THE ORIGIN OF THE TERRESTRIAL ATMOSPHERE: EARLY FRACTIONATION AND COMETARY ACCRETION.

Nicolas Dauphas, Enrico Fermi Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago IL 60637, USA (dauphas@uchicago.edu).

Despite decades of efforts aimed at unraveling its origin, the terrestrial atmosphere is still considered to be one of the most puzzling enigmas in earth sciences. Remote observations will provide information on the atmospheres of extra-solar planets, some of these may prove to be hospitable for life. Understanding the origin of Earth's atmosphere thus improves our knowledge of the sources and processes that permitted the emergence of life within the solar system and beyond. Noble gases are sensitive tracers for investigating this question. Indeed, they span a large range of atomic masses, have many isotopes, and are chemically inert.

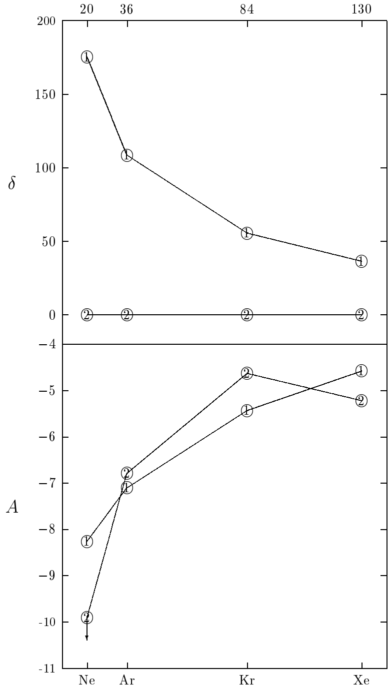

Fig. 1. δ is the isotopic composition in ‰ amu^{-1} and *A* is the logarithmic abundance; both are normalized to solar. Stage 1 corresponds to the escape episode while stage 2 refers to the accretion by the Earth of comets. The elemental composition of comets is derived from experiments [10] and the isotopic composition is assumed to be solar.

Atmospheric noble gases are depleted relative to the solar composition [1]. This depletion conforms to a first approximation to theory, the heavier noble gases being less depleted and isotopically less fractionated than lighter ones. This is however not true for xenon. Despite being heavier, xenon is more depleted and more fractionated than krypton. This feature is known as the Earth's “missing xenon paradox„. The most likely scenario for depleting and fractionating terrestrial noble gases is through hydrodynamic escape on the early Earth [2-5]. In this model, the rapid escape of a light gas would have exerted an aerodynamic drag on heavier gases. The balance between the upward aerodynamic drag and the downward gravitational potential would have resulted in a mass-dependent loss of noble gases. The massive hydrogen envelope could have been acquired by capture of nebular gases or could have resulted from the reduction or photodissociation of water. The appropriate energy could have been deposited as extreme ultraviolet radiation from the young sun or as gravitational energy released during impacts. Because of modeling uncertainties, it is difficult to know the appropriate fractionation law to apply. One may instead use a parameterized law such as the exponential law. Accordingly, the concentration C_1 of any volatile element at the end of the fractionation episode (stage 1) can be related to the solar composition $C_{\odot}$ through $C_1 = x\,C_{\odot}^{f}$, where x and f are two free parameters.

As discussed previously, a simplistic fractionation model cannot account for the missing xenon paradox. A way to get around this difficulty is to assume that fractionated gases were mixed with a source having a low Xe/Kr ratio and unfractionated isotopic ratios. Two possible sources can be advocated, the mantle [5, 6] and comets [7, 8]. The Xe/Kr ratio and Xe isotopic composition of the silicate Earth are close to those of the atmosphere [9] and it is unclear whether volatiles degassed from the mantle could have had the low Xe/Kr ratio and unfractionated Xe isotopic composition required by some models [5, 6], unless this early signature was subsequently erased by recycling. The noble gas composition of comets is unknown but laboratory experiments have attempted to reproduce the poorly known conditions that prevailed when ice condensed [10, 11]. These trapping experiments indicate that at a certain temperature, heavy noble gases are isotopically unfractionated while xenon is depleted relative to krypton. If gases from the fractionation episode were mixed with cometary material, then the resulting atmosphere could have had a near-solar Xe/Kr ratio, unfractionated krypton delivered by comets, and fractionated xenon inherited from the fractionation episode. A dual origin for the terrestrial atmosphere therefore provides an elegant solution to the “missing xenon paradox„. This possibility was recognized early [7] but has never been carefully evaluated. The trapping efficiency of ice depends on the formation temperature of comets [10]. The cometary contribution to the atmosphere of Earth can therefore parameterized as follows, $C_2 = y\,C_{\circ}(T_{\circ})$, where y is a scaling factor ($y = M_{\circ}/M_{\oplus}$ with $M_{\circ}$ the mass of comets accreted by the Earth) and $C_{\circ}$ is the concentration of comets which depends on the trapping temperature $T_{\circ}$.

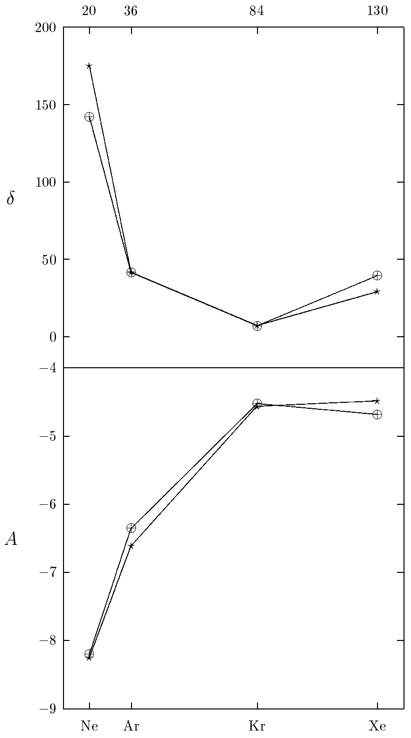

Fig. 2. Comparison between the observed (⊕) and the modeled (★) atmosphere.

The terrestrial atmosphere is the superposition of the early fractionation and cometary accretion episodes, $C_{\oplus} = x\,C_{\odot}^{\,f} + y\,C_{\circ}(T_{\circ})$. It is demonstrated that such a model could explain the isotopic and elemental abundances of Ne, Ar, Kr, and Xe in the terrestrial atmosphere. There are four free parameters, the scaling factors x and y, the fractionation parameter of the exponential law f, and the trapping temperature of comets $T_{\circ}$. The equation mentioned above can be written independently for eight nuclides (a pair of nonradiogenic isotopes for each rare gas). The system is overconstrained and a proper solution can only be obtained by minimizing the distance between simulation and observation. The set of parameters that minimizes this distance is $(x, f, y, T_{\circ}) = (7.093\times10^{-15}, 4.531, 5.224\times10^{-7}, 55.954)$. As illustrated in Fig. 2, the agreement between the observed and the modeled atmosphere is remarkable given the simplicity of the assumptions made.

Are the values of the parameters realistic? Hunten *et al.* [4] developed a convenient theoretical treatment of mass fractionation during hydrodynamic escape. The curvature of the fractionation law they derived is close to that advocated in the present contribution. The mass of comets accreted by the Earth is 3×10^{18} kg ($M_{\circ} = y\,M_{\oplus}$). Based on noble metals, it is estimated that the Earth accreted $0.7–2.7\times10^{22}$ kg after segregation of the core [12]. If the comets were delivered after core formation, they would represent only 10^{-4} by mass of the late veneer. The inferred trapping temperature of these comets is 56 K. Simulation of cometary trajectories in the early solar system indicates that the comets that impacted the Earth must have been trans-Uranian [13], in a region of the nebula where the temperature was probably lower than 70 K. The derived values of the parameters are thus physically realistic.

The terrestrial atmosphere may thus have had a dual origin, being a mixture between fractionated nebular gases and accreted cometary volatiles. Its relationship to the mantle is not straightforward to establish. If the atmosphere was derived from degassing, it implies that comets were incorporated in the main stage of planetary accretion and that fractionation occurred in a transient atmosphere surrounding the growing Earth. If not, then hydrodynamic escape occurred on a fully developed planet and comets may have been part of the late veneer. The later possibility would require that heavy noble gases be recycled in a mantle having solar composition. Whatever is the true scenario, the composition of the mantle can be faithfully reproduced with a parameterization of the form, $C_m = x\,C_{\odot}^{\,f} + y\,C_{\circ}(T_{\circ}) + z\,C_{\odot}$, where the last term represents the solar composition of the early silicate Earth. This signature may still be trapped in the deep mantle.

References: [1] Ozima M. and Podosek F.A. (1983) *Noble gas geochemistry*, Cambridge Univ. Press, Cambridge. [2] Zahnle K. and Kasting J.F. (1986) *Icarus, 68*, 462. [3] Sasaki S. and Nakazawa K. (1988) *Earth Planet. Sci. Lett., 89*, 323. [4] Hunten D.M. *et al.* (1987) *Icarus 69*, 532. [5] Pepin, R.O. (1991) *Icarus, 92*, 2. [6] Tolstikhin I.N. and O'Nions R.K. (1994) *Chem. Geol., 115*, 1. [7] Zahnle K. *et al.* (1990) *Geochim. Cosmochim. Acta, 54*, 2577. [8] Owen T. *et al.* (1992) *Nature, 358*, 43. [9] Moreira M. *et al.* (1998) *Science, 279*, 1178. [10] Bar-Nun A. and Owen T. (1998) In *Solar System Ices*, pp. 353-366, Kluwer Academic Publishers, Dodrecht. [11] Notesco G. et al. (1999) *Icarus, 142*, 298. [12] Dauphas N. and Marty B. (2002) *J. Geophys. Res., 107 (E12)*, 5129, doi: 10.1029/2001JE001617. [13] Morbidelli A. *et al.* (2000) *Meteoritics Planet. Sci. 35*, 1309.