Geochemical Perspectives Letters

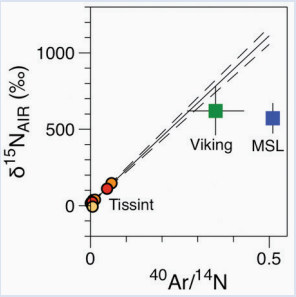
Noble gases and nitrogen in Tissint reveal the composition of the Mars atmosphere

G. Avice[1,2]*, D.V. Bekaert[1], H. Chennaoui Aoudjehane[3], B. Marty[1]

OPEN ACCESS

doi: 10.7185/geochemlet.1802

Abstract



Comparative planetology is crucial to unravel the origin and evolution of volatile elements on terrestrial planets. We report precise measurements of the elemental and isotopic composition of nitrogen and noble gases in the Martian meteorite Tissint. Ar-N_2 correlations confirm discrepancies between results from Viking and Martian meteorites and those from the Mars Science Laboratory (MSL) mission. The Martian atmospheric $^{40}Ar/^{36}Ar$ ratio is estimated to be 1714 ± 170 (1σ), lower than the value determined by Viking but in agreement with, and with higher precision than, data from MSL. We confirm a solar wind-like origin for Martian Kr and Xe. Excesses on light Kr isotopes are lower than those measured by MSL. Cosmogenic excesses in the Xe isotopic spectrum could have been produced in space during exposure of the Tissint parent body to cosmic rays.

Received 23 July 2017 | Accepted 24 January 2018 | Published 9 February 2018

Introduction

Until recently, knowledge of the elemental and isotopic compositions of volatile elements on Mars mainly relied on analyses of noble gases and nitrogen trapped in the so-called SNC Martian meteorites. Some of these (*e.g.*, EETA 79001, Zagami, ALH84001, Tissint, NWA 7034) contain glassy melt pockets or veins created during impacts on Mars that ejected fragments of Martian crust into space (Becker and Pepin, 1984; Marti *et al.*, 1995; Murty and Mohapatra, 1997; Bogard and Garrison, 1998; Chennaoui Aoudjehane *et al.*, 2012; Cartwright *et al.*, 2014). Melt pockets present noble gases and nitrogen compositions (*e.g.*, Becker and Pepin, 1984; Wiens *et al.*, 1986) comparable to those measured on Mars by the Viking lander (Owen *et al.*, 1977), strongly supporting their Martian origin (Treiman *et al.*, 2000).

Data from the Samples Analysis at Mars (SAM) instrument suite on-board the Curiosity rover (MSL mission, NASA) provided a new reference value for the Martian atmospheric $^{40}Ar/^{36}Ar$ ratio of 1900 ± 300 (1σ) (Mahaffy *et al.*, 2013), only 63 % of the value measured by Viking ($^{40}Ar/^{36}Ar$ = 3000; Owen *et al.*, 1977). SAM also measured a Ar/N ratio of 0.51 ± 0.01 (Wong *et al.*, 2013), whereas SNC and Viking analyses were similar and pointed to a lower Ar/N ratio of about 0.35. Martian atmospheric Xe measured by SAM (Conrad *et al.*, 2016) is mass-dependently fractionated, *i.e.* enriched in heavy isotopes relative to light ones, by 3–4 % *per* amu, a value comparable to that of terrestrial atmospheric Xe. When such fractionation is corrected for, a solar-like composition is obtained for the progenitor of Martian atmospheric Xe, contrary to the case of terrestrial Xe, which requires a different initial composition labelled U-Xe (Pepin, 1991; Avice *et al.*, 2017). Interestingly, SAM measurements also revealed isotopic excesses of $^{124,126}Xe$ and $^{80\text{-}82}Kr$ isotopes (Conrad *et al.*, 2016). These authors attributed these excesses to neutron capture and spallation reactions in the Martian regolith. Produced isotopes would have been subsequently degassed into the Martian atmosphere (Rao, 2002). However, Conrad *et al.* (2016) noted that krypton and xenon trapped in Martian meteorites do not present such excesses.

In an attempt to reconcile results from space missions and terrestrial investigations of SNCs and to refine the elemental and isotopic compositions of the Martian atmosphere, we analysed fragments of the Tissint meteorite, a depleted olivine-phyric shergottite that fell near Tata town, southern Morocco, in July 2011. Glassy melt veins are present and are larger than in other SNC meteorites (Chennaoui Aoudjehane *et al.*, 2005). Bubbles also appear in the glassy melt veins. These two features make glass-rich lithologies from Tissint ideal samples for investigating the composition of the Mars atmosphere. Tissint has a low cosmic-ray exposure age of 0.7 ± 0.3 Ma (Chennaoui Aoudjehane *et al.*, 2012) compared to other Martian meteorites (up to 20 Ma; Shukolyukov *et al.*, 2002), resulting in a low contribution of cosmogenic Xe isotopes. Careful measurement of the light Xe and Kr isotopes may thus permit the occurrence of spallogenic noble gas isotopes in the Martian atmosphere to be tested.

1. CRPG-CNRS/Université de Lorraine, 15 rue Notre-Dame des Pauvres, 54500 Vandoeuvre-lès-Nancy, France
2. California Institute of Technology, Division of Geological and Planetary Sciences, 1200 E. California Blvd, Pasadena, CA 91125, USA
* Corresponding author (email: gavice@caltech.edu)
3. Hassan II University of Casablanca, Faculty of Sciences Ain Chock, Géosciences Appliquées à l'Ingénierie et l'Aménagement (GAIA) Laboratory, Km 8 Route d'El Jadida, 20150 Casablanca, Morocco

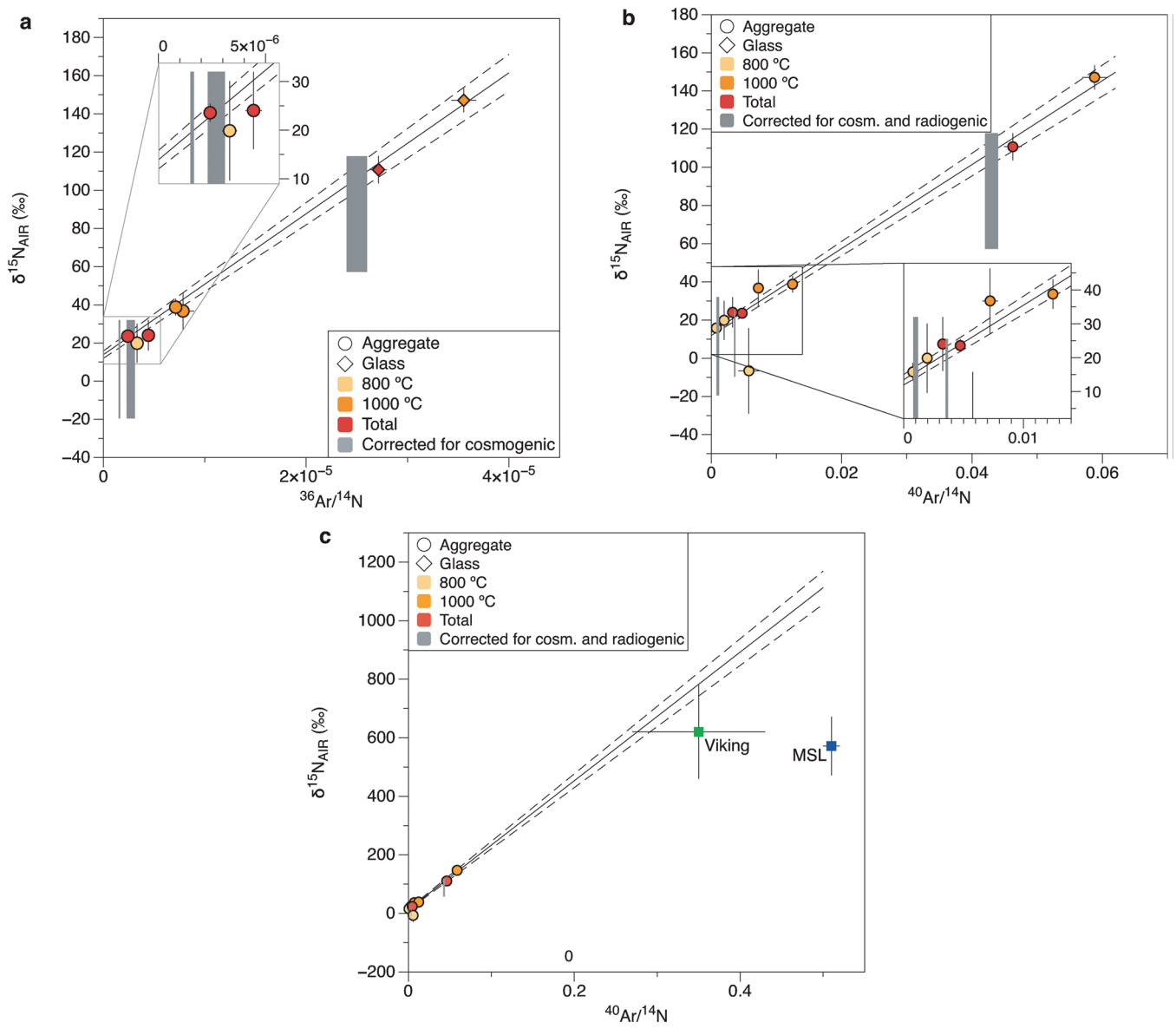


Figure 1 N-Ar isotope plots. **(a)** $\delta^{15}N$ *vs.* $^{36}Ar/^{14}N$ mixing diagram. The line corresponds to the relationship between an end-member with low $\delta^{15}N$ and $^{36}Ar/^{14}N$ values, and the Mars atmosphere with elevated isotope and elemental ratios and was computed using Isoplot software (courtesy of K. Ludwig, Berkeley Geochronology Center). Dashed lines correspond to 1σ error envelope. **(b)** Same as (a) but with the $^{40}Ar/^{14}N$ ratio. **(c)** Expanded view of (b) showing results from Viking (Owen *et al.*, 1977) and MSL (Wong *et al.*, 2013). Tissint data are compatible with the $^{40}Ar/^{14}N$ ratio defined by Viking. Errors correspond to 1σ.

Material and Methods

Two "Aggregates" and one "Glass" sample were dedicated to Ar-N measurements. Aggregates are handpicked glass separates with some matrix minerals attached to them whereas glass samples are handpicked glass shards without any visible matrix. Gases were extracted by step-heating using a CO_2 laser extraction setup and measured on a VG5400® mass spectrometer at CRPG (Nancy, France) (Chennaoui Aoudjehane *et al.*, 2012). Another set of samples consisted of two matrix (Bulk A and B), one glass-matrix (Bulk and Glass) and three glass-rich handpicked separates (Glass 1, 2 and 3) and was dedicated to Kr-Xe measurements. To avoid atmospheric contamination of fine-grained matrix samples, only handpicked pure glass separates were ultrasonically washed in acetone before measurement. Samples were wrapped in Al foil. Gases were extracted using two induction furnaces (Zimmermann *et al.*, 2017) and measured on a Helix MC Plus® (Thermofisher Scientific) mass spectrometer at CRPG (Supplementary Information). Errors were propagated following the method described by Bekaert *et al.* (2017).

Results

Results for the chemical composition of a Tissint sample are given in Table S-1. N/Ar isotope and elemental data define a linear trend between a component with a low $\delta^{15}N$ (10–20 ‰ for $^{40\text{-}36}Ar/^{14}N \sim 0$) and another component with elevated $\delta^{15}N$ and $^{40\text{-}36}Ar/^{14}N$ values (Fig. 1, Table S-2) released at higher temperature.

For Kr and Xe results, the reference for the Martian atmospheric record in meteorites is taken from Mathew *et al.* (1998). Temperature steps (Table S-3) define a mixing trend between two components having similar $^{136}Xe/^{132}Xe$ but strongly different $^{129}Xe/^{132}Xe$ ratios (Fig. 2). Gases released

during the 400 °C and 800 °C temperature steps have isotopic compositions close to the composition of the Earth's atmosphere whereas higher temperature step (1700 and 1800 °C) data show elevated $^{129}Xe/^{132}Xe$ ratios. Xe released during the high temperature step on sample Glass 3, with a $^{129}Xe/^{132}Xe$ ratio of 2.38 ± 0.01 (1σ), has an isotopic composition (Fig. 3a) very close to that of the Martian atmosphere previously defined (Mathew *et al.*, 1998).

For Kr, the first heating steps have isotope ratios close to those of the terrestrial atmosphere (Table S-3). Krypton extracted at higher temperature (1225 °C and 1700 °C) is enriched in light isotopes and depleted in heavy isotopes compared to the solar composition (Meshik *et al.*, 2014) (Fig. 3b).

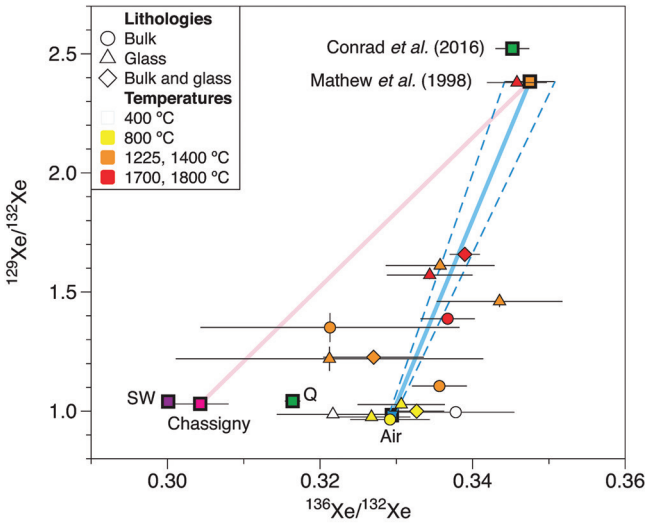


Figure 2 Three isotope plot of Xe measured in Tissint samples. Data define a mixing trend between the terrestrial (Ozima and Podosek, 2002) and Martian atmospheres (Mathew *et al.*, 1998). Chassigny is from Ott (1988) and is comparable to SW-Xe (Meshik *et al.*, 2014). Chondritic (Q-Xe) from Busemann *et al.* (2000). New results from the MSL mission (Conrad *et al.*, 2016) have similar $^{136}Xe/^{132}Xe$ but higher $^{129}Xe/^{132}Xe$ than previous studies. Errors correspond to 1σ.

Discussion

$^{15}N/^{14}N$ and $^{40}Ar/^{36}Ar$ isotope compositions and N-Ar elemental abundances. A cosmic-ray exposure (CRE) age of 1 Ma is considered to correct for cosmogenic noble gas and nitrogen isotopes produced in space by galactic cosmic rays (Wieler *et al.*, 2016 and Supplementary Information). Overall, despite high uncertainties in production rates of cosmogenic ^{15}N, the corrected data still define a mixing trend between two components (Fig. 1). The component with low $\delta^{15}N$ values probably corresponds to the Earth's atmosphere ($\delta^{15}N_{AIR}$ = 0 ‰) although a contribution from a Martian interior component with $\delta^{15}N_{AIR}$ between -20 ‰ and 0 ‰ cannot be excluded (Becker and Pepin, 1984). The second component, with elevated $\delta^{15}N_{AIR}$, represents the Martian atmosphere. Indeed, the mixing trend extended to higher $^{40\text{-}36}Ar/N$ ratios intercepts the value of the Martian atmosphere determined by Viking ($^{40}Ar/^{14}N$ = 0.35 ± 0.08; Owen *et al.*, 1977). This observation is valid for both cosmogenic-corrected (Fig. 1c) and uncorrected data. Our new data confirm a discrepancy previously noted by Wong *et al.* (2013), that the isotope and elemental compositions determined by the SAM instrument on-board MSL fall below the mixing trend defined by SNC data (Fig. 1c). From previous laboratory experiments on shock implantation of atmospheric gases on terrestrial basalts, it appears unlikely that the impact event on Mars could have fractionated isotope or elemental ratios of Ar and N_2 during their implantation into the glass phase produced upon impact (Wiens and Pepin, 1988). Interestingly, the difference between the MSL and the SNC data is likely due to different elemental $^{40}Ar/^{14}N$ ratios since $\delta^{15}N$ values are similar for both the Viking and the MSL measurements. The MSL $^{40}Ar/^{14}N$ ratio is 0.51 ± 0.01 (Mahaffy *et al.*, 2013) even after updating calibrations of the SAM instrument (Franz *et al.*, 2015). There is thus a remaining discrepancy for elemental ratios between Viking/SNC data and MSL data. Seasonal variations cannot account for changes in the Ar/N ratio given the long lifetimes (>1 Gyr) of Ar and N_2 in the Martian atmosphere (Krasnopolsky, 2017).

Taking a $\delta^{15}N$ value of 572 ± 82 ‰ (1σ) (Wong *et al.*, 2013) and an Ar/N ratio between 0.35 and 0.51 (see above) for the Martian atmosphere, correlations using all temperature steps give a value of 1714 ± 170 (1σ) for the Martian atmospheric $^{40}Ar/^{36}Ar$ ratio uncorrected for cosmogenic ^{36}Ar. This minimum value is more precise than and in excellent agreement with the value of 1900 ± 300 (1σ) determined by MSL (Mahaffy *et al.*, 2013). It is also in agreement with a previous value defined by measurements on SNCs (1800 ± 100) (Bogard *et al.*, 2001). The original value of 3000 ± 500 determined by the Viking mission (Owen *et al.*, 1977) was probably over-estimated.

Origin and evolution of the Martian atmospheric Xe. In agreement with previous studies (*e.g.*, Garrison and Bogard, 1998; Mathew *et al.*, 1998; Conrad *et al.*, 2016), Martian atmospheric Xe measured in sample Glass 3 is related by mass-dependent isotope fractionation (Pepin, 1991) to Solar Wind Xe (SW-Xe, Meshik *et al.*, 2014). This initial isotope composition does not leave space for a contribution of ^{244}Pu-derived fissiogenic Xe (Ozima and Podosek, 2002) to the Martian atmosphere (Conrad *et al.*, 2016) since the mass-fractionation of SW-Xe already matches the isotope composition of Martian atmospheric Xe. Furthermore, the Chassigny meteorite also contains solar-derived Xe, thus arguing for a unique solar source for Martian heavy noble gases. This observation differs from hypotheses on the origin of heavy noble gases on Earth with chondritic sources identified in the Earth's mantle (Holland *et al.*, 2009; Caracausi *et al.*, 2016) and a U-Xe initial isotopic composition for atmospheric Xe (Pepin, 1991; Avice *et al.*, 2017).

Mars is believed to have accreted ≤2.7 Myr after the start of solar system formation (Dauphas and Pourmand, 2011), when gas from the protosolar nebula was likely to be present (Wang *et al.*, 2017). Thus, Mars probably incorporated significant amounts of heavy noble gases from the nebula during its formation. On Earth, the impact responsible for the formation of the Moon happened <100 Myr after the formation of the solar system (Jacobson *et al.*, 2014) and probably erased most of the signatures of volatiles from the protosolar nebula even if some are still persistent in the Earth's mantle (*e.g.*, He and Ne evidence reviewed by Marty, 2012).

Despite being evolved from different progenitors, both Earth and Mars Xe present a similar mass-dependent isotope fractionation of 3–4 % *per* amu in favour of heavy isotopes. Studies of Archean rocks on Earth suggest that a prolonged atmospheric escape of Xe ions lifted by H ions acted on Earth and led to the fractionation observed today (Hébrard and Marty, 2014; Avice *et al.*, 2017). Despite evidence from the MAVEN mission for active – but variable – modern H escape (Chaffin *et al.*, 2014), meteorite studies suggest that escape of atmospheric Xe ceased much earlier (4.2–4.3 Gyr ago) on Mars relative to Earth (Cassata *et al.*, 2017). Modern escape of Martian atmospheric argon by pickup-ion sputtering has also been detected (Jakosky *et al.*, 2017) suggesting that – at least

the lightest – noble gases are still escaping from the Martian atmosphere. Mechanisms responsible for Xe escape remain to be explored through theoretical or modelling studies to understand why Mars and Earth, presenting such different physical and chemical parameters, exhibit comparable depletion and isotope fractionation of atmospheric xenon.

Light Xe and Kr isotopes: production in space or on Mars? Glass 3 data (with the highest $^{129}Xe/^{132}Xe$ ratios) have been corrected for spallogenic Kr and Xe isotopes produced in space over 0.7 to 1 Myr (Supplementary Information). A 1 Ma exposure age leads to an unrealistic low $\delta^{126}Xe$ of -475 ‰ (Fig. 3a) since the minimum value from either meteorite or *in situ* data is -140 ‰ (Mathew *et al.*, 1998). This may be due to (i) chemical heterogeneities in Tissint, with abnormally low contents of target elements for cosmogenic Xe production by spallation, or (ii) a lack of precision of cosmogenic production rates given in the literature for Xe. When taking a CRE age of 0.7 Ma, the corrected $^{126}Xe/^{132}Xe$ ratio is similar to the value given by Mathew *et al.* (1998) but also comparable to the value given by Conrad *et al.* (2016). The $^{124}Xe/^{132}Xe$ ratio seems to show excesses as measured by Conrad *et al.* (2016). Overall, our data cannot exclude that spallation-derived Xe is present in the Mars atmosphere.

Light Kr isotope ratios present low cosmogenic excesses compared to results obtained *in situ* by SAM (Conrad *et al.*, 2016) (Fig. 3b). The $\delta^{80}Kr$ value (normalised to ^{84}Kr and relative to SW) is only +164 ‰, compared to a value of +653 ‰ measured by MSL. Even if temperature steps up to 1225 °C can be accounted for by mixing between the terrestrial atmosphere (Ozima and Podosek, 2002) and the Martian atmosphere (taking Kr/Xe from Swindle, 2002) (Fig. S-1), 1700 °C temperature steps have too low $^{80}Kr/^{84}Kr$ ratios for a given $^{129}Xe/^{132}Xe$. If Tissint does not contain any cosmogenic Kr produced in space, the maximum $^{80}Kr/^{84}Kr$ is about 0.048, ≈30 % lower than the value proposed by Conrad *et al.* (2016). Excesses of spallation-derived Kr detected in the Martian meteorite NWA 7034 (Cartwright *et al.*, 2014) have been interpreted as evidence of incorporation of Martian regolith in NWA 7034. Results from our study suggest either that only a limited fraction of Martian regolith has been incorporated in Tissint or that the incorporated regolith did not contain significant amounts of spallation-derived Kr. The disagreement between our results and those obtained *in situ* remains difficult to explain. Models involving degassing of cosmogenic Kr and Xe, produced in the regolith, in the Mars atmosphere after the ejection of some of the Martian meteorites are unsatisfactory. Interestingly, Conrad *et al.* (2016) pointed out the presence of hydrocarbons preventing interpretations of ^{78}Kr data. These could also have interfered with ^{80}Kr (m/z = 80) measurements as well as "change-of-charge" effects involving energetic $^{40}Ar^{+}$ ions (Meshik *et al.*, 2014).

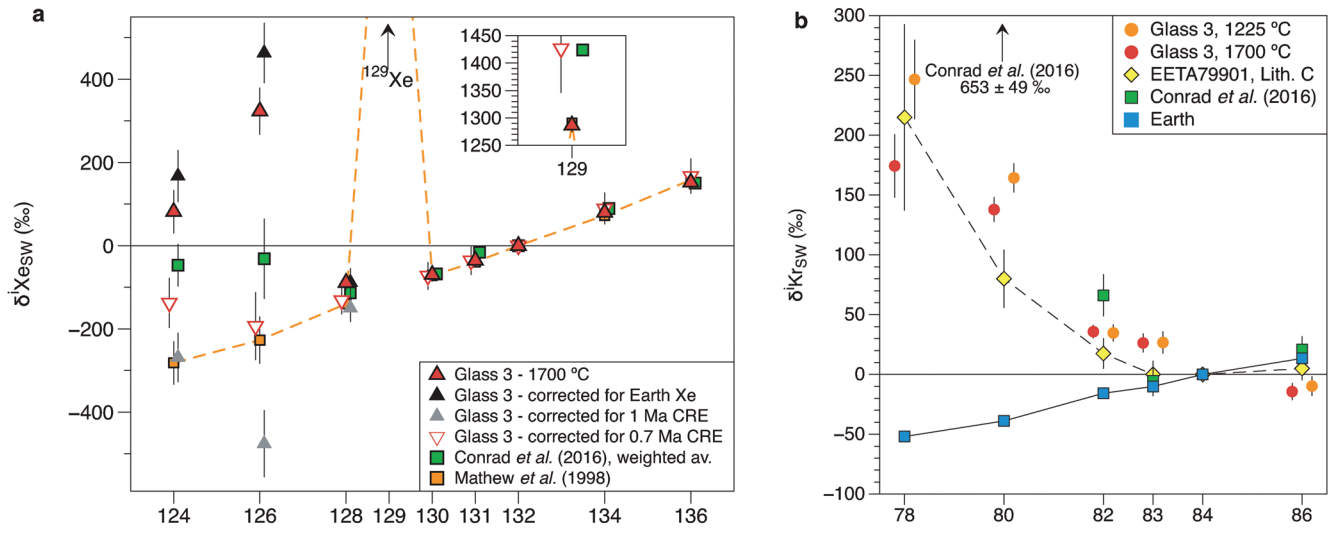


Figure 3 Isotope composition of Xe and Kr in Tissint. **(a)** Isotope spectrum of Xe released from sample Glass 3. The isotopic compositions of Xe measured by MSL (Conrad *et al.*, 2016) and in other Martian meteorites (Mathew *et al.*, 1998) are also displayed. All data are normalised to ^{132}Xe and to SW-Xe (Meshik *et al.*, 2014) and expressed in delta notation: $\delta^{i}Xe = 1000 * [(^{i}Xe/^{132}Xe)/(^{i}Xe/^{132}Xe)_{SW\text{-}Xe} - 1]$. ^{129}Xe excesses relative to SW-Xe are shown in the top-right sub-panel. Xe isotope spectra corrected for terrestrial Xe, for 1 Myr and 0.7 Myr of cosmic-ray exposure are also shown. **(b)** Isotope spectra of Kr extracted from sample glass compared to results obtained on lithology C (glass) of the EETA79001 meteorite (Swindle *et al.*, 1986) and *in situ* by MSL (Conrad *et al.*, 2016). Terrestrial Kr (Ozima and Podosek, 2002) is shown for comparison. Data are expressed in delta notation relative to solar-wind Kr (Meshik *et al.*, 2014). Errors correspond to 1σ.

Conclusions

At the time of the impact responsible for its ejection from the Martian crust into space, the Tissint parent body recorded the elemental and isotopic compositions of the Martian atmosphere. Overall, Tissint data are in agreement with *in situ* measurements on Mars with, for example, a $^{40}Ar/^{36}Ar$ ratio of about 1714 ± 170 (1σ) and a Martian Xe ultimately derived from SW Xe by mass-dependent isotope fractionation. However, several discrepancies still remain. First, SNC data point toward an Ar/N ratio lower than the value measured by MSL and close to the original value measured by the Viking mission. Uncertainties in cosmogenic production rates and isotope ratios for Xe prevent conclusions being drawn on the presence of spallation Xe in the Mars atmosphere but Kr data show a modest contribution of the spallation component compared to results obtained *in situ*. Our preferred values for the composition of the Martian atmosphere (Table 1) will likely become more precise when additional measurements of Martian gases analysed *in situ* or in new Martian meteorites become available.

Table 1 Range of values proposed for the elemental and isotope composition of the Martian atmosphere. The agreement between meteorites and Viking mission data suggests that the Ar/N ratio determined by Viking is correct (Owen *et al*., 1977). $^{40}Ar/^{36}Ar$ ratios from this study and from *in situ* measurements reported in Mahaffy *et al*. (2013). For $^{124\text{-}126}Xe/^{132}Xe$ ratios, we propose the values determined in this study for two different CRE ages (0.7 and 1 Ma). Values for $^{128\text{-}136}Xe/^{132}Xe$ ratios from Conrad *et al*. (2016). Krypton values from Swindle *et al*. (1986). Errors correspond to 1σ.

Argon - Nitrogen					
$^{40}Ar/^{14}N$	0.35 ± 0.08	Owen *et al*. (1977)	$^{40}Ar/^{36}Ar$	1714 ± 170 1900 ± 300	this study Mahaffy *et al*. (2013)
Xenon			**Krypton**		
$^{124}Xe/^{132}Xe$	0.0039–0.0045	this study (CRE = 0.7–1 Ma)	$^{78}Kr/^{84}Kr$	0.0078 ± 0.0005	Swindle *et al*. (1986)
	0.00468 ± 0.00025	Conrad *et al*. (2016)	$^{80}Kr/^{84}Kr$	0.0445 ± 0.0010	-
$^{126}Xe/^{132}Xe$	0.0030–0.0037	this study (CRE = 0.7–1 Ma)	$^{82}Kr/^{84}Kr$	0.2090 ± 0.0026	-
	0.00403 ± 0.0004	Conrad *et al*. (2016)	$^{83}Kr/^{84}Kr$	0.2034 ± 0.0023	-
$^{128}Xe/^{132}Xe$	0.07466 ± 0.00077	Conrad *et al*. (2016)	$^{86}Kr/^{84}Kr$	0.3027 ± 0.0030	-
$^{129}Xe/^{132}Xe$	2.5221 ± 0.0063	-			
$^{130}Xe/^{132}Xe$	0.1537 ± 0.0009	-			
$^{131}Xe/^{132}Xe$	0.8123 ± 0.0029	-			
$^{134}Xe/^{132}Xe$	0.4021 ± 0.0026	-			
$^{136}Xe/^{132}Xe$	0.3452 ± 0.0022	-			

Acknowledgements

L. Ferrière and the Natural History Museum, Vienna kindly provided some samples (NHMW_#7996_35a3a and NHMW_#7996_35a3b). We thank three anonymous reviewers for their comments and Liane G. Benning for editorial handling. This study was supported by the European Research Council (grants no. 267255 and 69618 to B.M.). L. Zimmermann is thanked for N-Ar measurements. CRPG contribution #2546.

Editor: Liane G. Benning

Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1802.

Cite this letter as: Avice, G., Bekaert, D.V., Chennaoui Aoudjehane, H., Marty, B. (2018) Noble gases and nitrogen in Tissint reveal the composition of the Mars atmosphere. *Geochem. Persp. Let.* 6, 11–16.

References

Avice, G., Marty, B., Burgess, R. (2017) The origin and degassing history of the Earth's atmosphere revealed by Archean xenon. *Nature Communications* 8, 1-9.

Becker, R.H., Pepin, R.O. (1984) The case for a Martian origin of the shergottites: Nitrogen and noble gases in EETA 79001. *Earth and Planetary Science Letters* 69, 225-242.

Bekaert, D.V., Avice, G., Marty, B., Henderson, B. (2017) Stepwise heating of Lunar anorthosites 60025, 60215, 65315 possibly reveals an indigenous noble gas component on the Moon. *Geochimica et Cosmochimica Acta* 218, 114-131.

Bogard, D.D., Garrison, D.H. (1998) Relative abundances of argon, krypton, and xenon in the Martian atmosphere as measured in Martian meteorites. *Geochimica et Cosmochimica Acta* 62, 1829-1835.

Bogard, D.D., Clayton, R.N., Marti, K., Owen, T., Turner, G. (2001) Martian volatiles: Isotopic composition, origin, and evolution. *Space Science Reviews* 96, 425-458.

Busemann, H., Baur, H., Wieler, R. (2000) Primordial noble gases in "phase Q" in carbonaceous and ordinary chondrites studied by closed–system stepped etching. *Meteoritics and Planetary Science* 35, 949-973.

Caracausi, A., Avice, G., Burnard, P.G., Füri, E., Marty, B. (2016) Chondritic xenon in the Earth's mantle. *Nature* 533, 82-85.

Cartwright, J.A., Ott, U., Herrmann, S., Agee, C.B. (2014) Modern atmospheric signatures in 4.4 Ga Martian meteorite NWA 7034. *Earth and Planetary Science Letters* 400, 77-87.

Cassata, W.S. (2017) Meteorite constraints on Martian atmospheric loss and paleoclimate. *Earth and Planetary Science Letters* 479, 322-329.

Chaffin, M.S., Chaufray, J.-Y., Stewart, I., Montmessin, F., Schneider, N.M., Bertaux, J.-L. (2014) Unexpected variability of Martian hydrogen escape. *Geophysical Research Letters* 41, 314-320.

Chennaoui Aoudjehane, H., Jambon, A., Reynard, B., Blanc, P. (2005) Silica as a shock index in shergottites: A cathodoluminescence study. *Meteoritics and Planetary Science* 40, 967-979.

Chennaoui Aoudjehane, H., Avice, G., Barrat, J.A., Boudouma, O., Chen, G., Duke, M.J.M., Franchi, I.A., Gattacceca, J., Grady, M.M., Greenwood, R.C., Herd, C.D.K., Hewins, R., Jambon, A., Marty, B., Rochette, P., Smith, C.L., Sautter, V., Verchovsky, A., Weber, P., Zanda, B. (2012) Tissint Martian Meteorite: A Fresh Look at the Interior, Surface, and Atmosphere of Mars. *Science* 338, 785-788.

Conrad, P.G., Malespin, C.A., Franz, H.B., Pepin, R.O., Trainer, M.G., Schwenzer, S.P., Atreya, S.K., Freissinet, C., Jones, J.H., Manning, H., Owen, T., Pavlov, A.A., Wiens, R.C., Wong, M.H., Mahaffy, P.R. (2016) In situ measurement of atmospheric krypton and xenon on Mars with Mars Science Laboratory. *Earth and Planetary Science Letters* 454, 1-9.

Dauphas, N., Pourmand, A. (2011) Hf–W–Th evidence for rapid growth of Mars and its status as a planetary embryo. *Nature* 473, 489-492.

Franz, H.B., Trainer, M.G., Wong, M.H., Mahaffy, P.R. (2015) Reevaluated Martian atmospheric mixing ratios from the mass spectrometer on the Curiosity rover. *Planetary and Space Science* 109-110, 154-158.

Garrison, D.H., Bogard, D.D. (1998) Isotopic composition of trapped and cosmogenic noble gases in several Martian meteorites. *Meteoritics and Planetary Science* 33, 721-736.

Hébrard, E., Marty, B. (2014) Coupled noble gas-hydrocarbon evolution of the early Earth atmosphere upon solar UV irradiation. *Earth and Planetary Science Letters* 385, 40-48.

Holland, G., Cassidy, M., Ballentine, C.J. (2009) Meteorite Kr in Earth's Mantle Suggests a Late Accretionary Source for the Atmosphere. *Science* 326, 1522-1525.

Jacobson, S.A., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Walsh, K.J., Rubie, D.C. (2014) Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact. *Nature* 508, 84-87.

Jakosky, B.M., Slipski, M., Benna, M., Mahaffy, P., Elrod, M., Yelle, R., Stone, S., Alsaeed, N. (2017) Mars' atmospheric history derived from upper-atmosphere measurements of $^{38}Ar/^{36}Ar$. *Science* 355, 1408-1410.

Krasnopolsky, V.A. (2017) Annual mean mixing ratios of N_2, Ar, O_2, and CO in the martian atmosphere. *Planetary and Space Science* 144, 71-73.

Mahaffy, P.R., Webster, C.R., Atreya, S.K., Franz, H., Wong, M., Conrad, P.G., Harpold, D., Jones, J.J., Leshin, L.A., Manning, H., Owen, T., Pepin, R. O., Squyres, S., Trainer, M., MSL Science Team (2013) Abundance and Isotopic Composition of Gases in the Martian Atmosphere from the Curiosity Rover. *Science* 341, 263-266.

Marti, K., Kim, J.S., Thakur, A.N., McCoy, T.J., Keil, K. (1995) Signatures of the Martian atmosphere in glass of the Zagami meteorite. *Science* 267, 1981-1984.

Marty, B. (2012) The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth and Planetary Science Letters* 313-314, 56-66.

Mathew, K.J., Kim, J.S., Marti, K. (1998) Martian atmospheric and indigenous components of xenon and nitrogen in SNC meteorites. *Meteoritics and Planetary Science* 33, 655-664.

Meshik, A., Hohenberg, C., Pravdivtseva, O., Burnett, D. (2014) Heavy noble gases in solar wind delivered by Genesis mission. *Geochimica et Cosmochimica Acta* 127, 326-347.

Murty, S., Mohapatra, R.K. (1997) Nitrogen and heavy noble gases in ALH 84001: Signatures of ancient Martian atmosphere. *Geochimica et Cosmochimica Acta* 61, 5417–5428.

Ott, U. (1988) Noble gases in SNC meteorites: Shergotty, Nakhla, Chassigny. *Geochimica et Cosmochimica Acta* 52, 1937-1948.

Owen, T., Biemann, K., Rushneck, D.R., Biller, J.E., Howarth, D.W., Lafleur, A.L. (1977) The composition of the atmosphere at the surface of Mars. *Journal of Geophysical Research* 82, 4635-4639.

Ozima, M., Podosek, F.A. (2002) *Noble Gas Geochemistry*. Second Edition, Cambridge University Press, Cambridge.

Pepin, R.O. (1991) On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. *Icarus* 92, 2-79.

Rao, M. (2002) Neutron Capture Isotopes in the Martian Regolith and Implications for Martian Atmospheric Noble Gases. *Icarus* 156, 352-372.

Shukolyukov, Y.A., Nazarov, M.A., Schultz, L. (2002) A New Martian Meteorite: the Dhofar 019 Shergottite with an Exposure Age of 20 Million Years. *Solar System Research* 36, 125-135.

Swindle, T.D (2002) Martian noble gases. In: Porcelli, D., Ballentine, C.J., Wieler, R. (Eds.) *Reviews in Mineralogy and Geochemistry Volume 47*. Mineralogical Society of America, Washington D.C., 171-190.

Swindle, T.D., Caffee, M.W., Hohenberg, C.M. (1986) Xenon and other noble gases in shergottites. *Geochimica et Cosmochimica Acta* 50, 1001-1015.

Treiman, A.H., Gleason, J.D., Bogard, D.D. (2000) The SNC meteorites are from Mars. *Planetary and Space Science* 48, 1213-1230.

Wang, H., Weiss, B.P., Bai, X.-N., Downey, B.G., Wang, J., Wang, J., Suavet, C., Fu, R.R., Zucolotto, M.E. (2017) Lifetime of the solar nebula constrained by meteorite paleomagnetism. *Science* 355, 623-627.

Wieler, R., Huber, L., Busemann, H., Seiler, S., Leya, I., Maden, C., Masarik, J., Meier, M.M.M., Nagao, K., Trappitsch, R., Irving, A.J. (2016) Noble gases in 18 Martian meteorites and angrite Northwest Africa 7812-Exposure ages, trapped gases, and a re-evaluation of the evidence for solar cosmic ray-produced neon in shergottites and other achondrites. *Meteoritics and Planetary Science* 51, 407-428.

Wiens, R.C., Pepin, R.O. (1988) Laboratory shock emplacement of noble gases, nitrogen, and carbon dioxide into basalt, and implications for trapped gases in shergottite EETA 79001. *Geochimica et Cosmochimica Acta* 52, 295-307.

Wiens, R.C., Becker, R.H., Pepin, R.O. (1986) The case for a Martian origin of the shergottites, II. Trapped and indigenous gas components in EETA 79001 glass. *Earth and Planetary Science Letters* 77, 149-158.

Wong, M.H., Atreya, S.K., Mahaffy, P.N., Franz, H.B., Malespin, C., Trainer, M.G., Stern, J.C., Conrad, P.G., Manning, H.L.K., Pepin, R.O., Becker, R.H., McKay, C.P., Owen, T.C., Navarro-González, R., Jones, J.H., Jakosky, B.M., Steele, A. (2013) Isotopes of nitrogen on Mars: Atmospheric measurements by Curiosity's mass spectrometer. *Geophysical Research Letters* 40, 6033-6037.

Zimmermann, L., Avice, G., Blard, P.-H., Marty, B., Füri, E., Burnard, P.G. (2017) A new all-metal induction furnace for noble gas extraction. *Chemical Geology*, doi: 10.1016/j.chemgeo.2017.09.018.