The production rate of cosmogenic deuterium at the Moon's surface

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ABSTRACT

The hydrogen (D/H) isotope ratio is a key tracer for the source of planetary water. However, secondary processes such as solar wind implantation and cosmic ray induced spallation reactions have modified the primordial D/H signature of 'water' in all rocks and soils recovered on the Moon. Here, we re-evaluate the production rate of cosmogenic deuterium (D) at the Moon's surface through ion microprobe analyses of hydrogen isotopes in olivines from eight Apollo 12 and 15 mare basalts. These in situ measurements are complemented by CO_2 laser extraction-static mass spectrometry analyses of cosmogenic noble gas nuclides (^{3}He, ^{21}Ne, ^{38}Ar). Cosmic ray exposure (CRE) ages of the mare basalts, derived from their cosmogenic ^{21}Ne content, range from 60 to 422 Ma. These CRE ages are 35% higher, on average, than the published values for the same samples. The amount of D detected in the olivines increases linearly with increasing CRE ages, consistent with a production rate of $(2.17 \pm 0.11) \times 10^{-12}$ mol(g rock)$^{-1}$ Ma^{-1}. This value is more than twice as high as previous estimates for the production of D by galactic cosmic rays, indicating that for water-poor lunar samples, i.e., samples with water concentrations ≤ 50 ppm, corrected D/H ratios have been severely overestimated.

1. Introduction

The discovery of indigenous H-bearing species (H_2, OH, H_2O, in the following referred to as 'water') in lunar volcanic glasses (Saal et al., 2008), olivine-hosted melt inclusions (Hauri et al., 2011), apatite (McCubbin et al., 2010), and highland plagioclase (Hui et al., 2013) – together with the detection of water ice in permanently shadowed polar regions of the Moon (Feldman et al., 1998) – has led to a paradigm shift in our knowledge and understanding of the water inventory of Earth's sole natural satellite. These findings have stimulated new investigations of the origin of volatiles within the Earth–Moon system, as well as of the physical and chemical conditions that prevailed in the post-impact protolunar disk (Barnes et al., 2016; Hauri et al., 2015; Pahlevan et al., 2016). A major caveat is that the primordial isotopic signature of water and other volatile elements in samples returned by the Apollo and Luna missions has been modified because the Moon's surface lacks full atmospheric shielding and magnetic field protection against the solar wind (SW) as well as against high-energy galactic (GCR) and solar cosmic rays (SCR).

Hence, SW-derived gases are implanted into the top few tens of nanometers of any regolith grain or rock exposed to the lunar surface environment (e.g., Hashizume et al., 2000), and cosmic ray induced spallation reactions – triggered by GCR and SCR particles that can penetrate lunar matter to depths of several meters and a few centimeters, respectively – are important sources of cosmogenic nuclides, such as deuterium (^{2}H or D) and noble gases (e.g., ^{3}He, ^{21}Ne, ^{38}Ar) in lunar samples with long cosmic ray exposure (CRE) ages (Rao et al., 1994; Reedy, 2015, 1981). Given the recently emerged interest in the origin of water on the Moon – both at the surface (Liu et al., 2012; Stephant and Robert, 2014) and in the mantle (e.g., Barnes et al., 2016; Füri et al., 2014; Saal et al., 2013) –, accurate knowledge of the cosmogenic D production rate (P_D) is critical for correcting measured D/H ratios for the cosmogenic contribution, and, ultimately, for comparing lunar hydrogen isotope signatures with those of potential Solar System sources (i.e., solar, terrestrial, chondritic, cometary).

Merlivat et al. (1976) estimated the GCR-induced production of cosmogenic deuterium to be 0.92×10^{-12} mol(g rock)$^{-1}$ Ma^{-1}, based on the abundances of water, hydrogen, and deuterium in eight sub-samples from different depths of basalt 70215. This P_D value entirely relies on the assumption that the measured deuterium is a mixture between D generated by the reduction of terrestrial water during the experimental process (with a D/H ratio of 138 ppm or $\delta D = -115‰$, where $\delta D = [(D/H)_{sample}/(D/H)_{SMOW} - 1] \times 1000$, with $(D/H)_{SMOW} = 155.76$

$\times 10^{-6}$) and cosmogenic D, which has been produced *in situ* by spallation reactions during space exposure over a period of 10^8 years. Importantly, Merlivat et al. (1976) concluded that the uniform distribution of cosmogenic D within basalt 70215 can be explained by continuous erosion of the uppermost rock surface (at a rate of ≥ 0.5 mm/Ma) which prevented the accumulation of cosmogenic D produced by SCRs. From theoretical calculations, Reedy (1981) derived a similar value (i.e., $\sim$1200 atoms/min/kg or 1×10^{-12} mol(g rock)$^{-1}$ Ma^{-1}) for the GCR production of D in lunar rocks from the target elements O, Mg, Al, Si, and Fe for the top 40 g/cm^2 of shielding. However, the additional D production by SCRs (for a rigidity $R_0 = 100$ MV and 2π exposure) would result in a higher P_D value of up to 2×10^{-12} mol(g rock)$^{-1}$ Ma^{-1} at the uppermost surface of mare basalts without any surface erosion.

To this date, a P_D value of 0.92 to 1×10^{-12} mol(g rock)$^{-1}$ Ma^{-1} has been used in all studies of lunar samples (e.g., volcanic glasses, apatites, plagioclases) to correct the measured D/H ratios for the cosmogenic contribution and to determine the isotopic signature of the indigenous water component. However, the production of a given nuclide depends on the abundance of multiple target elements and the irradiation conditions. Consequently, it is of key importance to note here that the P_D value determined by Merlivat et al. (1976) cannot be used to correct the D/H ratio of apatite because the chemical composition of the sample must be taken into account. Based on Reedy's model, the production rate of D would be $\sim$35% lower in apatite than in a mare basalt; all previous studies of water in extraterrestrial (lunar, eucrite) apatite have failed to address this issue.

Bulk lunar basalt samples may contain hydrous phases (such as OH-rich apatite) as well as surface-sited SW-derived hydrogen; thus, they are not well-suited for quantifying cosmogenic deuterium abundances. In contrast, "dry", nominally anhydrous minerals (such as olivine) in the interior of lunar basalts are expected to be dominated by deuterium produced *in situ* during cosmic ray irradiation. Therefore, in this study, we re-evaluate the production rate of cosmogenic deuterium at the Moon's surface by determining the deuterium content of olivine from eight Apollo 12 and 15 mare basalts (12004, 12009, 12018, 12020, 12075, 12076, 15016, 15535), which cover a wide range of previously published CRE ages, from $\sim$30 to 335 Ma (Table 1). In parallel to the hydrogen isotope analyses by secondary ionization mass spectrometry, we determined the noble gas characteristics of bulk rock fragments and olivine separates of the same basalts by CO_2 laser extraction-static mass spectrometry in order to quantify the abundances of cosmogenic noble gas nuclides (^{3}He, ^{21}Ne, ^{38}Ar) and to verify previously published CRE ages. In this way, we can compare the abundance of deuterium with the duration of cosmic ray irradiation to obtain the average production rate of cosmogenic deuterium for the past few hundreds of million years.

2. Samples and analytical techniques

The mare basalts studied here (12004, 12009, 12018, 12020, 12075, 12076, 15016, 15535) are all of the low-Ti variety (Neal and Taylor, 1992) and contain between 11 and 15 wt.% MgO (Supplementary Table S1). Up to four olivine grains of each basalt sample were mounted in indium together with four standards with known H_2O contents: StHs6/80-G andesitic glass (250 $\pm$ 7 ppm and δD = -95 ± 2‰; Jochum et al., 2006), MON9 pyrope (56 $\pm$ 6 ppm; Bell et al., 1995), synthetic forsterite (4.5 $\pm$ 1 ppm; Wetzel et al., 2015), and synthetic Suprasil 3002 quartz glass ($\leq$1.3 ppm; Wetzel et al., 2015). The major element composition of the olivine grains was determined using the Cameca SX100 at the Université de Lorraine (Service Commun de Microscopies Electroniques et de Microanalyses X) with a primary beam current of 12 nA and an acceleration voltage of 15 kV. Counting times on peaks and background were

Table 1

Abundances of cosmogenic noble gas nuclides (in 10^{-12} mol/g) and cosmic ray exposure (CRE) ages (in Ma) calculated using the production rate for ^{3}He and ^{21}Ne from Reedy (1981) and Leya et al. (2001), respectively. Previously published CRE ages are given for comparison.

Sample ID	^{3}He$_{cosm}$	^{21}Ne$_{cosm}$	^{38}Ar$_{cosm}$	T_3 Ma	T_{21} Ma	T_{CRE}[c] Ma
12004	21.46	3.32	2.99	42	60 ± 11	30–85
12004[a]	32.12	3.75	1.55	63	68 ± 12	
12004[b]	28.20	3.84	2.71	53	70 ± 12	
12009	52.56	13.02	10.68	103	241 ± 42	112–160
12009[a]	51.31	9.69	6.45	101	179 ± 31	
12018	63.78	14.05	10.27	125	242 ± 42	152–221
12018 ol	84.12	36.75	0.84	165	371 ± 75	
12018[a]	83.88	14.34	6.33	160	247 ± 42	
12018[b]	81.86	15.91	9.56	165	274 ± 47	
12020	18.38	4.36	3.79	36	73 ± 13	56–100
12020	26.12	6.46	4.08	51	111 ± 19	
12020[a]	45.95	5.28	2.91	90	91 ± 15	
12020[b]	34.88	5.29	2.64	67	91 ± 15	
12075	85.02	17.08	14.83	170	305 ± 54	240–300
12075 ol	86.31	30.36	1.24	173	319 ± 63	
12075[a]	133.84	18.94	11.57	268	338 ± 60	
12076	102.62	24.03	9.92	201	429 ± 76	240–270
12076[a]	102.61	17.68	11.88	201	316 ± 56	
15016	167.77	19.66	11.84	336	378 ± 66	285–335
15016	162.27	21.93	14.68	325	422 ± 73	
15535	56.01	12.38	2.65	112	238 ± 43	110
15535 ol	61.23	11.89	1.36	122	159 ± 31	

[a] Noble gas data from Bogard et al. (1971), recalculated.
[b] Noble gas data from Hintenberger et al. (1971), recalculated.
[c] Previously published cosmic ray exposure ages (Alexander et al., 1973; Bogard et al., 1971; Hintenberger et al., 1971; Husain, 1974; Kirsten et al., 1973; Marti and Lugmair, 1971; Stettler et al., 1973).

10 s for all elements. Results are reported in Supplementary Table S2 and show that the targeted olivines display a significant range in Fo contents (between Fo57 and Fo77).

The CAMECA 1280 HR2 ion microprobe at CRPG, Nancy, was used for the hydrogen isotope analysis of the olivines. The Au-coated sample mount was left in the airlock of the instrument at $\sim$5 $\times 10^{-9}$ Torr for 48 hours in order to ensure thorough removal of any terrestrial adsorbed water before introduction into the sample chamber. In addition, a liquid nitrogen cold trap was used to reduce the hydrogen background and maintain a pressure of $\leq$1.5 $\times 10^{-9}$ Torr during analyses. Spot analyses of hydrogen and deuterium were carried out using a 10 keV Cs$^+$ primary ion beam with a current of 10 nA and a normal-incidence electron gun (emission = 0.21 mA) for charge compensation. Standards and olivines were pre-sputtered for 180 s over an area of 30 $\times$ 30 μm prior to signal acquisition. For analysis, the $\sim$30 μm beam was rastered over an area of 20 $\times$ 20 μm, and a dynamical transfer operating system was used to compensate the primary rastering and to refocus the beam in the secondary part of the ion probe. To eliminate any hydrogen contamination from the crater edges, a 1800 μm field aperture limiting the analyses to ions from the central $\sim$10 μm of the beam and an electronic gate of 80% were used. The H$^-$ and D$^-$ ion intensities were determined for 4 and 20 s, respectively, for 30 cycles. Measurements were carried out in mono-collection mode on an electron multiplier at a mass resolving power ($M/\Delta M$) of $\sim$1250. Under these analytical conditions, typical count rates on StHs6/80-G were $\sim$118,000 cps for H$^-$ and 16 cps for D$^-$, whereas count rates on the 'driest' standard averaged 1747 $\pm$ 662 cps for H$^-$ and 0.22 $\pm$ 0.16 cps for D$^-$ (Supplementary Table S3).