

EXPERIMENTAL STUDY OF PHOTOIONIZATION AND FRACTIONATION OF NOBLE GASES AND OXYGEN IN THE STRATOSPHERE AT THE OZONE HOLE OVER ANTARCTICA. A. Meshik¹, G. Dominguez², R. C. Ogliore¹, O. Pravdivtseva¹, B. F. Rauch¹, ¹Physics Department CB1105, Washington University, 1 Brookings Drive, St. Louis, MO 63130, ameshik@physics.wustl.edu, ²Physics Department, California State University, 333 S. Twin Oaks Valley Road, San Marcos, CA 92096, gdominguez@csusm.edu.

Introduction: The Earth's atmosphere is leaking. According to the ESA Cluster mission our planet is losing around 90 tons of material per day from the upper atmosphere. Presently these losses occur mainly from the polar regions where photo-ionized volatiles can escape along the Earth's magnetic field lines. However, in the past, when our planet did not have its magnetic field, and when the young Sun was more active, the atmospheric losses were most likely much more significant than today. Therefore, studying the effects of elemental and isotopic fractionation of atmospheric gases in the stratosphere above the polar regions could potentially help us to understand the history of terrestrial atmosphere and, perhaps, the timing of establishing the Earth's magnetic field.

To study these effects, we designed, built, and successfully tested the Balloon Air Sampler (BAS) device that captured air at different altitudes over Antarctica in the 2018/19 season. BAS was deployed again during the current 2019/20 campaign.

Noble gases have a special place in geophysics and cosmochemistry. Their low terrestrial background and high yield in nuclear processes make noble gas isotopes excellent tracers of Solar System evolution [1]. Meanwhile noble gas geochemistry has a major problem. Carbonaceous chondrites retain a record of our Solar System's earliest days containing some of the most-primitive materials, including xenon, krypton and lighter noble gases. Their elemental ratios follow a certain well understood mass-dependent pattern with only one exception – Xe. Terrestrial Xe/Kr and Xe/Ar ratios are 20 times lower than the early Solar system Xe/Kr and Xe/Ar values. The problem of missing terrestrial Xe (called the “xenon paradox”) reflects some fundamental process characteristic of Earth's evolution that has been attacked by researchers for several decades. Despite extensive searching in sediments [2, 3], glacier ices [4, 5], silica [6], clathrates [7] *etc.* none of the studied materials could quantitatively account for the missing Xe. There is a possibility that the missing Xe could be hiding in the Earth's mantle and/or the core. Several experimental studies reported that Xe could form chemical bonds or Van der Waals compounds. A recent study found XeNi₃ at 150 GPa and > 1700°C [8]. XeFe₃, Xe₂O₅, Xe₃O₂ and Xe hydrates have been synthesized at similar extreme conditions [9, 10].

An alternative approach to solve the Xe paradox is not to bury the Earth's Xe in some terrestrial reservoir, but to lose it to space. At first glance, it seems unreasonable since in any gas escape mechanism the lighter Kr should be lost preferentially. However, among all noble gases Xe has the lowest first and second ionization potentials, and if ionized by UV in the upper atmosphere it may escape faster than other noble gases [11]. Therefore, to observe a selective Xe escape today, we need to sample the air at high altitude near the poles where UV flux is the highest and magnetic field lines are open.

Oxygen occupies a special place in cosmochemistry and geochemistry because it has three stable isotopes and may be found in both volatile and refractory phases in geochemical systems *writ large*. Its multi-isotopic nature makes it a particularly powerful tracer of non-equilibrium processes (e.g. photochemistry and radical-chemistry) in natural systems [12]. For example, O₃, a minor component of the atmosphere when judged in terms of abundance, helps to set the multi-isotopic composition of a variety of atmospheric species, imparting them with an isotopic signature that can be used to elucidate or constrain their oxidation pathways. Multi-isotopic measurements (¹⁸O/¹⁶O ¹⁷O/¹⁶O) of atmospheric compounds, when combined with chemical reaction network computations, may also be used to constrain the reaction rates of difficult to measure chemical reactions. The isotopic composition of water vapor in the stratosphere is believed to be set by a complex reaction network involving methane (CH₄), an important and powerful greenhouse gas, H₂O recycling, and poorly understood isotope exchange and HO_x chemical reactions. Measurements of the complete isotopic composition of water vapor (D/H, ¹⁸O/¹⁶O, ¹⁷O/¹⁶O) from the middle- and upper-atmosphere would help resolve these gaps in the atmospheric literature and provide additional constraints for atmospheric circulation models relevant for global climate change [13].

Experimental: Currently our BAS device consists of three identical samplers activated by three high precision absolute pressure sensors at designated different altitudes. Each air sampler consists of a 200 ml stainless steel cylinder welded to all metal ultra-high vacuum valve operated by gear motor actuators. The

cylinders are internally electro-polished, cleaned (UHV protocol + vacuum baking) and He-leak checked at temperatures cycled from room to -60°C . The cylinders were pumped out to $< 10^{-9}$ Torr using a dry vacuum pumping station, the valves were closed, and the inlet tubes were attached to the valve side ports with less than 0.1 ml “dead” volume. To exclude potential mass-fractionation at sampling our BAS device employs neither cryogenic trapping (e.g. [14]), nor mechanical compression (e.g. [15]). We use four parallel 4” long 0.005” ID stainless steel capillaries to ensure the absence of mass fractionation, especially at low stratospheric pressure and temperature. Each air inlet lasts 4 min. Valve opening or closing requires 2 minutes. BAS has been tested in laboratory at 1 Torr and -50°C (similar or more extreme than actual stratospheric conditions). To pass these tests we had to replace several electronic components and completely decrease all mechanical parts. The BAS device is shown in Figure 1.

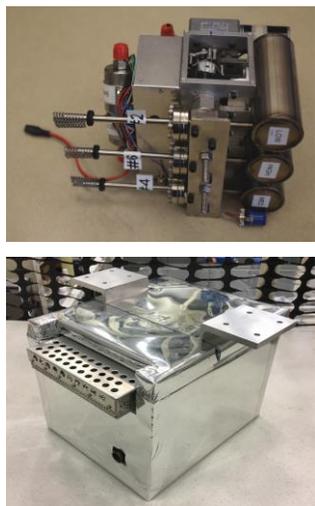


Fig. 1. BAS (Balloon Air Sampler) without (top) and with the enclosure, ready to be attached to the SuperTIGER flame (bottom). BAS has less than $1' \times 1' \times 1'$ outside dimensions, weighs less than 25 lbs and requires $< 30\text{W}$ during air sampling and $< 1\text{W}$ at standby. No power is needed after the sampling completion.

BAS has been successfully tested during the 2018-19 Antarctic expedition, when it flew as a piggyback on a long-duration balloon-borne instrument SuperTIGER (Super Trans-Iron Galactic Element Recorder). It is flying again during the current 2019-20 campaign and has likely already collected air samples at 18,000', 63,000' and 105,000' altitudes during the 5-hour balloon ascent carrying our BAS (Figure 2).

During the 2019-20 launch of the balloon, an additional reference air sample has been collected on the ground near the launch pad using a device with a collection system identical to those in BAS. We hope BAS will be recovered soon after the completion of the SuperTIGER mission (weather, landing location, and aviation support permitting). If the recovery turns out

to be impossible this year, we are confident that the valves will hold atmospheric pressure during the long Antarctic winter.

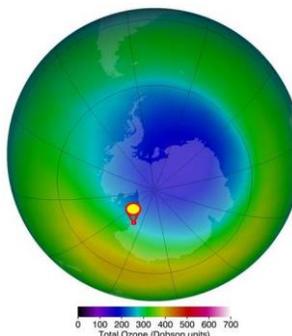


Fig. 2. Location of air samples taken on Dec-15-2019 is shown relative to an unusually small ozone hole (blue) in mid-December 2019 due to the reduction of chlorine and other ozone-depleting substances in the stratosphere.

The samples collected during two Antarctic seasons will be analyzed in the Noble Gas Lab at Washington University (WUNGL, [16]) and by Cavity Ring-down isotope spectroscopy at D-Lab in California State University, San Marcos [17].

Conclusion: Stratospheric air sampling from the ozone hole over the South Pole is the only way we will be able to study photoionization and escape of atmospheric volatiles along open magnetic field lines. We are looking for an opportunity to sample the stratospheric air closer to the South Pole, where the ozone layer has minimal thickness.

Acknowledgements: We thank the SuperTIGER team members W. R. Binns, R. G. Bose, D. L. Braun and P. F. Dowkontt (Washington University) who helped us to integrate BAS to SuperTIGER-2.

References: [1] Ozima M. and Podosek F. A. (2002) Noble gas geochemistry. 2nd Ed. Cambridge Univ. Press. [2] Podosek F. A., Bernatowicz T., Kramer F. E. (1981) *GCA*, 45, 2401–15. [3] Bernatowicz T., et al. (1984) *JGR*, 89 B6, 4597–611. [4] Wacker J. F. and Anders E. (1984) *GCA*, 62, 2335–45. [5] Bernatowicz T., Kennedy B. M. and Podosek F. A. (1985) *GCA*, 49, 2561–4. [6] Matsuda J. and Matsubara K. (1989) *GRL*, 16, 81–4. [7] Sill G. T., Wilkening L. (1978) *Icarus*, 33, 13–22. [8] Stavrou et al., (2018) *Phys. Rev. Lett.*, 120, 096001. [9] Howie R. T. et al. (2016). *Nature* (Scientific Reports No.6), 34896. [10] Sanloup Ch., et al. (2005) *Science* 310, 1174–7. [11] Hebrard E. and Marty B. (2014) *EPSL*, 385, 40–48. [12] Thiemens et al. (2012) *Ann. Rev. Phys. Chem.*, 63, 155–77. [13] Zahn et al. (2006) *Atmos. Chem. Phys.*, 6, 2073–2090. [14] Bieri R. H., Koide M., Martell E. A., and Scholz T. G. (1970) *JGR*, 75, 6731–6735. [15] Flocke, F., Herman R. L., Salawitch R. J. et al. (1999) *JGR*, 104 (D21), 26,625–26,642. [16] Meshik A. and Pravdivtseva O. (2016) *47th LPSC*, Abstract #1681. [17] Salvo et al. (2013) *Anal. Chim. Acta*, 804, 176–179.