The Role of Methanogens in the Preservation of Organic Matter in Smectite Mineral

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Organic matter burial in sediments is largely associated with clay minerals, especially, expandable clay minerals, and can be preserved over geological time. However, microbial activity can possibly influence this association and release organic matter from clay minerals via reductive or oxidative dissolution of clay minerals. In this study, the relationship between bioreduction of structural Fe(III) in smectite and organic matter release from the smectite structure was investigated. Two methanogens: mesophilic *Methanosarcina mazei* and thermophilic *Methanothermobacter thermautotrophicus* were selected to reduce structural Fe(III) in nontronite (an iron-rich smectite, NAu-2) that was intercalated with 12-Aminolauric acid (ALA), a model organic compound. As a comparison, sodium dithionite was used to chemically reduce structural Fe(III) in the same mineral. The reduction extents and rates were determined by wet chemistry and the amount of organic matter release due to reduction was determined by total organic carbon analysis. The effect of Fe(III) reduction on methanogenesis was determined by monitoring time-course methane production in comparison with no nontronite control. Reduction products were characterized by X-ray diffraction, infrared spectroscopy, and scanning electron microscopy. Our results indicated that the amount of organic matter release depended on the extent of Fe(III) reduction in nontronite. A low reduction extent of bioreduction (<30%) resulted in little organic matter release, whereas, a nearly complete chemical reduction by sodium dithionite released all intercalated ALA. The reductive dissolution of nontronite was a main mechanism for ALA release from the nontronite structure. Because biological reduction should be much more prevalent than chemical reduction in natural environment, the results of this study demonstrated that organic matter preserved within smectite structure should not be disturbed and released by microbial activities.