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On the correlation between the enantiomeric excess of L-isovaline and the level of aqueous alteration in carbonaceous meteorites

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A positive correlation was observed between the enantiomeric excess (ee) of L-isovaline (L-iVal) and the degree of aqueous alteration (AqA) of carbonaceous meteorites. The origin of this remarkable phenomenon has remained enigmatic from two points of view: First, the correlation is between seemingly unrelated observables−nothing about AqA is of chiral characteristics; and second, following the accepted assumption that circularly polarized light (CPL) was the origin of the observed meteoritic ee of L-amino acids (AAs), it remined unclear why some of the observed levels of the ee of L-iVal in that correlation are significantly higher than those observed in laboratory simulations or those obtained from circular dichroism (CD) g-factor calculations. The current proposition accounting for this picture attributes late AqA conditions of the meteoritic parent bodies as providing the grounds for amplification of early initially CPL-generated low levels of L-ee. For reasons summarized below, this interpretation, which treats the CPL event and the AqA process as occurring in wide-time separated eras, is re-visited. An alternative interpretation of the observed correlation and of the high ee-values, is provided. It focuses on hydrophilic dust-aggregates clouds in wet star-forming regions in early pre-solar times, where both the CPL event and the grounds leading to the later AqA processes of the parent bodies, occurred. This mechanism removes the time separation between the initial ee formation and the AqA of the parent body, and replaces it with parallel processes, providing a scenario to the observation of high ee's without total destruction, and to the apparent AqA/L-ee correlation. Although iVal is at the focus of this report, the steps of the development of the alternative mechanism and the conclusions that arise from it, are relevant and applicable to the general observations of L-ee's of meteoritic AA's.

KEYWORDS

meteorite, isovaline, aqueous alteration, dust, enantioselectivity

1 Background

1.1 The correlation

A pre-solar enantioselective event left behind it an enantiomeric excess (ee) of L-amino acids (AA) (Glavin, Burton, et al., 2020; Garcia et al., 2019), of D-sugar acids

(Cooper et al., 2018; Martinez et al., 2022) and of other organic molecules (Pizzarello and Yarnes, 2018; Pizzarello et al., 2010), all to be found billions of years later incorporated within carbonaceous chondrites (**CC**) (Cronin, 1989). The origin of that ee is one of the most enigmatic observations in the natural sciences, in particular because the same types of handedness excesses, characterize the biosphere of our planet, pointing to the possible role of meteorites in pushing ee-fluctuations in the pre-biotic era, into the evolutionary handedness preference of life on Earth. The intensive research in this field has led to various observations, and one of these which is particularly intriguing, is the observation of Glavin and Dworkin (Glavin and Dworkin, 2009) of a correlation between the level of ee of L-isovaline (L-iVal)–a common L-ee meteoritic AA (Burton and Berger, 2018)–and the level of aqueous alteration (AqA) of minerals that compose a range of CCs. It is a puzzling observation: Why should these seemingly unrelated meteoritic properties display a correlation? Why or how should an AqA process affect or contribute to an enhanced ee, when such processes have no inherent chirality in them? That L-iVal-ee/AqA correlation is a key observation because any suggested feasible scenario which links these two parameters, should be compatible with other related observations of the ee of organic molecules in CC meteorites, and should shed light on mechanisms that have led to ee's of various organic components of CCs. This report proposes a new interpretation for the processes that had led to that correlation, and it addresses some of the difficulties in the currently proposed interpretations.

Let us first mention some of the relevant background of the finding of the L-iVal-ee/AqA correlation: In a pioneering study in the 80's, Cronin reported on a correlation between the total amount of 10 AAs in five CM chondrites (including Murchison) and the level of AqA [Fig. 1 in Cronin, 1989]. Then, Pizzarello (Pizzarello et al., 2003) analyzed samples of the Murchison meteorite, obtained from various collections and from various locations within the same sample and found [Fig. 5 in (Pizzarello et al., 2003)] a rough linear correlation between the amount of iVal and the degree of AqA. The relatively high L-ee values were observed in that study (up to 15%), led Pizzarello to suggest that initial lower ee values obtained by the enantioselective destructive action of circularly polarized light (CPL), were amplified by the water altered properties of the minerals of the parent bodies. Such assumption of amplification seemed to be needed because both calculated and experimental ee values of AAs are much smaller, even at high levels of CPL-induced destruction (Meierhenrich, 2008). However, an attempt in that study to correlate the L-ee with the total amount of iVal (and therefore, indirectly, also with the degree of AqA through Cronin's correlation) showed "only partial correlation" between the two variables.

Six years later, Glavin and Dworkin proved such a correlation to exist (Glavin and Dworkin, 2009): They showed a correlation between the L-ee of iVal in Murchison and 5 other CC meteorites and their level of AqA. The correlation, which is rough but quite clear, was confirmed in later studies (Glavin et al., 2011; Martins et al., 2015; Burton and Berger, 2018; Glavin, McLain et al., 2020), covering a range of different CCs, such as CH, CB, CI, CM, CR, C2 chondrites (Burton et al., 2013), summarized also in (Elsila et al., 2016; Burton and Berger, 2018; Chan et al., 2023), and more. In fact, parent AqA was considered as an active parameter, contributing to the profiles of not only iVal but of other organic components as well, including the possible precursors of iVal (Herd et al., 2011; Glavin et al., 2012; Simkus et al., 2019).

1.2 The current interpretations of the correlation

1.2.1 The assumption that aqueous-alteration of the parent body affected an ee-amplification

The main current interpretation of the observed correlation follows the above mentioned Pizzarello interpretation, namely, that an initially CPL-induced small ee of L-iVal was amplified by an aqueous process, which is also reflected by the AqA level of the parent bodies of the CCs (Bailey et al., 1998; Glavin, Burton et al., 2020); that is, the more pronounced the AqA is, the higher ee is obtained. The prevailing assumption is that the initial CPL-inducing ee process, and the amplification and are separate events in time, perhaps even by millions of years. The focus on the AqA of the parent bodies has also highlighted the need to have liquid (or liquid-like) water, and we return to this key issue below. Chemistry provides a wealth of processes under aqueous conditions which can enrich a small ee with one of the enantiomers (Sallembien et al., 2022), some of which have been proposed to occur in the parent bodies. These propositions included Viedma-type crystallization ee-shifts (Iggland et al., 2011; Blackmond, 2011; Koga et al., 2021), autocatalytic reactions such as the Soai reaction (Kawasaki et al., 2009; Blackmond, 2020) and Frank's classical model (Frank, 1953), spontaneous enantiomorphs symmetry breaking upon crystallization [such as Kondepudi's experiments with sodium chlorate (Kondepudi et al., 1990)], and other spontaneous deracemizations [see (Buhse et al., 2020; Sang and Liu, 2019) for reviews]. These proposed mechanisms require specific optimally-tailored conditions, such as the need for supersaturated solutions, pure solvents, absence of co-solutes, optimal temperatures, and therefore it seems that these propositions are not general enough to explain the observed diverse meteoritic molecules with appreciable ee values spanning over various AAs, sugar acids and more. Note also the special conditions which are needed for autocatalytic reactions, tailored for each specific case (Hanopolskyi et al., 2020; Vinogradoff et al., 2024); the idea of a family of autocatalytic reactions responsible for all of the observed meteoritic ee's, is still waiting to be realized in synthetic chemistry (Cintas and Viedama, 2012).

Below we propose some additional amplification scenarios that seem to have a broader molecular scope, and we also propose that the CPL event and the (more general) amplification process, took place close in time, at the early pre-solar dust clouds era. But next let us review difficulties with the current leading assumption that the initial ee was produced by a CPL event, and then explain why we stick with it anyway.

1.2.2 The assumption of CPL as the enantioselective process

Enantioselective CPL decomposition of AAs under laboratory conditions is well documented (Meierhenrich, 2008; Garcia et al., 2019). Regarding the ability of CPL to decompose iVal enantioselectively, Takahashi et al. (2009) reported the induction of ee in thin films–100 nm–of racemic iVal (and two additional AAs–alanine and phenylalanine) by CPL irradiation at a wavelength λ = 216 nm. CD analysis indicated that R-CPL produced an L-iVal ee and L-CPL produced an excess of D-iVal, [Fig.'s 11, 12 in (Takahashi et al., 2009)]. The actual ee values were not calculated in that study, but in a recent detailed study by Bocková et al. (2023) an L-ee of 2% was reported to be induced in thin films of racemic iVal by R-CPL at 192 nm, namely, the same relation between the handedness of the CPL and the resulting ee, as observed by Takahashi.

Yet the CPL interpretation as the source of the universal handedness-ee's of various meteoritic organic molecules in general, is not free from difficulties: The first difficulty is that it is still unclear what was the actual electromagnetic wavelength range of the CPL and what was its specific circular handedness, which can explain the observation that whenever an ee is observed in meteoritic AA it is always L-ee (Glavin, Burton et al., 2020), that in sugar acids it is D-ee (Cooper and Rios, 2016; Cooper et al., 2018), that lactic acid was found with L-ee (Pizzarello et al., 2010), that the possible hydrolytic products of propylene oxide identified in Murchison are of R-ee (Pizzarello and Yarnes, 2018), and more. Returning to iVal, the complexity of the situation is evident from the analyses of its CD spectra: iVal has *opposite* CD spectral signs compared to other AAs in the solid state at the 140–190 nm range (Fig. 1 in (Meierhenrich et al., 2010), and in the 170–220 nm range in the gas phase [Fig. 2 in (Meinert et al., 2022)]. This may imply therefore that D-iVal should have been prevalent in meteorites along with the L-ee of the other meteoritic AAs. Similarly, based on gas-phase CD arguments, Cerf and Jorrisen (Cerf and Jorrisen, 2000) raised the point that tryptophan and proline should have been produced with a D-ee by that universal CPL burst which resulted in L-ee of the other observed meteoritic AAs (Jorissen and Cerf, 2002). Based on the gas phase CD analysis of propylene oxide and based on the observations of Pizzarello and Yarnes (2018) of the R-ee of hydrolytic products of that molecule, Garcia et al. (2022) suggested that L-CPL is the best candidate for the early cosmic CPL event. This, however, is opposite to the experimental observations for photolysis of iVal—R-CPL which led to L-ee of iVal—and to the prediction for iVal based on both gas phase and solid-state CD observations cited above. An interesting computational solution to this iVal enigmatic issue was proposed recently by Shoji et al. (2023), namely, that the L-ee excess of AAs has already been introduced photochemically at the at the amino-nitril precursors stage of the Strecker reaction by their enantioselective destruction with R-CPL irradiation with Lyman α photons (10.2 eV, 122 nm); under these conditions, the prediction is that the AAs—including iVal–will form with an L-ee.

The second difficulty relates to the possible source of the CPL. Although the potentially most relevant range of wavelengths is where photochemistry occurs, namely, form the far UV to the edges of the visible range (Oberg, 2016), CPL in that range has not been observed directly in dust-dense star forming regions due to the opaqueness of these clouds to that electromagnetic range (Bailey, 2001). Most of the UV propositions rely on the galactic IR-CPL observations (Bailey et al., 1998; Kwon et al., 2014), assuming that the mechanism which induces CPL in the IR, applies also for the photochemically relevant, dust obscured, UV range. That mechanism is not trivial: The current leading proposition involves scattering of light from a cloud of magnetically-aligned dust particles (Lucas et al., 2005; Hough et al., 2001; Fukushima et al., 2020). On one hand, it has been an appealing assumption, because that scattering mechanism was shown to induce high level of circular polarization, and because it uses common star-emitting UV sources within star-formation nebulae. However, on the other hand, the mechanism by which the needed alignment of the dust particles of the CPL-producing cloud is obtained, raises some questions: The most straight-forwards assumption, namely, that ferrimagnetic components in dusts particles such a magnetite, are responsible for that alignment, has indeed been put forwards (Shapiro, 1975), mainly because magnetite is found in CCs, but the accepted view is that this magnetite has formed in the parent bodies by AqA from metallic iron, and was not a component of pre-solar dusts (Pilchin, 2010). In fact, magnetite is not common in interstellar dust (Psaradaki et al., 2023), and magnetic alignment of dust particles which are diamagnetic–such as the silicates (Bowey and Adamson, 2002)–is not trivial to explain (Draine, 2001; Andersson et al., 2015). Mechanisms explaining the possibility of that scenario, such as based on radiative alignment torque, have been proposed (Andersson et al., 2015; Tram and Hoang, 2022), but the search for paramagnetic components as the relevant interpretation is still on-going (Roy et al., 2022). Furthermore, accepting that proposed mechanism of induction of circular polarization creates the following non-trivial condition: A specific mutual orientation of the three celestial components is needed for that CPL to form and then to hit the AA-bearing target–the UV emitting star, the scattering cloud and the CPL-receiving target. That specific mutual orientation also dictates the duration of the CPL-exposure event, and the handedness of the CPL experienced by the target (Bailey et al., 1998). In the context of using ee as an indicator for extraterrestrial life (Avnir, 2021), that would mean that galaxy-wide, no preferential handedness is expected for observed life, that is, life characterized by D-AAs and L-sugars, is equally expected.

The third difficulty–the need for an amplification process of initial low CPL-induced ee–was mentioned above in the context of the iVal correlation, but has a broader scope: Very high meteoritic ee values were observed for many organic molecules, examples being the 50% L-ee of isoleucine (Pizzarello et al., 2012), the 40%–80% D-ee of several sugar acids (Cooper and Rios, 2016), and many more, defying Kagan-type g-factor CPL ee-calculations (Balavoine et al., 1974), predicting much lowers ee values, and laboratory experiments that confirmed it (Meierhenrich, 2008).

2 A proposed mechanism for the title correlation, with some generalizations

2.1 We still adopt the CPL interpretation despite its difficulties

Despite these difficulties with the CPL interpretation, we proceed with it. This is so, because CPL still seems to be the current best enantioselective relevant process, which fulfills the following needed wish list, giving us:

- a general (photo)chemical process capable of affecting a non-zero ee of a wide variety of organic molecules;
- a feasible electromagnetic illuminating source of high enough flux and of wide-enough dimensions;
- a feasible mechanism which circularly-polarizes that irradiation creating the needed enantioselective driver;
- a mechanism which is on a limited-time scale to preserve the achieved ee's (Bailey, 2001).

Staying with CPL in the proposed mechanism, is also relevant in addressing the following questions:

- What irradiation configuration can provide wide-scope high L-ee values on one hand, and still leave appreciable amount of undestroyed AA on the other hand?
- Can a CPL-based mechanism be linked to the observed AqA of the parent bodies?

2.2 The element of the wide diversity and heterogeneity of meteorites

One of the main leads for the proposed mechanism is based on the observed wide variability and heterogeneity of meteorites. A manifestation of that wide heterogeneity can be found in the detailed CC classifications into nine types, each of which is further sub-divided into at least 6 sub-types (Kerridge and Matthews, 1988). Even within each subclass of the CCs, heterogeneity in the lithic components and in the profiles of organic components varies: Compare, for instance, the AAs characteristics of the two CM2 CCs, Aguas Zarcas and Murchison (Koga and Naraoka, 2017; Glavin et al., 2021): The two meteorites "agree" on the consistent excess of the L-AAs, but significantly differ in the ee values. The heterogeneity of meteorites does not stop here–it appears also *within* the same meteorite, as shown in Pizzarello's study of various samples of Murchison, revealing wide distribution in the amount of iVal, in the degree of AqA, and in the L-ee of iV (zero to 15%) (Pizzarello et al., 2003).

The main source of that pronounced diversity and heterogeneity of meteorites in general and CCs in particular, reflects the different histories of formation of their parent bodies from the various types of virgin dust clouds which occupied the dense star-formation zones (Elsila et al., 2016). These different histories of formation resulted from the characteristic profiles of the dust particle components, namely, the minerals, the carbon materials, the ice-mantle compositions, the load of larger organics, and the resulting hydrophobicity/hydrophilicity balance. The characteristics of these various dust clouds was affected also by their post-formation history, which may include transient exposure to irradiations, to temperature variations, to various molecular clouds, all occurring as the pre-solar assembly passes through these diverse environments (Sandford et al., 2020). Thorough mixing of such clouds is an incomplete, complex and lengthy process (Kamp et al., 2023), and the heterogeneity of the pre-solar nebula (Thiemens, 1988) is the result of that incomplete homogenization of the primary pre-solar clouds. The end products of this incomplete process are the various parent bodies, each of which has the composition which reflects the specific cluster of few clouds which contributed most to its formation.

The title question translates therefore into – *what history of formation can be proposed, that is compatible with the discusses correlation?*

2.3 Looking at earlier dusty times

The current assumption has been that the CPL production of a small ee, and its amplification into the currently observed meteoritic values by parent bodies AqA processes, took place at completely different times. We propose that focusing on processes that took place at early pre-solar system times, provides an alternative picture of events, where the initial CPL-induced ee, its amplification, and the set-up for a future AqA of the parent bodies (unrelated as a cause-and-effect process to the ee amplification), all occurred close in time, on the same celestial object: dust aggregates.

Above we stated that the wide heterogeneity is a key to the proposed mechanism: The fact that L-ee's of AAs are detected in different types of CCs with different amounts of AAs and different levels of L-ee values–even within the same meteorite–makes sense if one adopts the idea that the enantioselective act happened in a specific virgin dust cloud, *before* its partial mixings with various other types of dust clouds into the various parent bodies, took place. That is, we propose that a specific virgin cloud, with characteristics to be spelled out below, provided the necessary components in order to:

- have the needed transparency for the enantioselective photochemistry to take place;
- provide the conditions for attaining a high ee without near total destruction of the AA;
- set-up a scenario that led, later on after the parent bodies formation, to their AqA processes, the ee, but that have led to the observed correlation;

We are ready to ask the next question: *What were the properties of the specific virgin cloud, that are compatible with the iVal ee/AqA correlation, and which was incorporated in various proportions in the various CC meteorites parent bodies?*

2.4 The relevant virgin dust cloud and its dust particles

2.4.1 The cloud and its particles

The fact that the high L-ee was found to be associated with aqueously altered lithic material in the parent bodies, suggests that the relevant dust cloud–later on to be mixed with other dust clouds, some with AA's as well–was composed mainly of highly hydrophilic mineral particles (Rubin and Ma, 2017; Hazen and

Morrison, 2020; Morrison and Hazen, 2020). This hydrophilicity allows not only for an early-on AqA of the dust particles themselves (Bischoff, 1998), but also for forming the zones within the parent bodies capable of adsorbing water and promoting the later-stage AqA processes observed there. In other words, the proposed mechanism splits the high L-ee observation from the AqA of the parent bodies.

Thus, in what follows we focus on dust-particles which are composed of hydrophilic minerals, mainly the ubiquitous silicates (Draine, 2002), which later on form the hydrophilic components of most CCs. The relevance of silicates is for a number of reasons: They are very good adsorbers of water (Liu et al., 2018), of small molecular building blocks (as, for instance, for the AA Strecker reaction components) and of larger ones such as, for instance, ready-made AAs (Sebben and Pendleton, 2015) formed in the gas phase, and they are good seeds for icy mantle formation. In addition, silicate materials allow efficient photochemical reactions to take place on their surfaces (Avnir et al., 1978; Slama-Schwok et al., 1992), or within their icy mantels (de Marcellus et al., 2011); and, as just mentioned, they are highly prone to further AqA by water adsorption (Nguyen and Zinner, 2004). The silicates in the dust particles, come mainly from the rich groups of pyroxenes (mostly of various $(Mg,Fe)Si_2O_6$ compositions), and of olivines [of various $(Mg,Fe)_2SiO_4$ compositions, such as forsterite (Mg_2SiO_4)], in both their initially glassy/amorphous state and in their phase-transitioned crystalline form (Molster et al., 2002; Okamoto and Ida, 2022). The surfaces of these silicates are highly hydrophilic mainly due to the interfacial silanol moieties (SiOH) (Rimola et al., 2013), and to other hydroxylated moieties, such as MgOH (on forsterite surface).

The prevailing picture of these particles is of core-shell morphology, where the core is a low-porosity lithic core and the shell is a thick icy coating of hundreds and thousands of layers. Yet, an alternative picture of these mineral-ice particles has been advanced recently by Potapov et al. (Potapov et al., 2020; Potapov et al., 2021; Potapov and McCoustra, 2021). This refined picture has two main components: The first one is that a more realistic structure of the primary lithic aggregates is that of high surface area, high open porosity, ballistic particle-cluster derived aggregates, perhaps with scale-invariant (fractal) structure (Ossenkopf, 1993; Avnir et al., 1985; Rozanski et al., 1986; Pines et al., 1988; Avnir, 1989; Schmidt et al., 1989). The second component of that picture is that the highly convoluted geometry of such aggregates leads to heterogeneity in adsorption capabilities (Jaroniec et al., 1990), blurring the strict core-shell structure into a mix of exposed surfaces patches and narrow pores, covered with only partially with one or few icy monolayers. Our own experience the surface science of silica-based materials [for instance (Rojanski et al., 1986; Samuel et al., 1992)], generally agrees and supports Potapov's picture, and we adopt it in what follows.

2.4.2 The role of water

The hydrophilicity of the dust particles at our focus is already enough for serving our proposed mechanism, but the possibility for even further enhancement of the hydrophilicity exists, and has added value for setting the grounds for the later periods of AqA of the parent bodies, triggered by high amounts of water incorporation. Such desired maximal hydrophilicity is reached if the cloud has a history of passing through water-rich zones in the star forming regions (Facchini et al., 2024), not far from a snow line, rendering a possibility of some of the ice to be in one of the several forms of liquid water (see below), a phenomenon already observed for various celestial bodies (Suttle et al., 2020). The effect of water rich environments in enhancing the inherent hydrophilicity of the silicates is due to a variety of serpentinization reactions, which are common AqA process. For instance, the serpentinization of the olivine forsterite to chrysolite (mineral which are found in many CCs, including Murchison) is:

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2.$$

Note that this reaction introduces a very dense layer of silanols, Si-OH, at the interface of the chrysolite (Sprynskyy et al., 2011), of the order of 5 silanols/nm^2 (de Farias and Airoldi, 2011; Rimola et al., 2013), leading to high hydrophilicity the value of which is between that of water and methanol (Avnir et al., 1984). Many other serpentinized silicates and phyllosilicates are found in CCs as well [see listings in these reviews (Rubin and Ma, 2017; Henning, 2010; Norton and Chitwood, 2008)] such as cronstedtite, $Fe^{2+}{}_2Fe^{3+}[(Si, Fe^{3+})_2O_5]$ $(OH)_4$, and antigorite, $(Mg, Fe^{2+})_3Si_2O_5(OH)_4$. The latter is a common component of fine-grained meteorites (Pizzarello et al., 2003)–such fine graining increases the effective porosity (Corrigan et al., 1997) for organics loading, and increases the surface area available for interfacial reactions. There are other families of AqA minerals which are found along with the silicates in dust composites, such as the heavily hydroxylated sulfide tochilinite $[Fe^{2+}{}_{5-6}(Mg, Fe^{2+})_5S_6(OH)_{10}]$ (Metzler et al., 1992; Le Guillou and Brearley 2014), and these only add to the pronounced hydrophilicity of the dust particles at our focus. Indeed, there has been plenty of accumulated evidence for some degree of pre-accretion water alteration of dust minerals (Bischoff, 1998; Metzler et al., 1992; Whittet et al., 1997), including evidence of pre-accretion serpentinization (Tomeoka, 1991; Bischoff, 1998).

Such serpentinization processes are much more efficient in liquid water then in ice, but these are not the only to be affected: If ee-amplification processes are indeed to take part in the observed ee-values, then these either must have liquid water to take place at all, or at least must have it in order to be more efficient; frozen within ice limits reactive diffusional processes. Liquid water can be associated with the dust particles in a number of ways: In the form of quasi-liquid layers [known as qll (Kimura et al., 2020; Zeng and Li, 2019)] on the ice surface; at the ice-silicate interface; and as disorderly entrapped within narrow pores where the freezing point drops with pore radius (Schreiber et al., 2001). All of these options provide liquid or liquid-like behavior of water molecules at sub-freezing temperatures. It is the third option which is perhaps the most relevant for our purpose, as it allows the freezing point of water to go down as low as 100 K (van Miltenburg and van der Eerden, 1993) rendering ee-amplification reactions which need solution conditions, feasible. And indeed, what further points to the possibility that a water-rich, perhaps liquid phase period was part of the relevant history, is the very fact that we deal with AAs, and water-rich environments are compatible with the view that the formation of molecules, larger than bi- or tri-atomic (such as the AAs), took place in water rich interstellar molecular clouds (McClure et al., 2023).

We move now to the photochemistry that took place on these early dust particles.

2.5 The enantioselective photochemistry

2.5.1 Enantioselective photo-destruction

Of the two possibilities of CPL-induced enantioselective organic chemistry–destructive or synthetic–the first seems to be preferable (Bonner and Rubenstein, 1987; Shoji et al., 2023). This is so because photo-destruction is by far less-demanding than photosynthesis from the point of view of the chemical reaction mechanisms involved: Photo-destruction needs molecular electromagnetic absorption–a quite general molecular feature–leading to an excited or ionized state, from which a variety of spontaneous degradation processes follow (usually after intersystem crossing to the triplet state). Given the right wavelengths range, this is general for any organic molecule, be it an AA, a sugar derivative, a hydroxy acid, etc. Furthermore, photo-excitations into spontaneous decomposing states usually have low activation energies and are mainly non-thermal. Synthesis, on the other hand, is by far more molecule-specific and a multi-step process, with some steps needing higher temperatures and others delicately tailored reaction conditions. For instance, one of the proposed mechanisms for an interstellar formation of iVal involves specifically the chiral precursor 5-ethyl-5-methylhydantoin (Da Pieve et al., 2014), which is not relevant to organic molecules which are not AAs and which display a meteoritic ee, such as sugar acids. The main disadvantage of destructive enantioselective photochemistry is that the differences of this process between the two enantiomers is usually low, leading to massive destruction of both enantiomers in the process. Calculations and experiments suggest (Bailey, 2001) that reaching ee values as high as 15% would mean a heavy destruction of iVal. We need therefore *a mechanism that preserves appreciable amounts of the AA while inducing a relatively high ee*.

2.5.2 The location and duration of the CPL-induced enantiomer enrichment process

Next question to comment on is, where did the CPL event take place and how did the ee-enriched AA got associated with the hydrophilic lithic components? Again, there are two main options: The first is of CPL-induced enrichment that took place in the gas-phase on racemically synthesized AAs, followed by adsorption of the ee-enriched AAs onto the dust particles. The second option is that the CPL event took place with pre-existing AAs already on the dust, ice-coated particles (regardless of whether the AAs got there from the gas-phase, or were synthesized on the dust particles). The on-dust CPL photochemical process is the more accepted one and we proceed with it.

In our context, the open aggregate/thin coating model described above, seems to be more relevant for the photochemistry that took place, for the following reasons:

- The exposed surface area for the CPL irradiation of such a tumbling loose aggregate is by far larger than that of a compact spheroidal lithic core-ice shell particle.
- The transparency of a thick mantle which contains a zoo of organic molecules is low, if not opaque, diminishing the probability of efficient photochemistry to take place. The open aggregates offer better exposure.
- Photoprocesses inside a confined environment such as entrapment within solid ice cage, will blur the enantioselection by CPL: After the photodecomposition occurs, the enantioselective history is erased in the decomposed fragments. Now, in a closed confined cage, the probability of a reverse reaction of the fragments, reassembling into the original molecule, are higher than in an open system, and that re-assembly will reproduce the racemic situation.
- Let us also link this section to the discussion of the possible needed role of liquid water: The spell of temperatures higher than those of interstellar voids, requires the cloud to pass close to the irradiating star and to the CPL-converting aligned cloud, perhaps not far away from the snow line. Such near-by pass is also beneficial from the point of view of the CPL enantioselective event, by increasing the photons flux.

We now zoom out from the specific dust particles to the clouds from which they are composed. The relevant CPL photochemistry of the AAs must have taken place on the exposed outer rims of the AA-bearing cloud (Öberg, 2016), while the inside AAs remain protected from that irradiation by the shadows casted by the outer rim. That is, the collection of all dust particles at the outer reaches of the cloud are responsible for the high L-ee component of iVal, which was later on found in the parent bodies, at the cost of high level of total destruction. This level of destruction was however compensated by the dust components in the inner parts of the cloud which remained protected. More accurately, the irradiation of the cloud most probably created a cloud-penetrating profile of decreasing L-ee and increasing concentration of undestroyed AA. It is that concentration-gradient cloud which answers the dual need–a reservoir of dust particles carrying the high L-ee, and a reservoir of dust particles carrying undestroyed AAs, to be mixed later on into the parent bodies.

Above we mentioned the need for a specific alignment between the light emitting star, the CPL producing cloud and the target cloud. If we accept that the chance of such an alignment is realistic, then another needed aspect of that alignment follows, and that is that the perfect alignment had a window of time just right to achieve the high L-ee values, (Bailey, 2001). Another feature to be considered is that as the L/D ratio goes up during that time window, the rate of further destruction of the D enantiomer is decreasing (if not counterbalanced by the slower diffusional replenishment from deeper parts of the aggregate or the cloud, to which we return below in the discussion of possible amplification mechanisms). This sets the grounds for a steady state L-ee$_{max}$/D which can be achieved, where the higher photosensitivity/lower concentration of D is compensated by the lower photosensitivity/higher concentration of L.

2.6 The high ee values—alternative mechanisms

The concept that post-CPL irradiation ee-amplification processes are needed in order to explain the observed high meteoritic ee values of AAs and other organic molecules, was detailed in the previous sections. One "trivial" possibility is that, in fact, an amplification is not needed, and that the laboratory experiments and the g-parameter calculations are not copying accurately enough the CPL conditions that produced the meteoritic ee's. Just for the record, a brief list of parameters that are perhaps wroth a second look are: The relevant wavelength [the very short vacuum UV range (138 nm) was proposed as leading to higher ee's compared to the UV-Vis range (Da Pieve et al, 2014)]; the assumption that the Beer-Lambert law is retained throughout the irradiation (experimentally this is not the case–high concentrations, absorption by other components in the complex mixture, vertical concentration gradients in thin films—affect that assumption and the time-evolution calculations); the degree of the ellipticity of the CPL (Bonner and Bean, 2000) (there is an appreciable dependence of the g-factor on that property and on the incident angle (Chen et al., 2020); the temperature dependence of the g-factor (Konarev et al., 2016); and the effective pH (Nishino et al., 2002; Moore et al., 2023) (in porous materials, the thermodynamic meaning of pH collapses, and nominal pH values reach exceedingly extreme values—see (Frenkel-Mullerad and Avnir, 2005) for explanation of this phenomenon).

But as all of these still may leave us with the need for an amplification step, let us go back to that aspect of the mechanism. As summarized in the Introduction, the specific currently suggested amplification processes are not general enough to be relevant for the diversity of organic molecules found in meteorites with a measurable ee; and they assume that the CPL event and the amplification were detached processes, the latter of which operated only after the parent bodies formed. Here we offer some mechanisms which have a wider scope in chemistry, and which could *take place as part of the CPL event*, at the early dust aggregates stage, not needing to wait for parent body formation.

2.6.1 The SDE mechanism

Autocatalysis of an initial fluctuating small ee's into large ee, has been the focus of propositions to explain the emergence of homochirality on Earth and of meteoritic ee, and these have been already listed in Section 1.2.1, and commented on there. The catalytic growth of initial ee fluctuations involve, for instance, crystals (Viedma mechanism) or dissolved species in solution (Soai reaction, Frank reaction networks and more), and the main difficulty with so far proposed autocatalytic mechanisms is that they require highly specific tailored conditions. There is a related autocatalytic process, based on adsorption, which does seem to carry more general features, and which is based on *adsorption-driven* enhancement of an initial ee fluctuation. It is known as SDE (self-disproportionation of enantiomers (Han et al., 2021), which is the following: The usual observation is that when a racemate is exposed to an *achiral* adsorptive material, say on silica, reversible adsorption occurs, which leads to a 1:1 ratio of the enantiomers on the surface. However, normal fluctuations of this process create a situation that the coverage is never with an exact 1:1 enantiomers ratio, but there is a slight excess of one of the enantiomers on the surface. That changes the nature of the surface to be partially coated with a slight enantiomeric excess of one of the enantiomers. The SDE phenomenon is that a positive feed-back loop begins to operate: The partially chiral surface prefers more of its own handedness in the adsorption equilibrium process, and a clear surface/liquid deracemization is obtained. This phenomenon is also well documented for amino acids (Han et al., 2019). Now, if the liquid phase is *a priori* enriched with one of the enantiomers and then exposed to the adsorbing material, then the SDE phenomenon will form an enriched adsorbed layer with that enantiomer. The relevance for us is the following: The CPL photochemistry is more effective at the outer accessible portions of the open porous aggregate, creating there an excess of L-ee. If liquid-like conditions, described above, exist, then equilibration with inner protected parts of the aggregate takes place, and an SDE mechanism will form, creating an adsorbed, protected layer, enriched with the L enantiomer. The outer exposed reaches of the aggregate which are now again racemic, undergoing again that cycle, creating more L excess, which again is protected by adsorption in the inner parts, and so on.

2.6.2 The photodesorption mechanism

Mortaheb et al. (2019) demonstrated enantioselective CPL-triggered *desorption* [of (R)- and (S)-BINOL (1,1′-bi-2-naphthol)] from achiral optical borosilicate glass. In our context we recall that photodesorption from interstellar dust particles is one of the most elementary processes that coated dust particles undergo (Bertin et al., 2023; Öberg et al., 2009). Now, if a desorption process of AA molecules from the surface of the dust particles, is affected by the same CPL event that decomposes more efficiently the D-AA (thus enriching L), then the D-enantiomer will also be better desorbed, thus further enriching the L-AA. This better D desorption is envisaged, because more efficient energy absorption of that enantiomer means both more efficient decomposition *and* more efficient thermal desorption.

2.6.3 The molecular environmental effects

Shimizu made a particularly interesting photocatalytic reaction observation (Shimizu, 1999): They first found that CPL irradiation (at 351 nm) induced enantioselective enrichment in methionine and threonine, but not in proline. But then they found that enantioselective enrichment did happen for that proline, when mixed with L-valine (which was also enantioselectivity affected); that is, the L-valine apparently catalyzes the formation of the ee of proline. In our context, we need to recall that the environment of an AA at our focus in the dust aggregates, hosts many other organic molecules, including other racemic AAs. Not only that they may induce catalytic effects of the type observed by Shimizu, but they can undergo enantioselective degradations as well, rendering the environment non-racemic. Enantioselective processes in enantiomorphic environments are more efficient, and that maybe a general contributor for higher ee values, in a positive feed-back (autocatalytic) loop.

3 Summary and outlook

3.1 The build-up of the correlation and its time line

We now summarize proposed mechanism that had led to the title correlation, with a time-line:

Stage 1: The dust clouds: In a dense star-formation zone which contains various virgin molecular and dust clouds, we focus on clouds composed of high-hydrophilicity open-aggregate porous dust particles. These are mainly silicates in their native form and in their further enhanced hydrophilicity by dust aqueous serpentinization processes. These hydrophilic dust clouds set the grounds for efficient adsorption of AA precursors and for their synthesis, or, alternatively, for adsorption of gas-phase synthesized AAs. These clouds also set the grounds for the later AqA processes of the hydrophilic zones within the heterogeneous parent bodies. Water-rich environment is needed for that stage and for some of the next stages.

Stage 2: The enantioselective CPL irradiation: We adopt the currently accepted model, by which CPL irradiation had been the enantioselective event. Its origin is still shrouded in uncertainty, but again we proceed with the frequently cited proposition of a three celestial bodies event: A UV-emitting star which shines light on magnetically aligned cloud dust particles, which re-emits circularly polarized, then hitting our target AA-bearing cloud. A special alignment of the three moving celestial bodies is required for that to happen, and therefore it is a time-transient event. The whole event takes place at a distance from the star, which allows the existence of qll-water. Such vicinity also contributes to the efficiency of the photochemical event.

Stage 3: The photochemistry: The outer rims of that target cloud undergo enantioselective AA destruction leading to a maximal possible ee, accompanied by high level of destruction. A vertical gradient of decreasing ee and increasing undestroyed AA penetrated the cloud. The inner parts of the cloud carry undestroyed AAs, compensating for the high degradation at the exposed layers, and which later on appear in the mixed components of the parent bodies as their highly hydrophilic, aqueous-alteration prone zones.

Stage 4: Parallel amplification: If needed at all, amplification contributes to the apparent ee, by processes that are compatible with the wide range of meteoritic organic molecules displaying clear ee. Examples for such processes include the SDE mechanism, CPL driven enantioselective desorption, and the active participation of other chiral molecules that reside in the dust mantles.

Stage 5: Clouds mixing and formation of the parent bodies: The irradiated cloud undergoes an incomplete mixing process of the gradients formed, resulting in a heterogeneous cloud of zone-patches of high ee, medium ee, low ee and zero ee. Clouds of various compositions in the star forming region begin their combined collapse into the components of the pre-solar disc by a complex, incomplete, mixing and accretion processes. A wide variety of parent bodies and planetesimals form, leading later on to the wide variety of CCs, each of which represents, with its own profile of AAs and their ee's, the specific mixing neighborhood and history of the clouds.

Stage 7: Aqueous alteration of the parent bodies and the correlation: Parent bodies which have a high proportion of the highly hydrophilic cloud on which the CPL event took place (stage 3), also carry higher sensitivity to AqA. Thus, an apparent correlation emerges, which represents different formation histories of the parent bodies: The more of the virgin hydrophilic cloud component in the parent body, the higher will be the detected ee, and the higher will be the apparent AqA.

Stage 8: Billions of years later, a technological life-form emerges, and discovers the apparent correlation between the L-ee of iVal in CC meteorites, and the degree of AqA of their parent bodies.

3.2 Outlook

In conclusion, note that elements of the proposed mechanism are general enough to be possibly applicable for other significant ee observations of AAs and perhaps also for other ee-enriched organic molecules, such as sugar derivatives. These elements include focusing on the very early stages of the solar system formation, irradiation of the outer reaches of a dust cloud carrying racemates, which result in radiation induced high ee's at the rim, while carrying undestroyed in the inner part of the clouds; later-on mixing with other virgin dust clouds to obtain the rich library of heterogeneous parent bodies and their meteorites offspring; approaching apparent correlations with parent body characteristics as actually representing not a cause-and-effect, but parallel histories that had led to the apparent correlation, and more–all may tell the story of other significant ee observations.

The proposed mechanism is general enough to include other feasible enantioselective processes, as long as they involve an external-source process that is capable of interacting with the hydrophilic cloud, as described above. An example for that is the proposed relevant role of low-energy secondary electrons in the extraterrestrial synthesis of organic molecules (Wu et al., 2024). Spin polarization is required for the enantioselective action of such electrons (Rosenberg, 2019; Ozturk and Sasselov, 2022), the feasibility of which has been demonstrated by the seminal pioneering studies of Naaman and his colleagues (Naaman et al., 2022).

Data availability statement

Publicly available datasets were analyzed in this study. This data can be found here: Direct contact to david.avnir@mail.huji.ac.il.

Author contributions

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