all amino acids was determined by chemical derivatization and HPLC [39–41]. The results are shown in Table 1 [38]. In trial 1, a nearly racemic mixture was obtained. In trials 2–5, L-rich mixtures were obtained, and in trial 6, a D-rich mixture was obtained.

Table 1. ee values (%) of amino acids contained in crystals obtained by recrystallization from a mixture of excess D,L-Asn with 12 D,L-amino acids [38].

Trial	Asn	Ala	Arg	Asp	Gln	Glu	His	Leu	Met	Phe	Ser	Tyr	Val
1	0.23	−6.6	−2.4	1.2	2.3	−3.9	0.2	0.4	−9.8	−2.5	8.0	−5.5	−8.2
2	37.9	30.8	20.4	40.1	37.5	26.5	18.9	3.6	26.0	14.6	48.4	6.7	−0.4
3	33.1	43.0	35.2	48.5	52.2	41.8	18.8	8.0	40.0	22.5	56.6	14.5	5.0
4	79.4	91.0	82.6	100	94.9	92.0	70.0	42.4	40.6	71.2	100	ND	41.8
5	62.9	52.8	39.2	59.7	50.6	61.3	26.1	11.2	54.9	41.4	67.4	36.1	22.8
6	−94.6	−87.1	−43.0	−100	−72.4	−77.4	−66.9	−13.3	−62.0	−39.9	−90.1	−30.1	−6.3

ND: not detected

These results demonstrate that the coexisting amino acids with the same configuration as Asn were also preferentially cocrystallized in this experiment. This highlights a very important point; all these amino acids give the same enantiomer-rich crystals by the recrystallization. In other words, ***recrystallization is a mechanism that gives rise to a set of L-amino acids or D-amino acids.*** Therefore, the 19 independent mechanisms for each amino acid, as postulated in the Introduction, are not necessary to cause optical resolution of amino acids. This may be explained on the grounds that an amino acid has two polar groups to interact with each other by strong Coulomb forces during crystallization and their configuration predominantly determines the structure and ee of the crystal.

Interestingly, the ee of Ala and Glu, which did not give an ee by recrystallization with D,L-Asn alone, was induced from a mixture of these 13 racemic amino acids. It is surprising that the maximal ee was 100%, and that these ee values are much higher than those observed in the recrystallization of each amino acid with D,L-Asn alone. One can conclude that ***a racemic mixture of amino acids causes spontaneous and effective enantiomeric enrichment by itself***, even if asymmetric synthesis of a single amino acid does not occur without the aid of an optically active molecule.

A selection in the very early stage of the crystallization process may also determine the ee of entire crystals. It is easily understood that a strong chiral field is generated when the crystal surface of L-Asn or D-Asn appears in a racemic solution. Based on these results, we propose that enantio-selective crystallization of racemic amino acids induced by spontaneous resolution of a coexisting racemic molecule such as D,L-Asn, is a simple and realistic mechanism for the selection of L-amino acids in the biosphere [38]. Furthermore, the resulting ee was sufficiently high to account for the predominance of L-amino acids on the earth, if the L-selection occurred by crystallization comparing with the small ee of amino acids contaminated in meteorites [26].

D,L-Asn, the unique amino acid, is formed using contact glow discharge electrolysis against an aqueous solution containing alanine and formamide [42]. However, it is unknown whether D,L-Asn was produced in sufficient quantities by chemical evolution to allow crystallization. It is incidental

whether D,L-Asn gave either L-rich or D-rich crystals as described above; thus, it may be speculated that random crystallizations at many points may not have induced an L-rich world, but have lead to a racemic world. It is very interesting to consider whether an L-amino acid world was formed accidentally or necessarily generated by the interaction of D,L-amino acids, especially D,L-Asn with D-sugars or RNAs.

3. Other Hypotheses Explaining Homochirality of Amino Acids

Absolute asymmetric synthesis and optical resolution have been examined under physical fields [2,43,44]. Irradiation of Cr(III)tris-oxalato complex with unpolarized light in a magnetic field at 7.5 T parallel to the irradiation direction yielded an ee of -1×10^{-4} [6]. This was an epoch-making study, but based on this small value, it may be debated whether magnetochiral reaction has a realistic meaning in the formation of homochirality. A confined vortex motion induced an ee in the oxidation of isophorone and hydrogen peroxide [45], although a relationship of this study with the amino acid was unknown.

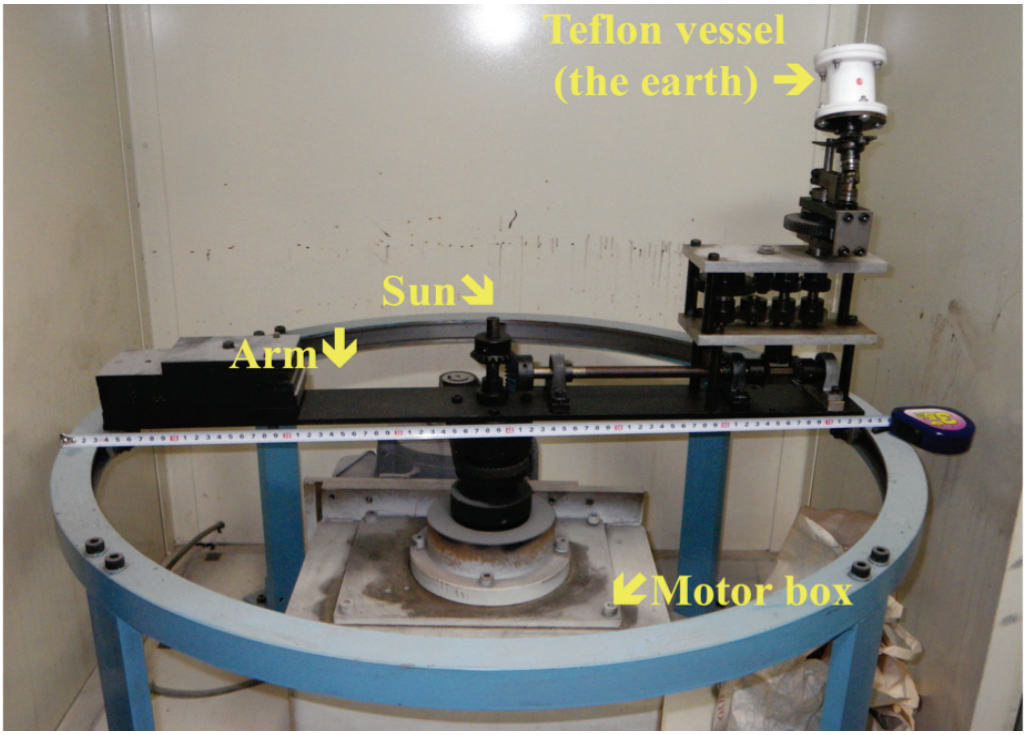
Two orientations of a molecule must be regulated to generate an ee. If the molecule orients by a flow of the solution, e.g., the smallest substituent moves forward, and the largest substituent locates at the outside position by the centrifugal force, the movement of the earth (revolving both around the sun and on its axis) possibly induces an ee. As the tilt of the earth's axis to its orbital plane is 23.5°, the movement of the earth itself is asymmetric. If chemical evolution occurred in the solution (including the gas phase) that synchronized with the movement of the earth, generation of an ee may be expected.

We constructed a model of the earth about 20 years ago (Figure 3). The radius of the arm was 30 cm. The inner diameter of a Teflon vessel was 4 cm, and the height of its inner cavity was also 4 cm. This vessel revolves three times around its axis per one rotation around the sun (center) using a motor and gears (Video 1). The maximum rotation speed was 150 rpm. Unfortunately, we have not succeeded in inducing appreciable ee in oxidation of methyl p-tolyl sulfide with sodium periodate, epoxidation of stilbene with m-chloroperbenzoic acid, or solvolysis of 1-chloro-1-phenyl-ethane with this model. To avoid the effects of side products, we determined the ee by HPLC, in which the standard deviation is usually ~1%–2%. Therefore, an ee smaller than 1% could not have been detected even if it had arisen. Recrystallization of D,L-Asn with this model gave crystals with either plus or minus ee and did not give only L- or D-rich crystals, showing that the results were similar to those obtained by recrystallization made in a stationary vessel. At present, no experimental evidence is available indicating that the asymmetric movement of the earth causes homochirality of amino acids.

Even simple stirring of the solution gave optically active crystals of sodium chlorate ($NaClO_3$), although this molecule is not chiral [19]. Since this process regulates only one direction, the yield of optically active crystals of $NaClO_3$ may be a very specific case, and this may not be applicable to amino acids. However, it is possible that optically active crystal surfaces provide an asymmetric field with amino acids. Selective adsorption of amino acids to crystals of nonchiral inorganic molecules is a possible mechanism for the condensation of either enantiomer. Quartz [46] underwent asymmetric preferential adsorption of Ala in anhydrous dimethylformamide solution. However, Bonner [47] casted doubt on any significant role of quartz in chiral selectivity on the basis of equal abundance of (+)- and (−)-quartz on the earth and the strictly anhydrous conditions required for optical resolution. Calcite

($CaCO_3$) displayed significant adsorption and chiral selectivity of Asp [48,49] and Ala [49] on pairs of mirror-related crystal growth surfaces, although it was not determined whether the ee of Asp or Ala was induced as a whole on the total crystal surfaces. If either crystal field preferentially oriented to the aqueous phase in the prebiotic sea, selection of an amino acid such as Asn, which causes optical resolution of other amino acids [30,38], may have been possible similar to the floating Gly crystal [24].

Figure 3. Earth model. The tilt of the axis of the Teflon vessel to its orbital plane is 23.5°. A red mark appears every 10 cm for measurement. The earth revolves both round the center (the sun) and on its axis.



4. Conclusions

Since the selection of homochirality takes place only once in the history of the earth, it may be almost impossible to prove the mechanism scientifically and to reproduce the situation with confidence. For example, even if a large quantity of D-amino acids remained somewhere after the L-selection, it is impossible to find them, because almost all living organisms equip with metabolic enzymes of D-amino acids like D-amino acid oxidase to consume them as an energy source. Therefore, discussions on this issue will last forever, and new and surprising ideas corresponding to the progress of science and technology will be proposed one after another. These ideas will affect chemistry, especially in fundamental concepts concerning interaction among molecules. Whether this is scientific or romantic, or both, is not for us to say.

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