THE H-NOBLE GAS SIGNATURE OF SINGLE APOLLO VOLCANIC GLASS BEADS. E. Füri1, L. Zimmermann1, E. Deloule1, and A.E. Saal2, 1Centre de Recherches Pétrographiques et Géochimiques, CNRS-UL, 54501 Vandoeuvre-lès-Nancy, France (efuri@crpg.cnrs-nancy.fr, laurentz@crpg.cnrs-nancy.fr, deloule@crpg.cnrs-nancy.fr). 2Department of Geological Sciences, Brown University, Providence, RI 029112, USA (Alberto_Saal@brown.edu).

Introduction: Between July 1969 and December 1972, the Apollo Program brought back 383 kg of lunar rocks and soil. Thanks to advances in analytical techniques, these samples still allow scientists to make giant leaps in their understanding of the formation and evolution of Earth's sole natural satellite. One paradigm-shifting discovery was that by Eric Hauri (1966-2018) and his colleagues of significant amounts of magmatic water in tiny beads of lunar volcanic glass collected during the Apollo 15 and 17 missions [1-3]. These findings spurred new research on lunar volatiles using secondary ionization mass spectrometry (SIMS) and noble gas mass spectrometry, for example.

A major caveat for assessing the origin of water within the Earth-Moon system is that the isotopic signature of primordial 'water' (i.e., H-bearing species) in lunar samples has been modified by contributions from the solar wind (SW) and/or cosmic ray induced spallation reactions. SIMS offers a non-destructive means for analyzing hydrogen isotopes in the interior of minerals or soil grains, away from the rim that contains implanted SW-derived volatiles. Nonetheless, in order to account for the production of cosmogenic nuclides (e.g., deuterium), the duration of exposure to cosmic rays must be known. Since solar and cosmogenic noble gas components are characterized by distinct isotope and/or elemental abundance signatures, noble gases represent a powerful tool for determining cosmic ray exposure (CRE) ages. Therefore, coupled H-noble gas analyses are key for resolving the volatile abundances observed in lunar samples into constituent components, and, ultimately, for determining the concentration and isotopic composition of indigenous water in the lunar mantle source.

Samples and analytical methods: Green and orange volcanic glasses collected during the Apollo 15 and 17 missions, respectively, are among the most primitive material yet collected on the Moon [4]. While noble gas studies in the 70's typically required several milligrams of glass for analyses by destructive techniques [e.g., 5,6], precise noble gas data can now be obtained for single glass beads, ≤25 μg in mass, by step-wise CO2 laser extraction and by using high-sensitivity, ultra-low-blank, multi-collector noble gas mass spectrometry [7]. By applying (at least) two heating steps, noble gases can be resolved into constituent components: a low temperature step (~600°C) allows extracting surface-sited (solar) gases, whereas the fusion step (~1500°C) is aimed at releasing volume-correlated (cosmogenic, radiogenic, indigenous) noble gases. Furthermore, noble gas analyses of single glass beads can be coupled with major element analyses by electron microprobe and volatile element (e.g., hydrogen) analyses by SIMS [8]. Such multi-element measurements are key for assessing the exposure history of lunar samples, as well as for understanding their formation and volatile element signature.

Results and discussion: Indigenous lunar noble gases have never been unambiguously found despite extensive searches over the past five decades [7,9]. Although the presence of indigenous neon and argon in gas-rich 15426 green glasses cannot be ruled out [5,7], the noble gas signatures of Apollo 15 and 17 volcanic glass beads is best explained by varying mixing proportions between SW-derived and cosmogenic components. Individual Apollo 74002 orange glasses record cosmogenic 21Ne exposure ages ranging from 10 to 39 Myr [8]. In contrast, the noble gas content of single 15426 green glasses varies by two orders of magnitude (Fig. 1; [7]), indicating that irradiation durations vary between 87±9 and 2139±303 Myr. This indicates that a few glass beads were exposed to cosmic, and possibly solar wind, irradiation at the (sub-)surface of the Moon for a much longer duration that the majority of the Apollo 15 and 17 pyroclastic glasses which could have resulted in inward diffusion of SW-derived gases, facilitated by radiation damage.

Fig. 1: 21Ne content of 22 single 15426 green glass beads. The 21Ne concentration range reported previously for five grain size fractions and two large spherules is indicated for comparison [5]. Modified after [7].
These observations demonstrate that, due to intense stirring of the regolith by impact gardening, each individual lunar volcanic glass bead records its own unique irradiation history, which is accessible only through analyses of single grains. Therefore, single grain analyses (as opposed to studies of bulk samples) are crucial for quantifying contributions from solar, cosmogenic, meteoritic/cometary, and indigenous volatiles sources to the lunar regolith.

While noble gas (Ne, Ar) isotopes provide constraints on the irradiation history of Apollo volcanic glass beads, accurate knowledge of the cosmogenic deuterium production rate ($P_D$) is also 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. The $P_D$ value derived recently [10], from analyses of olivine grains in lunar basalts with varying CRE ages, is more than twice as high as estimates for the production of deuterium by galactic cosmic rays derived ~40 years ago [11,12]. This much higher D production rate implies that for water-poor lunar samples, such as lunar volcanic glasses with water concentrations ≤50 ppm [3,8], corrected D/H ratios have been severely overestimated [10]. This has profound implications for constraining the origin of water in these samples, as well as for understanding the magmatic processes that may have affected their water content and isotopic composition (i.e., degassing of H$_2$ vs. H$_2$O [3,8,13] and/or mixing between different H-bearing components [10]). However, for the water-rich olivine-hosted melt inclusions – found within Apollo 17 orange glasses – the correction for cosmogenic deuterium is negligible, and the new $P_D$ value has virtually no effect on the corrected hydrogen isotope ratios. Thus, the most primitive Apollo 17 high-Ti melts point to a δD value of 274±42‰ for lunar water [3], provided that the melt inclusions retain the original pre-eruptive isotopic ratio. This value is currently best explained by late accretion of volatile-rich chondritic material to the Moon, although the possibility that some volatiles were inherited from the proto-Earth cannot be ruled out [3,10,14,15].

**Outlook:** The detection and characterization of indigenous noble gas component and to identify its provenance. Pristine samples that have never been exposed to space at the lunar surface, i.e., rock samples retrieved by drilling from depths of several meters or fresh crater ejecta, are key for assessing whether the lunar mantle retains indigenous noble gases that were supplied to the growing Moon by the delivery of volatile-rich chondritic matter or were inherited from the proto-Earth.