

1 (lines 1–6) summarizes some typical results. Over 500 experiments showed that, as expected, the D-amino acids were incorporated only into those floating glycine crystals whose (010) faces were exposed to the water solution, while the L-amino acids are incorporated only into the crystals with exposed (0 $\bar{1}$ 0) faces (Fig. 2a–c). HPLC analysis of plates grown on the glass bottoms showed similar resolution, albeit with a lower enantiomeric excess.

Without an amplification mechanism, it is unlikely that a systematic net resolution of the  $\alpha$ -amino acid additives would be obtained from crystals grown in this way in a closed system. If, on the other hand,  $\alpha$ -amino acids which have been partially resolved in the first random crystallization are able to induce correct orientation in the subsequent flotation of further glycine crystals, asymmetry may be both preserved and amplified. To test this idea, we investigated the ability of resolved  $\alpha$ -amino acids to orient glycine crystals at water–air interfaces (see Table 1 legend for the specific conditions for the experiments given below). In these conditions the results were fully reproducible.

We found that resolved hydrophobic  $\alpha$ -amino acid additives such as Leu, Phe, Phe-Gly and  $\alpha$ -aminobutyric acid of, say, D-configuration, have indeed a pronounced orientating effect; these additives induced the formation of pyramidal crystals all floating with their well developed (010) faces directed upwards (Table 1, lines 7, 8). On the other hand, in the presence of these same additives, crystals of two distinct habits were found on the glass bottom of the vessel—pyramids lying on their (010) face and plates lying on their (0 $\bar{1}$ 0) face (Fig. 2a)—indicating that there is no orientating effect here. Furthermore, in the presence of resolved alanine or other more hydrophilic amino acids, both plate-like and pyramidal floating crystals were obtained in the given range of additive concentrations (Fig. 2b and Table 1, lines 9, 10). Combinations of D-Leu and L-Ala (or L hydrophilic amino acids) in equal concentrations yielded, without exception, parallelepipeds floating with their (010) faces pointing upwards (Fig. 2c and Table 1, lines 11–19). A similar effect was found at a water/hexane interface. Finally, combinations of non-hydrophobic amino acids, (for example, D-Ala and L-Glu or L-Ser) did not lead to preferential orientation of the floating plate-like crystals (Table 1, lines 20–22). The absolute orientations of the floating crystals, that is, (010) or (0 $\bar{1}$ 0) directed upwards<sup>4</sup>, were established by visual observation: their morphology is such that the two enantiomorphic habits are not superimposable in the plane of the interface (Fig. 3a, d, f). The assignments were verified by X-ray diffractometry on several crystals from each batch. According to HPLC analysis of the above crystals, only minute amounts of the orientating hydrophobic additives are occluded through the upward-pointing face. This result indicates that the orientation of the floating crystals occurs at a very early stage of growth.

Based on the above findings, a novel induced resolution of  $\alpha$ -amino acids was then performed by crystallization of glycine in the presence of, for example, L-Leu and mixtures of other (D, L) amino acids (Table 1, lines 23–30). The floating crystals (Fig. 3d) were obtained with their (0 $\bar{1}$ 0) faces directed upwards, as deduced by X-ray diffractometry, and, as shown by HPLC analysis, occluded exclusively the D-amino acids through the exposed, growing (010) face; a typical chromatogram is depicted in Fig. 3e. Furthermore, even in conditions where polycrystalline crusts of glycine were formed (Fig. 3f), resolution occurred with an enantiomeric excess higher than 70% (Fig. 3g) in the examples studied.

The above experiments provide a simple model for the generation and amplification of optically active amino acids in prebiotic conditions. Consider, for example, that the first crystallization of glycine from the evolutionary 'soup' gave a crystal floating with its (010) face directed, by chance, upwards. Thus, the (010) face grew in contact with the solution containing racemic mixtures of  $\alpha$ -amino acids. During that process the crystal would have occluded the L-amino acids exclusively and thus the water solution would have been enriched in the corresponding D-enantiomers. The hydrophobic D-amino acids pres-

ent in excess in the water solution would, then, have preferentially directed new floating crystals with their (010) faces upwards and these in turn would, during growth, have occluded only L-amino acids from the solution, thus leading to further D-enantiomer enrichment of the solution.

We are now investigating the detailed mechanism of the orientating effect as well as the minimum enrichment required to trigger amplification. Preliminary studies using Leu as an additive have shown that a D/L-Leu mole ratio as low as 55:45, with a total Leu concentration in the range 2.0–2.2% wt/wt of glycine, results in an assembly of perfectly orientated floating, plate-like crystals of glycine.

The principles applied here may be extended to oligopeptides and to other organic and inorganic materials, provided they exhibit the appropriate crystal point symmetry and also develop enantiotopic faces capable of interacting selectively with D- and L-enantiomers.

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## Erratum

### Characterization of DNA sequences through which cadmium and glucocorticoid hormones induce human metallothionein-II<sub>A</sub> gene

Michael Karin *et al. Nature* **308**, 513–519 (1984)

IN Fig. 5a, the footprint due to receptor binding was not evident because a poor original was reproduced darkly. The figure is reproduced correctly below. The strong receptor footprint between –265 and –245, as well as the weak footprint around –324, are clearly visible.

