

水溶液中におけるピロタイトおよびアミノ酸からの鉄-硫黄クラスターの形成 Formation of iron-sulfur clusters from amino acids with pyrrhotite in aqueous solutions

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Iron-sulfur (Fe-S) clusters are agents that affect many biochemical processes as they are the active sites in relatively small proteins with molecular weights of 6,000 to 12,000. They are common to most ancient components of living matter and are present in a host of other organisms such as photosynthetic organisms, nitrogen-fixing bacteria, and submitochondrial fractions of mammalian origin [1]. The chemically simplest Fe-S clusters are the rhombic [2Fe-2S] and the cubane [4Fe-4S] types, and are usually integrated into proteins through coordination of the iron ions by cysteine or histidine residues. Interestingly, these biological Fe-S clusters resemble the iron sulfide minerals such as mackinawite (Fe_(1+x)S) and greigite (Fe₃S₄), which have been assigned an important role in the geochemical theory of the origins of life [2].

Cody *et al.* [3] reported the formation of carbonylated Fe-S species in the aqueous formic acid with nonanethiol and synthesized troilite (FeS) under hydrothermal conditions. They identified the carbonylated Fe-S species by UV-visible light and Raman spectroscopy. Here, we describe the results of the separation and identification of ferredoxins-like Fe-S clusters in amino acid aqueous solutions with pyrrhotite (Fe_(1-x)S) by using liquid chromatography-mass spectrometry (LC-MS).

Our experiments were run in glass vials charged with amino acid containing aqueous solutions and laboratory synthesized pyrrhotite (Fe_(1-x)S). Separation and identification of FeS clusters were performed with the use of ultra-performance liquid-chromatography (UPLC) coupled to UV spectroscopy and electrospray ionization-mass spectrometry (ESI-MS) detection (ACQUITY UPLC and TQD system, Waters).

Serine aqueous solution with pyrrhotite recovered from the reaction show clear yellow color. UV and ESI-MS spectra of the colored solution reveal the formation of Fe-S clusters, very similar to [2Fe-2S] and [4Fe-4S] units of ferredoxins. Proteins that contain ferredoxins are smaller than most other enzymes, having only 55 amino acid units, therefore, have been thought by some to be the most primitive enzymes [4].

Amino acids that include serine have been synthesized under hydrothermal conditions [5]. Pyrrhotite is one of the abundant sulfide minerals around sea-floor hydrothermal systems. The facile synthesis of ferredoxins-like Fe-S clusters from amino acid aqueous solutions with pyrrhotite in the present experiments suggests that these potentially catalytic species will form in natural settings, where reduced hydrothermal fluids with abiotic amino acids pass through metal sulfides-containing ore deposits. Our results lend support to the theory that the Hadean sea-floor hydrothermal systems could have provided an environment for the chemical evolution promoted by ferredoxins-like Fe-S clusters.

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