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ARCHAEAL BIOLOGY

Masters of methane

Methane is an important fossil fuel and an atmospheric gas that contributes to global warming. It is released during the fermentation of organic compounds by microorganisms; for example, by communities in the gut or in different environmental populations. The archaea that produce methane, known as methanogens, and the archaea and bacteria that metabolize methane, known as methanotrophs, contribute substantially to the global carbon cycle. Two new studies provide insights into the metabolic pathways of these microorganisms and a third study shows that a similar pathway exists for the oxidation of butane, another natural gas.

Methyl-coenzyme M reductase (MCR) is the key enzyme that catalyses the final step of methanogenesis and is thought to also catalyse the reverse reaction in the first step of anaerobic methane oxidation in archaea. To carry out these reactions, MCR depends on the coenzyme F430. Although the *mcr* gene cluster had been characterized previously, the genes required for the synthesis of the coenzyme F430 were unknown. The biosynthesis of coenzyme F430 is of interest both for the production of biofuels from methane and decreasing methane emission. Zheng *et al.* screened the genomes of methanogenic archaea for genes that encode chelatases, as these enzymes are responsible for the insertion of metal ions into tetrapyrrolic cofactors, such as coenzyme F430. Based on this analysis, the authors identified the coenzyme F430 biosynthesis (*cfb*) gene cluster. Heterologous expression and biochemical analysis of the five enzymes that are encoded in the *cfb* cluster confirmed their capacity to synthesize coenzyme F430.

Anaerobic oxidation of methane requires the concurrent reduction of other substrates. Thus far, nitrate, nitrite and sulfate have been confirmed as such substrates; however, metal oxides, which are abundant in many environments in which *mcrA*-encoding archaea have been found, would be more favourable electron acceptors. Ettwig *et al.* tested the ability of an enrichment culture from the sediment of a freshwater canal to oxidize methane in the presence of different electron acceptors. They showed that the anaerobic methanotrophic archaea in this culture could use nanoparticulate oxidized iron and manganese, which are the environmentally relevant forms of these metals, to support methane oxidation. Analysis of the partial genome from the enriched archaea and from previously sequenced related genomes suggested that these methanotrophs encode metabolic pathways that enable them to switch between different electron acceptors, including oxidized metals.

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In a third study, Laso-Pérez *et al.* tested the ability of an enrichment culture from deep-sea sediment to use butane instead of methane. Both gases are released from the seafloor and are potential growth substrates for resident microorganisms. The enrichment culture, which consisted of a consortium of anaerobic archaea and a sulfate-reducing bacterium, could indeed oxidize butane and contained none of the butane metabolic pathways that were previously identified in bacteria. Instead, the cultured archaea highly expressed an enzyme that was closely related to MCR and produced butyl-coenzyme M, the analogous metabolite to methyl-coenzyme M, which is produced in the first step of methane oxidation by MCR. The archaea also expressed the downstream enzymes that are required for complete butane oxidation. Furthermore, genetic analysis of previously sequenced environmental archaea suggested that this new butane-oxidizing pathway is widespread.

These three studies confirm the importance of archaea in global biochemical cycling and highlight their metabolic adaptation to the diverse environments that they inhabit.

Ursula Hofer

ORIGINAL ARTICLES Zheng, K. *et al.* The biosynthetic pathway of coenzyme F430 in methanogenic and methanotrophic archaea. *Science* **354**, 339–342 (2016) | Ettwig, K. F. *et al.* Archaea catalyze iron-dependent anaerobic oxidation of methane. *Proc. Natl Acad. Sci. USA* http://dx.doi.org/10.1073/pnas.1609534113 (2016) | Laso-Pérez, R. *et al.* Thermophilic archaea activate butane via alkyl-coenzyme M formation. *Nature* http://dx.doi.org/10.1038/nature20152 (2016)