massive dose of radiation. Thus, it is not a surprise that  $\alpha$ -methyl-amino acids have been found in meteorites in chiral excess (Pizzarello & Cronin 2000; Cronin & Pizzarello 2000). All the terpenes we have studied undergo invariably the radoracemization reaction. The unique exception has been represented by  $\beta(-)$ -pinene, which instead of the expected radoracemization reaction undergoes a radiation-induced polymerization, and the resulting poly- $\beta$ -pinene, having a highly ordered supramolecular structure, displays an optical activity which is 1.7 times higher than the starting monomer. Thus, in this specific case, the optical activity is not reduced but enhanced by the action of radiation and remains locked into a polymer which displays a considerable radiation resistance and may act as a chiral template and as a chiral surface for the prebiotic chemistry.

In line with the results of other scientists (Kminek & Bada 2006), it is expected that molecules in enantiomeric excess should be easily searched for and found; for instance, in the Martian subsurface as relicts of an extinct Martian biosphere or in the subsurface of smaller cometary and meteoritical





**Fig. 7.** Solid-state  $C^{13}$ -NMR spectra of poly- $\beta$ -pinenes. The spectrum at the top labelled 175-34 is from the poly- $\beta$ -pinene prepared by cationic polymerization in comparison with a poly- $\beta$ -pinene prepared by free radical polymerization (labelled 58-35) and with two poly- $\beta$ -pinenes obtained by radiation-induced polymerization at 600 and 300 kGy, respectively. The better definition of the NMR signals of the samples prepared with radiation or with a free radical mechanism is again evident. Instead the poly- $\beta$ -pinene produced by cationic mechanism shows less defined NMR bands and very low optical activity.

bodies as traces of the prebiotic chemistry of the early Solar System.

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