Noble Gases in Northwest Africa 12323 Shergottite: Trapped Martian Atmosphere and Cosmic Ray Exposure Ages. F. Vayrac¹, G. Avice¹, L. Ferrière², J.-A. Barrat¹, and B. Hoefnagels⁴, ¹Université Paris Cité, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France (vayrac@ipgp.fr). ²Natural History Museum Vienna, Burgring 7, A-1010 Vienna, Austria. ³Université de Bretagne Occidentale & Institut Universitaire Européen de la Mer, Plouzané, France, ⁴Big Bang Meteorites.

Introduction: The determination of the past and present composition of the atmospheres of Earth, Mars and Venus today is key to conduct comparative planetology, especially for understanding why these planets evolved so differently [1]. In the case of Mars, current data were obtained from in situ measurements collected by space probes and rovers [2] and from analyses of gases trapped within impact glasses from Martian meteorites (SNCs) [3].

Existing data suggest that Mars suffered from early episodes of atmospheric escape. This left the atmosphere depleted in primordial gases and comparatively enriched in radiogenic isotopes such as 129Xe produced by the β-decay of now extinct 129I (T1/2 = 15.7 Ma) leading to a very high 129Xe/132Xe ratio [4].

Exact values for the composition of the Martian atmosphere are still debated. For example, light Kr show low isotopes excesses derived from spallation in the Tissint shergottite compared to in situ measurements [5,6].

In this study, we report on extracted noble gases contained in bulk and glass fragments of the Northwest Africa 12323 (NWA 12323) [7] in order to expand the existing dataset of composition of the Martian atmosphere.

Material and Methods: NWA 12323 is a gabbroic shergottite mainly composed of prismatic grains of clinopyroxene and maskelynite [7]. It shows shock melt veins and some melt/glass pockets. Four "bulk" and one "glass" fragments of NWA 12323 were obtained from the Natural History Museum Vienna (Austria) to measure the elemental and abundance and isotopic composition of noble gases (Ne, Ar, Kr, and Xe). Noble gases were extracted by step heating using a laser and an induction furnace, for bulk and glass samples respectively and measured on a Noblesse (Nulnstruments) noble gas mass spectrometer at the Institut de physique du globe de Paris (France). Major and trace element abundances were obtained using an ICP-AES Ultima 2 and a HR-ICP-MS Thermo Element 2 in Plouzané (France).

Results and Discussion: Neon isotopes ratios. Ne isotopic composition was only determined for the bulk samples. Cosmogenic neon is produced by the spallation phenomenon induced by cosmic ray bombardment on specific major elements. For laser intensities equal to or less than 1,000 mA, Ne isotope ratios plot relatively close to the composition of terrestrial atmospheric neon. For laser heating steps above 5,000 mA, the isotopic composition is dominated by cosmogenic neon. The lowest 20Ne/22Ne ratio, of 0.866 ± 0.008, was recorded by the Bulk 1 sample at the 5,000 mA temperature/intensity step.

Cosmic Ray Exposure Age (CREA). To derive a CRE age, we estimated an abundance of 21Ne of 7.62 × 10^-5 cm^3 STP/g with the hypothesis that the Ne isotope composition reflects a pure mixing between atmospheric Ne (i.e., from Mars or from the Earth, 20Ne/22Ne = 8–10.1) and cosmogenic Ne (21Ne/22Ne = 0.715–0.945) (Fig. 1). A 21Ne production rate of 2.4 × 10^-5 cm^3 STP/g/Ma [8] was determined based on the chemical composition of NWA 12323 measured for CaO (9.35 wt%), FeO (20.44 wt%), Ni (79 ppm), Al2O3 (4.76 wt%), and MgO (11.82 wt%); and using values of SiO2 (51.1 wt%) for NWA 480 from [9] and considering the negligible importance of S in the equation (i.e., because SiO2 and S were not measured for NWA 12323 and considering their very similar composition). The computed 21Ne abundances allows to derive a CREA of 3.20 ± 0.71 Ma. This age is compatible with exposure ages determined for other shergottites, with a minimum age of 1.0 Ma for Tissint bulk and a maximum age of 5.5 Ma for NWA 6342 (see [10]).

![Fig 1. Three isotopes diagram 20Ne/22Ne vs. 21Ne/22Ne ratios for bulk samples of NWA 12323. Data from the Martian and Earth’s atmospheres [14, 15] and spallation end-members are plotted in orange and purple ranges for comparison, respectively. Errors are at 1σ.](image-url)
Argon isotopes ratios. Low $^{40}$Ar/$^{36}$Ar ratios, between 231 and 265, are recorded for the four bulk samples, to be compared with the Martian atmospheric ratio $^{40}$Ar/$^{36}$Ar = 1900 ± 300 [6] and Tissint ratio $^{40}$Ar/$^{36}$Ar = 1714 ± 170 [5]. Interestingly, the measured $^{38}$Ar/$^{36}$Ar ratios for NWA 12323 are high, up to 1.25 ± 0.05, a sign of the presence of cosmogenic argon ($^{38}$Ar/$^{36}$Ar$_{Mars}$ = 0.24 ± 0.03).

Xenon isotopes ratios. For xenon, $^{129}$Xe/$^{132}$Xe and $^{136}$Xe/$^{132}$Xe ratios are intermediate between the Earth's atmosphere and Mars' atmospheric xenon ratios measured for SNCs (Fig. 2). Xenon released during low temperature steps has a composition close to Earth's atmospheric xenon. At higher temperatures, especially for the glass at 1550°C, the xenon isotopic composition shows an elevated $^{129}$Xe/$^{132}$Xe ratio closer to the values reported for the Martian atmosphere [11] with a $^{129}$Xe/$^{132}$Xe ratio of 1.299 ± 0.031 (1σ). However, this excess is not as high as for in situ atmospheric data obtained by the SAM experiment on board the Curiosity rover [6] or for Tissint [5].

Our data comfort the hypothesis that melt/glass pockets in NWA 12323 trapped the Martian atmosphere at the time of their ejection. The rather low $^{129}$Xe/$^{132}$Xe ratios are likely due to a significant Earth's atmosphere contamination, what is expected considering that NWA 12323 is a find.

![Fig 2. Three isotopes diagram of $^{129}$Xe/$^{132}$Xe vs. $^{136}$Xe/$^{132}$Xe ratios for bulk and glass samples. Data from Earth's atmosphere [15], the Martian atmosphere recorded in meteorites [11] and from the MSL Curiosity mission [6] are plotted for comparison. Errors are at 1σ.](image)

Krypton isotopic composition. Excesses of light Kr isotopes ($^{78-80}$Kr) are recorded in the bulk samples, normalized to the isotopic composition of the solar wind [12], with an excess up to 964 ± 122 ‰ for the $^{78}$Kr/$^{84}$Kr ratio. Similar excesses in light Kr isotopes are also observed in the glass sample, but also in the Martian atmosphere and in Elephant Moraine 79001 meteorite [13]. The Kr isotopic composition shows significant excesses in $^{80}$Kr for some samples compared with data from [5, 13] but less than for in situ measurements. However, an explanation for the high $^{80}$Kr/$^{84}$Kr ratios has been proposed by [12]. The authors explain that, during noble gas mass spectrometry measurements, $^{40}$Ar$^+$ can interfere with $^{80}$Kr. Between the ionization source and the magnet, $^{40}$Ar$^+$ can capture an electron, transforms into $^{40}$Ar$^-$ but with twice energy meaning that it follows the same trajectory as $^{84}$Kr ions. This is the so-called "change-of-charge" effect. Bulk 1 and 3 samples also recorded an excess of spallation derived $^{83}$Kr compared to solar wind and in situ measurements.

The new data presented here can be added to the limited available dataset on past Martian atmosphere obtained for other SNCs. Atmospheric samples to be returned by the future Mars Sample Return mission will provide a new wealth of data on the current Martian atmospheric composition that will be interesting to compare with the past Martian atmosphere record derived from SNCs.

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