### Nitrogen composition of the ancient atmosphere from fluid inclusion analysis of Archean quartz

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### Introduction

Knowning the composition of the Archean atmosphere is extremely important for a number of reasons. First, the Sun was ~25 % fainter than Today and, because there is no evidence of glaciation in the Archean, rhe lower solar energy delivery was presumably compensated by a stronger greenhouse effect. Such an effect is not recorded in geological proxies of the paleo partial pressure of CO<sub>2</sub>, and it has been proposed that doubling the pN<sub>2</sub> in the Archean atmosphere could have broadened by Rayleigh scattering the adsorption line of radiatively active gases, strengthening the greenhouse effect [1]. Because nitrogen isotopes are fractionated by bacteria, the isotopic siganture of this element in old sedimentary rocks is used to investigate the early development of the biosphere. Thus the isotopic value of the atmosphere at different time periods is equally important to document. Previous works have proposed that it remained constant through time within a few permil [2].

## Nitrogen and argon isotopes in irradiated Archean quartz

We have analyzed nitrogen and argon isotopes in 3.5 Ga old hydrothermal quartz from the North Pole area, Pilbara, NW Australia. In the same sample we have previoulsy determined a Ar-Ar plateau age of 3.0±0.2 Ga indicating that the age of trapped fluids is within 3.0-3.5 Ga. The Xe isotope signature intermediate between Chondritic and Atmospheric was interpreted as representing atmospheric Xe trapped  $\geq 3.0$  Ga ago [3]. Gases were extracted by vacuum crushing and heating of the remaining powder, nitrogen and noble gases were purified independently, and nitrogen and argon isotopes and abundances were sequentially analyzed by static mass spectrometry (overall  $\delta^{15}N$  error : 1-2 %). In a first step we analyzed non-irradiated samples, and data are consistent with mixing between an hydrothermal end-member and a paleo-atmospheric component having a  $\delta^{15}$ N value close to the modern one. We then irradiated a second batch of samples in order to quantify the chlorine and potassium contents of the extraction steps from <sup>37</sup>Ar, <sup>38</sup>Ar and <sup>39</sup>Ar and to correct data for mixing (and ageing for Ar). The  $\delta^{15}$ N values are very similar to the ones obtained from the nonirradiated sample runs, showing neglible production of nitrogen isotopes during neutron irradiation. Premiminary results confirm  $\delta^{15}$ N values between 0 ‰ and 5 ‰, and suggest a partial pressure of atmospheric nitrogen comparable to the present-day one.

# The volatile element record of Earth's accretion

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#### Isotope signatures of volatile elements

The stable isotopes signatures of terrestrial nitrogen and hydrogen suggest strongly that most volatile elements on Earth originated from a cosmochemical reservoir that also sourced asteroidal bodies. However, in the Earth's mantle, a minor solar-like volatile component is present and best seen in the Ne (and possibly N and H) isotope composition(s) of mantle-derived rocks. Ne isotopes in minerals from mantle plume provinces discriminate against contribution of dust implanted with solar ions, and instead support trapping of volatile elements directly from the nebular gas. Atmospheric escape to space has been long advocated to account for the atmospheric <sup>20</sup>Ne/<sup>22</sup>He isotope ratio lower than the Solar value. I shall argue instead that mixing between solar and chondritic components accounts well for Ne isotope variations in the Earthatmosphere system. In a <sup>20</sup>Ne/<sup>22</sup>Ne versus <sup>36</sup>Ar/<sup>22</sup>Ne diagram, both the atmosphere and the MORB mantle plot on a mixing line joining the solar and the chondritic (A-type component) end-members [1]. Earth's accretion seen from volatile elements

The above geochemical compositions on one hand, and dynamical modelling of planetary formation [2] on another hand, are consistent with the following scenario. Planetary embryos of the size of Mars accreted and differentiated in a few Ma [3], while the nebular gas was still present. Solar-like atmospheres were gravitationnally bound and solar gases were dissolved in molten silicates, imposing reducing conditions that participated to metal segregation. Such conditions might have also permitted the trapping of minor amounts of solar, isotopically light, N and H. Such contribution is larger than the late veener advocated in the case of PGEs. Giant shocks that characterized the accretion of Earth, but not of Mars, did not completely dry up the proto-Earth : volatile elements were gravitationnaly bound as were less volatile, or non volatile, elements also vaporized during the Moon-forming impact. Delayed accretion of asteroidal bodies or of volatile-rich dust orginating from close to the snowline added chondritic-like volatiles : a contribution of  $2\pm1\%$  carbonaceous chondrite-type material is indeed sufficient to supply water, carbon, nitrogen, halogens, and most noble gases to the Earth (including the surface reservoirs) [1]. In the light of existing data, the contribution of comets might not have exceeded a few percents of that of asteroidal material. The isotopic fractionation of atmospheric xenon (and, to a lesser extent, of atmospheric krypton) is probably related to non-thermal escape processes involving selective ionization, possibly on embryos, or during the Hadean-Archean eons [4] when the young Sun was more energetic than Today in the far UV range [5].

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