Sulfidogenesis for metal removal and recovery from metalliferous oil shale

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Introduction

In ores like black shale, including **Estonian metalliferous oil shale** (MOS, previously graptolite argillite) a considerable part of metals (V, Ni, Mo, Re) are trapped into organometallic complexes. With traditional acidic bioleaching these metallo-porphyrins are poorly biodegradable resulting in extracting only metals present in ore as sulfides[1]. Bioleaching at neutral pH creates organic acids that can hinder the growth of autotrophic microorganisms. Organic compounds and metals left in the waste are hazardous to environment and wasted as a source of energy. Our previous studies have shown that heterotrophic facultative anaerobes and methanogenic archaea of MOS indigenous microbial community ARGCON5 (CELMS No EEUT ARGCON5) are able to decompose the organic matter of metalliferous oil shale under anaerobic conditions and at pH 7 resulting in generation of energetically valuable methane with releasing metals, like Co, Ni, Mo, Zn.[2] Toxic intermediates (NH_3, H_2, H_2S) are transformed into harmless end products (N_2, H_2O, S_0).

Question

What is the mechanism underlying the simultaneous methanogenesis and release of metals from metalliferous oil shale into the aqueous phase?

Figure 1. Pressure increase measurement with OxiTop system (WTW, Germany).

Hypothesis: sulfidogenesis for metal removal and recovery

Half reaction : $H_2 \rightarrow 2e^- + 2H^+$
Half reaction : $S + 2e^- \rightarrow S^{2-}$
Global reaction : $S + H_2 \rightarrow S^{2-} + 2H^+$

Half reaction : $4H_2 \rightarrow 8e^- + 8H^+$
Half reaction : $SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O$
Global reaction : $SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O$

$H_2S + Me^{2+} \rightarrow MeS\ (s) + 2H^+$
where Me^{2+} = metal, such as **Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}**

$C_3H_8O_3 + 7SO_4^{2-} \rightarrow 7H_2S + 12CO_2 + 16H_2O$
$C_3H_8O_3 + 7S + 3\ H_2O \rightarrow 7H_2S + 3CO_2$

Conclusions

Based on the results, the hypothesis on metal removal and recovery by **sulfidogenesis** – oxidation of simple organic compounds or H_2 by microorganisms under anaerobic conditions, generating sulfide from the reduction of sulfur compounds was posed.[5] Depending on pH, the metals released from metallo-porphyrins can form either soluble or insoluble metal sulfides.

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Materials and methods

Methanogenesis of argillite indigenous community ARGCON5 was monitored by pressure increase with OxiTop system (**Fig. 1**); The taxonomical content of the community in inoculum, exponential phase and stationary phase was determined with sequencing on Illumina MiSeq platform targeting v4 and v5 regions with the primer pair of 515F and 926R[3]. Generated OTU tables were classified using Silva database[4] with a threshold of 97% and further processed with QIIME (v. 1.9.1). Metal content was tested by ex-situ analysis of supernatant from cultivation media of experiments using ICP-MS.

Results

In comparison to hydrolytic bacteria, the abundance of sulfur- and sulfate-reducing bacteria increased remarkably in the course of anaerobic bioleaching of MOS with dominating genera being uncultured *Thermoanaerobacteraceae, Desulfotomaculum, Lutispora and Desulfitomaculum* (**Fig. 2**)

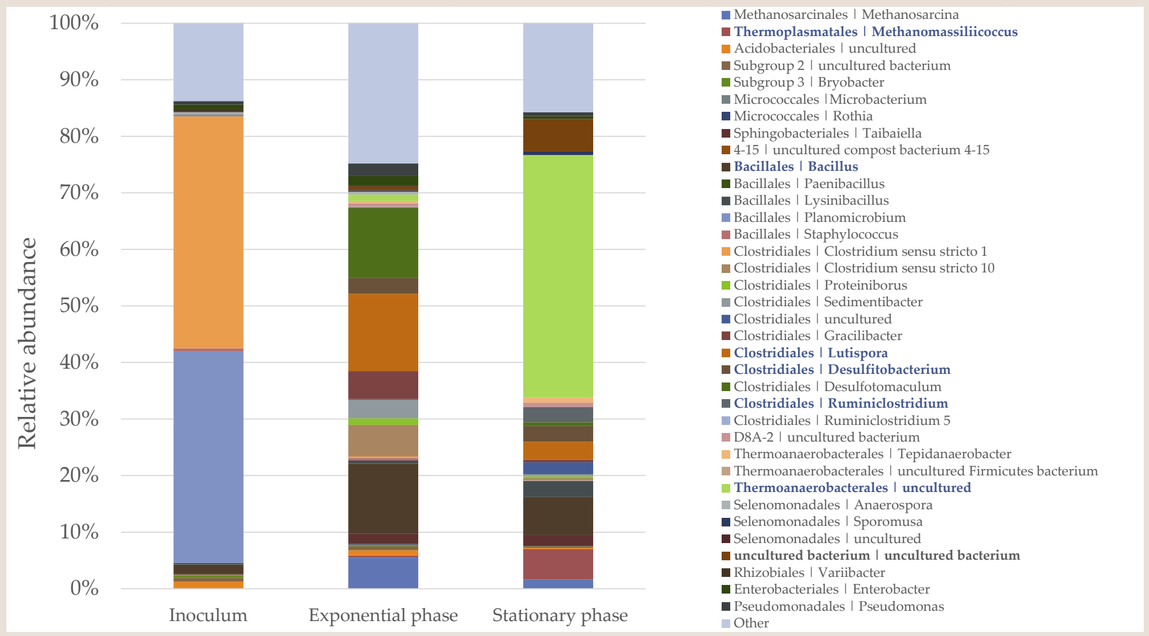

Figure 2. Species detected by pyrosequencing from the communities in experiment with inoculum ARGCON5 at diferent growth stages targeting v4 and v5 regions with the primer pair of 515F and 926R3; percentage of different taxa (operational taxonomic unit, OTU).

On the other hand, with some metals (**Li, V, Co, Ni, Mo**) their content in the liquid phase was the highest in exponential phase (**Fig. 3**).

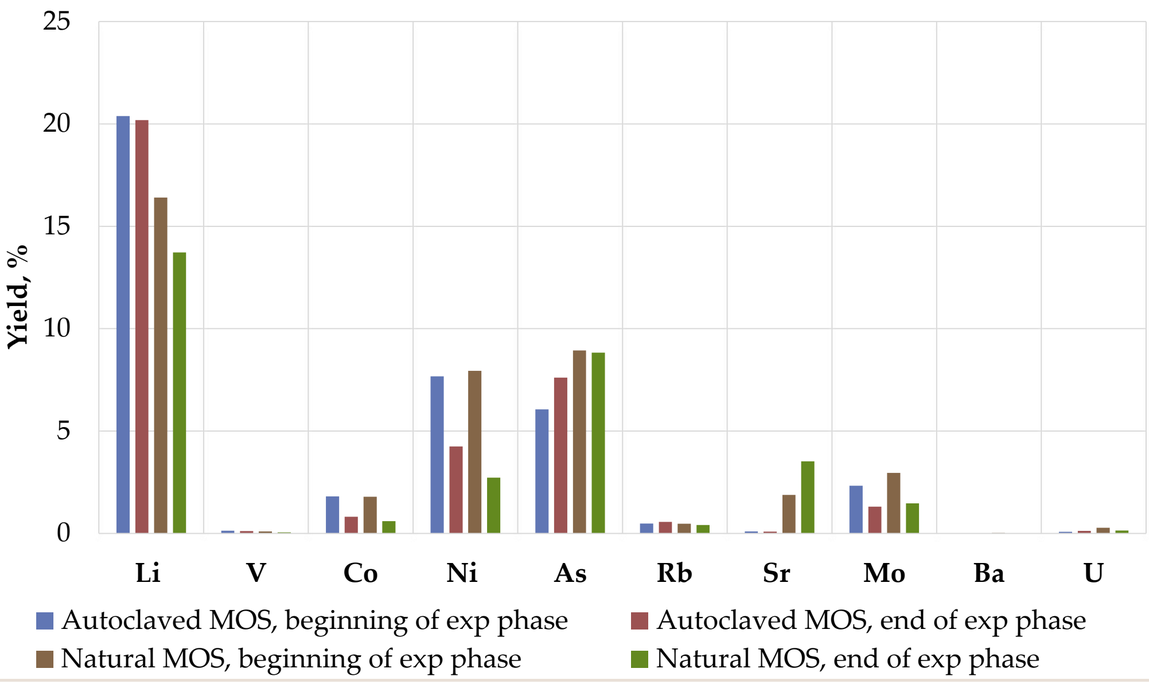

Figure 3. Metal yields in the bioleaching experiment of MOS with inoculum ARGCON5.

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