NOBLE GAS ANALYSIS FOR MARS ROBOTIC MISSIONS: EVALUATING K-AR AGE DATING FOR MARS ROCK ANALOGS AND MARTIAN SHERGOTTITES. J. Park[1,2], D. W. Ming[1], D. H. Garrison[1,3], J. H. Jones[1], ,D. D. Bogard[1] and K. Nagao[4]. [1]ARES, NASA Johnson Space Center, Houston, TX 77058, USA, [2]Lunar and Planetary Institute, Houston, TX, 77058, USA, [3]ESCD-Barrios, JE23, 2224 Bay Area Blvd, Houston, TX 77058, USA, [4]Laboratory for Earthquake Chemistry, Graduate School of Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan.

Introduction: The purpose of this noble gas investigation was to evaluate the possibility of measuring noble gases in martian rocks and air by future robotic missions such as the Mars Science Laboratory (MSL). The MSL mission has, as part of its payload, the Sample Analysis at Mars (SAM) instrument, which consists of a pyrolysis oven integrated with a GCMS. The MSL SAM instrument has the capability to measure noble gas compositions of martian rocks and atmosphere. Here we suggest the possibility of K-Ar age dating based on noble gas release of martian rocks by conducting laboratory simulation experiments on terrestrial basalts and martian meteorites. We provide requirements for the SAM instrument to obtain adequate noble gas abundances and compositions within the current SAM instrumental operating conditions, especially, a power limit that prevents heating the furnace above ~1100ºC. In addition, Martian meteorite analyses from NASA-JSC will be used as ground truth to evaluate the feasibility of robotic experiments to constrain the ages of martian surface rocks.

Difficulties and Suggested Solutions: There are several difficulties to measuring noble gases on Mars with the SAM instrument. To begin, the MSL instrument has no method to weigh the Martian rock samples. Furthermore, the furnace built into SAM will be heated to only ~1000 ºC, perhaps to ~1100 ºC, because of power limitations. Bogard [1, 2] pointed out that analyzing ^{40}Ar concentrations on Martian meteorites is difficult, because the total ^{40}Ar is not only from *in situ* ^{40}K decay, but also other Martian ^{40}Ar components, *e. g*., shock implanted ^{40}Ar from the martian atmosphere [3, 4] and ^{40}Ar acquired from the parent magma [5]. Consequently, Ar-Ar ages of basaltic shergottites often are much older than ages determined using other radiometric age dating methods, such as Sm-Nd [e.g., 6]. Bogard [1] suggested that K-Ar age dating of Mars rocks will require determining the excess ^{40}Ar which was inherited from the magma, because this excess ^{40}Ar possibly is a common property of Martian rocks. Bogard [1] also suggested that Ar diffusion data (i.e., D/a^2) from Martian meteorites can be used to evaluate the effect of the heating temperature limit (≤1100 ºC). That is, the diffusion data will define the heating time needed to totally de-gas noble gases from Martian rocks.

Experimental methods: *Samples.* MORB (Mid Ocean Ridge Basalt) samples and three Martian shergottites [EET79001, Zagami and Los Angeles (LA)] were prepared for noble gas measurements. We chose MORBs, because they are basaltic, as are martian meteorites, and because they have noble gas concentrations similar to martian meteorites (^{4}He= ~10^{-5} cc/g, ^{20}Ne= ~10^{-9}-10^{-10} cc/g, ^{40}Ar= ~10^{-6} cc/g, ^{84}Kr= ~10^{-11} cc/g, ^{132}Xe= ~10^{-12} cc/g [7]). Additionally, terrestrial samples are easily available, compared to the rarity of shergottites. Among the meteorites, we chose EETA79001, Zagami and LA001. These meteorites are well-characterized basaltic shergottites. *Grain sizes.* For sample preparation, we ground the samples sieving to 120, 230 and 325 mesh, which are equivalent to 125 µm, 65µm and 44 µm, respectively. The anticipated mean particle size for MSL samples was estimated to be ~70 µm (R. Anderson, per comm.). We prepared MORB and Martian meteorite samples with similar grain size distributions. *Experimental temperatures.* We performed two different types of experiments. First, a 9-10 step heating protocol from 400 ºC to 1400 ºC with 20-30 min heating intervals for the MORBs for the purpose of measuring Ne and Ar diffusion parameters. Then, we analyzed the prepared MORB and Martian meteorite samples for a simulated MSL noble gas investigation at temperatures of 400 ºC (30 min), 1100 ºC (60 min) and 1400 ºC (20 min). The first step should remove any adsorbed Ne and Ar. The second step should release most of the radiogenic ^{40}Ar. And the third step should determine how successful the second step was.

Results: Fig. 1 is an Arrhenius plot of D/a^2 vs. $1/T$, calculated from stepwise degassing of ^{20}Ne and ^{40}Ar from MORB sample PR2-3-1-100 compared to ^{40}Ar diffusion data for Zagami. Ar diffusion from MORB is seen to be similar to Ar diffusion from Zagami.

Based on Arrhenius plots, we can determine Ne and Ar diffusivity at temperatures achievable by SAM. That is, we can infer percent gas losses for given temperatures and heating times using the determined values of D/a^2. In the case of Ar with 60 min heating, the calculation suggests we can release ~90% of the total ^{40}Ar at a temperature of 1100ºC, and ~70% of the total ^{40}Ar at a temperature of 1000ºC. In the case of Ne with 60 min heating, we expect to obtain >99% of ^{20}Ne at a temperature of 1100ºC, and ~90% of ^{20}Ne at the tem-

perature of 1000ºC. Therefore, because of power limitations, we suggest longer heating times, perhaps ~120 minutes at 1100 ºC (or longer at 1000°C), may be

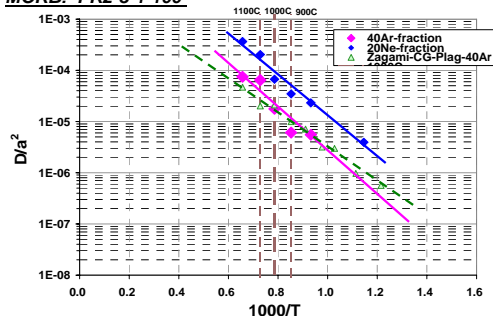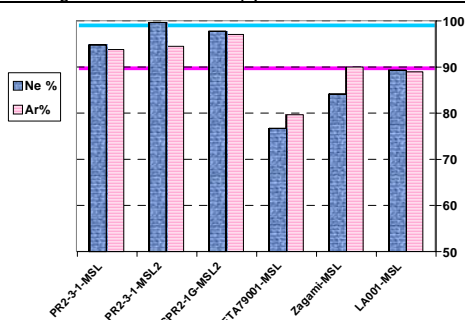Figure 1. Arrhenius plot for ^{20}Ne and ^{40}Ar from MORB and ^{40}Ar from Zagami.

Figure 1. Histogram of Ne and Ar degassing percentages.

necessary in order to sufficiently de-gas Ar from martian rocks.

The histogram in Fig. 2 shows the actual percent of Ne and Ar degassing from MORB samples and three martian meteorite samples using 400 ºC and 1100 ºC extractions. The horizontal lines show the expected degassing percent ages calculated for Ne (blue line) and Ar (pink line). MORB samples degassed more Ar than calculated. For the martian meteorites Zagami and LA, the extracted Ar is about 80-90% of total Ar, which is close to the calculated value. The EET79001 sample (Lithology A), is anomalously low. We are still working to understand the differences between our calculated and measured percent releases. Presumably, differences in (i) mineralogy, (ii) noble gas components, and (iii) previous thermal history all contribute.

Application to K-Ar age dating: To calculate K-Ar "ages" for Zagami, LA, and EET79001, we used reported K concentrations of 539 ppm [8], 1286 ppm [9] and 166 ppm [10], respectively. We calculated apparent K-Ar ages for these meteorites with (a) no correction, (b) with/without the 400 ºC extraction, and (c) with/without estimations of excess ^{40}Ar [2]. The calculated ages for Zagami, LA001 and EETA79001 range, respectively, from 249 to 825 Myr, from 177 to 393 Myr and from negative values to 1070 Myr. The respective reported K-Ar ages are 412-1778 Myr [6, 11],

359-453 Myr [6], and 517-3338 Myr [6, 11]. Determining K concentrations accurately will play a key role in getting accurate ages for Martian rocks. Common K concentrations on Mars as measured by Spirit APXS are reported as ~3000-7000 ppm with variations based on locations. Some places on Mars, e.g., Low Ridge and Husband Hill, are very enriched in K, having concentrations as high as ~ 25000 ppm [12, 13], favorable for K-Ar age measurements. However, these concentrations are probably dominated by soils. Rock concentrations of K are probably considerably lower.

Martian atmospheric noble gases: Fig. 3 shows noble gas elemental ratios compared to those in solar gas assuming a mass-dependent Rayleigh distillation process for Earth's atmosphere [7] and the Martian atmosphere [14-16]. The straight line for Earth suggests the terrestrial atmosphere originally had the solar nebula composition and then underwent Rayleigh distillation. This similarity suggests that perhaps both the Earth and Mars experienced atmospheric hydrodynamic escape [14].
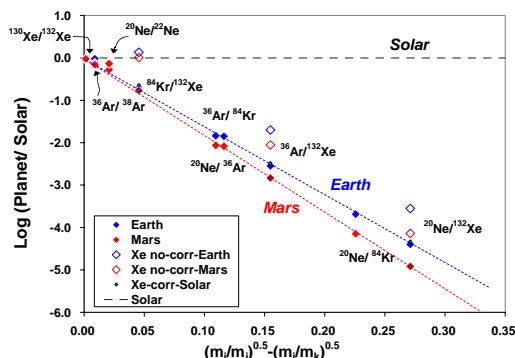

Figure 2. Noble gas isotopic and elemental ratios compared to those of solar gas that underwent Rayleigh distillation.

References: [1] Bogard D.D. (2008) *MaPS,* in press. [2] Bogard D.D. and Park J. (2008) *LPS XXXIX,* Abstract#1100. [3] Bogard D.D. and Johnson P. (1983) *Science, 221,* 651-654. [4] Marti K. et al. (1995) *Science, 267,* 1981-1984. [5] Bogard D.D. and Park J. (2008) *MaPS, 43,* 1113-1126. [6] Nyquist L.E. et al. (2001) *Space Science Rev., 96,* 105-164. [7] Ozima M. and Podosek F.A. (2002) Noble Gas Geochemistry. 286p. [8] McCoy T.J. et al. (1992) *GCA, 56,* 3571-3582. [9] Rubin A.E. et al. (2000) *Geology, 28,* 1011-1014. [10] Warren P.H. and Kallemeyn G. W. (1997) *MaPS, 32,* A135-136. [11] Schwenzer S.P. et al. (2007) *MaPS, 42,* 387–412. [12] Ming D.W. et al. (2006) *JGR, 111,* E02S12. [13] Ming D.W. et al. (2008) *JGR, 113,* E12S39. [14] Pepin R. O. (1991) *Icarus, 92,* 2-79. [15] Bogard D.D. (1997) *JGR, 102,* 1653-1661. [16] Park J. and Nagao K. (2006) *LPS XXXVII* Abstract #1110.