FRACTIONATED NOBLE GASES IN MARTIAN METEORITE ALH84001 – AN INDICATOR FOR WATER-ROCK INTERACTION, OR A SAMPLE OF ANCIENT ATMOSPHERE? S. P. Schwenzer[1,2,3], G. Bart[4,5], J. C. Bridges[6], S. A. Crowther[7], J. Filiberto[8,1], J. D. Gilmour[7], S. Herrmann[2], L. J. Hicks[6], S. P. Kelley[1,x], M. A. Miller[9], U. Ott[2,10], E. D. Steer[1,11], T. D. Swindle[5], and A. H. Treiman[3], [1]The Open University, Department of Environment, Earth and Ecosystems, Walton Hall, Milton Keynes MK7 5AA, UK; susanne.schwenzer@open.ac.uk. [2]Max-Planck Institute for Chemistry, Germany. [3]Lunar and Planetary Institute, USA. [4]University of Idaho, USA. [5]University of Arizona, USA. [6]University of Leicester, UK. [7]University of Manchester, Manchester, UK. [8]Southern Illinois University, Carbondale, IL 62901. [9]Southwest Research Institute, San Antonio, Texas 78228, USA. [10]MTA, ATOMKI, Debrecen, Hungary. [11]Nanoscale and MicroscaleResearch Centre (NMRC), University of Nottingham.

The composition of an atmosphere is the product of the processes which acted on it throughout its history. The Martian atmosphere today has a distinct noble gas isotopic fingerprint, mainly characterized by a high ^{129}Xe/^{132}Xe ratio of 2.6; the corresponding ^{84}Kr/^{132}Xe elemental ratio is 20.5 [1]. This was found by Viking [2] and confirmed by SAM on Curiosity [3]. Most importantly, the corresponding elemental and isotopic ratios have been measured in impact glasses in shergottite Martian meteorites [4,5]. In contrast, nakhlites and the unique ALH84001 Martian meteorite have lower ^{84}Kr/^{132}Xe ratios, which have presumably been caused by a range of processes from water-rock interaction to the existence of an ancient atmosphere.

Meteorite evidence: The relationships between the endmembers of Martian atmosphere, elementally fractionated Martian atmosphere, Martian interior and terrestrial air on the one hand, and the nakhlite and ALH84001 meteorites, on the other, in the ^{136}Xe/^{132}Xe vs. ^{84}Kr/^{132}Xe and ^{129}Xe/^{132}Xe vs. ^{84}Kr/^{132}Xe systems are illustrated in Fig. 1.

The plots show that both, the nakhlites and ALH84001 have a component of fractionated Martian atmosphere, which is clearly distinguishable from potential terrestrial contamination and – if extrapolated to a ^{129}Xe/^{132}Xe ratio of 2.6 – would have a ^{84}Kr/^{132}Xe ratio of about 8. Of course, the ancient Xe-isotope ratio could be lower, it has been estimated to be as low as ~2, e.g., in which case the corrensponding elemental ratio would be even lower about 5.

Terrestrial evidence: Terrestrial evidence for fractionation of noble gases is plentiful. Here we focus on observations of environments meteorites are found in most commonly: hot and cold deserts. Mohapatra et al. [21] investigated the effect of adsorbed terrestrial air contamination on the ability to measure the Mars interior component in hot desert finds, and concluded that elementally fractionated air (EFA) dominates the gas released at low temperatures.

Investigating a series of terrestrial samples from hot and cold deserts reveals that EFA is a ubiquitous occurrence (Fig. 2). Thus, a similar process could be expected to have acted on Mars, especially during a warm and wet period.

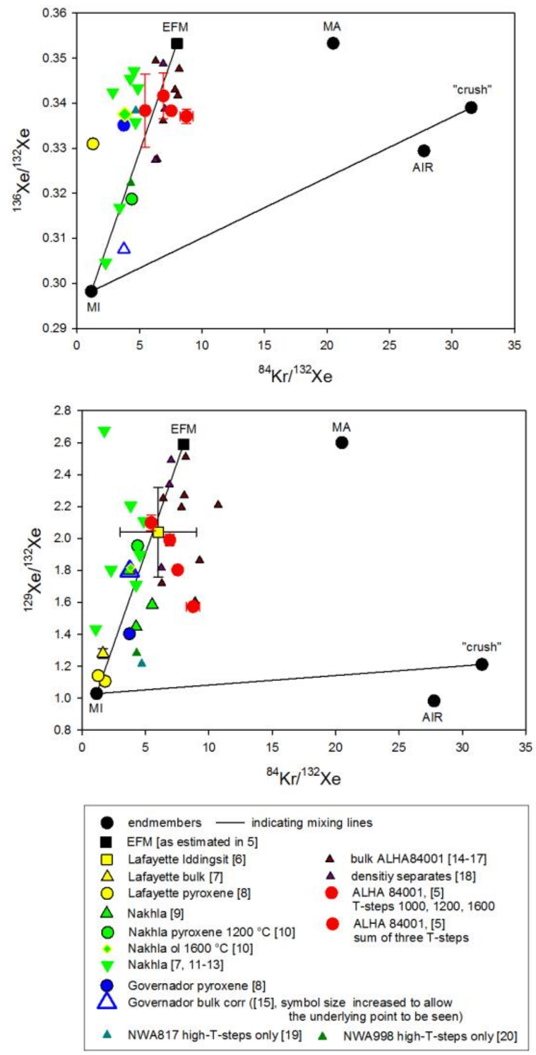

Fig. 1 a (top). ^{136}Xe/^{132}Xe vs. ^{84}Kr/^{132}Xe ratios, and 1 b (bottom) ^{129}Xe/^{132}Xe vs. ^{84}Kr/^{132}Xe ratios. Endmembersin both panels: MA = Martian atmosphere [1], MI = Martian Interior [9], EFM = Elementally fractionated Martian atmosphere [5], Air = terrestrial atmosphere [1], and 'crush' = gases released upon crusing instead of heating [13]. Data corrected for terrestrial atmosphere, see [5].

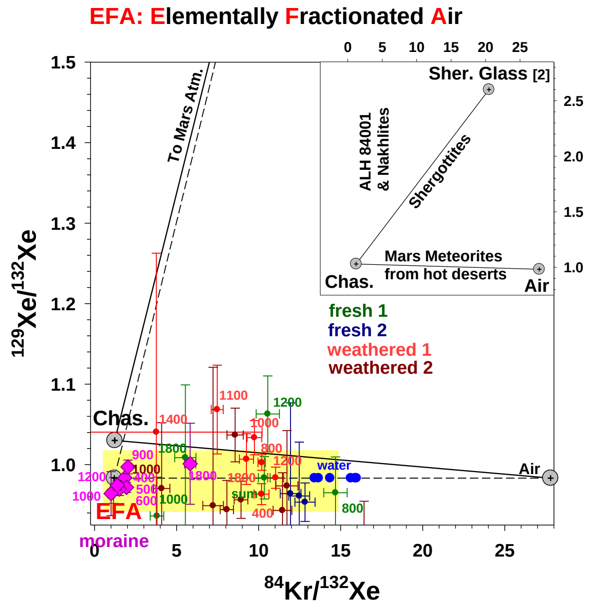

Fig. 2. Plot of four different samples of Antarctic dolerite samples: 'fresh' (green and blue symbols) denominates subsamples from a large boulder with fresh appearance (see [22]), weathered 1 and 2 (red symbols) are oxidized rim subsamples from small boulders from the same dolerite and the pink symbols indicate samples from a moraine, freeze-thaw environement. All numbers are degassing T-steps, the yellow box outlines the $^{84}Kr/^{132}Xe$ variation found in samples from terrestrial hot deserts. Noble gas data from [23,24]. Endmembers shown on Fig. 1.

Experimental evidence: It has long been recognized through experiments done on Apollo samples [25,26] that sample preparation, especially grinding, introduces heavy noble gases. More recently, similar observations have been made on Martian meteorites [27]. Thus, 'mechanical stress', but also exposing fresh surfaces to air [27], is well known to introduce heavy noble gases with a signature elementally fractionated in favour of the heavier element against the gas reservoir composition. Similarly, dissolution of air in water is known to result in elemental fractionation of Ar/Kr/Xe favouring the heavier element in solution [28]. Consequently, exposure of minerals to fluids and the resulting alteration, introduces a noble gas signature fractionated against the original gas reservoir.

We are currently undertaking experiments [29,30] to expose Mars relevant minerals (olivine, pyroxene, plagioclase, olivine glass, nakhlite composition glass, and mixtures thereof) to a simulated Mars atmosphere. Initial results point towards fractionation of the noble gas signature within the altered mineral surfaces. Ongoing measurements and modeling of the process is expected to give insights into the two step process of dissolution and incorporation of noble gases from a fluid phase, as well as potential changes to incorporation of noble gases due to differences in the chemistry of the alteration process (e.g., clay formation vs. oxide formation).

Concluding remarks: While it is well known that alteration of the mineral surface by mechanical stress or alteration processes can introduce elementally fractionated noble gases into minerals, details are yet to be explored. However, it is those details which will allow us to decide, which of the various processes brought forward in the literature (references see Fig. 1) can explain the incorporation of elementally fractionated Martian atmosphere into the nakhlites and ALH84001, and thus is the cause for the observed signatures. For the topic of this conference, ALH84001 is especially interesting, because it has been stated that the signature could be ancient Martian atmosphere [31] – or caused by water-rock interaction.

References: [1] Swindle T. D. (2002) *Rev. Min. Geochem., 47,* 171-190. [2] Owen, T. et al. (1977) *JGR, 82,* 4635–4639. [3] Conrad, P. G. et al. (2016) *EPSL, 454,* 1-9. [4] Bogard, D. D., Johnson, P. (1983) *Science, 221,* 651-654. [5] Schwenzer, S. P., Ott, U. (2006) 37th LPSC, abstr. #1614. [6] Swindle, T. D. et al. (2000) *MAPS, 35,* 107–115. [7] Ott, U. et al. (1988) *Meteoritics, 23,* 295–296. [8] Schwenzer, S. P. et al. (2006) 37th LPSC, abstr. #1612. [9] Ott, U. (1988) *GCA, 52,* 1937–1948. [10] Schwenzer, S. P. et al. (2002) *MAPS 37,* A127. [11] Mathew, K. J. & Marti, K. (2002) *EPSL, 199,* 2–20. [12] Busemann, H., & Eugster, O. (2002) *LPS XXXIII,* Abstr. #1823. [13] Wiens, R. C. (1988) *EPSL 91,* 55–65. [14] Mathew, K. J. & Marti, K. (2001) *J. Geophys. Res., 106 (E1),* 1401–1422. [15] Swindle, T. D. et al. (1989) *LPS, XX,* 1097–1098. [16] Swindle, T. D. et al. (1995) *GCA 59,* 793–801. [17] Miura, Y. N. et al. (1995) *GCA 59,* 2105–2113. [18] Murty, S. V. S. & Mohapatra, R. K. (1997) *GCA 61,* 5417–5428. [19] Mathew, K. J. et al. (2003) *EPSL, 214,* 27–42. [20] Mathew, K. J. & Marti, K. (2005) *JGR., 111,* E12S05. [21] Mohapatra, R. K. et al. (2009) *GCA, 73,* 1505-1522. [22] Steer, E. D. et al. (2013) *EPSC, 2013,* abstr. # EPSC2013-166. [23] Schwenzer, S. P. et al. (2007) *38th LPSC,* abstr. # 1150. [24] Schwenzer, S. P. et al. (2007) *38th LPSC,* abstr. # 1143. [25] Niedermann, S. &, Eugster, O. (1992) *GCA, 56,* 493–509. [26] Niedermeier & S., Leich, D.A. (1976) *Proc. 7th Lunar Sciene Conf., GCA, Suppl. 7,* 587–597. [27] Schwenzer, S. P. et al. (2012) *MAPS, 47,* 1049–1061. [28] Ozima & M., Podosek, F. A. (2002): Noble Gas Geochemistry. [29] Schwenzer, S. P. et al. (2016) *47th LPSC,* abstr.# 1889. [30] Schwenzer, S. P. et al. (2017) *48th LPSC,* abstr.# 1531. [31] Gilmour, J. D. et al. (1998) GCA, 62, 2555-2571.

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