

The distribution of chiral asymmetry in meteorites: An investigation using asymmetric autocatalytic chiral sensors

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Abstract

We separated and analyzed several organic and inorganic phases of the carbonaceous chondrite matrix to determine whether they contained any inherent asymmetry. Our intent was to determine any possible *foci* of asymmetry besides the one determined for meteoritic amino acids. As a probe, we employed a very sensitive asymmetric autocatalytic reaction. We were able to determine that asymmetry still resides in powders after extraction with water and solvents as well as in the insoluble organic material (IOM) obtained after demineralization. Asymmetry is not found any longer in the IOM after hydrothermal treatment and in meteorite powders from which all organics had been removed by O₂ plasma at low temperature. The data are interpreted to indicate a diverse molecular asymmetry residing in yet unknown meteorite organics; these organics might have had an inductive effect on organic molecular evolution upon exogenous delivery to the early Earth.

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1. Introduction

Carbonaceous chondrite meteorites offer a unique opportunity to study the a-biotic chemistry of carbon that preceded the onset of terrestrial life. According to molecular and isotopic analyses of the last 30 years, this chemistry was able to produce a large and complex suite of organics that range from insoluble kerogen-like material to small water-soluble compounds, such as amino acids, that are similar, sometimes identical, to biomolecules (see Pizzarello et al., 2006 for a recent review). It has been debated whether these meteorite organics could have participated in the molecular evolution that lead to life's origin upon their delivery to the early Earth. One problem facing this theory is the fact that the organics found in meteorites, as well as those produced via other synthetic models of un-catalyzed prebiotic chemistry, appear to have followed

stochastic rules and formed a random assemblages of abundant and diverse isomeric species. For example, over one hundred amino acids are observed in the Murchison meteorite while terrestrial proteins comprise just twenty. In view of the high structural specificity and strict selectivity of biomolecules, therefore, the challenge in appraising the possible contribution of exogenous organics to the origin of life resides not on their delivery, which was undoubtedly possible (Chyba and Sagan, 1992; Delsemme, 1992), but rather on finding plausible pathways of chemical selection by which they could have fostered molecular evolution (Pizzarello, 2006).

Amidst the general random distribution of meteorite organics, a selected sub-group of soluble compounds extracted from CM2 carbonaceous chondrites, the 2-amino-2-alkylamino acids, have been found to share with biomolecules the unique trait of chiral asymmetry and display enantiomeric excesses (*ee*) of the same configuration as protein amino acids (Cronin and Pizzarello, 1997; Engel and Macko, 1997; Pizzarello and Cronin, 2000; Pizzarello et al., 2003). Chirality is a general property of objects that

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can exist in two forms that are mirror image of each other and cannot be brought into congruence by rotation or translation (Prelog, 1976). Chirality can be best understood by the general term of “handedness” because the hands are a common example of chiral objects and their properties, of being made of the same parts but not superimposable, can be easily visualized (e.g., by considering the failed fit of one’s right hand into a left-hand glove). Chirality is inextricably linked to biochemistry because many carbon molecules are chiral, i.e., contain a carbon that is asymmetric by having four different substituents, and can be present in two forms called enantiomers (the more general term of enantiomorphs is used for inorganic or other two- and three-dimensional chiral forms). Of the two enantiomers, biochemistry chooses monomers of just one handedness, L-amino acids and D-sugars, in the building of polymeric proteins, RNA, DNA. The tertiary structures and function of biopolymers depend on this chiral homogeneity (homochirality) that is, therefore, considered essential to terrestrial life (Cronin and Reisse, 2005).

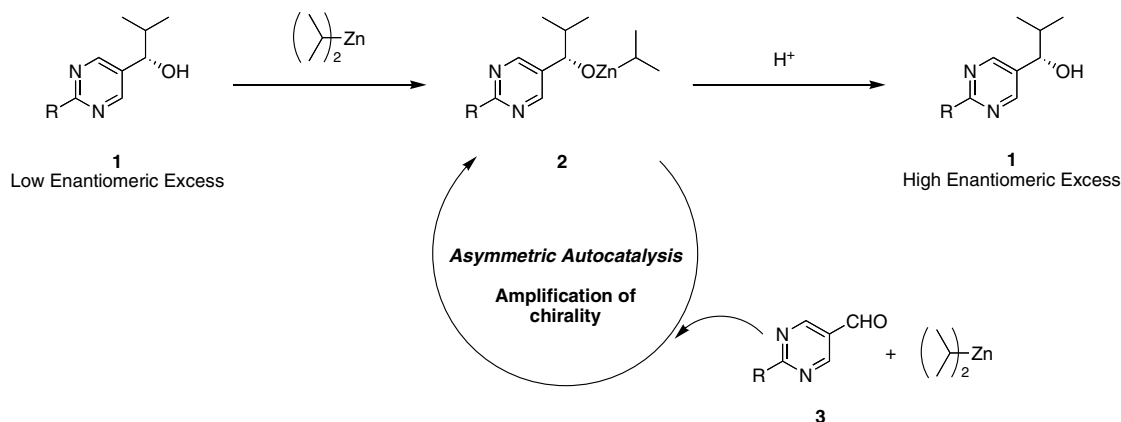
Outside the biosphere, on the other hand, we find several examples of chirality (e.g., in circularly polarized light or crystals such as quartz) but only two cases of molecular asymmetry, they are: (1) the parity-violating energy difference (PVED) between enantiomers of a chiral molecule, and (2) the enantiomeric excesses of CM2 amino acids. PVED is manifested in subatomic interactions of the weak force and entails a small energy difference between enantiomers of a molecule, which is estimated theoretically to be exceedingly low ($\sim 10^{-11}$ J/mol⁻¹, e.g., Quack, 2002) and has not been demonstrated directly (e.g., such difference would fall below the stochastic variations that already trigger the Soai reaction amplification). The *ee* in meteorites, on the other hand, have been extensively studied, may reach values of 15%, and their indigeneity was confirmed by isotopic analyses (Pizzarello et al., 2003; Pizzarello et al., 2004; Pizzarello and Huang, 2005). It is not known how these meteoritic *ee* were produced, however, both their uniqueness in nature and mimicking of a fundamental property of biomolecules are compelling points for a further inquiry on their origin and distribution.

The molecular analyses that lead to meteoritic *ee* discovery, while painstaking and complex, were helped by the chemical characteristic of amino acids. These compounds have two functional groups (the basic amino, $-\text{NH}_2$, and acidic carboxyl, $-\text{COOH}$) along the alkyl chains of their molecules and allow for a larger number of chiral molecules at shorter chain lengths, which are more abundant in meteorites (Pizzarello et al., 2006). The search for other compounds’ asymmetry has been complicated by the fact that any asymmetric carbon bonded to a hydrogen and adjacent to an electron-withdrawing group, such as the oxygen-rich carboxyl of organic acids, rather easily exchanges that hydrogen in water, converting from one configuration to the other. This process, called racemization, will further reduce the number of compounds that would have been able to withstand its effect during the asteroidal parent body aqueous phase and could be candidates for analysis of possible *ee*. In addition, there could be many possible recipients of asymmetry within the complex meteorite matrix and a methodology for their chiral analyses would not be easy to design.

We report here on chiral analyses aimed to by-pass this difficulty. We analyzed several constituent phases, organic as well as inorganic, isolated from the Murchison and Murray meteorites in order to detect any possible asymmetry residing in them besides that revealed for amino acids. We employed an asymmetric autocatalytic reaction, the Soai reaction (Soai et al., 1995; see also Soai et al., 2000; Mislow, 2003; Podlech and Gehring, 2005, for reviews), which is a powerful diagnostic technique capable of revealing chiral imbalances in varied media. This study is expected to identify possible *foci* of asymmetry within the large compositional diversity of CM chondrites and help narrowing the locale(s) for more detailed analyses to follow.

2. Asymmetric autocatalysis for the amplification of chiral imbalances

The concept of asymmetric autocatalysis, a reaction in which a chiral product acts as an asymmetric catalyst for its own production (Soai et al., 1995), is outlined in



Scheme 1. Reaction scheme of asymmetric autocatalysis.

Scheme 1. In this reaction, pyrimidyl alkanol **1** (R = alkyl or alkynyl group) having a small chiral imbalance is involved in the formation of the chiral zinc alkoxide **2**, which catalyses the addition of diisopropylzinc (*i*-Pr₂Zn) to the achiral aldehyde **3** and, because the catalysis is enantioselective, upon hydrolysis of **2** an initial enantiomeric excess of the alkanol will be amplified. The Soai reaction has shown to be able to amplify an even minor (ca. 0.00005%) initial enantiomeric excess of the alkanol to near enantiomeric purity through a few autocatalytic cycles (Sato et al., 2003a,b,c) and represents a good experimental proof of theoretical models (e.g., Frank, 1953) for the amplification of small chiral perturbations of racemic mixtures.

It can also be used as an exceedingly sensitive diagnostic tool to detect asymmetry in a variety of media. In fact, when starting the reaction with an achiral pyrimidine-5-carbaldehyde **3** *only* (i.e., in the absence of pyrimidyl alkanol *ee*), Soai and co-workers have shown that other enantiomeric imbalances can act as chiral triggers (“initiators”) in the autocatalytic reaction to afford pyrimidyl alkanol with very high enantiomeric excess and whose configuration correlates to that of the initiators (Scheme 2).

As it can be seen, these imbalances may reside in organic molecules, e.g., amino acids (Shibata et al., 1998; Soai et al., 2001), crystals, e.g., quartz (Soai et al., 1999) and sodium chlorate (Sato et al., 2000), inorganic structures such as helical silica (Sato et al., 2003a,b,c), circularly polarized light (Kawasaki et al., 2005), and even in the minute statistical fluctuations occurring during chiral syntheses (Soai et al., 2003; Kawasaki et al., 2006). The experimental outline to test the possibility of a similar effect by meteoritic samples is shown in Scheme 3. In these analyses 2-alkynylpyrimidyl-5-carboxaldehyde **3a** was employed because, prior to the analysis of the meteorite powders (see below, Table 1), this reagent had been extensively tested with protein amino acids that could have been the source of false-positive results (Soai et al., unpublished results).

Scheme 3 also shows that with repeat trials in the absence of a chiral initiator, stochastic chiral imbalances at the beginning of the reaction will be amplified to each alkanol product enantiomer about 50% of the time.

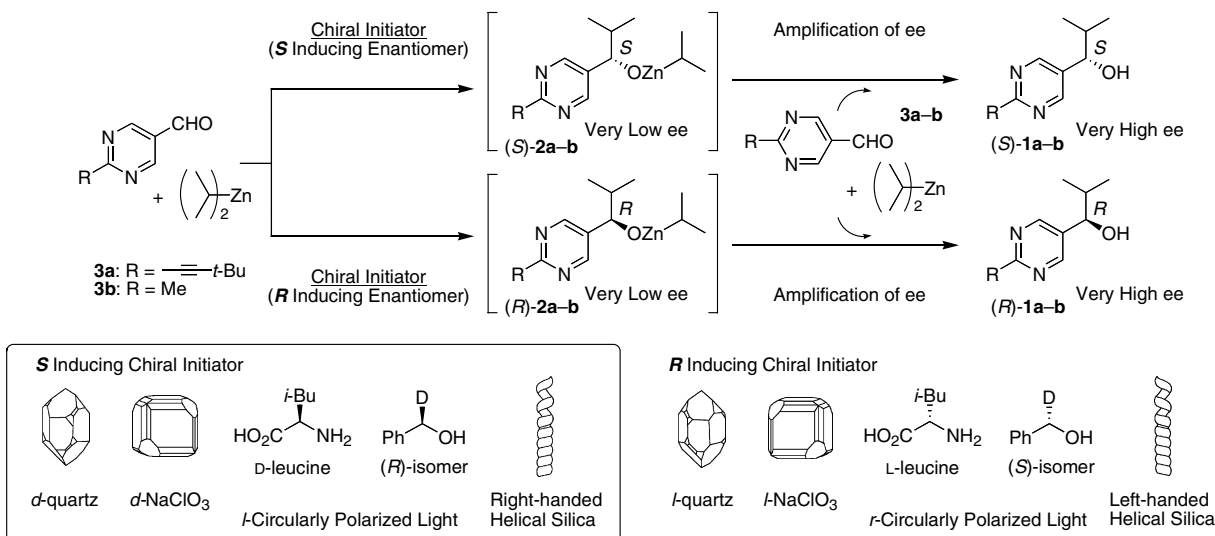
While an account of the complex mechanistic aspects of the Soai reaction is beyond the scope of this manuscript, recent publications (Sato et al., 2001; Sato et al., 2003a,b,c; Blackmond, 2004; Islas et al., 2005) may provide details of the reaction model that is currently envisioned.

3. Analytical methods

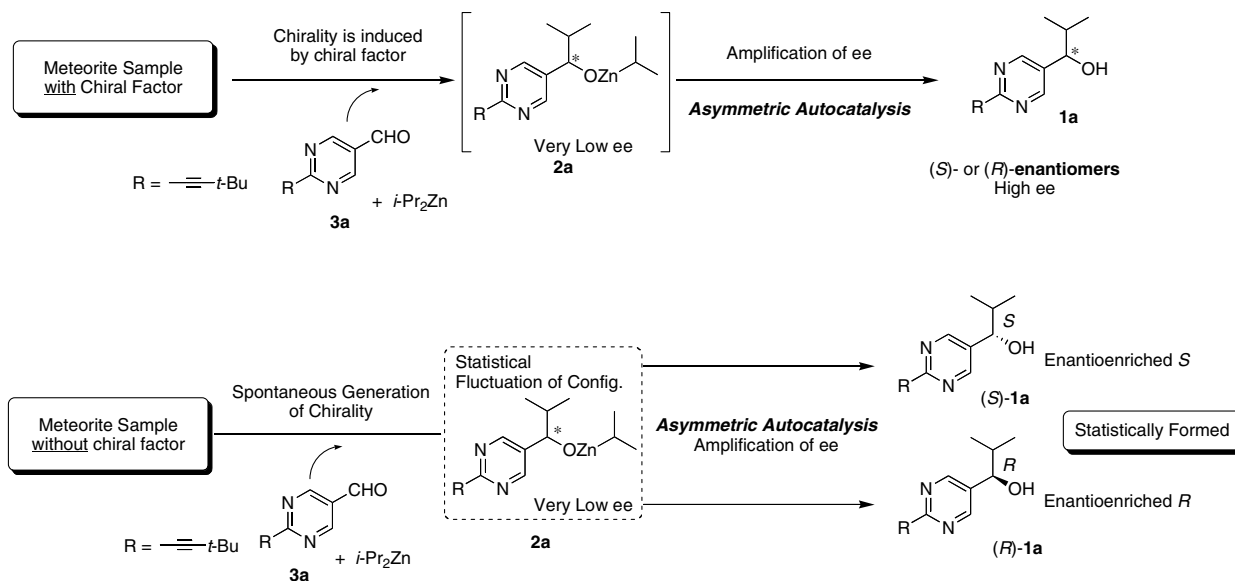
3.1. Meteorite sample preparation

Several samples of meteorites were used in this study, the Murchison (MN) and Murray (MY) powders had been extracted with water and solvents for previous studies (at 100 °C for 24 h; Pizzarello and Huang, 2005 and unpublished results) and kept covered at -10 °C. The Allende (AL) powders (1 g) were similarly extracted for this study.

The MY sample, consisting of 16 g, was further processed for isolation and treatment of the insoluble organic material (IOM). The demineralization procedure has been described before (Cronin et al., 1987), briefly, the powders were washed with a 8 N HF/3 N HCl solution in water, in Teflon containers, at room temperature, for 24 h with stirring, and followed by 6 N HCl rinses. The process was repeated several times until, upon drying, powders showed a stable weight. It was followed by several water rinses and one last methanol rinse. After withdrawing 50 mg of the IOM for NMR spectroscopic analyses (Yabuta et al., 2005) and chiral analyses (Table 3) aliquots (~20 mg) of the material were transferred to previously annealed gold capsules. The capsules were torch-sealed under argon gas and kept at 300 °C and 100 MPa (±5 MPa) for six days (Yabuta et al., 2005). The hydrothermally treated powders were then extracted with water and solvents (DCM/methanol, 9:2 v/v), dried in a



Scheme 2. Asymmetric autocatalysis initiated by chiral substances.



Scheme 3. Asymmetric autocatalysis using meteorite samples.

Table 1
Autocatalytic asymmetric induction by Murchison powders after water and solvent extraction

Entry	Pyrimidyl alkanol 1a		
	yield(%)	ee (%)	Config.
1	94	99	<i>R</i>
2	94	94	<i>R</i>
3	94	77	<i>R</i>
5	95	90	<i>R</i>
6	88	70	<i>R</i>
7	89	97	<i>R</i>
8	96	93	<i>R</i>
9	84	74	<i>R</i>

desiccator, combined for ~60 mg, and again analyzed for a chiral response (**IOM-H**).

MN powders (about 1 g) were exposed to O₂ plasma in a RF Plasma Asher (PC-2000 SBT Plasma Cleaner). In this instrument, the sample-containing chamber is evacuated and filled with O₂ gas to a pressure of 0.2 torr; RF power is then applied to produce oxygen atoms and radicals that effectively react with the organic material to give volatile molecules, H₂O, CO₂, and CO, which are easily pumped away (e.g., Glit, 1968). We employed room *T*, 3-h exposure, and followed the progress of organic material disappearance by scanning electron microscope (SEM) of the powders at time intervals.

3.2. The asymmetric autocatalysis test

For the extracted **MN** and **AL** samples, 50 mg of the meteorite powder were suspended in a toluene (0.5 mL) solution of pyrimidine-5-carbaldehyde **3a** (4.7 mg, 0.025 mmol), and a toluene solution of *i*-Pr₂Zn (0.08 mL, 0.08 mmol, 1.0 M toluene solution) was added dropwise over a period of 30 min. After stirring for 12 h at 0 °C,

toluene (1.0 mL) and a toluene solution of *i*-Pr₂Zn (0.2 mL, 0.2 mmol, 1.0 M toluene solution) was added successively at 0 °C. After stirring for 10 min at 0 °C, aldehyde **3a** (18.8 mg, 0.1 mmol) in toluene (1.0 mL) was added slowly and the mixture was stirred for 3.5 h at 0 °C. Toluene (6.0 mL) and toluene solution of *i*-Pr₂Zn (0.8 mL, 0.8 mmol, 1.0 M toluene solution) were added and the mixture was stirred for 15 min. Then, aldehyde **3a** (75.3 mg, 0.4 mM) in toluene (2.0 mL) was added slowly and the mixture was stirred for 12 h at 0 °C. Once again, after toluene (10.0 mL) and toluene solution of *i*-Pr₂Zn (2.0 mL, 2.0 mmol, 1.0 M toluene solution) were added, aldehyde **3a** (188.2 mg, 1.0 mmol) in toluene (5.0 mL) was added at 0 °C. After the mixture was stirred for 2 h, the reaction was quenched with 1 M hydrochloric acid (5 mL), and neutralized with a saturated sodium hydrogen carbonate solution (15 mL). The mixture was then filtered using Celite, and the filtrate extracted using ethyl acetate three times. The combined organic layers were dried over anhydrous sodium sulfate and evaporated in vacuo. Purification of the residue using silica gel thin layer chromatography (hexane:ethyl acetate = 2:1 v/v) gave the 5-pyrimidyl alkanol **1a**. For the **MN** **IOM** samples, 4 mg of the powder were used and the reactant and solvent amounts for the reaction were scaled accordingly. The enantiomeric excess was determined using HPLC with a chiral stationary phase (Chiralcel OD-H column, 4.6 × 250 mm, eluent: 5% of 2-propanol in hexane, flow rate 1.0 mL min⁻¹, 254 nm UV detector, retention time 11.6 min for (*S*)-**1a**, 17.9 min for (*R*)-**1a**).

3.3. Material

The water and all solvents used in the extractions of the bulk and **IOM** meteorite powders were triple and double distilled, respectively. The HCl used in the meteorite

demineralization was also double distilled while the HF was purchased from Aldrich (48 wt% in water, double distilled, PPB Teflon grade).

4. Results

The results of asymmetric autocatalysis in the presence of MN powders, washed previously with water and solvents, are summarized in Table 1. In entry 1, (*R*)-5-pyrimidyl alkanol with 99% enantiomeric excess was obtained in 94% yield. In the additional eight examinations, reproducible results were obtained, that is, (*R*)-5-pyrimidyl alkanols with high enantiomeric excess were isolated in all cases. This statistically valid one-enantiomer selection suggests the presence of some chiralities in the Murchison meteorite other than the water and solvent extractable compounds.

Results from asymmetric autocatalyses conducted in the presence of AL powders, also previously washed with water and solvent, are summarized in Table 2. As for the Murchison meteorite, an induction of (*R*)-pyrimidyl alkanol were observed that was highly reproducible in all nine cases. These results indicate that Allende as well as Murchison powders meteorite still contain chiral “entities” that reside in their insoluble organic and/or inorganic materials.

The Murray kerogen-like insoluble organic materials (IOM) were next tested for asymmetry by asymmetric autocatalysis and the results are summarized in Table 3. In all cases, (*R*)-pyrimidyl alkanol were again generated in a good reproducible fashion. The low *ee* yields in entries 1 and 2 (as well as entry 4 in Table 4) owe in part to the small amount of meteorite used (4 mg). Because CM demineralization yields are sometimes less than 3% and require the investment of many grams of meteorite, a micro scale reac-

Table 2
Autocatalytic asymmetric induction by Allende powders after water and solvent extraction

Entry	Pyrimidyl alkanol 1a		
	Yield(%)	<i>ee</i> (%)	Config.
1	95	99	<i>R</i>
2	92	99	<i>R</i>
3	91	88	<i>R</i>
5	90	94	<i>R</i>
6	97	93	<i>R</i>
7	91	96	<i>R</i>
8	95	96	<i>R</i>
9	84	61	<i>R</i>

Table 3
Autocatalytic asymmetric induction by Murray IOM

Entry	Pyrimidyl alkanol 1a		
	Yield(%)	<i>ee</i> (%)	Config.
1	90	22	<i>R</i>
2	95	27	<i>R</i>
3	93	74	<i>R</i>
4	98	89	<i>R</i>

Table 4
Asymmetric autocatalysis initiated by Murray IOM-H

Entry	Pyrimidyl alkanol 1a		
	Yield(%)	<i>ee</i> (%)	Config.
1	84	95	<i>R</i>
2	84	95	<i>R</i>
3	89	92	<i>S</i>
4	93	3	<i>S</i>

Table 5
Asymmetric autocatalysis initiated by meteorite powders treated with oxygen plasma

Entry	Pyrimidyl alkanol 1a		
	Yield(%)	<i>ee</i> (%)	Config.
1	86	72	<i>S</i>
2	92	49	<i>R</i>
3	87	69	<i>R</i>
4	85	52	<i>R</i>
5	80	75	<i>S</i>
6	88	59	<i>S</i>
7	78	4	<i>S</i>
10	94	87	<i>R</i>
11	76	76	<i>R</i>

tion was set up for autocatalytic reactions employing the IOM. At these low amounts of material, the effect of small initial imbalances in the reaction is more pronounced and additional *ee* amplification steps may be required. Once this initial amplification phase has taken place, however, Sato et al. (2003a,b,c) proved satisfactorily that *ee* values can be consistently amplified by consecutive asymmetric autocatalysis.

On the other hand, the IOM samples from which several percent amounts of organic compounds had been removed by hydrothermolytic treatment (IOM-H, Yabuta et al., 2005) gave results (Table 4) that are in sharp contrast with those in Tables 1–3. Here, both (*R*)- and (*S*)-pyrimidyl alkanol were obtained equally and indicate the absence in the IOM-H sample of chiral factors, i.e., results are stochastic.

Similar results (Table 5) were obtained upon conducting the asymmetric autocatalytic reaction in the presence of MN powders from which all the organic material had been removed by exposure to oxygen plasma. Results are summarized in Table 5, (*S*)-pyrimidyl alkanol was obtained in eleven repeat trials, and the opposite *R*-enantiomers were given in five times, respectively, again the statistical formation of (*S*)- and (*R*)-pyrimidyl alkanols and the absence of a chiral effect are observed.

5. Discussion

The results obtained by the analyses of the various meteorite samples we tested for asymmetry are novel, rather unexpected, and, as implied in the experimental design itself, will have to be followed by detailed molecular analyses for the full identification of the meteoritic material that tested positive for asymmetric induction. However, the

data we obtained are convincing and already allow inferences of a diverse chiral imbalance in meteorites as well as of the phases that may likely host such asymmetry.

The convincing part of the above results is that they appear to be un-affected by terrestrial contamination. Such contamination has been a constant risk in analyses of enantiomeric excess in CM2 organic material, due to the homochirality of biomolecules and the ease with which terrestrial contaminants can be transferred to the meteorites soon after their falls (e.g., see Han et al., 1969, in regard to the Allende meteorite). In our experiments, the positive chiral responses shown in Tables 2–4 are of the opposite configuration of those obtained experimentally with the same alcohol by the induction of terrestrial protein L-amino acids (Soai et al., unpublished results). This fact appears to eliminate the likelihood of interferences from contamination in our analyses, which is further ruled out by the lack of response from the treated IOM. In fact, we would expect contamination to be comparable for meteorites' powders and IOM, given that both samples were last processed in the same general experimental environment (e.g., water and solvents employed).

The data also rule out the presence of asymmetry in the mineral constituents of meteorites, a result somewhat unexpected in view of the fact that several of these constituents could crystallize and crystals are often chiral. We have to conclude that the mineral phase, even if chiral, does not contain enantiomeric imbalances and that asymmetry resides exclusively in the organic material of meteorites, possibly in yet unknown compounds of the labile components of CM as well as CV IOMs.

It has been long known by observation of the meteorite samples, e.g., the “soapy” characteristics of the water extracts and the simple comparison of the elemental composition of the total extracts with that inferred from the actual compounds detected (Epstein et al., 1987), that the water-soluble organic compounds we identify in meteorites represent only a portion of the total extracted. In our analyses of these organics we are clearly limited by the procedures and/or techniques employed. It is likely that more species, many according to the elemental analyses, could be characterized with more exhaustive procedures. Also, a study of Murchison carboxylic acids showed that sulfuric acid treatment of the already water-extracted meteorite powders releases several of the acids, which had apparently been trapped within the matrix (unpublished results). It is possible, therefore, that some of these water-soluble unknowns may carry enantiomeric excesses.

From the data, however, asymmetry appears to reside with more certainty in the insoluble, complex, and not yet fully characterized IOMs of both Murray and Allende. The IOM is the largest organic component in carbonaceous chondrites and consists largely of condensed aromatic, hydroaromatic, and heteroaromatic macromolecules that contain alkyl branching, functional groups such as OH and COOH, and are bridged by alkyl chains, ether, and sulfide linkages. A general understanding of its composition

comes mainly from spectroscopic analyses (e.g., Cody et al., 2002) and the study of its oxidative or pyrolytic decomposition products (e.g., Hayatsu et al., 1977; Sephton et al., 2004, and references therein). On the basis of ^{13}C isotopic analyses of Murchison IOM, Sephton et al. (1998) postulated that the material comprises at least two components: a more labile portion, which can be solubilized from the IOM under pyrolytic conditions (and presumably may have generated soluble compounds in the meteorites parent body under comparable exposure to temperature and pressure), and a refractory material.

Recently, we have carried out model experiments to ascertain the possible release of water-soluble compounds under conditions that would reasonably mimic the hydrous phase of the meteorite parent bodies. Results (Yabuta et al., 2005) showed that a rather complex group of water- and solvent-soluble organic compounds were freed from Murray IOM after HT treatment. Among others, a suite of dicarboxylic acids that ranges from three to seventeen carbon species, N-containing species such as benzimidazoles, quinolines, and quinoxalines, their methylated homologs, and a large variety of aromatic compounds. Therefore, it is in this suite of compounds solubilized from the IOM that we will have to search to identify the sources of molecular asymmetry that lead to the induction of the autocatalytic enantiomeric excesses recorded in Tables 1–3. It is intriguing that an asymmetric effect is seen also in the IOM of the Allende meteorite, a CV chondrites where little soluble material has been detected (Cronin and Pizzarello, 1990). Because terrestrial contamination can reasonably be excluded, as mentioned above, only repeat analyses after hydrothermal treatment of the Allende IOM comparable to those conducted for the Murray IOM may show if there is any hope to identify the source of this meteorite asymmetry at the molecular level.

The clear implication of a diverse asymmetry in cosmochemistry that can be drawn from the data should not be surprising in view of the fact that asymmetry is a fundamental trait of matter. Not all laws of physics are invariant with operations of symmetry (e.g., reflection upon a plane) and, as pointed out in the Introduction, it is believed that the enantiomers of a chiral molecule have an inherent, albeit minute, energy difference (PVED). How this basic asymmetry of matter at the sub-atomic level could relate to the chemistry of chiral molecules is poorly understood, because *ab initio* calculations have not been successful so far in giving consistent predictions (Quack, 2002). How PVED might have influenced the formation of the less known molecules in cosmic environments remains a question of vast importance.

The finding so far of *ee* only in those meteoritic amino acids that show a more direct lineage to interstellar processes (Pizzarello and Huang, 2005) would favor the suggestion that the cold cosmic regimes that lead to their syntheses may be responsible for their asymmetry as well. If so, the organic unknowns responsible for the asymmetric response we determined in this study may be related to the

same pre-solar processes. Once isolated and their chiral signature verified, it will be interesting to analyze these compounds' isotopic composition as well.

The results presented here may also have a prebiotic relevance in that molecular asymmetry seems to reside in a far larger fraction of the organic material of meteorites. Besides the possible contribution by the non-racemic amino acids of meteorites (Pizzarello and Weber, 2004), therefore, a more abundant and diverse exogenous material could have participated in the induction toward asymmetry in the molecular evolution of the early Earth.

6. Conclusions

It is shown convincingly that molecular asymmetry affects other organic constituents of the carbonaceous chondrites organic suite besides the non-racemic amino acids.

This asymmetry affects the labile portion of the insoluble material and may also involve yet unknown soluble compounds.

Asymmetry is seen also in Allende IOM, a meteorite that contains very few soluble organics.

A diverse and more abundant molecular asymmetry may have implication for prebiotic chemical evolution.

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References

- Blackmond, D.G., 2004. Asymmetric autocatalysis and its implications for the origin of homochirality. *Proc. Natl. Acad. Sci.* **101**, 5732–5736.
- Chyba, C.F., Sagan, C., 1992. Endogenous production, exogenous delivery, and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* **355**, 125.
- Cody, G., Alexander, C.M.O'D., Tera, F., 2002. Solid state (¹H and ¹³C) NMR spectroscopy of the insoluble organic residue in the Murchison meteorite: a self-consistent quantitative analysis. *Geochim. Cosmochim. Acta* **66**, 1851–1865.
- Cronin, J.R., Pizzarello, S., 1990. Aliphatic hydrocarbons of the Murchison meteorite. *Geochim. Cosmochim. Acta* **54**, 2859–2868.
- Cronin, J.R., Pizzarello, S., 1997. Enantiomeric excesses in meteoritic amino acids. *Science* **275**, 951–955.
- Cronin, J.R., Reisse, J., 2005. Chirality and the origin of homochirality. In: Gargaud, M. (Ed.), *Lectures in Astrobiology*, vol. 1. Springer-Verlag, Berlin, pp. 473–514.
- Cronin, J.R., Pizzarello, S., Frye, J.S., 1987. ¹³C NMR spectroscopy of insoluble carbon in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **51**, 299–303.
- Delsemme, A.H., 1992. Cometary origin of carbon, nitrogen, and water on the Earth. *Origins Life* **21**, 279–298.
- Engel, M.H., Macko, S.A., 1997. Isotopic evidence for extraterrestrial non racemic amino acids in the Murchison meteorite. *Nature* **389**, 265.
- Epstein, S., Krishnamurthy, R.V., Cronin, J.R., Pizzarello, S., Yuen, G.U., 1987. Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* **326**, 477–479.
- Frank, F.C., 1953. Spontaneous asymmetric synthesis. *Biochim. Biophys. Acta* **11**, 459–463.
- Glit, C.F., 1968. Use of electrically excited oxygen for the low temperature decomposition of organic substrate. *Anal. Chem.* **34**, 1454–1457.
- Han, J., Simoneit, A.L., Burlingame, M., Calvin, M., 1969. Organic analysis of the Pueblito de Allende meteorite. *Nature* **222**, 364.
- Hayatsu, R., Matsuoka, S., Scott, R.G., Studier, M.H., Anders, E., 1977. Origin of organic matter in the early solar system—VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1325–1339.
- Islas, J.R., Lavabre, D., Grevy, J.-M., Lamoneda, R.H., Cabrera, H.R., Micheau, J.-C., Buhse, T., 2005. Mirror-symmetry breaking in the Soai reaction: a kinetic understanding. *Proc. Natl. Acad. Sci. USA* **102**, 13743–13748.
- Kawasaki, T., Sato, M., Ishiguro, S., Saito, T., Morishita, Y., Sato, I., Nishino, H., Inoue, Y., Soai, K., 2005. Enantioselective synthesis of near enantiopure compound by asymmetric autocatalysis triggered by asymmetric photolysis with circularly polarized light. *J. Am. Chem. Soc.* **127**, 3274–3275.
- Kawasaki, T., Suzuki, K., Shimizu, M., Ishikawa, K., Soai, K., 2006. Spontaneous absolute asymmetric synthesis in the presence of achiral silica gel in conjunction with asymmetric autocatalysis. *Chirality* **18**, 479–482.
- Mislow, K., 2003. Absolute asymmetric synthesis: a commentary. *Collect. Czech. Chem. Commun.* **68**, 849–864.
- Pizzarello, S., 2006. The chemistry of life's origin: a carbonaceous meteorite perspective. *Acc. Chem. Res.* **39**, 231–237.
- Pizzarello, S., Cronin, J.R., 2000. Non racemic amino acids in the Murchison and Murray meteorites. *Geochim. Cosmochim. Acta* **64**, 329–338.
- Pizzarello, S., Weber, A.L., 2004. Prebiotic amino acids as asymmetric catalysis. *Science* **303**, 1151.
- Pizzarello, S., Huang, Y., 2005. The deuterium enrichment of individual amino acids in carbonaceous meteorites: a case for the presolar distribution of biomolecules precursors. *Geochim. Cosmochim. Acta* **69**, 599–605.
- Pizzarello, S., Zolensky, M., Turk, K.A., 2003. Non racemic isovaline in the Murchison meteorite: chiral distribution and mineral association. *Geochim. Cosmochim. Acta* **67**, 1589–1595.
- Pizzarello, S., Huang, Y., Fuller, M., 2004. The carbon isotopic distribution of Murchison amino acids. *Geochim. Cosmochim. Acta* **68**, 4963–4969.
- Pizzarello, S., Cooper, G.W., Flynn, G.J., 2006. The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In: Lauretta, D., McSween, H.Y., Jr. (Eds.), *Meteorites and the Early Solar System II*. University of Arizona Press, Tucson, USA, pp. 625–651.
- Podlech, J., Gehring, T., 2005. New Aspects of Soai's Asymmetric Autocatalysis. *Angew. Chem. Int. Ed.* **44**, 5776–5777.
- Prelog, V., 1976. Chirality in chemistry. *Science* **193**, 17–24.
- Quack, M., 2002. How important is parity violation for molecular and biomolecular chirality? *Angew. Chem. Int. Ed.* **41**, 4618–4630.
- Sato, I., Kadowaki, K., Soai, K., 2000. Asymmetric synthesis of an organic compound with high enantiomeric excess induced by inorganic ionic sodium chlorate. *Angew. Chem. Int. Ed.* **39**, 1510–1512.
- Sato, I., Omiya, D., Tsukiyama, K., Igarashi, H., Ogi, Y., Soai, K., 2001. Evidence of asymmetric autocatalysis in the enantioselective addition

- of diisopropylzinc to pyrimidine-5-carbaldehyde using chiral pyrimidyl alkanol. *Tetrahedron: Asymmetry* **12**, 1965–1969.
- Sato, I., Omiya, D., Igarashi, H., Kato, K., Ogi, Y., Tsukiyama, K., Soai, K., 2003a. Relationship between the time, yield, and enantiomeric excess of asymmetric autocatalysis of chiral 2-alkynyl-5-pyrimidyl alkanol with amplification of enantiomeric excess. *Tetrahedron: Asymmetry* **14**, 975–979.
- Sato, I., Kadowaki, K., Urabe, H., Jung, J.H., Ono, Y., Shinkai, S., Soai, K., 2003b. Highly enantioselective synthesis of organic compound using right- and left-handed helical silica. *Tetrahedron Lett.* **44**, 721–724.
- Sato, I., Urabe, H., Ishiguro, S., Shibata, T., Soai, K., 2003c. Amplification of chirality from extremely low to greater than 99.5% ee by asymmetric autocatalysis. *Angew. Chem. Int. Ed.* **41**, 1614–1616.
- Sephton, M.A., Pillinger, C.T., Gilmour, I., 1998. $\delta^{13}\text{C}$ of free and macromolecular aromatic structures in the Murchison meteorite. *Geochim. Cosmochim. Acta* **62**, 1821–1828.
- Sephton, M.A., Love, G.D., Watson, A.B., Verchovsky, A.B., Wright, I.P., Snape, C.E., Gilmour, I., 2004. Hydroxyrolysis of insoluble carbon matter in the Murchison meteorite: new insights into its macromolecular structure. *Geochim. Cosmochim. Acta* **68**, 1385–1393.
- Shibata, T., Yamamoto, J., Matsumoto, N., Yonekubo, S., Osanai, S., Soai, K., 1998. Amplification of slight enantiomeric imbalance in molecules based on asymmetric autocatalysis: the first correlation between high enantiomeric enrichment in a chiral molecule and circularly polarized light. *J. Am. Chem. Soc.* **46**, 12157–12158.
- Soai, K., Shibata, T., Morioka, H., Choji, K., 1995. Asymmetric autocatalysis and amplification of enantiomeric excess of a chiral molecule. *Nature* **378**, 767–768.
- Soai, K., Osanai, S., Kadowaki, K., Yonakubo, S., Shibata, T., Sato, I., 1999. *d*- and *l*-quartz-promoted highly enantioselective synthesis of a chiral organic compound. *J. Am. Chem. Soc.* **121**, 11235–11236.
- Soai, K., Shibata, T., Sato, I., 2000. Enantioselective automultiplication of chiral molecules by asymmetric autocatalysis. *Acc. Chem. Res.* **33**, 382–390.
- Soai, K., Sato, I., Shibata, T., 2001. Asymmetric autocatalysis and the origin of chiral homogeneity in organic compounds. *Chem. Rec.* **1**, 321–332.
- Soai, K., Sato, I., Shibata, T., Komiya, S., Hayashi, M., Matsueda, Y., Imamura, H., Hayase, T., Morioka, H., Tabira, H., Yamamoto, J., Kowata, Y., 2003. Asymmetric synthesis of pyrimidyl alkanol without adding chiral substances by the addition of diisopropylzinc to pyrimidine-5-carbaldehyde in conjunction with asymmetric autocatalysis. *Tetrahedron: Asymmetry* **14**, 185–188.
- Yabuta, H., Williams, L., Cody, G., Pizzarello, S., 2005. The insoluble carbonaceous material of CM chondrites as possible source of discrete organics during the asteroidal aqueous phase. *36th Lunar and Planetary Conference*, Houston, TX Abstract # 1367 [CD-ROM].