Accumulation of rare earth elements by siderophore-forming *Arthrobacter luteolus* isolated from rare earth environment of Chavara, India

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In this study, *Arthrobacter luteolus*, isolated from rare earth environment of Chavara (Quilon district, Kerala, India), were found to produce catechol-type siderophores. The bacterial strain accumulated rare earth elements such as samarium and scandium. The siderophores may play a role in the accumulation of rare earth elements. Catecholate siderophore and low-molecular-weight organic acids were found to be present in experiments with *Arthrobacter luteolus*. The influence of siderophore on the accumulation of rare earth elements by bacteria has been extensively discussed.

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1. Introduction

Rare earth elements (REEs) include the 14 lanthanides; cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Moreover, lanthanum (La) belongs to the REEs; often yttrium (Y) is included as well. Their average abundances in the earth's crust vary from 66 μg g^{-1} for Ce, 40 μg g^{-1} for Nd, and 35 μg g^{-1} for La to 0.5 μg g^{-1} for Tm, disregarding the extremely rare Pm. Several of REEs are not very 'rare' and accurately dispersed in a variety of forms, especially as accessory minerals in granites, pegmatites, gneisses and related common types of rocks (Fessenden and Fessenden 1986). The abundance of Ce is almost the same as the environmentally much more studied elements such as Cu and Zn; the scarcest lanthanides, Lu and Tm, are actually more abundant in the earth's crust than Cd and Se. They all usually form trivalent cations, although the divalent or the tetravalent oxidation state is known for most of them in chemical compounds. The effective ionic radius of the trivalent ions decreases gradually from La^{3+} (103.1 pm) to Lu^{3+} (86.1 pm).

There are developments on profiling primary and secondary soil minerals with REEs, concentrations of REEs in surface soils, factors influencing adsorption, solubility and transport in soils, including weathering and transformations of REE minerals, and vertical distribution in soil profiles (Tyler 2004). Weathering and leaching sequences are partly controlled by soil microorganisms and the production, dissolution, movement and precipitation of organic compounds. Various microorganisms have a high capacity of biosorption of REE ions, such as Gd^{3+} (Andres *et al*. 2000; Emmanuel *et al*. 2010).

Bacteria and fungal hyphae may cover mineral surfaces of REE phosphates and both plant roots and microorganisms are often good producers of oxalic acid/oxalate, a highly efficient solubilizer of phosphate minerals. Other

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explanations for enhanced metal release may be siderophore complexation at the mineral surface and the subsequent release of the soil solution or uptake by the cell. In a study of the soil bacterium *Arthrobacter* sp. (Brantley *et al*. 2001), heavy REEs were markedly fractionated, the uptake increasing from Ho to Lu.

The great diversity of organic compounds produced by microorganisms in litter decomposition is of great importance to the behaviour of REEs in soils. Soil organic matter (OM) has many negatively charged groups per unit dry weight and, thereby, a high capacity to absorb or chelate divalent and trivalent cations. Because organic compounds such as polycarboxylic and amino carboxylic acids are known to form very stable complexes with the REE, organic acids and siderophores may drastically increase REE mobility during fluid–rock interaction produced by microbes, perhaps changing REE distribution patterns.

The extreme specificity of metal–siderophore complexes formed (Morel and Hering 1993) would be very Fe(III) specific. Indeed, these 'extra' siderophores may therefore be involved in solubilization of metals other than Fe from soil minerals.

Beveridge and Fyfe (1985) summarized investigation of metal uptake by living cells in particular; gram-positive bacteria such as the *Arthrobacter* studied have a great ability to sequester metals in their cell wall. They argued that the first step is complexation at anionic surface sites, and the second step is precipitation of metal phases in the cell wall (Urrutia *et al*. 1992). Therefore, siderophore complexes are thought to be transported across the membrane by specific membrane proteins in an ATP-requiring process. Fe release from the siderophore may occur at the membrane or within the cytoplasm (Guerinot 1994). In order to study the accumulation of REE in siderophore-forming *Arthrobacter luteolus*, the present investigation was carried out.

2. Materials and methods

2.1 *Sample collection and isolation of bacterial strain*

The soil samples rich in REEs and also enriched with numerous microorganisms were collected in sterile polythene cover and brought to the laboratory in an icebox to avoid microbial contamination and proliferation during transport.

2.2 *ICP-MS analysis of soil*

An adopted method was used for the analysis of REEs in the soil samples (Date and Gray 1985). The known weight of processed sterile rare earth soil sample collected from Chavara (Quilon District, Kerala, India) was analysed using ICP-MS (Perkin Elmer Sciex ELAN DRC II).

2.3 *Bacterial identification*

The molecular and microbiological characteristics and accumulation study of the soil sample were carried out. Morphologically dissimilar and well-isolated colonies were randomly selected and streaked onto the nutrient agar medium plates to obtain pure cultures. The bacterial strain isolated from soil samples were identified up to generic level by employing the standard morphological and biochemical characteristics described in Bergey's manual of systemic bacteriology (Holt *et al*. 1994).

2.4 *DNA isolation*

Tris-EDTA (10 mM Tris-HCl, 1 mM EDTA; pH 8) buffer and lysozyme (10 mg/mL) were added in the pelleted cells of the dominant isolate and incubated for 30 min at room temperature. SDS and Proteinase K (10 U/μL) were added and incubated at 55°C for 2 h. DNA was extracted with phenol, chloroform and iso-amyl alcohol, and was precipitated with ethanol and dissolved in TE buffer (Wawer and Muyzer 1995).

2.5 *PCR amplification, cloning and sequencing of 16S rRNA genes*

16S rRNA genes of the bacterial isolates were amplified with genomic DNA isolates as template and 8F and 1490R primers (Teske *et al.* 2002) in the following composition and amplification cycle. PCR amplification, cloning and sequencing of 16S rRNA gene sequences were carried out as described (Anandkumar *et al.* 2009). The nucleotide database was searched with the sequences obtained with NCBI BLAST (Blastn) tool (*http://www.ncbi.nlm.nih.gov/BLAST*) (Altschul *et al*. 1997).

2.6 *Siderophore production*

The respective growth media (GASN and succinate) were inoculated with *Arthrobacter luteolus* (approximately 10^9 CFU/mL) and incubated at their optimum growth temperatures (28–30°C). Culture filtrates (15 days old) were screened for siderophore production by $FeCl_3$ test (Atkin *et al.* 1970), Chrome Azurol Sulphonate (CAS) assay and CAS agar plate test (Schwyn and Neilands 1987). The concentration of siderophores in two different media was calculated using method described (Meyer and Abdullah 1978).

2.7 *Detection of chemical nature of siderophores (hydroxymates and catecholates)*

The presence of hydroxymate and catecholate siderophores were identified by methods described (Arnow 1936; Neilands 1981). The spectral peaks were noted with UV–visible spectrophotometer (Shimadzu 160A). The chemical characterization of siderophore produced in the culture supernatant was chemically analysed by the following methods such as UV spectroscopy, FTIR spectroscopy and high-performance liquid chromatography (HPLC).

2.8 *Identification of possible outer membrane receptor protein*

Iron–siderophore complexes are transported via outer membrane receptor proteins; therefore, it was investigated for the presence of possible outer membrane receptor proteins in the outer membrane fractions isolated from the bacterial isolate. To identify possible outer membrane receptor protein(s), the outer membrane fractions were isolated and analysed using SDS-PAGE analysis (Laemmli 1970).

2.9 *Bioaccumulation studies – FTIR analysis*

Sterile nutrient broth was prepared in 500 mL conical flasks, and 1 g of processed sterile rare earth soil from Chavara was added to all the conical flasks. One of the conical flasks was kept as control and the other two were inoculated with 10^6 cells of the isolate. All the flasks were incubated without shaking at 37°C overnight. After incubation, the control and broths with bacterial cultures were centrifuged at 5000 rpm for 10 min. All the air-dried pellet samples were analysed by FTIR spectrum (NDXUS-672 model). The spectrum was taken in a mixed IR 400–4000 cm^{-1} with 16 scan speed and was recorded using Attended Total Reflectometer (ATR).

2.10 *ICP OES analysis*

The presence of REEs was measured in bacterial cultures after acid-digesting the cell pellet (Walsh *et al.* 1981). Accumulation of REEs (cerium and neodymium) in bacterial cell samples was analysed with rare earth soil (SOM1) using ICP-OES (Optima 5300 DV).

2.11 *Nucleotide sequence accession number*

The nucleotide sequence coding the gene 16S rRNA has been submitted with the accession number EF532916 to GenBank.

3. Results

The soil samples were processed for ICP-MS analysis. Among the 12 lanthanides analysed in the soil sample cerium, samarium and scandium were found to be abundant in different proportions in the soil sample given in table 1.

The isolate had gram-positive non-sporulating motile bacilli and a nitrate-reducing, citrate-utilizing, catalase- and urease-positive bacterium. The nucleotide database was searched with the sequences obtained using NCBI BLAST (Blastn) tool (*http://www.ncbi.nlm.nih.gov/BLAST*) and showed 99% similarity with 16S rRNA genes of *Arthrobacter luteolus* in the database sequences. Based on these characteristics and sequence analysis, the isolate was identified as *Arthrobacter luteolus.*

Upon confirmation of the presence of a siderophores in cultures, the culture supernatants were tested for the presence of hydroxymate and catecholate siderophores using specific assays. The formation of red or purple colour indicated the presence of siderophores. A peak between 420 and 450 nm of ferrated siderophores indicated its hydroxamate nature. The Arnow's assay result was positive for *Arthrobacter luteolus*, indicating the presence of catecholate siderophores. The maximum siderophore production ranged from 38 to 58 μM after 72 h of incubation, at 30°C (0.35 μM) with pH 7.0 (0.52 μM).

The UV spectral analysis of the siderophore production by *Arthrobacter luteolus* in the culture supernatant of succinate medium revealed the maximum absorption peak at 310 nm, which is the characteristics of catechol-type siderophore.

Table 1. ICP-MS analysis of soil sample

S. No.	Analyte	Mass	Conc. mean (ppm)
1	**Ce**	140	**55.88**
2	Yb	172	23.72
3	Eu	151	0.33
4	**Sm**	**147**	**65.21**
5	**Sc**	**146**	**58.62**
6	Pr	141	43.11
7	Gd	157	40.81
8	Tb	159	0.00
9	Dy	163	41.72
10	Er	166	20.36
11	Tm	169	4.54
12	Ho	165	10.80

Boldfaced letters and numbers indicate the abundance of rare earth elements (cerium Ce, samarium Sm and scandium Sc) among others in the sample.

The siderophore secreted from the *Arthrobacter luteolus* was also analysed and isolated with reversed-phase HPLC. HPLC analysis of the culture supernatant from the present study showed peaks at various retention times such as 1.543, 2.133, 2.763 and 2.910 min. The peak obtained at the retention of 2.9 indicated the presence of 2, 3- dihydroxybenzoic acid (DHBA) in the culture supernatant confirming the presence catechol type siderophore.

The possible outer receptor proteins involved in the ferric siderophore transport of *Arthrobacter luteolus* was identified. The SDS-PAGE result was shown in figure 1. Two bands are visible in all no-iron samples with molecular weights of approximately 78 kDa and 80 kDa, and the bands are absent in the high-iron samples. This indicates repression of these proteins under high-iron conditions, which is consistent with the behaviour of the iron-regulated genes of iron transport systems.

The FTIR spectral analysis of the produced siderophore by *Arthrobacter luteolus* revealed that the FTIR data showed the peak values at 3624.37, 3190.37, 2141.06, 1637.62, 1404.22, 1087.89, 991.44 and 661.61 cm^{-1}. The spectrum of the compound showed a band in the region 3624.37 assignable to the intermolecular H-bonded OH group. The frequency at 3190.37 represented the N–H group (amide NH) of the compound and 1637.62 the C=O group and 1404.22 the C–C group of the compound. Each of the values represented the functional groups for the enterobactin compound having the molecular formula $C_{15}H_{27}N_3O_{15}$, the catechol-type siderophore. Thus, it related to catechol-type 'enterobactin' siderophore. Centrifuged pellets of the isolate with the element were used for FTIR analysis. The medium without element was maintained as the control system. When compared to the control system, strong peaks of –OH and C≡C and carbonyl peak C=O were observed in the test system. C=O carbonyl peaks were observed in cultures and elements system. In the system containing only the bacterial isolate, no significant peaks were observed.

Based on an earlier ICP-MS analysis, four elements were considered for further bacterial accumulation studies, viz. Ce, Sm, Eu and Sc. The accumulation of REEs in the bacterial isolate was carried out by ICP-OES after acid-digestion of cell pellets. Significant levels of accumulation of samarium and scandium, 17.14 and 6.01 μmol/g of dry weight of cells respectively, were observed with the isolate (table 2), whereas a very small amount of cerium was found to be accumulated in the isolate (0.48 μmol/g). Concentrations of other elements in the isolate were found to be below the detectable limit.

4. Discussion

REEs comprise light REEs (LREEs) and heavy REEs (HREEs) including all the lanthanides and actinides (Henderson 1984). The communication by Jeya *et al.* (2008) also reported that the presence of LREEs in monazite sample was comparatively higher than other REEs in the samples of both Chavara and Manavalakurichi. Based on an earlier ICP-MS analysis, four elements were considered for further bacterial accumulation studies with *Arthrobacter luteolus*, viz. cerium, europium samarium and scandium. Gram-positive bacteria such as the *Arthrobacter luteolus* studied here have a great ability to sequester metals in their cell wall. During sequestration, the complexation at anionic surface sites followed by the precipitation of metal phases takes place in the cell wall (Beveridge and Fyfe 1985).

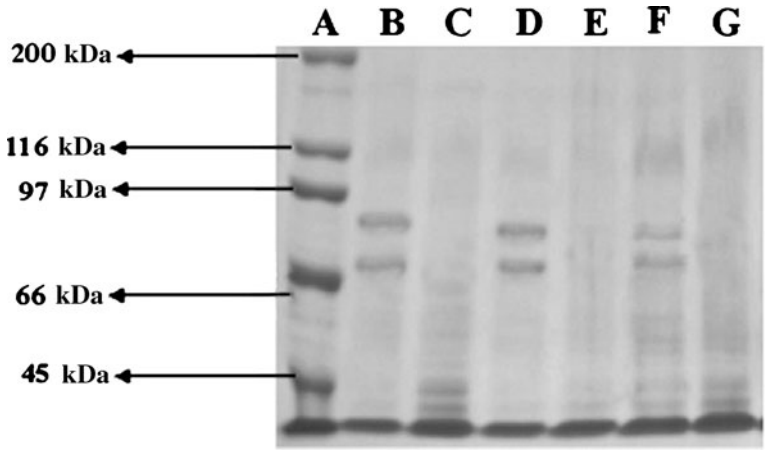

Figure 1. SDS – PAGE of possible outer membrane receptor protein. Bands having the molecular weights 78 and 80 kDa were observed only in the absence of iron and no bands in the case of high iron media. A – standard protein marker; B – OMP of *A. luteolus* (no iron); C – OMP of *A. luteolus* (high iron); D – OMP of *A. luteolus* (no iron); E – OMP of *A. luteolus* (high iron); F – OMP of *A. luteolus* (no iron); G – OMP of *A. luteolus* (high iron).

Table 2. Accumulation of REEs in *A. luteolus* by ICP-OES

S. No.	Sample composition	Rare earth element observed (μmol/g of dry weight of cells)			
		Ce	Sc	Sm	Eu
1	1 % element + bacterial isolate	0.48	6.01	**17.41**	BDL

Samarium (Sm) was accumulated by the bacteria more than Ce, Sc and Eu.
BDL – below detectable limit.

The catechol-type siderophore produced was chemically characterized by number of methods such as UV, FTIR and HPLC. Specifically, the *Arthrobacte*r sp. isolate has been shown to produce a catecholate siderophore using a chemical assay (Kalinowski *et al.* 2000). Typical absorption maxima for catechol were also detected for the siderophore with HPLC using UV detection. Suryakala *et al.* (2004) reported that the cell-free supernatant showed maximum absorption between 403 and 405 nm, which characterizes hydroxamate-type siderophore. The pyoverdine nature of siderophore of all isolates was evident from their absorption maxima within 407–412 nm. The present experiment showed the absorption between 200 and 300 nm and maximum absorption obtained at 310 nm. The result revealed that organisms produced catechol-type siderphore. In the present experiment, the analytical HPLC peak values occurred at various retention times and the peak at 2.9 min represents the presence of DHBA present in the sample (culture supernatant), because the catechol-type siderophores bind ferric iron with adjacent hydroxyls of catechol rings, and are almost always derived from DHBA (Crosa and Walsh 2002). Thus, it was confirmed for the catechol-type siderophore.

Both the *Streptomyces* sp. used in Liermann *et al.* (2000), and the *Arthrobacter* sp. investigated were found to produce catecholate siderophores. Published studies have shown that *Arthrobacter* typically uses hydroxamate siderophores (Matzanke 1991). However, very little is known about siderophores produced by soil bacteria; under iron starvation conditions the bacteria may be stimulated to produce the most Fe-efficient chelator. In general, catecholate siderophores have higher Fe-complex formation constants than hydroxamate siderophores. Therefore, it is possible that the *Arthrobacter* sp. produces organic acids such as pyruvic, a-ketoglutaric (Ahmed *et al*. 1984; Rozycki and Strzelczyk 1986), lactic or succinic acids (Kutzner 1981). HPLC analysis using UV detection of the *Arthrobacter* sp. culture supernatant shows typical absorption maxima for catechol at 214, 254 and 280 nm (Fessenden and Fessenden 1986).

Concentrations of metals in solution could reflect the competing effects of release from the mineral surface due to siderophore complexation and bacterial uptake. The REE concentration in the soil (availability) and the tendency toward complexation with the siderophore (extractability) contribute to the metal uptake into the cell.

Arthrobacter nicotianae also accumulated higher amounts of Sm than other REEs from a solution containing six LREEs (Tsuruta 2006). Although accumulation of LREEs by gram-negative bacterial species has been reported (Kamijo *et al.* 1998), the accumulation by gram-positive species in the present study has been observed. Initial concentration of REEs in soil had been taken account for the accumulation studies with *A. luteolus*. It has been shown that lanthanum, europium and terbium were accumulated during growth, between inner and outer membranes of the cell envelope (periplasmic space) of *Escherichia coli* (Bayer and Bayer 1991). Besides uptake into cell walls, metal uptake can also occur in the coating of macromolecules surrounding the cell wall. The glycocalyx can be an aggregation or rigid layer of carbohydrates or proteins that is easy (slime layer) or difficult (capsule) to wash off (Roane *et al*. 2009). Roane and Kellogg (1996) have suggested that glycocalyx provides protection to the cell against metal toxicity by complexing metals. Metals can also be taken into the cell through the cell membrane. Several workers have documented that most trace elements display a low solubility in lipids, limiting the rate of transport across bacterial membranes. Therefore, Fe–siderophore complexes are thought to be transported across the membrane by specific membrane proteins. Fe release from the siderophore may occur at the membrane or within the cytoplasm. Fe uptake may occur sequentially from the envelope (glycocalyx to cell wall and then to cell membrane) into the cytoplasm of *Arthrobacter*.

Biosorption encompasses the uptake of metals by the whole biomass (living or dead) through physico-chemical mechanism such as adsorption, ion exchange or surface precipitation. For example, the interaction between a mycobacterial siderophore (mycobactin) and europium ions have been shown by or spectrophotometric approach. Moreover, some siderophores such as ferrioxamine B could deplete europium fixation by goethite or boehmite (Andres *et al.* 2003).

The interaction of REEs between *Pseudomonas* sp. and organic ligands were studied by Ozaki *et al*. (2005). They noticed the adsorption of Eu(III) on bacterial cells in the presence of organic ligands with low chelating ability. Several investigators have quantitatively measured the

organic acids produced by bacteria and dissolution of metals by organic molecules produced in the surface complexes (Stone 1997; Kalinowski *et al*. 2000).

The fixation of heavy metal lanthanum by *Myxococcus xanthus* by extracellular polymeric substances was noticed as model of bacteria–lanthanide interactions (Merroun *et al.* 2003). In the present study the influence of REEs on bacterial reveals that REE enhances the production of acid and aromatic nuclei, which can be noticed in FTIR spectrum. The bacterium may influence the environment by producing mineral acids, chelating agents such as siderophores, or by-products of the metabolism (organic acids, *etc*.). The strong absorption peaks confirm the presence of the carboxyl groups in the bacterial polysaccharide structure; after metal binding by the biomass, the significant variations in the peak positions these regions strongly support the involvement of the carboxyl groups in REEs sorption. It can be assumed that REE induces the bacteria for the production of carboxylic acid.

The difference in quantity of siderophores produced by different organisms is logical. Several reports have shown strain-to-strain variation in production of siderophores (Reigh and O'Connell 1988). Oceans are relatively scarce of iron, where diffusion of siderophores away from the producer organism has raised questions about the types of siderophores marine bacteria produce (Martinez *et al.* 2003).

It is evident from the above results that REE uptake into bacteria cells is high, and the fractionation of LREEs such as samarium (Sm) and scandium (Sc) taken up into cellular material of *A. luteolus* is also very strong although very little enhancement in the release rate of metal has been detected during dissolution.

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