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Spontaneous assembly of iron-sulfur clusters at low concentrations of cysteine.

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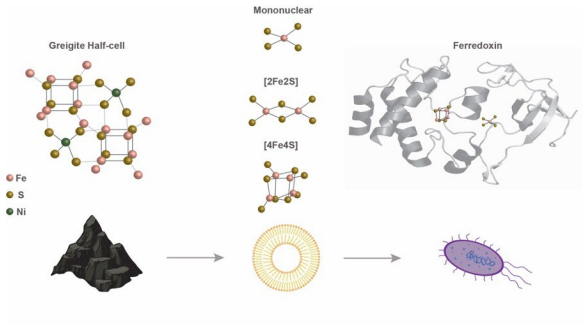

Iron-sulfur (FeS) proteins are ancient and fundamental to life, being involved in electron transfer and CO_2 fixation. FeS clusters have structures similar to the unit-cell of FeS minerals such as greigite, found in hydrothermal systems. The alkaline vent hypothesis is a compelling explanation for the origin of life [1,2,3]. It centres on vents comprising Fe-Ni-S materials produced by serpentinization in the Hadean submarine crust. However, the prebiotic pathway from mineral surfaces to biological clusters is unknown. The gap could hypothetically be crossed by FeS clusters chelated by amino acids or short polypeptides [4,5] (see Figure). It is noteworthy that cysteine is the only thiol-containing coded amino acid in biology, essential for anchoring the Fe in iron-containing prosthetic groups. In this presentation, I will present new research that shows FeS clusters form spontaneously through interactions with micromolar concentrations of the amino acid cysteine in water at alkaline pH. Bicarbonate ions stabilize the clusters and even promote cluster formation alone at concentrations >10 mM, probably through salting-out effects. We demonstrate robust formation of [4Fe4S], [2Fe2S] and mononuclear iron clusters using ^{57}Fe-Mössbauer spectroscopy, UV-Vis spectroscopy and ^{1}H-NMR. Our findings reveal that the structures responsible for biological electron transfer and CO_2 reduction form spontaneously from monomers at the origin of life.

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