Oxidation in the pristine Cenozoic atmosphere
Co-evolution with life and climate
[PaleOX]

Grant requested 342 000 €

Projet duration 48 months

Coordinator partner Sophie SZOPA - JCJC

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Tutelle gestionnaire : CNRS

1. PROJECT SUMMARY

The level of oxygen in the Earth's atmosphere is unique in our solar system and reflects the long history of life on Earth. It also leads to a singular oxidizing chemistry that regulates the levels of atmospheric reactive trace gases. This is of importance since some of these reactive gases, even if in trace amount, can strongly interact with life and climate. Indeed, reactive trace gases might have been key factors in massive life extinctions in the deep past via abrupt climate warming, the collapse of the stratospheric protective ozone layer, or intense acid rains.

During the Cenozoic era (the last 66 Ma), environmental conditions have vastly varied but these changes, less abrupt or more localized than previously in the Earth history, have allowed life to diversify continuously and allowed in particular the mammalian evolution. If there were changes in the atmospheric composition, notably oxidizing capacity, during this period, those changes should therefore have been spatially limited or of moderate amplitude. Yet the Cenozoic era covers a wide variety of environmental conditions related to a gradual cooling of the climate of great amplitude (> 20 ° C) from a hot world, with a very strong greenhouse effect allowing tropical vegetation at high latitudes and very active carbon and nitrogen biogeochemical cycles, to the current glacial climate. In such varied climate and environments, one can expect modifications in the regulation of reactive compounds by atmospheric chemistry.

Over the last decade, field observations and then laboratory and theoretical works have revealed chemical mechanisms involved in the pristine atmospheres, such as the recycling of radicals over forests or a new halogenated chemistry over the oceans. This has definitely changed our vision of the oxidising capacity of the atmosphere in untouched areas.

In PaleOX, we aim to explore how the oxidizing capacity of the atmosphere has evolved throughout the Cenozoic era and how this has affected the lifetime of reactive short-lived climate forcers such as ozone or methane. To this end, PaleOX aims to study the atmospheric reactivity for five key periods of the Cenozoic by bridging the gap between the cutting-edge past climate modelling methodologies and the state of the art in atmospheric chemistry. A new Earth system model with up-to-dated representations of pristine atmospheric chemistry at its heart will be assembled to simulate consistently atmospheric chemical composition and climate at different stages of the Cenozoic. In parallel, unreleased samples of volcanic sulfate deposits coupled with advanced analysis of their isotopic composition will bring new information on the importance of past atmospheric oxidation pathways, bringing valuable constrains to the numerical analyses.

The ultimate goal of this project is to determine how the self-cleaning capacity of the atmosphere changed during the Cenozoic era taking into account information and assumptions about the evolution of vegetation, fires and climatic constraints based on various proxies available in the literature. The fact that modelling methodologies currently used to study deep time climates tend to neglect interactions between chemical cycles of short lived climate forcers and climate will be examined. The possible role of these chemistry-climate links in modulating climate change and gradients will be explored and conditions of surfaces (e.g. UV levels, concentrations of compounds that can alter the functioning of ecosystems, acid deposition) will be characterized. The feedback loops induced by changes in chemical composition of the atmosphere will be assessed in various contexts.

2. SUMMARY OF PEOPLE INVOLVED IN THE PROJECT

Institute	Last name	First name	Current position	Involvement (person.month)	Role & Responsabilities in the project
LSCE Laboratoire des Sciences du Climat et de l'Environnement UMR CNRS-UVSQ-CEA	SZOPA	Sophie	CR-CEA	40	Project Coordinator, chemical scheme development, Global modelling of atmospheric chemistry
	LATHIERE	Juliette	CR-CNRS	15	Terrestrial biogenic emission modelling
	SEPULCHRE	Pierre	CR-CNRS	10	Paleoclimate modelling
	BOPP	Laurent	DR-CNRS	8	Marine biogeochemical modelling
	COZIC	Anne	IR-CEA	10	High performance computing for ESM, model coupling
	CAUD	Nada	IR-CEA	2	Scientific Mediation
ISTEP Institut des Sciences de la Terre de Paris (UMR UPMC-CNRS)	MARTIN	Erwan	MC-UPMC	10	Collection and preparation of samples for S and O MIFS, interpretation of isotope analysis
LATMOS Laboratoire Atmosphères, Milieux, Observations Spatiales (UMR UPMC-UVSQ-CNRS)	BEKKI	Slimane	DR-CNRS	10	Atmospheric chemistry modelling including S and O MIFS
	MARCHAND	Marion	CR-CNRS	10	
	ONISHI	Tatsuo	IR-UPMC	10	
LGGE Laboratoire de glaciologie et de géophysique de l'environnement (UMR UJF-CNRS)	SAVARINO	Joël	DR-CNRS	5	S and O MIFS determination and interpretation
	CAILLON	Nicolas	IR-CNRS	5	

3. MODIFICATIONS COMPARED WITH THE INTENTION LETTER

No significant change was made compared with the intention letter.

4. CONTEXT, POSITION AND OBJECTIVES OF PALEOX

4.1. GENERAL CONTEXT

On the scale of Earth's history, the evolution of life, climate and tectonics are indubitably interweaved. In this system, chemical compounds, even in trace amounts in the atmosphere, can play a decisive role in maintaining or on the contrary shrinking favourable conditions for the development of life.

A striking example lies in the hypotheses proposed to explain some of the five largest mass extinctions, which occurred at the beginning of the Phanerozoic (540 Ma to 66 Ma) and have led, each time, to the extinction of more than 70% of living species (Raup & Sepkoski, 1982). Individual or additive causes have been proposed to explain these extinctions (asteroid impact, oceanic anoxia, etc.). Among those involving atmospheric chemistry are: the collapse of the stratospheric ozone layer due to hydrogen sulfide (H_2S), released in large quantities by the ocean under anoxic conditions (Kump et al., 2005); strong acidic rains due to magmatic emissions caused by volcanic traps (Payne and Clapham, 2012) or rapid climate warming induced by the massive release of methane (CH_4) by oceanic chlatrates (Berner, 2002). The exact role of each of these changes is still under debate and possible cumulative effects are suspected. For example, in the case of the Permian / Triassic extinction (~ 250mA), the effect of the high methane content was probably amplified by the presence of enhanced levels of H_2S (Lamarque et al., 2006). Indeed, both of these compounds are oxidised by the hydroxyl radical (OH), the main atmospheric oxidant for most trace and source gases. Consequently, highly enhanced levels of one of them can decrease the OH concentrations and so increase the lifetime of the other, intensifying its potential impact. In this case, the combination of both compounds could have led to a methane-driven stratospheric ozone collapse. The resulting increase of the UV-B reaching the Earth surface could have been determinant for the mass extinction.

Beyond the problematic of the huge mass extinctions, such examples question the removing processes regulating the trace gases content in the atmosphere and how they were able to maintain, so far, sustainable conditions for the evolution of life as we know it (diversification of mammals, appearance of savannah, grasslands, etc.) and the emergence of Hominids throughout the Cenozoic (from 66mA to present).

The current atmosphere of the Earth is oxygen-rich. Even if still dominated by dinitrogen, a significant level of oxygen (>10%) was reached about 540 million years (Ma), through the diversification of multicellular organisms taking advantage of the photosynthesis (Holland, 2006). Its level has varied since then between 0.7 and 1.8 times the present atmospheric level (PAL). The biosphere has allowed the free oxygen release that gives the Earth its uniqueness within our solar system. Oxygen has notably enabled the densification and the elevation of an ozone layer protecting DNA-based living organisms from destructive UV radiations and thus allowed the land colonization by life. Oxygen also induces a peculiar chemistry in the atmosphere, powered by solar energy, which slowly "burns" molecules that are injected by the biosphere. In this process, radicals play a major role, in the lower atmosphere, by chemically attacking the carbon, nitrogen or sulfur based species injected in the atmosphere. The strength of this removal, referred as **"oxidising capacity", determines the lifetime of trace gases and consequently modulates their levels and impacts in the atmosphere.**

So far, no information exists regarding the atmospheric chemical reactivity on geological times. However, it was recently established that volcanic sulfates, through mass-independent isotopic signatures, could constitute records of the oxidation pathways encountered by sulfur during its removal from the atmosphere. Such oxidation end products can be preserved for millions of years (under specific conditions) and can

therefore be used as indicators of atmospheric chemical processes. Therefore, **volcanic sulfates offer opportunities to constrain past oxidation pathways.**

As illustrated by the figure on the right, atmospheric composition is crucial in the Earth system functioning. By filtering solar radiations reaching the Earth, by controlling the acidity of rain or by regulating the content of harmful compounds, atmospheric chemistry can favour or alter the conditions favourable to living organisms. By interacting with solar radiations as well as infrared terrestrial emissions, atmospheric composition partly controls climatic conditions. Although carbon dioxide is often the main driver (considering atmospheric composition) of climate change, reactive species such as ozone, methane and nitrous oxide contribute significantly to the
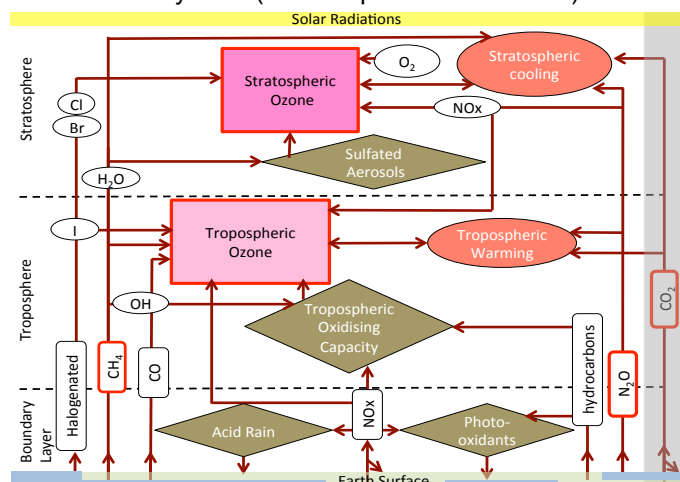

Figure 1: Interactions and feedbacks between important chemical systems in the troposphere and stratosphere. Compounds in red boxes act in the radiative equilibrium of Earth. (adapted from Wayne, 2000)

Earth's radiation energy balance. Multi-proxy analyses have allowed the partial reconstruction of the puzzling past conditions, but the levels of reactive trace species are unknown prior 800 ka. Hence, **although deep time climates are more and more investigated by numerical models, the role of non-CO$_2$ atmospheric compounds and, in particular, short-lived climate forcers is largely neglected or, at least, simply prescribed in most coupled paleoclimate simulations.**

Roughly, the Cenozoic era (the last 66mA) is characterized by a global cooling of the planet (Figure 2). It starts with a warm greenhouse world with, for example, terrestrial temperatures at high latitudes potentially 20°C warmer than modern ones during the early Eocene (~ 55-50Ma) (e.g. Huber & Caballero, 2011). Then the climate progressively cools down allowing the growth of large continental ice sheets in both hemispheres in the last millions of years. This era has also seen the huge diversification of plants and mammals. **The Cenozoic era thus encompasses a wide variety of climatic as well as environmental conditions, which have necessarily shaped the functioning of the atmospheric photochemical reactor.**
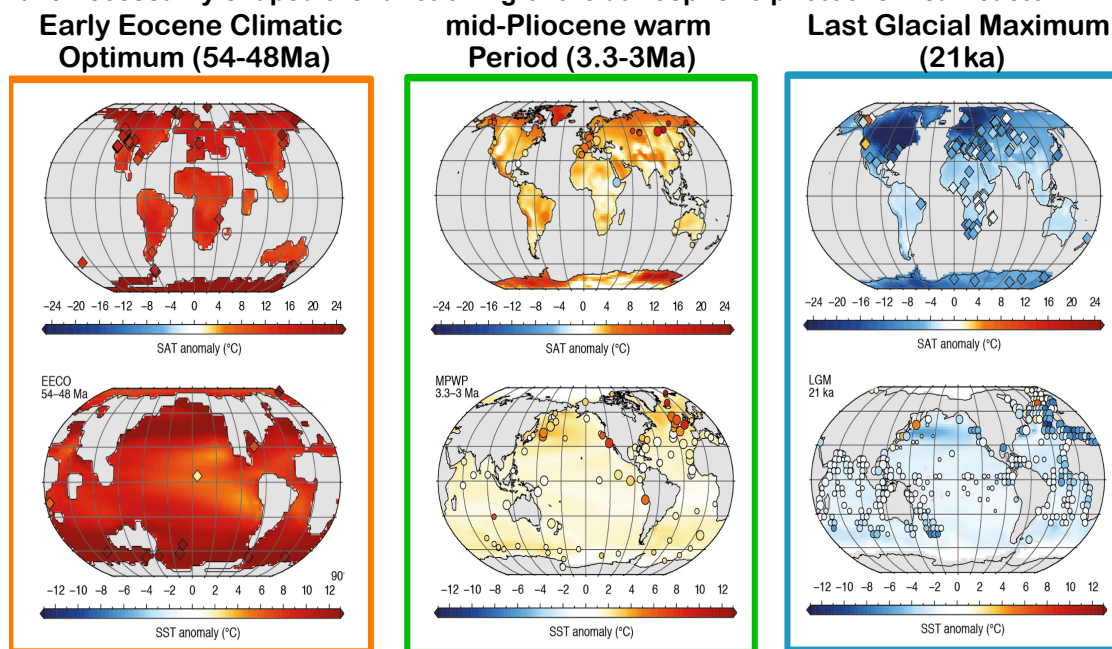

Figure 2: Comparisons of data and multi-model mean simulations for Early Eocene Climatic Optimum, mid-Pliocene warm-Period and Last Glacial Maximum, showing sea surface temperature (SST) and land surface air temperature (SAT) anomalies relative to preindustrial values, *from Masson-Delmotte et al., Climate Change, 2013*

However, many questions remain regarding the links and feedbacks between the evolution of life, atmospheric chemistry and climate: has the oxidizing capacity of the atmosphere varied throughout time or has it been regulated by chemistry of biogenic compounds? What is the breakdown of organic oxygenates on a living planet? What is the radiation spectrum reaching Earth and thus affecting life and in conditions so different? What was the functioning of the chemistry when oxygen levels were significantly lower or higher than nowadays? Has the surface atmospheric composition (ozone levels, for example) played a significant role in the evolution of the biosphere? Could the content in reactive gases explain some of the discrepancies between models and data for the past warm conditions?

4.2. OBJECTIVES OF PALEOX

In PaleOX, we propose to use state-of-the-art chemistry-climate modelling supported by sulfate isotopic composition measurements **to explore how the oxidising capacity of the atmosphere may have evolved throughout the Cenozoic era (the last 66 million years of Earth's history) taking explicitly into account feedbacks between atmospheric chemical composition, oxidizing capacity, and climate** and how it has affected the lifetimes of reactive short-lived climate forcers.

We will explore how the atmospheric composition (in particular non-CO$_2$ greenhouse gases such as ozone, methane, nitrous oxide) impacted climate and surface conditions prevailing on Earth at different stages of the Cenozoic. For this purpose, we will intensively use an existing 3-D numerical model of the atmosphere embedded in a well-established Earth system model to investigate the past atmospheric composition. The PaleOX team will first tackle the representation of the chemistry occurring in pristine atmospheres to simulate realistically the production and loss of reactive compounds in the troposphere and stratosphere. Then, for the first time, a large range of climate and environmental Cenozoic conditions will be consistently investigated to assess the evolution of photooxidative chemistry and, in particular, of the atmospheric oxidizing capacity. The results from this huge modelling effort will be analysed in light of the information obtained via original isotopic analysis of sedimentary deposits testifying of the past oxidative reactivity and

performed through PaleOX. These <u>unique dataset of isotopic measurements</u> will provide new insights into atmospheric oxidation pathways prevailing in past atmospheres, thanks to the collection of original samples of volcanic sulfates deposited during the Cenozoic era in arid or semi-arid regions and representing different atmospheric conditions. This project will provide a unique opportunity to question the role played by chemically reactive trace gases in the radiative budget of the Earth since the apparition of an oxidising atmosphere. This overall work will also provide clues on surface conditions prevailing on Earth during the evolution of life.

4.3. SCIENTIFIC AND TECHNICAL BARRIERS TO LIFT

The prerequisites to address such questions and the subsequent objectives are:

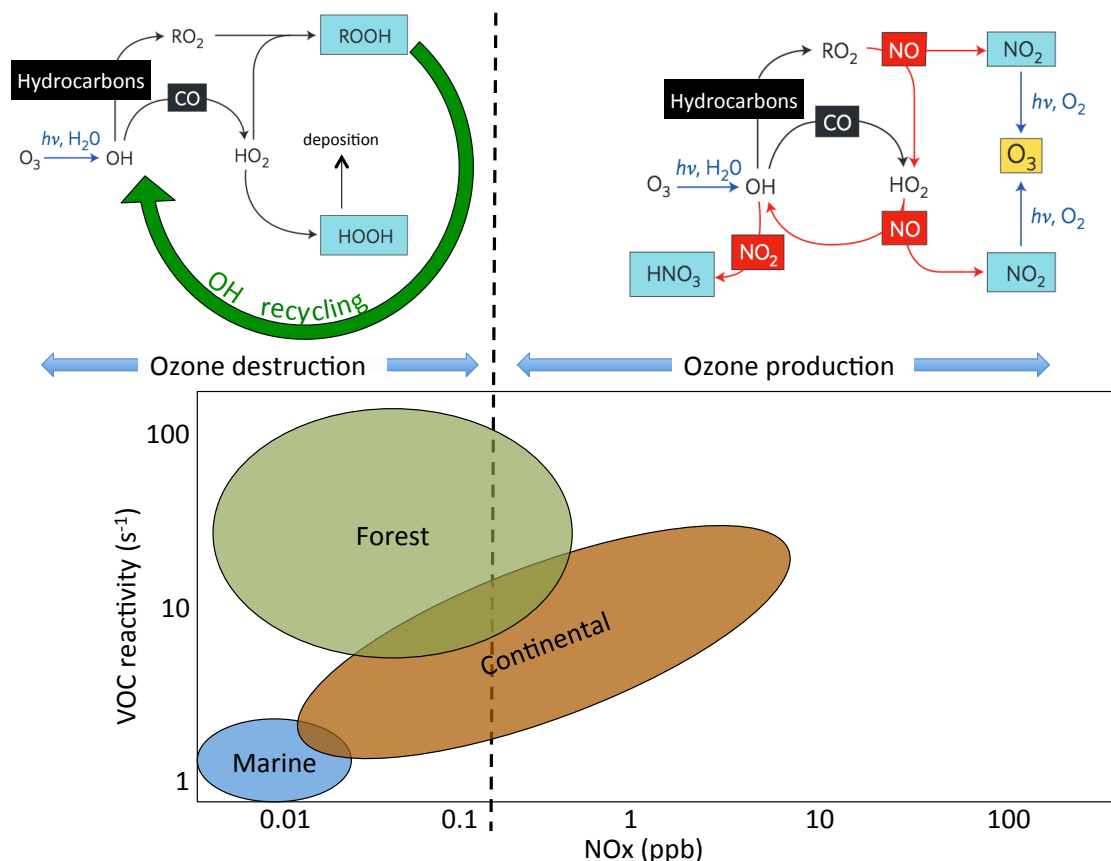- **Understanding pristine atmospheric chemistry**

Figure 3: Simplified illustration of tropospheric OH chemistry. On the left, when levels of nitrogen oxides (NO and NO₂) are low, the oxidation of CO, hydrocarbons as well as CH₄ (not represented) lead to the consumption of ozone and OH can only be sustained by OH recycling (in green), recently revealed; on the right, under the influence of NO and NO₂, which recycle the peroxy radicals (HO₂ and RO₂) in OH, ozone is produced and radicals cycle is maintained. *hν denotes the absorption of light; O₃, ozone; HNO₃, nitric acid; HOOH, hydroperoxide; ROOH, organic hydroperoxides ; ppb, part per billion. c,* **Classification of different types of pristine environments in the planetary boundary layer according to VOC reactivity and NOx concentration.** *The VOC reactivity refers to the sum of volatile organic compound concentrations multiplied by their reactivity with the OH radical* **[*adapted from Rohrer et al., 2014*]**

First, let's see how the oxidizing capacity is regulated in the pristine low-atmosphere. As illustrated in Figure 3, the photolysis of ozone in the presence of water vapour starts the radical chain, which initiates the oxidation of the reduced compounds emitted in large part by the biomass. As an example, plants and trees, and to a lesser extent oceans, emit currently in the atmosphere more than a gigatonne of hydrocarbons per year (Goldstein and Galbally, 2007). In the presence of NOx, which are emitted by lighting in the free troposphere and by soils over terrestrial areas, the radicals can be recycled by the NO/NO₂ interplay. Far from any NOx source, the peroxy radicals mainly react together to form hydroperoxides (HOOH or ROOH) and the propagation of radical chain is stopped. Considering only those pathways, oxidation of hydrocarbons, CO and CH₄ should lead to very low OH close to their biogenic sources, and potentially accumulation of hydrocarbons. However, during the last decade, the fate of hydroxyl radical (OH) was debated due to unexpected high concentrations measured over various forests, notably, in Europe (Carslaw et al. 2001), North America (Tan et al. 2011) and Amazonia (Lelieveld et al., 2008). Interferences were recently discovered in the OH measurement techniques used for some of these observations (Mao et al. 2012, Novelli et al. 2014) which probably implies an overestimation of the OH observations in some cases.

However, these observations have led to an impressive experimental, theoretical and detailed chemistry modelling work over the past 15 years which has greatly improved our understanding of the isoprene chemistry and more generally on the hydroxyl recycling. This OH-recycling during the oxidation of isoprene, the mostly emitted biogenic hydrocarbon, in presence of low-NOx concentrations, is now explained. It is due to isomerization of peroxy radical intermediates leading to hydro-peroxy-aldehydes, which can produce OH during their photolysis (e.g. Peeters et al., 2014, Paulot et al., 2009, Taraborrelli et al., 2012, Fuchs et al., 2013, Hofzumahaus et al., 2009). Considering this mechanism, Taraborrelli et al. (2012) explained how isoprene oxidation can alternately be a source or a sink of OH depending on the environmental conditions (solar radiation, OH levels). Using an explicit representation of these processes in a global model, Peeters et al. (2014) predict that, on average, 30% of the oxidation of emitted isoprene occurs through isomerization pathways, which should lead to a higher percentage of hydroxyl recycling. Taraborrelli et al. (2012) conclude that isoprene oxidation can act as a buffer for hydroxyl radical concentration by serving as both a sink and source for these radicals.

Another recent improvement regarding our knowledge of chemistry in pristine atmosphere concerns the first radicals produced during the oxidation processes of organic compounds: peroxy radicals (RO_2 in Fig. 3). The manner they react together (peroxy cross-reactions) is decisive for oxidizing capacity since these reactions can either lead to stable products or to new radicals sustaining the reactivity of the system. The reaction between an important peroxy (acetyl peroxy) and HO_2 radical was debated during the last decade and the branching ratios between radical propagating versus radical sink pathways were re-evaluated. Even if temperature dependence of this ratio is still unexplored, the recent work of Gross et al. (2014) suggests that the propagation pathway is dominant and would be, in clean air, the dominant route for HO_2 to OH conversion.

Finally, the hydroxyl and peroxy radicals are not the only radicals leading to the removal of compounds in the troposphere and other radicals were extensively investigated over the last years. One example is the chemistry induced by halogenated radicals produced by oxidation of halomethanes emitted by oceans, wetlands and fungi (Gribbles, 2004). Recently, Saiz-Lopez et al. (2014) showed that iodine chemistry, induced by oceanic emissions in supersaturated ocean waters, could lead to up to 27% of the tropical ozone loss in the upper troposphere indicating that iodine would be the second strongest ozone-depleting family throughout the global marine upper troposphere. However this chemistry is not commonly incorporated in global climate-chemistry models.

> **These recent findings raise issues about the cycling of radicals when unpolluted conditions prevailed on Earth. In the early times of the Cenozoic, how can the exchange of organic compounds between atmosphere and living vegetation have buffered the level of radicals when subtropical forests were extended up to north and south poles? In such world, was the sensitivity of the atmospheric cleansing capacity to climate variations different from the present-day sensitivity? What was the role of the marine compounds in ozone destruction in pristine chemistry and, for example, when ice sheets were covering much of high latitudes in both hemispheres?**
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> **In order to tackle these questions, the first objective of this project is to develop an up-to-date representation of atmospheric chemistry devoted to the study of the oxidising chemistry in pristine atmospheres. Entirely based on the latest kinetic data and chemical mechanisms, the chemical scheme will be suited to simulate tropospheric as well as stratospheric reactive chemistry.**

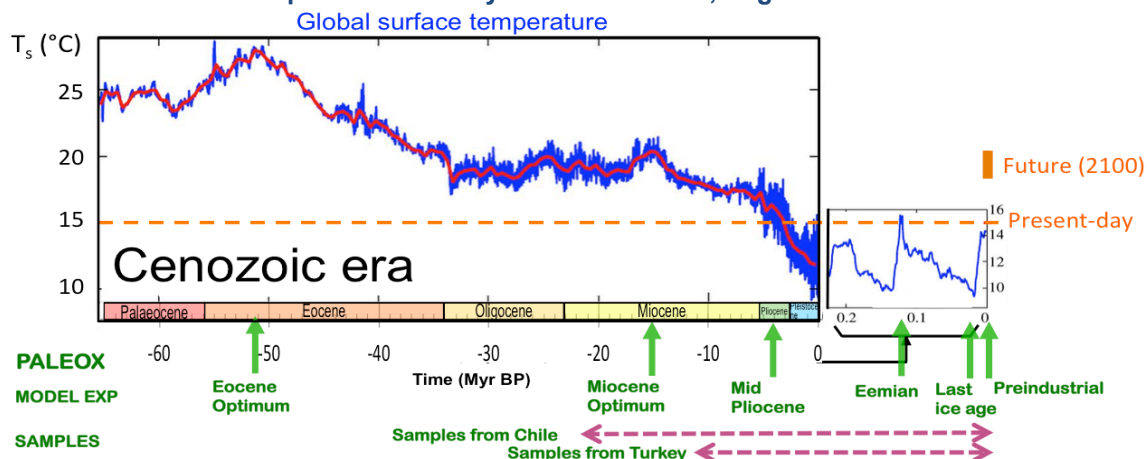- **Evolution of atmospheric chemistry drivers: Climate, Vegetation & Wildfires**

Figure 4: Surface temperature estimate for the past 65.5 Myr, including an expanded time scale for the past 200 000 years (adapted from Hansen et al., 2013). Surface air temperature expected at the end of the 21st century, according to multi-model RCP8.5 projections are superimposed.

Second, the conditions in which the atmospheric chemistry occurred have to be documented: namely climate conditions, vegetation distributions but also solar and volcanic activities. Over the Cenozoic Era, broad features of continents, plants and animals were very roughly similar to nowadays. It is important to notice that if the evolution of oceanic temperature, precipitation, life, tectonic or vegetation distribution has been recorded in various natural archives, there is no direct record of atmospheric concentrations of reactive trace gases beyond 800ka (unlike atmospheric CO_2). Oxygen isotopes from marine organisms indicate large variations in deep ocean temperatures, which correspond to even larger global surface temperature variations (Fig. 4). Hence, compared to the end of the 20th century, the global surface temperature anomaly probably culminated to +14°C during the early Eocene maximum (-50Ma) whereas this deviation reached probably -4°C during the last glacial maximum (21ka). Pollen records document major changes in the biome repartitions over this Era. The distribution of vegetation types greatly varied over Cenozoic. As an example, the tropical/subtropical climate of the Eocene allowed temperate forests to cover Antarctica, and palm trees over high latitudes whereas the end of the Cenozoic era have seen the sudden rise to ecological dominance of grasses using C4 photosynthesis (e.g. graminae) 8 to 3 Ma [Edwards et al. 2010]. Regarding, wildfires, the largest natural emissions of reactive compounds in the atmosphere, the presence of charcoal in sediments and the frequency of inertinite in coal allow to reconstruct past trends in fires since they took place 420Ma [Scott & Glasspool 2006, Bond & Scott 2010]. In addition, huge efforts of data synthesis for past conditions have been carried out these last years in order to simulate past climates and assess their realism against proxy data (PMIP Braconnot et al. 2012; PlioMIP Haywood et al. 2010, EoMIP Lunt et al., 2012). **These recent syntheses will be the foundations of our atmospheric chemistry-climate simulations.**

- **Modelling of the Biogeochemical cycles in the Earth system**

In the Earth System, biosphere, oceans and atmosphere are continuously interacting, exchanging both energy and matter. Complex tools are required to synthetize the state-of-the-art understanding on these reservoirs in order to represent their functioning and interactions. As stated in the last IPCC report (Flato et al. 2013), the Earth System Models are the most comprehensive tools to quantify the past and future evolutions of climate and the role of complex feedbacks. One of the recent leaps in climate modelling is the representation of atmospheric chemistry and composition in an interactive way in some of the ESM. Such models then allow the analysis of feedbacks between processes such as the biosphere response to changes in atmospheric composition or oceanic circulation due to stratospheric modifications.

One of them, the IPSL-ESM, was a pioneer in encompassing the full biogeochemical cycle of carbon, allowing to demonstrate one of the most emblematic feedback in the climate system. This ESM is the ideal tool to deal with the biosphere/atmosphere interactions regarding reactive compounds. For instance, the global terrestrial vegetation model simulates dynamically the emissions of biogenic organic compounds and incorporates the effects of ozone deposition on vegetation. The oceanic biogeochemical model allows to simulate ocean/atmosphere exchanges of reactive trace gases. In addition, the increased capabilities of large scale computing facilities and level of parallelization of ESMs now enable to simulate the atmospheric transport and chemistry within ESMs, thus opening the way to question the hypothesis existing on the role of past atmospheric chemistry, notably climate feedbacks involving the cycles of short-lived climate forcers.

- **Natural archives testifying the Cenozoic atmospheric reactivity**

However, gathering information on the drivers of atmospheric chemistry for defining initial and boundary conditions for chemistry-climate modelling is not sufficient. We also need some observational proxies/constraints of atmospheric chemistry, notably the critical oxidative capacity, to frame and evaluate the evolution of atmospheric chemical reactivity in numerical experiments.

One of the most difficult tasks to establish the chemical state of the atmospheres in ancient times is to find suitable and reliable proxies of this state. No direct measurement of the oxidation capacity of the atmosphere is possible at million years times scales. Even at present day, the measurement of the oxidation capacity is not a trivial task (Joeckel et al., 2003). The reason is that radical species (Monks, 2005), due to their extremely high reactivity cannot be archived. Geochemists are therefore constrained to look for markers in nature that, due to their specific properties, can record the chemical conditions prevailing when the marker was archived. As time passed, the number of such marker decreases rapidly due to lack of stability of either the marker or the archive/recorder itself (ice core, trees rings, lake or ocean sediments, rocks, etc.). However, sulfate and more specifically its sulfur and oxygen stable isotopes content have been shown to be impressively stable and unaltered over millions of years (e.g Paytan et al., 2004, Crowe et al., 2014). Being the end oxidation of the sulfur compounds, sulfate has become one of the most used marker of the past oxidation state of the atmosphere (Bao et al. 2003, Farquhar & Wing 2003, **Alexander et al. 2004**, Paytan et al. 2004, Bindeman et al. 2007). It has been demonstrated that either sulfur (Farquhar et al. 2000, **Savarino et al. 2003**, Paytan et al. 2004, Ohmoto et al. 2006, Kaufman et al. 2007) or oxygen (Bao et a. 2009, Bao et al. 2000, **Alexander et al. 2002,** Bao et al. 2010, Alexander et al. 2012) isotopes of sulfate are indicators of the past environmental conditions, notably UV levels and oxidation pathways. Bao (2015) has even defined **the sulfate as a time capsule for Earth's O_2, O_3 and H_2O.**

As part of the sulfur biogeochemical cycle, compounds containing reduced sulfur (e.g., H_2S, COS, CS_2, SO_2, dimethylsulfide (DMS)) are emitted regularly and continuously from a variety of surface sources into the atmosphere (Rodhe, 1999; Warneck, 2000), and are routinely oxidized to sulfate or sulfuric acid (S(VI)), the final and stable form of sulfur. Most sulfur emissions, including volcanic degassing and anthropogenic releases, are destined to the troposphere.

Sulfur dioxide (S(IV)) oxidation in the troposphere is achieved through either gas-phase (homogeneous) or aqueous-phase (heterogeneous) processes. A variety of oxidants (e.g., OH radicals; H_2O_2, O_3, O_2 and metals in liquid phase) are involved in the S(IV)-to-S(VI) conversion, which is the common step in the conversion of the majority of reduced sulfur compounds to sulfate (**Savarino et al., 2000**; Warneck, 2000) as shown in the Fig. 5 The relative contribution of heterogeneous oxidation pathways may reflect the atmospheric moisture content and/or the abundance of oxidants active through the aqueous phase (Lee and Thiemens, 2001; Lee et al., 2001). The atmospheric sulfur-containing end product, sulfate, plays an important role in the atmospheric climatic system, before its removal through wet or dry deposition from the atmosphere.
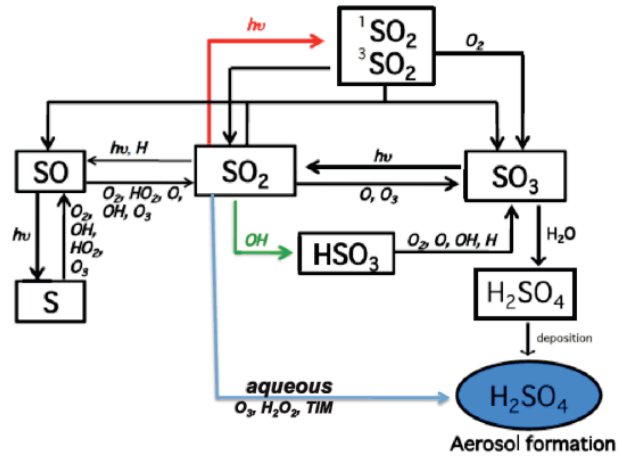
Figure 5: Schematic of chemical reactions in atmospheric sulfur chemistry. The red arrow indicates the photo-excitation of SO_2, a possible candidate for the creation of S-MIF; the green arrow indicates the oxidation of SO_2 by OH, the dominant pathway in the stratosphere; the blue arrow indicates aqueous oxidation of SO_2 by O_3, H_2O_2 and TIM (TransitionMetal Ion), the dominant pathways in the troposphere. adapted from [Hattori et al., 2013].
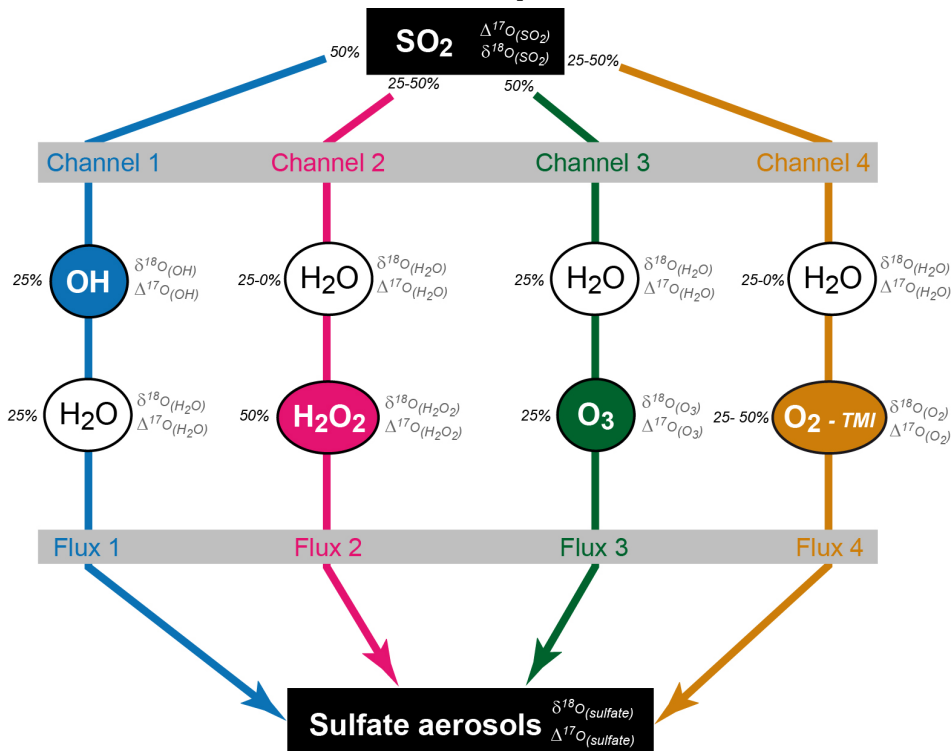
Figure 6: Simplified diagram showing the 4 dominant oxidation channels through which volcanic SO_2 is converted to sulfate aerosols in the atmosphere. Although chemical fluxes 1, 2, 3 and 4 cannot be measured directly, oxygen isotopic composition of sulfate provides constraints in their estimations according to the following mass balance (the same equation is used for $\Delta^{17}O$):

$$\delta^{18}O_{(sulfate)} = flux1.\left[0.5.\delta^{18}O_{(SO_2)} + 0.25.\delta^{18}O_{(OH)} + 0.25.\delta^{18}O_{(H_2O)}\right]$$
$$+ flux2.\left[(0.25\ or\ 0.5).\delta^{18}O_{(SO_2)} + 0.5.\delta^{18}O_{(H_2O_2)} + (0\ or\ 0.25).\delta^{18}O_{(H_2O)}\right]$$
$$+ flux3.\left[0.5.\delta^{18}O_{(SO_2)} + 0.25.\delta^{18}O_{(O_3)} + 0.25.\delta^{18}O_{(H_2O)}\right]$$
$$+ flux4.\left[(0.25\ or\ 0.5).\delta^{18}O_{(SO_2)} + (0.25\ or\ 0.5).\delta^{18}O_{(O_2)} + (0\ or\ 0.25).\delta^{18}O_{(H_2O)}\right]$$

Percentages correspond to the proportion in sulfate of oxygen originating from the different compounds during each oxidation chain (mainly from _Savarino et al._ 2000). The resulting O-isotopes compositions of sulfate

aerosols are: Channel 1: $\delta^{18}O$ = -5 to 1 ‰ and $\Delta^{17}O$ = 0‰ // Channel 2: $\delta^{18}O$ = 14 to 27 ‰ and $\Delta^{17}O$ = 8‰ // Channel 3: $\delta^{18}O$ = 13 to 25 ‰ and $\Delta^{17}O$ = 1‰ // Channel 4: $\delta^{18}O$ = 4 to 15 ‰ and $\Delta^{17}O$ = -0.17 to -0.08‰. (from *Martin et al.* **2014**)

Savarino et al. (2000) demonstrated that multiple oxygen isotope (^{16}O, ^{17}O, and ^{18}O) analysis of sulfate produced from SO_2 oxidation could be used to determine the contributions from different oxidation pathways through the transfer of mass-independent isotopic anomalies of the oxidants. This approach has been applied to continental tropospheric aerosol sulfates (Alexander et al., 2012; **Alexander et al., 2005**) and tropospheric sulfate deposited in the Antarctic ice sheet during the last glacial cycle (**Alexander et al., 2002**). In addition, the discovery of mass-independently fractionated (MIF) sulfur isotope composition in sulfate and sulfide samples (Farquhar et al., 2000; **Farquhar et al., 2001**; Farquhar et al., 2002) suggests that photo-oxidation of SO_2 in the primitive atmosphere produced characteristic sulfur isotope anomalies. Therefore, mass independent isotope chemistry appears to be a suitable and potentially highly effective tool (Thiemens, 1999, 2006) to study oxidation reactions of atmospheric sulfur species.

The best option as paleo-chemistry indicator is thus the Mass Independent Fractionation of oxygen and sulfur isotopes since they record the atmospheric oxidation pathways experienced by volcanic sulfates during their transit and oxidation in the past atmosphere (see Fig. 6). Such observations rely both on the mastery of cutting-edge analytical procedures and the identification of suitable samples bearing information on the reactivity of the successive Cenozoic atmospheres. Note that few groups in the world are able to carry out quality measurements of sulfur and oxygen mass independent isotopic anomalies. The Savarino's group (LGGE) is one of them.

How did the atmospheric conditions evolve during Cenozoic era and how could it have modified the oxidising capacity?

Solar and volcanic activities, biogenic emissions and climate are important drivers of the atmospheric chemistry. During, the Cenozoic era (66 Ma to present), many environmental changes occurred leading potentially to modifications in the dominant chemical features. It is important to notice that if the evolution of oceanic temperature, precipitation, life, tectonic or vegetation distribution has been recorded in various natural archives, there is no direct record of atmospheric concentrations of reactive trace gases beyond 800ka, unlike atmospheric CO_2, which can be assessed using different archives over the era. However, the records in natural archives provide clues on the evolution of vegetation, climate, or wildfire intensity, which all condition the physico-chemistry of atmosphere. In this way, oxygen isotopic analysis recording deep ocean temperatures allow to estimate global surface temperatures (Hansen et al., 2013). Such temperatures could have been up to more than 14°C hotter than present-day due to high atmospheric CO_2 levels, during the early Eocene optimum (~50Ma), at the beginning of the Cenozoic era. On the opposite, during the last glacial maximum (~21ka) the global temperature was probably 4°C colder than nowadays.

One of the main features regarding vegetation evolution during the Cenozoic era is the sudden rise to ecological dominance of grasses using C4 photosynthesis (e.g. graminae) 8 to 3 million years ago (Edwards et al., 2010). The distribution of vegetation types greatly varied over Cenozoic. As an example, the tropical/subtropical climate of the Eocene allowed temperate forests to cover Antarctica, and palm trees over high latitudes. These repartition, obviously changed as climatic conditions evolved. In addition to intensification of carbon cycle due to warmer climate, biogenic emissions of hydrocarbons are suspected to have been significantly larger during warm periods of the Cenozoic. For the last glacial maximum, if colder conditions limits biogenic emissions, the lower CO_2 level could have been more favourable to emissions. Indeed, recent findings of Possell et al. (2005) and Wilkinson et al. (2009) have shown that elevated CO_2 levels, such as the current ones, can inhibit the natural isoprene emission, compared to preindustrial.

Hence, emissions during the last glacial maximum could have been larger than the present-ones. Wildfires are responsible for the largest natural emissions of reactive compounds in the atmosphere (almost all the carbon monoxide and 2/3 of the NOx naturally emitted under preindustrial conditions). The presence of charcoal in sediments and the frequency of inertinite in coal are indicators of past trends in fires since they took place 420Ma (Scott & Glasspool, 2006; Bond & Scott 2010). If oxygen is almost fixed in the atmosphere (and exceeds 13% of the atmospheric content allowing the combustion to occur), the occurrence and spread of wildfires depends on the availability of biomass as fuel, on lightning as source of ignition and on sufficiently dry periods to allow ignition and spread of fires.
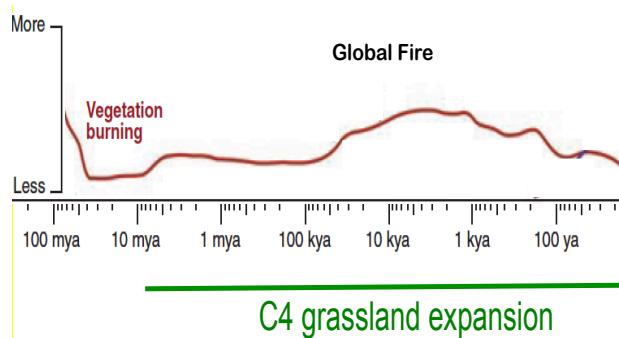

Figure 7: Qualitative schematic of global fire activity through time, based on pre-Quaternary distribution of charcoal, Quaternary and Holocene charcoal records, in relation to appearance of C4 vegetation type. *adapted from Bowman et al., 2009.*

All these conditions have greatly varied throughout the Cenozoic era, but the main driver of wildfire activity over long timescales being the temperature (Bowman et al., 2009), large pyrogenic emissions are suspected in the past. Hence, a large increase in charcoal occurrence is reported in deep marine sediments (Bond & Scott, 2010) over the past 7 Ma probably reflecting the expansion of pyrophityc vegetation such as C4 grasslands. An extensive palaeofire database was built by Power et al. (2010) to characterize the changes in fire regimes since the Last Glacial Maximum and allow to link the broad scale changes in charcoal abundance with large-scale climate controls, local changes in vegetation and fuel load. These charcoal data indicate that fire between 21ka and 18ka were similar or lower than present day fires with little change in spatial patterns.

From such information, the use of global 3D atmospheric circulation-chemistry numerical models is required to investigate the atmospheric chemistry, which could have occurred under environmental conditions of the Cenozoic. Indeed, the photochemistry of trace constituents is in perpetual disequilibrium and is driven by the relative kinetic rates of competing chemical reactions. The representation of gradients in concentrations are thus of high importance and 3D atmospheric models with sufficient horizontal and vertical resolutions are required to correctly account for reactive atmospheric chemistry.

4.4. STATE-OF-THE ART

- **Paleochemistry Modelling**

So far, few studies have been done using such models to approach paleo-conditions. Two of them have recently investigated warm conditions of the Cenozoic:

First, Beerling et al. (2011) studied particularly warm climate of the early Eocene (55 Ma ago). According to these authors, under such warm climate, enhanced nitrogen cycling induces a N_2O increase, and higher wetland emissions lead to a large CH_4 increase (x4 to x5 compared to the preindustrial level). Isoprene emissions are also increased and so are lightning NOx due to enhance convection. The Brewer-Dobson circulation, which favours the stratosphere/troposphere exchanges, is also considerably enhanced. In the pre-anthropogenic atmosphere, tropospheric ozone is regulated by the photo-oxidation of biogenic organic compounds, mainly isoprene and methane. As a consequence, in their simulations, tropospheric ozone concentrations increase significantly, being more than 60% higher than at preindustrial time. In addition, the OH concentration is significantly reduced (14 to 50%) whereas its production is enhanced by wet condition. Its oxidation reactions with CH_4 and isoprene are faster due to higher temperatures. Overall, the oxidising capacity is reduced and the reactive greenhouse gases (N_2O, CH_4 and O_3) are maintained at high concentrations in these conditions.

The effect of trace greenhouse gases (CH_4, N_2O, O_3) increase on climate is then quantified. Beerling et al. (2011) show that this effect is amplified by positive feedbacks, through albedo change due to melting of continental snow and reaches +1.4 to 2.7K for Eocene. This work clearly highlights the interest to take into account the coupling between trace gas chemistry and ecosystem in paleoclimate studies and open the way for other Earth system modelling studies focussing on reactive chemistry. However, it is important to notice that this work does not consider the recent finding on OH recycling during the oxidation of isoprene (discussed p. 2) nor stratospheric chemistry, which could significantly affect the results for CH_4 and N_2O. For example, stratospheric ozone levels determine the amount of UV reaching the troposphere and ultimately a large part of tropospheric chemical reactivity, notable the production of tropospheric OH. This project would allow to revisit this work without these limitations.

Second, Unger & Yue (2013) investigated the chemistry-climate feedbacks in the mid-Pliocene (~3 Ma). This epoch is of interest because its global climate is as warm, compared to preindustrial period, as the climate projected for the end of the on-going century (+2-3°C compared to present-day) but the structure of temperature differences are not explained by known natural forcings. This period is also characterised by a larger extension of vegetation compared to preindustrial, warmer and wetter climate, and more intense wildfires. Compared to preindustrial, tropospheric ozone burden is found to be 25% higher in the troposphere and 5% higher in the stratosphere. This stratospheric increase, due to a higher tropical upwelling and lower ozone chemical destruction in the stratosphere, leads to an important (20%) decrease of ozone photolysis leading to OH production (see Fig. 2). As a consequence, OH is 20-25% lower and the lifetime and burden of reactive species (CO, CH_4) is significantly increased. Unger & Yue have simulated the role of ozone, organic and inorganic aerosols on climate. They show that the net warming effect of reactive gaseous species (CH_4, N_2O, tropospheric O_3) reaches ~75% of that of CO_2. As concluded by Unger & Yue, the fast feedbacks of short lifetime greenhouses gases such as ozone have been, so far, dismissed from paleoclimate sensitivity studies but these results, as well as those of Beerling et al. clearly challenge this methodology.

More 3D modelling investigations of atmospheric chemistry have been done for cold climates since the methane cycle is constrained over the last 800.000 years by analysis of bubbles trapped in ice cores (Loulergue et al., 2008). Such observations offer a framework to consider long term variations of the oxidizing capacity during glacial-interglacial cycles of the Pleistocene (~2.6Ma to ~12ka) and Holocene (~12ka to present). Hence, Levine et al. (2012) performed a large set of simulations with a 3D chemistry

transport model considering the last glacial maximum (~21 ka), and several states compatible with abrupt Dansgaard-Oeschger (D-O) events (between 21 and 110 ka). Their aim was to explore the possible range of oxidizing capacity of the atmosphere due to climate and natural emissions. Their modelling results suggest minor changes in oxidizing capacity over that period and conclude that changes in OH sink does not drive the rapid changes observed in methane concentrations (100-200ppb) at that time. Comparing the tropospheric OH burden during the last glacial maximum to the preindustrial one, four recent 3D modelling studies offer a wide range of variations, from -29% to +28% (Murray et al., 2014, Valdes et al., 2005, Kaplan et al., 2006, Achakulwisut et al., 2015). It is not surprising since the sensitivity of OH is highly dependant of the model used as shown by Naik et al. (2013), who investigated the OH modification between preindustrial and present-day as simulated by 17 global models. They show a large inter-model diversity in the sign and magnitude of preindustrial to present-day OH changes. Such uncertainty of the long-term trends in OH can be largely explained according to these authors to different hypothesis on natural precursor emissions but also incriminate the chemical mechanisms in the current generation of chemistry-climate models. Indeed, the recent study of Achakulwisut et al. (2015) **underlines how the chemistry representation, and notably the consideration of OH recycling in pristine atmosphere, can drastically affect the sensitivity of OH to atmospheric temperature and biogenic emissions**.

- **Isotope analysis to contrain paleochemistry**

Since the discovery of isotopic mass-independent fractionation of sulfur and oxygen (S- and O-MIF) on Earth (Farquhar et al. 2000; Thiemens and Heidenreich, 1983), the isotopic composition of sulfates offers a new and revolutionary way to study the evolution of the atmosphere chemistry and its consequences on the climate (e.g. Bao et al. 2008; Farquhar and Wing, 2003). Although no S-MIF is observed in rocks younger than 2.3 Ga, it is the case in Archean rocks and this transition in S-isotopes became the iconic argument in favour of the atmosphere's oxygenation. Indeed, experiments show that UV photolysis of SO_2 leads to S-MIF and can only happen in an oxygen-poor atmosphere, with no shielding of UV by ozone (Farquhar et al. 2001; Ono et al. 2013; Whitehill et al. 2013). The O-MIF on Earth is mainly observed in ozone (Mauersbeger, 1987) and linked to it formation processes themselves (Mauerserger et al. 2003). Naturally, all atmospheric O-bearing compounds that derive from the O_3 are most likely O-MIF (e.g. Thiemens 2006). Despite the last 20-15years of intense research on MIFs, no real consensus on the precise origin of the S- and O-MIF in the atmosphere has been reached.

Sulfur-bearing gases (mainly SO_2 and H_2S) released during volcanic eruptions are oxidized in the atmosphere into sulfate aerosols (mainly H_2SO_4) via different possible oxidation channels (**Martin et al. 2014**; **Figure 6**). Therefore, the O-isotopes composition of volcanic sulfates registers the oxidation pathways from which volcanic S-bearing gases have been through. Since 2.3 Ga, the only location on Earth where S-MIF can be generated is in the stratosphere, where the O_3 UV shielding is less efficient. As a consequence, S-MIF measured in volcanic sulfate testifies the fact that they've been generated into the high atmosphere (most likely the stratosphere), following a large volcanic eruption (**Savarino et al. 2003, Martin and Bindeman 2009**).

Finally, volcanic eruptions that occur constantly at different locations on the globe are the perfect tool to 'probe' the past atmosphere. Sulfate aerosols formed during volcanic eruptions travel in the atmosphere depending on the air-mass circulations and sediment on the ground after few weeks (in the troposphere) or years (in the stratosphere), and much quicker when entrapped with volcanic ash (e.g. Robock 2000). The best natural archive for these sulfate aerosols deposition are ice-cores (**Savarino et al. 2003, Baroni et al. 2008**) or volcanic ash deposits (Bao et al. 2003, **Martin and Bindeman 2009**, **Martin 2014**). Ice-cores archives are time-limited while volcanic ash deposits can be preserved at geological timescale. Indeed, S-MIF have been measured in sulfides from 3.2 Gyears old volcanic ash bed (Philppot et al. 2012) and MIF signatures on few Myears old ash layers (**Martin and Bindeman 2009**) and few tens of Myears with cenozoic volcanic deposits (up to 34Myears old; Bao et al. 2003, Bao 2005, Bao et al. 2010).

Therefore, as also recently suggested in Bao's review on sulfates (2015), **isotopic composition of sulfate preserved in volcanic ash deposits represents an accessible and underexploited geological archive for atmospheric conditions, including oxidant capacity, in the past.**

4.5. POSITIONING OF PALEOX IN THE NATIONAL AND INTERNATIONAL CONTEXT

This project complements advantageously an on-going ANR project "FOFAMIFS" (PI: J. Savarino) which aims at evaluating the sensitivity of the oxygen and sulfur isotope of sulfate to the oxidation state of the atmosphere (http://www.agence-nationale-recherche.fr/?Projet=ANR-14-CE33-0009). FOFAMIFS relies on laboratory experiments performed in environmental simulation chambers and an atmospheric sampling strategy to cover a variety of atmospheric environments. Therefore PaleOX, being essentially a modelling exercise, will use and extend the knowledge gathered during FOFAMIFS project.

5. SCIENTIFIC AND TECHNICAL PROGRAM, PROJECT ORGANISATION

5.1. SCIENTIFIC PROGRAM AND PROJECT STRUCTURE

The goal of the project is to establish a systematic evaluation of the atmospheric reactivity and its main drivers under contrasted environmental conditions based on analysis of original samples on the one hand and state-of the art modelling on the other hand.

A first axis will aim to frame the past atmospheric conditions by :
- Collecting and analysing sediments which can testify the past oxidizing pathways
- Collecting numerical simulation representative of past climates

A second axis will target the development of a state-of-the art chemical model for pristine atmosphere and the assessment of chemical precursors emissions for past conditions.

A third axis will focus on the simulations of the atmospheric chemistry for five snapshots: at the Eocene optimum, Miocene, Mid-pliocene, Eemian conditions and finally cold conditions of the Last Glacial Maximum (Fig 4). In order to achieve these ambitious objectives, this work will be performed using an Earth system-modelling framework based on the IPSL-CM model (Dufresne et al., 2013) whose general architecture is displayed on Figure 8. This climate-modelling infrastructure, which already describes interactively the carbon biogeochemical cycle, contains an ideal level of description of the terrestrial as well as oceanic biospheres for this project. It also offers an internationally recognized appraisal on paleoclimatology to provide a unique framework for the simulations of paleo-chemistry proposed here.
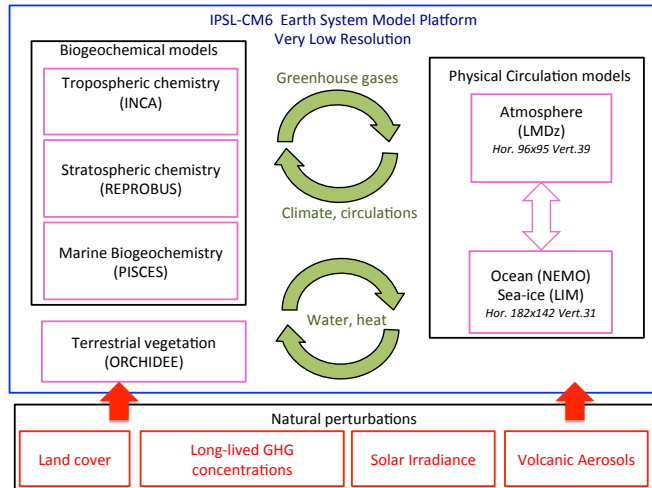
Figure 8: The IPSL-CM Earth System Model

These numerical realizations will, for the first time, document the atmospheric composition at different stages of the Cenozoic. This evolution will first be addressed considering the slowly changing drivers of atmospheric chemistry (vegetation, climate and resulting wildfires).

The overall strategy of PaleOX relies on three axes whose interdependences are shown hereafter.
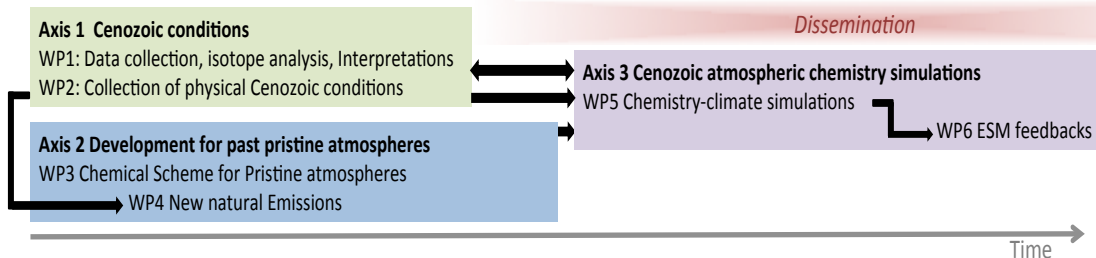
Axis 1: Reconstructions of the Cenozoic Era conditions

WP1: Isotopes analysis of Cenozoic volcanic deposits [resp. E. Martin, participants: E. Martin, J. Savarino, N. Caillon, S. Bekki]

→ The aim is to collect or gather samples dating back to various periods of the Cenozoic era and whose analysis can testify of the oxidative capacity of the atmosphere.

Volcanic eruptions are sporadic but mark out milestones in the progressive evolution of Earth. The huge quantity of sulfur then injected in the atmosphere is oxidised and converted into sulfate aerosols that, associated to volcanic clasts, end up deposited on the Earth's surface. When occurring in arid or semi-arid regions, these sulfates can be at least partially preserved in volcanic deposits for millions of years (**Martin & Bindeman 2009**, Bao et al. 2003, Bao 2005, Bao et al. 2010). The isotopic composition of these sulfates is a good indicator of their formation and fate in the atmosphere (**Savarino et al. 2003a, Savarino et al., 2003b**). The combined use of oxygen and sulfur Mass-Independent Fractionation Signatures (O- and S-MIFS) of sulfates archived in ice cores (**Baroni et al. 2007**, **Baroni et al. 2008**), tuffaceous ash beds (**Martin & Bindeman, 2009**) or fresh volcanic ash (**Martin et al. 2014**) have evidenced their potential to constrain the important oxidation channels through which volcanic sulfate has been generated in the atmosphere. However, two challenges have to be taken up when dealing with Cenozoic archives: the conservation of (1) volcanic sulfates and (2) their isotopic composition. **Martin and Bindeman (2009)** and Bao et al. (2003,

2005, 2010) were able to interpret and discuss the atmospheric oxidation pathways of volcanic S-bearing gases from the isotopic composition of sulfates preserved in volcanic deposits up to 34 Million years old. Therefore it is possible 'probe' the oxidant capacity (via the sulfur oxidation channels) of the Cenozoic atmosphere by considering well characterized volcanic deposits that have been preserved in arid to semi-arid environments. Then, it is required to master sulfate extraction from natural samples, like recently demonstrated in the ISTeP involved in this project (**Legendre et al. 2016**) and to master S- and O-isotopes measurements with a high precision in dozens of natural samples on a systematic way, which is the case in the LGGE team involved in the project, which was pioneering in applying these techniques to ice cores. The interpretation of the results will be supported by 2D-modelling of the atmospheric sulfur cycle performed by the LATMOS.

In this WP, we identified two main targets liable to contain Cenozoic volcanic sulfates:

1- Central Anatolia (Turkey) displays the Cappadocian ignimbrites and associated ash layers deposited during plinian to ultra-plinian eruptions from the Miocene until the Quaternary [Temel et al. 1998]. These volcanic sites are ideal for this project as the deposits have been preserved in semi-arid environments and the chronostratigraphy is perfectly known [Le Pennec et al., 1994, 1998, 2000, 2005; Paquette and Le Pennec 2012; Aydar et al. 2012, Argo et al. 2014]. The sampling missions will be carried out with the collaboration of Jean-Luc Le Pennec (DR, IRD), who has been working in this area for the last 30 years. His expertise in the regional geology and volcanology as well as its Turkish connections are certainly one of the key point in the success of this axis. Different volcanic deposits from 3 Ma to 25 Ma are targeted, and air-fall deposits are preferred rather than massive ignimbrites. This is important in order to favour secondary volcanic sulfate (generated in the atmosphere) rather than primary volcanic sulfate (magmatic) or xeno-sulfates (extracted from the subrstatum during the volcanic eruption or secondary precipitation of sulfate in the ignimbrite due to hydrothermal circulation). It is noteworthy that even in altered and/or diagenitized volcanic deposits it is possible to decipher the different origins of sulfate and to go back to the volcanic signature (**Martin and Bindeman 2009**). A three weeks mission in 2017 is required to collect volcanic deposits samples from different ages between 3 and 25 Ma.

2- The Altiplano in the Andes (South America), where many ignimbrites and ash layers have been continuously deposited and well preserved since at least 25 Ma (M. Brandmeier, 2015 and references therein) are also interesting for this project. Indeed the fact that this is one of the driest places on Earth for the last ~150 Ma (Hartley et al. 2005) assure a good preservation of sulfate in volcanic deposits. However, the high dispersion of volcanic deposits on a vast area, the scarcity of good outcrops due to a relatively flat topography and the difficult access due to the high altitude and lack of trails make the field work conditions difficult. Furthermore, the chronostratigraphy of this vast area is not as well established as in the Cappadoce (see above), which will require longer and much harder field work than a 'simple' sampling mission (detailed chronostratigraphy requires field observations, sampling and dating). However, as this is a very promising region for this project and potentially the widest and totally unexploited geological archive for atmospheric conditions in the Cenozoic, we plan on doing at least an exploration mission during this project. First, a mission in North Chile and South Peru (in 2018) in order to collect some samples for which the age is relatively well known, such as the Ríos Cotahuasi Ocoña and Colca–Majes canyons in Southern Peru that incise volcanic deposits successions from 0.5 to 19 Ma (Thouret et al. 2007) and the deposit of the La Pacana caldera forming super-eruption that took place 4-5 Myears ago (Lindsay et al. 2001). Here again the collaboration with Jean-Luc Le Pennec is crucial. Indeed as a researcher at the IRD, he works also in these regions and he has well-established connections with the local scientific community. If needed, we will establish new datings of volcanic samples in this region through collaboration with Hervé Guillou, who is an expert in K-Ar and Ar-Ar techniques applied to tephrochonology. Depending on the results of the first mission and second one can be planned for 2019 in order to aim for very specific deposits.

Proper samples containing proxies of paleochemistry are tricky to identify and collect. A risk remains regarding the presence of enough sulfates of secondary origin in the samples. However, the feasibility of MIF analysis in Cenozoic ash beds has been demonstrated by Bao et al. (2010). The analysis of the Turkish samples would be a low to medium risk/high gain study. The study of Altiplano samples is more risky because the suitable sampling sites are not yet well identified, however, we will benefit from the expertise and networks of J.L. Le Pennec and H. Guillou, both senior scientists, to gather and date proper samples. This part is more exploratory but is realistic and would clearly lead to high gain results.

WP2: Physical conditions for simulations over Cenozoic Era [resp. P. Sepulchre, participants : S. Szopa, P. Sepulchre]

→ The aim is to gather oceanic and atmospheric physical conditions for five contrasted stages of the Cenozoic chosen to encompass the diversity in climate, CO_2 atmospheric levels and vegetation distributions (in green on Fig. 1). These periods are the last glacial maximum (20ka), mid Pliocene (3Ma), Eemian (128ka), the optimum of Miocene (24-15Ma) and the Eocene optimum (52-50Ma).

To do so, we will build on modelling set-up already defined for several of these past periods in recent climate model intercomparisons EoMIP, PlioMIP, PMIP (respectively described in Lunt et al., 2012, Haywood et al.,

2010, Braconnot et al., 2012) and original climate simulations recently performed at LSCE (e.g. Kageyama et al., 2013a & 2013b, Contoux et al., 2012, **Hamon et al. 2013**, Woilliez et al., 2014, **Chaboureau et al. 2014**). The later can provide extensively analysed modelling set-ups. In addition, for all these stages, the coupled ocean and atmosphere general circulation models of the IPSL-ESM have simulated oceanic and atmospheric physical conditions (Fig 9). For each of these simulations, the models were runs over thousands of years with the same external forcings (ice-sheet extent, coastline, land-surface types, long-lived

greenhouse gases) and boundary conditions (essentially insolation) to reach the equilibrium in the ocean-atmosphere system. These simulations can provide the conditions (paleogeography, sea surface temperature) required to simulate adequately the climate using the chemistry-climate model built in the 2nd axis and also based on components of the IPSL-ESM.

We will harness these huge synthesis efforts on climate drivers (solar radiations, paleogeography, vegetation distribution, CO_2 atmospheric levels, notably) and climate parameters (temperatures, oceanic salinity, etc.…) to build a set of initial and boundary conditions for all the periods of interest. These conditions will be used in the production of natural emissions and for atmospheric chemistry simulations (WP4 and Axis 3).
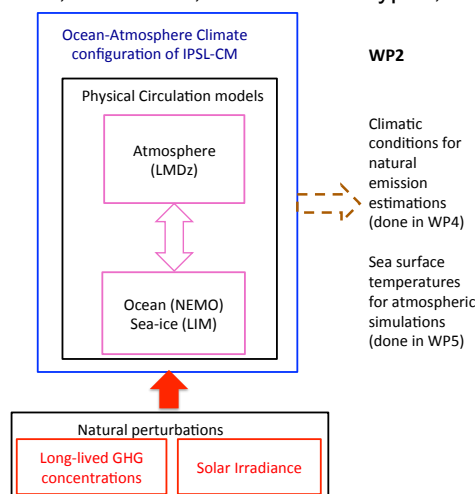

Figure 9: Ocean-atmosphere climate model previously used for paleoclimate modelling and which provide climate conditions for use in WP2.

There is no risk in this WP because it relies on existing simulations. The work will mainly consist in the collection of information and their analysis to discuss and compare the climate conditions at different periods.

Axis 2: Developments for deep time pristine atmospheric chemistry

WP3: Development of an up-to-date scheme for pristine chemistry [resp. S. Szopa, participants : S. Szopa, S. Bekki, M. Marchand. T. Onishi, A. Cozic]

→ This WP aims at developing an original chemical mechanism representing seamlessly the tropospheric and stratospheric chemistry for pristine atmosphere. The aim is to reproduce faithfully ozone and radical budgets and thus to quantify the oxidising capacity and the lifetime of radiatively and chemically active species (N_2O, CH_4, O_3).

Indeed, if the authors who have investigated 3D chemistry of the past are remarkably innovative in their approach, they also admit limitations in the way chemistry is modelled: either because they neglect the representation of higher hydrocarbon oxidation in the troposphere (e.g. Lamarque et al., 2006) or because they consider fixed stratospheric conditions (e.g. Beerling et al., 2011). In this project, we propose to develop a chemical scheme allowing to consider fully interactive photo-oxidative chemistry suited to background conditions occurring in troposphere and stratosphere over short timescales. The new scheme will be developed taking as a basis the tropospheric INCA and stratospheric REPROBUS chemical models already implemented in the LMDz atmospheric circulation model. We will particularly take care of the radicals' chemistry (peroxy, hydroxyl and halogenated) involved in the oxidation of reduced natural compounds. The recent techniques in High Performance Computing and the increase in supercomputer capabilities allow to develop chemical schemes with hundreds of tracers for 3D modelling. The chemical scheme will then be coupled with the climate model to investigate its performance on present-day for low-polluted atmospheres and on preindustrial conditions by extensive model/observation comparisons.

Methodology

The three dimensional chemistry-climate model will be based on the existing LMDz-INCA model (Hauglustaine et al., 2004, Folberth et al., 2006). The PI commonly used it in multimodel exercices aiming to simulate preindustrial, present and future tropospheric conditions (e.g. **Szopa et al., 2013**), transcontinental transport of pollution, or to study the climate/chemistry interactions. Thanks to the international model intercomparisons, the model's capabilities as well as its sensitivity to physico-chemical changes are well documented for the recent versions. The INCA chemistry module computes the tropospheric chemistry considering naturally emitted species (biogenic organic compounds, lightning and soil NOx, CH_4 from wetlands or oceanic CO emissions for example) as well as anthropogenic species and wet and dry deposition. In the absence of human perturbations, the oxidative chemistry regulates the lifetime of organic and inorganic compounds injected by oceanic biomass and terrestrial vegetation, soils, wetlands, wildfires, lightning and sporadically volcanic emissions of reactive compounds. The number of organic primary precursors to be considered is thus reduced but the importance of chemical radical recombination is increased.

The application of recent techniques in High Performance Computing to climate models and the increase in supercomputer capabilities allow to develop chemical schemes with hundreds of tracers for 3D modelling. The 3D model will be used nominally at a 3.75°x1.9° horizontal resolution with 39 vertical levels extending from surface up to 70km, which has been the reference configuration of the LMDz climate model for a few years (Dufresne et al., 2013)[1].

The ambitious aim of this chemical mechanism is to include both a seamless representation of tropospheric and stratospheric chemistry describing both photooxidative inorganic chemistry and a detailed representation of the oxidation of organic compounds in order to avoid bias in ozone and radical budgets (and thus oxidising capacity). To do so, the main developments will concern:

- an extension of the interactive chemistry to the stratosphere with an interactive coupling of ozone and shortwave heating rates as recommended in Sassi et al. (2005). The stratospheric chemistry of CH_4 and O_3 will be based on the REPROBUS scheme (Lefèvre et al., 1994, 1998, Jourdain et al., 2008) without the reactions induced by the anthropogenic CFC chemistry.
- Recent updates on recycling of OH during isoprene oxidation through peroxy isomerisation as well as reevaluation of peroxy branching ratios will be considered
- The iodine chemistry will be incorporated as well as chemistry of short lived halogenated emitted by ocean and ice.
- All the photolysis rates will be calculated on-line to account for radiative changes

If the number of chemical species becomes too computationally expensive for 3D modelling, we will make reductions based on tests in box model (as done in Szopa et al., 2005). The impacts of such reductions will then be fully quantified.

Evaluation strategy:

Before removing the chemistry related to anthropogenic compounds (e.g. aromatic, long chain alkanes) which is unnecessary in pristine context, the model will be used to simulate a present-day climatology. This climatology will be compared to the recent evaluations performed by comparing ensemble of models with large observation datasets. We will pay particular attention to the representation of background chemistry by comparing concentrations with field data collected over oceans (e.g. Prados-Roman et al., 2015), indigenous forests (e.g. Carslaw et al. 2001, Tan et al. 2001, Lelieveld et al., 2008) and free troposphere (for example comparisons with the data from In-service Aircraft for a Global Observing System, IAGOS European Research infrastructure, as we did in **Elias et al., 2011**).

Then, a preindustrial simulation will be performed and confronted to scarce data and intermodel comparison results (such as for example the Atmospheric Chemistry and Climate Intercomparison Project, ACCMIP, by Naik et al., 2013, Young et al., 2013, Lamarque et al., 2013). This simulation will be the baseline to discuss all the other past simulations.

The development and implementation of a new chemical scheme for pristine atmosphere is the cornerstone of the project. As a specialist of the atmospheric chemistry of the atmosphere, the PI will be particularly involved in this axis to ensure the realization of this ambitious chemical scheme without delay. This crucial step should not exceed 2 years to allow the work of axis 2 to start. Then, the extensive qualification of this new global chemistry model versus observation for present day and past case studies will be done independently of the other Axes, which will progress in parallel.

•   1 engineer hired through this project (28 months) will ensure the on line coupling between radiations and trace gases, will help in the implementation and test of chemical schemes (1D and 3D) and will carry on the realisation of preindustrial and present-day climatologies.

(test in box-model, analysis of preindustrial and present-day climatologies) and perform and analyse the comparisons with observations

This axis will benefit from the expertise of M. Marchand and S. Bekki for the development regarding stratospheric chemistry. The technical developments will be done under the supervision of A. Cozic (engineer in charge of the INCA model development at LSCE) to ensure to consistency with the general IPSL model infrastructure and T. Onishi (engineer developing the REPROBUS infrastructure at LATMOS).

WP4: New datasets of natural emissions [resp. J. Lathière, participants: J. Lathière, L. Bopp, S. Szopa]

→ This WP aims is to assess the natural emissions of reactive gases considering climate and land surface conditions occurring at different stages of the Cenozoic.

For that purpose, the terrestrial and marine biosphere models from the IPSL ESM will be used. These models can relevantly be used since the Cenozoic era is characterized by a large variety of climate conditions but with the advantage of modern marine and terrestrial fauna and near present-day oxygen level. The vegetation model ORCHIDEE allows to simulate the biogenic compound fluxes in line with climate conditions, land type distribution and CO_2 level [**Lathière** et al. 2005]. The wildfire emissions, methane initial

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[1] The computing resources required are discussed in the section "C. Resources & budget"

conditions and sources, and terrestrial N_2O will be based on literature and international collaborations. The implementation of processes leading to the emissions of CO, organic and halogenated compounds in the PISCES model is currently going on and will provide, for the first time, cartography of these emissions for past conditions. Oceanic N_2O and OCS emissions will be simulated using PISCES.

Methodology

ORCHIDEE and PISCES will be used to assess the emissions of reactive gases considering climate and land surface conditions gathered in the WP2. The use of these models is relevant since the Cenozoic era is characterized by a large variety of climate conditions but with the advantage of modern marine and terrestrial fauna and near present-day oxygen level. The vegetation model ORCHIDEE allows to simulate the horizontal distribution of biogenic compound fluxes (namely isoprene, terpenes, oxygenated organic compounds) in line with climate conditions, land type distribution and CO_2 level (both for vegetation fertilisation and isoprene emission inhibition). However wildfires are not yet sufficiently robust in this model to be used to estimate the emission with a sufficiently high level of confidence for past conditions. The fire emissions will be based on literature and international collaborations (e.g. global paleofire working group under the auspice of the PAGES program). The same goes for methane initial conditions and sources and terrestrial N_2O. The implementation of processes leading to emission of CO, organic and halogenated compounds in the PISCES model is currently going on and will provide cartography of these emissions for past conditions. Oceanic N_2O emissions will be simulated using PISCES. The sensitivity of the chemistry to natural emissions will be quantified in cold and hot conditions during the third year of the project.

Ancient conditions are sometimes poorly constrained and hypotheses will be required to investigate atmospheric chemistry in the 5 past periods studied in this project. For this reason, simulations will be performed in a pertinent range for the most critical hypothesis, which are:

- Sensitivity to <u>terrestrial biospheric emissions</u> hypothesis

Natural hydrocarbon emissions by terrestrial vegetation, NOx emissions from soils as well as CH_4 emissions by wetlands depends on climate and surface conditions. The different representation in model estimating these emissions at the global scales induce, for present day, variations by factor 2, 3 and 1.6 respectively (Lamarque et al., 2013, Ciais et al., 2013).

In addition, for the past, we have to face two difficulties: the vegetation distribution is poorly constrained and the functions describing the emission sensitivity to temperature and photosynthetically active radiations are calibrated for present-day biomes and conditions. Consequently, a range of possible biogenic emissions has to be considered and the sensitivity of atmospheric chemistry to these emissions as function of climate conditions has to be quantified.

- Sensitivity to <u>wildfires emissions</u> hypothesis

The interannual variability of fires leads to global emissions varying with a factor of two from one year to another for present-day. Over longer time scales, it is reasonable to think that fire intensity could have led to emissions varying by a factor of 3. Different cases based on preindustrial maps, literature and/or cartographies of emissions obtained via collaboration with extern modelling groups will be tested.

- Sensitivity to <u>oceanic emissions</u> hypothesis.

Oceanic circulation, stratification, salinity or nutrient availability changed in the past. Using PISCES, a range of oceanic emissions, for each of the 5 past stages will be simulated and will be used.

This axis will be managed by J. Lathière and benefit from the involvement and expertise of L. Bopp respectively for terrestrial and marine emissions.

Axis 3: Simulations of the Cenozoic atmospheric chemistry and its interactions in the Earth System

WP5: Paleo-chemistry-climate simulations [resp. S. Szopa, participants: S. Szopa, S. Bekki, M. Marchand]

→ This WP aims to perform snapshot simulations at the earth scale for the 5 periods of WP2 with the new chemistry-climate model. The sensitivity of the chemistry to natural emissions will be quantified in cold and hot conditions. It will provide new distributions of atmospheric compounds. The results will be discussed in light of the insights on oxidizing pathways inferred through isotopic proxies (O-MIF, S-MIF) analysis.

We will then analyse the role of trace greenhouse gases, quantify the possible evolution of the self-cleansing capacity of the atmosphere and the impact on the lifetime of important compounds. The UV radiations reaching the Earth will be assessed and surface conditions characterised.

Methodology

Here, the effect of changing environmental conditions on atmospheric chemistry will be quantified by using the offline chemistry-climate configurations at 5 contrasted stages of the Cenozoic (Fig 10). The simulation will consist in 10-year snapshots after a 20-year spin-up. The emissions of compounds needed as boundary conditions for the chemistry are the subject of the WP4. We will perform the simulations from the most recent to the most ancient five following periods since oldest periods require more hypotheses due to the increasing scarcity of data constraints. The selected periods and their specificities are:
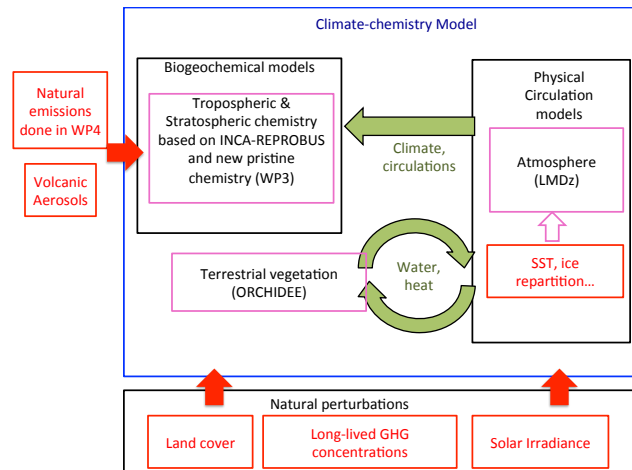

Figure 10: Climate–chemistry model at the heart of this axis

- The Last Glacial Maximum: thanks to ice core analysis, this glacial cold period is relatively well constrained, particularly regarding CO_2, N_2O, CH_4 concentrations. During ice age, ice caps extend over Laurentides and Fennoscandia leading to reduction of vegetation northward and expansion of tundra over northern continents. In the tropics, steppes replace tropical forest, and the terrestrial productivity is probably lower. Combined effects of foliar expansion, and ecosystems redistribution in vegetation associated to cold conditions could have led to twice lower biogenic emissions during the LMG period compared to preindustrial conditions (Lathière et al., 2005). There is no consensus on marine productivity changes.

- The mid Pliocene (3Ma) and Eemian (128ka) are all the more interesting as their warm climate can be considered as analogues of the climate expected at the end of 21st century. However, an important difference is the level of CO_2, which reaches 330-400ppm (part per million) during the mid-Pliocene whereas ice core observations indicate that it remains lower than 270-280ppm during the Eemian. Vegetation of the mid Pliocene is probably leading to higher biogenic emissions (e.g isoprene). Wildfires are also suspected to have been twice more efficient to emit CO, NOx and hydrocarbons (Unger & Yue, 2013).

- The optimum of Miocene (between 24 and 15Ma) is a warm climate episode, probably a few degrees hotter that the future projection for 2100, which occurred in a more general cooling period. This optimum is not explained by CO_2 level, which does not exceed those of the preindustrial atmosphere and thus leaves room for interpretation based on other forcing such as other greenhouse gases. The tropical vegetation is extending far from tropics, for example, in Europe.

- The Eocene optimum is characterised by a particularly hot climate, No icecaps are present at that time. Prior this optimum (56 Ma), an abrupt and severe warming occurred with global temperature increased by 5-8°C. This brutal warming called Paleocene-Eocene Thermal Maximum (PETM) is attributed to destabilisation of clathrates buried in oceanic sediments whereas underlying mechanisms for this release are not fully explained. In any case, isotopic observations confirm the huge release of CH_4 in the atmosphere. This period offers possibility to assess the chemistry in high-CH_4 conditions and hot climate conditions. In particular, large modifications of oxidizing capacity and stratospheric ozone destruction should be strongly different from preindustrial conditions. It could for example lead to modifications of the UV radiations reaching Earth during this period, which has also seen rapid evolution of terrestrial and marine organisms.

PaleOX will provide new distributions of atmospheric compounds for different past cases. On this basis, we will be able to quantify the sources and sinks for relevant oxidants. The exchanges between reservoirs such as stratosphere/troposphere fluxes and the lighting production of NOx, driven by climate modulations will be scrutinized. The oxidizing capacity of atmosphere and its impact on the budget and lifetime of reactive greenhouse gases will be established as well.

Thanks to these new climatologies of atmospheric composition, we will analyse the role of trace greenhouse gases on climate (WP6) and allow the climate modelling community to take them into account in its modelling exercises (via their distribution on the PaleOX web portal). We will also quantify the UV radiation reaching Earth and will characterise surface conditions. These data will provide indications for the other scientific communities (palaeontologists or exobiologists).

This axis is the core of the project, making it possible to apply the chemistry model developed in the 2nd axis to understand chemistry evolution. It will last 3 years from the preparation of the simulation framework prior the simulations (Axis 1 + corresponding emissions) in order to scan carefully the hypothesis required for each period (in particular the oldest). Since the various climates were already investigated with ocean-atmosphere configuration of the ESM, there is no technical risk in this axis. However, if for any reason some delays appear in this axis, we would probably cancel the simulation of the Miocene.

PaleOX will devote one PhD student to the analyses of these simulations, which would be launched and monitor with the help of the computer scientist hired in the project.

The chemistry-climate interactions in these simulations will be analysed by the PhD student supervised by S. Szopa, S. Bekki and M. Marchand. This axis will benefit from the expertise of P. Sepulchre for past climates.

WP6: Earth System Model feedbacks [resp. S. Szopa, participants : S. Szopa, L. Bopp, J. Lathière, M. Marchand, S. Bekki, A. Cozic]

→ Atmospheric chemistry relies on climate and emissions. In return, atmospheric chemistry modifications can impact the radiative budget on Earth, the composition of the air breathed by living organisms or the acidity of the precipitation. This WP aim to investigate the complex feedbacks between the biosphere, the climate and the atmospheric chemistry for most extreme conditions of the Cenozoic.

Climate models consider with more and more details the changes in reactive greenhouse gases for preindustrial to future projections [Stocker et al. 2013]. However, when used to assess their ability to reproduce the past climate proxy (EoMIP, PlioMIP, PMIP), they use fixed and spatially homogeneous distribution of ozone or methane, often corresponding to preindustrial distribution. First, we will quantify the impact of short-lived N_2O, CH_4 and O_3 on climate for the different stages of the Cenozoic selected and see, for example, how the meridional gradients in climate can be affected by the distribution of these non-CO_2 greenhouse gases.

When considering only a temperature change, many feedbacks can occur in the Earth system, which can reinforce or dampen the climate change: some involving directly the climate processes (via albedo, cloud cover change, etc..) and some linked to biogeochemical cycles as for example the carbon-cycle feedbacks. Regarding atmospheric chemistry, feedbacks between vegetation and ozone chemistry have to be considered. Indeed, terrestrial biosphere emits large quantity of hydrocarbons (involved in ozone chemistry) but ozone deposition can significantly alters vegetation functioning, decreasing plant productivity and thus CO_2 uptake. Stratospheric ozone changes can also impact oceanic circulation and thus marine productivity of precursors. Finally, inorganic iodine emissions were recently found to be linked with abiotic processes enhanced by increases of sea surface temperature and atmospheric ozone concentrations [MacDonald et al. 2014]. In the atmosphere, iodine chemistry can, in turn, lead to significant destruction of ozone in the marine boundary layer but also in free and upper troposphere [Saiz-Lopez et al. 2014].

Such interactions and feedbacks can only be considered using Earth system models. The IPSL-CM model has a high level of description of the biosphere (among existing ESM models) and we propose to set up and tighten the relevant couplings to consider interactions with an "atmospheric chemistry centered" point of view. This work would lead to a unique ESM which could be used to investigate the feedbacks related to modifications of the oxidising atmosphere. Hence, the ORCHIDEE model simulates interactive emissions from the terrestrial biosphere with up-to-date representation of the CO_2 inhibition effect on isoprene emissions as well as the ozone effect on vegetation. The oceanic emissions are considered in the PISCES biogeochemical model for several precursors of atmospheric chemistry and will be completed through this project as well as extended to ice emissions of halogenated compounds to better investigate the LGM conditions. Then, the feedbacks and resulting atmospheric composition will be studied for most extreme conditions uppermost (Eocene, LGM) and the mid-Pliocene "future condition analogue". The effect on climate and in particular on spatial gradients will be carefully examined.

The analysis of such complex feedbacks is tricky. To achieve this goal, we will perform two sets of simulations. First, the impact of chemistry on climate will be investigated using the 3D fields of reactive components having a radiative effect (CH_4, N_2O, O_3) simulated in the WP5 and the ocean-atmosphere configuration of the IPSL-ESM. Based on multicentennial simulations, the impact on climate will be assessed and compared to a similar simulation but considering only the CO_2 as atmospheric forcing. If climate is drastically affected by these changes in atmospheric composition, the feedback will be considered using an asynchronous offline coupling methodology. For this set of runs, the model is the IPSL Earth System Model (IPSL-CM6-VLR).

Second, a simulation with the complete new ESM including the new interactive chemistry developed in 1st axis will be performed for one scenario with hot climate conditions to evaluate the role of the feedbacks involving atmospheric chemistry in the Earth System. For this simulation, the model is the IPSL Earth System Model (IPSL-CM6-VLR, including interactive chemistry developed in the axis 2).

PaleOX will devote time of the computer engineer, hired within the project to prepare the new ESM configuration including the original chemistry of WP3 and relevant couplings for atmospheric chemistry.

The analysis of the runs will be done in collaboration with the experts of each components of the IPSL model to maximize the scientific benefits of these complex and comprehensive simulations.

5.2. THE TEAM

- **Early achievements track-records of the PI and opportunities given by a JCJC project**

Since my PhD dedicated to the development of detailed photo-chemistry models, I have oriented my research on global tropospheric chemistry modelling, with the general aim of quantifying the trends of chemically reactive compounds at the Earth scale induce by human activities. The long term trends and interannual variability of ozone were also in my targeted scope. I took part to several international initiatives involving about 20 global chemistry-climate models allowing to intercompare the sensitivity of the models. These works have allowed to better assess, through ensemble of simulations, the role of intercontinental transport of pollution as well as to estimate the future ozone considering several scenarios. Using both global and regional models, I demonstrated the impact of global ozone change in the near future on air quality issues in Europe. These simulations were used by climate modellers, economists and ecologists to assess the impact of atmospheric trace constituent changes.

After 3 years as a team leader, I dedicated 2 years to the administration of my institute (as deputy director) and, at national level, to the french scientific community working on atmospheric and oceanic sciences (through my implication in CNRS committees). It brings me a global view of the Earth science field and convinced me to lead a project at the frontier between atmospheric chemistry and paleoclimatology.

Based on my strong background in tropospheric chemistry modelling, this project is a new direction in my career with an important shift toward deep past of the Earth. PaleOX would allow me to manage my own team on a single and original aim, establishing my scientific leadership on paleochemistry modelling which is new in France over such timescales. Fully convinced by the benefit of multi-model exercises, I would promote the sharing of past scenarios among atmospheric chemistry modellers allowing to do intercomparisons of paleochemistry studies.

- **Skills of The PaleOX team**

The coordinator, **S. Szopa** (Ingénieur Chercheur CEA, since 2009) first developed detailed models of photo-chemistry during her PhD obtained in 2003. With 2 children born after her PhD and recruited as a permanent researcher only in 2009, the coordinator is still in an early stage of her career and lies in the JCJC range (according to the ANR definition : i.e. PhD after 1st of Jan 2005 - 1year/child born after PHD). She is author or co-author of 68 peer-reviewed papers in international scientific journals (http://www.researcherid.com/rid/F-8984-2010). S. Szopa has a good experience in project coordination (e.g. led the contribution of the IPSL institute to IPCC chemistry-climate activities (CMIP5) in 2009-2012, coordinator of 2 LEFE-INSU projects in 2011-2014 and 2015-2016 and co-coordinator of a PRIMEQUAL-project (2010-2013) and management.

Three other researchers playing key role in this project belong to the JCJC ANR category.

E. Martin (Assistant Professor, since 2010) is in charge of the volcanic sulfate sampling in this project. He first studied the evolution of magmas in several geodynamical contexts and the formation of primitive continental crust. He has a strong field experience as well as a mastery of the stable isotope quantification. He recently performed a study based on the analyses of the sulfates deposited after 10 eruptions, which occurred since 1947. This publication has demonstrated the potential of the S and O isotope fractionation to better understand the chemical pathways in the troposphere.

J. Lathière (Chargée de Recherche, since 2008) is specialized in biosphere‐atmosphere interactions and has 11 years of experience in biogenic emissions. Her research activity at the LSCE focuses notably on the coupling between a vegetation model (ORCHIDEE) and atmospheric chemistry model (LMDz-INCA).

P. Sepulchre (Chargé de Recherche, since 2009), studies the evolution of climate over the last 50 million-years and its link with biological evolution.

PaleOX is highly interdisciplinary, requiring stimulating exchanges with different scientific fields. The team associated in this project covers this interdisciplinary and can bridge the atmospheric chemists and paleoclimate modellers. The association with geochemists who enlighten clues on atmospheric oxidation channel recorded in rock archives is a unique opportunity to constrain for the first time the Cenozoic atmosphere at different periods. In order to cover all the skills needed, 9 other engineers and researchers will take part, at different levels, to the project. Hence, the S-MIFS and O-MIFS measurements will be performed by N. Caillon and J. Savarino at LGGE. The stratospheric chemistry and sulfur cycle modelling will be done in collaboration with M. Marchand, S. Bekki T. Onishi at LATMOS.

It is important to notice that the project will benefit from an existing dynamic since E. Martin, S. Bekki and M. Marchand, N. Caillon participate to the FOFAMIFS-ANR project (see p.12) supervised by J. Savarino. This on-going project (2014-2018) is establishing robust methodologies to quantify and interpret S-MIFS and O-MIFS. The PaleOX project will thus benefit from already existing collaborations and effective interactions between these participants.

The core team will be strengthened by the recruitment of 1 computer scientist for two years, 1 assistant engineer for 6 months and 1 PhD for three years. Their involvements are detailed on Table 2.

5.3. TASKS SCHEDULE AND MANPOWER ALLOCATION

Table 1: Deliverables in each WP and time schedule of the project (in green are the field campaigns and main numerical simulations)

Months: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48

Axis 1 - Reconstruction of the Cenozoic Era conditions

WP1 Isotopes analysis of Cenozoic volcanic deposits
- Evaluation of the chronostratigraphy for Cappadoce / Establishment of the sampling strategy
- Sampling of turkish deposits
- sulphate extration and purification
- O- and S- isotope measurments of turkish deposits
- 2D atmospheric modelling - Discussion of the representativity of volcanic isotopes
- Altiplano Field exploration
- Altiplano Field tephrochronology
- Sampling of Altiplano deposits
- Sulphate extraction and purification of Altiplano deposits
- O- and S- isotope measurments
- 2D atmospheric modelling - Discussion of the representativity of volcanic isotopes

WP2 Collection of physical Cenozoic conditions
- Design of the 5 past scenarios (SST, insolation, Land surface types, coastline for each simulation, LL_GHG)

Axis 2 - Development for past pristine atmospheres

WP3 Chemistry Model
- Full tropo and strato model to test on present day conditions
- Present day climatology to be compared with observations
- Preindustral climatology to be compared with observations and to multimodel
- Evaluation of the model performance for present-day and preindustrial conditions

WP4 New natural emissions
- Evaluation of Biogenic emission range (from ORCHIDEE) for each scenario
- Evaluation of Oceanic emission range (from PISCES) for each scenario
- Evaluation of Wildfires emission range (from litterature and collaboration) for each scenario
- Sensitivity studies to Natural emissions

Axis 3 - Cenozoic atmospheric chemistry simulations

WP5 Paleo chemistry-Climate simulations
- Last Glacial Maximum Simulation
- Eemian Simulation
- Mid-Pliocene Simulation
- Optimum Miocene Simulation
- Paleocene-Eocene Thermal Maximum Simulation
- Analysis of the simulations, realism of the results, comparison with previous study and ISOTOPE ANALYSIS, evolution of oxidizing capacity throughout time
- Climatologies of 3D distribution of reactive compounds and corresponding surface UV radiation distributed

WP4 Earth System Feedbacks
- Simulation of the climate feedback due to composition change (ESM forced by WP5 concentrations) for each of the 6 past conditions
- Quantification of chemistry effect on climate
- IPSL-CM5 model with interactions between: Climate and 3D atmospheric N_2O, CH_4, O_3/Chemistry and terrestrial biosphere/Atm Chemistry and marine biogeochem
- Simulation with the IPSL-CM5 model first with all the couplings for hot climate conditions (100 yrs + 1base line 100yr)
- Quantification of the feedbacks

Dissemination/Outreach

PaleOX Meetings ↑ ↑ ↑ ↑ ↑

Table 2: Involvements of the participants in the WP

	SZOPA	LATHIÈRE	SEPULCHRE	BOPP	COZIC	CAUD	MARTIN	BEKKI	MARCHAND	ONISHI	SAVARINO	CAILLON	PhD PaleOX	Research Engineer	Assistant Engineer	M2 isotopes	M2 modelling	M2 mediation	Collab. JL Le Pennec (IRD-LMV)	Collab. H. Guillou (CEA-LSCE)
Coordination (S. Szopa)																				
Axis 1 - Reconstruction of the Cenozoic Era conditions																				
WP1 Isotopes analysis of Cenozoic volcanic deposits (resp. E. Martin)																				
Evaluation of the chronostratigraphy for Cappadoce / Establishment of the sampling strategy																				
Sampling of turkish deposits																				
sulphate extraction and purification																				
O- and S- isotope measurments of turkish deposits																				
2D atmospheric modelling - Discussion of the representativity of volcanic isotopes																				
Altiplano Field exploration																				
Altiplano Field tephrochronology																				
Sampling of Altiplano deposits																				
Sulphate extraction and purification of Altiplano deposits																				
O- and S- isotope measurments																				
2D atmospheric modelling - Discussion of the representativity of volcanic isotopes																				
WP2 Collection of physical Cenozoic conditions (resp. P. Sepulchre)																				
Design of the 5 past scenarios (SST, insolation, Land surface types, coastline for each simulation, LL_GHG)																				
Axis 2 - Development for past pristine atmospheres																				
WP3 Chemistry Model (resp. S. Szopa)																				
Full tropo and strato model to test on present day conditions																				
Present day climatology to be compared with observations																				
Preindustral climatology to be compared with observations and to multimodel experiment (few data)																				
Evaluation of the model performance for present-day and preindustrial conditions																				
WP4 New natural emissions (resp. J. Lathière)																				
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Simulation with the IPSL-CM5 model first with all the couplings for hot climate conditions (100 yrs + 1base line 100yr)																				
Quantification of the feedbacks																				
Dissemination/Outreach																				

5.4. SCIENTIFIC JUSTIFICATION OF REQUESTED RESSOURCES

Budget (in k€) for 48 months

Salary	217	94	1 PhD (LSCE-LATMOS)
		98	1 computer engineer (28 mth) (LSCE-LATMOS)
		18	1 chemical analysis engineer (6 mth) LGGE
		2	1 master student (1 on analysis)
		2	1 master student (1 on modeling)
		2	1 master students (1 on vulgarization)
Analytical fees	25	10	10 Ar-Ar datations (LSCE) for tephrochronology on Altiplano volcanic deposits
		5	samples' preparation - Maintenance (not covered by the institute) and running the ISTEP geochemical lab for sulfate extraction and purification
		10	samples' analysis (LGGE) [100 samples' analysis (both O- and S-MIFS)]
			irMS (oil and turbo pumps servicing, filament, source cleaning) 50 % of the unit price
			Consumables (Helium, isotope standards, chemical reagents, wet chemistry consumables, vacuum and GC connections, GC columns) 50 % of the unit price
Local computing fees	10	10	Computers, hardware and storage
Missions	45	25	Chili and Turkey [2x2.5k€ x 2persons + 4x5k€ x 2persons]
		15	European Geosciences Union General Assembly (EGU) [1k€ x3 persons]
			American Geophysical Union fall meeting (AGU) [2k€ x3 persons]
			Goldschmidt conference (Boston, 2018) [2k€ x3 persons]
		5	ANR meetings + Internal project meetings
Divers	45	20	Open access publication fees
		12,7	administrative fees (4%)
		12,7	infrastructure fees (4%)
TOTAL	342		

Computing resources

The computing time for 3D simulations will be asked yearly via application to the call for projects of the french supercomputing consortium, GENCI. (See more at: http://www.genci.fr/en/content/using-genci-resources#sthash.Majhk2Ap.dpuf)

The requested CPU time as well as the real time needed to achieve the simulations are estimated hereafter for each version of the IPSL model used in this project. The CPU time is totally consistent with the usual CPU time we obtained so far for similar project via the national GENCI program.

Configuration	Axis	Estimation of CPU and real-time
LMDz-INCA+ new chemistry from axis 1	2 WP3	Considering 200 tracers, a decade=7,000h in CPU time i.e. less than 10 days in real time on 32 processors.
Ocean-Atmosphere from IPSL-CM6-VLR	3 WP5	100 years in 4 real days (corresponding to 13000h in CPU time)
IPSL-CM6-VLR with full couplings (including chemistry)	3 WP6	Based on the performances of existing versions with chemistry, it would simulate 100 years in 18 real days (corresponding to 53000h in computing time). Slow processes such as deep water exchanges in the ocean require at least 1000 years of simulations to reach climate equilibrium. As an option to decrease CPU, we can either study the feedbacks over shorter periods (150 years) neglecting the potential deep oceanic circulation change and then simulates several past conditions or we can focus on one long simulation reaching the ocean-atmosphere equilibrium.

6. IMPACT OF THE PROJET, STRATEGY FOR PROTECTION, EXPLOITATION AND DISSEMINATION OF THE RESULTS

Through this project, we will compare in a consistent way how the self-cleansing capacity of the atmosphere evolved during the Earth cooling and how, as a consequence, the lifetime of toxic or climatically active compounds was modified. The evolution of the ozone budget and its main drivers will be investigated. Finally the simulation of surface air quality and UV radiation will allow to better characterize the conditions in which ecosystems evolved and some of the environmental stresses they endured.

Numerous hypotheses are required to model past environments. One important objective will consist in systematically scanning and quantifying the range of uncertainty for the most important hypotheses regarding atmospheric composition. Beyond this objective, it will also document the sensitivity of the global atmospheric chemistry in extreme conditions.

Then, the impact of the changes in atmospheric composition on climate will be fully quantified. Finally, the objective is to analyse the feedbacks, which can occur in the Earth system via the biosphere or in the climate loops.

If modelling realisations have short lifetimes due to perpetual improvements of the state of the art, the data we will provide through isotope analysis will represent durable landmarks for paleochemistry studies.

Outreach

This project will, for the first time, document the variability of the oxidizing capacity in contrasted conditions, establishing a comprehensive baseline of the prehuman atmosphere and thus putting in perspective the recent and future human pressure on the atmospheric composition. Beyond the atmospheric chemistry field, PaleOX will provide elements for geologists (mainly sedimentologists and paleontologists) communities giving ranges of atmospheric stresses for different periods. Finally, such snapshots of atmospheric composition and in particular the content of organic compounds in oxidative atmosphere for different states of the Earth can provide elements, such as atmospheric biomarker signatures, for exoplanet observations.

A specialist of scientific mediation, N. Caud, (in charge of the LSCE communication) will join the project to supervise the production of sketch notes and videos, abordable for schoolchildren, and having attractive and modern designs. The aim of these supports will be to promote the way we, as scientists, interrogate the world we live and its evolution and how, starting from questions, we develop a reasoning based on "material proofs" and numerical experiments. The underlying aim will be to promote the scientific reasoning and the way we gather the "proofs" rather than detailing statically the inventory of knowledge. These reflexion will be conducted with a master (M2) student in a scientific mediation cursus.

At the end of the project, in addition to peer-review publications, all the simulations will be made available to end-users under the form of a web portal on which major results will be displayed. The Earth system model is developed under open source license and the development, such as the chemical scheme, will be available for the modelling community.

Challenges

The investigation of the paleochemistry is pioneering: whilst atmospheric composition changes can lead to dramatic effects on climate and life, only few proxies remain to reflect this reactivity over geological times which is thus almost unexplored so far. As a result, the possible importance of rapid atmospheric chemistry and short-lived greenhouse gases has been overlooked in past climate studies. Nowadays, numerical tools combined with original proxies can be used to assess such hypotheses. To do so, such tools have to reflect the complexity of atmospheric chemistry as well as its relations with the other reservoirs. Since a few years, some Earth System models now describe the contemporary atmospheric chemistry and are used to investigate its role on the current climate change. Fed and constrained by huge but synthetized interdisciplinary knowledge on the state of the Earth, they can be used to investigate past atmospheres.

The paleoclimate community has done a remarkable effort in the last years to homogenise existing data and assess their representativity. It provides a precious basis to investigate past atmospheric chemistry using ESM. In the meantime, high performance computing has improved and now allows to simulate the fate of hundreds of atmospheric constituents in the context of the Earth system evolution over multi-year periods with a reasonable computing cost (**Szopa** et al. 2013). Note that the computing time needed fits in usual project allocations of the French supercomputing consortium.

Paleo-atmospheric chemistry clearly lacks proxies to constrain the evolution of reactive species. In this projet we plan to collect previously unmined samples. A risk remains regarding the presence of enough sulfates of secondary origin in the samples. However, the feasibility of MIF analysis in Cenozoic ash beds has been demonstrated by (Bao et al. 2010). The analysis of the Turkish samples would be a low to medium risk/high gain study. The study of Altiplano samples is more risky because the suitable sampling site is not yet well identified, however, we will benefit from the expertise and networks of J.L. Le Pennec and H. Guillou, both senior scientists, to gather and date proper samples. This part is more exploratory but is realistic and would clearly lead to highly valuable results.

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