Methanogenesis is the final process of the anaerobic food web where consortia of microorganism degrade organic material to the catabolic end product methane. 1-2% (ca. $10^9$ tons per year) of the photosynthetically formed plant material on Earth is remineralized in this way. About two-thirds of the produced methane is biologically reoxidized to CO$_2$ and about one third escapes into the atmosphere (acts there as a green house gas). Biochemically, methane formation is based on a stepwise reduction of cofactor-bound and -activated one-carbon compounds. Only a special group of archaeal microorganisms (the methanogens) is endowed with the enzymatic capabilities and the unusual one-carbon carrying and electron donating cofactors required. Our interests are focused on the structural characterization of the participating enzymes in order to understand the mode of cofactor binding and the catalytic mechanism on an atomic level. Both an overview about the enzyme structures analyzed so far and a more detailed description of an unique Fe hydrogenase is presented.