

THE ORIGIN OF HOMOCHIRALITY IN AMINO ACIDS THROUGH WEAK NEUTRAL CURRENTS AND ORTHO:PARA DISEQUILIBRIUM IN THE AMINO GROUP. R. Popa¹, V.M. Cimpoiasu² and R.I. Scorei², ¹Portland State University, rpopa@pdx.edu, ²University of Craiova, Romania.

Introduction: Although many mechanisms were proposed to explain the origin of biochirality this phenomenon still confounds logical interpretation. Until recently it was believed that the only fundamental source of homochiral asymmetry in nature is Parity Non Conservation (PNC) through the weak force. Yet this asymmetry has too little chemical effects ($\sim 10^{-17} kT$) [1] to be relevant to the origin of biochirality. In the last few years we found evidence that chiral asymmetry exists between amino acid enantiomers regarding proton exchange, and that this difference is better visible in the presence of $H_2^{17}O$ [2]. This asymmetry is observed by Time Domain 1H Nuclear Magnetic Resonance (TD- 1H NMR) and is much larger than the effect of PNC ($10^{-7} kT$). We hypothesized that in amino acids this asymmetry is rooted in neutral ring currents from the chiral center influencing the nuclear spin coupling and the electromagnetic organization of the α -amino group [2].

Results and discussions: We purified asparagine enantiomers by crystallization from racemic solutions. We verified our hypothesis by studying how magnetic fields and the presence of $H_2^{17}O$ influences chiral disruption during the crystallization of Asparagine. We also analyzed the effect of pH on the *L-D* proton exchange asymmetry. We found significant differences in the rate of crystallization between enantiomers, and describe the effect of $H_2^{17}O$ in this chiral disruption. Using signal magnitude in TD- 1H NMR we also found that $H_2^{17}O$ has a significantly lower abundance of *para* (P17) relative to $H_2^{16}O$ (P16), according to $P17 = 1.0984 * P16 - 0.0984$. Consistent with our hypothesis chiral differences between asparagine enantiomers were pH -dependent and the relevant pH was different between amino acids (Asn vs. Ala). In Asn the largest chiral asymmetry was found in the 5.91-6.42 pH range, with proton exchange enantio-differences (*L-D* $\Delta\Delta G^\circ$) equivalent with $\sim 1.14 \text{ kJ}\cdot\text{mol}^{-1}$ for 200 mM Asn incubated with 100 mM $H_2^{17}O$.

Summary: Based on our results we propose that $H_2^{17}O$ does not amplify chiral asymmetry during TD- 1H NMR, but contributes to the stabilization of an already existing asymmetry caused by the neutral ring currents from the chiral center. Because the pK of $H_2^{17}O$ is different from the pK of $H_2^{16}O$, it is most likely that during TD- 1H NMR $H_2^{17}O$ behaves as a molecule-size probe of the state of the amino group.

Concluding Remarks: We report finding differences in proton exchange reactivity between asparagine enantiomers, and propose that they are caused by chiral-asymmetric organization of the amino group. These results are significant for understanding the origin of prebiotic chirality and biochirality. These chiral differences are significantly larger (10 scales of magnitude) relative to the effect of PNC and thus can be made relevant to chemistry upon coupling with amplification mechanisms such as crystallization or catalysis. Also, because the organization of the neutral currents is similar relative to the chiral center of all α -amino acids this effect will be homochiral at specific pH values.

References: [1] Szabó-Nagy A. and Keszthelyi L. (1999) *PNAS.*, 96,4252-4255. [2] Popa R., Cimpoiasu V.M. and Scorei R.I. (2009), *Astrobiology*, 9:697-701.