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ture dependencies of the magnetic neutron scattering at these incommensurate wave vectors, which may be stronger in a non-Fermi liquid.

The second striking feature of this experiment is that significant magnetic scattering at these incommensurate wave vectors or nearby exists for a range of frequencies. This scattering means that these magnetic excitations are not elementary, but are composite objects. Spin-flip neutron scattering couples to spin-1 excitations, composite or elementary, because neutron scattering flips a spin of $^1/_2$, from up to down or from down to up. If the excitation is elementary, for example, a spin wave, a given momentum transfer will lead to a given frequency or energy transfer and not a range of frequency transfers. Thus, it is unlikely that these magnetic fluctuations give rise to pairing in a simple way. These excitations could arise from a nearby quantum critical point, but the theory of the quantum critical point (*3*, *5*) has to be generalized appropriately to include incommensurate fluctuations.

To me, the very same observations that have led Aeppli *et al.* to suspect quantum criticality seem to negate its existence. They have found that the amplitude of the magnetic scattering rises strongly as the temperature is lowered, and the widths of peaks at the incommensurate momenta scale in a simple way, where frequency and temperature can be interchanged almost exactly. So far, so good; these are indeed the characteristics of a quantum critical point. But if we look more closely, we discover that in the limit as frequency and temperature go to zero, the length scale is finite, about 30 Å, instead of infinity. So, in the zero-temperature limit, we are in a quantum (as opposed to thermally) disordered state (*3*, *5*). This state would imply an energy scale of order 6 meV (70 K in temperature units) or greater [in this estimate, I have used the only quoted scale, approximately equal to $(1/3)Ja$]. For quantum criticality as we understand it, scattering should disappear below this energy transfer. This does not seem to be the case, and it is not contained in the functional form of the scattering function chosen by the authors.

There are many avatars of quantum magnetism, including spin liquid, magnetic stripe phases, and quantum critical points. It remains to be seen if any of them are useful in solving a problem that has occupied a sizable fraction of the physics community over the last decade.

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BIOCHEMISTRY

Methane: Small Molecule, Big Impact

James G. Ferry

Why so much interest in methane? Each year microbes produce about 400 million metric tons of this gas, a huge mass that has a profound effect on humankind. Methanogenesis occurs in vast natural and human-made environments, but only when the conditions are anaerobic. This situation can be found inside animals (the rumen of cows or insect hindguts), in watery landscapes (natural wetlands or rice paddies), or at other human-made sites (sewage digestors, landfills, and biogas generators). Indeed, the estimated 1% annual increase in global methane is mainly attributed to human activities (*1*).

Methane-producing microbes are phylogenetically distinct from all other prokaryotes and eukaryotes. They make several novel cofactors and enzymes, and their existence has led to the present three-domain concept of phylogeny (Archaea, Bacteria, and Eukarya) (*2*). On page 1457 of this issue, Ermler and colleagues report a milestone for methane aficionados—the crystal structure of methyl–coenzyme M(CoM) reductase, a key enzyme common to all methane-producing pathways (*3*). This is the third structure reported for nickel-containing enzymes, following those of urease (*4*) and hydrogenase (*5*).

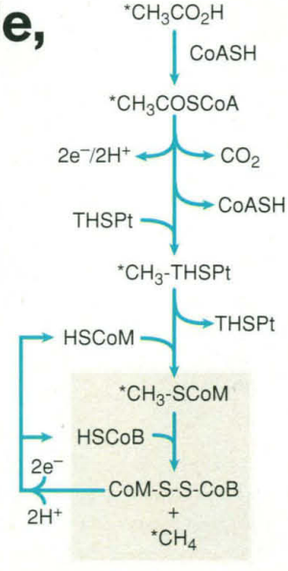

Fig. 1. Pathway for the conversion of acetate to methane by the methanoarchaea. The box highlights the reaction catalyzed by methyl-CoM reductase.

Most methane diffuses from the anaerobic to the aerobic biosphere where oxygen-requiring microbes oxidize it to carbon dioxide; thus, the microbial production and consumption of methane is a significant component of the global carbon cycle. In addition, each year about 45 million metric tons of methane escapes into the troposphere. A molecule of methane is far more effective than a molecule of carbon dioxide in absorbing and radiating energy back to Earth. Thus, methanogenesis contributes significantly to the greenhouse effect.

Production of methane requires a food chain of at least three interacting metabolic groups of obligately anaerobic microbes (see Fig. 2, next page) (*6*). The fermentative group decomposes cellulose and other complex molecules to volatile carboxylic acids (mainly acetate) and hydrogen gas. Only acetate, carbon dioxide, hydrogen, and formate are substrates for the methanoarchaea; thus, the hydrogen-producing acetogenic group is necessary to further metabolize butyrate and propionate. The methanoarchaea use two separate pathways in which methane derives from either the methyl group of acetate (reaction 1) (see Fig. 1) or the reduction of carbon dioxide with electrons from hydrogen or formate (reactions 2a and 2b).

$$CH_3COO^- + H^+ \bullet CH_4 + CO_2 \quad (1)$$

$$CO_2 + 4H_2 \bullet CH_4 + 2H_2O \quad (2a)$$

$$4HCO_2H \bullet 3CO_2 + CH_4 + 2H_2O \quad (2b)$$

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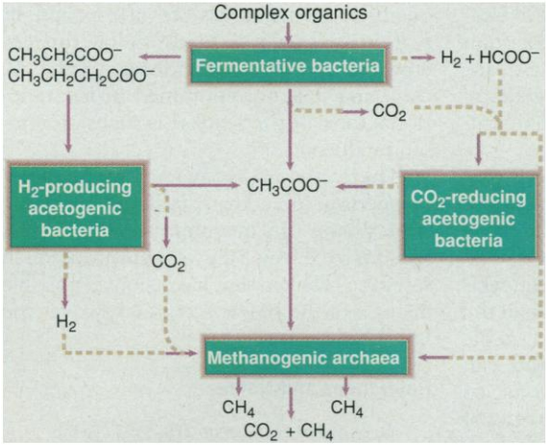

Fig. 2. Microbial food chain. Three types of microbes are required for the decomposition of complex biomass to methane and carbon dioxide. The principle intermediates and the major route of carbon flow is shown in red.

Most of the methane in anaerobic food chains is derived from the methyl group of acetate (Fig. 1) (6). In methanosarcina (7), acetate is activated to acetyl–coenzyme A (CoA), which is cleaved by the nickel-containing CO dehydrogenase/acetyl-CoA synthase, yielding enzyme-bound methyl and carbonyl groups.

The subsequent steps all require unusual coenzymes and cofactors with novel structures only found in the methanoarchaea (8). After cleavage, the methyl group of acetate is transferred to the cofactor tetrahydrosarcinapterin (THSPt) and then from CH_3-THSPt to coenzyme M (HS-CoM). The CH_3-S-CoM is reductively demethylated to methane by methyl-CoM reductase, which uses coenzyme B (HS-CoB) as an electron donor. An additional product of the reaction catalyzed by methyl-CoM reductase is the heterodisulfide CoM-S-S-CoB, which is reduced by heterodisulfide reductase to regenerate the reactive sulfhydryl forms of the coenzymes. The reduction of CoM-S-S-CoB is accomplished with an electron pair originating from oxidation of the carbonyl group of acetyl-CoA.

In the other pathway (reactions 2a and 2b), carbon dioxide is reduced to the methyl level with hydrogen or formate by use of still other novel cofactors unique to the methanoarchaea (8). The methyl group is attached to tetrahydromethanopterin (THMPt), a structural and functional analog of THSPt. Conversion of CH_3-THMPt to methane is the same as for the acetate pathway except the pair of electrons for reduction of CoM-S-S-CoB originate from the oxidation of hydrogen or formate. Thus, methyl-CoM reductase is a key enzyme in both pathways.

The aa'bb'gg' methyl-CoM from the CO_2-reducing *Methanobacterium thermoautotrophicum* contains two molecules of an unusual nickel-porphinoid prosthetic group F_{430}. What does the new crystal structure tell us about the catalytic mechanism and the functions of the novel F_{430}, HS-CoM, and HS-CoB structures? Each F_{430} is positioned at the bottom of identical narrow channels formed by residues from the aa'bg or a'ab'g' subunits; however, separation of the F_{430} molecules by about 50 Å clearly marks two independent catalytic sites. The high-resolution crystal structures with either HS-CoM and HS-CoB or CoM-S-S-CoB bound to the enzyme allowed Ermler *et al.* to propose a detailed and highly plausible mechanism largely consistent with previous studies. The protein environment and arrangement of the coenzymes relative to F_{430} suggests a nucleophilic attack of Ni(I) on CH_3-S-CoM and formation of an unusual [F_{430}]Ni(III)-CH_3 intermediate. The Ni(III) oxidizes HS-CoM, producing a thiyl radical intermediate. Finally, protonolysis releases methane, and the thiyl radical couples with -SCoB to form the heterodisulfide. Evidence for the proposed carbon-nickel bond is eagerly awaited. Such an intermediate has only been proposed for one other enzyme, found in a CO_2-reducing acetogenic anaerobe (9, *10*).

The Archaea domain is filled with diverse microbes with uncommon metabolic activities, portending uncommon structures. Two other crystal structures are reported for enzymes from the methanoarchaea; one of these, a novel class of carbonic anhydrase, displays an unusual protein folding pattern (*11*). On the basis of this limited sample, one can expect many more novel proteins. These discoveries will surely be expedited by the recently completed sequence of the genomes from the methanoarchaeons M. *thermoautotrophicum* (*12*) and *Methanococcus jannaschii* (*13*). Less than half of the predicted protein coding regions can be assigned a role from database sequences. These are truly exciting times for microbial structural biology.

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ECOLOGY

Marine Managers Look Upstream for Connections

John C. Ogden

The Florida Keys are the focus of a major national effort to manage a large land-sea area. In response to drastic declines in coral reefs and fishes and to create a buffer zone from shipping, Congress in 1990 created the 9500-km^2 Florida Keys National Marine Sanctuary. Although it is now exceeded in size by the Monterey Bay National Marine Sanctuary, its unique management plan includes virtually every conceivable human interaction with the marine environment. A state-federal partnership implementing this pioneering effort at coastal marine resources management was signed on 1 July.

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Over the 6 years of its development, by far the most contentious element of the management plan was the no-take marine reserves, in which all fishing and collecting is banned. These reserves are widely perceived as the best option for conservation of marine biological diversity in shallow waters, particularly in the tropics, where most organisms live in intimate association with specific sites (*1*).

A portion of a coral reef, even if only a few hectares in size, that is protected from human disturbances will develop larger populations of organisms composed of larger individuals within periods as short as a few years (*2*). In the Florida Keys, where coral reefs are heavily visited by tourists, this fact alone argues strongly for the establishment of reserves. People like to see big fish. In eco-