Chapter 1

Introduction: On the Early Evolution of the Atmosphere of Terrestrial Planets: COST Action CM#0805

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Abstract The early setting and evolution of planetary atmospheres of rocky planets is a hot, but still immature research topic. A better understanding of the processes at work at that early epoch in the history of our solar system is certainly required, particularly at this historical juncture when we are just discovering the first exoplanets similar to Earth. These new worlds need to be put in their astrophysical and cosmochemical context, as we understand stars in the Cosmos as physical entities similar to the Sun, but with different masses, composition, and distinctive evolutionary stages. Exoplanets discovered so far exhibit large diversity as a direct consequence of having experienced differing births, evolutionary stages, and being subjected to stochastic processes in the early stages of their growth and evolution. To understand what is going on in the first stages of planetary evolution we must promote interdisciplinary research. That should yield better answers about the role played in planetary setting and evolution by processes such as accretion, chemical differentiation, outgassing, impacts, and the different energy fluxes from their host stars. Our current knowledge regarding the initial atmospheric evolution of the Earth is scarce. State-of-the-art analyses of primitive meteorites, together with returned

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asteroidal and cometary materials will be able to offer us more realistic starting chemical compositions for the primordial building blocks of terrestrial planets. Searching for chemical signatures in Earth-like exoplanets could be an interesting future field of research, and the matches found will provide new points to be compared with increasingly sophisticated atmospheric models. Then, new evidence in other worlds can contribute to a better understanding of the transition point from a hostile to a habitable world. To define the role of N in such context was one of the main goals to promote this COST CM0805 workshop.

Introduction: The Earliest Setting of Planetary Atmospheres

The origin, and evolution of the atmospheres of terrestrial planets is of crucial importance to understand many cosmochemical, and astrobiological related issues (Holland 1962; Kasting 1993, 1997). We asked ourselves if the contents of the (Lewis and Prinn 1984) book or of the review chapters published in Atreya et al. (1989) compilation should be revisited in the context of recent computational capabilities, and geochemical evidence. After several space missions devoted to gain insight on remote solar system objects we know much more, for example, on the composition of comets and primitive meteorites. Also a significant progress has been made in photochemistry of planetary atmospheres since Yung and DeMore (1999) book dedicated to that issue. Consequently, we think that this proceedings book is making a significant contribution to these fields because different researchers have put all the effort in providing new clues in their respective fields on aspects scarcely treated in scientific literature. This book provides an interesting update to different research areas concerning the origins and the early evolution of planetary atmospheres.

Exoplanet research might provide additional clues for our understanding of the Earth transition from a hot accretionary phase to become a habitable world. Solar system planets have evolved with time to the present stage, and we have lost part of this information during their evolutionary way. Clues on the first stages in planetary evolution can be obtained from new discoveries around other stars as the exoplanets can be in different evolutionary stages, and be the product of similar or different formation processes. Many questions arise in the interpretation of these findings as e.g.: what is the potential role of N_2 in these atmospheres? How complex can be the organics formed in N-rich planetary environments? What are the processes involved in this chemical evolution?

In this context, the abundance of N and other volatile elements in planetary atmospheres can provide highly valuable information about the processes that brought them to terrestrial planets. N₂ is assumed to be a by-product after the release of NH₃ during outgassing, but it can be easily dissociated by EUV solar radiation in the upper atmosphere. An example of how important is assessing the depletion mechanisms of chemical species in planetary atmospheres. In any case, our current knowledge of the initial atmospheric composition of the Earth is scarce because we still have not identified paleosols older than 3.8 Gyr. Despite this, zircon grains suggest that liquid water, and probably other volatiles, were present on the

Earth's surface about 4.3 Gyr ago, even though we initially imagined our early world marked by volcanic activity (Valley et al. 2001).

Nitrogen is also one of the atoms of life and its delicate balance with oxygen in the Earth's atmosphere conditions the habitability of the surface. Cyanhydric acid, and nitric oxide, among other N-bearing compounds, could have played roles in the chemical evolution of early life. The biomarker character of nitrogen containing molecules in planetary systems was a theme of this meeting. Nitric oxide is also one of the main elements of the formation of the Earth's ionosphere and thus contributes, together with the magnetic field, to the habitability of the planet. These are some of the main issues that motivate us to organize this workshop.

Book Contributions in These Proceedings

The book starts with a general overview on the origin of N, and the role of Solar System minor bodies in the delivery of volatiles to Earth. This review chapter is written by Trigo-Rodríguez (2013). Oxygen isotopic data is particularly suggestive that enstatite and ordinary chondrites were the main primordial building blocks of the Earth (Wasson 2000). Such meteorites host several orders of magnitude less abundance in volatiles than those contained in some water-rich asteroids and comets. Does this suggest that the atmospheres of N-rich planetary bodies like Earth and Titan are the consequence of post-accretional delivery of volatile-rich bodies as predicted by recent models of the migration of giant planets?

Probably existed different pathways for massive delivery of N at early times. Nrich planetary atmospheres like Earth and Titan are consequence of the continuous delivery of volatiles along their evolutionary histories. Our current scenario for the delivery of volatiles is quite different from the envisioned by Chyba et al. (1990) and Chyba and Sagan (1992) as a byproduct of more complete, but still naïve, understanding of the bulk chemistry of undifferentiated asteroids and comets: authentic planetary building survivors.

The following chapter by Delgado-Bonal and Martín Torres (2013) deals with the abiotic sources of nitrogen fixation in early Earth, and their role in triggering a selection pressure favoring the evolution of nitrogenase and an increase in the nitrogen fixation rate. They introduce a mathematic method to analyze the amount of fixed nitrogen, both biotic and abiotic, through Earth's history.

In the field of exoplanets this book compiles very relevant contributions. Lammer et al. (2013) discuss the stability of Earth-like N₂-rich atmospheres and the main implications that such gaseous environments have for atmospheric, and planetary evolution and habitability. Evidence for such type of atmospheres in recently discovered exoplanets is discussed. Miguel and Kaltenegger (2013) introduce the reader into the fascinating topic of the new exoplanets called as super-Earths. These are planets with less than ten Earth masses that are very close to the Sun, that are unknown in our Solar System. A general review of the nitrogen chemistry in hot Jupiters atmosphere is given in the chapter by Venot et al. (2013).

It is usually considered that the earliest atmosphere of the Earth was produced by mantle outgassing, but it seems obvious that impacts participated in its evolution, as discussed in the Trigo-Rodríguez and Martín-Torres (2013) chapter. Impacts delivered water and organic compounds to a world mostly formed by anhydrous building blocks and even promoted catalytic reactions in the atmospheres of rocky planets. The authors invoke the need to accurately evaluate endogenous and exogenous sources of volatiles according to the geological and lunar evidence. They also discuss how laboratory experiments could be crucial to explain the evolution of the terrestrial atmosphere in that period.

Muller (2013) chapter deals with the intriguing presence in the Earth's atmosphere of N_2O . Since the discovery of this compound in 1938, N_2O sources and sinks have been a puzzle. N_2O has now been identified as produced by anaerobic bacteria's in soils which are sufficiently acid. The chapter also discusses the possible importance of N_2O as a biomarker in the characterization of exoplanet atmospheres.

The book starts a section with several chapters on Titan. The chapter by Sekine (2013) reviews pre- and post-Cassini-Huygens theories for the formation of a N_2 atmosphere in Titan. Before the arrival of Cassini, it was considered that Titan's N_2 atmosphere formed as a result of a major differentiation during accretion and subsequent chemical reactions (such as shock heating and photolysis) in a hot and prolonged proto-atmosphere, mainly composed of NH_3 and CH_4 . However, the new gravitational data provided by Cassini has revealed that Titan's core consists of a low-density material, suggesting that it remains relatively cold throughout its history.

Another fascinating result of the Cassini-Huygens (NASA-ESA) mission was to identify different common features among the atmospheres of Earth and Titan. An example is the assessment that molecular nitrogen is the major component of Titan's dense atmosphere, and is the basis for a very complex chemistry (Nixon et al. 2013). This chemically inert molecule is activated in the upper atmosphere by VUV radiations and particle impact ionization, causing its partial dissociation and ionization. The chapter by Carrasco et al. (2013) describes laboratory analyses performed with the goal of explaining the way in which nitrogen is retained in Titan's organic aerosols. As N2 is a rather chemically inert molecule, the processes leading to the high nitrogen content of Titan's aerosols are far from being understood. Recent laboratory analogues and experimental results are then presented. Balucani et al. (2013) are discussing N fixation by photochemical processes in the atmosphere of Titan and the implications for prebiotic chemistry. Titan upper atmosphere chemistry involving nitrogen active forms and hydrocarbons is discussed, and the plausible intermediate molecular species that, via addition reactions, polymerization and copolymerization form the N-rich organic aerosols are presented.

The Moyano-Cambero et al. (2013) chapter describes the applications of Martian meteorite studies to assess the atmospheric composition of Mars over time. Most Martian meteorites have experienced significant shock during the impact that released them from the red planet, and during the flight through the Martian atmosphere some of the gases were retained in the shock-altered glasses. As different radiogenic systems allow dating such processes, these meteorites can be considered

as time capsules capable of providing valuable information on the atmospheric evolution of Mars. Different SNCs were released by impacts at different times, having then different atmosphere-implantation ages, so in practice we can obtain clues on the composition of Mars' atmosphere at different times. Taking this information into account, they have developed a simple model of the evolution of Mars' atmosphere.

Finally, four authors (Moyano-Cambero, Martín-Torres, Serrano and Trigo-Rodríguez) contributed to the text by writing the book glossary. This quite exhaustive compilation will make general concepts and definitions accessible to students, and researchers of other areas. It is particularly useful for making this book understandable to a general reader, one of our main goals after all.

Putting the COST CM#0805 Workshop in Context

The scientific meeting that has led to these proceedings was organized by the Institute of Space Sciences (CSIC) and the Institut d'Estudis Espacials de Catalunya (IEEC) with the collaboration of the Scientific Secretariat of the Institute for Catalan Studies (IEC). Spanish Ministry of Science funded the complementary action called AYA2011-13250-E that has allowed the publication of this book. The workshop took place from 21 to 23 September, 2011 in the IEC historical building located in Carme street 47, nearby the famous Ramblas. A memorable poster session took place at IEC historical cloister on Wednesday 21st (see Fig. 1.1).



Fig. 1.1 A general view of workshop participants in the IEC historical cloister during the coffee break preceding the poster session (Alina Hirschman/CSIC-IEEC)



Fig. 1.2 A group picture of workshop participants in the IEC historical cloister during the coffee break preceding the poster session (Helmut Lammer/AAS)

All participants agreed that the meeting location was a perfect place to discuss many interdisciplinary issues concerning the formation and the evolution of planetary atmospheres. Consequently, this meeting resulted in a rewarding experience for all participants (Fig. 1.2), most of them granted by an European COST action.

The Proceedings Book

This interdisciplinary book is fruit of a common effort of authors and editors for promoting research on these disciplines. The book is published with funds received on 2011 from the Spanish Ministry of Science in a complementary action called

AYA2011-13250-E. We are all grateful to Spanish government for being sensitive to our research on the first stages in the evolution of planetary atmospheres.

As editors of this volume we are also especially grateful to all distinguished authors for preparing texts of high quality despite having long peer-review publication duties ahead in their agendas. We also thank the additional effort made by internal reviewers to read and correct the book contributions. They deserve all the credit to produce this comprehensive and enthusiastic book of proceedings that compiles most of the work presented during the COST CM#0805 workshop of Barcelone. We sincerely hope that all this common effort is useful for having many readers keeping the track on this fascinating research area.

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