

Isolation of a Bacterial Lanthanide and Pyrroloquinoline Quinone by Methanol Dehydrogenase

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Abstract

The cell biology of metals is relatively new to the field of lanthanides; their particular fuse into chemicals was just exhibited in 2011, with the confinement of a bacterial lanthanide-and pyrroloquinoline quinone-subordinate methanol dehydrogenase. Numerous research efforts have since been focused on elucidating the molecular details involved in selectively recognizing and utilizing these metals, as well as the widespread use of lanthanide in environmentally important bacteria. The biology's use of lanthanides, as well as the lanthano-enzymes and -proteins (the lanthanome) that are currently known, are the subject of this review, along with the specific chemical challenges and benefits that come with it. In addition, we discuss the emerging knowledge of the coordination chemistry and biology of the pathways for lanthanide acquisition, trafficking, and regulation. These studies have shown that biological pathways for the use of other metals share many similarities. Last but not least, we talk about some of the many unanswered questions in this developing field and the potential applications they could have.

Keywords: Metal homeostasis; Methanol dehydrogenase; Lanmodulin

Introduction

Over the course of the past ten years, it has become clear that lanthanide ions are necessary metals in the biology of many widely distributed and environmentally significant bacteria, particularly methylotrophs. Methylotrophic bacteria can grow solely on reduced one-carbon compounds, such as methanol, methylamine, and, in some instances, methane. Lanthanides have been shown to play a crucial role in the catalysis of a number of alcohol dehydrogenases (ADHs) that are dependent on pyrroloquinoline quinone (PQQ), including methanol dehydrogenase (MDH), and in methylotrophs and even non-methylotrophs, contrary to previous hypotheses that they do not have any specific biological function [1-3]. The requirement that these metal ions be selectively acquired, trafficked, and inserted into enzymes has led to the discovery of a rich bioinorganic chemistry of these metals and the identification of some of the dedicated machinery for these processes. In addition to these essential catalytic functions, these metal ions must also be inserted into enzymes. The "lanthanome" of proteins and other biomolecules involved in this biochemistry has been coined.

Methylotrophs can be found in a wide range of environments, including soil, aquatic systems, and plants. Methanol undergoes aerobic methylotrophic metabolism, beginning with MDH's oxidation to formaldehyde, followed by oxidation to formate, and finally assimilation into biomass or carbon dioxide. Through a first step of methane oxidation to methanol by particulate or soluble methane monooxygenase enzymes, some methylotrophs (methanotrophs) can also use methane as a source of carbon. Previously, the calcium-dependent, MxaFI-type MDHs (Ca-MDH) were thought to be responsible for PQQ-dependent methanol oxidation. However, it is now clear that the lanthanide-dependent, XoxF-type enzymes (Ln-MDHs) are much more widespread than the Ca-MDHs. As a result, our knowledge of methylotrophic metabolism and biochemistry as a whole has greatly expanded as a result of recent advancements in the essential utilization of lanthanides [4]. The understanding of the roles that lanthanides play in the microbial world has steadily advanced since the first MDH lanthanoenzymes were discovered and characterized in 2011 and 2012.

The characterization of the first organism, *Methylacidiphilum fumarolicum*, which not only can use but also needs lanthanides for growth, followed these landmark early studies in 2014. Expansion of lanthanoenzymes to include PQQ-dependent ADHs with multi-carbon substrates in 2016, extension to non-methylotrophs in 2017 first reports and characterization of a genetic locus for chelator-mediated uptake of trivalent lanthanide characterization of the first protein known to selectively bind and handle lanthanides within the cell. The most recent lanthanide storage observation and more discoveries are being made. As listed in this Unique Issue, the examination exercises committed to understanding how progress metals are specifically perceived and used in science are tremendous [5-7]. The involvement of the d electrons in metal-ligand interactions is one of the many chemical properties of transition metal ions that biology can use to differentiate between them. the trend in metal-ligand affinities across the first row (Irving-Williams series) and the effects it has on buffered cellular concentrations of metal ions, hard-soft acid-base properties, preferences for coordination geometry, and redox activity. The chemistry of the lanthanide series of elements, on the other hand, makes biological application of these elements a unique and intriguing challenge for biology. Their bonding with ligands is largely ionic, and their ionic radius, coordination number, and Lewis acidity only slightly differ across the series. All are primarily in the +III oxidation state.

As a result, using lanthanides has several advantages for biology: They are useful catalysts due to their high oxidation states and Lewis acidity, and they can be selectively obtained from the environment due to their reasonable abundance, relatively large sizes, and exceptionally high coordination number [8]. Therefore, biological use of lanthanides,

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particularly the lighter lanthanides, is understandable from a chemical standpoint.

Based on sequencing data, it has been hypothesized that the primordial MDH is a lanthanide-dependent XoxF type enzyme, likely to have emerged in Bacteria following their separation from Archaea. The fact that the XoxF-type enzymes are found in numerous methylotrophic and non-methylotrophic organisms and are more diverse than their calcium-dependent counterparts lends credence to this hypothesis. In addition to the ExaF/PedH enzymes that encode lanthanide- and PQQ-dependent ethanol DHs, five phylogenetically distinct clades of XoxF have been identified to date, although other XoxF-like proteins may also exist.

The ability of the lanthanide-dependent ADHs to be activated by multiple metal ions sets them apart from other metalloenzymes. The effects of the lanthanide contraction indicate that are not simply substitutes for one another, despite their chemical similarity. Ionic radius, coordination number, and Lewis acidity differences may differentially impact various steps in the reaction, which has been the subject of theoretical investigation. The contribution of the growth rates of lanthanide-using bacteria and the complex relationship between XoxF activity and the identity of the incorporated are two examples [9]. Using an artificial dye-based assay, systematic activity studies of the enzymes of *M. fumariolicum* and *M. extorquens* as well as the PedH ADH described below reveal distinct lanthanide dependences of the enzymes, which roughly correspond to the lanthanide-dependent growth rates of each organism.

Numerous lanthanide-linked pathways and their molecular players have been quickly discovered through genetic and biochemical research, but more research is needed to fill in the details: take-up, chaperones, cofactor gathering, detecting, guideline, other lanthanoenzymes, stockpiling, whether there are cytosolic elements of lanthanides separated from capacity, and that's just the beginning. In a wider range of organisms that utilize lanthanide, it is unknown how similar these pathways are-or if any of them are even present at all. Differences in the specific sets of lanthanides utilized by various bacteria imply diversity in the details of uptake, trafficking, and utilization, which are likely linked to the distinct environmental niches of these organisms. Despite being unified in their preference for the more abundant LREEs,

The lessons learned can be applied to other biological systems and even the fields of bio metallurgy and medicine, despite the fact that the majority of mechanistic work to date has focused on the function of lanthanides in bacteria. According to a brief review, tasty clues point to lanthanide functions in plants and even higher organisms. Moreover,

since the revelation of the utilization of REEs in science, it has been evident that there may be convenient and huge translational effect from utilizing lanthanide-using microorganisms or the ligands that they blend (little particles, proteins) to address difficulties in REE extraction and detachments and in REE-based clinical imaging and remedial applications [10]. Actinides are likely included in these applications as well. Scientists now have access to the fundamentals of the highly evolved chemistry of lanthanides found in biology, which they can use and develop for themselves.

Declaration of competing interest

The authors declare that they have no known competing interests.

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