ÉCOLE DOCTORALE SCIENCES DE LA TERRE

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TITRE du SUJET : Metals as tracers of the evolution of molecular oxygen on Earth

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Equipe d'accueil : *à préciser et supprimer la ligne inutile*
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The biosphere of the present Earth is strongly and globally oxygenated to the exception of a few number of anaerobic niches. Correspondingly, oxygen represents by far the major bioenergetic fuel to non-photosynthetic life. However, molecular oxygen was likely not a significant component of the protoplanetary disc giving rise to our solar system where the oxygen atom was mainly sequestered in H_2O. In line with this argument, palaeogeochemical data are mainly interpreted to indicate an anoxic early Earth and a dramatic rise of O_2-levels during the second half of the planet's history. Until recently, the "standard" model shared by geochemistry and biology stipulated that at around 2.45 billion years ago, O_2 levels rose from practically nil to about 1/5 of their present values followed by a second wave some 750 million years ago. The first wave of O_2 production named the Great Oxidation Event (GOE) is considered to be due to the action of oxygenic photosynthesis carried out by cyanobacteria and possibly triggered by major geodynamic processes. Recently, this standard model has become challenged to varying extent from both geochemistry and biology. Whereas emergent geochemical and biological results suggest that the onset of photosynthetic O_2 production and the presence of oxygenated pockets in the environment may pre-date the 2.45 Ga old step by several 100 million years, other voices prone the presence of appreciable O_2-levels already in the early Archaean (*i.e.* at the time when the last universal common ancestor (LUCA) is supposed to have given birth to the prokaryotic diversity of the extant biosphere).

During the last decade there has been a attempt to track the rise to ecological dominance of oxygenic photosynthesis using several new or emerging geochemical proxies such as redox-sensitive metals (Fe, Cu, Zn, Ni, Mo, Re, Cr, U). However, the geologic record of these systems is largely incomplete. Further, if we have learned one lesson from previous and on going debate about the Archean geochemical record, it is that we need to seriously consider the burial and diagenetic history of rocks and the potential for a false signal for Archean oxygenic photosynthesis or an oxygenated atmosphere/surface oceanic waters.

Microbial mats thriving on land, in modern stromatolites or in deep seafloor settings are thought to be ancient relics of past microbial life on early Earth. Organisms that grow in these systems adsorb and concentrate many metallic cations required for growth. Among these, Mo, Ni, Co and W occur as catalytic centers in metal-activated enzymes that are used only in specific types of metabolism. For instance, Mo is present in the enzymes used for nitrogen fixation (phototrophic organisms), Ni is found in enzymes that catalyze carbon reduction reactions in methanogens and acetogens, and W is used by hyperthermophiles and methanogenic archae. Other metals such as Fe, Zn, Cu, As, Cr… are not specific to a metabolic activity but are commonly used as nutrients or in detoxication processes. In addition to direct uptake, metals can also be incorporated by adsorption during secondary processes. Bacteria secrete exopolymer that forms the matrix (biofilm) of the bacterial mat. Large surface area and chemical reactivity of this biofilm is considered ideal for metal cation scavenging. Accordingly, trace metals such as Mo, Ni, Co and W but also Fe, Cu, Zn, As, Cr in ancient kerogenous laminae could potentially act as a biomarker for specific types of metabolism, if it can be shown that secondary adsorption processes during diagenesis and metamorphism can be excluded. With the exception of Fe, which has been extensively studied as a potential biomarker owing to its ubiquitous role in the biosphere, other metals such as Cu, Zn, Cr, Ni, As, Mo, Cr, Co have until recently only superficially analysed for their abundances and isotopic compositions. Clearly, such paleo-biogeochemical studies are of high scientific interest. The implications are the detection of biogeochemical changes in the rock record to constrain the various feedback mechanisms that controlled the relationships between microbial metabolisms (sulphur processers, methanogens/methanotrophs and photosynthesizers) and the evolution of the hydrosphere-atmosphere system that led to the GOE.

An analytical protocol is required for unravelling the respective imprint of microbial *vs* diagenetic processes and to document the characteristic abundance, distribution and speciation of metals within the organic fraction present in modern and ancient microbial mats, but also throughout the overall hosting stromatolitic structure. The core of this PhD is to develop an analytical protocol on the emerging Nanoscopium beamline at SOLEIL synchrotron facility. Nanoscopium is aimed at providing quantitative information with high sensitivity on density variation, elemental distribution, and chemical speciation in the 5-20 keV energy range and at high spatial resolution (≤ 100 nm). The study of highly heterogeneous geo-biological samples necessitates fast statistically significant measurements of large sample areas followed by high spatial resolution local characterisation of the zones of interests. Additional measurements will be performed at various scanning X-ray beamlines worldwide (ALSL, SLS, ESRF). Prior to synchrotron analysis, all samples will be first investigated for their mineralogy, composition and internal microstructure using a Raman Spectrosocopy, SEM and cathodoluminescence.

We have obtained in the recent years a large number of modern and ancient biogenic samples, which represent a unique collection worldwide. These include:

i) Four drill cores collected in Precambrian environmental and temporal context (PDP2, 3.5 Ga Dresser Formation, Australia; BBDP, 3.2 Ga Mapepe Formation, South Africa; PDP1, 2.72 Ga Tumbiana Formation, Australia; TCDP, 2.45 to 2.2 Ga, Turee Creek Group, Australia). All drill cores contain stromatolitic relics.

ii) Modern microbial mats from shallow water stromatolites (Bahamas, Shark Bay and high altitude stromatolites) containing consortia of phototrophs, sulfate-reducing bacteria and methanogens and displaying different degrees of lithification (collaboration with Pieter Visscher from Connecticut University).

iii) These investigations on natural samples will be completed by laboratory cultivated microbial strains (in collaboration with Wolgang Nitscke of the Laboratoire de Bioénergétique et Ingénierie des Protéines de Marseille) and artificially fossilized microbial mats containing various organic fractions in different types of mineral matrix. The use of in-situ analytical techniques will allow understanding the process of fossilization itself. This in turn will provide a framework for interpreting unambiguously traces of life throughout the Precambrian rock record.