Ecole doctorale Environnements-Santé
Dossier de projet de thèse « Contrat doctoral Etablissements »
ANNEE 2024

TITRE DU PROJET : Oxygen in Transition (OxiT): The emergence of complex life at a time of extreme environmental change

1) Renseignements administratifs sur la direction de thèse[1] (1 page maximum) :

Directeur de thèse HDR :
Nom : THOMAZO
Prénom : Christophe

Co-directeur de thèse éventuel :
Nom : PINTI
Prénom : Daniele Luigi

2) Descriptif du projet de thèse (devra inclure les rubriques suivantes) :

- nom et label de l'unité de recherche : **Biogéosciences, UMR CNRS 6282, Equipe SEDS**

- localisation : **DIJON, Université de Bourgogne UFR SVTE**

- nom du directeur de thèse et du co-directeur s'il y a lieu : **Christophe Thomazo & Daniele Pinti**

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- description du projet (2 pages maximum)

An outstanding question in the study of early Earth's is how and when free oxygen accumulated in the atmosphere and oceans, eventually culminated in the fully oxygenated world that we inhabit. The accumulation of O_2 in the atmosphere and gradual oxygenation of the oceans had profound impacts on the biosphere and biogeochemical cycles, and eventually opened the door to increased biological complexity. But whereas variations in atmospheric O_2 over the last ca. 1 million years can be readily measured in ice cores, estimation of atmospheric O_2 in Earths' deep history is a long-standing challenge. A handful of qualitative geological constraints, such as the disappearance of certain oxygen-sensitive detrital minerals in the sedimentary record, coupled with the appearance of continent red beds, have long been understood to record the onset of an oxidizing atmosphere ca. 2.5–2.3 billion years ago in what is known as the Great Oxidation Event (GOE). Similarly, a Neoproterozoic Oxidation Event (NOE) is commonly inferred based on the appearance of large, mobile, O_2-respiring animals near the end of the Precambrian, ca. 700–540 Ma (e.g. *Butterfield, 2009; Och and Shields-Zhou, 2012*). A breakthrough in quantifying the trajectory of the first oxygenation rise (GOE) was made using mass independent fractionation of sulfur isotopes, which is highly sensitive to the presence of ozone in the stratosphere, hence free oxygen in the atmosphere. Data now indicate quite clearly that this event occurred ca. 2.4–2.3 Ga (*Farquhar et al., 2000; Poulton*

[1] ATTENTION : selon l'article 16 de l'arrêté du 25 mai 2016, le total d'encadrants ne peut pas dépasser 2, sauf si l'un des encadrants appartient au monde socio-économique, qui peut venir en sus, ou en cas de co-tutelle; Le décompte des co-encadrements se fera au prorata du nombre d'encadrants : 1 pour 1 encadrant, ½ pour deux encadrants.

et al., 2021). Unfortunately, no other availability proxy allows us to track directly the continued rise or subsequent fluctuations in atmospheric O_2 levels, and researchers are left to infer this trajectory mainly through the abundance and isotopic ratios of redox sensitive elements (e.g. C, S, N, Fe, P, Mo, U, Cr, rare earth elements) as preserved in the sedimentary record. Many of these redox sensitive elements (RSE) and isotope ratios appear to broadly trace the stepwise oxygenation of Earth's environment implied by the GOE and NOE (Fig. 1).

Recent compilations of RSE concentrations and stable isotope ratios suggest that the oxygen contents of the atmosphere increased significantly during the early Paleoproterozoic Eon, after the initial rise indicated by mass-independent S data, such that the GOE is now thought to have lasted from ca.2.43–2.06 Ga, spanning the longest-lived positive carbon isotope excursion geological record (ca. 2.22–2.06 Ga), known as the Lomagundi Event (LE; Fig. 1). It has been suggested that the Lomagundi Event, which reflects the extensive burial of cyanobacterial-derived (i.e., oxygenic) organic matter, triggered an "oxygen overshoot" to roughly modern atmospheric O_2 levels, but which was followed by a crash in primary productivity (*Hodgskiss et al., 2019*) and to low but stable O_2 levels ca. 2.0–1.8 Ga (e.g., *Scott et al., 2014*). This interval of time also saw the last gasp of massive deposition of iron formation on continental margins (an indicator of the titration of iron from the deep ocean) which was likely linked to the establishment of more widespread sulfidic conditions in the oceans, itself resulting from the expansion of oxidative weathering on the continents and the delivery of sulfate to the oceans. These conditions then characterized much of the next billion years of Earth history, prior to the NOE. This protracted interval (ca. 1.8–0.8 Ga) of apparently low but present atmospheric O_2, more abundant sulfur in the oceans, and muted fluctuations in RSEs, is commonly referred to as the "boring billion" years in Earth's history (*Buick et al., 1995*).

Whereas renewed focus on middle Earth history have revealed more dynamic biogeochemical complexity than previously recognized, the overwhelming focus of research has been into the transition out of the "boring billion" and into the NOE (e.g. *Guilbaud et al., 2015*), its association with the diversification and ecological expansion of eukaryotes (*Riedman and Sadler, 2018*), and potential connection to the Cryogenian snowball glaciations between ca. 720–635 Ma. Much less progress has been done in understanding the biogeochemical transition from the GOE to the boring billion and its stable but low O_2 levels— hereafter named "Oxit". On the other hand, both molecular phylogenetic studies (e.g. *Betts et al., 2018*) and the microfossil record (*Porter and Riedman, 2023*) increasingly suggest that eukaryotes originated approximatively at the same time as Oxit, i.e. ca. 2.0–1.8 Ga. The apparent temporal overlap between these major events in the history of Earth raises many questions, because eukaryotes require free oxygen in the environment but their constituent forebears were anaerobic bacteria and archaea.

The primary objectives of this project are to establish the redox landscape in which eukaryotes first appeared and to understand how biogeochemical cycles responded to the Lomagundi O_2 overshoot and the Oxit transition to low, stable O_2 levels that followed and persisted for up to a billion years. Hence, this project is formulated to test *the hypothesis that it was this stabilization at lower oxygen levels after Oxit that established the paleoenvironmental landscape in which eukaryotes appeared.*

The project will leverage ongoing and strongly complementary research by Thomazo, Pinti, and colleagues in their respective laboratories by merging their collective analytical expertise and experience in reconstructing paleoenvironmental conditions from the ancient sedimentary record. To realize the project objectives, this collaboration will take advantage of existing drill cores through key sedimentary successions spanning Oxit, ranging between ca. 2100 to 1300 Ma (Fig. 1). The team will generate biogeochemical datasets using the stable isotopic compositions of C, N, S measured in organic matter and biogenic minerals to trace ancient metabolic pathways, along with redox sensitive elemental abundances. These data will be supplemented by noble gas measurements to discriminate between biological and geological processes causing isotopic fractionation to avoid ambiguous interpretations (*Pinti et al., 2009*). Argon analyses will be run in parallel with Xe isotopes measurements on kerogen to track the atmospheric evolution during the Oxit and the middle Proterozoic as a result of mass-dependent fractionation processes related to Xe-ionization by UV (*Bekaert et al., 2018*). These Xe isotope data can be used as an indirect chronological tool for dating ancient sedimentary sequences and to track changes in oxygen (and ensuing ozone).

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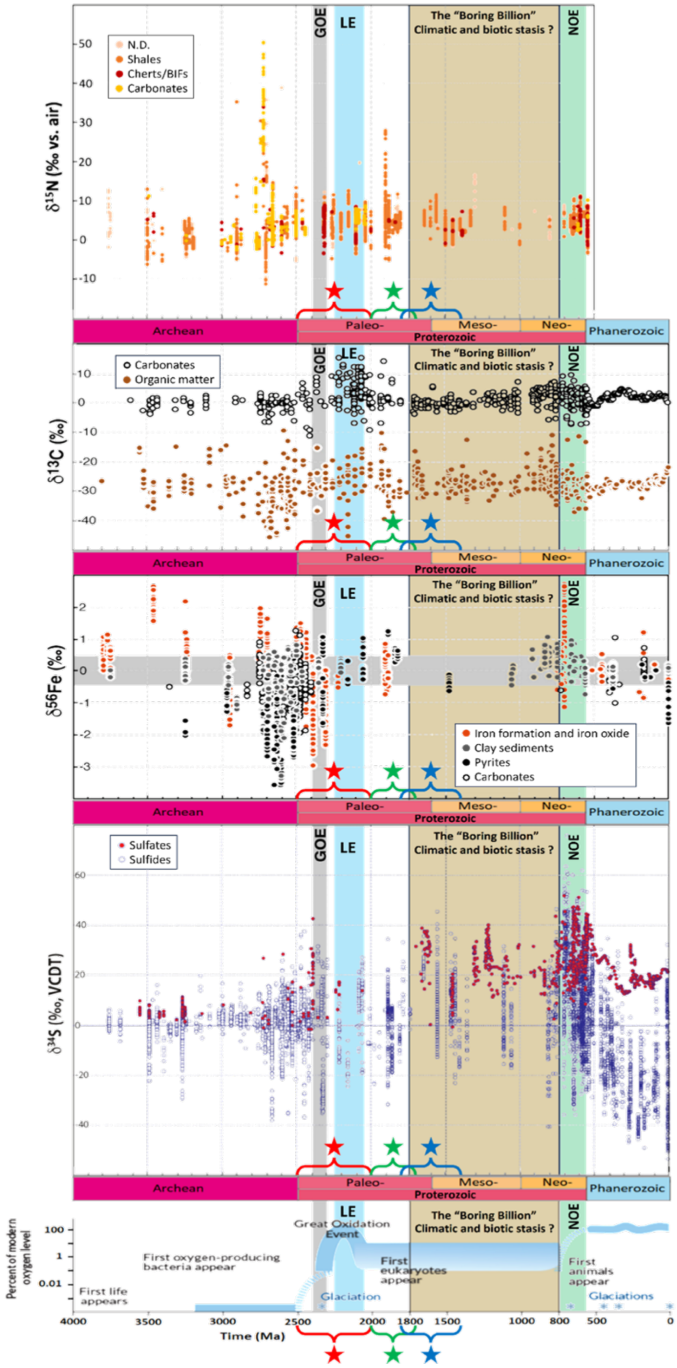

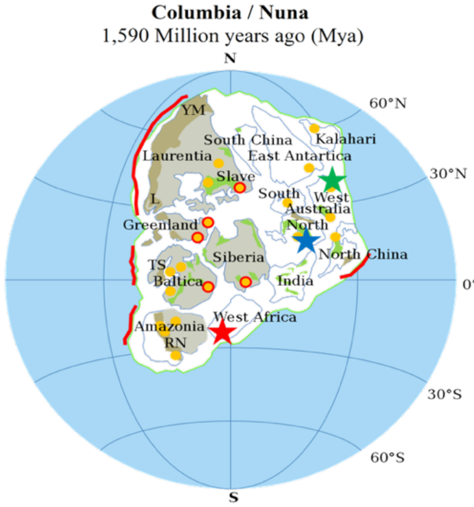

Target of this project:

★ **Francevillian Basin** (Gabon)
2,500 Ma – 2,000 Ma
Up to 2,000m thick
Intracratonic basin, influenced by continental inputs
Sandstone, siltstone, black shales, dolostone,

Analyses already done:
- $\delta^{13}C_{organic}$; $\delta^{13}C_{carbonate}$
- $\delta^{34}S$; $\Delta^{33}S$; $\Delta^{36}S$
- Few $\delta^{15}N$

Analyses considered:
→ $\delta^{15}N$
→ $\delta^{56}Fe$
→ Noble Gases (Ar, Xe)

★ **Earaheedy Basin** (West Australia)
2,000 Ma – 1,700 Ma
Up to 3,000m thick
Coastal deposit, outside the continental shelf
Siliciclastic rocks, platform carbonates, stromatolites

Analyses already done:
- $\delta^{13}C_{org}$; $\delta^{13}C_{carb}$

Analyses considered:
→ $\delta^{15}N$
→ $\delta^{56}Fe$
→ $\delta^{34}S$; $\Delta^{33}S$; $\Delta^{36}S$
→ Noble Gases (Ar, Xe)

★ **MacArthur Basin** (North Australia)
1,800 Ma – 1,400 Ma
Up to 12,000m thick
Intracratonic shallow basin linked with an open ocean
Mainly stromatolites, shales, shallow water carbonates, evaporite, conglomerates

Analyses already done:
- $\delta^{56}Fe$
- $\delta^{13}C_{carb}$

Analyses considered:
→ $\delta^{13}C_{carb}$
→ $\delta^{15}N$
→ $\delta^{34}S$; $\Delta^{33}S$; $\Delta^{36}S$
→ Noble Gases (Ar, Xe)

Figure 1: N, C, Fe, S isotopic secular variations and geobiological events through the Precambrian (left, unpublished data compilation). Targeted geological sample of this project and paleogeography of these basins after the assembly of the Columbia / Nuna supercontinent (right).

- **Financement du projet** – partie Recherche (montants acquis, type de contrat) : **Directeur HDR CT :** Projet IUF EVO-Lines (32k€ disponible pour 2024-2025), crédits récurrents équipes (≈ 4k€) pour l'année 2027. **Co-directeur DP :** crédits récurrents CRSNG à la découverte (40k$ CAD disponibles pour 2024-2026).

- **connaissances et compétences requises** : Maîtrise des concepts de la géochimie des éléments majeurs, traces et des isotopes ; Maîtrise des méthodes d'analyses par spectrométrie de masse isotopique ; Connaissance des méthodes de sédimentologie descriptive d'une carotte de forage. Une expérience des protocoles de chimie en solution d'extraction des espèces soufrés et ferreuses et de purification des gaz sur ligne à vide constitue un « plus ».

<u>Résumé en français et anglais (limité chacun à 1800 caractères)</u>

The study of early Earth's oxygenation is crucial for understanding the evolution of our planet and its biosphere. While recent research has shed light on tipping point events such as the Great Oxidation Event (GOE) and the Neoproterozoic Oxidation Event (NOE), the transition periods remain less explored. This project aims to fill this gap by investigating the redox and geobiological landscape during critical periods, particularly focusing on the transition from the GOE to the "boring billion" and the subsequent Oxit era when oxygen levels stabilized at low levels.

The PhD candidate, will analyze sedimentary cores spanning this Oxit period (from 2100 to 1300 million years ago) for their stable isotopes of carbon, nitrogen, and sulfur in organic matter and minerals in order to trace ancient metabolic pathways and reconstruct biogeochemical cycling. Additionally, he will study redox-sensitive elemental abundances to characterize water column paleo-redox environment. The project will also involve argon and xenon isotopic analyses to track atmospheric evolution, providing insights into oxygen and ozone levels during the Oxit and middle Proterozoic periods. All together, these data will help establish the environmental conditions when eukaryotes first emerged, shedding light on their relationship with oxygen levels.

By integrating various analytical techniques and leveraging existing research, this project seeks to unravel the complex interplay between oxygenation events and biogeochemical cycles evolution. Ultimately, it aims to test the hypothesis that stabilization of Earth's conditions at low oxygen levels during the Oxit created the paleoenvironmental conditions conducive to the emergence of eukaryotes.

L'étude de l'oxygénation de la Terre primitive est cruciale pour comprendre l'évolution de notre planète et de sa biosphère. Bien que des recherches récentes aient mis en lumière des événements remarquables tels que le grand événement d'oxydation (GOE) et l'événement d'oxydation néoprotérozoïque (NOE), les périodes de transition restent moins explorées. Ce projet vise à combler cette lacune en étudiant le paysage redox et géobiologique pendant la période dite du « milliard ennuyeux ».

Le doctorant analysera les isotopes stables du carbone, de l'azote et du soufre, dans la matière organique et les minéraux, de carottes sédimentaires sur la période allant de 2100 à 1300 millions d'années afin de retracer les métabolismes et de reconstruire les cycles biogéochimiques océaniques associés. De plus, il étudiera les abondances d'éléments sensibles à la concentration d'oxygène de la colonne d'eau afin de caractériser l'environnement paléo-rédox. Le projet impliquera également des analyses isotopiques de l'argon et du xénon comme traceur de l'évolution de l'atmosphère, fournissant ainsi un aperçu des niveaux d'oxygène et d'ozone pendant la période du « milliard ennuyeux ». Ensemble, ces données aideront à établir les conditions environnementales lors de l'émergence des eucaryotes, mettant ainsi en lumière leur relation avec les niveaux d'oxygène du système Terre et la diversité des métabolismes bactériens associées.

En intégrant diverses techniques d'analyse et en tirant parti des recherches existantes, ce projet cherche à démêler l'interaction complexe entre les événements d'oxygénation et l'évolution des cycles biogéochimiques. À terme, il vise à tester l'hypothèse selon laquelle la stabilisation des conditions terrestres à de faibles niveaux d'oxygène a créé les conditions paléoenvironnementales propices à l'émergence des eucaryotes.

<u>**Préciser le domaine de compétence dans la liste ci-dessous** (2 choix possibles maximum – ne pas modifier les intitulés : ils sont imposés par certains sites web) **:**</u>

Terre, univers, espace

<u>Mots clés :</u> Géochimie, sédimentologie, géobiologie