

DIAGENESIS ON MARS: INSIGHTS INTO NOBLE GAS PATHWAYS AND NEWLY FORMED MINERAL ASSEMBLAGES FROM LONG TERM EXPERIMENTS. S. P. Schwenzer¹, J. C. Bridges², M. A. Miller³, L. J. Hicks², U. Ott^{4,5}, J. Filiberto^{6,1}, C. Chavez⁷, H. Smith⁷, A. H. Treiman⁸, S. P. Kelley¹, J. M. Moore⁷, T. D. Swindle⁹, M. A. Bullock¹⁰ – ¹The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, Susanne.schwenzer@open.ac.uk; ²Space Research Centre, University of Leicester, UK; ³Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78228; ⁴ATOMKI, Debrecen, Hungary; ⁵MPI, Mainz, Germany; ⁶Southern Illinois University, MC 4324, Carbondale, IL 62901; ⁷NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035; ⁸Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058; ⁹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ; ¹⁰Southwest Research Institute, 1050 Walnut St., Suite 300, Boulder, CO 80302.

Introduction: Alteration mineral assemblages on Mars, including carbonates and clays, have been detected in meteorites [1-5], from orbit [6-10] and with rover-based instrumentation [11,12]. Thermochemical modeling has shown that those alteration minerals can form in a wide variety of temperatures and chemical environments [13-17]; for example diagenesis has been identified within the fluvio-lacustrine sediments at Gale Crater studied by MSL Curiosity [12-21].

Noble gases, on the other hand, show two different endmembers of atmospheric components: an unfractionated component measured by the lander-based instrumentation [22,23; isotopes only from MSL] and in the little to unaltered shergottite Martian meteorites; and an elementally fractionated component in the altered groups of Martian meteorites, the nakhlites and the orthopyroxenite ALH84001. The source of the fractionated atmosphere in those meteorites has been debated since its discovery (for a literature review see [24-25]). The experiments carried out here are designed to investigate the degree of elemental fractionation experienced by the heavy noble gases in a Mars analog setting.

Experimental set up: We use the Aqueous Simulation Facility at NASA Ames (see [26,27] for details of the facility and our experiments), running long-duration alteration experiments for 1, 3 and 9 months at 35 °C with a simulated Mars atmosphere (98 % CO₂ and

Table 1. Chemical composition of phases used. Ol=Fe-bearing forsterite, Pyx=augite, Plag=andesine, BS = blasting sand, referred to as glass. Our runs contained a variation of combinations from pure minerals 1:1 mixtures and mixtures of three or all four phases.

	Ol	Pyx	Plag	BS
SiO ₂	41.8	52.1	63.4	31.84
Al ₂ O ₃		2.4	21.6	4.43
TiO ₂		0.6		0.33
FeO	7.1	9.5	0.06	55.03
CaO	0.1	19.1	2.3	1.48
MgO	56.7	14.6		0.78
Na ₂ O		0.3	8.6	0.38
K ₂ O			3.8	1.23

2 % Ar, 30 ppm Kr and 8 ppm Xe) and a variety of mineral compositions as Mars analogs including the nakhlite meteorites (Tab. 1). Here we report on the first two experiments, while the 9 month long experiment is due to finish in May 2017. Earlier results were reported by Bullock et al. [26] and Schwenzer et al. [27].

Mineralogy: We previously reported [27] that chemical changes occur even after a 1 month experiment duration. Etch pits, leaching and the formation of carbonate and a mixture of amorphous and crystalline clay with ~0.7 nm d-spacing have been found. We have since investigated the clays with X-ray Absorption Spectroscopy (XAS).

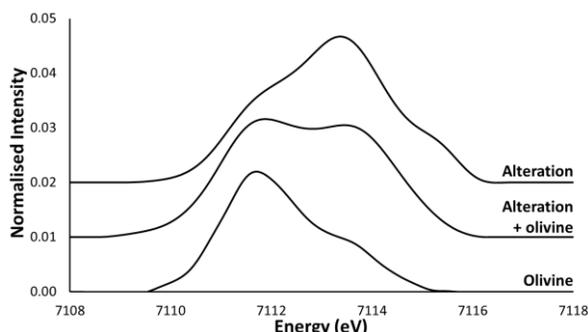


Figure 1. Fe-K XAS pre-absorption edge feature, showing a positive shift in the centroid energy measured in two alteration veins compared to that of the surrounding olivine.

XAS summary. The altered olivine sample (M-18, first run; [27]) has been measured for Fe-K XAS, using the I-18 X-ray Microfocus Beamline at the Diamond Light Source synchrotron. Analysing the Fe-K 1s→3d pre-edge peaks, a centroid position is taken as the intensity-weighted average of the spline-baseline-subtracted pre-edge peaks and can be used to estimate the ferric content of the sample [28-30]. The measured M-18 olivine has a 1s→3d pre-edge centroid at ~7112.2 eV, and the alteration veins were found to have a higher energy in the centroid of up to ~7113.1 eV (Fig. 1). This positive shift in the energy suggests an increase in the ferric content in the alteration material, over that of the surrounding ferrous olivine, with a fer-

ric-ferrous ratio of $\text{Fe}^{3+}/\Sigma\text{Fe} \leq 0.5$ for the clay alteration. This is equivalent to a chemical composition of MgO 44.8, Al_2O_3 0.9, SiO_2 51.8, FeO 1.1, Fe_2O_3 1.3 wt.-%. These Fe-K XAS results are similar to the increased ferric content of the alteration material observed in the nakhlites, where the Fe-silicate alteration was found to be highly ferric [5].

Noble gas results: Measurable amounts of adsorbed/incorporated heavy noble gases were found in our one month long experiment [27]; here we present results from the next, three months long experiment.

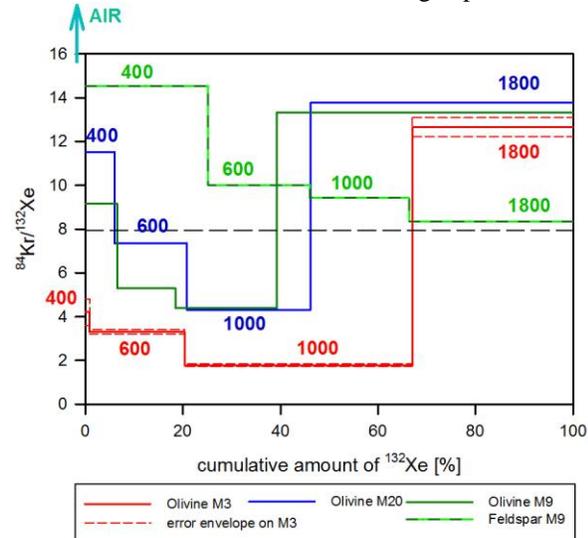


Figure 2. Noble gas results from olivines and a feldspar; three months-long run. Terrestrial air plots outside the diagram ($^{84}\text{Kr}/^{132}\text{Xe} = 27.8$), and the experimental gas mixture's $^{84}\text{Kr}/^{132}\text{Xe}$ is 7.95 as indicated by the thin dashed black line, but the $^{84}\text{Kr}/^{132}\text{Xe}$ in the fluid is likely half of this ratio. The measurement error envelope is given on the olivine M3 measurement and similar for all measurements.

Noble gases in altered olivines. Noble gases were measured in three olivines and one feldspar from two different alteration settings of the three month long run. Olivines M3 and M20 are from vessels with pure olivine, while vessel M9 contained a mixture of (wt.-%, for chemistry see Tab. 1) 25 % Plag, 25 % Pyx, 10 % Ol and 40 % blasting sand. This mixture is closest in its Fe^{2+} content to Martian rock compositions. The composition of the incoming Mars gas (30 ppm Kr and 8 ppm Xe) has a corresponding $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of 7.95.

Release patterns are similar for all olivines, with $^{84}\text{Kr}/^{132}\text{Xe}$ being higher in the 400 °C step than in the two following steps, and then high again in the last step. The 1800 °C step is similar within error in all three olivines and attributed to the gas trapped upon formation. The 400 °C step is attributed to adsorbed air from sample handling outside the controlled atmos-

pheres, while the 600 °C and 1000 °C steps are attributed to gas trapped during the experimental run.

Olivines M3 and M20 are from vessels with olivine only, but show different degrees of alteration and display different degrees of fractionation. Olivines M9 and M20 release 4.28×10^{-12} and 4.36×10^{-12} ccSTP/g of ^{132}Xe , respectively, with a $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of 4.7 ± 0.2 and 5.4 ± 0.1 in the 600 and 1000 °C steps combined. In contrast, M3 released 1.21×10^{-11} ccSTP/g of ^{132}Xe with a $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of 2.2 ± 0.1 in the two intermediate T-steps. Feldspar M9 displays a very different pattern, with higher $^{84}\text{Kr}/^{132}\text{Xe}$ ratios in the first T-step and 7.09×10^{-12} ccSTP/g of ^{132}Xe with a $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of 9.7 ± 0.4 in the two intermediate T-steps, indicating different incorporation characteristics for Kr and Xe at the alteration surfaces of those minerals.

The observations could be explained by adsorption/incorporation site differences in the minerals as modeled by atomistic simulations [31]. Other explanations include small differences in water to rock ratio, precipitating phases and thermochemical conditions within the vessel, or a fractionation gradient along the daisy chain of the experimental set up. Investigations of the mineralogy and the fluids of the 3 months long run, as well as more noble gas measurements are in progress.

References: [1] Harvey, R.P. & McSween, H.Y. jr (1996) *Nature*, 382, 49–51. [2] Treiman, A.H. (1998) *MAPS*, 33, 753–764. [3] Treiman, A.H. (2005) *Chem Erde*, 65, 203–270. [4] Changela, H.G. & Bridges, J.C. (2010) *MAPS*, 45, 1847–1867. [5] Hicks, L.J. et al. (2014) *GCA*, 136, 194–210. [6] Bibring, J.-P. et al. (2006) *Science*, 312, 400–404. [7] Ehlmann, B.L. et al. (2011) *Nature*, 479, 53–60. [8] Ehlmann, B.L. et al. (2014) *An. Rev. Earth Planet. Sci.*, 42, 291–315. [9] Carter et al. (2015) *Icarus*, 248, 373–382. [10] Turner et al. (2016) *JGR*, 121, 608–625. [11] Arvidson, R.E. (2014) *Science*, 343, DOI: 10.1126/sci-ence.1248097. [12] Vaniman, T.D. et al. (2014) *Science*, 343, DOI:10.1126/science.1243480. [13] Griffith, L.L. & Shock, E.L. (1995) *Nature*, 377, 406–408. [14] Zolotov, M.Y. & Shock, E.L. (2005) *GRL*, 32, doi:10.1029/2005GL02 4253. [15] Schwenzer, S.P. & Kring, D.A. (2009) *Geology*, 37, 1091–1094. [16] Melwani Daswani et al. (2016) *MAPS*, 51, 2154–2174. [17] Zolotov M.Y. & Mironenko, M.V. (2016) *Icarus*, 275, 203–220. [18] Stack, K. M. et al. (2014) *JGR*, 119, DOI:10.1002/2014JE 004617. [19] Nachon, M. et al. (2017) *Icarus*, 281, 121–136. [20] Bridges, J.C. et al. (2015) *JGR*, 120, DOI:10.1002/2014JE 004757. [21] Schwenzer, S.P. et al. (2016) *MAPS*, 51, 2175–2202. [22] Owen, T. (1977) *JGR*, 82, 4635–4639. [23] Conrad, P.G. et al. (2016) *EPSL*, 454, 1–9. [24] Filiberto, J. et al. (2016) *MAPS*, 51, 1935–1958. [25] Schwenzer, S.P. et al. (2016) *DINGUE* #4, CRPG, Nancy, France. [26] Bullock, M.A. et al. (2015) 46th LPSC, abstr. #1235. [27] Schwenzer, S.P. et al. (2016). 47th LPSC, abstr. #1889. [28] Wilke M. et al. (2001) *Am. Min.*, 86, 714–730. [29] Berry A.J. et al. (2003) *Am. Min.*, 88, 967–977. [30] Hick L.J. et al. (2017) *MAPS*, (in rev.). [31] Du, Z. et al. (2008) *GCA*, 72, 554–573.

Additional Information: We acknowledge NASA MFRP and OU internal funding.