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Impact-induced D/L chiral changes of valine in early Earth's oceans

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It has widely known that proteins are composed of L-amino acid mononers and that nucleic acids contains exclusively D-sugars. Homochirality selection may be contributed to the consequence of life materials and their generation conditions. Regarding the enantiomeric excess in biomolecules, there are several proposals at present. Because the enantiomeric excess occurs in photoreactions by circularly polarized light, it has been believed that interstellar environments play an important role to the formation of chiral amino acids identified in chondrites and interstellar ices. However, it is also important to know whether the enantiomeric excess of amino acids occurs during oceanic impacts or not, because the enantiomeric enrichments are known under critical states of fluids due to density fluctuations.

We have investigated the shock-induced chiral changes of valine in aqueous solution coexisting with given solids. Powders of olivine, hematite, and calcite were selected to represent solids. Hypervelocity plane impact experiments were carried out using a propellant gun. Sample solution of each of L- and D-valine in sealed steel containers was subjected to impact at velocities of about 1 km/s. The calculated shock pressures are 5-6 GPa by the impedance match solution. The recovered solutions were analyzed with LC/MS (2695 separation module; Waters Corp. and Quattro micro API; Waters Corp) after the FDLA derivatization that makes a difference in hydrophobicity between D- and L-valine. The enantiomeric excess (ee(%)=100(L-D)/(L+D)), the yield of the initial valine, and shock pressure are plotted to see their relationship. The results indicate a difference among the solid. Although there was no significant change from the racemic valine solution, the reaction from L-valine to D-valine was significantly faster than that from D-valine to L-valine in calcite. The adsorption of calcite powders was checked to display no difference between D- and L-valine. These results may suggest that oceanic impacts may change the chirality of amino acids in oceans. However the enrichment of L-amino acids on the Earth need another mechanism.

Keywords: Impact-induced D/L chiral changes, D/L valine, Calcite