

Rapid expansions in biological metal utilization

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The fundamental chemistry of trace elements dictates the molecular speciation and reactivity both within cells and the environment at large. Using protein structure and comparative genomics, we elucidate several major influences this chemistry has had upon biology. All of life exhibits the same proteome size-dependent scaling for the number of metal-binding proteins within a proteome. This fundamental evolutionary constant shows that the selection of one element occurs at the exclusion of another, with the eschewal of Fe for Zn and Ca being a defining feature of eukaryotic proteomes. Remarkably, most of known metalloenzymes evolved during two transitional eras. First, development of protein structures for metal homeostasis coincided with the emergence of metal-using proteins, which predominantly bound metals abundant in the Archean ocean. Potentially, this promoted the diversification of emerging lineages of Archaea and Bacteria through the establishment of biogeochemical cycles. In a later expansion, over 75% of known Zn binding structures evolve at the same time as the Eukaryotic superkingdom emerged. These Zn-binding proteins are fundamental to eukaryotic cellular biology, while the localization to the nucleus indicates that they are diagnostic features of this superkingdom. Zn bioavailability may have been a limiting factor in eukaryotic evolution. In both scenarios, the newly evolved metalloenzymes would drastically change cell biology and by extension, geochemistry.

The role of extracellular organic matter (EOM) in the nucleation and growth of microbial carbonates

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Microbes are key players in the global carbon cycle, where they influence the balance between the organic and inorganic carbon. Microbial populations can be organized in microbial mats, which can be defined as organosedimentary biofilms that exhibit tight coupling of element cycles. Complex interactions between mat microbes and their surrounding environment can result in the precipitation of carbonate minerals (i.e., microbialite). This process refers as 'organomineralization *sensu lato*', which differs from 'biomineralization' (e.g., in shells and bones) by lacking genetic control on the mineral product. Organomineralization can be: (1) *active*, when microbial metabolic reactions are responsible for the precipitation ("*biologically-induced*" mineralization) or (2) *passive*, when mineralization within a microbial organic matrix is environmentally driven (e.g., through degassing or desiccation) ("*biologically-influenced*" mineralization). Two tightly coupled components that control carbonate organomineralization *s.l.*: (1) the alkalinity engine and 2) the extracellular organic matter (EOM), which is ultimately the location of mineral nucleation.

The EOM is composed of two main carbon pools: the high molecular weight extracellular polymeric substances (EPS) and the low molecular weight organic carbon compounds (LMW-OC). Both pools play a critical role in carbonate precipitation by providing Ca^{2+} and CO_3^{2-} as well as a nucleation template for mineral growth. EOM contains several negatively charged functional groups, which, depending on the pH, can be deprotonated (each group has unique pK value(s)) and, thus, bind cations. This binding capacity can deplete the surrounding environment of cations (e.g., Ca^{2+} , Mg^{2+}) and, thus, inhibits carbonate precipitation. Therefore, organomineralization is only possible if the inhibition potential is reduced through (1) oversaturation of the EOM binding capacity or (2) EOM degradation.

Studying microbe-mineral interactions, particularly the role of EOM in carbonate formation, is essential in the investigation of early life (e.g., definition of biosignature), especially at the interface between the biotic and prebiotic worlds, where newly formed organic matter could have strongly influenced the nucleation and growth of minerals, notably carbonate.