**COMBINED STEPWISE HEATING AND VACUUM CRUSHING ANALYSES OF NOBLE GASES IN SHERGOTTITES.**

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**Introduction:** Martian meteorites, typical Shergottites-Nakhlites-Chassignites and several unique meteorites, are valuable and possibly sole direct samples from Mars until future sample-return. Trapped noble gases in these meteorites have similar compositions to Martian atmosphere, which provides a strong evidence of their Martian origin [1][2]. Accurate and precise information of the trapped gases may also complement the previous observation and exploration data of Mars. Hence, elucidation of noble gas records in the Martian meteorites is helpful to understand the evolutional history of Martian surface system. However, noble gases in the meteorites are known to be complicated mixtures of several sources, such as Martian surface (or atmosphere), Martian interior (or mantle), radiogenic products, cosmogenic products, and terrestrial air (e.g.[3]–[9]). Moreover, meteorites found in hot deserts also contain elementally fractionated terrestrial air (EFA), which was incorporated by desert weathering [7]. Previous studies of heating analyses and crushing analyses of some shergottites revealed different elemental/isotopic signatures between the different analytical methods [6][7], suggesting that distinct components are retained in distinct site in the same meteorites.

In order to retrieve the exact Martian atmospheric records from the meteorites, one needs to know the trapping mechanism and sites of the noble gases. As the first step, we have conducted combined stepped heating and vacuum crushing of several shergottites.

**Samples:** Tissint and SaU 008 are olivine-phyric shergottites. Tissint, fell in Morocco in 2011, is characterized by its numerous shock-melted glasses with small bubbles (<10μm – ca. 100μm), which might contain Martian atmospheric components [10]. A previous heating analysis of the Tissint glass reported its significant concentration of the Martian atmospheric noble gases [8]. Meanwhile, heating analyses of pairs of SaU008 showed the incorporation of EFA[7][9]. Similar EFA effects were also observed in NWA 7397, a slightly weathered poikilitic shergottite [11][8]. NWA 10441 is a recently found highly shocked and moderately weathered shergottite. It is composed of ca. 15% of shock-melted glasses with a lot of vesicles [12].

**Analytical Methods:** The noble gas analyses (He, Ne, Ar, Kr, and Xe) were conducted with a VG3600 at the University of Tokyo. A ca. 100–200 mg chip of the each sample was separated into two groups; one for the stepped heating and the other for the vacuum crushing. The former fraction was heated in steps of 400°C, 600°C, 800°C, 1000°C, 1300°C, and 1800°C. The latter fraction was crushed with 2–10 MPa hydraulic ram to extract noble gases presumably from bubbles and/or fluid inclusions. The crushed samples were then picked-up and also stepped heated for the comparison. Tissint crushing fraction was divided into fusion crust-enriched (FC) and the other sample (Bulk). All samples and vacuum lines were baked at ca. 200°C in vacuum for overnight before the analyses.

**Results & Discussion:** *Neon*: Both pre-crushing and post crushing, most stepped heating data plotted lower-right in the $^{20}Ne/^{22}Ne$–$^{21}Ne/^{22}Ne$ diagram (Fig. 1), which means ≥ 90% of cosmogenic Ne. Although some high-temperature steps of NWA 7397 plot close to the terrestrial air composition, it is not clear whether they are Martian origin or terrestrial contamination. On the other hand, all vacuum crushing data are shown in the upper-left side in Fig. 1, suggesting cosmogenic Ne can be effectively cut off by crushing method. The upper-left endmember might be either Martian atmospheric Ne or terrestrial air. However, it is difficult to distinguish the two because we do not know the exact $^{20}Ne/^{22}Ne$ ratio of Martian atmosphere currently, while some estimated values were proposed from meteorite analyses [9]. Furthermore, our crushed data are indistinguishable from a mixing line between terrestrial air and cosmogenic Ne (fig. 1). For determination of the upper-left endmember, further investigation is required.

*Argon:* Middle to high temperature steps of the heating analyses showed higher $^{40}Ar/^{36}Ar$ ratios up to ca. 1600 (Fig. 2). The high $^{38}Ar/^{36}Ar$ ratios indicate significant effects of cosmogenic Ar components. After cosmogenic $^{36}Ar$ and radiogenic $^{40}Ar$ corrections, trapped $^{40}Ar/^{36}Ar$ ratios became ~500–800, suggesting mixing of Martian atmospheric Ar of $^{40}Ar/^{36}Ar$ ~2400 [1] and terrestrial air. At the same time, all crushing data were identical to terrestrial value ($^{40}Ar/^{36}Ar$ ~300[13]; Fig. 2). This might be because either (i) the expected bubbles in glassy phases of the meteorites did not contain Martian atmospheric Ar, which would have been extracted by the crushing or (ii) the crushing was not enough to break the bubbles.

*Krypton and Xenon:* Figure 3 shows the relationship between $^{129}Xe/^{132}Xe$ ratios and trapped Kr/Xe elementally ratios ($^{84}Kr/^{132}Xe_{trapped}$) after cosmogenic and fission effects corrections. All crushed data plotted almost on the mixing line between terrestrial air and EFA or Martian interior (Chassigny-like) components. High temperature steps in the heating analyses showed some enrichments in $^{129}Xe$, indicating mixing of Martian atmospheric Xe ($^{129}Xe/^{129}Xe$ ≥2.4 [1][14]) and terrestrial air. No significant difference was observed between pre-crush and post-crush samples. It is noteworthy that both Tissint and the desert meteorites showed the similar mixing patterns in Fig. 3. Low temperature steps in the heating plotted in the lower-left side, close to EFA or Chassigny-like endmember. Since Tissint is fall, it is unlikely that Tissint contains EFA by weathering on the Earth. The lower-left endmember might be either the Martian Chassigny-like component or the terrestrial fractionated air that was incorporated by other rapid processes during the fall.

**References:** [1] Owen T. et al (1977) *JGR* 82: 4635-4639. [2] Becker R. H. and Pepin R. O. (1984) *EPSL* 69: 225-242 [3] Ott U. (1988) *GCA* 52: 1937-1948. [4] Bogard D. D. and Johnson P. (1983) *Science* 221: 651–654. [5] Schwenzer S. P. (2007) *Meterit. Planet. Sci.* 42: 387-412. [6] Wiens R. C. (1988) *EPSL* 91: 55–65. [7] Mohapatra R. K. et al. (2009) *GCA* 73: 1505–1522. [8] Wieler R. et al. (2016) *Meterit. Planet. Sci.* 51: 407-428. [9] Park J. (2005) phD thesis. [10] Chennaoui Aoudjehane H. et al. (2012) *Science* 338: 785-788. [11] Ruzicka A. et al. (2015) Meteoritical Bulletin, No. 102. [12] Meteoritical Bulletin Database, (No.104, in prep). [13] Ozima M. and Podsec F. A. (2002) Noble Gas Geochemistry. [14] Condrad P. G. et al. (2016) *EPSL* 454: 1-9.

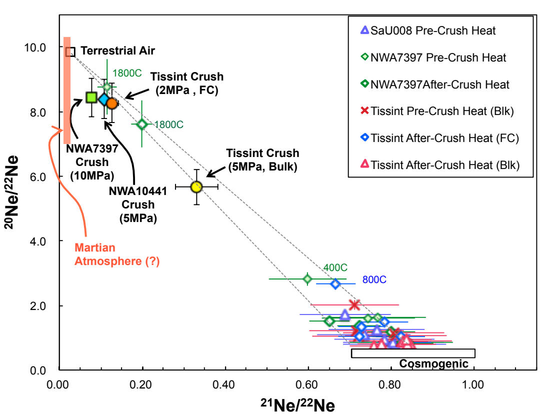


Figure 1. Neon three-isotope plot ($^{21}Ne/^{22}Ne$ vs. $^{20}Ne/^{22}Ne$) of the stepped heating and the vacuum crushing of the shergottites. The data were not corrected for cosmogenic effects. Tissint was divided into fusion-crust-rich (FC) and the other sample (Blk). Endmembers are: terrestrial air [13]; cosmogenic Ne [8]; possble Martian atmosphere [7][9].

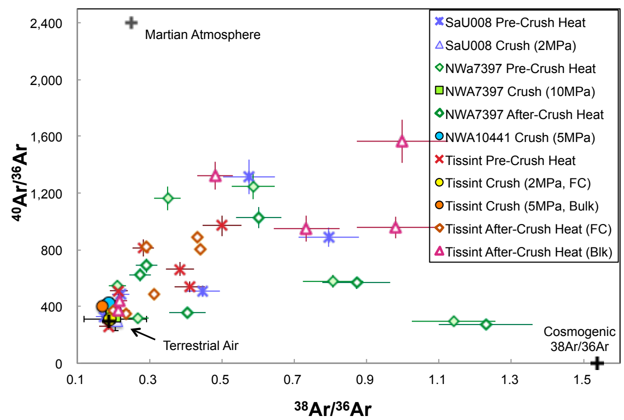


Figure 2. Argon three-isotope plot ($^{38}Ar/^{36}Ar$ vs. $^{40}Ar/^{36}Ar$) of the stepped heating and the vacuum crushing of the shergottites. The data were not corrected for cosmogenic or radiogenic effects. Endmembers are: terrestrial air [13]; Martian atmosphere [1].

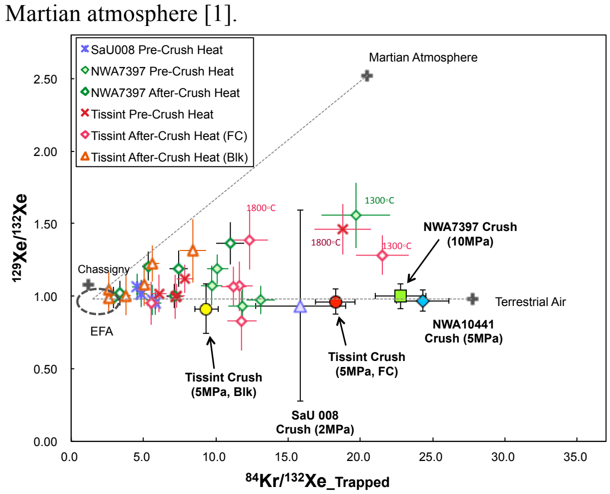


Figure 3. Relationship between $^{84}Kr/^{132}Xe$ elementally ratios and $^{129}Xe/^{132}Xe$ of the stepped heating and the vacuum crushing of the shergottites. The trapped $^{84}Kr/^{132}Xe$ ratios were obtained by cosmogenic and fision effects corrections. Endmembers are: Martian atmosphere [1][14]; Martian interior (Chassigny) [3]; elementally fractionated air (EFA) [7]; terrestrial air [13]