

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

1. Context and Scientific objectives of PaleOX

About 500 million years ago (Ma), the diversification of life had released, through photosynthesis, enough oxygen to lead to an atmosphere still dominated by nitrogen but oxygen-rich (varying between 0.7 and 1.8 Present Atmospheric Level). The biosphere thus provided the free oxygen that makes Earth so peculiar in our solar system. Oxygen has notably allowed the densification and lifting of an ozone layer protecting DNA-based living organisms from destructive UV radiations and allowing the land colonisation. Oxygen also induces a peculiar chemistry, triggered by the solar energy, which slowly burns the organic molecules produced by the biosphere. This chemistry relies on highly reactive intermediates such as radicals or ozone whose amount determines the oxidising capacity of the atmosphere and thus the atmospheric lifetimes of reactive gases.

So far, no information exists regarding the atmospheric chemical reactivity toward geological times. However, it was recently established that volcanic sulphates record, through mass-independent isotopic signatures, the oxidation pathways they encountered during the atmospheric sulphur removal. Such end products can be preserved over millions of years and can thus be used as indicators of atmospheric chemical processes. Hence, volcanic sulphates offer possibilities to constrain the past oxidation pathways.

Atmospheric composition is crucial in the Earth system functioning: By filtering the solar radiations reaching the Earth, controlling acidity of rain or regulating harmful compounds, atmospheric chemistry can favour or alter living organisms; By interacting with solar radiations as well as the infrared terrestrial emissions outgoing in space, atmospheric composition partly controls climate conditions. Whereas carbon dioxide is often the main driver (considering atmospheric composition) of climate change, reactive species such as ozone, methane or nitrous oxide contribute significantly to Earth radiative equilibrium. Multi-proxy analyses have allowed partial reconstruction of the puzzling past conditions but the levels of reactive trace species are unknown back in time prior to 800ka. Hence, although deep time climates are more and more investigated with numerical models, the role of non-CO₂ atmospheric compounds is neglected.

The Cenozoic era (the last 66Ma) has encompassed an incredible range of environmental conditions, from a very warm greenhouse world to the current ice world and has seen the huge diversification of plants and mammals. However, many questions remain regarding the links and feedbacks between the evolution of life, atmospheric chemistry and climate: Is the oxidising capacity of the atmosphere varying throughout time or is it regulated by chemistry of biogenic compounds? What is the distribution of organic oxygenated compounds on a living planet? What is the radiative spectrum reaching Earth and thus affecting life in so different conditions? How was the chemistry functioning when oxygen levels were significantly lower or higher than present-day? Have the surface atmospheric composition (ozone levels for instance) always been harmless for life or did it play a role on biosphere evolution? Could the content in reactive gases explain some of the discrepancies between models and data for past warm conditions?

In PaleOX, we will use state-of-the-art chemistry-climate modelling supported by sulphate isotopic composition measurements with the aim of revealing how the oxidising capacity of the atmosphere has evolved throughout the Cenozoic era (the last 66 million years of Earth's history) and how it has affected the lifetimes of reactive greenhouse gases.

We will explore how the atmospheric composition (in particular non-CO₂ 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 an 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 unique dataset of isotopic measurements will provide new insights into atmospheric oxidation pathways prevailing in past atmospheres, thanks to the collection of original samples of volcanic sulphates 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.

2. Scientific description of the project

2.a. Scientific and technological objectives

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

- **Understanding pristine atmospheric chemistry**

First, atmospheric chemistry needs to be represented in 3D climate-chemistry models adequately to reproduce the mechanisms occurring in a non-humanly perturbed atmosphere. Nowadays, anthropogenic emissions drastically shift the oxidative photochemistry of the atmosphere, altering the stratospheric ozone layer and leading to an overproduction of ozone in the vicinity of populated basins. Models were mainly developed to investigate the human footprint on its atmospheric environment and the consequences on the milieu. Thus they focus on the representation of the main drivers of the chemistry leading to societal issues. However, in the absence of anthropogenic activities, chemical regimes are different and reactions considered as negligible in polluted areas can play a key role in 'clean' atmosphere. Thus, there is a need to adapt these models to pristine chemistry if the past atmospheres are targeted. Radicals especially are highly important since they initiate the oxidation of reduced compounds. Hence, they determine (in addition to photolysis for chromophoric compounds) the atmospheric lifetime of many compounds and, for some of them, their conversion into

aerosol particles. The level of radicals, in particular hydroxyl radical (OH), is thus crucial as it largely determines the oxidizing capacity of the atmosphere. During this oxidation process, radicals can be recycled or destroyed. In this matter, the level of nitrogen oxides (NO_x) is decisive as it governs the radical propagation, but is drastically affected by anthropogenic combustion emissions. During the last decade, our understanding of background chemistry improved a lot, in particular regarding the chemistry of radicals. For example, the recycling of hydroxyl radical was recently debated due to unexpected high concentrations measured over tropical forests. This recycling, which occurs when the most emitted biogenic hydrocarbon (isoprene) is oxidised in low-NO_x concentrations, is now explained by a new pathway for peroxy radical intermediates. Overall, substantial progress has been recently made in our understanding of chemistry of natural atmospheres. **In PaleOX, we will develop a new chemical model dedicated to the representation of pristine chemistry to be used in global chemistry-climate models or in Earth System Models (ESM).**

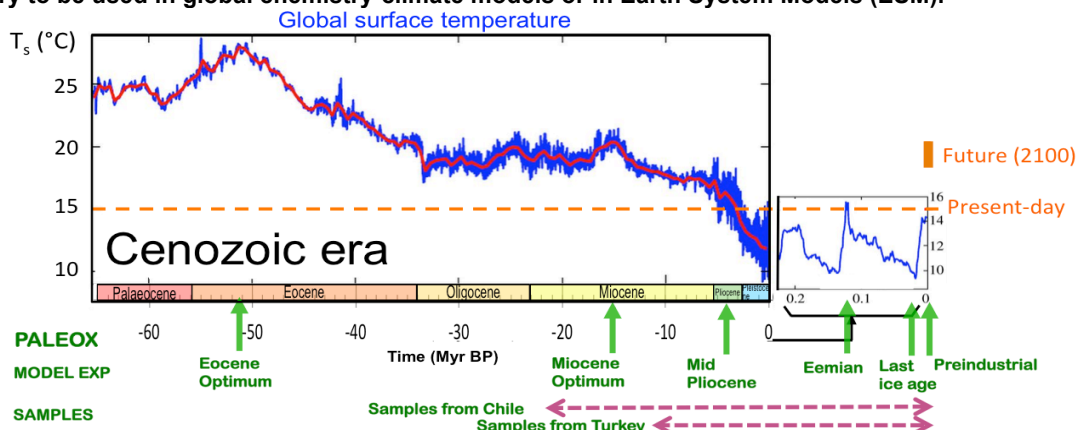


Figure 1: Surface temperature estimate for the past 65.5 Myr, including an expanded time scale for the past 200 000 years (adapted from Hansen et al., 2013¹). Surface air temperature expected at the end of the 21st century, according to multi-model RCP8.5 projections are superimposed.

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

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 CO₂). Oxygen isotopes from marine organisms indicate large variations in deep ocean temperatures, which correspond to even larger global surface temperature variations (Fig. 1). 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. gramineae) 8 to 3 Ma [2]. 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 [3,4]. In addition, huge efforts of data synthesis for past conditions have been done, these last years, in order to simulate past climates and assess their realism against proxy data (PMIP⁵, PlioMIP⁶, EoMIP⁷). **These recent syntheses will be the foundations of our atmospheric chemistry 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 synthesize the state-of-the-art understanding on these reservoirs in order to represent their functioning and interactions. As stated by the last IPCC report [8], 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 strides in climate modelling is the consideration of atmospheric chemistry 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 and is the ideal tool to deal with the biosphere/atmosphere interactions regarding reactive compounds. Hence, 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 current capability of large scale computing facilities and level of parallelization of

1 Hansen et al. 2013. Climate sensitivity, sea level and atmospheric carbon dioxide, Phil. Trans. R. Soc

2 Edwards et al. 2010. The Origins of C4 Grasslands: Integrating Evolutionary and Ecosystem Science, Science,

3 Scott & Glasspool 2006. The diversification of Paleozoic fire systems and fluctuations in atmospheric oxygen concentration, Proc. Natl. Acad. Sci. USA,

4 Bond and Scott 2010, Fire and the spread of flowering plants in the Cretaceous. New Phytologist,

5 Braconnot et al, 2012. Evaluation of climate models using palaeoclimatic data, Nature Climate Change.

6 Haywood et al. 2010. Pliocene Model Intercomparison Project (PlioMIP): experimental design and boundary conditions, Geosci. Model Dev.

7 Lunt et al., 2012. A model-data comparison for a multi-model ensemble of early Eocene atmosphere-ocean simulations: EoMIP. Clim. Past

8 Flato et al. 2013. Evaluation of Climate Models. In Contribution of WGI to the AR5 of the IPCC. Cambridge University Press.

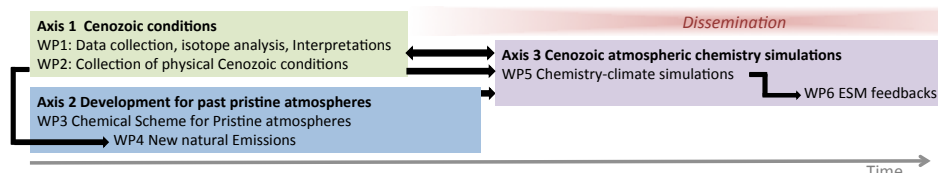
ESMs now enable the simulation of atmospheric transport and chemistry of a large number of tracers with reasonable computational cost and thus open the way to question the hypothesis existing on the role of past atmospheric chemistry.

- **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 oxidative capacity, to frame and evaluate the evolution of atmospheric chemical reactivity in numerical experiments. The best option as paleo-chemistry indicator is the Mass Independent Fractionation (MIF) of oxygen and sulphur isotopes since they record the atmospheric oxidation pathways experienced by volcanic sulphates during their transit and oxidation in the past atmosphere. 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 sulphur and oxygen mass independent isotopic anomalies. The Savarino's group (LGGE) is one of them.

2. b. Scientific program and project structure

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 - Volcanic eruptions are sporadic but mark out milestones in the progressive evolution of Earth. The huge quantity of sulphur then injected in the atmosphere is oxidised and converted into sulphate aerosols that, associated to volcanic clasts, end up deposited on the Earth's surface. When occurring in arid or semi-arid regions, these sulphates can be preserved in volcanic deposits for millions of years. The isotopic composition of these sulphates is a good indicator of oxidation pathways they undergone during their formation [9,10]. The combined use of oxygen and sulphur Mass-Independent Fractionation Signatures (O- and S-MIFS) of sulphates archived in ice cores [11,12], tuffaceous ash beds [13, 14] or fresh volcanic ash [15] have evidenced their potential to constrain the important oxidation channels through which volcanic sulphate has been generated in the atmosphere. However, two challenges have to be taken up when dealing with Cenozoic archives: (1) the identification of sites with documented chronostratigraphy and sufficiently rich in secondary sulphates (arid to semi-arid environments) and (2) the capability to extract and measure S and O isotopes with a high precision in dozens of natural samples on a systematic way. This last point is perfectly mastered by the LGGE team involved in the project which was pioneering in applying these techniques to ice cores. Regarding the samples, we identified two main targets liable to contain Cenozoic volcanic sulphates:

- The Cappadocian ignimbrites and ash layers (Central Anatolia, Turkey) deposited during plinian to ultra-plinian eruptions from the upper Miocene until the Quaternary [16]. For this site, a set of samples will be obtained via a collaboration with J.L. Le Pennec (IRD), who established the chronostratigraphy of these eruptions [17].

- The Atacama desert in Northern Chile, one of the driest place on Earth for the last ~150 Ma [18], reveals vast and well preserved volcanic deposit outcrops mid-Cenozoic in age [19,20]. A sampling campaign will be carried on in collaboration with colleagues from Chile (A. Castruccio, University of Chile - Santiago and E. Campos, Universidad Católica del Norte - Antofagasta).

The collection and isotopic analysis of volcanic deposits will bring new information on the oxidation pathways and their evolutions for contrasted periods.

WP2: Physical conditions for simulations over Cenozoic Era - The aim is to gather oceanic and atmospheric physical conditions for five contrasted stages of the Cenozoic chosen to encompass the diversity in climate, CO₂ 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 and original climate simulations recently performed at LSCE [21]. We will harness these huge synthesis efforts on climate drivers (solar radiations, paleogeography, vegetation distribution, CO₂ atmospheric levels, notably) and climate parameters (temperatures, oceanic salinity, etc....) to build a set of initial and boundary conditions

9 Savarino et al. (incl Bekki), 2003. UV-induced mass-independent sulfur isotope fractionation in stratospheric volcanic sulfate, *Geophys. Res. Lett.*
 10 Savarino, Bekki et al., 2003. Evidence from sulfate mass independent oxygen isotopic compositions of dramatic changes in atmospheric oxidation following massive volcanic eruptions, *J. Geophys. Res.*

11 Baroni, et al. (incl Savarino). 2007. Mass-independent sulfur isotopic compositions in stratospheric volcanic eruptions. *Science*.

12 Baroni, Savarino et al. 2008. Anomalous sulfur isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores, *J. Geophys. Res.*

13 Bao et al. 2010. Massive volcanic SO₂ oxidation and sulphate aerosol deposition in Cenozoic North America, *Nature*

14 Martin & Bindeman (2009) Mass-independent isotopic signatures of volcanic sulfate (...) ash deposits in Lake Tecopa, Calif. *Earth Planet. Sci. Lett.*

15 Martin, Bekki, et al. 2014. Volcanic sulfate aerosol formation in the troposphere, *J. Geophys. Res.*

16 Temel et al. 1998 Ignimbrites of Cappadocia _Central Anatolia, Turkey/: petrology and geochemistry *J. Volcanol. Geoth. Res.*

17 Le Pennec et al. 2005. Stratigraphy and age of the Cappadocia ignimbrites, Turkey: (...). *J. Volcanol. Geoth. Res.*

18 Hartley et al. 2005. 150 million years of climatic stability: evidence from the Atacama Desert, northern Chile. *J. of the Geol. Society*

19 de Silva, 1989. Geochronology and stratigraphy of the ignimbrites (...) of northern Chile. *J. Volcanol. Geoth. Res.*

20 Wörner et al. 2000. Geochronology (...) of Cenozoic magmatic rocks from Northern Chile (18-22°S) (...). *Revista geológica de Chile.*

21 Chaboureaud et al. (incl Sepulchre), 2014. Tectonic-driven climate change and the diversification of angiosperms. *Proc. Natl. Acad. Sci.*

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).

Axis 2: Developments for deep time pristine atmospheric chemistry

WP3: Development of an up-to-date chemical scheme for gaseous chemistry - 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). The simulations for the present-day atmosphere will be validated using the large measurement datasets available nowadays focusing on the few remaining low-polluted areas of the Earth. 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.

WP4: New datasets of natural emissions - In this WP, the terrestrial and marine biosphere models from the IPSL ESM will be used to assess the natural emissions of reactive gases considering climate and land surface conditions gathered in WP2. 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 [22]. The wildfire emissions, methane initial 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 emissions will be simulated using PISCES.

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

WP5: Paleo-chemistry-climate simulations - The new chemistry-climate model will be used to perform snapshot simulations at the earth scale for the 5 periods of WP2. 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.

WP6: Earth System Model feedbacks - Climate models consider with more and more details the changes in reactive greenhouse gases for preindustrial to future projections [23]. However, when used to assess their ability to reproduce the past climate proxy (EoMIP, PliMIP, 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.

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 [24]. 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 [25].

Such interactions and feedbacks can only be considered using Earth system models. This WP will be based on the use of IPSL-ESM model including the new chemical scheme produced in this project. It also includes the ORCHIDEE and PISCES models, which respectively simulate the terrestrial biosphere and oceanic biogeochemistry. Then, we will investigate the complex feedbacks and resulting atmospheric composition for most extreme conditions (Eocene, LGM) and for the "future condition analogue" (mid-Pliocene).

3. 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. 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 synthesized 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

22 Lathière et al. 2005. Past and future changes in biogenic VOC emissions simulated with a global vegetation model, *Geophys. Res. Lett.*

23 Stocker et al. 2013. Technical Summary. In Contribution of WG1 to the AR5 of the IPCC. Cambridge University Press.

24 MacDonald et al. 2014. A laboratory characterisation of inorganic iodine emissions from the sea surface: (...), *Atmos. Chem. Phys.*

25 Saiz-Lopez et al. 2014. Iodine chemistry in the troposphere and its effect on ozone, *Atmos. Chem. Phys.*

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 [26]. Note that the computing time needed fits in usual project allocations of the French supercomputing consortium.

Proper samples containing proxies of paleochemistry are tricky to identify and collect. We will benefit from the expertise and network of H. Guillou, tephrochronologist, to gather proper samples. A risk remains regarding the presence of enough sulphates of secondary origin in the samples. However, the feasibility of MIF analysis in Cenozoic ash beds has been demonstrated by [13]. The analysis of original samples would be a medium risk/high gain study.

4. The PaleOX team

The coordinator, **S. Szopa** (Chargée de Recherche, since 2008) first developed detailed models of photo-chemistry during her PhD obtained in 2003²⁷. She has a strong experience on global tropospheric chemistry modelling. In particular, she studied the trends of chemically reactive compounds at the Earth scale and their links with human activities. She is author or co-author of 67 peer-reviewed papers in international scientific journals (<http://www.researcherid.com/rid/F-8984-2010>). She took part in several international initiatives (involving more than 20 global chemistry-climate modelling teams) focussing on the role of intercontinental transport of pollution as well as estimating the future ozone under several scenarios. S. Szopa has a strong 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 sulphate 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 communities. 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.

Consortium	LSCE (CEA-CNRS-UVSQ)	ISTEP (UPMC-CNRS)	LATMOS (CNRS-UVSQ-UPMC)	LGGE (UJF-CNRS)
Main Scientists ("Jeunes chercheurs/Jeunes Chercheuses")	S. Szopa (CR-CEA), J. Lathière (CR-CNRS), P. Sepulchre (CR-CNRS), L. Bopp (DR-CNRS), H. Guillou (DR-CEA), A. Cozic (IR-CEA)	E. Martin (MC-UPMC)	S. Bekki (DR-CNRS), M. Marchand (CR-CNRS), T. Onishi (IR, UPMC)	J. Savarino (DR-CNRS) N. Caillon (IR-CNRS)
Expertise	Global Modelling of Tropospheric chemistry, paleoclimate and vegetation and oceanic phytoplankton modelling, tephrochronology	S and O MIFS, sampling, interpretation	Atmospheric chemistry modelling including S and O MIFS	S and O MIFS determination and interpretation
Permanent Staff (Man.Months)	85	10	30	10

5. 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 vulgarisation, N. Caud, will join the project to supervise the production of presentations and sketch notes, affordable for schoolchildren, explaining the past of atmospheres as well as the motivations and proceedings of the project.

At the end of the project, 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.

6. Budget (in k€) for 48 months

Salary	235	1 PhD + 1 computer engineer (28 mth) + 1 chemical analysis engineer (6 mth) + 3 master students (1 on analysis/ 1 on modeling /1 on vulgarization)
Equipements	25	Including 15 for samples' preparation and analysis
Missions	45	
Divers	38	13 for administrative fees + 25 for publication fees
TOTAL	343	

²⁶ Szopa et al. (incl. Bekki, Marchand, Lathière) 2013. Aerosol and Ozone changes as forcing for Climate Evolution between 1850 and 2100. *Clim. Dynamics*

²⁷ With 2 children born after her PhD, the coordinator is in the JCJC range (i.e. PhD after 1st of Jan 2005 - 1year/child born after PHD)