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COMMENT

Do methanogenic archaea cause reductive pyrite dissolution in subsurface sediments?

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Pyrite (FeS_2) is the most abundant iron-sulfur mineral in the seabed. A strong thermodynamic and kinetic drive makes pyrite the main terminal product of reduced iron and sulfur transformations under sediment conditions. One of the main pathways of pyrite formation is the oxidation of iron sulfide by hydrogen sulfide [1]:

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

The process may be enhanced by methanogenic archaea that effectively consume H_2 for the reduction of CO_2 to CH_4 [2]. A similar enhancement may be caused by H_2 oxidation by sulfate reducing bacteria in the sulfatic sediment.

Pyrite is stable at low temperature in the absence of oxygen and oxidative weathering, and its formation history can therefore be recorded back in sedimentary rocks over geological timescales [3, 4]. The burial of pyrite and organic matter in marine sediments provides an important global sink for reducing power, of importance for the oxidation state of Earth's surface. Below a sub-seafloor depth where potential oxidants, such as metal oxides or sulfate, have been exhausted, the buried organic matter continues to be slowly degraded by microorganisms. Methane and CO_2 are thereby the ultimate products of organic carbon mineralization. Pyrite, in contrast, may undergo slow recrystallization but remains a stable end-product of iron-sulfur diagenesis in the deep, anoxic and methanic sediment.

A new study by Payne et al. [5] questions that last statement. The authors performed batch culture experiments with two species of methanogenic archaea, *Methanococcus voltae* and *Methanosarcina barkeri*, using formate, methanol or acetate as substrates. FeS_2 or mackinawite ($FeS_{(mack)}$) was provided as the only source of iron and sulfur. The fine-grained FeS_2 was either laboratory-synthesized according to Berner [6] or was produced by grinding pyrite crystals. The striking observation was that the methanogens apparently performed a reductive dissolution of the FeS_2. The released iron and sulfur were used for the synthesis of archaeal cell biomass. The dissolution required physical contact between cells and minerals and proceeded even by 1 mM free sulfide in the medium. For comparison, it would require sub-nM concentrations of both Fe^{2+} and H_2S to bring pyrite to dissolution in a purely chemical system [7]. The authors did not suggest a mechanism for the reductive pyrite dissolution but indicated that it may have played a role for the iron and sulfur cycles through Earth's geological history. In the following, I will briefly consider both of these aspects.

The formation of pyrite is strongly exergonic in anoxic sediments. Therefore, the reductive dissolution is expectedly an energy-requiring process. In the experiments of Payne and coworkers, the dissolution served the formation of cellular biomass, including the synthesis of proteins and complex cofactors. The requirement for physical contact between cells and FeS_2 grains indicated that the reductive dissolution involved an electron transfer from the methanogens to the mineral surface. Such an electron transfer is known from the syntrophy between bacteria and methanogens, whereby heterotrophic bacteria give off electrons to a mineral surface while methanogenic archaea receive the electrons for the reduction of CO_2 to CH_4. The minerals may be iron sulfides, such as mackinawite, greigite (Fe_3S_4) or FeS_2, or they may be magnetite (Fe_3O_4) or black carbon, all of which can function as electric conductors and capacitors [8–10].

The transfer of electrons from bacteria to minerals generally involves outer-membrane multiheme *c*-type cytochromes (OMCs) and electrically conductive pili [9]. It is less known how methanogens receive or give off electrons, but some *Methanosarcina* species have OMCs, and methanogens have appendages that serve attachment. This may have enhanced the observed formation of methanogenic biofilms on pyrite surfaces, and perhaps enabled an electron transfer, in the experiments by Payne et al. [5]. However, an important aspect of the inter-species electron transfer from bacteria to methanogens via minerals is that the minerals are not chemically altered but only serve as electrical conduits for energy metabolism. In contrast, the reductive dissolution of pyrite had the function to supply Fe and S for biosynthesis, presumably at the expense of catabolic energy.

If pyrite indeed serves as a source of Fe and S for methanogens in the sub-seafloor, is it then of quantitative significance for the sedimentary iron and sulfur cycles? I will use an example from our studies in the Baltic Sea (Bornholm Basin, Station BB02) to illustrate this, based on the following simple arguments:

a) the growth yield of methanogens under optimal conditions in pure culture is ca 2 g dry biomass per mol CH_4 produced [11, 12];

b) the sulfur content of methanogens is about 1% by weight of the dry biomass, i.e., 0.02 g S or 0.6×10^{-3} mol S is assimilated per mol CH_4 produced [13];

c) the highest rates of methanogenesis just beneath the sulfate zone in the Baltic Sea sediments are about 10^{-9} mol CH_4 cm^{-3} d^{-1} [14];

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d) assuming that the methanogens have optimal growth yield, their rate of S assimilation for biosynthesis is then: $10^{-9} \times 0.6 \times 10^{-3} = 0.6 \times 10^{-12}$ mol S cm^{-3} d^{-1} $= 2 \times 10^{-10}$ mol S cm^{-3} yr^{-1};

e) pyrite accumulates down through the sulfatic zone and into the upper methanic zone in these sediments at a rate of 4×10^{-7} mol cm^{-3} yr^{-1} [15], which is three orders of magnitude faster than its potential dissolution by biosynthesis of methanogens;

f) at the peak of methanogenesis rates, located at 80 cm depth in the sediment deposited 900 years ago, the pyrite concentration is 6×10^{-4} mol S cm^{-3}. A complete turnover of pyrite by reductive dissolution would therefore take $>10^5$ years.

In conclusion, even in the unlikely case that pyrite served as the only Fe and S source for methanogens and these had optimal growth yield, reductive pyrite dissolution would not be detectable in the iron and sulfur budgets of these marine sediments. Sediments further offshore than the example given here will tend to have lower rates of both pyrite formation and methanogenesis, thereby maintaining this general conclusion. Furthermore, in those marine sediments where most methanogenesis takes place, other iron-sulfur minerals are generally present, albeit at lower concentration, such as mackinawite, greigite, marcasite, or iron-sulfur nano-clusters [7]. Pyrite would therefore seem to be the least attractive source of iron and sulfur for biosynthesis today.

For much of Earth history, however, the sedimentary sulfur cycle was completely different because of the lack of atmospheric oxygen in the early Earth (>2.2 Ga). This meant that sulfate was not abundant in the ocean and oxic dissolution of pyrite did not occur. The only currently known route for pyrite dissolution was through the anoxic Fe(III) pathway. One interesting possibility of Payne et al.'s results is that they are observing the vestiges of a relic microbial metabolism from ancient time, when reductive pyrite dissolution may have been a more significant assimilatory sulfur and iron resource.

Microbiologically, the observation that pyrite may be reduced by methanogens for biosynthetic purpose is very interesting in terms of the processes of electron transfer and chemical alteration. Geochemically, it is intriguing how a highly stable iron-sulfur mineral like pyrite may be attacked and dissolved anaerobically by microorganisms. Future studies should focus on the nature of the FeS_2 formed synthetically in the laboratory and the surface properties of highly crystalline pyrite after grinding into a powder. The new results by Payne et al. [5] also call for more detailed studies of the electron transfer between archaea and conductive or semiconductive minerals. Such a conductive-particle-mediated interspecies electron transfer (CIET; [16]) could perhaps also be involved in the syntrophy between anaerobic methane-oxidizing archaea and sulfate reducing bacteria in the sub-seafloor.

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COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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