FRACTIONATED MARTIAN ATMOSPHERE – THE CASE OF THE NAKHLITES, REVISITED WITH EXPERIMENTS. S. P. Schwenzer[1,2,3], Ott[2,4], U., Hicks[5], L. J., Bridges[5], J. C., Filiberto[6,1], J., Bart[7,8], G. D., Swindle[8], T. D., Miller[9], M. A., Treiman[3], A. H., Crowther[10], S. A., Gilmour[10], J. D., Herrmann[2], S., Mohapatra[2,10], R., Seidel[11], R. G. W., Kelley[1,12], S. P., Bullock[10], M. A., Chavez[14], C., Smith[14], H., Moore[14], J. M. – [1]The Open University, School of Environment, Earth and Ecosystem Sciences, Walton Hall, Milton Keynes MK7 5AA, UK; Susanne.schwenzer@open.ac.uk; [2]Max-Planck Institute for Chemistry, 55128 Mainz, Germany, [3]Lunar and Planetary Institute, USRA, Houston, TX 77058, USA; [4]MTA Atomki, 4026 Debrecen, Hungary; [5]University of Leicester, Leicester LE1 7RH, UK; [6]Southern Illinois University, Carbondale, US; [7]University of Idaho, Moscow, Idaho, USA; [8]Lunar and Planetary Laboratory, University of Arizona, Tucson AZ, U.S.A.; [9]Southwest Research Institute, San Antonio, USA; [10]University of Manchester, Manchester, UK; [11]The Open University, School of Physical Sciences, Milton Keynes, UK; [12]University of Edinburgh, Endinburgh, UK; [13]Southwest Research Institute, Boulder, CO USA; [14]NASA Ames Research Center, Moffett Field, CA, USA.

Introduction: Noble gases in Martian meteorites have three endmembers. First, the Martian atmosphere as measured by Viking [1,2] and found in the shergottites [3]. This component, more specifically its match between *in situ* measurements on Mars and data from the shergottite meteorites, established the link between the SNC meteorites and Mars. The second component, found in Chassigny [4], is considered to be Martian interior. The third component has atmospheric $^{129}Xe/^{132}Xe$ but lower Kr/Xe elemental ratios than Martian atmosphere (as seen in $^{84}Kr/^{132}Xe$ on the plot $^{129}Xe/^{132}Xe$ vs $^{84}Kr/^{132}Xe$ [4]). For reviews on the components see [5-7]. The fractionated Martian atmosphere is the subject of this abstract.

Formation hypotheses: There are four ways to explain elemental fractionation of atmospheric noble gases in the nakhlites: a) an internal (possibly crustal) gas reservoir, with its host rocks melted or assimilated into the meteorites' parent magmas [8]; b) elementally fractionated Martian atmosphere in the rocks' aqueous alteration minerals [9]; c) fractional adsorption of atmospheric noble gases onto mineral surfaces [10]; and d) incorporation of an unfractionated ancient Martian atmosphere, which was significantly different from today's [11]; see also [7, 12]. Terrestrial samples and alteration experiments have demonstrated that elemental noble gas fractionation in hot and cold desert environments is the rule rather than the exception [13-15], and that elemental fractionation is replicable in the laboratory environment [16].

Data sets: In this study of nakhlites we use a literature compilation of existing noble gas data [7,12], PhD thesis [17] and unpublished data from MPI Mainz, unpublished data from LPL [18], unpublished data from University of Manchester [19-21], and data from our experimental study [22-26].

Mainz data. At MPI, we measured mineral separates and bulk rock using an MAP215-50 noble gas mass spectrometer. All separates and bulk rocks showed a tendency towards $^{84}Kr/^{132}Xe$ ratios lower than expected from a mixture of Martian interior and un-fractionated Martian atmosphere. The most fractionated $^{84}Kr/^{132}Xe$ ratios were observed in olivine and mesostasis (Fig. 1), in which the 1200°C T-step of 'Nakhla olivine (a)' shows the highest $^{129}Xe/^{132}Xe$ (2.4±0.1) and the largest fractionation ($^{84}Kr/^{132}Xe$ = 0.9±0.9) from the unfractionated atmospheric $^{84}Kr/^{132}Xe$ ratio (of 20.5). The $^{136}Xe/^{132}Xe$ ratio of this T-step also has Martian atmospheric signatures of 0.373±0.011, indicating that the sample is not contaminated by terrestrial air ($^{136}Xe/^{132}Xe$= 0.3294±0.0004).

Tucson data. Governador Valadares (GV) and Nakhla samples were analyzed in a VG5400. Most samples returned many T-steps with low $^{129}Xe/^{132}Xe$, suggesting air contamination. $^{136}Xe/^{132}Xe$ confirmed the assumption that low $^{129}Xe/^{132}Xe$ data are a good indication for terrestrial air contamination, but also demonstrated that GV gases were not significantly affected by contamination. The highest $^{129}Xe/^{132}Xe$ ratio of 1.884±0.016 was measured in the 1000°C T-step of GV bulk (Fig. 2).

Manchester data. Samples were analyzed on the RELAX mass spectrometer [22,23]. The highest $^{129}Xe/^{132}Xe$ of 2.282±0.061 was found in mesostasis, accompanied by a Martian atmospheric $^{129}Xe/^{136}Xe$.

Experimental data. We tested the fluid hypothesis (b) by experimentally altering minerals analogous to those found in Martian meteorites [24-28]. The experimental apparatus was a daisy chain of vessels, with CO_2-headspace gas flow containing 2 vol.% Ar, 30 ppm Kr, and 8 ppm Xe. We calculated a generalized solution to the differential equation for this daisy chain problem and found that the peak concentration of gas exiting the third vessel would be achieved after 50 min, while that exiting the 30th vessel would be realized after 700 min when each vessel is 250 mL and the volumetric gas flow is 10 standard cm^3/min. This has, however, not been achieved for the reason of limited gas throughput (i.e., excess unfractionated gas mixture) compared to the system size, which in addition to the experimental complexities also shows the difficulties we face when investigating natural systems. However,

comparing the elementally fractionated gas signature measured in olivine from the first vessel ($^{84}Kr/^{132}Xe=1.77\pm0.11$; 1000 °C T-step) to the head-space gas ($^{84}Kr/^{132}Xe=7.9$) shows considerable elemental fractionation.
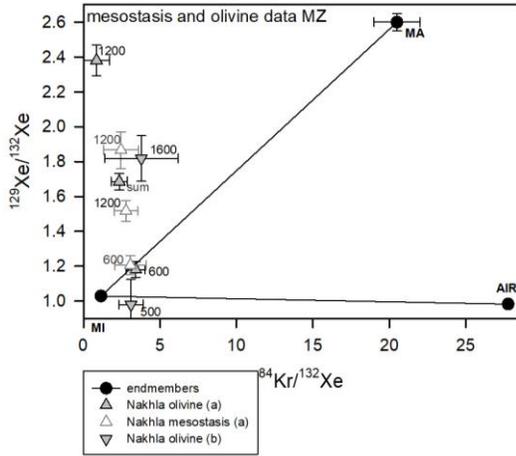

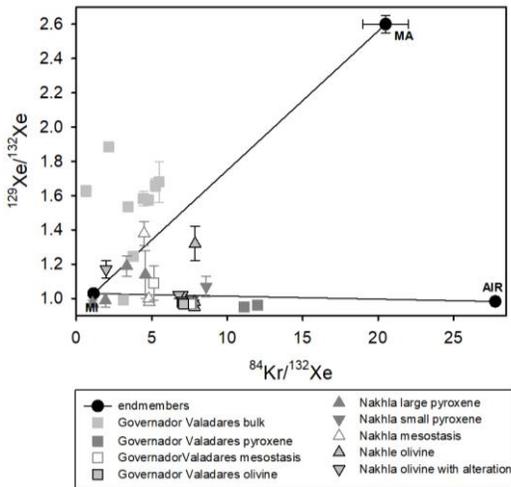*Figure 1. Olivine and mesostasis data measured at MPI Mainz [17] and unpublished data.*

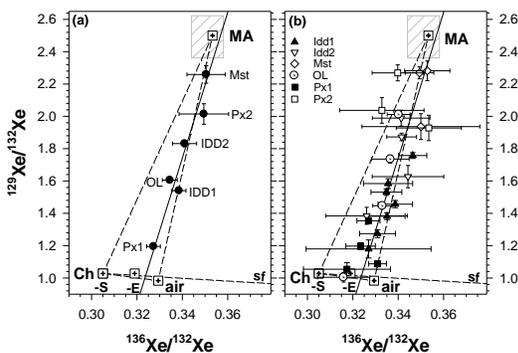*Figure 2. Bulk and mineral separate data from Tucson [18].*

Figure 3. Bulk and mineral separate data from Manchester [19-21].

Summary and conclusions: Elemental fractionation occurs in all nakhlites with the highest fractionation factors ($\alpha=[(^{84}Kr/^{132}Xe)_{frac}/(^{84}Kr/^{132}Xe)_{atm}]$) observed in the 1200°C step of Nakhla olivine (MZ data, $\alpha = 0.04$). Reported here is an α of 0.1 for the 1000 °C step from AZ corresponding to the highest $^{129}Xe/^{132}Xe$ ratio of this data set; however, we note that the 1400 °C step of GV from AZ has a similarly low α (0.03). For comparison, air noble gases dissolved in terrestrial water are fractionated with $\alpha \approx 0.5$ (depending on T and salinity), but much greater fractionation occurs upon incorporation into terrestrial alteration minerals [13-15] and in our experiments (α =0.22).

The wide range of α in Martian, terrestrial, and experimental systems demonstrates that more experimental and terrestrial analog data are required to understand the complexity of noble gas incorporation into secondary alteration minerals. Especially important experimental issues to address are the differences between a static and a dynamic flow regime – and the influence of mineral surface changes. The Martian system has the added complexity that the Kr/Xe ratio at the time of incorporation is not known, thus the experimental and terrestrial data are vital to narrow the number of possible hypotheses for the incorporation of fractionated Martian atmosphere into the nakhlites.

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