

Experimental study on role of sulfide-peptide complexes in the first metabolism

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Metal sulfides are thought to have played an essential role in chemical evolution processes leading to the origin of life (the iron-sulfur world hypothesis). Greigite (Fe_3S_4) contains the cubic Fe_4S_4 unit, which is similar to the iron sulfur cluster, which constitutes the catalytic center of various iron-sulfur proteins such as carbon monoxide dehydrogenase/acetyl-CoA synthase. Although greigite is thought to have been the origin of iron-sulfur clusters, the catalytic activity of this mineral has not been assayed for hydrothermal reactions in which inorganic carbons (i.e., CO_2 and CO) are reduced to form organics. In chemical evolution processes, it has been hypothesized that metal sulfides were conjugated with peptides to form sulfides-peptide complexes, which had greater stability and higher catalytic activity than the metal sulfides themselves. However, no experimental evidence that supports this hypothesis has been reported. Thus, the aims of this study are to (i) obtain a more comprehensive understanding of the catalytic nature of metal sulfides, including greigite, under hydrothermal conditions wherein inorganic carbons are converted to organics and (ii) obtain evidence for enhancement of the catalytic activity of metal sulfides by complex formation with peptides.

The catalytic activity of metal sulfides (FeS , Fe_3S_4 , NiFe_2S_4 , FeS_2 , CoS , NiS , and ZnS) for the conversion of CO_2 or CO was assayed under various hydrothermal conditions (20–100°C, pH 4–10, 2–100 atm, with/without reductants). Metal sulfides containing Fe and/or Ni catalyzed CO_2 reduction by H_2 to afford formate. Among them, the greigite species (Fe_3S_4 and NiFe_2S_4) showed the highest catalytic activity. Similarly, greigite catalyzed CO reduction by HS^- more efficiently than did any other metal sulfides tested, producing 2–6 mM acetate after 24 h reaction under 100°C and 2 atm. At higher reaction pressures, CO_2 was predominantly reduced by H_2 to methane, indicating dissolved gas concentration strongly influence reaction products. These results suggest that greigite has superior catalytic activity and plays a central role in establishing the first metabolism. In order to construct sulfide-peptide complexes, greigite-binding peptides were screened by using phage display random peptide libraries. After three rounds of biopanning, several consensus peptide sequences that were rich in polar amino acids (especially histidine) were obtained and found to attach to greigite. Preliminary experiments to study sulfide-peptide complexes are underway, and the results would be reported in due course.

Keywords: Origin of life, Iron sulfide, Primitive enzyme, Iron-sulfur protein, Chemical evolution, Acetyl-CoA pathway