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Biomineralization: Nanoparticle Synthesis and Its Geochemical Implication

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1. Introduction

Microbial metal reduction plays an important role in the cycling of Fe and Mn and organic matter in natural environments. Many metal-reducing bacteria can reduce a variety of metals and radionuclides including U(VI), Tc(VII), Co(III), Cr(VI), As(V), and Se(VI) as well as degrade petroleum hydrocarbons. Metal-reducing bacteria participate in a variety of geochemical processes such as weathering and formation of minerals, formation of ore deposits, and cycling of organic matter. Metal-reducing bacteria can precipitate or transform amorphous/poorly crystalline or crystalline Fe(III) oxides into crystalline iron phases such as magnetite (Fe_3O_4), siderite ($FeCO_3$), vivianite [$Fe_3(PO_4) \cdot 2H_2O$], and maghemite(Fe_2O_3).

Metal-reducing bacteria that grow under diverse environmental conditions. Their habitats may be cold polar seas, deep-sea sediments, deep subsurface sedimentary rock, highly saline lakes, carbonate springs, inter-tidal flat sediments, groundwater, or soda lakes. The objective of this presentation summarizes recent research results on metal reduction and biomineralization by psychrophilic, mesophilic, thermophilic, and alkaliphilic metal-reducing bacteria isolated and/or enriched from diverse environments.

2. Metal-Reducing Bacteria from Diverse Environments

Table 1 shows thermophilic, mesophilic, psychrophilic, and alkaliphilic metal-reducing bacteria isolated and/or enriched from a variety of environments such as deep marine sediments, sea water near hydrothermal vent, deep subsurface environments, inter-tidal flat sediments, groundwater, and a leachate-pond containing high levels of salt and boric acid.

Table 1. Metal-reducng bacteria isolated and enriched from diverse environments

Isolates	Growth condition	Site Description	Geology/ Sample Type	Genus & species	References
TOR-39	Thermophilic (40-75°C)	Taylorsville Triassic Basin, Northern Virginia	Shale, Siltstone, and Sandstone	*Thermo-anerobacter ethanolicus*	Liu et al., 1997
X513 X514 X561	Thermophilic (40-75°C)	Piceance Basin Wasatch Formation, Western Colorado	Cemented sandstone; cross-bedded siltstone and shale	*Thermo-anerobacter ethanolicus*	Roh et al., 2002

PV-4	Psychro-tolerant (0-37°C)	Naha vents, Coast of Hawaii	Iron-rich microbial mat associated with a hydrothermal vent	*Shewanella Loihica*	Roh et al., 2006
W3-6-1 W3-7-1	Psychro-tolerant (0-37°C)	Deep Pacific Ocean Marine Sediments	Marine sediment	*Shewanella pealeana*	Stapleton et al., 2005
QYMF	Alkaliphilic pH = 8.0 - 11	Boron-rich sites at the U. S. Borax mine in Borax, CA	Leachate-pond containing high level of salt (~12 % NaCl) and boric acid (2-8 g/L B) at pH 9-10	*Alkaliphilus transvaalensis*	Ye et al., 2004
Haejae-1	Mesophilic	Inter-tidal flat sediments, Haejae, Chonnam Province	Inter-tidal flat sediments	*Clostridium sp.*	Kim et al. (in prep.)
Kaeri-1	Mesophilic	Groundwater from KAERI Underground Research Tunnel, Daejeon	Groundwater	*Pseudomonas sp.* *Desulfuromonas michiganensis*	Oh *et al.* (in prep.)

3. Metal Reduction and Biomineralization

Metal-reducing bacteria isolated and/or enriched from diverse environments have the capacity to reduce various metals and radionuclides (Table 2), which can lead to immobilization of these contaminants in subsurface environments. Thermophilic microorganisms isolated from Taylorsville and Piceance Basin were found to reduce Co(III), Cr(VI), Fe(III), Mn(IV), and U(VI) to reduced species such as Co(II), Cr(III), Fe(II), Mn(II), and UO_2 at temperatures up to 75°C(Zhang et al., 1996; Roh et al., 2002). Mesophilic, psychrotolerant, and alkaliphilic metal-reducing bacteria were also able to reduce Co(III), Cr(VI), Fe(III), Mn(IV), As(V), and Se(VI) to reduced species such as Co(II), Cr(III), Fe(II), Mn(II), As(III), and Se(0) (Roh et al., 2006, 2007, 2008; Stapleton et al., 2005; Ye et al., 2004).

Table 2. Metal reduction and mineral formation by thermophilic, mesophilic, psychrotolerant, and alkaliphilic metal-reducing bacteria

Isolates/ Enrich-ments	Growth temp. range	Electron donors	Electron acceptors	Minerals formed
TOR-39 X513 X561	40-75°C	Lactate Pyruvate Acetate Formate Glucose	Fe(III) Mn(VI) U(VI) Cr(VI) Co(III)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Maghemite (Fe_2O_3) Uraninite (UO_2) Rhodochrosite ($MnCO_3$)
X514	40-75°C	Lactate Pyruvate Acetate Formate Glucose Hydrogen	Fe(III) Mn(VI) U(VI) Cr(VI) Co(III)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Rhodochrosite ($MnCO_3$)
PV-4 W3-6-1 W3-7-1	0-37°C	Lactate Formate Pyruvate Hydrogen	Fe(III) Co(III)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Vivianite [$Fe3(PO_4)_2 \cdot 8H_2O$]

QYMF	25°C, pH up to 11	Lactate Acetate Hydrogen	Fe(III) Co(III) Cr(VI)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]
Haejae-1	~25°C	Lactate Formate Glucose Pyruvate	As(V) Fe(III) Cr(VI) Mn(IV)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]
Kaeri-1	~25°C	Lactate Formate Glucose Pyruvate	As(V) Fe(III) Cr(VI) Mn(IV) Se(VI)	Magnetite (Fe_3O_4) Siderite ($FeCO_3$) Rhodochrosite ($MnCO_3$) Se(0)

The thermophilic bacteria were able to reduce several Fe(III)-species including Fe(III)-citrate, Fe(III)-EDTA, and poorly crystalline Fe(III)-oxides using acetate, lactate, formate, glucose, pyruvate, and hydrogen as the electron donors. The mesophilic, psychrotolerant, and alkaliphilic metal-reducing bacteria were also able to reduce the Fe(III)-species using lactate, formate, pyruvate, and hydrogen as the electron donors.

Table 2 shows mineralogical characterization of crystalline minerals formed by the metal-reducing bacteria. The thermophilic, mesophilic, and psychrotolerant metal-reducing bacteria were capable of reducing poorly crystalline Fe(III) oxides and transform them into nm-sized magnetite (Fe_3O_4) crystals. The metal-reducing were capable of reducing poorly crystalline Fe(III) oxides and transform them into Fe(II) containing minerals such as siderite ($FeCO_3$) under H_2/CO_2 atmosphere or using HCO_3^- in the media. The thermophilic bacteria reduced uranyl carbonate [$UO_2(CO_3)_3^{4-}$] and MnO_2 and formed sparingly soluble minerals including uraninite (UO_2) and rhodocrosite ($MnCO_3$). Mesophilic, psychrotolerant, and alkaliphilic bacteria precipitated vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] with PO_4 (25mM) containing media when soluble Fe(III), Fe(III)-citrate and Fe(III)-EDTA, were used as the electron acceptor. Vivianite formation was only observed when soluble Fe(III), Fe(III)-citrate and Fe(III)-EDTA, was used as the electron acceptor.