MASS DEPENDENCY OF ISOTOPE FRACTIONATION OF GASES UNDER THERMAL GRADIENT AND ITS POSSIBLE IMPLICATIONS FOR PLANETARY ATMOSPHERE ESCAPING PROCESS

Tao Sun[1,2*], Paul Niles[1], Huiming Bao[2], Richard Socki[3], [1]ARES, Johnson Space Center, NASA, Houston, TX, 77058; [2]Department of Geology and Geophysics, Louisiana State University; [3]Jacobs, Johnson Space Center Houston, TX, 77058, *tao.sun@nasa.gov

Introduction:

Physical processes that unmix elements/isotopes of gas molecules involve phase changes, diffusion (chemical or thermal), effusion and gravitational settling. Some of those play significant roles for the evolution of chemical and isotopic compositions of gases in planetary bodies which lead to better understanding of surface paleoclimatic conditions, e.g. gas bubbles in Antarctic ice [1], and planetary evolution, e.g. the solar-wind erosion induced gas escaping from exosphere on terrestrial planets [2]. A mass dependent relationship is always expected for the kinetic isotope fractionations during these simple physical processes, according to the kinetic theory of gases by Chapman, Enskog and others [3-5]. For O-bearing (O^{16}-O^{17}-O^{18}) molecules the $\alpha^{17}O/\alpha^{18}O$ is expected at 0.5 to 0.515, and for S-bearing (S^{32}-S^{33}-S^{34}-S^{36}) molecules, the $\alpha^{33}S/\alpha^{34}S$ is expected at 0.5 to 0.508 , where α is the isotope fractionation factor associated with unmixing processes. Thus, one isotope pair is generally proxied to yield all the information for the physical history of the gases. However, we recently [6-8] reported the violation of mass law for isotope fractionation among isotope pairs of multiple isotope system during gas diffusion or convection under thermal gradient (Thermal Gradient Induced Non-Mass Dependent effect, TGI-NMD). The mechanism(s) that is responsible to such striking observation remains unanswered.

In our past studies, we investigated polyatomic molecules, O_2 and SF_6, and we suggested that nuclear spin effect could be responsible to the observed NMD effect in a way of changing diffusion coefficients of certain molecules, owing to the fact of negligible $\Delta^{36}S$ anomaly for SF_6 [7]. On the other hand, our results [6-8] also showed that for both diffusion and convection under thermal gradient, this NMD effect is increased by lower gas pressure, bigger temperature gradient and lower average temperature, which indicate that the nuclear spin effect may not be the significant contributor as the energies involved in the hyperfine effect are much smaller than those with molecular collisions, especially under convective conditions.

Current Study:

We investigated thermal diffusion of monatomic gas molecule, Neon, for its Ne^{20}-Ne^{21}-Ne^{22} systematics. Neon is one of the best targets to (de)validate the nuclear spin role in the TGI-NMD phenomena because 1) it is devoid of molecular structure related properties, e.g. mass distribution, 2) its collisions can be regarded as truly elastic which is the basis of kinetic theory of gases and 3) it has isotopes with (Ne^{21}) and without (Ne^{20}, Ne^{22}) non-zero nuclear spin numbers.

We employed a conventional vertical two-bulb (equal volume, stainless steel) apparatus for determination of the thermal diffusion factor,

$$\alpha_T = Ln\ q_{hot-cold}/Ln(T_{cold}/T_{hot}),$$

where q is equivalent to the isotope fractionation factor α and T is temperature. In our study, we only present q profile instead of α_T. The Neon experiments were performed in a purely diffusion setting (lower reservoir at lower temperature). We also performed O_2 thermal diffusion experiments in the same setting for comparison between monatomic and polyatomic molecules.

Results and Discussions:

The results for Neon gas showed a perfect consistency with the theoretical mass dependent prediction in a wide pressure range with very close mass exponent, 0.512 (Figure 1). This strongly suggests that the nuclear spin (hyperfine effect) is not the direct cause of the TGI-NMD effects. O_2 gas results showed that when gas pressure is sufficiently high, the TGI-NMD effect disappears in the tested temperature range, in sharp contrast with the low pressure results (Figure 2). When placed in context with our previous work, results suggest that monatomic gas molecules do not have a TGI-NMD effect while polyatomic gas molecules do when pressure is not too high. Also data show TGI-NMD effects may exist for gases other than O_2 and SF_6.

Implications:

A typical planetary atmosphere possesses thermal structure of 100s of kelvin temperature changes along 100s of kilometers' altitude associated with drastic pressure changes. Above troposphere, diffusion becomes more predominant than the turbulence controlled mixing motion near surface, which would result in gas separation by mass differences of isotopes and elements. Prior to the eventual gas loss, isotope fractionation should be present between the top and the bottom of the atmosphere, and such fractionation is partly introduced by a combination of physical processes: chemical diffusion, gravitational settling and thermal diffusion [2, 9, 10]. The first two

are known to be mass dependent and are well studied, while the role of thermal diffusion remains largely unexplored. Our laboratory investigation suggests that thermal diffusion may play an important role in the isotopic composition of gases within a planetary atmosphere. Additional information may be gained by combining the steady behavior of noble gas and active response of other gases to the physical settings of the atmosphere, i.e. pressures, temperatures, with respect to the mass dependency of the isotope fractionation. Upcoming results from the MAVEN mission will also yield important constraints on the importance of TGI-NMD processes at the top of the martian atmosphere.
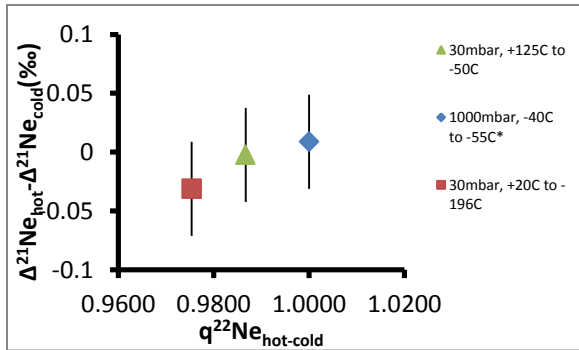

Figure 1, Isotope fractionation factor ($q_{hot-cold}$) and $\Delta\Delta^{21}O$ ($\Delta^{21}O_{hot}-\Delta^{21}O_{cold}$) of Neon gas thermal diffusion. $\Delta^{21}O=\delta^{21}Ne-0.512*\delta^{22}Ne$, where 0.512 is theoretical predicted mass exponent for Neon. * datum was obtained from personnel communication with Dr. Jeff Severinghaus at Scripps Institute of Oceanography.
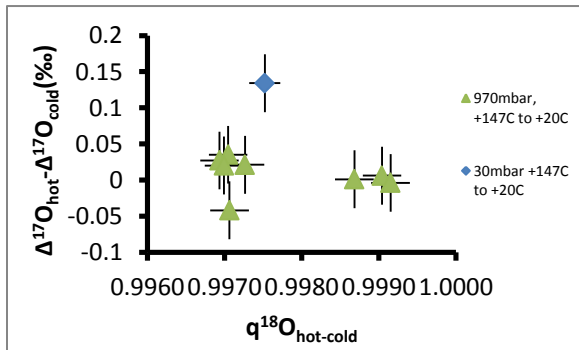

Figure 2, Isotope fractionation factor ($q_{hot-cold}$) and $\Delta\Delta^{17}O$ ($\Delta^{17}O_{hot}-\Delta^{17}O_{cold}$) of O_2 gas thermal diffusion. $\Delta^{17}O=\delta^{17}O-0.509*\delta^{18}O$, where 0.509 is theoretical predicted mass exponent for O_2.

References

[1] Severinghaus, J.P., Sowers, T., Brook, E.J., Alley, R.B., and Bender, M.L. 1998, *Nature* **391**, 141-146
[2] Lammer, H., Kasting, J.F., Chassefière,E.

Johnson,R.E., Kulikov, Y.N., Tian, F., 2008, Space Science Review 139, 399-436 [3] Jones, R.C. and W.H. Furry, Reviews of Modern Physics, 1946. 18(2): p. 151-224. [4] S. Chapman, T.G.C., *Thermal conduction and Diffusion in Gases*. 3 ed. 1991. [5] Hirschfelder, J.O., R.B. Bird, and E.L. Spotz, Journal of Chemical Physics, 1948. 16(10): p. 968-981. [6] Sun, T and Bao, H.M., *Rapid Communication in Mass Spectrometry*, 2010, v.25 p.20-24. [7] Sun, T and Bao H.M., *Rapid Communication in Mass Spectrometry*, 2011, v.25 p.765-773. [8] Sun T., Niles, P.B., Bao, H.M., Socki, R.A., Liu, Y., LPSC, 2013 [9] Monchick, L., John Hopkins APL Technical Digest, 1986, v.7, p.39-41 [10] Geiss, G. and Buergi, A., Astronomy and Astrophysics, 1986, v.159, p.1-15