

**NOBLE GAS FRACTIONATION IN HYDROUS ROCK ALTERATION UNDER DIAGENETIC PRESSURE AND TEMPERATURE CONDITIONS** S. P. Schwenzer<sup>1</sup>, M. A. Bullock<sup>2</sup>, J. C. Bridges<sup>3</sup>, C. L. Chavez<sup>4</sup>, J. Filiberto<sup>5</sup>, L. J. Hicks<sup>3</sup>, S. P. Kelley<sup>1</sup>, M. A. Miller<sup>6</sup>, J. M. Moore<sup>4</sup>, H. D. Smith<sup>4</sup>, T. D. Swindle<sup>7</sup>, A. H. Treiman<sup>8</sup> – <sup>1</sup>The Open University, Walton Hall, Milton Keynes MK7 6AA, UK; <sup>2</sup>Southwest Research Institute, 1050 Walnut St., Suite 300, Boulder, CO 80302 (bullock@boulder.swri.edu); <sup>3</sup>Space Research Centre, University of Leicester, UK, <sup>4</sup>NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035; <sup>5</sup>Southern Illinois University, MC 4324, Carbondale, IL 62901; <sup>6</sup>Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78228; <sup>7</sup>University of Arizona, Tucson, AZ; <sup>8</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058.

**Introduction:** Noble gases observed in Martian meteorites stem from a complex set of sources: Martian interior [1], Martian atmosphere [2], a ‘crush’ component [3], fractionated Martian atmosphere [1], cosmic irradiation [4] and (fractionated) terrestrial air contamination [5]. Disentangling those sources and the pathways of incorporation of the Martian fractionated noble gas component has the potential to reveal environmental conditions on Mars throughout its history, but especially during Noachian times through the oldest of the Martian meteorites - ALH84001 - and in the mid-Amazonian through the nakhlites.

Fractionation of noble gases under natural conditions is a multi-step process that can involve dissolution into a fluid, adsorption onto a mineral surface, and incorporation into a crystal. Each step might involve fractionation (e.g., [6]). In addition, impact metamorphism is known to incorporate noble gases in a non-fractionating way [7]. Understanding the processes and their contribution to the final signatures found will enable disentangling terrestrial contamination from Martian signatures - and understanding the Martian signatures themselves. We present experimental results from mineral alteration under diagenetic conditions that allow tracking the noble gas incorporation alongside the mineralogical changes and fluid characteristics in a well-defined setting.

*Table 1. Chemical composition of the phases used in the experiments. Ol=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. In this abstract we mainly focus on olivine and plagioclase from mixtures.*

	Ol	Pyx	Plag	BS
SiO <sub>2</sub>	41.8	52.1	63.4	31.84
Al <sub>2</sub> O <sub>3</sub>		2.4	21.6	4.43
TiO <sub>2</sub>		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 <sub>2</sub> O		0.3	8.6	0.38
K <sub>2</sub> O			3.8	1.23

**Experimental:** We conducted experiments in the Mars brines experimental apparatus at NASA Ames [8,9]. Here we present data from the short 1 month experiment with mineral mixtures composed of olivine, pyroxene and plagioclase (Tab. 1), and a three month experiment with mineral mixtures composed of the same minerals but added ‘blasting sand’, which is a glass of fayalitic composition and serves as Martian analogue Fe<sup>2+</sup>-source (Tab. 1). 50 g of each mineral or mineral mixture was immersed in 100 ml purified water at 35 °C under a synthetic Martian atmosphere (98 % CO<sub>2</sub>, 2 % Ar, 30 ppm Kr and 8 ppm Xe (<sup>40</sup>Ar/<sup>132</sup>Xe = 9236, <sup>84</sup>Kr/<sup>132</sup>Xe = 7.93)). We studied the mineralogical changes in the samples through SEM (FEI Quanta 650 with EDS IXRF Systems 550i) and Raman (Horiba/Jobin Yvon LabRam HR Evolution; Excitation Wavelength: 532 nm) investigations at SwRI San Antonio, and details of the clay formation in olivine through FIB-TEM (JEOL 2100, 200 kV) at University of Leicester. Mineral chemistry of unreacted minerals was obtained on a Cameca SX 100 at the OU (Tab. 1).

**Results:** We investigate three parameters of our experimental products: the alteration mineralogy, the fluid chemistry and the noble gas composition.

*Mineralogy.* Mineralogical changes include etch pits, compositional changes and the formation of alteration phases. Compositional changes of mineral surfaces vary with the co-dissolving minerals. Comparing olivines on their own to olivines in mixtures with pyroxene and plagioclase show significant differences, most of which can be explained by the ion activity supplied by co-dissolving minerals in the mixtures (Fig. 1). Olivine dissolves incongruently [10], with Mg being leached first and an SiO<sub>2</sub>-rich layer forming on the surface. This is observed in our experiments (Fig. 1). Further changes depend on the nature of the mineral mix in the reaction vessel. Ca and Al are enriched on surfaces of olivines in mixed mineral reactions. Al-enrichment is especially prominent in the olivine + plagioclase run, indicating phyllosilicate formation with Al from the plagioclase on the surface of the olivine. Interestingly, Fe is leached from the olivine’s surface, if no other Fe-bearing mineral is present, but no change is observed, if pyroxene as another Fe-source is present (Fig. 1).

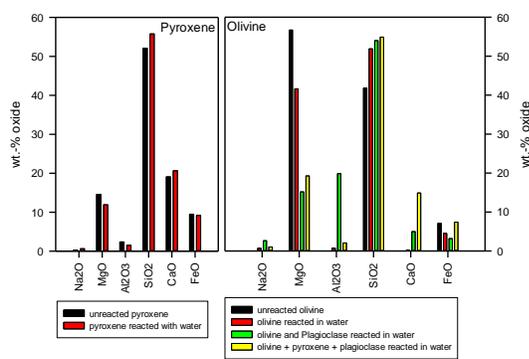


Fig. 1. Chemical changes at mineral surfaces of Run 1.

The reactions of pyroxenes are similar. If pyroxene dissolves on its own, Mg is depleted at the surface, but in the presence of olivine an enrichment is observed.

The chemical changes are consistent with our Raman observations of additional SiO<sub>2</sub> bonds at the mineral surfaces, which we attribute to the formation of a silica layer, and Ca-Mg-carbonate formation.

Investigation of visible phyllosilicate veinlets in olivine from M18 supports the changes observed in the chemistry. Numerous alteration veins were identified in the olivine (Mg# = 0.93). These are up to 20 mm wide in anastomosing networks. The veins contain clay-like silicate material with lesser amounts of iron oxide. The clay has ~46-54 wt% SiO<sub>2</sub> and 40-49 wt% MgO, 2-9 wt% FeO (average Mg# = 0.95). HR-TEM analysis showed a largely amorphous nature to the clay but with crystalline patches. These have lattice spacings of 3.8 Å and are consistent with a serpentine structure where the combined tet-oct repeating unit is ~7.6 Å.

**Fluids.** The surface chemical and mineralogical changes are in direct connection to the fluid compositions observed. Most notably, Fe and Al are below detection limit in all solutions, which supports the observation of oxide and phyllosilicate precipitation. Si is highest in the pure olivine sample fluid, which also has the highest Mg-concentration. This indicates dissolution, but also limited precipitation of secondary phases compared to mineralogically mixed samples.

**A preliminary look at the noble gases.** Noble gases will be measured at the Lunar and Planetary Laboratory, using stepwise heating protocols and a cold trap to separate the heavy noble gases. Preliminary data, presented here, were obtained at The Open University using a MAP215 mass spectrometer and infrared-laser stepwise heating protocols, but no cold trap. The stepwise heating allows separation of adsorbed air, more tightly bound noble gases, as might be incorporated into etched surfaces or within alteration mineral formation, and noble gases sited within crystals, e.g., radiogenic <sup>40</sup>Ar in feldspars. We note that the plagioclase

has about a factor of 2 more <sup>40</sup>Ar and a factor of 3 more <sup>132</sup>Xe than the olivine, but only slightly more <sup>84</sup>Kr. We therefore assume that the differences are not due to different surface areas, but the higher <sup>40</sup>Ar stems from radiogenic <sup>40</sup>Ar, and the higher Xe might be the result of differences in surface adsorption or secondary mineral formation. We will measure in more detail to disentangle those processes, which can include adsorption but also incorporation into the newly formed surface, as has been modeled by [11].

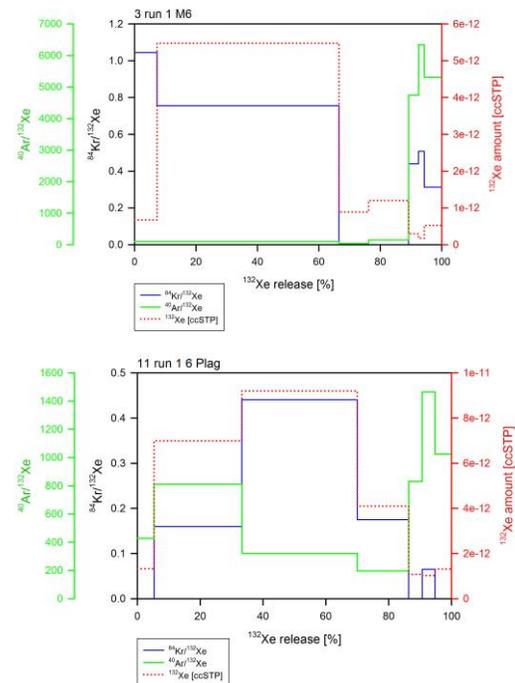


Fig. 2. Stepwise heating noble gas measurements of olivine (top) and plagioclase (bottom) from run 1.

**Conclusions:** Systematic changes in mineral surface chemistry show that SiO<sub>2</sub> is generally enriched on dissolving mineral surfaces, but all other element enrichments or depletions depend on the environment. Most interestingly, the alteration on olivine from the dissolution of pure olivine has led to the formation of Mg-rich serpentine and iron oxide veins in just one month of alteration.

**References:** [1] Ott U. (1988) *GCA*, 52: 1937–1948. [2] Bogard D.D. and Johnson P. (1983) *Science*, 221: 651–654. [3] Wiens R.C. (1988) *EPSL* 91: 55–65. [4] Eugster O. (2003) *Chem. Erde*, 63: 3–30. [5] Mohapatra et al. (2009) *Geochim. Cosmochim. Acta* 73, 1505–1522. [6] Ozima, M. & Podosek, F. A. (2002) *Noble Gas Geochemistry*. 286 p.; Cambridge University Press. [7] Bogard, D.D. et al. (1986) *JGR*, 91, *Proc. 17th Lunar Planet. Sci. Conf.*, 99–114. [8] Bullock, M.A., Moore, J.M. (2004) *GRL*, 31: doi:10.1029/2004GL019980. [9] Bullock et al. (2015) *LPSC* 46, abstr. 1235. [10] Stefánsson, A. et al. (2001) *Chem. Geol.*, 172, 251–276. [11] Du, Z. et al. (2008) *GCA*, 72, 554–573.

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