

**SEPARATING ALL NOBLE GAS COMPONENTS (HE-XE) RELEASED FROM A STARDUST ANALOGUE SAMPLE MIXTURE BY CLOSED SYSTEM STEP ETCHING (CSSE) – A MAJOR STEP TOWARDS ANALYZING ALL COMETARY NOBLE GASES.** P. Will<sup>1,2</sup>, H. Busemann<sup>2</sup>, M. E. I. Riebe<sup>2</sup> and C. Maden<sup>2</sup>, <sup>1</sup>Physics Department and McDonnell Center for Space Sciences, Washington University, 1 Brookings Drive, Saint Louis, MO 63130 (patrizia.will@erdw.ethz.ch), <sup>2</sup>Institute of Geochemistry and Petrology, ETH Zürich, 8092 Zürich, Switzerland.

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**Introduction:** Comets mostly formed in the cold, outer realms of the early solar nebula where they accreted dust grains, organic matter, and frozen volatiles [1]. Their volatile record shows only little evidence for processing in the early solar nebula [2]. Deciphering the cometary noble gas composition will thus likely enhance our understanding of the volatile processing in the early solar nebula [3], the origin of cometary ices [1], the volatile delivery to the inner solar system, and the origin of planetary atmospheres.

The NASA Stardust mission to comet 81P/Wild 2 for the first time returned particles of known cometary origin for ground-based laboratory analyses [4]. The particles were captured by collectors consisting of ultralow-density silica aerogel that were exposed to the cometary dust stream. Heating of the particles and instantaneous volatile release upon impact produced bulbous cavities with walls of quenched aerogel melt that taper off into fine tracks covered by abraded particle dust, and a terminal particle [4]. The various noble gas components potentially sited along the tracks, in the dust and in the terminal particles could not be resolved by conventional step-heating techniques and a complete characterization of the cometary He-Xe noble gas inventory has not been achieved so far. Detection of the trapped heavier cometary noble gases might further be hampered by the small gas amounts expected and the adsorbed atmospheric contamination of the aerogel [5].

The unique closed-system step etching (CSSE) technique developed at ETH Zürich [e.g., 6] is a promising technique to resolve the noble gas components sited in the various, potentially present, silicate and organic carrier phases by choosing appropriate acids. Moreover, noble gas components of cometary ices potentially trapped along the bulbous entry cavities and possibly distinct from the components trapped in coma particles, as well as the inevitably adsorbed air, might also be resolved by the CSSE technique.

The long-term goal of this project is to analyze the noble gas components (He-Xe) released from a Stardust sample track, i.e. the terminal particle and the bulbous cavity, using CSSE. Before analyzing a precious Wild 2 sample, we carried out a Stardust analogue test etching experiment to i) test the feasibility of separating all noble gas components released from silicate and carbona-

ceous carrier phases, ii) determine the etching conditions required to selectively release air from the silica aerogel and cometary noble gases from the silicate minerals, and iii) assess the capability of CSSE for depth-dependent resolution of the cometary noble gas components and their isotopic compositions. Here we demonstrate the success of our approach.

**Sample material:** The Stardust analogue sample mixture contained 4.9 mg of unflown silica aerogel, 2.0 mg of the HF/HCl-resistant residue (insoluble organic matter, IOM) of the reduced CV3 chondrite Vigarano [7], and 0.1 mg of the solar wind-rich lunar anorthositic regolith breccia Pecora Escarpment (PCA) 02007 [8].

**Preparatory sample analyses:** Aerogel and PCA 02007 were analyzed for their noble gas contents by bulk fusion in one heating step to 1700 °C for 30 min. The HF/HCl-resistant residue of Vigarano was examined by CSSE in 19 vapor and liquid acid etch steps ranging from 0.25-288 h at room temperature (RT) to 100 °C [9]. The sample amounts required for the Stardust analogue test etching experiment were determined based on these results.

**Stardust analogue test etching experiment:** The sample mixture was first etched using concentrated hydrofluoric (HF) acid (37 %, 21.5 m) to dissolve the siliceous aerogel and lunar regolith particles. In total, 31 etch steps ranging from 45 s to 136 h in acid vapor at RT, and 5 etch steps between 2-21 h at -70 to +60 °C were carried out. Thereafter, nitric (HNO<sub>3</sub>) acid (65 %, 14.4 m) was applied to open the oxidisable noble gas carrier(s) residing in the HF/HCl-resistant organic residue of Vigarano. In total, 10 etch steps of 0.25-135 h duration in acid vapor at -20 °C to RT, and 10 etch steps from 2-160 h in liquid acid at -70 to +90 °C were carried out before gas release dropped close to blank level and the CSSE experiment was terminated.

All isotopes of He-Xe were analyzed with a custom-built noble gas mass spectrometer equipped with a Baur-Signer ion source [10]. Details of the noble gas analytical procedures are given in [11].

**Results and discussion:** i) All noble gas components could successfully be separated. First, the aerogel released extremely high amounts of atmospheric noble gases ( $5.4 \times 10^{-7} \text{ cm}^3 \text{ }^{132}\text{Xe/g}$  aerogel), then the lunar silicate minerals liberated solar wind (SW) and cosmo-

genic noble gases (Figs. 1 and 2), and lastly the primordial Q-gases [7] were released from the IOM. Critical conditions to selectively etch aerogel were  $< 2.2$  h at  $-20$  °C in HF acid vapor, and  $> 12.5$  h ( $-20$  °C, acid vapor) to attack the lunar the silicate minerals.

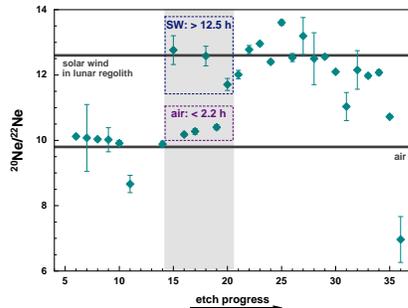


Figure 1.  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios of HF-etch run. Ratios changed from atmospheric to SW composition when etching conditions were harshened sufficiently to attack regolith material.

ii) The noble gas components residing at different depths within a noble gas carrier could successfully be resolved. After initial release of air superficially adsorbed to the aerogel, nearly pure surface-correlated SW and then increasing amounts of volume-correlated cosmogenic noble gases were released from the lunar regolith particles (Fig. 2). Likewise, the Xe isotopic signature of the Vigarano IOM was initially dominated by  $^{129}\text{Xe}_{\text{rad}}$  and only later pure Xe-Q was released (not shown). This behavior is known from etch experiments of meteoritic organic matter [7].

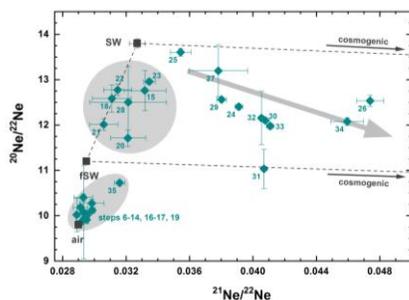


Figure 2. Ne three-isotope plot of the HF-etch run. After initial release of air from aerogel, the lunar regolith particles first released rather surface-correlated SW-Ne and, with progressive etching, higher proportions of volume-correlated  $\text{Ne}_{\text{cos}}$  were released.

iii) The mass-dependent isotopic fractionation of the SW with increasing implantation depth could successfully be resolved (Fig. 3). Step 15 shows a  $^3\text{He}/^4\text{He} = (5.0 \pm 0.1) \times 10^{-4}$  indicating SW and potentially minor amounts of cosmogenic He. The  $^3\text{He}/^4\text{He}$  ratios then continuously decreased to  $\sim 3 \times 10^{-4}$ . Diffusive degassing is excluded based on the low etching temperatures and the expected preferential diffusive loss of  $^3\text{He}$  over

$^4\text{He}$ . Release of Q-gases during HF-etching is excluded based on other isotopic systems clearly indicating SW.

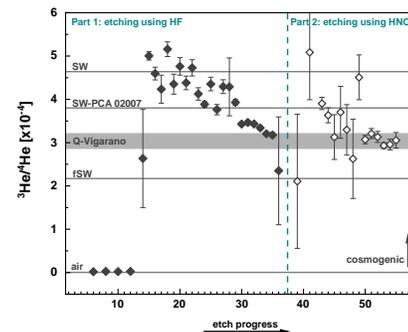


Figure 3.  $^3\text{He}/^4\text{He}$  ratios with progressive etching. After an initial release of air from aerogel, SW with decreasing  $^3\text{He}/^4\text{He}$  ratios was released (see text for details), and lastly Q-gases were liberated by oxidation with  $\text{HNO}_3$ .

Remarkably, large amounts of even air-He were incorporated into the aerogel and released during the first steps of the etch experiment.

**Conclusions:** The CSSE technique successfully i) separated noble gas components hosted by the different well-intermingled carrier phases as could also be found in the collectors of the Stardust mission [12], ii) resolved mass-dependent isotopic fractionation of SW-He and SW-Ne [13] with implantation depth, despite the sample being a complex mixture of materials, iii) resolved noble gas components sited at different depths of a mineral phase, here the surface-correlated SW and the volume-correlated cosmogenic noble gases. CSSE is thus perfectly suited to resolve the noble gases sited in aerogel, which could contain cometary gases trapped during Wild 2 particle impact (e.g., from ices) in addition to the unavoidable air contamination, and other cometary phases such as siliceous or organic dust.

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**References:** [1] Stern S. A. et al. (2000) *Astrophys. J.*, 544, L169-L172. [2] Mumma M. J. et al. (1993) in *Protostars and Planets III* (eds. Levy E. H. et al.) 117-1252. [3] Marty B. et al. (2008) *Sci.*, 319, 75-78. [4] Brownlee D. et al. (2006) *Sci.*, 314, 1711-1716. [5] Will P. et al. (2017) DINGUE V meeting, abstract. [6] Wieler R. et al. (1991) *GCA*, 55, 1709-1722. [7] Busemann H. et al. (2000) *Meteoritics & Planet. Sci.*, 35, 949-973. [8] Will P. et al. (2017) 80<sup>th</sup> Ann. Meeting Met. Soc., abstr. #6353. [9] Will P. et al. (2019) 82<sup>nd</sup> Ann. Meeting Met. Soc., abstr. #6494. [10] Baur H. (1980) PhD thesis, ETH Zürich. [11] Riebe M. E. I. et al. (2017) *Meteoritics & Planet. Sci.*, 52, 2353-2374. [12] Joswiak D. J. et al. (2017) *Meteoritics & Planet. Sci.*, 52, 1612-1648. [13] Benkert J.-P. et al. (1993) *JGR*, 98, 13147-13162.