Deep ocean **quest**

On a mission to discover more about the role of metals in the marine environment, **Dr Olivier Rouxel** outlines cutting-edge research that focuses on geobiological interactions and metal cycling

Europole Mer is a research consortium on marine science and technology in Brittany providing direct funding for projects fostering scientific excellence, international expansion and collaboration. Could you introduce your Europole Mer-funded project on metals in the deep sea environment?

Our research focuses on understanding the behaviour of metals in the marine environment and their relationships with different Earth System processes such as hydrothermalism and mineral formation, their evolution in the oceans throughout ancient Earth history and the roles they play at the heart of the oceans' major biogeochemical cycles. The main goal of the International Chair funded by Europole Mer was the formation of an interdisciplinary research group investigating geobiological interactions and metal cycling in extreme marine environments.

Much of our research involves examining the isotope signatures of metals to interrogate the geochemistry of modern seafloor hydrothermal systems, as well as the rock record of metals in Earth's ancient oceans more than 2.5 billion years ago.

The concentrations of elements found in the deep sea depend on complex interplay between biological and geological processes. What methodology have you developed to explore metal biogeochemical cycles?

We use stable isotope techniques – many elements have several different stable isotopes (ie. non-radioactive) that differ only in the number of neutrons in their nucleus that may be selected for, or separated in characteristic ways by, different biological and geological processes. Variations in the isotopic ratios of light elements such as carbon, sulphur and oxygen have been widely studied over the last five decades and have provided the foundation for the field of stable isotope geochemistry.

With the advent of new generations of instruments (specifically multi-collector inductively-coupled plasma mass spectrometers), large numbers of heavier stable isotopes such as iron, copper, germanium, nickel and zinc isotopes are now accessible to stable isotope studies. By developing new techniques for their analysis – as well as establishing which processes impart their unique signatures – we are providing new tools for unprecedented discovery in the geochemical and biogeochemical cycling of metals.

One of your PhD students is conducting the first examination of nickel isotopes to trace nickel sources and enrichment processes in marine metalliferous deposits. How will this research advance existing knowledge of the development of polymetallic nodules or manganese crusts?

Polymetallic nodules and manganese crusts occurring at the seafloor are predominantly composed of mangenese- and iron-rich mineral phases showing various enrichments in metals of economic interest such as cobalt, nickel, rare earth elements and platinum.

Although geological and geochemical models have long been proposed to account for the genesis of these deposits, we still lack a basic understanding of their metal sources and precipitation mechanisms. In this project, we have aimed to develop and apply novel geochemical tools based on metal isotope ratios to address this issue. Our initial investigation of nickel isotopes has proved that this tracer can be used to decipher both different metal sources (hydrothermal versus seawater) and processes of enrichment (seafloor versus water column processes).

What is a spectrometry platform and in what manner has it benefited your research?

Project partners, the French Research Institute for Exploitation of the Sea (Ifremer) and the European University Institute of the Sea (IUEM) offer state-of-the-art research and analytical facilities through their ocean spectrometry platform (www.pso-brest.org). Specifically, this is home to six mass spectrometers dedicated to the analysis of natural materials. The acquisition of a flagship MC-ICP-MS instrument (Neptune, Thermo Scientific), installed in the Laboratory of Geochemistry and Metallogeny at Ifremer – with which the research team has in-depth experience – fulfills the primary analytical needs of our research programme.

Does your research have any implications that extend beyond its academic focus?

Anthropogenic pressure on deep-sea environments is ever-increasing and includes fishing activities, exploration for oil and mineral resources, pollution and global change. Some deep-sea areas have been incorporated into projects to establish protected marine areas, while others are now areas where exploration is authorised for metal-rich hydrothermal sulphide deposits, manganese nodules and manganese crusts. Hence, research activities in the deep sea have strong societal and economic impacts beyond their primarily academic focus, including the exploration and characterisation of potential mineral and energy resources and specific biological 'hotspots', the dissemination of scientific and technical information to the industrial sector and the general public, providing expertise and impact studies of industrial activities in the deep sea, and conservation of deep-sea ecosystems.

Exploring the **deep ocean**

Global change could have a significant impact on ocean function but, in order to predict this, researchers must better understand global geochemical cycles. The **LabexMER** consortium is making significant headway in this endeavour

THE SEAFLOOR AND subseafloor feature extreme variations in temperature, pH, pressure, salinity, and inorganic and organic compounds. These extreme conditions lead to a complex interplay between metabolic activity and diversity and geochemical changes. While these regions are a source of long-held scientific fascination, much remains to be understood about these environments and the likely effects of environmental change and anthropogenic activities upon them.

UNDERSTANDING DEEP-SEA ENVIRONMENTS

The French National Research Agency (ANR)-funded LabexMER consortium is improving understanding of ocean functioning in the context of climate change by combining the best marine science research teams and laboratories in west France. These respective investigations focus on the ocean at different scales: global, coastal and the deep ocean.

Dr Olivier Rouxel is one of the coordinators of the consortium's deep ocean-focused project, which is characterising and quantifying fluid circulation and geobiological interactions in extreme deep-sea environments. This will lead to a better understanding of these interactions in the dynamics and functioning of deep-sea ecosystems as well as their contribution to global geochemical cycles.

The work utilises state-of-the-art tools and methods to conduct research at sea and in the laboratory. Five multidisciplinary teams from the French Research Institute for Exploitation of the Sea (Ifremer) and the European Institute for Marine Studies (IUEM) are involved in the work, each specialising in either marine geology, geochemistry, biology or microbiology.

CONTRASTING GEOBIOLOGICAL INTERACTIONS

The teams are studying deep-sea environments where contrasting geobiological interactions occur. These include seafloor hydrothermal systems along mid-ocean ridges in the Atlantic and Pacific Oceans; submarine volcanoes that are both active and inactive; areas of the abyssal plains; and cold seeps, methane hydrate formation and cold-water corals at continental margins in the Mediterranean Sea and the equatorial Atlantic Ocean.

The consortium is also exploring and investigating sites within the French Exclusive Economic Zones – sea zones in which France has special rights over the exploration and use of marine resources. These include the Polynesian seamounts and active oceanic ridges. "Most of these sites need a strong effort for exploration at regional and local scales," Rouxel explains.

THREE RESEARCH AREAS

Three major research areas will be addressed within the project. The first investigates the tectonic, magmatic and sedimentary processes that control fluid circulation and its spatial and temporal variability. Questions include the depth of fluid penetration in the ocean lithosphere, how fluids and different types of substrata interact, the geometry of circulation, the relationship between deep fluid circulation and the deep biosphere and the relationships between the development of faults and magmatism. "This research is absolutely crucial for understanding chemical and heat exchanges between the Earth's crust and the ocean, the origin and nature of the biosphere in these extreme environments, as well as the energy sources and the mineral resources that are concentrated at the deep ocean-crust interface," Rouxel enthuses.

The second area of research aims to elucidate the environmental factors that control the dynamics of biological and functional diversity of deep-sea ecosystems. Understanding the interactions between biological compartments and environments in the complex ecosystems that thrive at ocean ridges and continental margins is a major challenge. The teams are taking an interdisciplinary, multi-scale approach, studying everything from the molecule to the ecosystem, using innovative sampling technology and data acquisition strategies.

The third area involves the teams investigating the impact of microbial community activity on the environment and major biogeochemical cycles. Submarine hydrothermal and cold-seep environments host very diverse microbial communities that contribute to the only relatively recently discovered subsurface biosphere. Rouxel is studying these ecosystems by focusing on the biogeochemical cycles of carbon, sulphur and metals in seafloor hydrothermal fields and ridge flank settings.

MANAGING PRESSURE ON THE DEEP OCEAN

The deep ocean harbours major economic and societal interests. The LabexMer project will ultimately lead to better management of human activities that involve the exploration or exploitation of deep-sea biological, mineral or energy resources by providing the scientific arguments to best define conservation strategies for the unique ecosystems that exist alongside them.

Understanding metals in the marine

Although crucial to the functioning of the Earth's natural cycles, the behaviour of metals in the deep sea is not well known. Using cutting-edge analytical tools, research led by the **French Research Institute for Exploitation of the Sea** is helping to elucidate the evolution of marine metal biogeochemical cycling

METALS CONSTITUTE ESSENTIAL catalysts at the heart of the biological enzymes that control the planet's major elemental cycles, particularly carbon and nitrogen. The important role of trace metals within marine ecosystems and the global carbon cycle has been well demonstrated. However, relatively little is understood about the sources of dissolved metals and the metal biogeochemistry of the ocean's largest dissolved metal reservoir, the deep sea.

An improved understanding of the major parameters controlling the distribution and bioavailability of metals in the environment is urgently required to predict how metal delivery to the global ocean may respond to climatic or anthropogenic changes affecting ocean chemistry and circulation, the continental flux of metals or pollutants and the biological carbon pump.

THE ROLE OF METAL CYCLING

Dr Olivier Rouxel is a geoscientist at the French Research Institute for Exploitation of the Sea (Ifremer) who has dedicated his career to studying metal isotopes in marine environments. Dr Stefan Lalonde joined him as a postdoctoral fellow in 2010 and is now faculty at the adjacent European Institute for Marine Studies (IUEM). Their current research focuses on geobiological interactions and metal cycling in the ocean and involves developing and applying cutting-edge geochemical techniques to better understand the fundamental behaviour of metals in modern and ancient environments.

One relatively recent hypothesis is that changes in marine metal reservoirs may be linked to variations in hydrothermal activity, geological processes and ocean circulation, which have in turn led to the emergence and decline of specific microbial metabolisms over billions of years: "This has incredibly profound implications," Rouxel asserts. "Although the details of the interaction between changes in marine metal reservoirs and biological evolutionary innovations are likely to be complicated, it is critical for unravelling the co-evolution of life, the Earth System and the role of metal cycling."

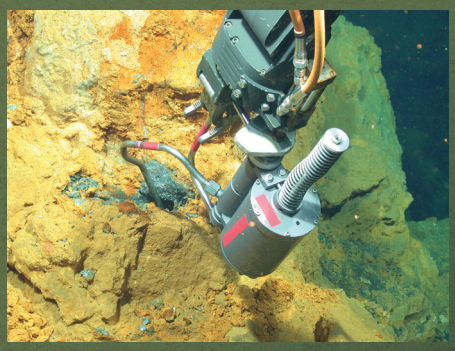
CUTTING-EDGE APPROACH

Rouxel and Lalonde are taking a cutting-edge approach to marine investigation; measuring trace amounts of metals and their isotope ratios in order to study the evolution of marine metal biogeochemical cycling through time. The team's work is strongly orientated towards analytical development, and is focused on using state-of-the-art laboratory equipment to take these measurements.

Prior to the appearance of complex multicellular life around 600 million years ago, Earth's oceans contained only microbial life. Over 3 billion years of their history is recorded in ancient marine sedimentary deposits that are preserved on Earth today. "Microbes often don't fossilise very well, so we turn to the chemical signatures they leave in sediments to reconstruct their activity in the deep past," Lalonde explains. By fractionating the isotopes of metals during biological processes – such as metal uptake, the microbially-catalysed oxidation or reduction of metals, and the biologically-mediated formation of new sedimentary metal minerals – microbes leave isotopic signatures that provide more information than can be obtained through abundance studies alone. Lalonde adds: "By understanding how these isotope signatures are generated through biogeochemical cycling in modern systems, and looking for their first appearance or changes in these signatures over time, we can seek out the trials and tribulations of life's ancient microbial ancestors, the diverse metabolisms they evolved to use and when in Earth's history that occurred".

OCEANIC IRON

Iron is a particularly important element whose marine cycling is under scrutiny. Iron is essential for the growth of marine phytoplankton and plays an important role in many biochemical reactions such as photosynthesis and nitrate reduction. Rouxel's team has constrained iron isotope systematics in seawater, establishing that iron derived from deep sea sediments and seafloor hydrothermal systems in the deep



Hydrothermal fluid sampling at Loihi Seamount (JASON2 on the R/V *Kilo Moana*, FeMO 2009 cruise). © WHOI

Changes in marine metal reservoirs are the result of a complex interplay among mantle, oceanic and biospheric processes

ocean has characteristic isotope signatures that are distinct from riverine and atmospheric iron sources, such that their relative importance to the seawater iron budget may be resolved using isotope tools.

Rouxel has also been investigating how iron oceanic cycles may have changed in deep geological time over billions of years, and how such changes may be linked to the evolution of the redox state of the atmosphere/ocean system. Based on the iron and sulphur isotope compositions of ancient sedimentary sulphides, his team has identified a direct link between the first accumulation of atmospheric oxygen around 2.3 billion years ago and changes in the oceanic iron and sulphur cycles. Banded Iron Formations, ancient iron-rich sedimentary rocks that were deposited in the deep ocean for much of Earth's early history, are a direct testimony to these profound changes. The iron isotope record of progressive oxygenation of the marine realm helps explain not only changes in the way they formed but also their distribution in time. This is no small feat considering that these multibillion-year-old Banded Iron Formations, deposited at the bottom of ancient seas but now found on land, constitute by far the Earth's most important and exploited source of iron ore.

DEEP-SEA HYDROTHERMAL BIOSPHERE

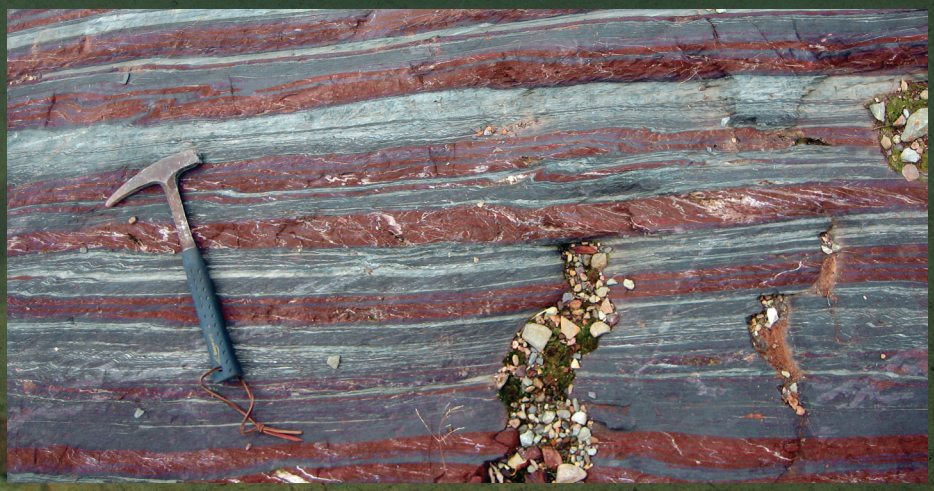
The project also encompasses the deep-sea hydrothermal biosphere, focusing on the bacteria and archaebacteria living near hydrothermal sources. Submarine hydrothermal environments host very diverse microbial communities that are based on chemosynthesis, involving CO_2-fixing metabolisms and metabolisms based on the reduction-oxidation of locally available chemical species such as hydrogen, sulphur and iron. Yet the mechanisms by which deep-sea microbial communities use the chemical energy stored in sulphide minerals, in particular from sulphur and iron, are poorly understood.

To study these mineral/microbe interactions, Nolwenn Callac, a PhD student in Rouxel's team, has performed a pioneering study combining functional gene sequencing and laboratory cultures with sulphur and iron isotopic signatures to better elucidate the 'key players' in the microbial ecosystems inhabiting seafloor hydrothermal systems. Through international collaboration, the project also provided the first comprehensive evidence of an active biosphere in deeply buried basalts on the flanks of deep-sea mid-ocean ridges, as Rouxel explains: "The subseafloor basaltic crust represents the largest habitable zone by volume on Earth. Hence, it is crucial to determine the abundance, activity, diversity and limits of the deep biosphere and its potential role in chemical exchange between seawater and the seafloor".

MODERN ANALOGUES OF ANCIENT MARINE ENVIRONMENTS

Another important aspect of Rouxel's research focuses on modern seafloor metalliferous deposits such as seafloor massive sulphides, polymetallic nodules and ferromanganese crusts, which provide unique analogues of ancient deposits. "Their study is crucial for the establishment of genesis models for seafloor metalliferous deposits and their relationships to oceanic and crustal evolution through time," he enthuses. Key examples include Red Sea seafloor hydrothermal systems that are characterised by anoxic deep water and extensive exhalative metalliferous deposits, and the sediment-hosted seafloor hydrothermal system in the Guaymas basin that approximate ancient black shales profoundly affected by late-stage hydrothermal metal input.

By taking a comparative approach to studying these environments, Rouxel's group aims to elucidate the mechanisms of metal redox cycling and microbiological interactions in the water column as well as in the sedimentary pile. Ultimately, through the combination of this fitting methodology and the dedicated work of the entire team, the researchers are on track to produce a greatly improved ancient oceanographic rock record.



Banded iron formation (2.7 Ga, Ontario, Canada). © Stefan Lalonde

INTELLIGENCE

METALS IN THE DEEP SEA

OBJECTIVES

The emerging paradigm that changes in marine metal reservoirs were caused not only by oceanic and geological events but also by the rise and fall of specific microbial metabolisms over billions of years has profound implications for understanding biological and Earth System co-evolution. The project's main research interest involves the use of stable isotopes for the study of the biogeochemical cycling of metals and metalloids in modern and ancient marine environments. Central to this is the use of geochemical proxies to improve understanding of how metals are mobilised from source regions, transported into the coastal and deep ocean and recycled within the water column.

PARTNERS

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