Chapter 8
N_2O as a Biomarker, from the Earth and Solar System to Exoplanets

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Abstract Since its discovery in the earth's atmosphere 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 influence of agriculture is still to be determined as the nitrogen cycle is broken by both the addition of inorganic fertilizers and the simultaneous oxygenation of soils by mechanized agriculture. The situation was even complicated recently by the discovery of an abiotic N_2O production in the Antarctic brines (Samarkin et al. 2010). In the last 10 years, a global increase has been observed and N_2O is considered as a greenhouse gas in the current IPCC report. It is destroyed by direct oxidation by oxygen atoms in the stratosphere where it is also sensitive to photodissociation. The observation of N_2O from space is possible as several of its bands are in infrared atmospheric windows, especially the strong 7.8, 4.5 and the weaker 3.7 μm bands. Terrestrial N_2O would be both a by-product of a subterranean biosphere and of the current agricultural practices. Its oxidation produces also tropospheric nitric oxide in the unpolluted troposphere, in limited quantities, No also plays an important role for biological processes.

N_2O on the contrary to methane and formaldehyde has never been even tentatively identified nor on Mars nor on another planet. Martian methane still awaits a definitive confirmation from the EXOMARS orbiter payload in 2016 but its most probable origin would be the release of methane pockets produced under the surface by a deep biosphere while the new earth Antarctic process could also be a possibility. By analogy with the earth model, a similar mechanism would apply to the production of nitrous oxide, however, the absence of a blocking ozone layer is a sufficient reason to make the observation of N_2O impossible because of its

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sensitivity to UV radiation, however UV bands of NO are observed in the upper Martian atmosphere since Mariner 6 and 7 and confirmed by SPICAM on Mars-Express (Bertaux et al. 2005).

These considerations show the necessity of a better understanding of the nitrogen cycles on Mars in order to point to uncharted sources in the Martian subsurface which could prove Martian nitrogen compounds to be biomarkers.

Introduction: What Is a Biomarker?

A biomarker is essentially a proxy for the existence of life; the typical biomarker is the fossil. A fossil is an inert artefact which only life could produce and which allows the identification of the life form that produced it, as they age fossils deteriorate and finally, the oldest fossils require extensive analysis to prove their biological origin. In the case of astronomical objects, the main source of information is the light that originates from them and it is thus tempting to look for spectral traces of life which are essentially the signatures of the gases usually associated with life or some very specific signatures of surface life forms as for example the chlorophyll "red edge" of earth vegetation. The exercise began with spectroscopy in 1867 when Pierre Janssen, the founder of the Meudon observatory, found a difference between the spectra of Mars and the moon obtained at the Etna summit and attributed it to absorption by water vapour and oxygen, it took 20 years to prove (Campbell 1894) that this observation was not possible with the instruments used during the Mount Etna expedition. However, most of the astronomical community and educated public accepted in the early twentieth century that colour changes, polar caps and the presence of an atmosphere were biomarkers for Mars and took the habitability of the planet for granted (Jouan 1900). This situation dramatically changed when the few images returned by Mariner 4, together with the first measurements of the pressure showed a moon-like landscape where a pressure of 6 hPa made the triple point of water difficult to attain (Anderson 1965). The situation changed again when the extensive cartography of Mars by the missions MARINER 9 and VIKING 1 and 2 showed that Mars had traces of liquid erosion and deposition basins hinting that earlier it had been habitable, reviving thus the interest for search of life on the planets. I was in this context that Sagan et al. (1993) made the exercise of attempting to detect earth's life from space using a flyby of the GALILEO payload aimed at the study of the Jupiter system (Fig. 8.1). The same exercise was repeated with most planetary spacecrafts including VIRTIS on VENUS-EXPRESS (Fig. 8.2). The molecules detected on earth are water vapour, ozone, methane and nitrous oxide. The detection of oxygen in the infrared is not easy and as well, the instrumental quality and the configuration of the instruments do not allow the detection of other oxides of nitrogen and related acids, life related carbon molecules as formaldehyde and glyoxal now routinely monitored by earth observation satellites are also too weak to appear on these spectra.

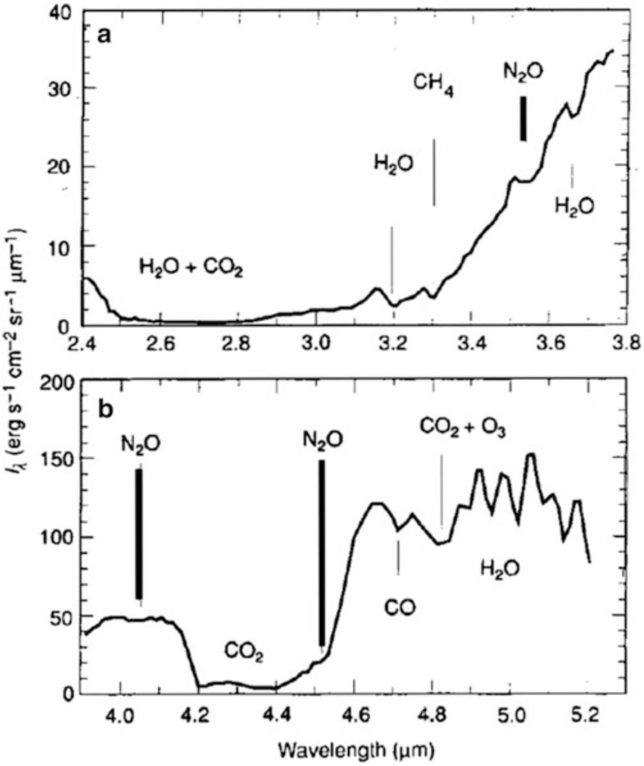

Fig. 8.1 Nadir spectrum obtained by the GALILEO payload (Sagan et al. 1993), all the molecules identified have a relation with life, N_2O is one of them

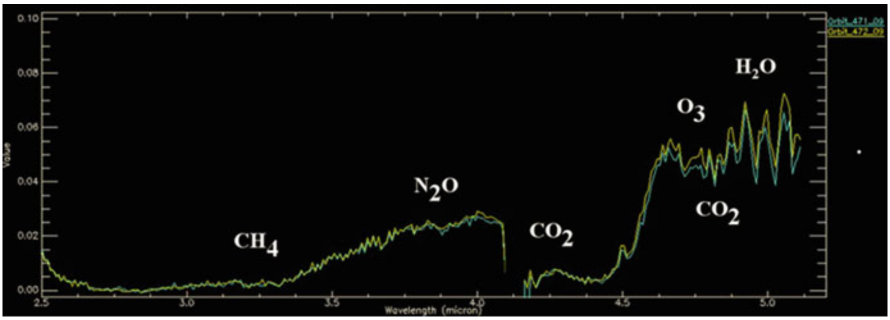

Fig. 8.2 Earth observed in 2007 from the Venus orbit by the VIRTIS instrument on board VENUS-EXPRESS (ESA/VIRTIS/INAF-IASF/Obs. de Paris-LESIA, http://www.esa.int/esaSC/SEMUOW4N0MF_index_0.html) The difference between the two curves comes from a change in the configuration of continents, the same complement of gases appear on both images

The biomarker name used for the first time by Sagan et al. (1993) applies perfectly to this set of molecules taken as a whole: water and especially liquid water is necessary for life membranes mobility, ozone is both an indication of oxygen and an effective UV shield for DNA molecules, methane on the earth is produced at 95% by contemporary bacteria's and the same analysis has been applied to nitrous oxide. Also, the earth's DNA of composed of only five atoms: hydrogen, carbon, oxygen, nitrogen and more marginally phosphorous. The recent discovery that a life form adapted by substituting DNA phosphorous with arsenic in the California Mono Lake (Wolfe-Simon et al. 2011) is only a small step towards the extension of the definition of life. This paper when it appeared in print was accompanied in the same SCIENCE issue by eight technical comments starting a debate on the nature of the observed adaptation, these criticisms which were also peer reviewed address both the method used by the authors and fundamental arsenic and phosphorus biochemistry properties. The authors clarified their printed text and added a response to these technical comments, they also made their strains available to researchers for further analysis. The Mono lake itself will continue to be studied as its pH of 10 and increasing salinity make it a unique eco-system.

N_2O Specificities as a Biomarker on Earth

Nitrogen oxides on earth form a very important family of gases, extending to all domains of biological and atmospheric physics. N_2O is however very specific as it is the only one for which no production in the gaseous phase on the earth have ever been observed in situ, it photodissociates extremely easily and its presence in the earth's troposphere is only possible under the protection of the ozone layer, in the absence of industrial pollution, it is the main source of stratospheric nitric oxide. Theoretically, gaseous phase production mechanisms could exist beginning with the direct reaction: $N2 + O(1D) + M$ producing $N_2O + M$, in the current upper atmosphere, the nitrous oxide produced than would rapidly react with O(3P) to produce NO. It is however not excluded that exceptional situations in earth history could have led to a measurable N_2O atmospheric source. In the present mesosphere and higher, however, NO is produced by the reaction of the photodissociation products of oxygen and nitrogen containing molecules, its photoionization leads to the ionospheric layers so important for radio-propagation.

The N_2O biological production has been linked to anaerobic bacteria's in acid soils with low level of oxygen. The denitrification of soils is a complex process that produces according to conditions N_2O, NO and N_2 (Hénault and Germon 1995). On earth, N_2O was only discovered on infrared solar spectra by Adel in 1938 (Adel 1939, 1951), its value at various ground stations was measured during the 50s and showed considerable fluctuations around an average mixing ratio of 2.5 E-7 between 1955 and 1975. Since 1975 this value has increased to about 3.2 E-7 according to the current WMO report on greenhouse gases: (http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/GHG_bull_6en.pdf). N_2O constitutes now 6%

of the greenhouse gases forcing on climate, the current increase being related to the development of artificial fertilization while ploughs cannot introduce more oxygen in the soil that they already did 20 years ago.

NO in an unpolluted troposphere is not only produced by the denitrification of soils but also by the oxidation of N_2O, in limited quantities, it has an important biological role as a neuro-transmitter and also plays a regulation role in the UV resistance of deinococcus radiodurans, the most*** resistant life-form known to exist (Patel et al. 2009). Deinococcus radiodurans was first isolated by Anderson et al. (1956) while studying the sterilisation of food by irradiation, it has been studied since and it is thought now that its resistance comes from an exceptional DNA repair capability which mechanism is still not fully known.

Abiotic Production of N_2O on Earth

The eighteenth century identification by Priestley (Davy 1800) was made through the analysis of the decomposition of ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

This process was later used to produce N_2O for anaesthetic uses in the nineteenth century "As nitrous oxide ... appears capable of destroying physical pain, it may probably be used with advantage during surgical operations in which no great effusion of blood takes place..."(Davy 1800). The process is very unlikely to be reproduced naturally as it requires a controlled high temperature. More recently, an inorganic source of nitrous oxide was identified in a hypersaline pond of the dry valleys of Antarctica (Samarkin et al. 2010). This source is completely marginal compared to the biological source and does not reflect itself in the satellite observations of N_2O in the earth's troposphere. These Antarctic dry valleys are interesting as they can be viewed as a Mars analogue.

The atmospheric direct production mechanisms have already been discussed and are negligible in the present earth atmosphere.

Nitrogen Oxides on Mars

Nitrogen oxide has been observed in day glow and night glow by UV instruments since MARINER 6-7 in the upper atmosphere of Mars, the observation is still performed in 2012 by the SPICAM instrument on Mars-Express (Bertaux et al. 2005), NO is produced in the most simple inorganic way by direct reactions between nitrogen and oxygen atoms. It is in no way a biomarker. Nitrogen exists on Mars, it has been observed by VIKING and in trapped gas on Martian meteorites, its mixing ratio is of 2.7% (Viking value). Enrichment in ^{15}N leads to think that most

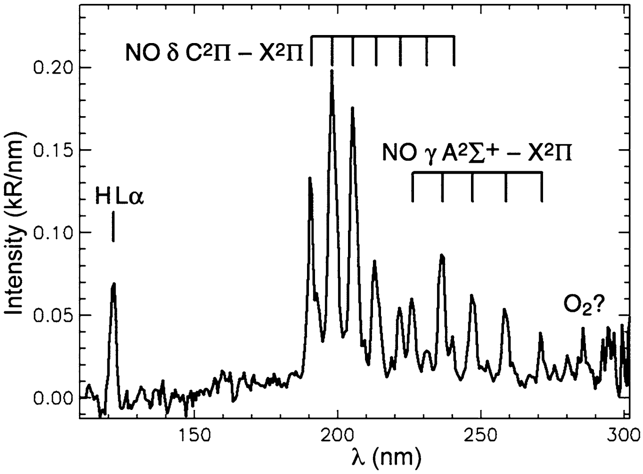

Fig. 8.3 Observation of nightglow of NO by the SPICAM instrument on the ESA Mars Express satellite, the figure corresponds to a NO layer centred at the altitude of 117 km (Bertaux et al. 2005)

of Mars nitrogen has escaped a long time ago. It is not consistent with an active biological source which would produce fresh nitrogen continuously, more striking also is the fact that this mixing ratio is similar in meteorites which have formed at least million years before present, this would point to a very old escape of nitrogen from Mars and is in contradiction with the current reports of methane atmospheric releases from a submartian production hypothesized to be biospheric. The most instrumentally sound of these communications is the Mumma et al. (2009) mapping of a release in the Terras Sabeas region of Mars. This and other observations of Martian methane are now controversial as they are not reproducible and as the observed large space and time fluctuations have until now no clear explanations. Alternative spectroscopic interpretations of the data have been proposed but as they depend on either terrestrial methane or carbon dioxide isotopologues, they do not explain either the observed variations. Anyway, no observation makes mention of a nitrous oxide line in either ground based of space-borne data (Fig. 8.3).

Other oxides of nitrogen than NO have still to be observed, the presence of strong UV due to the absence of an ozone layer and the effects of strong oxidants make this observation difficult with the current spacecraft instrumentation. The payload of the ESA EXOMARS trace gas orbiter should be able to perform an inventory of the Martian atmospheric composition in both limb and nadir and put an end to the current controversies.

The Future: Exoplanets and Conclusions

The infrared observation of N_2O will never be easy as its bands overlap with the infrared bands of other likely molecules as HDO, methane, ozone and of course unknown bands of molecules which are less abundant in earth conditions, including isotopologues. However, N_2O has its chances in the planets of UV weak stars where it could accumulate and be destroyed neither by direct UV radiation nor by reactive photodissociation products. These effects as well as the production of nitrogen oxides by galactic cosmic rays have been envisaged by Grenfell et al. (2007). The review of potential gaseous signatures by Des Marais et al. (2002) indicates also N_2O as a quasi-sure biomarker but puts a lot of restrictions on observational possibilities, the worse being possibly the contamination by water vapour. On the contrary of methane, only the middle infrared is usable for N_2O detection. In view of the contamination possibilities, the design of a specialized instrument could be envisaged with as first application the thematic mapping of N_2O on earth which has until now received a lower priority compared to methane.

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