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**Solar Wind Noble Gas Fractionation in Lunar
Ilmenites: A Study Based on Depth Profiling
Analyses and Numerical Simulations**

希ガス局所分析および数値シミュレーションに基づく
月イルメナイトの太陽風起源希ガスの分別に関する研究

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Abstract

Solar wind (SW) noble gases preserved in lunar regolith serve as powerful tracers of past solar activity due to their high volatility and chemical inertness. They can provide insights not only into past SW compositions but also into the energy distribution of the SW and the duration of SW irradiation on the lunar surface, thereby offering constraints on regolith gardening processes. Since the Apollo missions, numerous studies have attempted to reconstruct past SW signatures using lunar samples. However, conventional noble gas analytical techniques, limited by insufficient spatial resolution, cannot resolve the nanoscale distributions of implanted noble gases within the uppermost ~ 100 nm of grains. Because SW noble gases are implanted within this near-surface region, such limitations have restricted our ability to investigate the fractionation processes operating at the nanoscale.

Recently, a Time-of-Flight Secondary Neutral Mass Spectrometer (ToF-SNMS), LIMAS, was developed and has achieved high-resolution ^4He analyses in extraterrestrial materials. Previous LIMAS studies evaluated past SW energy distributions and regolith gardening timescales based on ^4He depth profiling and ^4He imaging. Because ^4He is known to be lost from minerals, assessing the degree of ^4He loss is essential for robust interpretation. However, LIMAS analyses had been primarily focused on ^4He , and Ne and Ar isotopes had scarcely been analyzed.

This study applies LIMAS to achieve nanoscale depth profiling of noble gases, including Ne and Ar isotopes. **Chapter 2** describes the optimization of analytical conditions for LIMAS, previously used primarily for ^4He analysis. This optimization enabled the simultaneous measurement of major elements in ilmenite, a typical lunar mineral, together with five noble gas isotopes: ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar . The detection limits were

lower than the expected noble gas concentrations in lunar ilmenite. In addition, the reproducibility and stability show that the bulk $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, as well as depth variations in the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio, can be sufficiently resolved.

Chapter 3 reports high-spatial-resolution depth profiling of SW noble gases in three ilmenite grains from Apollo 17 soil 71501 using the LIMAS depth-profiling technique. The depth profile of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio supports the demise of the previously inferred *solar energetic particle component*, which had been discussed without quantitative depth scales. The similar $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios among grains, regardless of their bulk values, indicate that SW-He and SW-Ne are lost from ilmenite through defect-mediated effusion.

In **Chapter 4**, SW implantation–sputtering was modeled using ion-implantation simulations and compared with literature data for lunar ilmenite. The reported bulk compositions and depth distributions of the $^{20}\text{Ne}/^{22}\text{Ne}$, $^{36}\text{Ar}/^{84}\text{Kr}$, and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios are broadly consistent with model predictions after sputtering of several tens of nanometers. The sputtering timescale was estimated to be $< 0.01 \text{ \AA yr}^{-1}$. However, the relationship between ^{36}Ar fluence and the evolution of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio inferred from previous studies suggests a higher effective sputter rate. This highlights the difficulty of estimating SW exposure durations from noble gas concentrations and depth profiles.

Chapter 5 summarizes the thesis. In this study, an in situ noble gas depth-profiling technique using ToF-SNMS was developed and applied to lunar ilmenite, and numerical simulations were conducted to reveal the time evolution of noble gas depth profiles. I conclude that noble gas depth profiling by LIMAS can serve as a powerful tool for investigating nanoscale fractionation processes and for approaching past SW characteristics.

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Contents

1	General Introduction	1
1.1	Solar wind noble gases in extraterrestrial materials	1
1.1.1	Solar wind	1
1.1.2	Solar wind composition of noble gases	2
1.1.3	Solar wind noble gases in lunar soils	3
1.2	Isotope nanoscope LIMAS	10
1.2.1	Overview of LIMAS	10
1.2.2	Solar wind- ⁴ He analyses by LIMAS	11
1.3	Purpose of this thesis	12
2	Development of Depth Profiling Analysis for Five Noble Gas Isotopes	13
2.1	Introduction	13
2.2	Materials and Methods	15
2.2.1	Sample information	15
2.2.2	Depth profiling by LIMAS	16
2.2.3	Calibration for concentrations and isotope ratios of noble gas . . .	17
2.2.4	Identification of target ion species	18
2.2.5	Ion implantation simulation	20
2.3	Results and Discussions	21
2.3.1	Time-of-flight spectra of ion implanted samples	21
2.3.2	Depth profiles of noble gas in minerals	23
2.3.3	Discrepancy between the measured and simulated profiles	33
2.3.4	Detection limits of noble gases	34

2.3.5	Reproducibility of noble gas analysis by LIMAS	37
2.3.6	Applicability to other extraterrestrial samples	40
2.4	Conclusions	42
3	Depth-dependent Mass Fractionation of Solar Wind Noble Gases	43
3.1	Introduction	43
3.2	Materials and Methods	47
3.2.1	Sample preparation	47
3.2.2	Depth profile analysis	47
3.2.3	Calibration for noble gas concentrations and isotopic ratios	49
3.2.4	Numerical simulation of ion implantation	51
3.3	Results	53
3.3.1	3D-distributions of the measured ions	53
3.3.2	Depth profiles of measured ions	57
3.3.3	Numerical simulations of noble gas depth profiles	60
3.4	Discussion	63
3.4.1	Characteristics of space weathered rim in depth profiles	63
3.4.2	The demise of the “SEP component”	64
3.4.3	Elemental fractionation at the surface of lunar ilmenite	69
3.5	Conclusions	72
4	Solar Wind Implantation–sputtering Modeling	73
4.1	Introduction	73
4.2	Modeling of Ion Implantation into the Moon	75
4.2.1	SRIM parameters	75
4.2.2	SRIM simulation	77
4.3	Surface sputtering model	82
4.3.1	Model description	82
4.3.2	Implantation–sputtering equilibrium	84
4.4	Comparison between model and lunar samples	87
4.4.1	Noble gas compositions	87

4.4.2	Timescale of sputtering	89
4.4.3	Discrepancy of noble gas characteristics between modeled and actual lunar samples	91
4.5	Conclusions	94
5	Summary of the Thesis	95

Chapter 1

General Introduction

1.1 Solar wind noble gases in extraterrestrial materials

1.1.1 Solar wind

The intense radiation and plasma outflow from the Sun strongly influence the physical and chemical evolution of planetary materials (e.g., Denevi et al. 2023, Pieters and Noble 2016) and can even erode planetary atmospheres (e.g., Lammer et al. 2008, Seki et al. 1998, Terada et al. 2017). Recent studies have also highlighted the possible contribution of solar particles irradiated into the precursor of the Earth to the origin of terrestrial volatiles (Daly et al. 2021, Marty 2020, Péron et al. 2018, Yamamoto et al. 2025). Therefore, understanding how solar activity, as well as the composition of the Sun, has evolved through time is therefore essential for reconstructing the history of the Earth and the solar system (Sonett et al. 1991).

Attempts to infer the past Sun have commonly relied on observations of solar-type stars of different ages and on theoretical models (e.g., Airapetian and Usmanov 2016, Vidotto 2021, Wood et al. 2005). However, these approaches probe other solar-type stars, not the Sun itself. The most direct approach to investigate the past Sun is to analyze materials that were exposed to solar corpuscular radiation. Such materials retain particles emitted by the Sun at various ages and therefore preserve information about the chemical composition and energy distribution of the solar plasma at the time of irradiation.

Solar corpuscular radiation can be classified to broadly two components: the *Solar*

Wind (SW) and *Solar Energetic Particles* (SEPs). The SW is a quasi-stationary plasma flow continuously emitted from the solar corona. Its composition is dominated by protons ($\sim 95\%$) and α particles ($\sim 5\%$), with trace abundances of heavier species that closely reflect the solar composition. The typical speed of the present-day SW is $\sim 400 \text{ km s}^{-1}$ (corresponding to $\sim 1 \text{ keV}$ per nucleon; Reisenfeld et al. 2013). In contrast, SEPs are eruptively emitted during solar flares and coronal mass ejections and typically possess energies of a few MeV. Observational studies of young solar-type stars indicate that such stars are significantly more active, implying that SEP fluxes in the early Solar System were much higher than today. Thus, the SW/SEP ratio of the past Sun is of interest.

To analyze solar particles preserved in extraterrestrial materials, noble gases serve as powerful tracers due to their high volatility and chemical inertness (e.g., Lodders et al. 2025). In the following sections, I review the noble gas composition of the present-day SW and summarize noble gas studies on lunar regolith samples.

1.1.2 Solar wind composition of noble gases

The first laboratory analyses of the SW composition were carried out during the Apollo missions through the Solar Wind Composition (SWC) experiment (Geiss et al. 2004, and references therein). In this experiment, metallic foils were exposed to the SW at Apollo landing sites during the Apollo missions, and were returned to Earth for laboratory analysis. These measurements provided the first analytical determinations of noble gas compositions derived from the SW (e.g., Bühler et al. 1969, Geiss et al. 1970; 2004; Table 1.1). However, even the longest exposure duration during the Apollo 16 mission was only about 45 hours, only He, Ne, and Ar could be measured with sufficient precision, whereas the concentrations of Kr and Xe in the collected foils were too low to be detected reliably.

To obtain higher-precision measurements of the SW composition, including Kr and Xe, NASA conducted the Genesis mission in the early 2000s (Burnett et al. 2003, Wieler and Burnett 2025). In this mission, SW particles were collected for 2.3 years at the Earth–Sun L1 Lagrange point using artificial collector materials with well-defined chemical compositions (Jurewicz et al. 2003). Compared with extraterrestrial materials, the Genesis samples were irradiated by a well-characterized SW flux under controlled condi-

tions. In addition, the speed distribution of the SW irradiating the Genesis spacecraft was simultaneously monitored by the Advanced Composition Explorer (ACE) at the same L1 Lagrange point (Reisenfeld et al. 2013). Furthermore, the 2.3-year exposure period was short enough that either cosmogenic noble gases or sputtering effect can be neglected.

Although the collected amounts of Kr and Xe were still small and their analyses remain challenging, continued methodological improvements have nevertheless enabled their reliable measurement (Meshik et al. 2014; 2020, Vogel et al. 2011). The noble gas compositions obtained from the Genesis collector materials are now used as the modern reference for the SW (Table 1.1).

I note here that the values listed in Table 1.1 should be regarded as representative, and that some variations exist among laboratories. For example, the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio reported by Heber et al. (2009) is 13.78 ± 0.03 , whereas those reported by Meshik et al. (2007) and Pepin et al. (2012) are 13.972 ± 0.025 and 14.001 ± 0.042 , respectively. These discrepancies may be related to interference corrections (e.g., $^{12}\text{C}^{16}\text{O}^{16}\text{O}^{++}$ on $^{22}\text{Ne}^+$, as suggested by Pepin et al. 2012) or to differences in backscattering corrections. The analyzed target materials in Heber et al. (2009), Meshik et al. (2007), and Pepin et al. (2012) were diamond-like carbon on silicon (DoS), aluminum deposited on sapphire (AlO₃), and gold, respectively. Backscattering effects depend on the atomic mass of the target material; these effects are corrected for AlO₃ and gold based on ion implantation simulations, whereas the backscattering effect in DoS is negligible based on simulation. Therefore, the characteristics of SW implantation into solid materials are a key factor in determining further accurate SW compositions.

1.1.3 Solar wind noble gases in lunar soils

The initial analysis of the Apollo 11 return samples in 1969 revealed that lunar breccias and fines contain substantial amounts of noble gases (Lunar Sample Preliminary Examination Team 1969). In particular, their $^{20}\text{Ne}/^{22}\text{Ne}$ ratios were higher than those of the terrestrial atmosphere and were consistent with theoretical expectations for the SW, suggesting that these samples retained SW-derived noble gases. This interpretation was subsequently confirmed by the correlation with sample size (surface-correlation) and by

the agreement with the SW compositions measured by the SWC experiment (e.g., Bühler et al. 1969, Eberhardt et al. 1970, Heymann et al. 1970, Hintenberger et al. 1970, Pepin et al. 1970, Podosek et al. 1971). Since then, numerous studies have been conducted as a important archives of the solar noble gas studies. Here, I review previous research focusing on the composition of SW noble gases in lunar samples.

Mineral specific elemental compositions

Measurements of the noble gas compositions in lunar samples revealed that noble gases are strongly fractionated from the present-day SW compositions obtained by the SWC experiment (Hintenberger et al. 1970, Hohenberg et al. 1970, Pepin et al. 1970). Subsequent analyses of mineral-separated samples demonstrated that all minerals systematically show depletion of light noble gases, and that the degree of depletion varies among mineral species (Signer et al. 1977; Fig. 1.1). Among the minerals, ilmenite show relatively higher retentivity of noble gases (red plots in Fig. 1.1).

These findings led to the widely accepted interpretation that the loss of light noble gases from lunar materials is caused by mineral dependent gas concentration equilibrium between SW implantation and gas losses (Signer et al. 1977). Signer et al. (1977) suggested that such mineral dependencies could occur by mineral dependent trapping efficiencies, sputtering, or diffusion losses, and they concluded that the dominant process is diffusion. This light-element loss complicates the reconstruction of past SW elemental abundances (Pepin et al. 1999, Wieler 2016), and remains an issue even in recent studies (e.g., Zhang et al. 2025).

Noble gas isotopic signatures in lunar soils

Since the early analyses of lunar samples, it has been recognized that the isotopic ratios of He, Ne, and Ar in lunar soils are isotopically heavier than the SWC data, similar to the elemental fractionation observed relative to the SW (Eberhardt et al. 1972, Geiss et al. 1970). At that time, several mechanisms were discussed, including isotopic fractionation in diffusive loss, differences in trapping efficiencies, and mixing with an isotopically heavy component (see Wieler 2023 for the further history). Among these possibilities, the

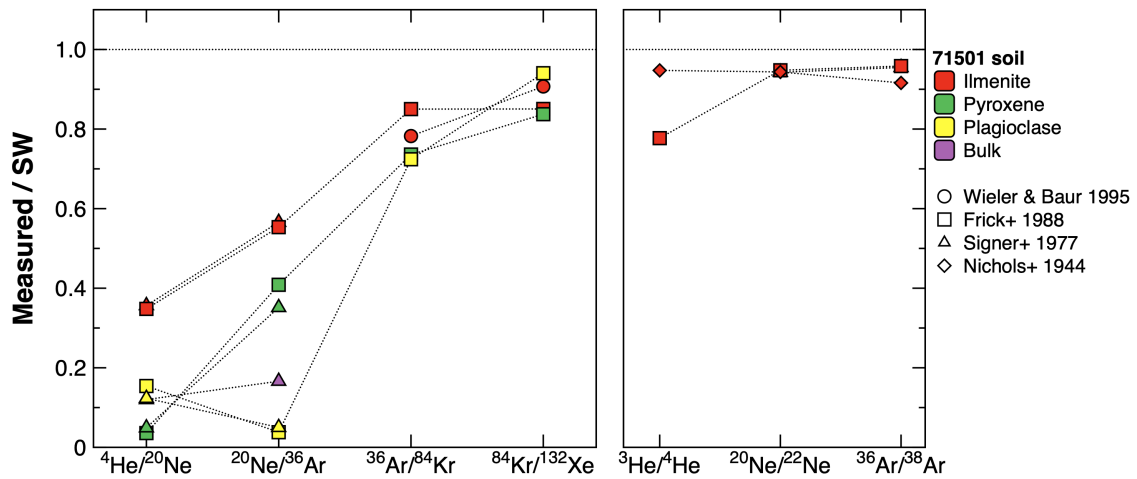


Figure 1.1: Noble gas elemental ratios of mineral separates from Apollo 17 71501 soil relative to the SW value (Heber et al. 2009). Data are from Signer et al. (1977), Frick et al. (1988), and Wieler and Baur (1995). Plots with different colors are data of different mineral separates.

contribution of an isotopically heavier component relative to the SW component became the major explanation for about 30 years. Such isotopically heavier neon signatures were also found in gas-rich meteorites and were labeled Ne-C (Black 1972).

The isotopically heavy component was attributed to SEPs, which is irradiated by much higher energies than the SW and therefore were expected to be implanted deeper than the SW. When lunar soils were acid-etched to remove their surface layers, the resulting noble gas compositions of the deeper portions were systematically lower than those from the total analyses (Etique et al. 1981). This observation supported the idea that heavy isotopic signatures originate from *SEP component*. Furthermore, the neon isotopic compositions of solar flare particles observed by a spacecraft was significantly heavier than the SW component (Mewaldt et al. 1979), which strengthened the interpretation.

Subsequently, Wieler et al. (1986) developed an analytical technique called Closed System Stepwise Etching (CSSE), in which a sample is chemically etched progressively in a vacuum line made by gold, and connected to a noble gas mass spectrometer. This method allows the qualitative depth profiling of noble gases. When CSSE was applied to lunar samples, the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio measured in the earliest etching steps was found to be close to the SW component, followed by a gradual decrease in the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio (Benkert et al. 1993, Wieler et al. 1986). This pattern was interpreted as the progressive

etching of SW reservoirs in the shallowest layers, progressively revealing deeper reservoirs influenced by an isotopically heavy SEP component.

However, the SEP component hypothesis faces challenges. The most prominent of which is that it requires an large amount of SEP noble gases. Benkert et al. (1993) estimated the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of the SW and SEP components to be 13.8 and 11.2, respectively. If one attempts to explain the $^{20}\text{Ne}/^{22}\text{Ne} \sim 13.0$ measured by Benkert et al. through mixing two components, it requires a proportion of SW:SEP $\approx 7:3$. This requires an SEP flux far higher than the present-day SW:SEP ratio of solar corpuscular radiation (Mewaldt et al. 2001). Therefore, alternative mechanisms capable of explaining the isotopically heavy compositions relative to the SW values in lunar samples had been discussed even at that time.

The demise of the SEP component

After the Genesis sample return, CSSE analyses were applied to the Genesis bulk metallic glass collectors. Although the SW speed distribution was monitored throughout the 2.3-year exposure period and the SEP flux during this interval is known to have been low (Reisenfeld et al. 2013), the Genesis collector nevertheless exhibited a $^{20}\text{Ne}/^{22}\text{Ne}$ depth profile closely resembling those observed in lunar samples and the depth profile was well reproduced by ion implantation simulation based on SW speed distribution with a uniform isotopic composition (Grimberg et al. 2006; 2008). This finding effectively marked the demise of the SEP-component hypothesis (Wieler et al. 2007). The observed $^{20}\text{Ne}/^{22}\text{Ne}$ trend were instead explained by depth-dependent isotopic fractionation arising from the different kinetic energies between the isotopes (Grimberg et al. 2006, Wieler et al. 2007), now referred to as fractionated solar wind (fSW). The SW-like ratios observed at the earliest etch steps of lunar samples are explained by surface sputtering, which removes the topmost surfaces including fSW fractionated to isotopically lighter values (Grimberg et al. 2006).

The misinterpretation of the SEP component is likely due to the lack of an quantitative depth scale in the CSSE technique, because SEPs should be implanted into micrometer depth scales, whereas the fSW trend will exist at nano-scale depths. Still, it remains

unclear, however, whether the entire depth-dependent trend of $^{20}\text{Ne}/^{22}\text{Ne}$ trend in lunar samples can be explained solely by fSW, because lunar soils may have been irradiated by actual SEPs due to their much longer exposure durations compared with the Genesis collectors.

Noble gas trapping sites

Recent transmission electron microscopy (TEM) studies combined with electron energy loss spectroscopy (EELS) have achieved direct detection of He in the near-surface regions of lunar samples (Burgess and Stroud 2018, Cymes et al. 2024, Kling et al. 2025, Zhang et al. 2026). These studies have identified He–K edges in EELS spectra associated with bubbles and defects in ilmenite, chromite, and olivine, as well as in iron nanoparticles within lunar glasses.

Crushing experiments on lunar samples conducted by Funkhouser et al. (1971) reported an extraction efficiency of only $\sim 10^{-3}$ relative to the total noble gases released by melting experiments. Noble gases hosted in bubbles and large defects, which are detectable by EELS, should be easily extracted by crushing. Therefore, this result implies that a significant fraction of noble gases in lunar materials is trapped in much smaller planar defects or interstitial sites, which remain difficult to detect directly by current TEM-based techniques.

Noble gas depth profiling in lunar samples

Noble gas depth profiling studies on lunar regolith grains were already conducted in the late 1970s using the Gas Ion Probe technique (Müller et al. 1976, Kiko et al. 1979). In these studies, samples were sputtered with a Xe^+ ion beam, and the released noble gases were ionized by electron impact, allowing measurements of quantitative depth distributions of noble gases with lateral dimensions of $\sim 100\text{ }\mu\text{m}$ and a depth resolution of $\sim 10\text{ nm}$. These measurements demonstrated that noble gases are concentrated within the uppermost surface region ($< 1\text{ }\mu\text{m}$ depth) of lunar regolith grains, with depth distributions that vary among individual grains and mineral types (e.g., Müller et al. 1976, Warhant et al. 1979).

However, due to background limitations, only ^4He and ^{22}Ne could be analyzed, and depth profiles of elemental and isotopic ratios were not obtained. As a summary of this section, previous noble gas analytical techniques were unable to provide quantitative depth profiles of noble gas compositions that are essential for interpreting past SW compositions and energy distributions, thereby limiting the scope of such discussions.

Table 1.1: Noble gas elemental and isotopic compositions reported in previous studies

	$^4\text{He}/^{20}\text{Ne}$	$^{20}\text{Ne}/^{36}\text{Ar}$	$^{36}\text{Ar}/^{84}\text{Kr}$	$^{84}\text{Kr}/^{132}\text{Xe}$	$^3\text{He}/^4\text{He} (\times 10^{-4})$	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{36}\text{Ar}/^{38}\text{Ar}$
SWC ^a	570 ± 70	49 ± 7	–	–	4.26 ± 0.22	13.7 ± 0.3	5.4 ± 0.3
Genesis ^b	656 ± 2	42.1 ± 0.2	2390 ± 240	9.9 ± 0.6	4.64 ± 0.02	13.78 ± 0.02	5.470 ± 0.006
71501 ilmenite ^c	231	24	1951	8.7	4.00	13.02	4.94

^a Data from Geiss et al. (2004) with 2σ errors.

^b $^4\text{He}/^{20}\text{Ne}$, $^{20}\text{Ne}/^{36}\text{Ar}$, $^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, and $^{36}\text{Ar}/^{38}\text{Ar}$ are from Heber et al. (2009); $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ are from Vogel et al. (2011). Errors are 2σ .

^c Average of 71501 ilmenite data from Frick et al. (1988), Nichols et al. (1994), Signer et al. (1977), Wieler and Baur (1995).

1.2 Isotope nanoscope LIMAS

1.2.1 Overview of LIMAS

Time-of-flight secondary neutral mass spectrometer (ToF-SNMS) called LIMAS (JEOL) was developed for in situ analyses of noble gases in extraterrestrial materials (Bajo and Yurimoto 2024, and references therein). A schematic figure of LIMAS is shown in Fig. 1.2.

LIMAS combined liquid ^{69}Ga focused ion beam (Ga-FIB) to sputter the sample as neutral particles, a femtosecond (fs) laser system to post-ionizing the sputtered neutrals, and a multi-turn ToF-MS (MULTUM II; Okumura et al. 2004) for mass separation. The use of a Ga-FIB together with an aberration corrector enables high spatial resolution analyses (Nagata et al. 2019). In ^4He imaging, a spatial resolution of ~ 100 nm has been achieved with beam currents up to 1 nA (Wada et al. 2025). Strong-field tunneling ionization induced by the fs-laser provides high ionization efficiency, ionizing up to 70% of the ^4He atoms in the ionization region (Yurimoto et al. 2016). The fs-laser also produces a large number of multiply charged ions, requiring high mass-resolving power to separate isobaric peaks.

LIMAS uses MULTUM II, a compact multi-turn ToF-MS that achieves high ToF (or mass) resolution by circulating ions through the same electrostatic orbit many times. MULTUM II attached to LIMAS attains a mass resolution of up to 6.2×10^5 (FWHM) by 1000 multi-turns (Tonotani et al. 2016). The high resolution comes with a challenge that fast ions may overtake slower ions (Bajo et al. 2022). Therefore, careful optimization of the ToF and selection of the m/z range is essential. Ions without interest must be removed with ion gates while ensuring that the ToF of the target ions do not overlap at the timing of detection.

Due to these analytical difficulties, LIMAS has been applied primarily to in situ analyses of ^4He , which is the most abundant SW-derived noble gas species (Bajo et al. 2015; 2016; 2024; 2025, Obase et al. 2025, Wada et al. 2025, Yurimoto et al. 2016).

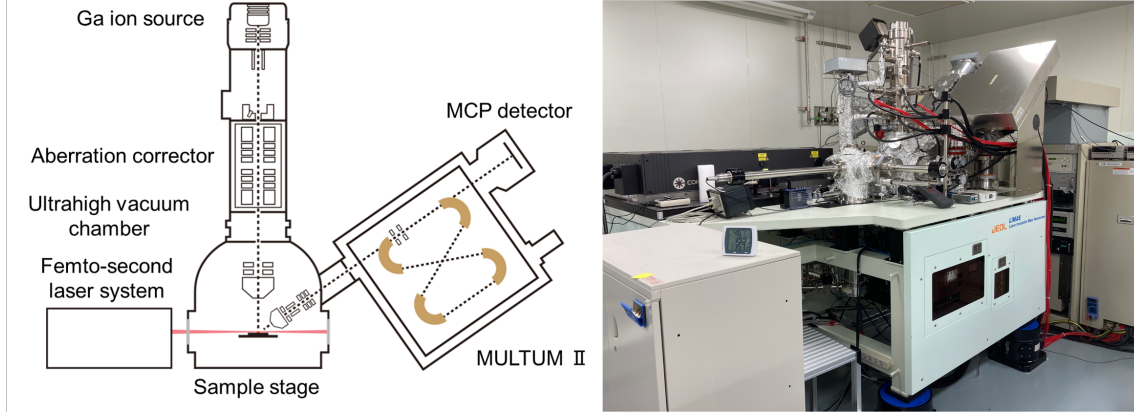


Figure 1.2: Schematic illustration (left) and photo (right) of LIMAS at Hokkaido University.

1.2.2 Solar wind- ^4He analyses by LIMAS

Using LIMAS, high-spatial-resolution depth profiling of ^4He was achieved, and ^4He depth profile of the Genesis collector (diamond-like-carbon on a silicon) was measured (Bajo et al. 2015). Their study showed that the measured ^4He depth distributions agree well with those predicted by SRIM ion implantation simulations (Ziegler et al. 2010), which were calculated using the SW speed distribution observed during the Genesis collection period (Reisenfeld et al. 2013). This agreement demonstrated that depth profiles of noble gases in extraterrestrial materials can be used to reconstruct the past SW energy distributions.

Obase et al. (2025) extended this approach by conducting ^4He depth profiling and SRIM simulations for silicate grains from asteroid 25143 Itokawa. By comparing the measured depth profiles with those predicted from the present-day SW speed distribution, they showed that during the period when the measured Itokawa particles were exposed to the SW (a ~ 100 -year snapshot within the last few million years), the flux of energetic particles must have been more than 250 times higher than the present-day energy distributions.

Recently, ^4He imaging has also been performed, revealing that a variety of minerals in gas-rich meteorite (Northwest Africa 801) retain ^4He near the grain surfaces (Bajo et al. 2024, Wada et al. 2025). These ^4He signatures represent that surface concentrated ^4He are implanted on their parent bodies regolith, and quantitative ^4He measurements have been used to discuss surface gardening processes on meteorite parent bodies.

1.3 Purpose of this thesis

As reviewed above, SW noble gases preserved in extraterrestrial materials provide not only information of the SW composition, but also serve as potential indicators of the SW energy distribution. Furthermore, noble gases can be used as tracers of SW irradiation to investigate regolith gardening processes on airless bodies. Recent studies using LIMAS have advanced this field through nanoscale depth profiling and imaging of ^4He .

However, as clearly demonstrated by lunar samples, ^4He is not retained at 100% re-tentivity in minerals. Samples from asteroid Itokawa and gas-rich meteorites also exhibit $^4\text{He}/^{20}\text{Ne}$ ratios lower than the SW value, similar to lunar samples (Nagao et al. 2011, Obase et al. 2021). This could disturb the SW irradiation duration and possibly, the ^4He depth distributions. For more robust interpretations of SW noble gases, it is essential to quantitatively evaluate the degree of ^4He loss in each samples. This requires simultaneous analysis of Ne and Ar isotopes, allowing elemental and isotopic ratios to be used to identify fractionation degree.

The primary aim of this thesis is to expand the analytical capability of the isotope nanoscope LIMAS by optimizing measurement conditions to enable simultaneous detection of He, Ne, and Ar isotopes. In particular, new analytical settings were developed to allow measurement of ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar in representative minerals of lunar and asteroidal materials, i.e., ilmenite and olivine, respectively.

Based on this novel technique, nanoscale noble gas depth profiles were obtained for lunar ilmenites. First, the quantitative depth profile of $^{20}\text{Ne}/^{22}\text{Ne}$ ratio allow a reassessment of the SEP hypothesis, which had previously been discussed without a quantitative depth scale. Second, the depth profiles of $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ provide new constraints on the process responsible for the loss of He and Ne from lunar samples.

Finally, sputtering, which is commonly invoked to explain the isotopically heavy Ne in lunar samples, also alters the depth distributions and concentrations of SW noble gases. To evaluate this effect, a numerical model combining ion implantation and surface sputtering was developed and compared with prior lunar data. This enables discussion of the possibility and implications of sputtering on lunar noble gases, including the evolution of their depth profiles and concentrations.

Chapter 2

Development of Depth Profiling Analysis for Five Noble Gas Isotopes

2.1 Introduction

In the 1970s, combining ion beam sputtering and electron ionization, gas ion probe technique (beam diameter, 200 μm ; depth resolution, ~ 10 nm) was used for the ^4He and ^{22}Ne depth profiling of lunar samples (Müller et al. 1976, Kiko et al. 1979). However, other noble gas isotopes such as ^{20}Ne and ^{36}Ar were difficult to measure in natural samples due to their high background. In addition, all sputtered particles will be ionized from the crater bottom and crater edge, which in principle limits the depth resolution.

Recent developments in secondary ion mass spectrometry have led to improvements in the detection limits and spatial resolution of the depth profiling of helium and argon implanted into semiconductors and metals in engineering applications. However, the rastering areas of these measurements have been limited to several tens of micrometers (Ray et al. 1988, Yamazaki 2001). In cosmochemical studies, the depth distribution of noble gases in extraterrestrial materials has been measured by the Closed System Stepwise Etching (CSSE) technique, in which a sample is chemically etched stepwise in a vacuum and the noble gases extracted from the sample surface are measured with a noble gas mass spectrometer (Wieler et al. 1986, Benkert et al. 1993, Grimberg et al. 2006). This

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technique succeeded to determine the depth trend of noble gas compositions, however, it lacked an absolute depth scale.

In recent years, a time-of-flight secondary neutral mass spectrometer (ToF-SNMS), LIMAS (JEOL), was developed and succeeded high-resolution ^4He analysis, reaching a ^4He detection limit of $2 \times 10^{-20} \text{ cm}^{-3}$ with a $\sim 2 \text{ }\mu\text{m}$ primary beam spot size (Bajo et al. 2024). Bajo et al. (2015) conducted ^4He depth profiling in the diamond like carbon target of NASA/Genesis (Burnett et al. 2003) using LIMAS to obtain the ^4He depth profile. The depth profile was consistent with that of ion implantation simulations performed using the Stopping and Range of Ions in Matter (SRIM) software (Ziegler et al. 2010) under the solar wind speed distribution observed by a spacecraft. The authors proposed that ^4He depth profiling of extraterrestrial materials could reveal the energy distribution of the past solar wind. However, conventional analyses of noble gases in extraterrestrial materials suggest that especially light noble gases (i.e., He and Ne) are partially degassed to a certain degree during or after solar wind irradiation (e.g., Signer et al. 1977, Nichols et al. 1994, Palma et al. 2002, Nagao et al. 2011, Wieler 2016, Zhang et al. 2025). Therefore, the simultaneous analyses of Ne and Ar isotopes in addition to ^4He to evaluate noble gas retention with high and quantitative spatial-resolution is of high interest.

In this study, a depth profiling technique for He, Ne, and Ar isotopes in minerals was developed. Polished ilmenite and olivine substrates implanted with ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar were prepared as analogues of solar wind-implanted lunar and asteroidal materials. Detection limits and analytical reproducibility were evaluated for future noble gas analyses of natural samples.

2.2 Materials and Methods

2.2.1 Sample information

Polished substrates of ilmenite crystal ($(\text{Fe}_{0.7}\text{Mg}_{0.3})\text{TiO}_3$) from Monastery mine, South Africa, and olivine crystal ($(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$) from San Carlos, USA, were prepared as representative lunar and asteroidal materials for ion implantation. Ion implantation of ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar and ^{40}Ar were carried out using an ion implanter (IMX-3500RS, ULVAC) at the Toray Research Center, Inc. The irradiation energies and doses for each noble gases are summarized in Table 2.1. Ion implantation was performed under room temperature and the angle of incidence was set to 0° . Ilmenite and olivine were fixed on a p-type silicon wafer and ion implantation was carried out simultaneously. Hereafter, these samples are referred to as HNA-IL and HNA-OL, respectively. The ion-implanted silicon wafer was also used here in the process of mass assignment because the ToF spectra were much simpler than those of ilmenite and olivine, which is referred to as HNA-Si. The ion implantation doses were certified to $\pm 5\%$ accuracy.

Table 2.1: Conditions of ion implantation

Isotope	Energy / keV	Dose / atoms cm^{-2}
^4He	20	2.00×10^{15}
^{20}Ne	60	1.00×10^{14}
^{22}Ne	60	1.00×10^{13}
^{36}Ar	110	1.00×10^{13}
^{40}Ar	110	1.00×10^{14}
* Implantation experiment was conducted at room temperature.		

Polished substrates of Monastery ilmenite and San Carlos olivine without ion implantation, i.e., blank-IL and blank-OL, respectively, to evaluate the background of the noble gas isotopes. The ilmenite and olivine substrates were coated with ~ 10 nm of gold before noble gas measurements to reduce electrostatic charge-up due to primary beam irradiation during depth profiling.

2.2.2 Depth profiling by LIMAS

Depth profiling was performed using LIMAS at Hokkaido University (Bajo and Yurimoto 2024, and references therein). Pulsed ^{69}Ga ion beam (30 keV, ~ 30 nA) was irradiated on the sample surface with focused ion beam (FIB) system. Primary ion pulse of 400 ns width was focused to a ~ 2 μm spot and rastered to an area of $\sim 18 \times 25$ μm^2 (30×30 pixels). Sputtered neutral particles were post-ionized by a femtosecond (fs) laser (Astrella, Coherent) with an energy of 6 mJ and a pulse width of 35 fs. Post-ionized ions were injected into multi-turn ToF mass spectrometer called MULTUM II (Okumura et al. 2004) with an acceleration voltage of -5 kV. Ions without interest is removed from the trajectory by adjusting the timing of the ion injection and ion gate control in MULTUM II. The ions were flown for several hundred microseconds to separate interfering ions and then detected by the high-speed ion detection system using two-stage micro-channel plates (MCP; F1217-011, Hamamatsu Photonics). This single sequence from sputtering to ion detection is referred to as a mass scan, and the signal intensity is given in the unit of ion counts per mass scan (cpms). The repetition rate of the mass scan is set to 1 kHz, which is synchronized with the fs laser system. The timing control and data acquisition systems are based on the description in Bajo et al. (2016; 2019).

During depth profiling, 100 mass scans (takes 0.1 sec) were collected for one pixel to obtain a ToF spectrum, and all ToF spectra for each pixel were recorded. Rastering of 30×30 pixels was repeated for more than several hundred measurement layers until the implanted noble gas decreased enough to a constant intensity, which is considered to be the background of the noble gas isotope signals. The depth profile was obtained using data from the inner 10×10 pixels area to reduce the crater edge effect, which is discussed later. After depth profiling, residual gas was measured without primary beam irradiation, referred to as blank ^iM (^iM : ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar ions). To compare the background of the noble gas signals, blank-IL and blank-OL were analyzed by the same analytical conditions of HNA-IL and HNA-OL.

After the depth profiling, the depth of the sputtering crater was measured using a three-dimensional (3D) confocal laser microscope (VK-X200, Keyence). A typical sputtering crater is shown in Fig. 2.1. The sputtering rate, which is defined by the sputtering depth

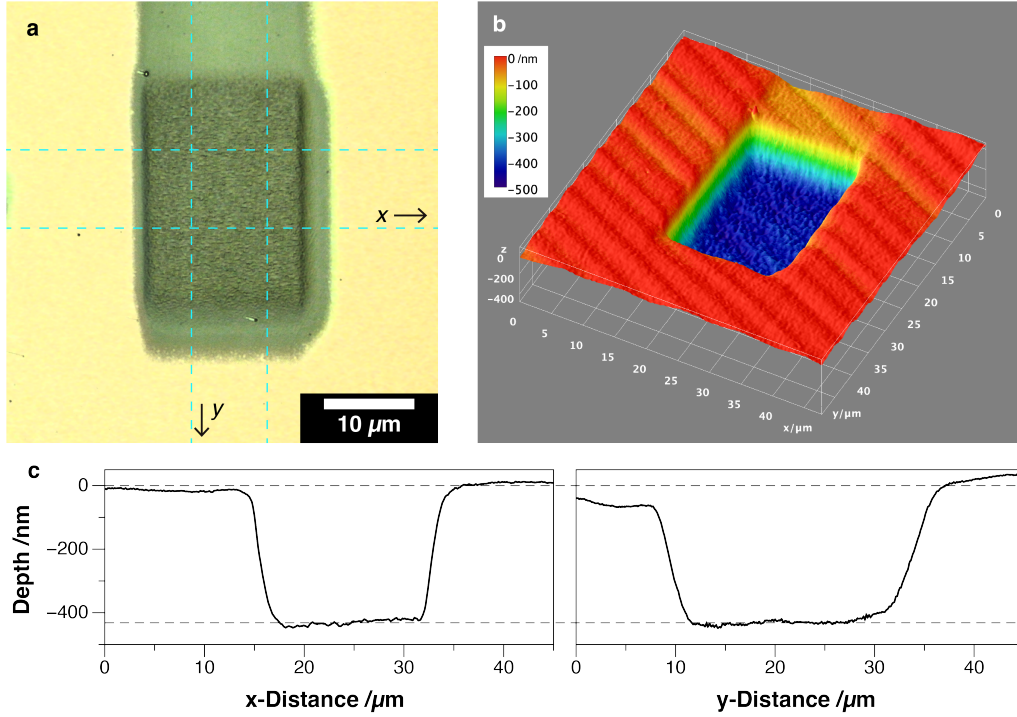


Figure 2.1: LIMAS sputter crater on HNA-IL measured by 3D confocal laser microscope. (a) Laser + RGB image. (b) 3D image. (c) Line profiles taken for x and y directions. Bright area in (a) is coated by gold. Wave on the sample surface in (b) is an artifact due to the measurement step of the laser microscope. Line profiles are averaged from inside of the broken line in (a) for x and y direction, respectively, so the effect of the wave is negligible. Averaged height of the sample surface and the crater bottom are shown as broken line in (c), and the depth of this crater is calculated to be 432 nm.

per measurement layer, was calculated by dividing the crater depth by the total number of measurement layers. The precision of the crater depth measurement is $\pm 5\%$ (1SD).

2.2.3 Calibration for concentrations and isotope ratios of noble gas

Isotope concentrations for noble gas isotope ^iM at depth layer k ($C_{i\text{M},k}$) can be calculated by using relative sensitivity factors (RSFs) as follows.

$$\text{RSF}_{i\text{M}} = \phi_{i\text{M}} \times \left[\sum_{k=1}^n \left(\left. \frac{[^i\text{M}_{\text{std}}]}{[\text{R}_{\text{std}}]} \right|_k - \left. \frac{[^i\text{M}_{\text{std}}]}{[\text{R}_{\text{std}}]} \right|_{\text{BL}} \times \frac{d}{n} \right) \right]^{-1} \quad (2.1)$$

$$C_{i\text{M},k} = \text{RSF}_{i\text{M}} \times \left(\left. \frac{[^i\text{M}_{\text{sam}}]}{[\text{R}_{\text{sam}}]} \right|_k - \left. \frac{[^i\text{M}_{\text{sam}}]}{[\text{R}_{\text{sam}}]} \right|_{\text{BL}} \right) \quad (2.2)$$

where ϕ_{iM} is ion dose of isotope iM , while $[^iM]$ and $[R]$ are ion intensities of isotope iM and matrix isotope for reference, respectively. The std, sam, and BL subscripts stands for standard, for unknown sample, and for baseline, respectively. d is the depth of the sputter crater and n is the number of measured layers at depth d . $^{16}O^{2+}$ was used as a matrix ion for both HNA-IL and HNA-OL.

The ion intensity ratios of noble gas ions in depth layer k can be converted to elemental/isotopic ratios with RSFs which is calculated as following equations.

$$RSF_{i,j} = \frac{\phi_{iM}}{\phi_{jN}} \times \left[\frac{\sum_{k=1}^n ([^iM_{std}]_k - [^iM_{BL, std}])}{\sum_{k=1}^n ([^jN_{std}]_k - [^jN_{BL, std}])} \right]^{-1} \quad (2.3)$$

$$\left(\frac{^iM}{^jN} \right)_k = RSF_{i,j} \times \left(\frac{[^iM_{sam}]_k - [^iM_{BL, sam}]}{[^jN_{sam}]_k - [^jN_{BL, sam}]} \right) \quad (2.4)$$

2.2.4 Identification of target ion species

To simultaneously measure 4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , ^{40}Ar , and major elements as matrix ions, an analytical conditions for mass spectrometry were optimized, in which each ion signal of interest is separated from isobaric ions and other signals that can overlap due to overtaking of ions with smaller m/z . The ToF T for each ion is calculated by the following equation:

$$T = L \sqrt{\frac{m/z}{2eV}} + T_o \quad (2.5)$$

where L is the flight path length, m/z is the mass-to-charge ratio of the ion, e is elementary charge, V is the acceleration voltage, and T_o is an offset time between trigger signal from the timing controller and the first injection pulse electrode. For the calculation, the flight path length was fixed as 0.910 m from the sample surface to the MCP, and 1.317 m as a single lap of MULTUM II. Therefore, L is $0.910 + 1.317N$ (m), where N is lap number in MULTUM II. V was fixed at 5 kV, and T_o is 500 ns.

The values of T for multiple ions were calculated using Eq. (2.5) by adjusting the valence and isotopes to identify ToF conditions where all noble gases and major elements of olivine and ilmenite (i.e., O, Mg, Si, Ti, and Fe) did not overlap. The noble gas ion were measured at a shorter ToF than the major element ions, as the tails of the intense peaks interfered with the smaller peaks of the noble gas isotopes. As a result, ToF windows were

found for measuring m/z 4 ($^4\text{He}^+$), 8 ($^{16}\text{O}^{2+}$), 9 ($^{36}\text{Ar}^{4+}$), 10 ($^{20}\text{Ne}^{2+}$, $^{30}\text{Si}^{3+}$, and $^{40}\text{Ar}^{4+}$), 11 ($^{22}\text{Ne}^{2+}$), 12 ($^{24}\text{Mg}^{2+}$ and $^{48}\text{Ti}^{4+}$), and 20 ($^{20}\text{Ne}^+$ and $^{40}\text{Ar}^{4+}$), along with either 18 ($^{36}\text{Ar}^{2+}$) or 28 ($^{28}\text{Si}^+$ and $^{56}\text{Fe}^{2+}$), at a ToF of 455–461 μs by activating the ion gate. The calculated ToF spectra of these m/z are shown in Fig. 2.2. The ToF windows of m/z 18 ($^{36}\text{Ar}^{2+}$ and $^{54}\text{Fe}^{3+}$) or 28 ($^{28}\text{Si}^+$ and $^{56}\text{Fe}^{2+}$) were needed to be selected because these ions overlap in the spectrum.

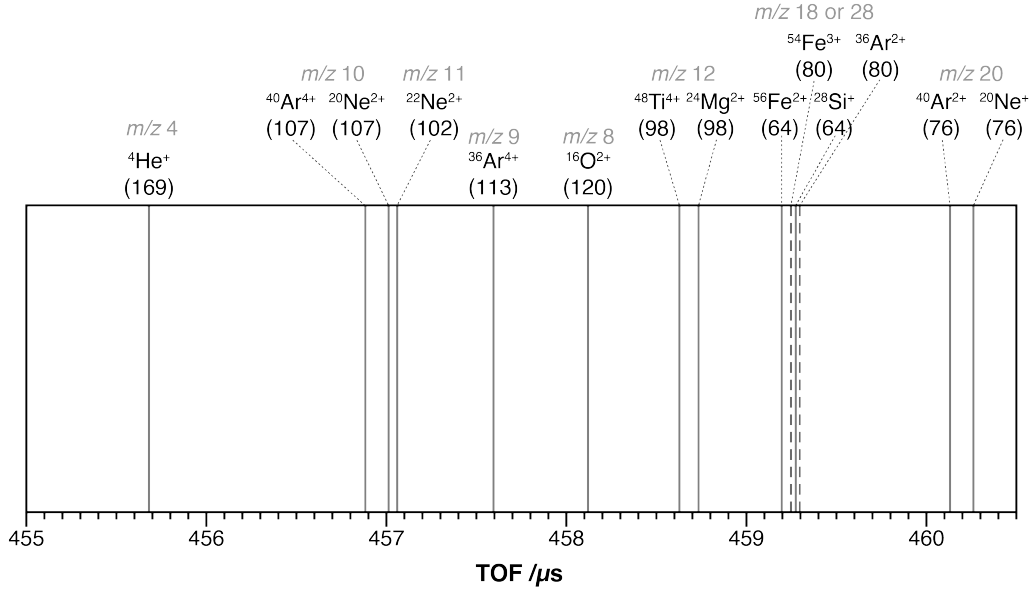


Figure 2.2: Calculated ToF for objective ions (m/z 4, 8, 9, 10, 11, 12, 20 along with either 18 or 28.). Numbers written below the ion are the lap numbers in MULTUM II.

In analysis of natural samples, many other ion peaks from minor and trace elements are detected in addition to the target ions in the ToF spectra. The ion peaks of major elements and implanted noble gases can be first assigned by comparing with calculations and respectively checking the depth profiles, which showed constant intensity during analysis and peaked depth profile. In addition, the ions of residual gases such as O, N, and Ar can be assigned through blank analysis. The exact m/z of the unknown peaks, such as minor and trace element ions, can be calculated from the ToF difference ΔT between the unknown and the known ion peak if they fly the same lap number. The following equation is used for the calculation.

$$m/z = \left(\sqrt{(m/z)_{\text{known}}} - \Delta T \times \frac{\sqrt{2eV}}{L} \right)^2 \quad (2.6)$$

2.2.5 Ion implantation simulation

The depth profile of the noble gases in the substrates were simulated using the Transport of Ions in Matter (TRIM) in the SRIM program (Ziegler et al. 2010). The simulation parameters for ilmenite and olivine are $(\text{Fe}_{0.7}\text{Mg}_{0.3})\text{TiO}_3$ and $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ for stoichiometry, and 4.47 and 3.35 cm^{-3} for density, respectively. The implantation energy was set as the same as HNA-IL and HNA-OL as listed in Table 2.1. The numbers of simulated ions were 10^6 for ^4He and ^{20}Ne , 5×10^5 for ^{40}Ar , and 10^5 for ^{22}Ne and ^{36}Ar , respectively. The depth profiles were binned into 5 nm bins and corrected to concentration based on doses. The noble gas depth profiles obtained are shown in Fig 2.3.

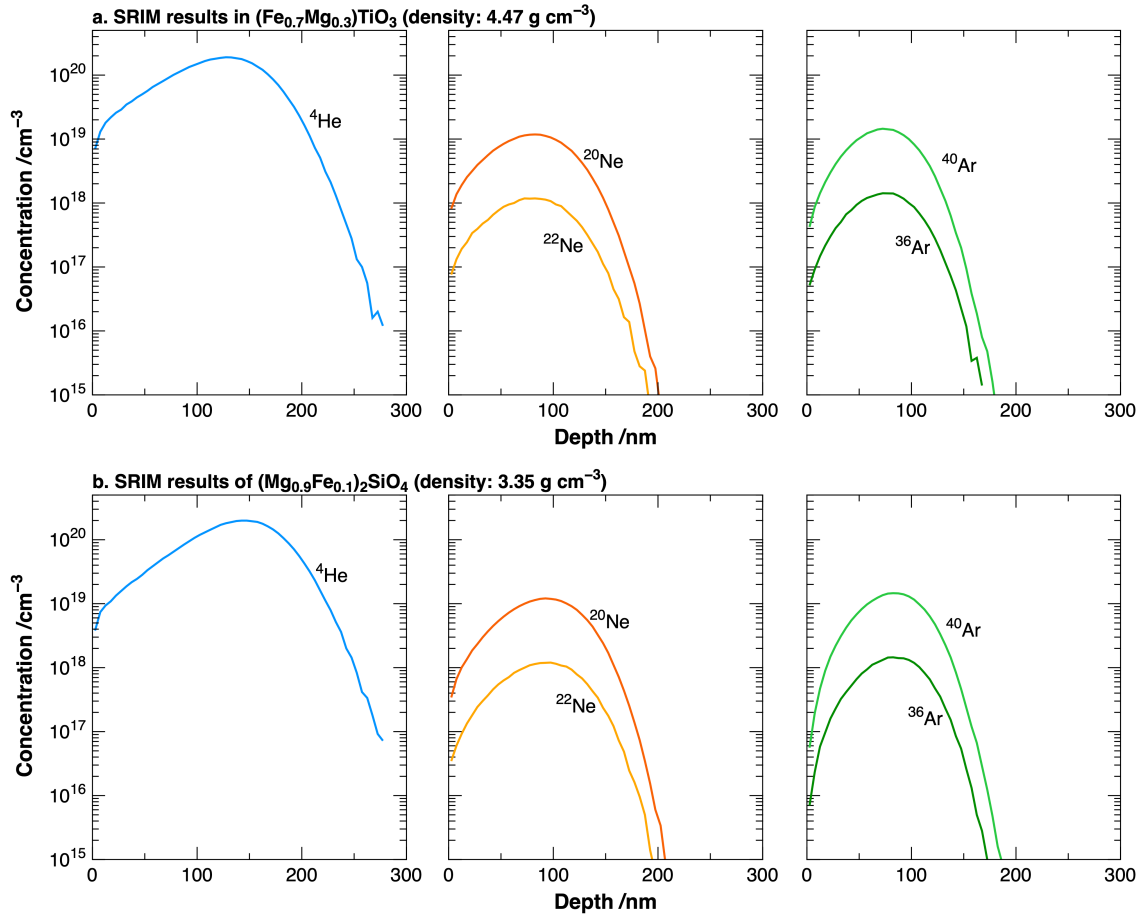


Figure 2.3: Depth profiles of noble gases obtained from the SRIM simulation. See text for detailed parameters used in the simulation. The depth profiles are obtained by calculating in 5 nm bins.

2.3 Results and Discussions

2.3.1 Time-of-flight spectra of ion implanted samples

Fig. 2.4a shows the ToF spectra obtained from HNA-Si. The full width at half maximum (FWHM) of the peak at 455.656 μs was 9 ns, which $m/\Delta m$ is $\sim 25,000$. The ion intensity was defined by integrating the signal of ± 9 ns from the peak ToF, which covers 99.05% of the peak at 455.656 μs . This range was set based on the FWHM of the peak for each analysis.

The peak assignments were applied by the procedure mentioned in the Section 2.2.4 (Fig. 2.4a). The two high-intensity peaks at 456.923 and 459.389 μs remained constant throughout the analysis (Fig. 2.4b) and were assigned to $^{30}\text{Si}^{3+}$ and $^{28}\text{Si}^+$, respectively. A long tail was observed after the $^{30}\text{Si}^{3+}$ and $^{28}\text{Si}^+$ peaks, which was a signal in the MCP induced by a large number of ions striking the channels of MCP (hereafter referred to as dark currents; Bajo and Yurimoto 2024). The peaked profile of $^4\text{He}^+$, $^{20}\text{Ne}^{2+}$, $^{22}\text{Ne}^{2+}$, $^{36}\text{Ar}^{4+}$, $^{40}\text{Ar}^{5+}$, $^{36}\text{Ar}^{3+}$, $^{40}\text{Ar}^{2+}$, and $^{20}\text{Ne}^+$, derived from ion implantation is shown in Fig. 2.4a. The peak at 458.119 μs representing adsorbed $^{16}\text{O}^{2+}$ was intense at the beginning of the depth profile and decreased rapidly toward blank intensity (Fig. 2.4b). Five peaks were observed in the ToF window of m/z 28. Based on the ToF of the $^{28}\text{Si}^+$ peak (459.389 μs) and Eq. (2.6), the peaks at 459.537 μs , 459.633 μs , and 459.839 μs are assigned as $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}^{2+}$, and $^{12}\text{C}^{12}\text{CH}_4^+$, respectively (Fig. 2.4a). The peak at 459.432 μs was assigned to the secondary ion of ^{28}Si because this peak was also detected with irradiating primary beam and without fs laser (without post-ionization). The $^{12}\text{C}^{3+}$ peak, which interfered the $^4\text{He}^+$ peak, was removed using the ion gate in the ion trajectory (Fig. 2.4a). The peaks of the target ions from the HNA-IL and HNA-OL samples were assigned using the same assignment procedure Figs. 2.5 and 2.7.

For HNA-IL, $^4\text{He}^+$ did not show interference from other peaks (Fig. 2.5a). The right-hand side slope of the $^{24}\text{Mg}^{16}\text{O}_2^+$ peak overlapped to the $^{20}\text{Ne}^+$ (Fig. 2.5g). $^{20}\text{Ne}^{2+}$ was not interfered from other ion peaks, while $^{22}\text{Ne}^{2+}$ was not fully resolved from an unknown peak (Fig. 2.5b). $^{36}\text{Ar}^{4+}$ was interfered from the left-hand side slope of the $^{27}\text{Al}^{3+}$ peak (Fig. 2.5c). However, it was less interfered from other peaks, as $^{36}\text{Ar}^{2+}$ and

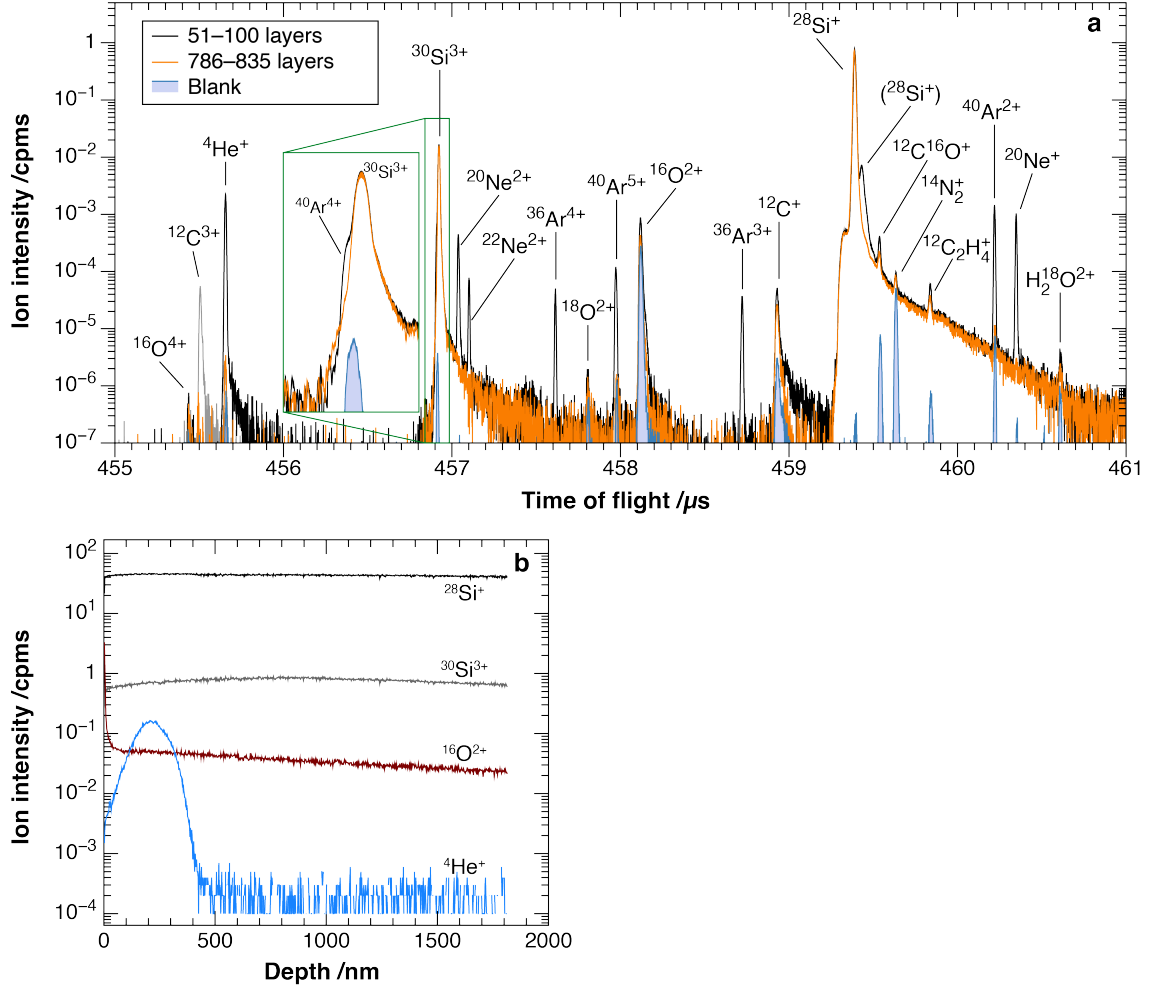


Figure 2.4: (a) ToF spectra and (b) depth profile of $^{28}\text{Si}^+$, $^{30}\text{Si}^{3+}$, $^{16}\text{O}^{2+}$, and $^4\text{He}^+$ taken from HNA-Si. Black, orange and blue line in (a) is spectra obtained from the depth of noble gas peak (51–100 layers: 110–217 nm), last 50 layers in the measurement (786–835 layers: 1708–1814 nm), and the blank signal, respectively. Gray line drawn at the range of 455–456 μs is a spectrum taken after 835 layers without removing $^{12}\text{C}^{3+}$ peak with ion gate. The ToF of the spectrum of 786–835 layers and blank are with slight offset (approximately 10 ns) to correct the ToF drifting during analysis.

$^{36}\text{Ar}^{3+}$ was not fully resolved from $^{54}\text{Fe}^{3+}$ and ($^{24}\text{Mg}^{2+} + ^{48}\text{Ti}^{4+}$), respectively (Fig. 2.6 and potentially seen in Fig. 2.5e but not observed). The ToF spectra of $^{40}\text{Ar}^{2+}$, $^{40}\text{Ar}^{4+}$, and $^{40}\text{Ar}^{5+}$ showed overlapped by ^{40}Ca ions due to the insufficient mass resolution of the analytical conditions (Figs. 2.5g, 2.5b, and 2.5d). The mass resolution using FWHM of the $^{40}\text{Ar}^{2+}$ peak in the HNA-Si spectrum was approximately 27,000 (Fig. 2.4a), but the $m/\Delta m$ between ^{40}Ar and ^{40}Ca is 190,000. Here, $^{40}\text{Ar}^{4+}$ was mainly used to match the valence with $^{36}\text{Ar}^{4+}$, and also analyzed $^{40}\text{Ar}^{2+}$ for comparison. The $^{55}\text{Mn}^{5+}$ peak was removed by the ion gate during noble gas measurements (Fig. 2.5). This operation did not affect the $^{40}\text{Ar}^{4+}$ peak, as it was operated when the ion packets of m/z 10 and 11 were well separated before a ToF of $\sim 456.9 \mu\text{s}$.

For HNA-OL, $^4\text{He}^+$ did not interference from other peaks (Fig. 2.7a). $^{20}\text{Ne}^+$ had interference from the $^{24}\text{Mg}^{16}\text{O}_2^+$ peak for the same reason as in the HNA-IL measurement (Fig. 2.7g). The tail from the $^{30}\text{Si}^{3+}$ peak, which is produced by the dark currents, slightly overlapped with both $^{20}\text{Ne}^{2+}$ and $^{22}\text{Ne}^{2+}$ peaks (Fig. 2.7b). $^{36}\text{Ar}^{4+}$ did not show interference from other peaks (Fig. 2.7c). Figs. 2.7g, 2.7b, and 2.7d show the ToF spectra of $^{40}\text{Ar}^{2+}$, $^{40}\text{Ar}^{4+}$, and $^{40}\text{Ar}^{5+}$, respectively, where ^{40}Ca ions overlap with ^{40}Ar ions similar with the HNA-IL measurement.

2.3.2 Depth profiles of noble gas in minerals

Blank-IL and blank-OL were measured with the same analytical condition and the depth profiles are shown in Fig. 2.8. The background of noble gas ions for blank-IL and blank-OL are listed in Table 2.2 with blank ^iMs (ion intensities of each residual noble gases in the sample chamber) measured continuously throughout each analysis. The noble gas background was defined as the average of 10^6 mass scans after sputtering ~ 100 nm depth to avoid contaminations on the sample surface. The error was defined as the standard deviation (1SD) of five data points obtained by binning the data into 2×10^5 mass scans. Similarly, blank ^iM is defined as the average of 10^6 mass scans, with the error determined as the 1SD of five data points by binning into 2×10^5 mass scans.

The backgrounds of blank-IL and blank-OL agree with the blank ^iMs within the standard deviation (Table 2.2) for ions with less interference from other peaks (i.e., $^4\text{He}^+$ and

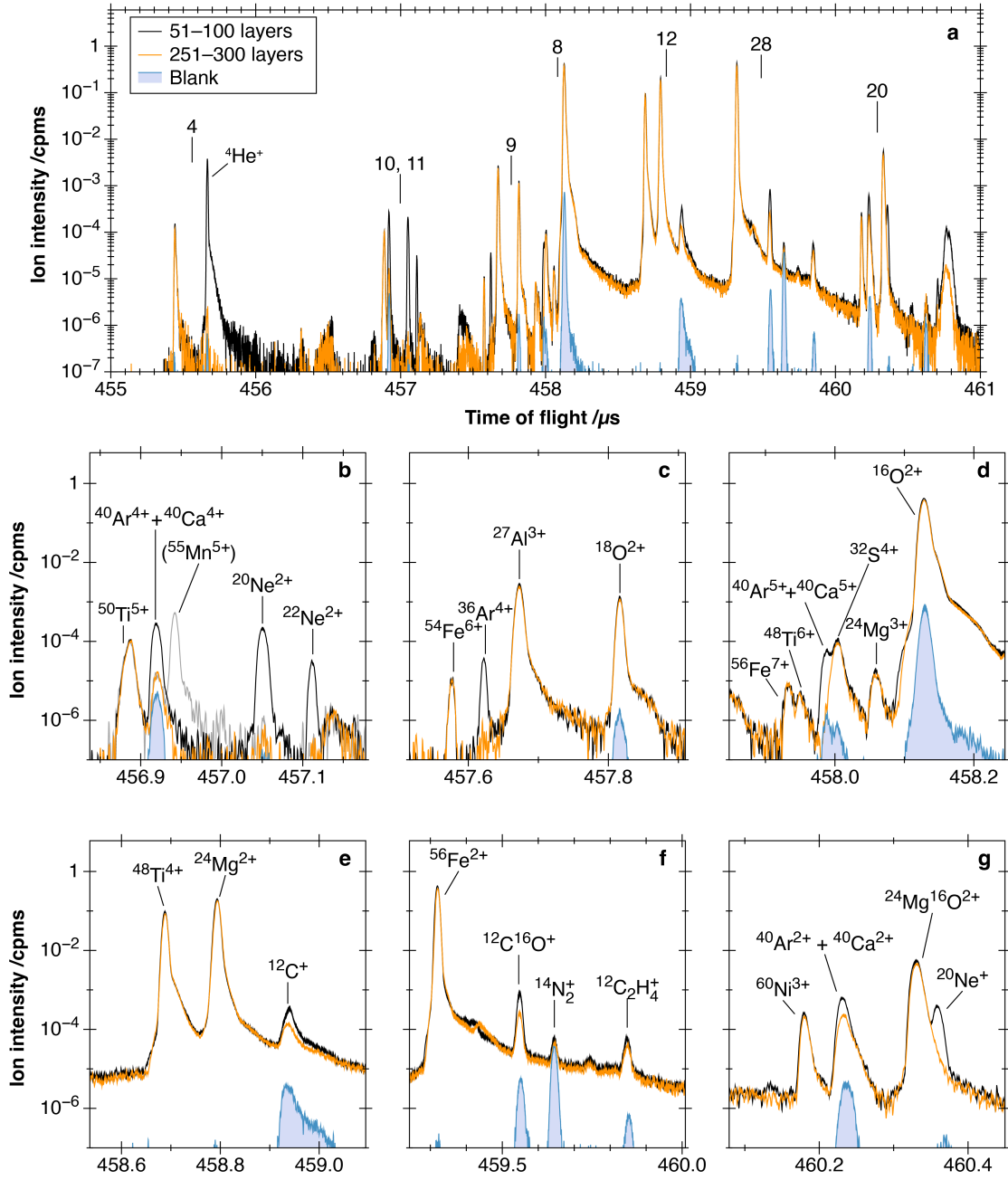


Figure 2.5: ToF spectra from HNA-IL. (b)–(g) are magnified spectra of (a). Each colors shows spectra from noble gas peak, last part of the analysis, and blank signal after analysis, respectively. The $^{55}\text{Mn}^{5+}$ peak shown by gray line in (b) is taken after 300 cycles. It is removed by ion gate because the peak interferes with the $^{40}\text{Ar}^{4+}$ and $^{40}\text{Ca}^{4+}$ peaks.

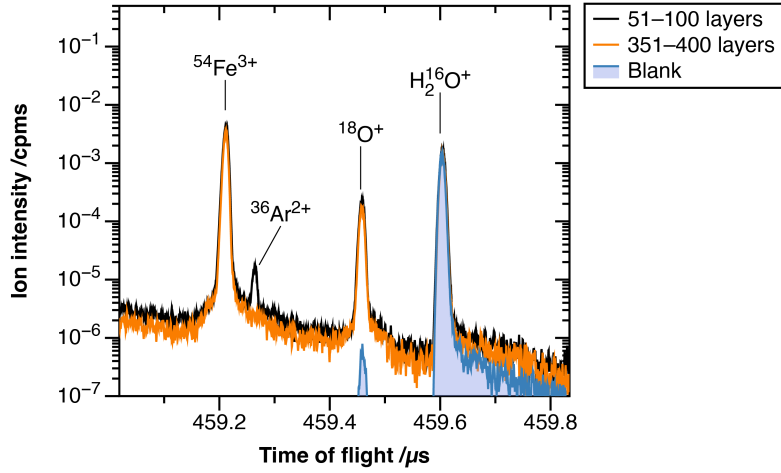


Figure 2.6: TOF spectrum of m/z 18 taken from HNA-IL, which is from data #5 in Table 2.4. This TOF window is not measured in Fig. 2.5.

$^{20}\text{Ne}^{2+}$ for blank-IL, and $^{36}\text{Ar}^{4+}$ for blank-OL). Therefore, the influence of noble gases originally contained in the minerals is smaller than that of residual gases in the sample chamber. For $^4\text{He}^+$ in blank-OL, the background is twice as high as the blank $^4\text{He}^+$. The similar results were observed by Bajo et al. (2024), who mentioned the possible sputtering of ^4He adsorbed onto the sputtered fresh surface from residual gas in the sample chamber. Therefore, the degree of adsorption may vary between materials. For the other ions, the higher backgrounds for blank-OL and blank-IL compared with blank $i\text{M}$ s are due to the interferences mentioned in the previous section.

The depth profiles of noble gases and selected major element ions of HNA-IL and HNA-OL are shown in Figs. 2.9 and 2.10. For both samples, all noble gas ions showed a peak at a depth of several tens to ~ 100 nm, which decreased to a background intensity deeper than 300 nm. The measured depth profiles were slightly distributed at the shallower depth than the simulated profiles (Fig 2.3), which is discussed later. The background is defined as the average of the last 10^6 mass scans for each noble gas isotope (Figs. 2.9a and 2.10a). The error of the background was evaluated by binning those data into 5 data points and calculating the standard deviation (2×10^5 mass scans per each point). The background and blank $i\text{M}$ values are summarized in Table 2.2.

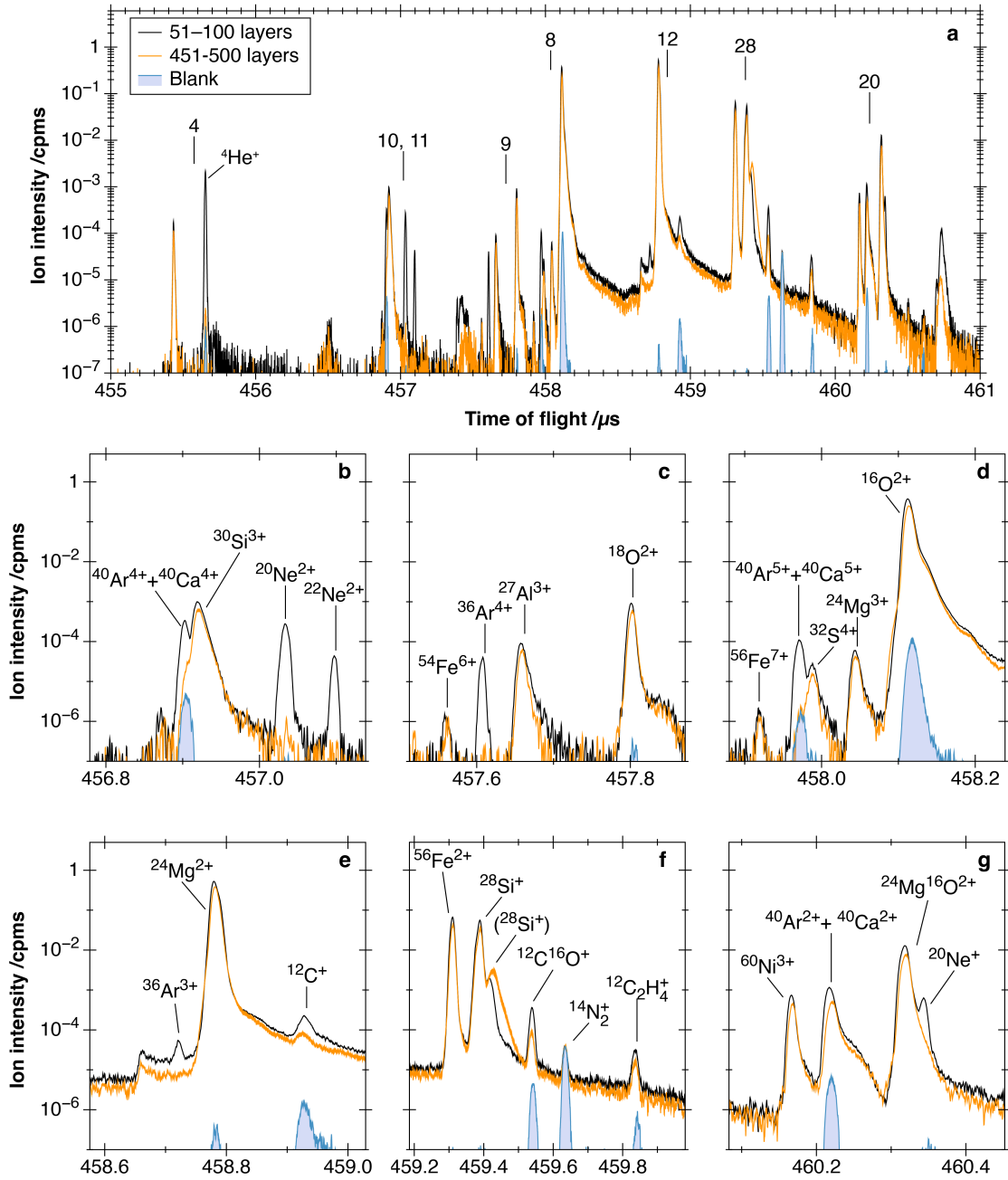


Figure 2.7: ToF spectra from HNA-OL. (b)–(g) are magnified spectra of (a). Each colors shows spectra from noble gas peak, last part of the analysis, and blank signal after analysis, respectively. ($^{28}\text{Si}^+$) in (f) is a secondary ion peak of ^{28}Si .

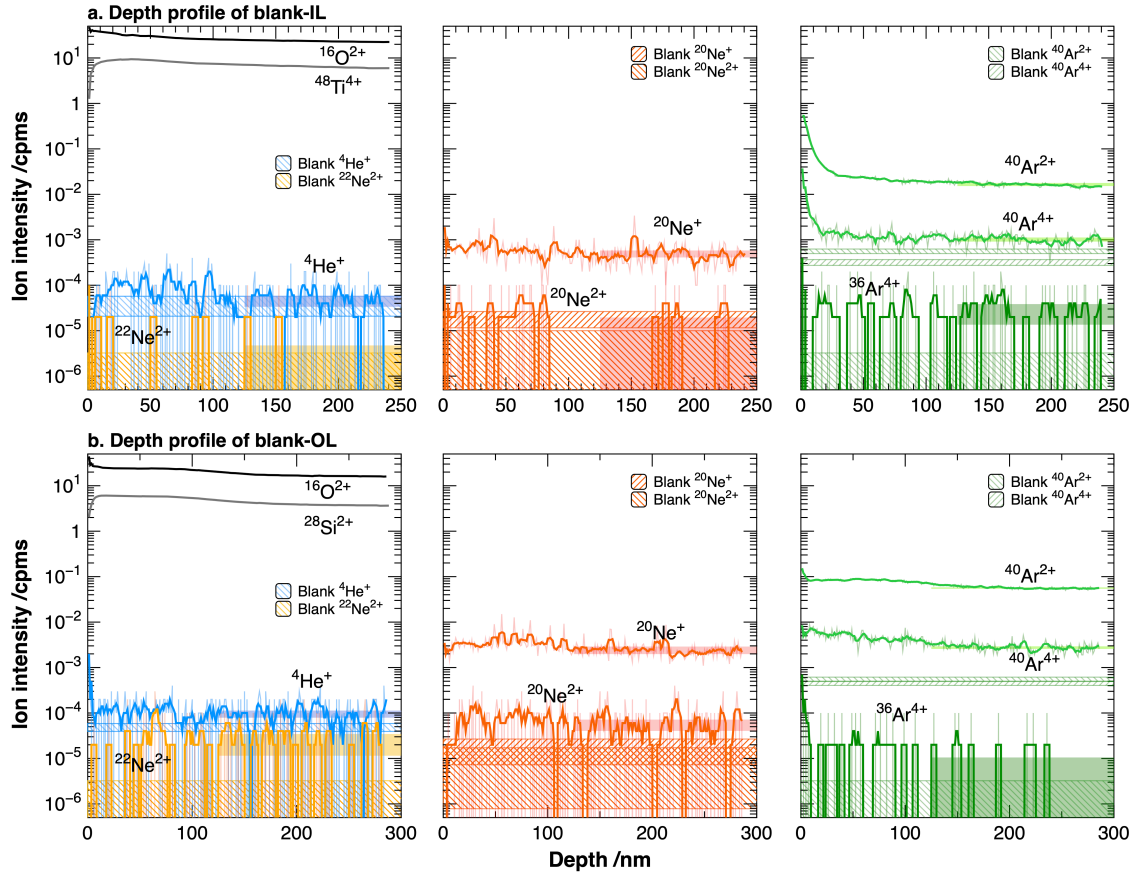


Figure 2.8: Depth profiles obtained from (a) blank-IL and (b) blank-OL. The raw data is shown as a light-colored line with the moving average as a dark solid line. The moving average was calculated over an interval of 5 data points. Blank i Ms and backgrounds for each ions are shown as a colored range corresponding to the average $\pm$ 1SD (Table 2.2)

Table 2.2: Ion signals for ${}^4\text{He}^+$, ${}^{20}\text{Ne}^{2+}$, ${}^{22}\text{Ne}^{2+}$, ${}^{36}\text{Ar}^{4+}$, and ${}^{40}\text{Ar}^{4+}$ (Units: cpms).

	${}^4\text{He}^+$	${}^{20}\text{Ne}^{2+}$	${}^{22}\text{Ne}^{2+}$	${}^{36}\text{Ar}^{4+}$	${}^{40}\text{Ar}^{4+}$
Blank-IL	$(4.6 \pm 1.2) \times 10^{-5}$	$(8.0 \pm 11.5) \times 10^{-6}$	$(2.0 \pm 2.7) \times 10^{-6}$	$(2.6 \pm 1.2) \times 10^{-5}$	$(1.0 \pm 0.1) \times 10^{-3}$
Blank ${}^i\text{M}$	$(3.9 \pm 1.8) \times 10^{-5}$	$(5.0 \pm 5.0) \times 10^{-6}$	$(1.0 \pm 2.2) \times 10^{-6}$	$(1.0 \pm 2.2) \times 10^{-6}$	$(3.2 \pm 0.5) \times 10^{-4}$
Blank-OL	$(9.6 \pm 1.7) \times 10^{-5}$	$(5.6 \pm 1.6) \times 10^{-5}$	$(2.3 \pm 1.2) \times 10^{-5}$	$(4.0 \pm 6.5) \times 10^{-6}$	$(2.8 \pm 0.2) \times 10^{-3}$
Blank ${}^i\text{M}$	$(4.9 \pm 1.0) \times 10^{-5}$	$(9.0 \pm 8.2) \times 10^{-6}$	$(1.0 \pm 2.2) \times 10^{-6}$	$(1.0 \pm 2.2) \times 10^{-6}$	$(4.5 \pm 0.4) \times 10^{-4}$
HNA-IL	$(1.1 \pm 0.1) \times 10^{-4}$	$(2.9 \pm 1.6) \times 10^{-5}$	$(5.0 \pm 6.1) \times 10^{-6}$	$(4.6 \pm 1.0) \times 10^{-5}$	$(6.6 \pm 0.4) \times 10^{-4}$
Blank ${}^i\text{M}$	$(1.6 \pm 0.8) \times 10^{-5}$	$(6.0 \pm 5.5) \times 10^{-6}$	$(1.0 \pm 2.2) \times 10^{-6}$	n.d.	$(1.5 \pm 0.2) \times 10^{-4}$
HNA-OL	$(1.1 \pm 0.3) \times 10^{-4}$	$(3.1 \pm 0.7) \times 10^{-5}$	$(4.0 \pm 4.2) \times 10^{-6}$	$(6.0 \pm 4.2) \times 10^{-6}$	$(8.1 \pm 0.3) \times 10^{-3}$
Blank ${}^i\text{M}$	$(3.0 \pm 1.0) \times 10^{-5}$	$(5.0 \pm 5.0) \times 10^{-6}$	n.d.	n.d.	$(1.4 \pm 0.2) \times 10^{-4}$

n.d.: not detected ($< 10^{-6}$ cpms)

The backgrounds of $^4\text{He}^+$ for HNA-IL and HNA-OL were higher than those of blank-IL and blank-OL, respectively (Table 2.2), which may be ascribed to the crater-edge effect. The ion image of $^4\text{He}^+$ accumulated for the last 100 measurement layers of HNA-IL is shown in Fig. 2.11a. The $^4\text{He}^+$ intensity of the outer few pixels was significantly higher than that of the central area, broadening the depth profile shown in Fig. 2.11b from the crater-edge effect. The averaged intensity of the last 100 measurement layers with changing data integration area is shown in Fig. 2.11. The intensity was nearly constant after removing the outer 7 pixels. The depth profiles shown in Fig. 2.9 removed the outer 10 pixels, sufficiently reducing the crater-edge effect. The higher backgrounds than those of blank-IL and blank-OL may have been caused by the weak halo of the primary beam. Nagata et al. (2019) reported that a very weak halo spreads out from the center of the primary beam in LIMAS. The weak halo consistently sputtered the high-concentration layer exposed on the crater edge, interfering with the signals from the crater bottom. This phenomenon was referred to as the weak halo effect. Both $^4\text{He}^+$ and $^{20}\text{Ne}^{2+}$ in HNA-IL and HNA-OL exhibited background intensities approximately three orders of magnitude lower than their peak intensities (Figs. 2.9a and 2.10a), supporting the idea of a common cause for the higher background.

The backgrounds of other ions of HNA-IL and HNA-OL were similar to those of blank-IL and blank-OL due to the respective interfering ions. The backgrounds of $^{20}\text{Ne}^{2+}$ and $^{40}\text{Ar}^{4+}$ were respectively lower than those of $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^{2+}$. For ^{20}Ne ions, this is because the $^{20}\text{Ne}^+$ peak is interfered by $^{24}\text{Mg}^{16}\text{O}^{2+}$ peak while the $^{24}\text{Mg}^{16}\text{O}^{4+}$ interfering with $^{20}\text{Ne}^{2+}$ was not observed. This is considered to be due to the balance between the fourth-ionization energy and the dissociation energy of the $^{24}\text{Mg}^{16}\text{O}$ molecule. For ^{40}Ar ions, $^{40}\text{Ca}^{4+}$ is much less ionized than $^{40}\text{Ca}^{2+}$, because the ionization energies of argon and calcium for the divalent ions are 27.6 and 11.9 eV, respectively, whereas for the tetravalent ions, they are 59.6 and 67.3 eV, respectively, showing an inversion in their relative magnitudes (Kramida et al. 2024). Considering these observations, $^{20}\text{Ne}^{2+}$ and $^{40}\text{Ar}^{4+}$ peaks for ^{20}Ne and ^{40}Ar were used for measurements, respectively.

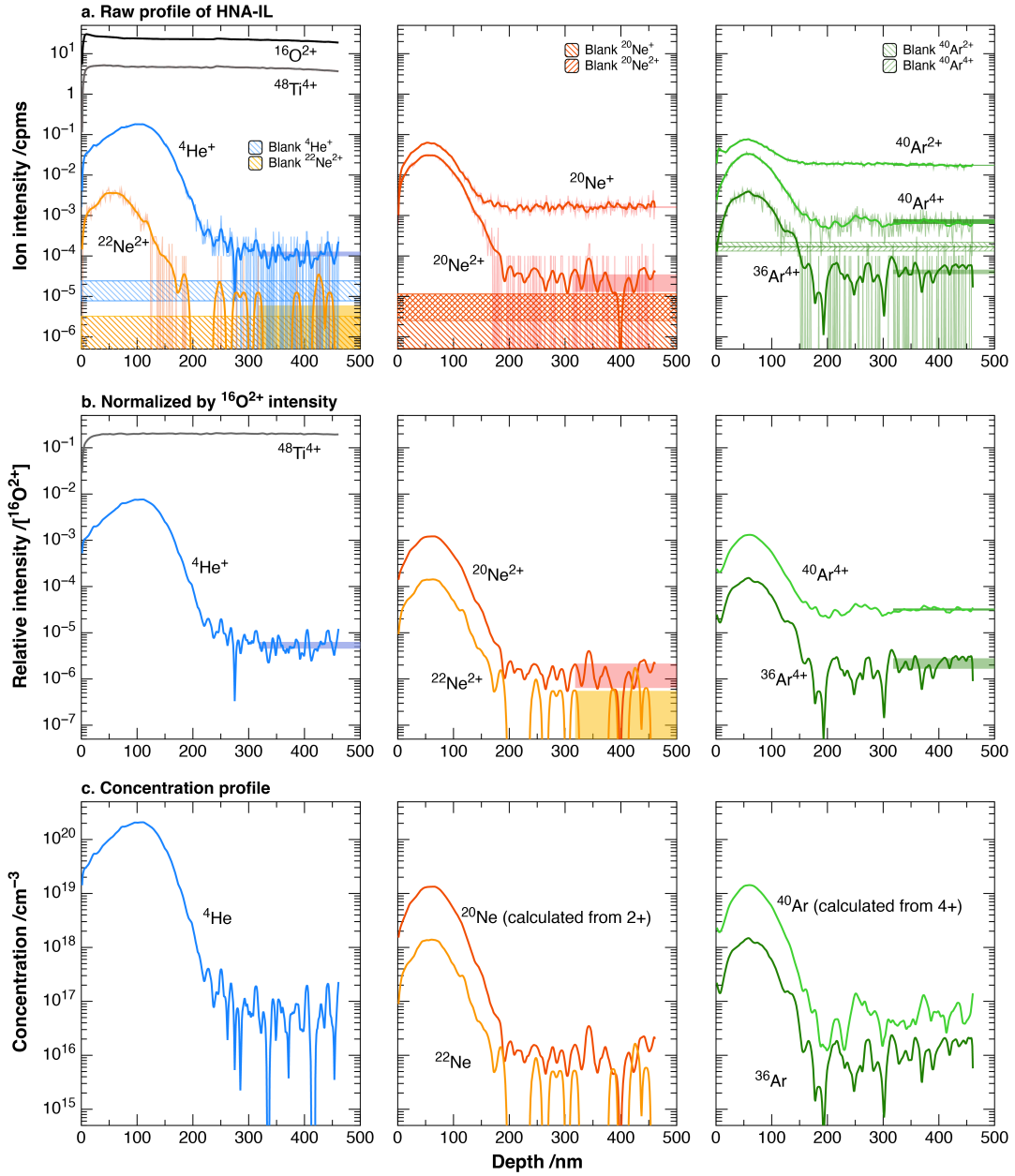


Figure 2.9: Noble gas depth profiles of HNA-IL. (a) Raw profile of noble gas and major element ions. The raw data is shown in a light-colored line, and the moving average in a dark solid line. The moving average is calculated over an interval of 5 data points. Blank i Ms and backgrounds for each ion are shown as colored range, which corresponds with the average $\pm 1\text{SD}$ (Table 2.2). (b) Ion intensities normalized by $^{16}\text{O}^{2+}$ intensity. The moving average with an interval of 5 data points are shown. $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^{2+}$ is omitted to simplify the figure. The colored range is the baseline with 1SD for each ion. The mean value is calculated using the last 10^6 mass scans and the standard deviation is calculated by binning data points into 5 points, as same as backgrounds. (c) The baseline was subtracted from the normalized profile and corrected to concentration using Eqs. 2.1 and 2.2. The moving average with an interval of 5 data points are shown.

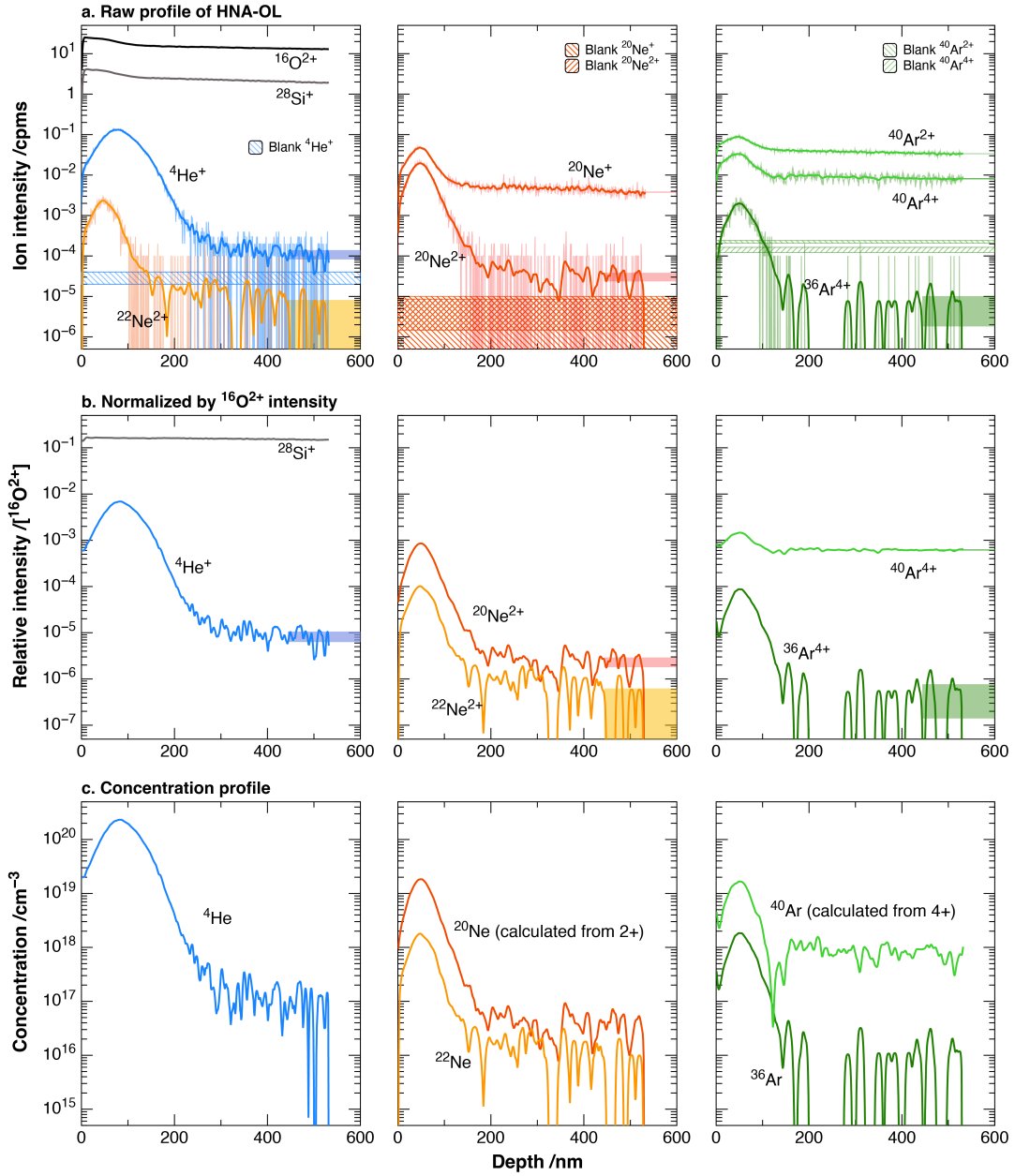


Figure 2.10: Noble gas depth profiles of HNA-OL. (a) Raw profile of noble gas and major element ions. The raw data is shown in a light-colored line, and the moving average in a dark solid line. The moving average is calculated over an interval of 5 data points. Blank ⁱMs and backgrounds for each ion are shown as colored range, which corresponds with the average $\pm 1\text{SD}$ (Table 2.2). (b) Ion intensities normalized by ¹⁶O²⁺ intensity. The moving average with an interval of 5 data points are shown. ²⁰Ne⁺ and ⁴⁰Ar²⁺ is omitted to simplify the figure. The colored range is the baseline with 1SD for each ion. The mean value is calculated using the last 10⁶ mass scans and the standard deviation is calculated by binning data points into 5 points, as same as backgrounds. (c) The baseline was subtracted from the normalized profile corrected to concentration using Eqs. 2.1 and 2.2. The moving average with an interval of 5 data points are shown.

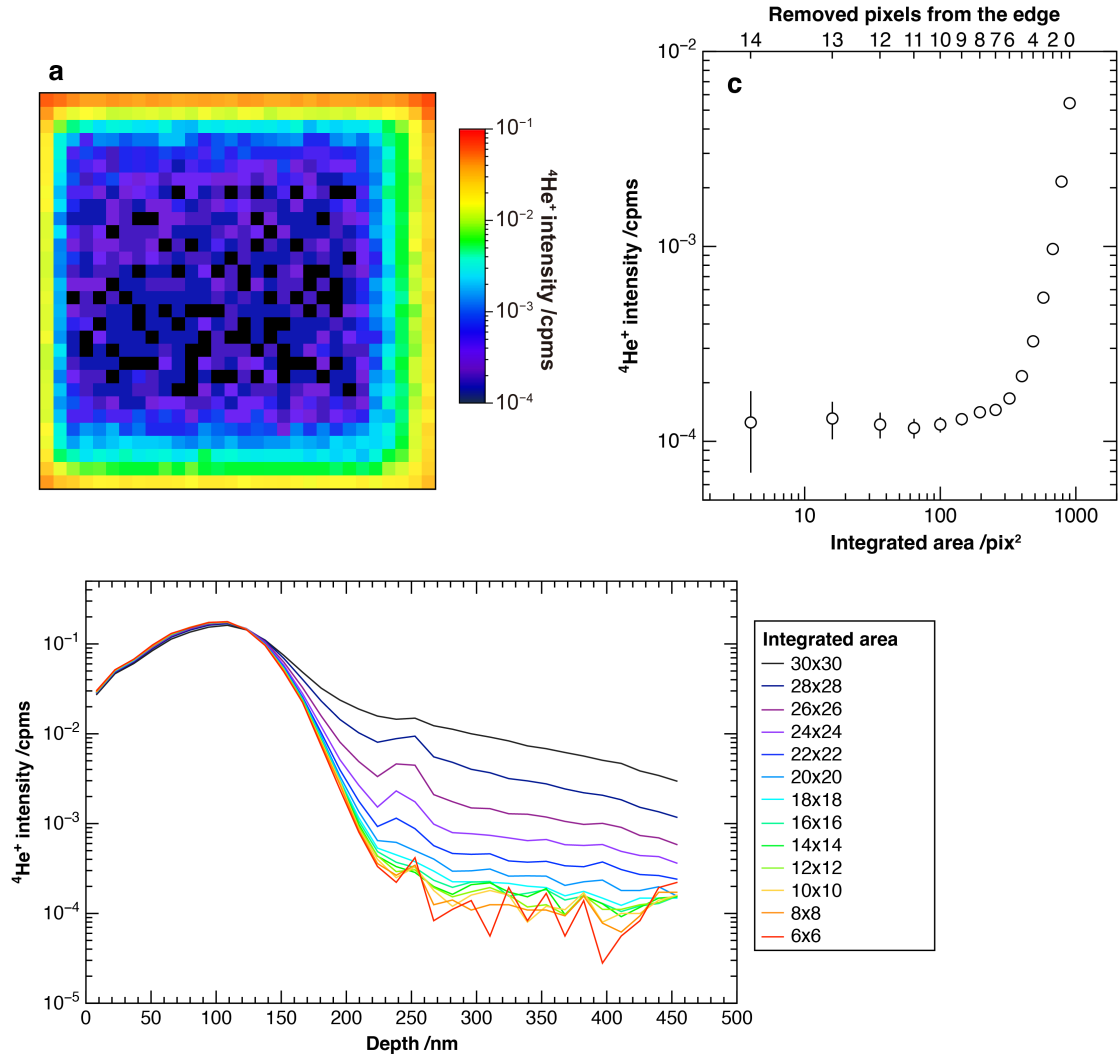


Figure 2.11: (a) $^4\text{He}^+$ image of HNA-IL accumulated for the last 100 layers, (b) depth profile binned within 10 measurement layers with changing integration area, and (c) averaged $^4\text{He}^+$ intensity of the last 50 measurement layers versus integration area from the center. Outer 7 pixels are significantly affected by crater edge, so the shapes of the profile after the peak taken from large integrated areas are worse than those from smaller area.

2.3.3 Discrepancy between the measured and simulated profiles

The peak depth of noble gases in HNA-IL and HNA-OL were shallower than the simulated profiles. Similar inconsistency has been observed in previous ion implantation experiments (e.g., Ross and Sévigny 2003, Gorondy-Novak et al. 2017). The TRIM calculation assumes an amorphous material, and thus differs from actual ion implantation experiments in some perspectives, such as the stopping power depending on the crystal structure or the charge-up of the samples surface. The discrepancy observed here is likely due to the uncertainties of SRIM model in low energy implantation or charge-up of the sample surface rather than changes of the profile after implantation due to, for example, noble gas diffusion in solids. The inconsistency between measured and simulated profiles present that the true depth profile can only be obtained by depth profiling for the ion implantation samples.

I note here that this effect is less effective for natural solar wind irradiation because solar wind includes both cations and electrons, and thus, electronic charge-up will not occur.

Here, whether that the ion implanted samples contain the expected fluence of the noble gas even with a discrepancy between measured and simulated profiles. If the irradiated ^4He was ideally trapped in the target substrates, the number of ^4He atoms sputtered from the analyzed area ($6.0 \times 8.3 \mu\text{m}^2$) is 9.8×10^8 atoms. The useful yield of ^4He in the HNA-Si, HNA-IL, and HNA-OL analyses are calculated to be 1.30×10^{-4} , 1.26×10^{-4} , and 1.28×10^{-4} , respectively. The useful yields of HNA-IL and HNA-OL are almost the same as that of HNA-Si. In contrast to HNA-IL and HNA-OL, the measured ^4He depth profile of HNA-Si agrees well with the simulated profile (Fig 2.12). Si wafer can preserve implanted ^4He up to doses of 10^{16} cm^{-2} with energy of 15 and 27 keV (Yurimoto et al. 2016). For olivine and ilmenite, Futagami et al. (1990) demonstrated that the ^4He dose and the trapped ^4He were comparable at doses below 10^{16} cm^{-2} and energies of 3.6 keV. The comparable useful yield between samples obtained in this study and results from previous studies strongly suggests that the sample prepared here is appropriate as a reference material for in situ noble gas analyses.

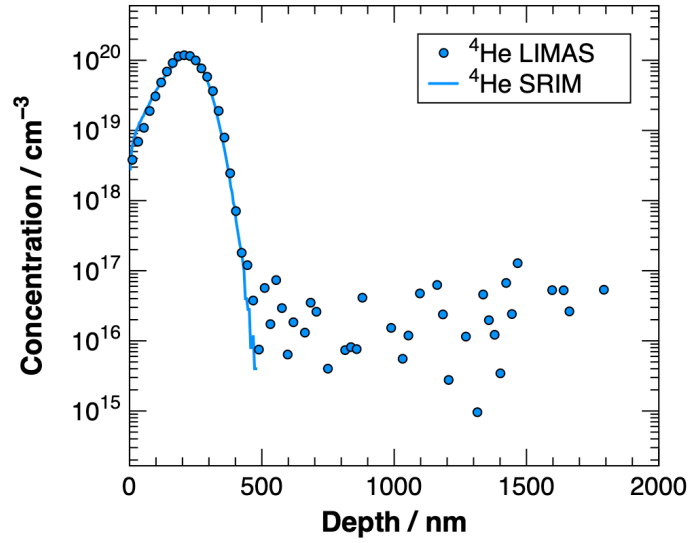


Figure 2.12: The measured and simulated ^4He concentration profile of HNA-Si. Both profiles well match with each other until the concentration reaches to $\sim 10^{17} \text{ cm}^{-3}$.

2.3.4 Detection limits of noble gases

The ion intensity profile of HNA-IL and HNA-OL are normalized with $^{16}\text{O}^{2+}$ profile (Fig. 2.9b and 2.10b) to calculate RSF_{IM} using Eq. 2.1 (Figs. 2.9b and 2.10b). The baseline was calculated using the last 10^6 mass scan. The baseline was subtracted from the relative intensity and calculated the concentration profile using Eq. (Figs. 2.9c and 2.10c). The detection limits were defined by multiplying RSF_{IM} to 3SD of the baseline. The standard deviation was calculated by binning the last 10^6 mass scan within 2×10^5 mass scan. The detection limits for each noble gases ranged from 9×10^{15} to $9 \times 10^{17} \text{ cm}^{-3}$ depending on each interference and standard deviation of base lines. Detection limits of all noble gases obtained here are summarized in Table 2.3. The detection limits of ^{40}Ar was different between two samples. This is due to the differences in calcium abundance in Monastery ilmenite and San Carlos olivine. In addition, detection limits of ^4He and ^{20}Ne also differed between the two samples, which could be due to slight differences in the wak halo effect.

Solar wind noble gases are concentrated on the very surface ($<100 \text{ nm}$) of extraterrestrial materials (Müller et al. 1976). Based on single grain analyses of lunar ilmenites (Nichols et al. 1994), the concentrations of ^4He , ^{20}Ne , ^{22}Ne , and ^{36}Ar are estimated to be approximately 10^{21} , 10^{19} , 10^{18} , and 10^{18} cm^{-3} , respectively, assuming that all noble gases were concentrated to the top 100 nm of the spherical grain. The detection limits

achieved here were approximately two orders of magnitude lower than the concentrations in lunar soils, allowing for the depth profiling of ^4He , ^{20}Ne , ^{22}Ne , and ^{36}Ar from the grain surface with extremely high spatial resolution with dynamic range of approximately two orders of magnitude.

Table 2.3: Detection limits and interferences for HNA-IL and HNA-OL

HNA-IL				HNA-OL		
Isotopes	Measured ion	Detection limit /cm ⁻³	Major interference	Measured ion	Detection limit /cm ⁻³	Major interference
⁴ He	⁴ He ⁺	7×10^{16}	WHE or Residual gas	⁴ He ⁺	2×10^{17}	WHE or Residual gas
²⁰ Ne	²⁰ Ne ²⁺	3×10^{16}	WHE or Residual gas	²⁰ Ne ²⁺	4×10^{16}	³⁰ Si ³⁺ tail
²² Ne	²² Ne ²⁺	9×10^{15}	WHE or Residual gas	²² Ne ²⁺	2×10^{16}	³⁰ Si ³⁺ tail
³⁶ Ar	³⁶ Ar ⁴⁺	2×10^{16}	²⁷ Al ³⁺ + residual gas	³⁶ Ar ⁴⁺	2×10^{16}	WHE or Residual gas
⁴⁰ Ar	⁴⁰ Ar ⁴⁺	5×10^{16}	⁴⁰ Ca ⁴⁺ + residual gas	⁴⁰ Ar ⁴⁺	9×10^{17}	⁴⁰ Ca ⁺ + ³⁰ Si ³⁺

WHE: Weak halo effect

2.3.5 Reproducibility of noble gas analysis by LIMAS

Eleven measurements on HNA-IL were conducted to calculate RSFs for concentrations of each noble gas isotope and at selected elemental and isotopic ratios (Fig. 2.13, Table 2.4). Each measurement run took about 12 hours, and the eleven measurements were conducted over a period of 6 months. The standard deviations by counting statistics for each run were less than 5%. The reproducibility of RSFs including $RSF_{i,j}$ and RSF_{iM} showed a variation of 11–31%, which was much larger than the statistical errors (Fig. 2.13).

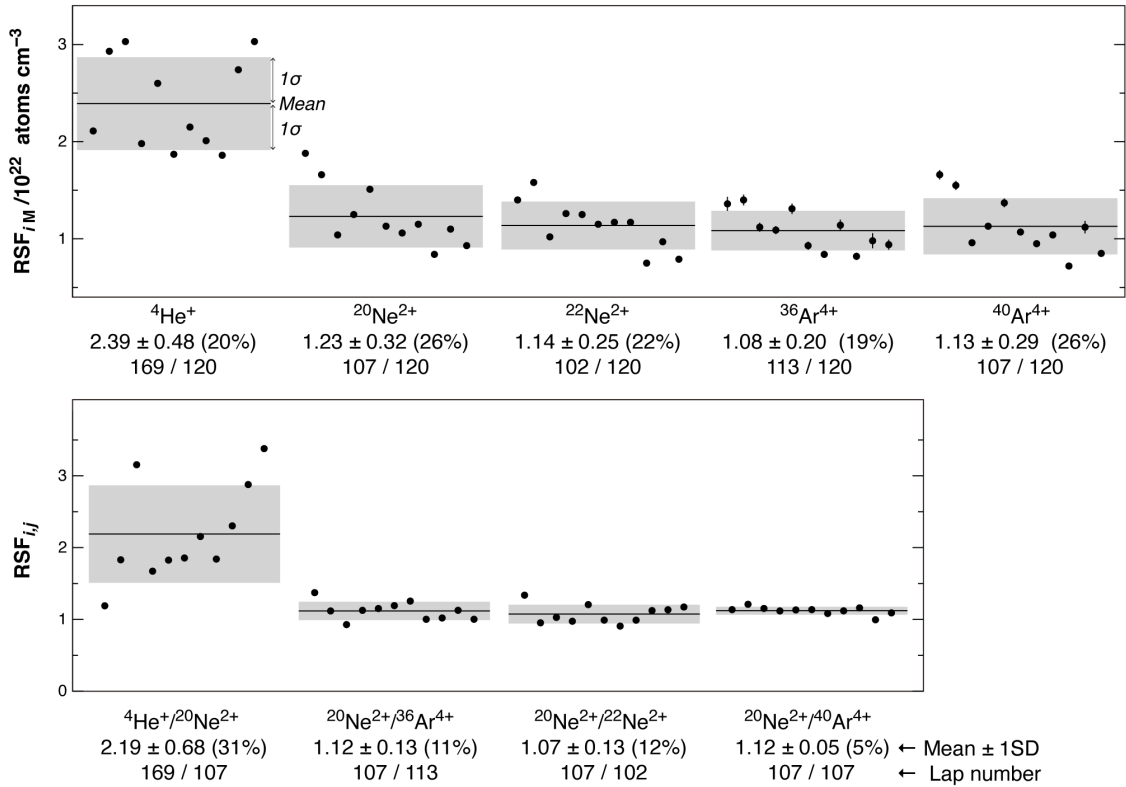


Figure 2.13: Reproducibility of RSFs in 11 HNA-IL measurements. Error bars are counting error in 1SD, which most of it is smaller than the symbol. Mean value with 1SD is noted below. Data are listed in Table 2.4.

The instrumental mass fractionation in the LIMAS arises primarily from two factors: (a) change of laser post-ionization efficiency due to the differences in ionization efficiencies between isotopes or elements, and (b) the differences in ion transmittance into MULTUM II and within MULTUM II between different lap numbers (Tonotani et al. 2016) for ions. These could also vary between independent measurements. $^{20}\text{Ne}^{2+}$ and $^{40}\text{Ar}^{4+}$ are both measured after 107 laps in the MULTUM II, and thus, $RSF_{20,40}$ is only affected

Table 2.4: RSFs from 11 HNA-IL measurements

#	RSF _{iM} / $\times 10^{22} \text{ cm}^{-3}$					RSF _{i,j}		
	⁴ He	²⁰ Ne	²² Ne	³⁶ Ar	⁴⁰ Ar	4,20	20,36	20,22
1	2.11	1.88	1.40	1.36	1.66	1.19	1.37	1.34
2	2.93	1.66	1.58	1.40	1.55	1.83	1.12	0.95
3	3.03	1.04	1.02	1.12	0.96	3.15	0.93	1.03
4	1.98	1.25	1.26	1.09	1.13	1.67	1.13	0.97
5	2.60	1.51	1.25	1.31	1.37	1.83	1.15	1.21
6	1.87	1.13	1.15	0.93	1.07	1.86	1.19	0.99
7	2.15	1.06	1.17	0.84	0.95	2.15	1.25	0.91
8	2.01	1.15	1.17	1.14	1.04	1.84	1.00	0.99
9	1.86	0.84	0.75	0.82	0.72	2.30	1.02	1.12
10	2.74	1.10	0.97	0.98	1.12	2.88	1.13	1.13
11	3.03	0.93	0.79	0.94	0.85	3.38	1.00	1.17
Average	2.39	1.23	1.14	1.09	1.13	2.19	1.12	1.07
1SD (%)	19	25	21	18	24	31	11	12

by factor (a). Its standard deviation is 5%, which is the highest reproducibility, and this indicates that relative ionization efficiencies between Ne^{2+} and Ar^{4+} are stable within independent measurements. On the other hand, $\text{RSF}_{20,22}$ is affected solely by factor (b) because isotopes would have similar ionization efficiency each other, and the standard deviation was 12%. This is only due to the change of relative ion transmittance between ions with 102–107 laps in the MULTUM II between independent measurements. The standard deviations of $\text{RSF}_{20,36}$ and $\text{RSF}_{4,20}$ are 11% and 31%, respectively. The former reflects the propagation of the reproducibility of factors (a) and (b), with factor(b) being the dominant contributor because factor (a) little affects between Ne^{2+} and Ar^{4+} . The latter shows the worst reproducibility because the flight path length of $^4\text{He}^+$ is ~ 1.5 times longer than Ne and Ar ions measured here (Fig. 2.2), and it would be more sensitive to factor (b). In addition, ionization efficiency of $^4\text{He}^+$ may also variates relative to Ne^{2+} and Ar^{4+} because of the extreme high ionization energy (Kramida et al. 2024). The standard deviations of RSF_{iM} are in the range of 19–26% in 1SD. Both factors (a) and (b) affects here. In addition, the calculation of the RSF_{iM} uses the sputtering rate (d/n in Eq. 2.1), which includes the measurement errors of the laser microscope of $\sim 5\%$.

Fig. 2.14 shows the measured and SRIM simulated $^{20}\text{Ne}/^{22}\text{Ne}$ depth profiles. The simulation suggests that the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of HNA-IL in the 0–100 nm range was maintained at 10. The measured ^{20}Ne and ^{22}Ne data were binned to make the counting error for the $^{20}\text{Ne}/^{22}\text{Ne}$ less than 10%, which is lower than the reproducibility of $^{20}\text{Ne}/^{22}\text{Ne}$ analyses (standard deviation of $\text{RSF}_{20,22}$). As a result, 13 data points were obtained within the 0–100 nm range. The mean value of these points was 10.1 ± 0.9 , which the 1SD is comparable to the counting error of each data point. This indicated that the isotopic ratio during the single depth profiling were sufficiently uniform within the error. The depth profile of neon isotopic ratio could be measured at a depth resolution of ~ 10 nm with a precision of 10% for each depth.

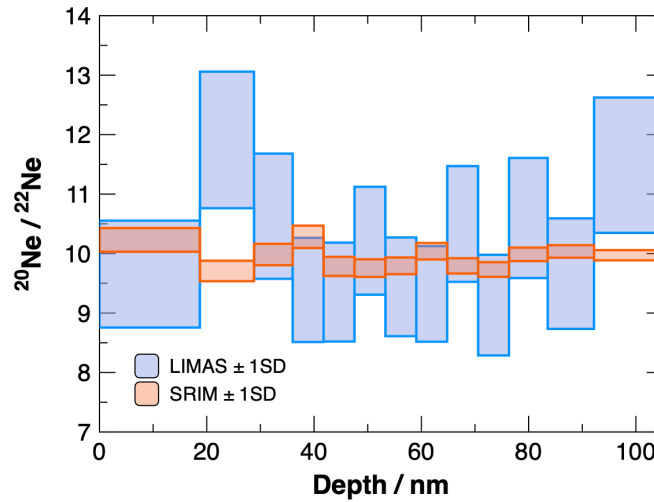


Figure 2.14: $^{20}\text{Ne}/^{22}\text{Ne}$ ratio with depth from HNA-IL and SRIM. LIMAS data are binned to make the counting error to less than the $\pm 10\%$, which error is shown as a blue range. SRIM depth profile calculated within 5 nm bin is shown with the counting error in 1SD. SRIM result shows that $^{20}\text{Ne}/^{22}\text{Ne}$ in the < 100 nm region is almost constant at 10. The relative standard deviation of 15 plots measured by LIMAS is 8%, which indicates that the counting error constrain the uncertainty for each data point in depth.

The reproducibility of the RSFs estimated here was evaluated by repeated measurements of the same reference sample. However, the random error between a reference sample and natural mineral grains may be larger than that estimated from repeated analyses of a single sample. Otsuki et al. (2021) repeatedly analyzed both a polished section of Monastery ilmenite and multiple grain samples prepared by crushing the same ilmenite, and evaluated the reproducibility of the average ion intensity ratios ($^{24}\text{Mg}^+ / ^{16}\text{O}^+$,

$^{48}\text{Ti}^{2+}/^{16}\text{O}^+$, and $^{56}\text{Fe}^{2+}/^{16}\text{O}^+$). As a result, the standard deviations obtained from ten repeated analyses of the polished section were 10–18%, whereas those from fourteen analyses of six individual grains were larger, ranging from 15–33%. This indicates that the reproducibility for particle samples may be degraded by approximately a factor of 1.5 to 2 compared to polished reference samples.

The single-grain analyses of lunar ilmenites showed that the concentrations of ^4He , ^{20}Ne , and ^{36}Ar varied by two to three orders of magnitude among individual grains (Nichols et al. 1994). Consequently, the reproducibility of RSF_{IM} ($\sim 20\%$ for all isotopes) was sufficient for the concentration analyses, even considering the degradation of reproducibility for particle samples. $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios provide insights into the degassing of light noble gases from lunar soils. The single-grain analyses of lunar ilmenites revealed $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios of 34–495 and 6–40, respectively, which are the minimum and maximum values of ilmenite grains separated from lunar soil 71501 reported by Nichols et al. (1994). Thus, the reproducibility of $\text{RSF}_{4,20}$ and $\text{RSF}_{20,36}$ (31% and 11%, respectively) was sufficient to estimate the bulk $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios in lunar ilmenites. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of lunar ilmenite was ~ 14 at the surface and ~ 11 in the subsurface region (Benkert et al. 1993). The reproducibility of $\text{RSF}_{20,22}$ ($\sim 12\%$) and the $^{20}\text{Ne}/^{22}\text{Ne}$ depth profile obtained using the LIMAS suggested that the fractionation of Ne isotopes could be visualized with actual depth, allowing for the more precise characterization of the implantation profile of solar wind noble gases in extraterrestrial materials.

2.3.6 Applicability to other extraterrestrial samples

This study demonstrates a measurement technique optimized for ilmenite and olivine, because measurements on lunar and asteroidal regolith samples are on the focus. The results of this study indicate that one critical factor for the optimization is to consider the sample composition, which influences detection limits due to interfering ions. For example, in materials with higher aluminum or silicon content, interferes such as $^{27}\text{Al}^{3+}$ to $^{36}\text{Ar}^{4+}$ or $^{30}\text{Si}^{3+}$ and $^{40}\text{Ca}^{4+}$ overlapping with $^{20}\text{Ne}^{2+}$ and $^{40}\text{Ar}^{4+}$ may become significant. In such cases, the ToF conditions and selected ions to be measured optimized in this study

may not be ideal, necessitating modifications to measurement parameters according to the discussion in this study. Preparation of ion-implanted reference samples is also necessary in such cases.

A possible application of this method in addition to lunar and asteroidal regolith materials is for noble gases implanted in presolar grains or interplanetary dust particles, whose samples sizes are much smaller than typical lunar or asteroidal sample sizes. To ensure high depth resolution for the depth profiling, a large smooth surface relative to the primary beam diameter is required. Therefore, a smaller primary beam diameter is needed. In order to achieve it, the primary beam current must be reduced. However, reducing the beam current leads to lower ion intensities per mass scan, which, in turn, raises the detection limit for noble gases.

Despite these challenges, the method presented here represents a novel approach to obtaining depth profiles of He, Ne, and Ar isotopes and their compositions based on an absolute depth scale, which has not been previously achieved.

2.4 Conclusions

^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar co-implanted ilmenite and olivine substrates were prepared as a reference materials of solar wind irradiated regolith materials. The analytical conditions of the LIMAS were optimized for multi-isotope depth profiling of ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar , and major elements of ilmenite and olivine. All target ions, except for ^{40}Ar , were well separated from the interference ions and determined using the ion assignment procedures for ilmenite and olivine substrates.

The depth profiles of ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar were obtained by sputtering an area of $\sim 6 \times 8 \mu\text{m}^2$, and the detection limits for ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar were respectively 7×10^{16} , 3×10^{16} , 9×10^{15} , 2×10^{16} , and $5 \times 10^{16} \text{ cm}^{-3}$ for ilmenite, and 2×10^{17} , 4×10^{16} , 2×10^{16} , 2×10^{16} , and $9 \times 10^{17} \text{ cm}^{-3}$ for olivine.

The reproducibility of RSFs to calculate noble gas compositions and concentrations were evaluated. The reproducibility of RSFs between independent measurement runs was in the 5% to 31% range (1SD). The stability of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios during depth profiling was restricted by counting errors. Therefore, this analytical method can be used to analyze solar wind noble gases in extraterrestrial materials. Based on the depth profiling of noble gases, this approach can reveal past solar activity and the underlying mechanisms of solar wind implantation and degassing processes.

The original data of Figs. 2.9 and 2.10 are available as online material of Otsuki et al. (2025). <https://doi.org/10.1039/d4ja00430b>.

Chapter 3

Depth-dependent Mass Fractionation of Solar Wind Noble Gases

3.1 Introduction

The lunar regolith has been exposed to the solar wind (SW), thus preserving past SW records (e.g., Eberhardt et al. 1970, Obase et al. 2025, Obase and Nakashima 2023, Pepin et al. 1970, Wieler 2023). Noble gases, particularly He, Ne, and Ar, are sensitive tracers for implanted SW in lunar materials, as they are significantly depleted in the materials due to their highly volatile nature. The implanted solar noble gases are known to be concentrated near the grain surfaces (Hintenberger et al. 1970, Eberhardt et al. 1972, Müller et al. 1975). Ever since these early studies and for a long time thereafter, variable isotopic compositions of noble gases released in stepwise heating analyses were thought to possibly reveal the presence of a second isotopically heavier component of solar Ne in addition to the classical SW (e.g., Pepin et al. 1970, Reynolds et al. 1970, Hohenberg et al. 1970, Black 1972, Etique et al. 1981). Caution was also expressed, however, that the data might be a consequence of slightly different implantation depths of the different Ne isotopes in the SW or isotopic fractionation upon stepwise degassing. Support for the two-component interpretation seemed to be provided by the first in-situ analyses of solar energetic particles (SEP, in the energy range of tens of MeV per nucleon), which

This chapter is based on manuscript under review in the *Earth and Planetary Science Letters*.

indeed yielded $^{20}\text{Ne}/^{22}\text{Ne}$ values considerably lower than the SW composition (Mewaldt et al. 1979), although fluxes of high-energy SEPs measured in space are many orders of magnitude too low to easily explain the lunar data. A later key argument in favor of the existence of the isotopically heavy Ne as an independent component of solar origin was provided by experiments releasing noble gases by stepwise in-vacuo etching of lunar soils, in which later steps released Ne with $^{20}\text{Ne}/^{22}\text{Ne}$ values of about 11.2, much lower than the SW ratio of about 13.8 known from the Apollo Solar Wind Composition experiment (cf. Geiss et al. 2004). The isotopically heavy Ne was by then dubbed “SEP-Ne” (e.g., Wieler et al. 1986, Benkert et al. 1993). The “SEP-component” in extraterrestrial samples became widely accepted, despite the fact that its apparent unexpectedly large abundance remained a problem. A few more historical details are given by Wieler et al. (2007) and Wieler (2023).

To rule on the “SEP conundrum”, a special Bulk Metallic Glass (BMG) target was flown on the Genesis mission (Burnett et al. 2003, Jurewicz et al. 2003). This material etches very homogeneously in nitric acid, and stepwise in-vacuo etching resulted in a very good depth resolution of the isotopic composition of implanted noble gases implanted by the bulk solar wind during the 2.3 years of Genesis exposure. This allowed Grimberg et al. (2006; 2008) to conclude that “SEP” is not an independent component but indeed reflects the fact that different isotopes of an element implanted with identical speed distribution have slightly different implantation depths. This conclusion was mainly based on two observations. First, the variations of the Ne isotopic composition during the stepwise etching were very similar in the BMG and the lunar samples. In particular, the lowest observed $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in the BMG (known to not contain sizeable amounts of Ne with energies higher than SW values) were very close to the values of trapped “SEP-Ne” in the lunar samples. Second, the Ne isotopic depth profile in the BMG could be very well reproduced by SRIM simulations (Ziegler 2004) for a uniform composition of SW with the measured speed distribution during the Genesis exposure period.

The heavy pseudo-component is therefore now termed fractionated solar wind (fSW) (Wieler et al. 2007). Strictly speaking, of course, the Genesis experiment could not conclusively exclude that lunar samples with their long exposure history might contain a record of hypothetical high activity phases of the Sun (cf. Sonett et al. 1991), though

likely hidden within the more abundant fSW gases. To evaluate this possibility by noble gas depth profiling in grains from the lunar regolith will be the main goal of the present study.

In addition, the elemental ratios of the past SW noble gases are important for understanding, for example, the origin of the Earth's ultravolatile elements (Marty 2020, Péron et al. 2017, Yamamoto et al. 2025). This requires also an understanding of elemental fractionations of noble gases in potential source materials contributing to the terrestrial noble gas budget. Lunar samples are strongly depleted in ^4He , ^{20}Ne , and partly ^{36}Ar relative to the SW composition, depending also on the mineral type (Signer et al. 1977), and the lunar regolith is therefore important to study such fractionation processes. Diffusion is commonly advocated to be the major loss process (e.g., Heber et al. 2003, Signer et al. 1977, Zhang et al. 2025), but previous studies have lacked quantitative depth scales, preventing a quantitative evaluation of the degassing process.

Noble gas depth profiling studies on lunar regolith grains were conducted already in the late 1970s by the Gas Ion Probe technique (Müller et al. 1976, Kiko et al. 1979). Samples were sputtered with a Xe^+ ion beam, and the released noble gases were ionized by electron impact, allowing measurement of the quantitative depth distribution of noble gases with lateral dimensions of $\sim 100\ \mu\text{m}$ and depth resolution of $\sim 10\ \text{nm}$. These measurements demonstrated that noble gases reside within the uppermost surface region ($< 1\ \mu\text{m}$ depth) of lunar regolith grains, with depth distributions varying among individual grains and mineral types (e.g., Müller et al. 1976, Warhaut et al. 1979). However, due to background limitations, only ^4He and ^{22}Ne could be analyzed, and depth profiles of elemental and isotopic ratios were not obtained.

Recently, multi-noble gas depth profiling has been successfully achieved at Hokkaido University using a time-of-flight secondary neutral mass spectrometer (ToF-SNMS), LIMAS (JEOL) (e.g., Bajo and Yurimoto 2024, and references therein). This instrument combines a ^{69}Ga focused ion beam, femtosecond (fs) laser tunneling ionization, and the multi-turn ToF mass spectrometer (MULTUM II; Okumura et al. 2004), enabling high-spatial-resolution depth profiling of ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar in representative lunar and asteroidal materials, e.g., ilmenite and olivine (Otsuki et al. 2025: **Chapter 2**).

In this study, LIMAS was used to perform high-resolution, nano-scale noble gas depth

profiling. By in situ depth profiling of SW noble gases in three Apollo 17 ilmenite grains, the quantitative depth profile of noble gas concentrations and their elemental/isotopic ratios were investigated. Based on these analyses, the neon isotopic ratios in lunar ilmenite was concluded to be explained solely by fSW and reassesses fractionation process of noble gas in lunar materials. In addition, the major process dominating the ^4He and ^{20}Ne loss from lunar ilmenite is suggested to be a defect-mediated effusion.

3.2 Materials and Methods

3.2.1 Sample preparation

The three ilmenite grains from lunar sample 71501 were used for this study (sample IDs; 71501#3, 71501#6, and 71501#7). They were selected from the same ilmenite separate already studied by Benkert et al. (1993), Nichols et al. (1994), and Wieler and Baur (1995). Ilmenite has the highest retentivity for SW-He and -Ne among the major minerals in the lunar regolith (Signer et al. 1977). Samples from soil 71501 have been exposed to the SW as individual grains within the last 100 Ma (Arvidson et al. 1976, Wieler et al. 1983), relatively recently for lunar standards. The samples of this study are therefore expected to have been less disturbed by secondary processes such as surface erosion than grains from samples with higher SW antiquities (e.g., Heber et al. 2003).

The ilmenite grains were embedded on metal substrate (either indium or gold) with relatively flat surface portions facing upward. The grains were coated with ~ 10 nm thick gold layers to reduce electrostatic charging during analysis. Secondary electron images (SEI) were obtained using a field emission scanning electron microscope (FE-SEM; JSM-7000F, JEOL) at an accelerating voltage of 3 kV and a beam current of ~ 10 pA to identify flat surfaces for the LIMAS analyses (Fig. 3.1). An energy-dispersive X-ray spectrometer (EDS; X-Max 150, Oxford) attached to the FE-SEM were used for elemental analyses under primary electron beam conditions at 15 kV and 0.5 nA. The HNA-IL used in **Chapter 2** (ion implanted Monastery ilmenite) was used as a reference material for LIMAS analyses.

3.2.2 Depth profile analysis

A high-spatial resolution and multi-isotope depth profiling was performed by LIMAS. An analytical condition used here is basically the same as used in **Chapter 2**. A ^{69}Ga focused ion beam (Ga-FIB; 30 keV, ~ 30 nA) with a beam diameter of ~ 2 μm and a pulse width of 400 ns was scanned across an area of $\sim 18 \times 25$ μm^2 (30×30 pixels) on the sample surface. The sputtered neutrals from each pixel were subsequently post-ionized using a femtosecond laser (Astrella, Coherent) of 795 nm wavelength operating at 6 mJ

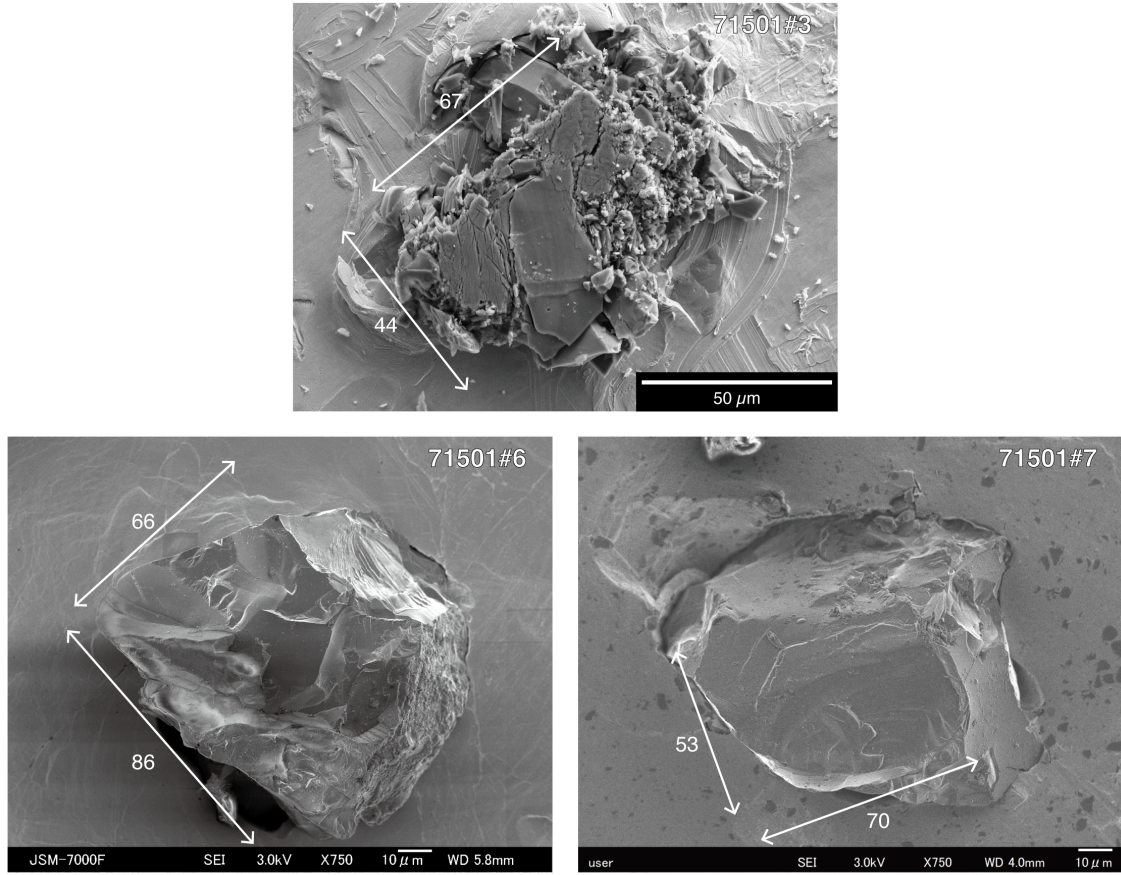


Figure 3.1: Secondary electron images by FE-SEM for 71501#3, #6, and #7. Arrows and numbers in each figure represent the length of long and short axis in unit of μm used for concentration calculation in section 3.4.2.

energy and 35 fs pulse width. The positive ions in the m/z range of 4–28 were then injected into a multi-turn ToF mass spectrometer, MULTUM II (Okumura et al. 2004), with an acceleration voltage of -5 kV. Ions without interest were removed from the ion trajectory during mass separation using ion gates. The ToFs of the ions were set to 455–461 μs . The entire sequence from sputtering to ion detection is referred to as a mass scan, and the signal intensity is given in the unit of ion counts per mass scan (cpms). 100 mass scans were collected from every pixel. Scanning were repeated for 800, 845, and 242 measurement layers for 71501#3, 71501#6, and 71501#7, respectively. During the measurement of 71501#3, $^4\text{He}^+$ signals between layers 94 and 101 and the signals from all other ions at the 94th measurement layer were not acquired due to a technical problem. These gaps were filled with the average values of the neighboring measurement layers.

Samples were introduced into the airlock ($\sim 3 \times 10^{-6}$ Pa) several days prior to the

measurements to minimize adsorbed atmospheric noble gases. Ga-FIB induced SEIs (FIB-SEIs) were obtained by LIMAS to determine the area for depth profiling. The FIB-SEIs were obtained with a primary beam acceleration voltage of 30 kV and ~ 4 pA current. Noble gas depth profiling was conducted following the procedure described in (Otsuki et al. 2025: **Chapter 2**). The measured ions were $^4\text{He}^+$, $^{20}\text{Ne}^{2+}$, $^{22}\text{Ne}^{2+}$, $^{36}\text{Ar}^{4+}$ for noble gases, $^{16}\text{O}^{2+}$, $^{24}\text{Mg}^{2+}$, $^{48}\text{Ti}^{4+}$, and $^{56}\text{Fe}^{2+}$ for major element of ilmenite, and $^{27}\text{Al}^{3+}$ and $^{28}\text{Si}^+$ for minor/trace elements of ilmenite. ^{40}Ca and ^{40}Ar overlapped peak was also measured (see section 2.3.1). The 3D distributions and the depth profiles of the overlapping peaks show a similar behavior to that of the minor/trace elements. Therefore, this peak is hereafter regarded as entirely originating from ^{40}Ca . For 71501#3, $^{54}\text{Fe}^{3+}$ was measured instead of $^{56}\text{Fe}^{2+}$ and $^{28}\text{Si}^+$ was not measured. The ToF spectra from the three measurements are shown in Fig. 3.2

3.2.3 Calibration for noble gas concentrations and isotopic ratios

The measured noble gas intensities were corrected for background signals including residual gases and interfering ions determined at **Chapter 2**. The $^{27}\text{Al}^{3+}$ signal was slightly interfering on $^{36}\text{Ar}^{4+}$, while other noble gas ions suffered no interferences (Fig. 3.2). Noble gas concentrations, fluences, and elemental/isotopic ratios ($^4\text{He}/^{20}\text{Ne}$, $^{20}\text{Ne}/^{36}\text{Ar}$, and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios) were then calibrated using relative sensitivity factors (RSFs) obtained from a reference sample analyses which was conducted in the same analytical session prior to the measurement of the lunar ilmenite grains. RSF_{iM} and $\text{RSF}_{i,j}$ were calculated using Eqs. 2.1 and 2.3. $^{16}\text{O}^{2+}$ was used for reference ion. The noble gas concentration and ratios at depth layer k were calculated according to Eqs. 2.2 and 2.4, respectively. The total noble gas fluence and bulk elemental/isotopic ratios were calculated as follows:

- Bulk fluence:

$$F_{iM} = \text{RSF}_{iM} \times \left[\sum_{k=1}^n \left(\left. \frac{[iM_{\text{sam}}]}{[R_{\text{sam}}]} \right|_k - \left. \frac{[iM_{\text{sam}}]}{[R_{\text{sam}}]} \right|_{\text{BG}} \right) \times \left(\frac{d}{n} \right)_{\text{sam}} \right] \quad (3.1)$$

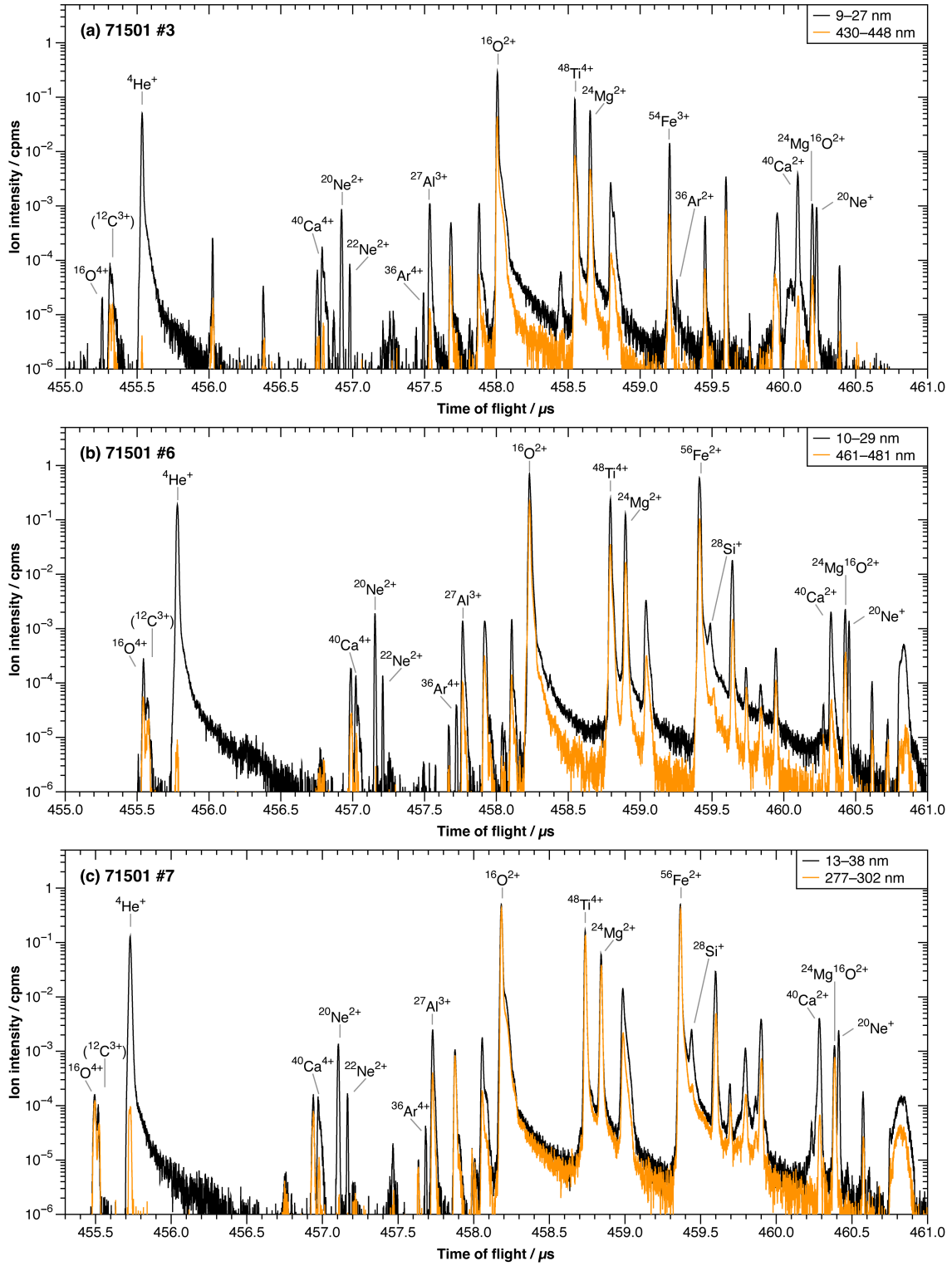


Figure 3.2: Time-of-flight (ToF) spectra for (a) 71501#3, (b) 71501#6, and (c) 71501#7. Black lines are ToF spectra accumulated from the surface 10–30 measurement layers and orange lines are from 20 measurement layers from deeper sites. Analyzed ions and some other ions are labelled, where $^{12}\text{C}^{3+}$ is partly removed from the ion trajectory using ion gate. ToFs are corrected for ToF drifts during analysis.

- Bulk elemental and isotopic ratio:

$$\left(\frac{iM}{jN}\right) = \text{RSF}_{i,j} \times \left[\frac{\sum_{k=1}^n ([iM_{\text{sam}}]_k - [iM_{\text{sam,BG}}])}{\sum_{k=1}^n ([jN_{\text{sam}}]_k - [jN_{\text{sam,BG}}])} \right] \quad (3.2)$$

where subscripts sam and BG refer to lunar ilmenite sample and the background signals, respectively. The background values were determined as the average of the last 100 measurement layers, after the signal intensity decrease to a steady value. These signals are mainly due to residual gases and interfering ions. For $^4\text{He}^+$ in 71501#7, only residual gas intensity was subtracted from the measured ion intensities because its profile did not reach to a constant value within 242 measurement layers (~ 300 nm). The sputter rate (d/n) in the lunar sample analyses were assumed to be the same as that of the reference sample in each analytical session, which were 0.90, 0.96, and 1.26 nm per measurement layer for 71501#3, 71501#6, and 71501#7, respectively.

The RSF values used in this study are listed in Table 3.1. The uncertainties in each analyses were calculated by respectively propagating the 1σ error of the background value, counting statistics, and the reproducibility of the RSFs. The error of RSFs were taken from the reproducibility evaluated at section 2.3.5. Note that the reproducibility of grain samples analyses have a possibility of degrading relative to polished substrates (see section 2.3.5).

Table 3.1: RSFs in each analysis

Sample	$\text{RSF}_{iM} / \times 10^{22} \text{ atoms cm}^{-3}$				$\text{RSF}_{i,j}$		
	^4He	^{20}Ne	^{22}Ne	^{36}Ar	$^4\text{He}/^{20}\text{Ne}$	$^{20}\text{Ne}/^{36}\text{Ar}$	$^{20}\text{Ne}/^{22}\text{Ne}$
71501#3	1.87	1.13	1.15	0.93	1.85	1.19	0.98
71501#6	1.86	0.85	0.75	0.82	2.30	1.02	1.12
71501#7	2.06	1.00	0.84	1.30	2.18	0.76	1.19

3.2.4 Numerical simulation of ion implantation

To estimate the noble gas depth distributions expected from a simple SW implantation, an ion-implantation simulations using SRIM (Ziegler et al. 2010) was conducted. The target was assumed as pure ilmenite-like material with composition of FeTiO_3 and density of

4.7 g cm^{-3} . The speed distribution and compositions were based on the present-day SW observed by the SWICS/ACE spacecraft (Gilbert et al. 2007), and the Genesis target material (Heber et al. 2009), respectively. Because speed distributions are available only for ^4He and ^{20}Ne , those of ^{22}Ne and ^{36}Ar were assumed to be identical to that of ^{20}Ne . Detailed procedure is explained in the next chapter. The simulations were conducted using the TRIM.DAT file, which gives the specification of parameters of the incidence energy calculated from the speed distribution and the incidence angle for each implanted ion. Totally $\sim 100,000$ ions were simulated according to the speed distribution. The ion incidence angle was set to 45° , which is conventionally used to represent the effect of lunar surface roughness (Brötzner et al. 2025, Wurz et al. 2007).

3.3 Results

3.3.1 3D-distributions of the measured ions

Rectangular areas with a relatively flat surface were selected for the FIB-scanning area (Figs. 3.3a, 3.4a, and 3.5a). The 3D distributions of $^{20}\text{Ne}^{2+}$, $^{16}\text{O}^{2+}$, and $^{27}\text{Al}^{3+}$ are shown in Fig. 3.3b, Fig. 3.4b, and Fig. 3.5b. Ion images of the first 20 measurement layers (~ 20 nm in total depth) of other measured ions are shown in Figs. 3.3c, 3.4c, and 3.5c.

Across all three grains, the major element ions of ilmenite ($^{54}\text{Fe}^{3+}$, $^{56}\text{Fe}^{2+}$, $^{48}\text{Ti}^{4+}$, $^{24}\text{Mg}^{2+}$, and $^{16}\text{O}^{2+}$) exhibit high and homogeneous intensities within the flat areas, indicating chemically uniform ilmenite suitable for noble gas depth profiling. Minor heterogeneity in ion intensities near cracks (71501 #3, Fig. 3.3) or along stepped structures (71501 #7, Fig. 3.5) were identified.

The $^{20}\text{Ne}^{2+}$ distribution is uniform in the flat surface but decreases rapidly with increasing depth, consistent with implanted SW. In contrast, the distributions of $^{27}\text{Al}^{3+}$, $^{28}\text{Si}^{+}$, $^{40}\text{Ca}^{2+}$, and $^{40}\text{Ca}^{4+}$ show uniformly high intensities at the first 20 measurement layer image in the flat surface area, suggesting the presence of a thin layer bearing ^{27}Al , ^{28}Si , and ^{40}Ca on the surface. For grains 71501#3 and #6, localized high-intensity spots of these ions were observed, likely corresponding to feldspathic particles adhering to the ilmenite surface, while grain 71501#7 shows no such adhered feldspathic material but exhibits minor heterogeneity associated with stepped structures (Fig. 3.5b). In grain 71501#3, $^{27}\text{Al}^{3+}$ ions exhibit a linear distribution on the right side in the image, and the intensity does not decrease with increasing depth (Fig. 3.3b). EDS analysis after the LI-MAS analysis shows that a chromite vein is present along this linear distribution region.

The intensity of $^{20}\text{Ne}^{2+}$ shown in Figs. 3.3b, 3.4b, and 3.5b decreases with increasing depth and the outer few pixels at the edge of the fourth and fifth $^{20}\text{Ne}^{2+}$ images exhibit higher intensities compared to the inner pixels. This is due to crater edge effects (Otsuki et al. 2025). These pixels include signals from crater edges with shallower depths than the crater bottom and were therefore excluded from the areas for depth profiling. The signals from cracks, stepped structures, adhered particles, and veins were also excluded from the depth profiling.

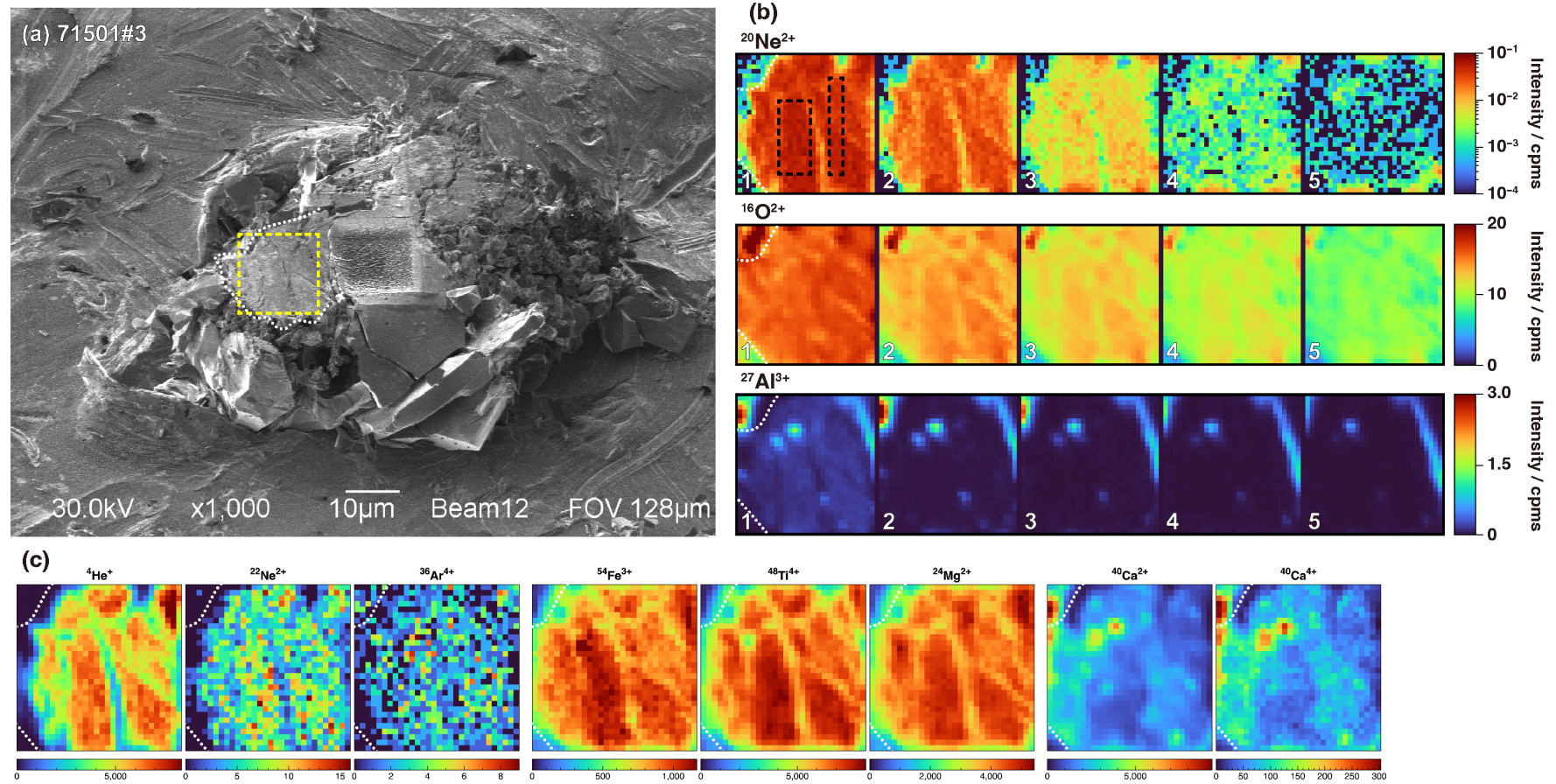


Figure 3.3: (a) FIB-SEI of 71501#3. The rectangle indicates the area shown in (b) and (c). A crater on the right-hand side of the rectangle represents the area of a test measurement performed prior to this analysis. The white dotted line approximately corresponds to the surface area used for depth profiling. (b) 3D distribution of ion intensities of 71501#3 for $^{20}\text{Ne}^{2+}$ (top), $^{16}\text{O}^{2+}$ (middle), and $^{27}\text{Al}^{3+}$ (bottom). Each image corresponds to a stack of 20 measurement layers (~ 17 nm). The numbers in each image correspond to depth layers: #1, 0–17 nm; #2, 17–35 nm; #3, 35–53 nm; #4, 53–71 nm; and #5, 71–89 nm. The color scale of $^{20}\text{Ne}^{2+}$ is logarithmic, while those for $^{16}\text{O}^{2+}$ and $^{27}\text{Al}^{3+}$ are linear. The black dotted rectangle shows the area used for depth analysis. (c) Ion images integrated over the first 20 measurement layers. The unit on the color bars for each ion is ion counts.

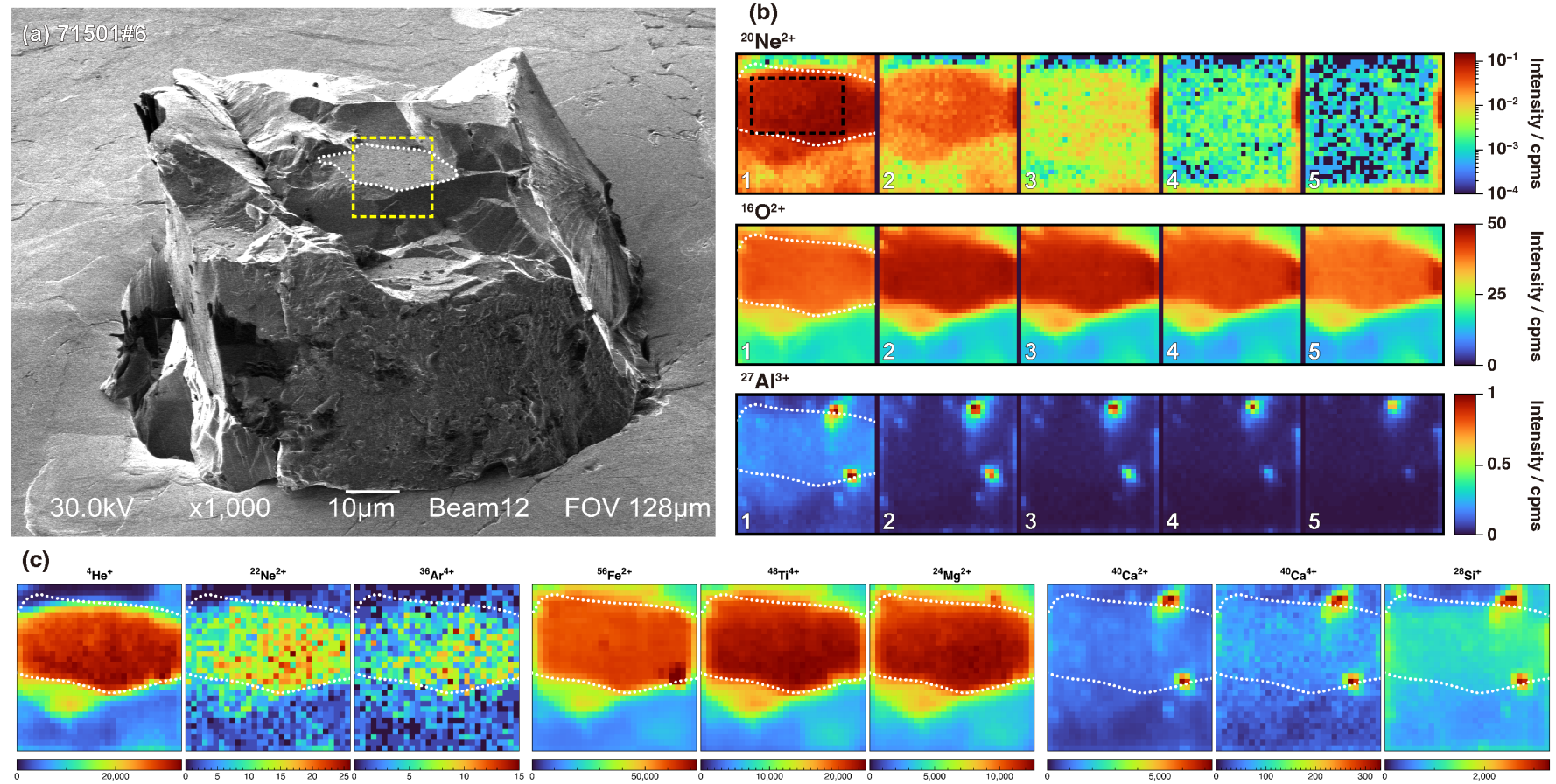


Figure 3.4: (a) FIB-SEI of 71501#6. The rectangle indicates the area shown in (b) and (c). The white dotted line approximately corresponds to the flat surface area used for depth profiling. The grain is rotated slightly to the right relative to the orientation in Fig. 3.1. The white dotted line approximately corresponds to the edge of the grain. (b) 3D distributions of ion intensities of 71501#6 for $^{20}\text{Ne}^{2+}$ (top), $^{16}\text{O}^{2+}$ (middle), and $^{27}\text{Al}^{3+}$ (bottom) from the yellow rectangle in (a). Each image corresponds to a stack of 20 measurement layers (~ 19 nm). The numbers in each image correspond to depth layers: #1, 0–18 nm; #2, 18–37 nm; #3, 37–57 nm; #4, 57–76 nm; and #5, 76–95 nm. The color scale of $^{20}\text{Ne}^{2+}$ is logarithmic, while those for $^{16}\text{O}^{2+}$ and $^{27}\text{Al}^{3+}$ are linear. (c) Ion images integrated over the first 20 measurement layers. The unit on the color bars for each ion is ion counts.

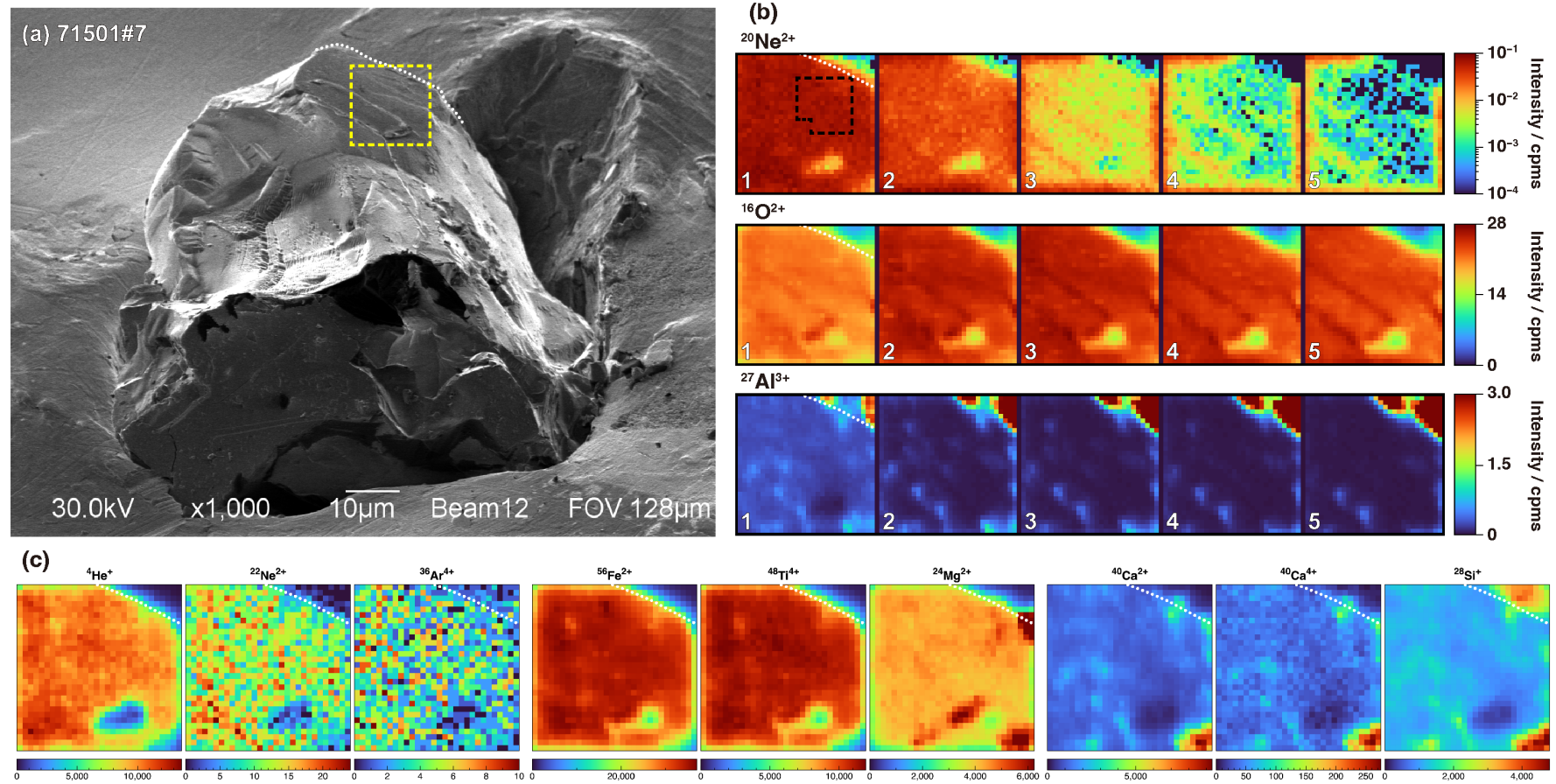


Figure 3.5: (a) FIB-SEI of 71501#7. The rectangle indicates the area shown in (b) and (c). The white dotted line approximately corresponds to the edge of the grain. The grain is rotated approximately 90° to the right relative to the orientation in Fig. 3.1. (b) 3D distribution of ion intensities of 71501#7 for $^{20}\text{Ne}^{2+}$ (top), $^{16}\text{O}^{2+}$ (middle), and $^{27}\text{Al}^{3+}$ (bottom). Each image corresponds to a stack of 20 measurement layers (~ 24 nm). The numbers in each image correspond to depth layers: #1, 0–24 nm; #2, 24–49 nm; #3, 49–74 nm; #4, 74–100 nm; and #5, 100–125 nm. The color scale of $^{20}\text{Ne}^{2+}$ is logarithmic, while those for $^{16}\text{O}^{2+}$ and $^{27}\text{Al}^{3+}$ are linear. The black dotted rectangle shows the area used for depth analysis. (c) Ion images integrated over the first 20 measurement layers. The unit on the color bars for each ion is ion counts.

3.3.2 Depth profiles of measured ions

Fig. 3.6 shows the depth profiles of ion intensities normalized to the $^{16}\text{O}^{2+}$ signal averaged over the entire analyzed area. All ion intensities are initially low due to the gold coating on the sample surface but then increase rapidly as the gold layer is sputtered away. Here, the zero-depth point was defined as the first measurement layer.

The relative intensities of the major elements of ilmenite, $^{24}\text{Mg}^{2+}$, $^{48}\text{Ti}^{4+}$, and $^{56}\text{Fe}^{2+}$ (or $^{54}\text{Fe}^{3+}$), are stable at depths below ~ 10 nm from the surface, whereas the noble gas ions ($^4\text{He}^+$, $^{20}\text{Ne}^{2+}$, $^{22}\text{Ne}^{2+}$, and $^{36}\text{Ar}^{4+}$) are highest near the surface at around 10–20 nm and then decrease steadily. Also, the trace elements ($^{27}\text{Al}^{3+}$, $^{28}\text{Si}^+$, and $^{40}\text{Ca}^{4+}$) are concentrated near the surface, peaking at <10 nm before decreasing until approximately 30 nm, followed by nearly constant intensities at larger depths.

Noble gas concentrations and fluences

The relative ion intensities of noble gases were converted to concentration profiles using RSFs and Eq. 2.2 (Fig. 3.7), and the fluences were calculated using Eq. 3.1 (Table 3.2). For grains 71501#3 and 71501#7, all detected noble gases show peaks within a depth range of 10–25 nm (Fig. 3.7). Grain 71501#6 exhibits for all noble gas isotopes the highest intensity at the topmost surface in a sharp peak, followed by the second peak at approximately 15 nm. Afterwards the concentrations decrease, but at all depths until 100 nm, the ^4He , ^{20}Ne , and ^{22}Ne from depths shallower than 100 nm were all above the detection limits of our analysis, which are 7×10^{16} , 3×10^{16} , and 9×10^{15} atoms cm^{-3} , respectively. These detection limits were determined from the background values obtained through measurements of the ion-implanted reference material (**Chapter 2**). On the other hand, the ^{36}Ar concentration reached the detection limit of 2×10^{16} atoms cm^{-3} , at depths of 50–80 nm for the 71501 samples. Therefore, data beyond these depths were excluded from the depth profiles of elemental ratios for ^{36}Ar .

Elemental and isotopic ratios

Elemental and isotopic ratios of measured noble gases were calculated from the depth profiles and Eqs. 2.4 and 3.2. The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio was calculated using data up to 55, 55,

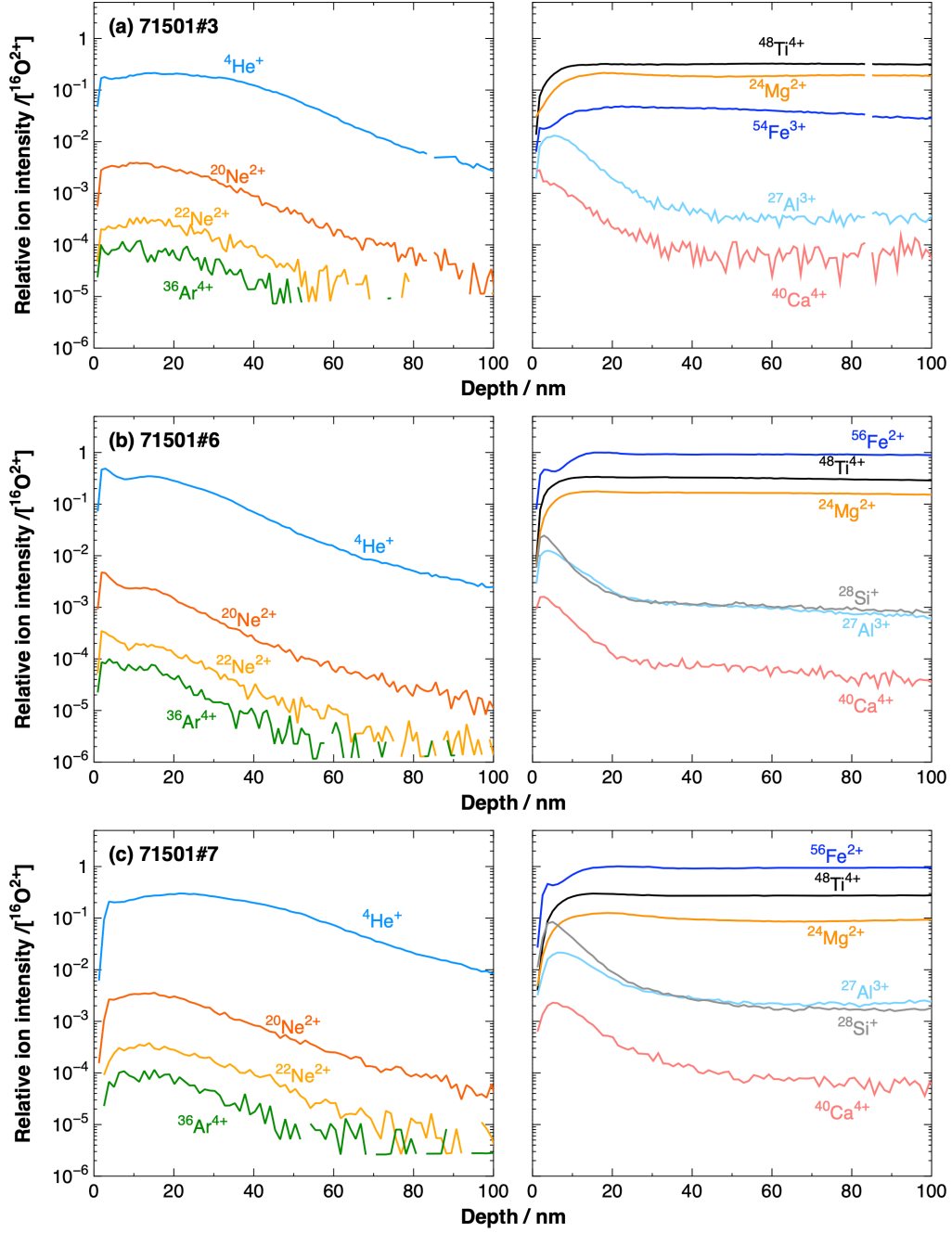


Figure 3.6: Depth profiles of 71501 ilmenite grains for noble gases (left) and major and minor/trace element ions (right), normalized by the $^{16}\text{O}^{2+}$ intensity. Noble gas ions ($^4\text{He}^+$, $^{20}\text{Ne}^{2+}$, $^{22}\text{Ne}^{2+}$, and $^{36}\text{Ar}^{4+}$) exhibit peaked profiles characteristic of SW implantation. Major element ions ($^{56}\text{Fe}^{2+}$ or $^{54}\text{Fe}^{3+}$, $^{48}\text{Ti}^{4+}$, and $^{24}\text{Mg}^{2+}$) show relatively stable intensities beyond approximately 10 nm from the surface. In contrast, $^{27}\text{Al}^{3+}$, $^{28}\text{Si}^+$, and $^{40}\text{Ca}^{4+}$ signals are concentrated in the outermost layer and decrease more rapidly than the noble gas profiles.

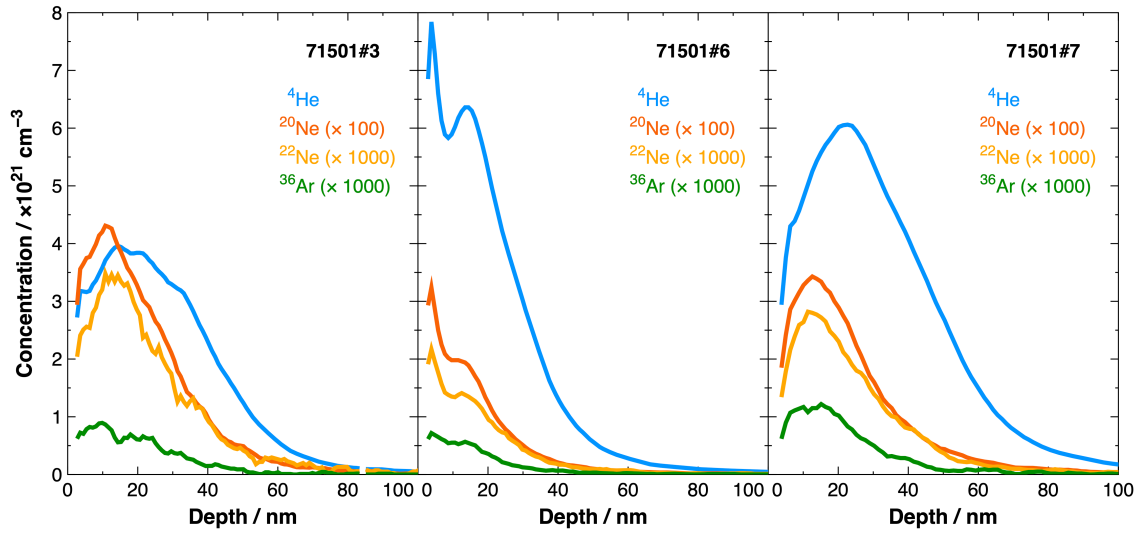


Figure 3.7: Depth profiles of noble gas concentrations measured by LIMAS. Profiles are shown as five bin moving averages. All noble gases are concentrated within the top 50 nm.

and 80 nm for 71501#3, #6, and #7, respectively. Bulk elemental ratios are summarized in Table 3.2. Except for the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of 71501#3, the bulk $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios for each grain were consistent with the range of single-grain analyses reported by Nichols et al. (1994), and remarkably, the mean values of the ilmenite grain separates measured by Benkert et al. (1993). The $^4\text{He}/^{20}\text{Ne}$ ratios of 141–380 in this study were lower than the present-day SW- $^4\text{He}/^{20}\text{Ne}$ ratio of 656 (Heber et al. 2009) and also the trapping corrected value for ilmenite of 578 (SRIM in Table 3.2). The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of 71501#3 (50.1 ± 10.1) was comparable with the SW- $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of 42.1 (Heber et al. 2009), whereas those of 71501#6 (36.8 ± 5.0) and 71501#7 (28.9 ± 5.8) were lower than the SW composition. The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of 71501#7 was also lower than the trapping corrected value of 40.1.

The depth profiles of noble gas elemental and isotopic ratios were calculated by binning the data to reduce the statistical error to less than approximately 10%. Depth profiles of $^4\text{He}/^{20}\text{Ne}$, $^{20}\text{Ne}/^{36}\text{Ar}$, and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios from all three grains are shown in Fig. 3.8. Bar width represent statistical errors of the ion counts. The stability of RSFs during a single analysis has been much better than 10%, although RSFs between independent analyses varied by approximately 10% for $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ analyses, and by approximately 30% for $^4\text{He}/^{20}\text{Ne}$ analysis (**Chapter 2**).

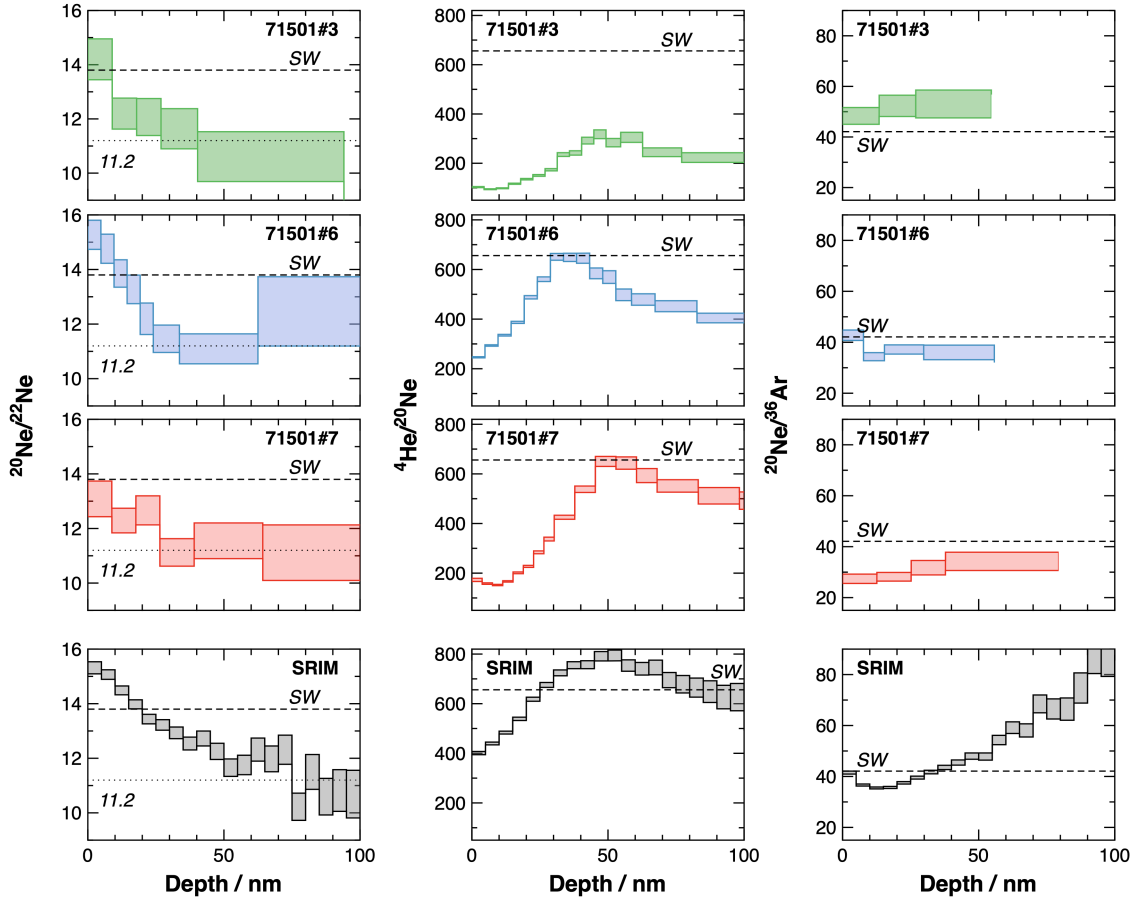


Figure 3.8: Depth profiles of $^4\text{He}/^{20}\text{Ne}$ (left), $^{20}\text{Ne}/^{36}\text{Ar}$ (center), and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (right) of 71501 ilmenites and from SRIM simulations. The width and height of each box represent the bin widths and the 1σ statistical errors, respectively. Solar wind (SW) values ($^{20}\text{Ne}/^{22}\text{Ne} = 13.78$, $^4\text{He}/^{20}\text{Ne} = 656$, and $^{20}\text{Ne}/^{36}\text{Ar} = 42.1$; Heber et al. 2009) and the conventionally so-called SEP value ($^{20}\text{Ne}/^{22}\text{Ne} = 11.2$; Benkert et al. 1993) are shown as broken and dotted lines, respectively.

The $^{20}\text{Ne}/^{22}\text{Ne}$ ratios show a decreasing trend with increasing depth. The $^4\text{He}/^{20}\text{Ne}$ ratio increases with increasing depth, peaking around 30–50 nm at values approximately 2.5–4 times higher than the surface $^4\text{He}/^{20}\text{Ne}$ ratios. The profile then decreases again with increasing depth. On the other hand, the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio did not exhibit significant variation with depth.

3.3.3 Numerical simulations of noble gas depth profiles

The depth profiles of isotopic and elemental ratios obtained from the SRIM simulations are shown in Fig. 3.8. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio exhibits a value of approximately 15 at the

surface and gradually decreases with increasing depth. The $^4\text{He}/^{20}\text{Ne}$ ratio shows a single-peak profile, increasing from ~ 400 at the surface to ~ 800 before decreasing again. The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio starts at ~ 40 near the surface, slightly decreases, and then gradually increases with increasing depth.

The SRIM simulations indicate that the trapping efficiencies differ among isotopes, with values of 0.806, 0.915, 0.926, and 0.961 for ^4He , ^{20}Ne , ^{22}Ne , and ^{36}Ar , respectively. Consequently, the bulk compositions after implantation become fractionated from the original SW composition, yielding $^{20}\text{Ne}/^{22}\text{Ne} = 13.6$, $^4\text{He}/^{20}\text{Ne} = 578$, and $^{20}\text{Ne}/^{36}\text{Ar} = 40.1$, all of which are lower than the SW values to different degrees (Table 3.2). Based on these values, the $^{20}\text{Ne}/^{36}\text{Ar}$ ratios of 71501#3 (50.1 ± 10.1) and 71501#6 (36.8 ± 5.0) are comparable to the noble gas compositions expected to be trapped in ilmenite, whereas the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of 71501#7 and the $^4\text{He}/^{20}\text{Ne}$ ratios of all grains still remain lower than those predicted by the SRIM (Table 3.2)

Table 3.2: Fluence and bulk ratios of noble gases in 71501 ilmenites

	Fluence / atoms cm ⁻²				Bulk ratios		
	⁴ He (×10 ¹⁶)	²⁰ Ne (×10 ¹³)	²² Ne (×10 ¹²)	³⁶ Ar (×10 ¹²)	⁴ He/ ²⁰ Ne	²⁰ Ne/ ³⁶ Ar	²⁰ Ne/ ²² Ne
This study							
#3	1.7 ± 0.3	12.6 ± 3.3	10.9 ± 2.4	2.5 ± 0.7	141 ± 44	50.1 ± 10.1	12.3 ± 1.5
#6	2.0 ± 0.4	5.6 ± 1.5	4.2 ± 0.1	1.5 ± 0.3	380 ± 118	36.8 ± 5.0	13.4 ± 1.7
#7	2.8 ± 0.6	10.3 ± 2.7	8.4 ± 1.9	3.3 ± 0.7	290 ± 90	28.9 ± 5.8	12.1 ± 1.5
71501 ilmenites							
B93					221	25.5	12.9
N94					278	26.0	13.1
					(34–495)	(6.0–39.5)	(9.7–13.7)
Solar wind							
H09					656	42.1	13.78
SRIM*					578	40.1	13.6

Errors are 1σ. B93: Benkert et al. (1993). Average of three total CSSE data of 71501 ilmenites. N94: Nichols et al. (1994). Mean value and its range in 90 grains of 71501 ilmenite are shown. H09: Heber et al. (2009).

*SW compositions corrected for trapping efficiencies of each isotope into ilmenite based on the SRIM simulation.

3.4 Discussion

3.4.1 Characteristics of space weathered rim in depth profiles

The uniformly high $^{27}\text{Al}^{3+}$, $^{28}\text{Si}^{+}$, $^{40}\text{Ca}^{2+}$, and $^{40}\text{Ca}^{4+}$ distributions observed within the first 20 measurement layers (Figs. 3.3, 3.4, and 3.5) suggest the presence of a vapor-deposited rim. Such rims are formed through micrometeorite-impacts into the lunar regolith or by sputtering induced by SW irradiation (Keller and McKay 1993; 1997, Pieters and Noble 2016). Transmission electron microscopy observations have revealed that such rims are typically less than 20 nm thick and contain not only Si but also Ca and Al (Burgess and Stroud 2018). In this study, enrichments of $^{27}\text{Al}^{3+}$, $^{28}\text{Si}^{+}$, and $^{40}\text{Ca}^{4+}$ were observed in the outermost layers, consistent with those characteristics of the vapor-deposited rim (Fig. 3.8).

By assuming that the sputter rate of the vapor-deposited rim is identical to that of ilmenite, the $^{27}\text{Al}^{3+}/^{16}\text{O}^{2+}$ ratio decreased to 50% of its maximum intensity within 12, 11, and 16 nm for 71501#3, 71501#6, and 71501#7, respectively (Fig. 3.8). This depth range is comparable to the typical thickness of vapor-deposited rims (Burgess and Stroud 2018), although the thickness inferred here may be slightly too high due to the depth resolution of LIMAS analyses, which is limited by the projected range of 30 keV Ga ions (Bajo et al. 2015). Therefore, the depth profiles within the approximately topmost 10–15 nm depths are likely affected by the vapor-deposited rim.

The first peaks of noble gases in 71501#6 at depths shallower than 8 nm are from the vapor-deposited rim, and second peaks of noble gases observed at 20–30 nm depths are from the host ilmenite. In contrast, grains 71501#3 and #7 exhibit single peaks at ~10–20 nm depths, which correspond to the second peak of 71501#6. The double-peaked profile of 71501#6 suggests that vapor-deposited rims can effectively trap noble gases and that SW irradiation continued during or after rim formation. The presence of a vapor-deposited rim indicates that the analyzed surface has not been damaged or altered after SW irradiation, either on the lunar surface or during laboratory treatment.

3.4.2 The demise of the “SEP component”

As described in the 3.1, observations of fSW by the Genesis BMG target allowed us to largely dismiss the idea of a high-energy “SEP component” in lunar (and meteoritic) samples with its putative very large abundance. However, what was missing so far was direct evidence that the extraterrestrial samples had trapped their solar gases only in very surficial grain layers, as is expected by the known energy distribution of the SW. Such a direct proof is now given in this work, as the quantitative depth distributions of SW ^4He , ^{20}Ne , ^{22}Ne , and ^{36}Ar in three carefully selected plane surface areas of rather pristine-looking lunar ilmenite grains. Figs. 3.6 and 3.7 show that all measured noble gases are largely concentrated in the grains topmost 50 nm, with tails extending to some 100 nm for He and Ne and ~ 80 nm for Ar.

Figure 3.8 shows that the depth distribution of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios also follows the SRIM-simulated profiles for a present-day SW speed distribution implanted into FeTiO_3 target. The three figures therefore provide the first direct and further evidence that the observed depth-dependent isotopic fractionation can be explained by implantation fractionated SW, without the need to postulate an abundant isotopically heavier high-energy component implanted deeper into the grains.

To compare the noble gas concentrations measured in this study with those reported previously, the noble gas concentrations in units of $\text{cm}^3 \text{ STP g}^{-1}$ for each grain were calculated (Table 3.3). The volume of each grain was calculated assuming a cuboid shape, using the measured long and short axes, with the height set equal to the long axis to avoid underestimation of the volume (Fig. 3.1). The mass of each grain was determined using an ilmenite density of 4.7 g cm^{-3} . The noble gases were likely implanted uniformly over the entire grain surface, because the average ^4He concentration would be $\sim 8 \times 10^{21} \text{ atoms cm}^{-3}$ within a 50 nm SW-implanted layer in ilmenite, assuming a cuboid grain shape based on single-grain data from Nichols et al. (1994). If instead SW irradiation were assumed to occur on only one face of the cuboid, the average ^4He concentration would be $\sim 5 \times 10^{22} \text{ atoms cm}^{-3}$, exceeding the atomic densities of Fe and Ti in ilmenite ($\sim 2 \times 10^{22} \text{ atoms cm}^{-3}$). Therefore, it was assumed that SW implantation occurred across the entire grain surface (Table 3.3).

Figure 3.9 compares the noble gas concentrations of the single grains in this study with those reported by Nichols et al. (1994), who analyzed 90 grains (^{36}Ar data were not reported for 21 grains). The concentrations obtained in this study are consistent with the typical range observed for lunar ilmenites (Fig. 3.9). The average concentrations reported by Nichols et al. (1994) are comparable to those obtained by CSSE analyses (Benkert et al. 1993). Considering that the noble gases analyzed in this study were confined to the uppermost few hundred nanometers of $\sim 100\text{ }\mu\text{m}$ -sized grains, these results indicate that the “bulk” noble gases measured in previous studies are dominated by SW noble gases implanted within the topmost few hundred nanometers of ilmenite. This further demonstrates that the so-called SEP component in lunar samples proposed by previous studies does not require a distinct isotopically heavy component but instead reflects depth-dependent isotopic fractionation of solar wind (fSW).

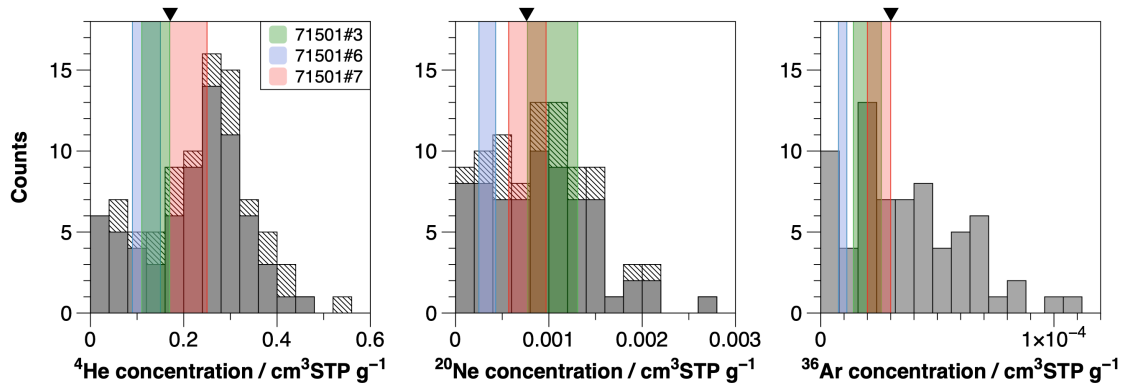


Figure 3.9: Comparison of noble gas concentrations between the three grains analyzed in this study and single grain analyses reported by Nichols et al. (1994). The green, red, and blue shaded regions indicates the concentrations of the three grains with errors (Table 3.3). The histogram shows the single grain data, where the hatched areas in the ^4He and ^{20}Ne panels represent grains for which ^{36}Ar was not reported. The black arrows above each panel indicate the mean values of the single grain data.

Figure 3.10 compares the LIMAS depth profiles as well as the elemental ratio profiles $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ with the respective CSSE results of the 71501 ilmenite grain separates reported by Benkert et al. (1993). The LIMAS depth profiles of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios representing the uppermost 100 nm reasonably reproduce the isotopic fractionation trends observed by the CSSE analyses. Both datasets show a broadly similar decrease in $^{20}\text{Ne}/^{22}\text{Ne}$ ratios with increasing ^{36}Ar release. In particular, all three grains in this study

exhibit $^{20}\text{Ne}/^{22}\text{Ne}$ ratios similar to the value around 11.2 observed near the end of the gas release from the grain separates. Because the lowest $^{20}\text{Ne}/^{22}\text{Ne}$ values were observed at depth of ~ 50 nm, Fig. 3.10 further confirms that the component formerly known as “SEP-Ne” is in fact, implantation-fractionated SW-Ne, now also known as fSW.

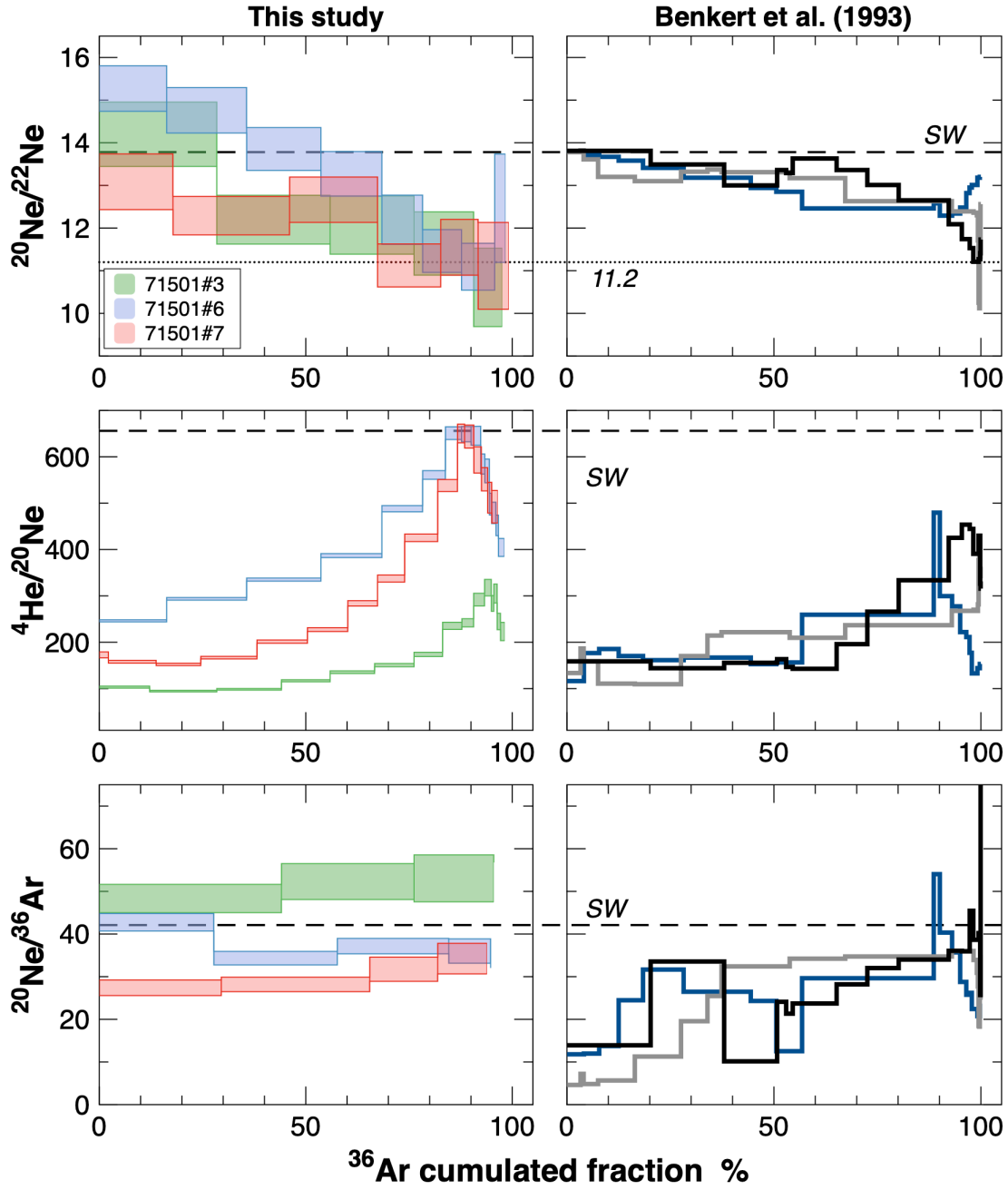


Figure 3.10: Variations of the $^4\text{He}/^{20}\text{Ne}$, $^{20}\text{Ne}/^{36}\text{Ar}$, and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of 71501 ilmenites plotted against the cumulative released fraction of ^{36}Ar . The results of this study (left) are compared with the CSSE results (right; Benkert et al. 1993). The binned numbers of measurement layers in this study are the same as those in Fig. 3.8. The three lines with different colors in the right panels represent independent etch runs of different 71501 ilmenite separates.

Table 3.3: Calculated grain sizes and noble gas concentrations of 71501 ilmenite.

	Surface area / cm ²	Mass / g	Concentration / atoms cm ³ STP g ⁻¹		
			⁴ He	²⁰ Ne	³⁶ Ar
#3	2.1×10^{-4}	9.4×10^{-7}	$(1.4 \pm 0.3) \times 10^{-1}$	$(10.4 \pm 2.7) \times 10^{-4}$	$(2.0 \pm 0.6) \times 10^{-5}$
#6	3.6×10^{-4}	2.3×10^{-6}	$(1.2 \pm 0.3) \times 10^{-1}$	$(3.4 \pm 0.9) \times 10^{-4}$	$(9.4 \pm 1.8) \times 10^{-6}$
#7	2.5×10^{-4}	1.2×10^{-6}	$(2.1 \pm 0.4) \times 10^{-1}$	$(7.7 \pm 2.0) \times 10^{-4}$	$(2.5 \pm 0.5) \times 10^{-5}$
B93			1.71×10^{-1}	7.62×10^{-4}	3.01×10^{-5}
N94			2.31×10^{-1}	9.16×10^{-4}	3.62×10^{-5}
			$(7.70 \times 10^{-4} - 5.46 \times 10^{-1})$	$(3.60 \times 10^{-6} - 2.65 \times 10^{-3})$	$(6.00 \times 10^{-7} - 1.10 \times 10^{-4})$

*Errors are 1σ . Concentrations of 71501 #3, #6, and #7 are calculated assuming that SW irradiation occurred over the entire grain surface (see text).

B93: Benkert et al. (1993). Average of three total CSSE data of 71501 ilmenites. N94: Nichols et al. (1994).

3.4.3 Elemental fractionation at the surface of lunar ilmenite

The observations in previous studies (e.g., Table 3.2) that Ne in bulk lunar ilmenite separates is isotopically heavier than the SW value imply a loss of Ne preferring its light isotopes. Also, the low $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios compared to the SW composition suggests a preferential loss of the light noble gases.

For isotopic ratios, surface sputtering associated with the SW irradiation has been proposed as a process responsible for producing the isotopically heavy neon observed in lunar samples (Becker 1998, Grimberg et al. 2006, Moreira and Charnoz 2016, Péron et al. 2017). However, the sputtering process alone cannot account for the lower $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, because surface removal by sputtering removes the lower values of the SRIM depth profiles near the surface and would therefore increase the bulk values, which is discussed in the next chapter. On the other hand, thermal diffusion has commonly been invoked to explain the selective loss of light noble gases (e.g., Benkert et al. 1993, Signer et al. 1977, Zhang et al. 2025). Here, the responsible process based on the observed depth profiles were discussed.

$^4\text{He}/^{20}\text{Ne}$ ratio

The $^4\text{He}/^{20}\text{Ne}$ depth profiles of the three analyzed grains exhibit similar single-peak distributions (Fig. 3.8), showing a consistent trend with the CSSE results (Fig. 3.10). This single-peak fractionation pattern is also reproduced by the SRIM simulations (Fig. 3.8), although the measured $^4\text{He}/^{20}\text{Ne}$ ratios are systematically lower than the simulated ones. The measured ^4He fluences of $(1.6\text{--}2.5) \times 10^{16} \text{ cm}^{-2}$ in the lunar ilmenite grains (Table 3.2) are comparable to the experimental retention limit of implanted ^4He in ilmenite, approximately $10^{16} \text{ atoms cm}^{-2}$, reported by ion implantation experiments simulating the present-day SW (Futagami et al. 1990). Similar behavior has been observed in Si wafers, where implantation fluences above $\sim 10^{16} \text{ atoms cm}^{-2}$ cause the sudden decrease in ^4He concentration profile, while the overall shape of the depth profile remains unchanged (Yurimoto et al. 2016). This trend has been attributed to ^4He effusion through defect networks generated during ion beam irradiation (Yurimoto et al. 2016).

Consideration of the possible trapping sites of ^4He in ilmenite further supports this

interpretation. ^4He -filled vesicles and planar defects have been observed in SW-irradiated ilmenite (Burgess and Stroud 2018, Kling et al. 2025, Zhang et al. 2026). Crushing experiments conducted under room temperature have shown that the amount of noble gases released by crushing is only about 10^{-3} of that released by total melting experiments (Funkhouser et al. 1971). Because crushing preferentially releases noble gases trapped at mechanically weak sites, such as large vesicles, most of the remaining noble gases must reside in sites that are resistant to mechanical destruction. Whether these sites correspond to interstitial sites or small planar defects remains unclear. However, in either case, they must represent mechanically robust trapping environments and would not easily release noble gases in natural conditions.

With increasing SW implantation fluence, planar defects are expected to develop and eventually evolve into larger vesicles. Once such vesicles or defects connect to the surface, efficient ^4He loss can occur. Carefully controlled stepwise crushing experiments could therefore provide further insight into the specific trapping sites and degassing processes of noble gases.

Taken together, these observations suggest that most grains of 71501 ilmenite had reached the ^4He retention limit, and that the dominant mechanism controlling ^4He loss in ilmenite could be a retention limit governed by defect-mediated helium escape. This also suggests that thermal diffusion for ^4He loss plays only a minor role for ilmenites.

$^{20}\text{Ne}/^{36}\text{Ar}$ ratio

Similar trends were observed between LIMAS and CSSE depth profiles for the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio, except for the surface values (Fig. 3.10). The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio from LIMAS remains almost uniform from the topmost surface to ~ 80 nm (^{36}Ar cumulative fraction $\sim 90\%$), whereas the CSSE analyses show lower $^{20}\text{Ne}/^{36}\text{Ar}$ ratios in the initial few steps (^{36}Ar cumulative fraction $\sim 20\%$; Figs. 3.8 and 3.10). The lower $^{20}\text{Ne}/^{36}\text{Ar}$ ratios of 5–10 seen in CSSE are not reproduced by SRIM (Fig. 3.8). Benkert et al. (1993) suggested that the earliest steps of the CSSE assemblage (several milligrams in total) might have included noble gases from acid-susceptible phases such as silicate glass patches on ilmenite (note that the glass patches mentioned here are different from the vapor-deposited rim in Sec-

tion 3.4.1). Results in this study are consistent with this interpretation because the glass patches did not exist in the measurement area in this study.

The $^{20}\text{Ne}/^{36}\text{Ar}$ ratios predicted by SRIM between depths of 10 nm and 40 nm are broadly similar to the LIMAS and CSSE results. The discrepancy of the initial few steps of the CSSE results is discussed in the previous paragraph. The SRIM profile deeper than 50 nm shows a strongly increasing $^{20}\text{Ne}/^{36}\text{Ar}$ ratio with increasing depth, but this would not sizably affect the bulk $^{20}\text{Ne}/^{36}\text{Ar}$ ratio due to the low concentrations of Ne and Ar in the deeper layers, for which measured ^{36}Ar concentrations were below the background level. The lower $^{20}\text{Ne}/^{36}\text{Ar}$ ratio compared with the SW composition for bulk analyses in previous studies (Table 3.2) may partly be due to contributions from acid-susceptible phases on the ilmenite surface, but the lower ratios in the pristine-looking ilmenite surface in this study would be due to selective ^{20}Ne loss from ilmenite. The defect-mediated effusion discussed in the context of ^4He loss likely applied to the ^{20}Ne loss, because the shape of the depth profiles of $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios are preserved between LIMAS and SRIM simulation (Fig. 3.8), and the absolute ratios change downward in parallel.

3.5 Conclusions

High-resolution noble gas depth profiling of Apollo 17 ilmenite grains using LIMAS was conducted. The measured depth profiles reveal depth-dependent fractionation of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio, and those trends are similar to the previously reported CSSE results and the depth profiles simulated by SRIM. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio decreases systematically with depth and reaches ~ 11.2 (conventionally the so-called SEP component) at approximately 50 nm, corresponding to $\sim 90\%$ of the ^{36}Ar cumulative fraction. In addition, the noble gas concentrations obtained from the surface 100 nm match the results of previous bulk analyses. These observations demonstrate that the conventionally so-called SEP component in SW-irradiated materials reflects depth-dependent fractionated SW within the topmost ~ 60 nm from the surface, rather than SEPs inferred to have been implanted into micrometer depths. This is the first direct nano-scale measurement of fSW in lunar ilmenite.

The depth-dependent fractionation of the $^4\text{He}/^{20}\text{Ne}$ ratio was also observed, whereas the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio was less fractionated with depth relative to the $^4\text{He}/^{20}\text{Ne}$ ratio. The bulk $^4\text{He}/^{20}\text{Ne}$ ratios of all three grains and the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of grain 71501 #7 were lower than the SW composition, but these could not be explained by differences in trapping efficiencies. High ^4He fluences on the order of 10^{16} cm^{-2} are consistent with the experimental retention limit of ^4He in ilmenite, indicating that the $^4\text{He}/^{20}\text{Ne}$ ratios lower than the SW value are governed by the ^4He retention limit controlled by defect-mediated effusion. The $^{20}\text{Ne}/^{36}\text{Ar}$ ratio, previously thought to be highly fractionated at the topmost ilmenite surface, is shown to have been affected by contamination due to glass patches on ilmenite, and the actual $^{20}\text{Ne}/^{36}\text{Ar}$ ratio at the surface is less fractionated. However, the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio of grain 71501 #7 was still lower than the SW value, even when the effect of the glass patches was excluded. This suggests that the neon loss is governed by a defect-mediated effusion process.

Chapter 4

Solar Wind Implantation–sputtering Modeling

4.1 Introduction

The elemental ratio and isotopic ratio of solar wind (SW) noble gases implanted into lunar materials are typically lower than the present-day SW value. Especially for the light elemental ratios ($^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$), those values are lower than approximately half of SW value and showing mineral dependencies (Fig. 1.1; Frick et al. 1988, Signer et al. 1977, Wieler and Baur 1995). In the previous chapter, these lower elemental ratios were concluded to be due to a defect-mediated effusive loss. In contrast, the heavier elemental ratios ($^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$) show much weaker fractionation and only minor mineral dependence, leading to the common view that noble gases heavier than argon are generally well retained in lunar materials (e.g., Vogel et al. 2011, Wieler 2016).

The characteristics of isotopic ratios observed in lunar samples are widely interpreted as the result of sputtering induced by SW irradiation. Sputtering has been used to explain the isotopically heavier signatures in lunar materials and the SW-like compositions observed at the topmost surface (Benkert et al. 1993, Grimberg et al. 2006, Heber et al. 2003, Péron et al. 2018, Wieler et al. 2007, Wieler 2016). Sputtering has also been used to explain the SW-like values of $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios observed in the topmost surface in lunar soils (Vogel et al. 2011). These sputtering models assume the

implantation–sputtering equilibrium. However, if the equilibrium had been reached, Ar, Kr, and Xe should all have been lost by sputtering. In this case, there is no requirement that the bulk $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios remain only weakly fractionated, as observed (Wieler et al. 1996). Furthermore, if SW sputtering is a common process for SW irradiated solids, then all SW noble gas signatures must be interpreted with the expectation that sputtering has modified them. In particular, ^{36}Ar concentrations are frequently used to estimate SW exposure durations (e.g., Nichols et al. 1994, Obase and Nakashima 2023), but if ^{36}Ar is significantly lost by sputtering, its concentration will no longer scale linearly with exposure duration. However, a comprehensive study unifying noble gas concentrations, compositions, and irradiation timescales has not been established.

The previous chapter demonstrated that SRIM-based ion implantation simulations (without sputtering) well reproduce the measured depth distributions of noble gas concentrations and compositions. Based on this confirmation, this chapter models the sputtering-induced-evolution of both bulk compositions and depth profiles of SW noble gases in lunar ilmenites using the SRIM simulated profiles. The modeled results are then compared with measurements from lunar samples to evaluate which noble gas signatures can be explained solely through sputtering. Finally, the sputtering timescale is evaluated to discuss how SW noble gas data in lunar samples should be interpreted, and what information can be reliably extracted from them.

4.2 Modeling of Ion Implantation into the Moon

To estimate the depth profiles of noble gases in materials irradiated by the SW on the lunar surface, ion implantation simulations using SRIM (Ziegler et al. 2010) were conducted. Here, the incidence angle was estimated by assuming spherical lunar surface. The incidence angle of the SW onto the lunar surface materials varies due to geometric factors on the spherical surface and the effects of the Moon's rotation. In addition, it is necessary to account for shielding of SW while the Moon is passing through the terrestrial magnetotail (e.g., Poppe et al. 2024). Here, these factors were combined to reproduce SW implantation at the Moon, specifically for the Apollo 17 landing site (A17 site; 20°N, 31°W), from which the 71501 samples used in **Chapter 3** were collected.

4.2.1 SRIM parameters

The target material was set to FeTiO₃ with a density of 4.7 g cm⁻³ based on ilmenite composition. The elemental and isotopic ratios were taken from the present-day SW composition (Heber et al. 2009). Although the SW composition is known to be different depending on the SW speed regime, this effect is sufficiently small for the purpose of this study and was therefore neglected here (the differences between slow and fast SW are 4.2‰ amu⁻¹ for the Ne isotopic ratio and 20‰ and 22‰ for the ⁴He/²⁰Ne and ²⁰Ne/³⁶Ar ratios, respectively; Heber et al. 2012). The following sections describe the incidence angle and energy distribution of the simulated ions.

The incidence angle at the Apollo 17 landing site

Let the latitude and longitude of a given point on the Moon be denoted by ϕ and λ , respectively (with the center of the nearside defined as $\phi = 0$, $\lambda = 0$). Let θ represent the position of the Moon in its orbital path (where the full moon corresponds to $\theta = 0$). At a point (ϕ, λ, θ) , the SW incidence angle Θ^* is given by:

$$\Theta^* = \arccos[\cos(\phi) \cos(\theta - \lambda)] \quad (4.1)$$

If the SW flux at 1 astronomical unit (au) is F , then the flux F^* at this location can be expressed as:

$$F^* = F \cos(\phi) \cos(\theta - \lambda) \quad (4.2)$$

Here, it is assumed that the SW flows parallel to the Sun–Earth axis and that the Moon is shielded from the SW by the terrestrial magnetotail for one-quarter of its orbit (i.e., $0 \leq \theta < \pi/4$, $7\pi/4 < \theta \leq 2\pi$), following Fegley and Swindle (1993). The tilt of the lunar rotation axis ($\sim 1.5^\circ$) is neglected.

Based on these assumptions, Fig. 4.1a and b show the incidence angle and the flux at each orbital position for the A17 site, respectively. The orange shaded area in the figure corresponds to the periods when the A17 site is exposed to the SW. By integrating the flux, the SW flux at the A17 site is estimated to be $0.12F$ (Fig. 4.1b). Furthermore, the flux at each incidence angle is shown in Fig. 4.1c, indicating that for most of the exposure period, the SW arrives at incidence angle greater than 30° .

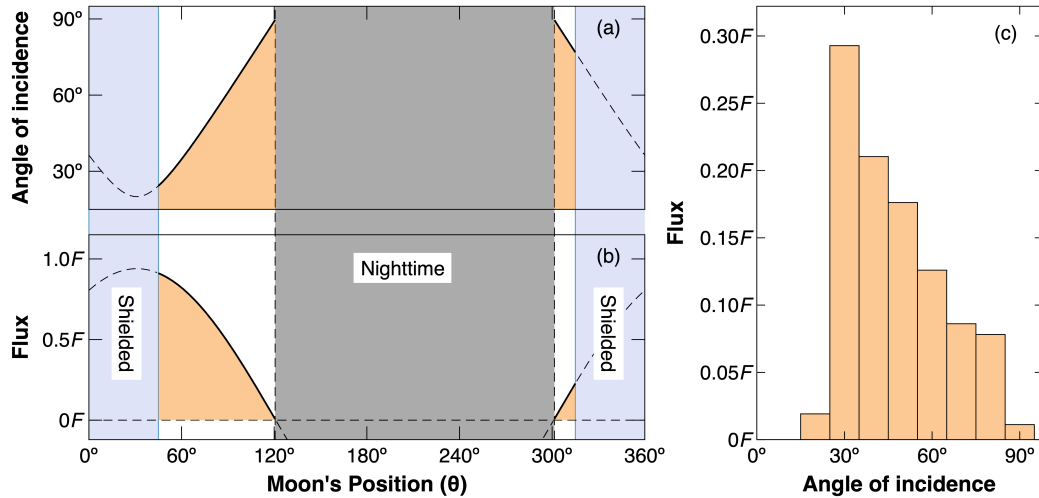


Figure 4.1: Angle of incidence and SW flux at the A17 site. Panels (a) and (b) show the angle of incidence and corresponding SW flux, respectively, as functions of the Moon's position (θ) in its orbit, calculated as $\Theta^* = \arccos(\cos(20^\circ) \cos(\theta - 31^\circ))$, and $F^* = F \cos(20^\circ) \cos(\theta - 31^\circ)$, where F is the SW flux at 1 au. The orange-shaded region indicates periods when the site is exposed to the SW, while the gray and blue-shaded regions represent nighttime and intervals when the Moon is passing the Earth's magnetotail, respectively. Panel (c) shows a histogram of SW flux as a function of incidence angle in 10° bins, indicating that most of the exposure occurs at incidence angles greater than 30° .

Speed distribution of the solar wind

Here, the speed distribution of the present-day SW as observed by the Solar Wind Ion Composition Spectrometer (SWICS) on the Advanced Compositions Explorer (ACE) spacecraft was used (Gilbert et al. 2007). Note that the Apollo 71501 soil was irradiated by the SW at approximately 100 Ma, and the speed distribution at that time may have differed from the present-day one. In addition, although both local and global magnetic fields are known to exist on the Moon (Blewett et al. 2011, Farrell et al. 2023, Poppe et al. 2024), their possible influences on SW deceleration and elemental or isotopic fractionation were neglected in this study.

For the present-day SW speed distribution, the full available dataset from ACE SWICS 2.0 Level 2 Data (Gilbert et al. 2007), covering the period from 1999:35 to 2011:233, was used. Using the Eq. (1) from Reisenfeld et al. (2013), the speed distributions of ^4He and ^{20}Ne were calculated in 100 km s^{-1} bins over the range of $300\text{--}1800 \text{ km s}^{-1}$. The speed distributions for other species (^{22}Ne , ^{36}Ar , ^{38}Ar , ^{84}Kr , and ^{132}Xe) were assumed to be identical to that of ^{20}Ne , and the fluxes were scaled according to the present SW compositions (Heber et al. 2009, Meshik et al. 2014).

Both the ^4He and ^{20}Ne speed distributions show a peak near 400 km s^{-1} , with fluxes approximately two orders of magnitude lower by $\sim 900 \text{ km s}^{-1}$ (Fig. 4.2). Fractions with speed exceeding 1000 km s^{-1} were mainly observed during the so-called "Halloween event" that occurred in late October 2003 (Reisenfeld et al. 2013).

4.2.2 SRIM simulation

SRIM simulations were conducted using TRIM.DAT mode in the TRIM program, which gives the specification of parameters of the incidence energy calculated from the speed distribution and the incidence angle for each implanted ion, with 100,000 ions distributed according to the speed distribution (Fig. 4.2). The simulations were performed for incidence angles ranging from 0° to 90° in 10° increments. The stopping positions of the ions were counted in 1 nm depth bins to obtain depth profiles. The results for each incidence angle were then weighted by the relative SW flux at that angle (Fig. 4.1c) and summed to estimate the expected depth profiles at the A17 site.

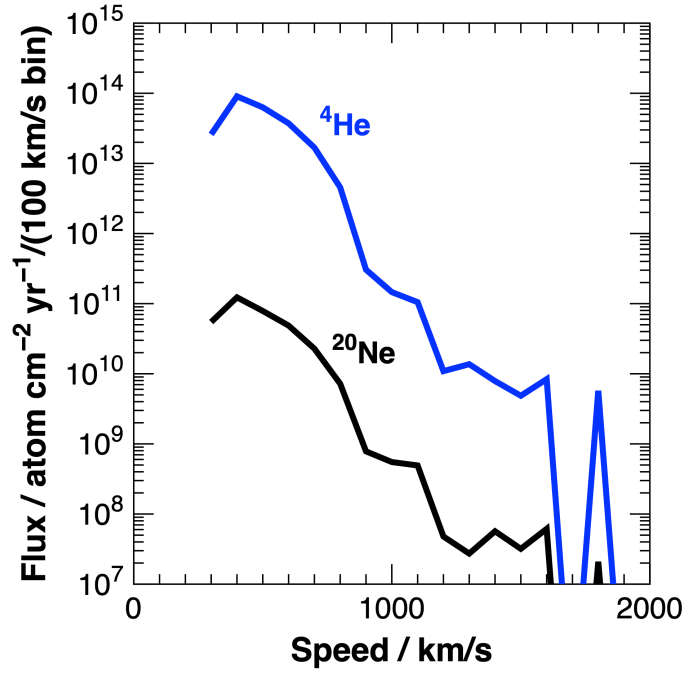


Figure 4.2: Speed distributions of ^4He and ^{20}Ne compiled from ACE SWICS 2.0 Level 2 Data.

Simulation results

Fig. 4.3 shows the simulation results for ^{20}Ne at each incidence angle, as well as the weighted sum according to the flux fractions. As the incidence angle increases, the depth profile shifts toward shallower depths, and the fluence decreases because backscattered ions (i.e., ions that escape before stopping in the target) increase (Fig. 4.3a). At the A17 site, the majority of the SW is implanted at $\sim 30^\circ$ (Fig. 4.1c), resulting in a ^{20}Ne depth profile peaking at a depth of ~ 10 nm (Fig. 4.3b)

Fig. 4.4 shows the depth profiles of all noble gas elements, where the number of simulated ions is normalized to 1, showing that the trends of depth distributions differ clearly among the elements. Not only the shapes, but also the trapping efficiency (β : calculated by $[\text{trapped ions}] / [\text{simulated ions}]$) differ, with lighter elements having lower values. Because the simulated ion numbers are normalized to 1, the elemental and isotopic ratios of bulk compositions corrected for the SW composition can be simply calculated

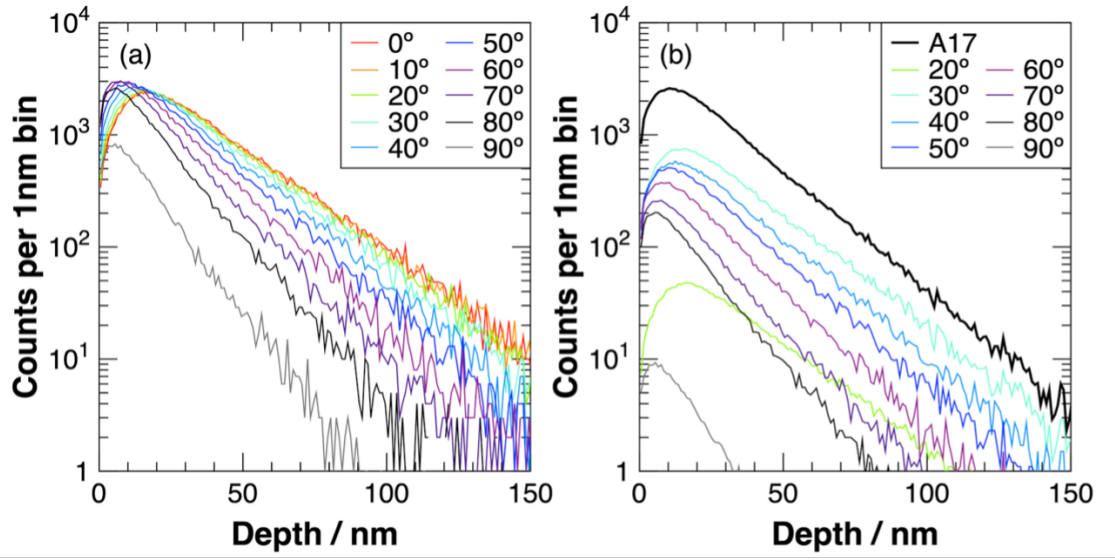


Figure 4.3: Simulation results of ^{20}Ne depth profiles. (a) With changing the incidence angle. (b) Depth profile estimated at irradiation conditions at A17 site.

as:

$$\frac{[A]}{[B]} = \frac{\beta_A}{\beta_B} \left(\frac{\Phi_A}{\Phi_B} \right)_{\text{SW}} \quad (4.3)$$

where β_A and β_B are the trapping efficiency of nuclide A and B and $(\Phi_A/\Phi_B)_{\text{SW}}$ is the SW composition of A/B . Note that the flux correction for the lunar surface geometry cancels out in this formulation. It is clear that the trapped SW noble gases are already fractionated after implantation, depending on the ratio of trapping efficiencies between two nuclei. The calculated bulk ratios relative to the SW values are shown in Fig. 4.5. In particular, lighter elements are more strongly fractionated due to their lower trapping efficiencies. Moreover, for isotopic ratios, the differences in trapping efficiencies between ^3He and ^4He is larger than those of other isotopic pairs, resulting in even greater isotopic fractionation. The elemental and isotopic compositions fractionated by differences in trapping efficiencies are as follows: $^4\text{He}/^{20}\text{Ne} = 576$, $^{20}\text{Ne}/^{36}\text{Ar} = 40.0$, $^{36}\text{Ar}/^{84}\text{Kr} = 2290$, $^{84}\text{Kr}/^{132}\text{Xe} = 9.76$, $^3\text{He}/^4\text{He} = 4.51 \times 10^{-4}$, $^{20}\text{Ne}/^{22}\text{Ne} = 13.7$, and $^{36}\text{Ar}/^{38}\text{Ar} = 5.45$.

The black lines in Fig. 4.6 shows the depth distributions of isotopic ratios and selected elemental ratios. Because the depth profiles of each elements exhibit distinct trends, those of the elemental ratios also differ. The $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios are lower than the

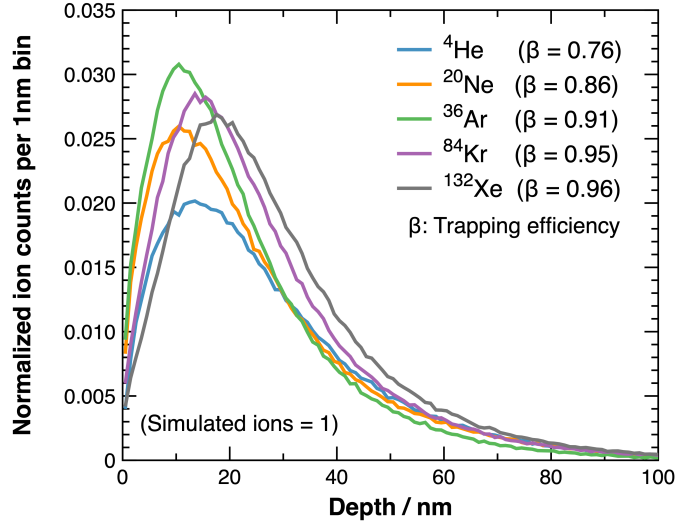


Figure 4.4: Depth distributions of noble gas elements simulated under the A17 site conditions. The ion counts are normalized, with the total number of simulated ions set to one. The vertical axis shows normalized ion counts per 1 nm depth bin. Each element shows a distinct distribution, and the trapping efficiencies (β) is shown for each elements.

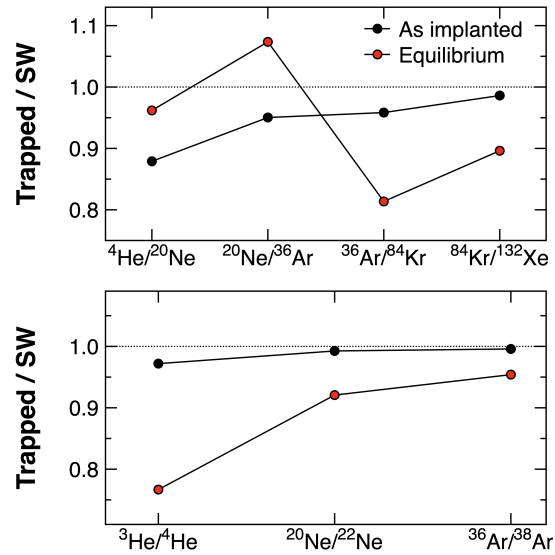


Figure 4.5: The trapped noble gas compositions relative to the SW compositions of as-implanted results (red) and at implantation–sputtering equilibrium (black). The SW compositions are from Heber et al. (2009) (${}^4\text{He}/{}^{20}\text{Ne}$, ${}^{20}\text{Ne}/{}^{36}\text{Ar}$, ${}^3\text{He}/{}^4\text{He}$, ${}^{20}\text{Ne}/{}^{22}\text{Ne}$, and ${}^{36}\text{Ar}/{}^{38}\text{Ar}$) and Meshik et al. (2014) (${}^{36}\text{Ar}/{}^{84}\text{Kr}$ and ${}^{84}\text{Kr}/{}^{132}\text{Xe}$).

SW value at the surface and increased toward deeper depths, whereas the $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios are higher than the SW value at the surface and decreased toward deeper depths. In contrast, all isotopic ratios are higher at the surface and decrease with depth.

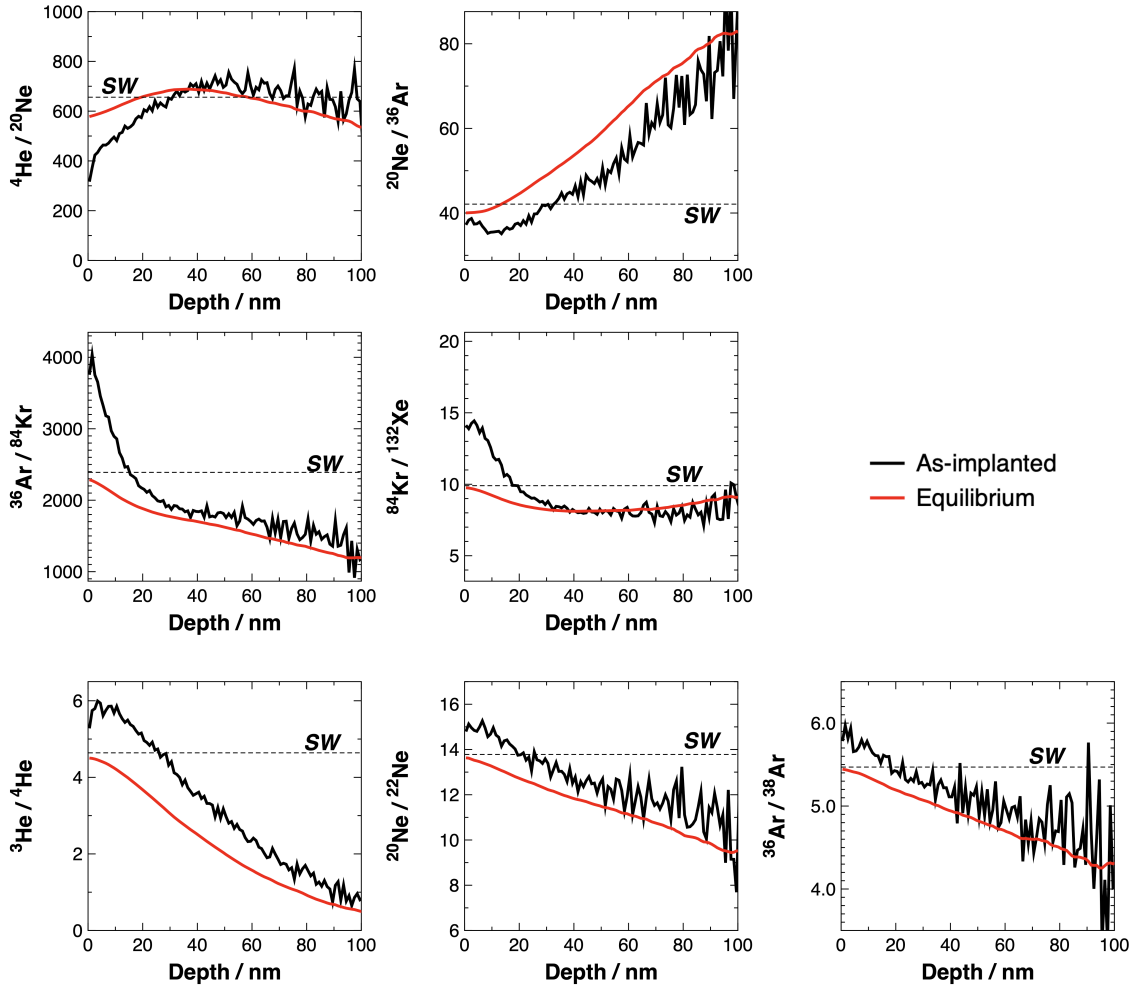


Figure 4.6: Depth distributions of elemental ratios and isotopic ratios of as-implemented (black) and at implantation-sputtering equilibrium (red). The SW compositions indicated by broken lines are from Heber et al. (2009) ($^4\text{He}/^{20}\text{Ne}$, $^{20}\text{Ne}/^{36}\text{Ar}$, $^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, and $^{36}\text{Ar}/^{38}\text{Ar}$) and Meshik et al. (2014) ($^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$).

4.3 Surface sputtering model

4.3.1 Model description

Here, the noble gas depth profiles obtained in the previous section are referred to as the as-implanted profiles. Based on these profiles, the modification of noble gas compositions by surface sputtering was modeled. A simple case involving repeated ion implantation and surface removal was considered, and a schematic illustration is shown in Fig. 4.7. This formulation allows the time evolution of the depth profile to be described as a sequence of implantation–sputtering steps.

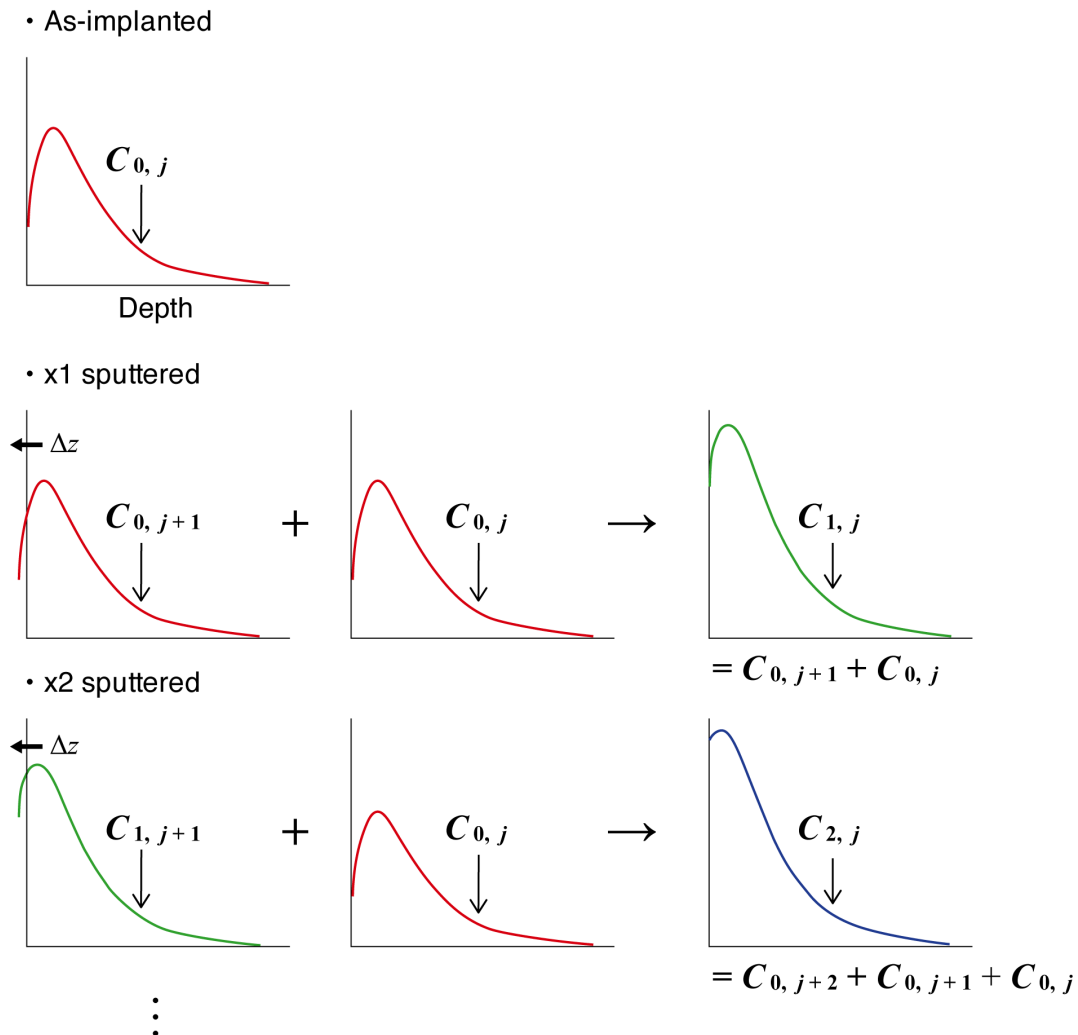


Figure 4.7: A schematic diagram of the implantation–sputtering model. An arrow indicates a given depth, and its concentration (or ion count) is represented as the sum of the subsequent cells.

Let the shape of the depth distribution of noble gases be given by $f(z)$, and consider its discretized and normalized form f_j as follows:

$$f_j = \int_{j\Delta z}^{(j+1)\Delta z} f(z)dz \quad (4.4)$$

$$\sum_{j=0}^{\infty} f_j = 1 \quad (4.5)$$

Let the depth distributions of concentration after n times sputtering steps be given as $C_{n, j}$. It can be expressed as

$$C_{n, j} = \beta \Phi^* \Delta t f_{n, j} \quad (4.6)$$

where β is the trapping efficiency of noble gases, Φ^* is the SW flux corrected for the A17 site conditions, Δt is an infinitesimal time corresponding to a single sputtering step of infinitesimal depth (Δz , where $s\Delta t = \Delta z$ and s is the sputter rate), and $f_{n, j}$ is the depth distribution after n sputtering steps. Hereafter, the as-implanted profile is described as $f_{0, j}$.

After n sputtering steps, the depth distribution at a given depth can be expressed as the sum of the ion counts in all subsequent n cells (Fig. 4.7). Therefore, the depth distribution and concentration can be written as:

$$f_{n, j} = \sum_{m=0}^n f_{0, j+m} \quad (4.7)$$

$$C_{n, j} = \beta \Phi^* \Delta t \sum_{m=0}^n f_{0, j+m} \quad (4.8)$$

Here, the infinitesimal depth (Δz) should be sufficiently small relative to the depth distributions and was set to 0.01 nm. To achieve this, the as-implanted profiles obtained with 1 nm depth bins (Fig. 4.4) were subdivided into 0.01 nm bins. Each 1 nm interval was divided into 100 smaller bins, and a constant value equal to 1/100 was assigned to each sub-bin. The corrected SW flux (Φ^*) was calculated by multiplying the present-day SW flux reported by Heber et al. (2009) by a shielding and rotation correction factor of 0.12 (see Section 4.2.1).

4.3.2 Implantation–sputtering equilibrium

Noble gas concentrations and fluences

Because the noble gas concentrations beyond ~ 100 nm in the as-implanted profile is negligible, Eqs. 4.7 and 4.8 converge after sputtering deeper than this region. In this case, the surface ($j = 0$) concentration approaches $C_{\infty, 0} = \beta \Phi^* \Delta t$ because f_j is normalized as shown in Eq. 4.5.

Figs 4.8a and 4.8b shows the evolution of ^{36}Ar depth profiles and the trapped ^{36}Ar amount with increasing sputtering depths. The depth profile progressively shifts toward the surface and reaches equilibrium after sputtering approximately 100 nm in depth. At this stage, the surface ion counts converge to 1 as described above (Fig. 4.8a). The trapped amount also saturates at a constant value, deviating from 100% trapping after sputtering of about 10 nm (Fig. 4.8b).

By assuming the sputter rate (s), the depth profile and trapped amount can be converted to concentration (cm^{-3}) and fluence (cm^{-2}), respectively. Fig. 4.8c shows the ^{36}Ar concentration profiles at implantation–sputtering equilibrium, calculated for three orders of sputter rate: 0.1, 0.01, and $0.001 \text{ \AA yr}^{-1}$. For these sputter rates, the peak ^{36}Ar concentrations are estimated to be approximately 10^{18} , 10^{19} , and 10^{20} cm^{-3} , respectively (Fig. 4.8c). The ^{36}Ar fluences at equilibrium are estimated to be about 3×10^{12} , 3×10^{13} , and $3 \times 10^{14} \text{ cm}^{-2}$, respectively (Fig. 4.8d). The ^{36}Ar concentrations and fluences may not exceed these values.

Depth distributions of elemental and isotopic compositions

Fig. 4.9a shows the evolution of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio with progressive sputtering. Because the surface concentration at equilibrium can be described as $C_{\infty, 0} = \beta \Phi^* \Delta t$, the noble gas elemental/isotopic ratios at the surface approach $\beta_A/\beta_B \times (\Phi_A/\Phi_B)_{\text{SW}}$, where β_A and β_B are the trapping efficiencies of isotopes A and B , and $(\Phi_A/\Phi_B)_{\text{SW}}$ is the A/B ratio of the implanting SW. This means that the surface ratio can be estimated from the of trapping efficiency ratio when the present-day SW composition is assumed.

For example, the trapping efficiencies of ^{20}Ne and ^{22}Ne are $\beta_{20} = 0.861$ and $\beta_{22} = 0.870$, respectively, and the surface $^{20}\text{Ne}/^{22}\text{Ne}$ ratio is estimated to be 13.65 at the equi-

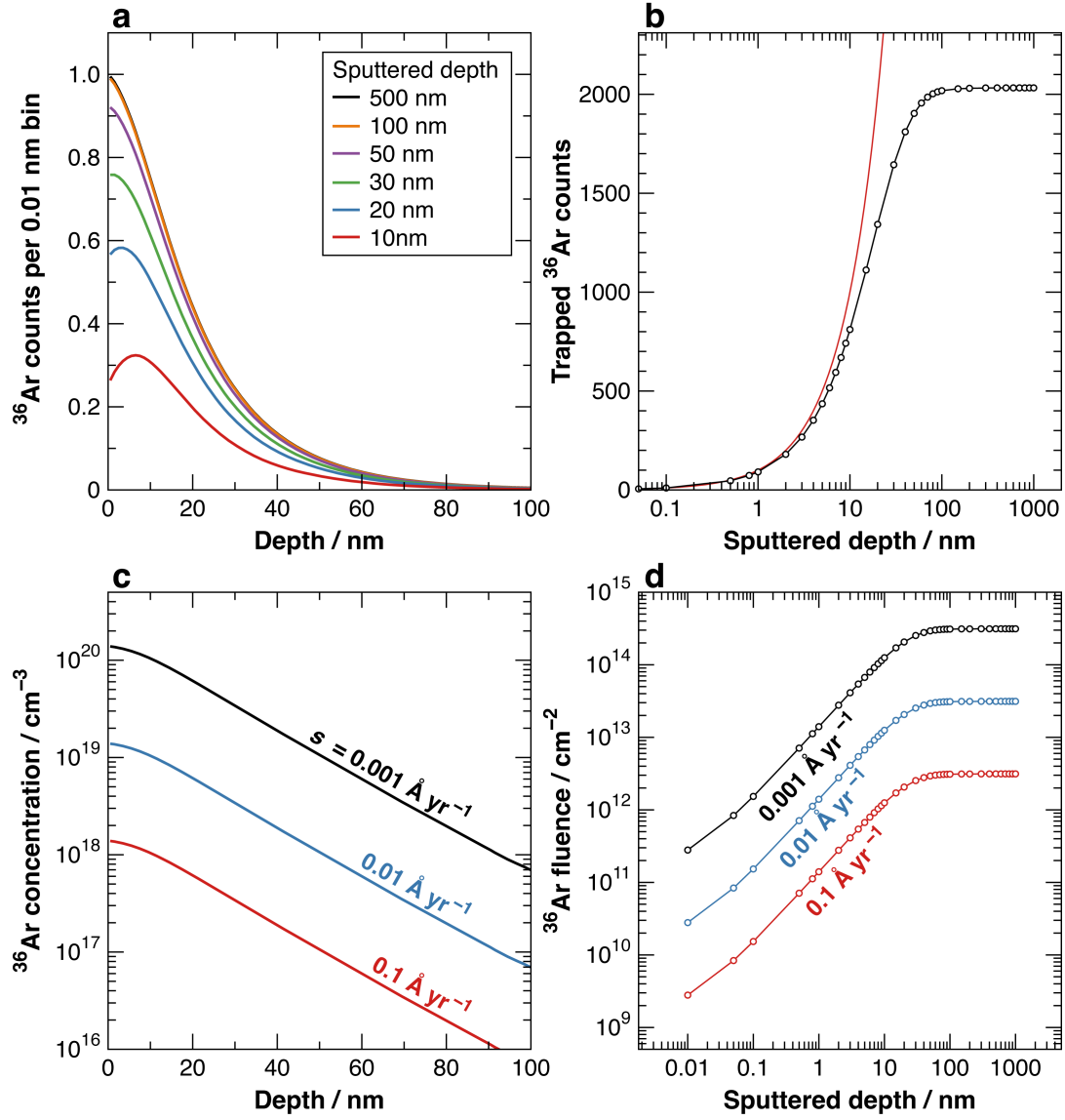


Figure 4.8: Evolution of ^{36}Ar depth profiles and trapped amounts during progressive sputtering. (a) Depth profiles of ^{36}Ar after sputtering different depths, showing a progressive shift of the implanted distribution toward the surface. (b) Increase in the total trapped ^{36}Ar with increasing sputtering depth, approaching saturation after sputtering of approximately 100 nm. (c) ^{36}Ar concentration profiles at the equilibrium calculated for different sputter rates ($s = 0.1, 0.01, \text{ and } 0.001 \text{ \AA yr}^{-1}$). (d) Evolution of the ^{36}Ar fluence with increasing sputtering depth.

librium (Fig. 4.9a). This applies to other elemental and isotopic ratios as well: the depth distributions progressively shift toward the surface and converge to equilibrium with the surface composition approaching to the SW compositions (red lines in Fig. 4.6).

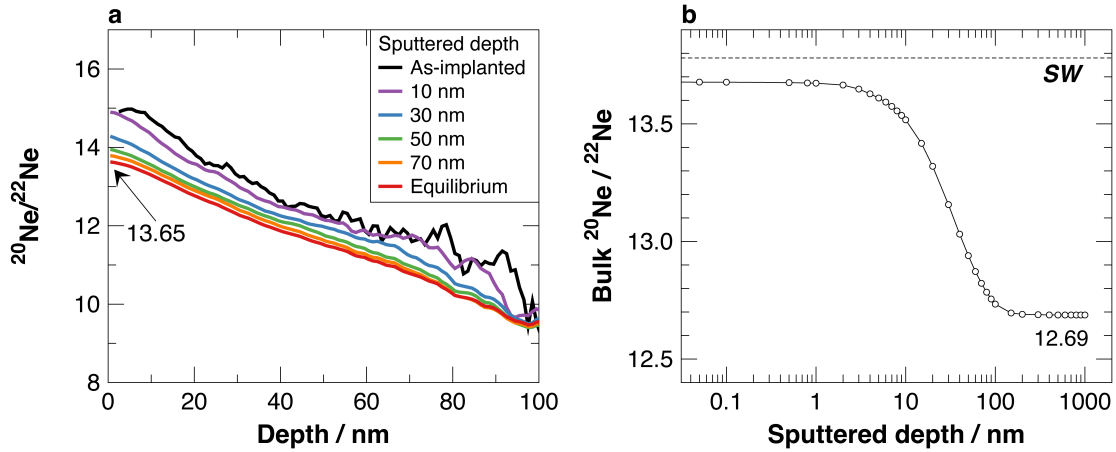


Figure 4.9: Depth profiles of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios for different sputtered depths. The surface ratio approaches 13.65, which is predicted from the SW composition and trapping-efficiency ratio. (b) Evolution of the bulk $^{20}\text{Ne}/^{22}\text{Ne}$ ratio as a function of sputtered depth. The bulk ratio begins to decrease after ~ 1 nm of sputtering and reaches its equilibrium value of 12.69 after ~ 100 nm of sputtering. The SW value of $^{20}\text{Ne}/^{22}\text{Ne} = 13.78$ is from Heber et al. (2009).

Bulk compositions

The bulk compositions also change with sputtering and reach equilibrium. The bulk compositions relative to the present-day SW value is shown as red plots in Fig. 4.5. Because the trends of the depth distributions differ among noble gas pairs, both the magnitude and the direction of sputtering-induced changes vary from pair to pair. For isotopic ratios, all systems become isotopically heavier with depth (Fig. 4.6), resulting in isotopically heavier value with increasing sputtering. In contrast, for elemental ratios, the $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios are fractionated toward heavier components at the topmost surface and therefore become lighter with sputtering, whereas the $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios are fractionated toward lighter components at the surface and thus become heavier through sputtering. The bulk noble gas compositions estimated for equilibrium are as follows: $^4\text{He}/^{20}\text{Ne} = 631$, $^{20}\text{Ne}/^{36}\text{Ar} = 45.2$, $^{36}\text{Ar}/^{84}\text{Kr} = 1945$, $^{84}\text{Kr}/^{132}\text{Xe} = 8.87$, $^3\text{He}/^4\text{He} = 3.56 \times 10^{-4}$, $^{20}\text{Ne}/^{22}\text{Ne} = 12.7$, and $^{36}\text{Ar}/^{38}\text{Ar} = 5.22$.

4.4 Comparison between model and lunar samples

In this section, the modeled noble gas characteristics are compared to the data of 71501 ilmenite reported in previous studies. For isotopic ratios, only the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio is considered, because the $^3\text{He}/^4\text{He}$ and $^{36}\text{Ar}/^{38}\text{Ar}$ ratios may be significantly affected by cosmogenic ^3He and ^{38}Ar , respectively.

4.4.1 Noble gas compositions

The bulk $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 71501 ilmenite ranges from 12.9–13.1 (Benkert et al. 1993, Frick et al. 1988, Nichols et al. 1994, Signer et al. 1977). Single-grain measurements by Nichols et al. (1994) show $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of 12.59–13.71 (corrected for cosmogenic component). These $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are consistent with the modeled values after sputtering of several tens of nanometers (Fig. 4.10a). Remarkably, the single-grain data fall entirely within the range expected from sputtering-driven evolution, and most grains exhibit ratios corresponding to sputtering of several tens of nanometers (Fig. 4.10b). Fig. 4.10c and 4.10d show the modeled $^{20}\text{Ne}/^{22}\text{Ne}$ depth profiles and the CSSE results of Benkert et al. (1993), respectively. The surface values of the CSSE profiles are also consistent with modeled profiles that have experienced at least ~ 50 nm of sputtering.

Fig. 4.11a compares a previously reported noble gas elemental ratios of 71501 ilmenites with the modeled ratios after 70 nm sputtering. For $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, although sputtering drives these ratios upward, the ratios measured in 71501 ilmenites are significantly lower than the SW values. This indicates that $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios in lunar soils are not controlled by sputtering, and that another process dominates their evolution. As discussed in **Chapter 3**, this process is defect-mediated effusion.

In contrast, the bulk $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios of 71501 ilmenites are comparable to the modeled values for 70 nm sputtering (Fig. 4.11a), which is 0.8–0.9 times lower relative to the SW values ($^{36}\text{Ar}/^{84}\text{Kr} = 1940$ and $^{84}\text{Kr}/^{132}\text{Xe} = 8.9$). When comparing the depth profiles, the $^{36}\text{Ar}/^{84}\text{Kr}$ ratio is consistent with the 70 nm sputtered profile, rather than as-implanted profile (Fig. 4.11b). The $^{84}\text{Kr}/^{132}\text{Xe}$ ratio, however, appears inconsistent with the modeled profile, although the absence of reported uncertainties prevents a

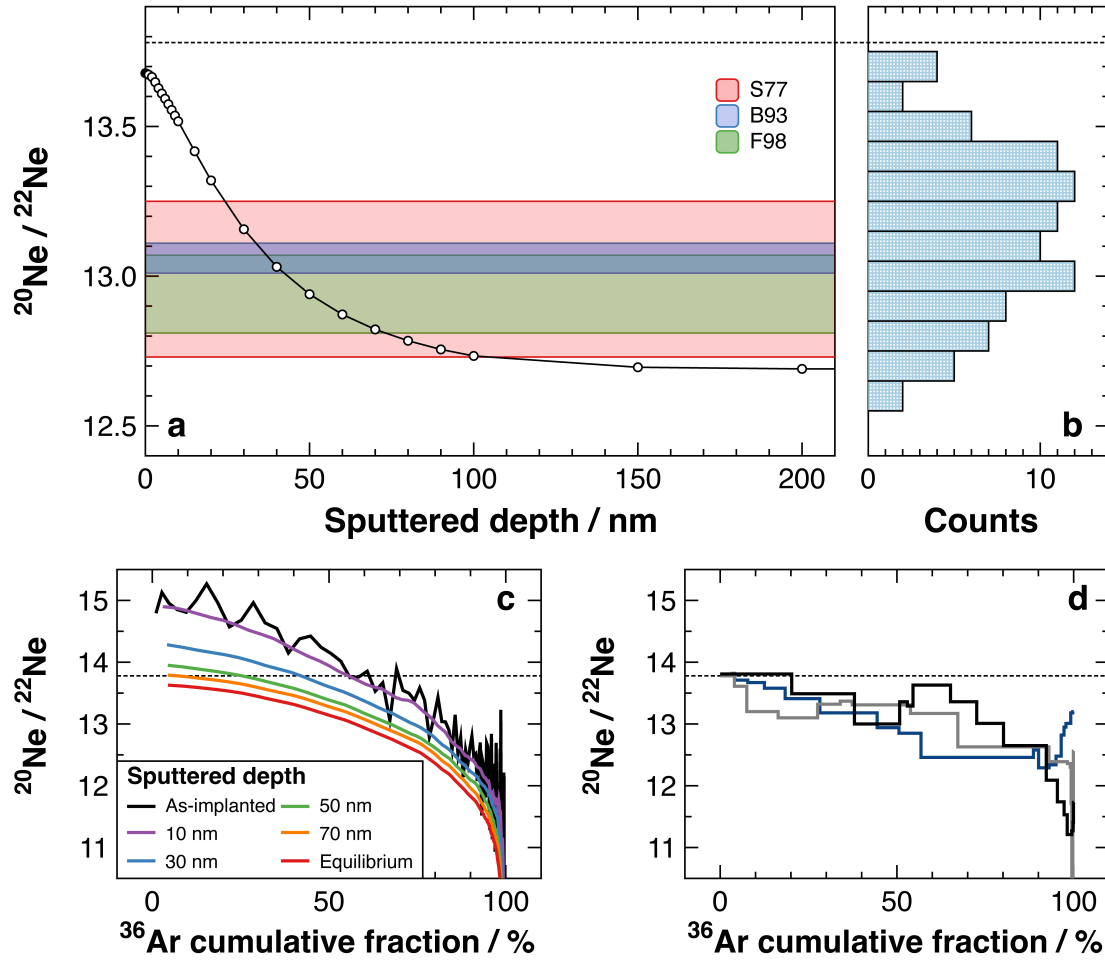


Figure 4.10: Modeled bulk $^{20}\text{Ne}/^{22}\text{Ne}$ ratios as a function of sputtered depth, compared with previously reported bulk values from red: Signer et al. (1977), green: Benkert et al. (1993), and blue: Frick et al. (1988). The range indicates the 1σ errors. (b) Histogram of the single-grain $^{20}\text{Ne}/^{22}\text{Ne}$ ratios from Nichols et al. (1994). The $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are corrected for cosmogenic components according to $(^{20}\text{Ne}/^{22}\text{Ne})_{\text{cos}} = 0.85$ and $(^{21}\text{Ne}/^{22}\text{Ne})_{\text{cos}} = 0.92$ based on Nichols et al. (1994). (c) Modeled depth profiles for different sputtered depths. (d) CSSE depth profiles from Benkert et al. (1993). Both the bulk and depth measurements are consistent with modeled $^{20}\text{Ne}/^{22}\text{Ne}$ ratios that have experienced several tens of nanometers sputtering.

definitive interpretation. Wieler and Baur (1995) attributed this trend to depth-dependent fractionation of $^{84}\text{Kr}/^{132}\text{Xe}$ ratio. Nevertheless, it is difficult to conclude here from the CSSE data alone, because it exhibits significantly lower $^{84}\text{Kr}/^{132}\text{Xe}$ ratio at 50% ^{36}Ar release, values not reproduced in the modeled profiles.

In any case, these comparisons show that the bulk and depth profiles of $^{20}\text{Ne}/^{22}\text{Ne}$, $^{36}\text{Ar}/^{84}\text{Kr}$, and the bulk $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of 71501 ilmenites can all be well explained by sputtering of several tens of nanometers.

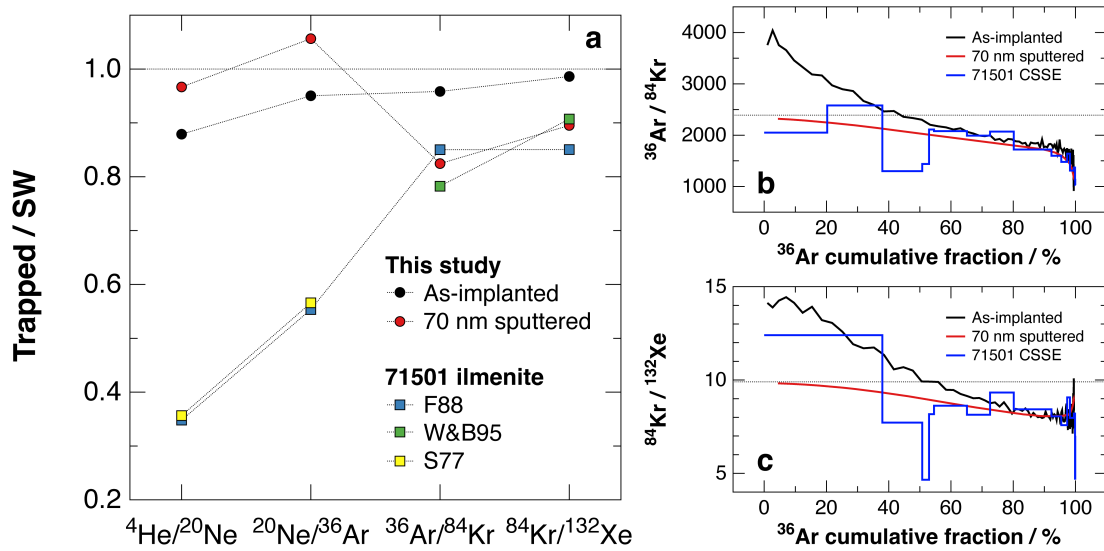


Figure 4.11: (a) Elemental ratios normalized to the SW values for the as-implemented and 70 nm sputtered values, compared with previously reported bulk ratios of 71501 ilmenites. F88: Frick et al. (1988), W&B95: Wieler and Baur (1995), S77: Signer et al. (1977). The SW values are from Heber et al. (2009) for $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, and Meshik et al. (2014) for $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios. (b) Modeled and CSSE depth profiles of $^{36}\text{Ar}/^{84}\text{Kr}$ ratio. (c) Modeled and CSSE depth profiles of $^{84}\text{Kr}/^{132}\text{Xe}$ ratio. The CSSE data are from 71501 ilmenite reported in Wieler and Baur (1995).

4.4.2 Timescale of sputtering

Based on the results presented above, it is clear that understanding the sputter rate of lunar surface materials is essential for interpreting the evolution of SW noble gas compositions. However, previously estimated sputter rates span more than two orders of magnitude. For example, Zinner et al. (1977) inferred an upper limit of $0.0035 \text{ \AA yr}^{-1}$ from the maximum fluences of SW-derived Fe and Mg in lunar samples. Kerridge (1991) estimated an upper

limit of $0.0024 \text{ \AA yr}^{-1}$ by comparing ^{36}Ar concentrations in samples that experienced long- and short-term SW irradiation with their solar-flare track ages. In contrast, Bibring et al. (1977) obtained much higher estimates of $\geq 0.2 \text{ \AA yr}^{-1}$, based on the morphology of micron-sized grains and the inferred residence times of regolith on the lunar surface.

Here, the noble gas concentrations of lunar samples can be used, together with the modeling results, to apply an approach similar to that of Zinner et al. (1977). Nichols et al. (1994) reported a maximum ^{36}Ar fluence of $2.6 \times 10^{13} \text{ cm}^{-2}$ for 90–125 μm -sized single grains of 71501 ilmenite, calculated by assuming a spherical grain and homogeneous irradiation from all directions. The modeled maximum ^{36}Ar fluences are approximately 3×10^{12} , 3×10^{13} , and $3 \times 10^{14} \text{ cm}^{-2}$ for sputter rates of 0.1, 0.01, and $0.001 \text{ \AA yr}^{-1}$, respectively (Fig. 4.8). Therefore, a sputter rate of $0.01 \text{ \AA yr}^{-1}$ can be regarded as an upper limit based on this approach.

Based on the upper limit estimated by Kerridge (1991: $<0.0024 \text{ \AA yr}^{-1}$) and the upper limit estimated in this study, sputtering of 10 nm, where the ^{36}Ar fluence begins to deviate significantly from 100% trapping, corresponds to approximately 42 kyr and 10 kyr, respectively. Similarly, sputtering of 100 nm, where clear saturation occurs, corresponds to about 420 kyr and 100 kyr for the two sputter rate, respectively. Therefore, if lunar surface grains have experienced simple SW irradiation as assumed in the present model, the maximum duration over which SW irradiation can be faithfully recorded is on the order of ~ 100 kyr.

However, actual SW irradiation on the Moon is unlikely to be as simple as assumed in the model, and may thus involve uncertainties. Fig. 4.12 compares the relationship between ^{36}Ar fluence and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios estimated by the present model, assuming sputter rates of $0.1 \text{ \AA yr}^{-1}$, $0.01 \text{ \AA yr}^{-1}$, and $0.0024 \text{ \AA yr}^{-1}$, with the single grain results of Nichols et al. (1994). The single grain results clearly show that the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio decrease at a lower ^{36}Ar fluence than the calculation results of the model assuming $0.01 \text{ \AA yr}^{-1}$ and $0.0024 \text{ \AA yr}^{-1}$. Furthermore, the trajectory of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio toward a heavier values ratio appears to deviate from the model predictions. The fluence calculations for the single grain data assume uniform irradiation from all directions and a spherical geometry. However, even if this were the cause, it is unlikely that all grains would systematically deviate from the modeled trend. The following section investigates

the causes of this discrepancy.

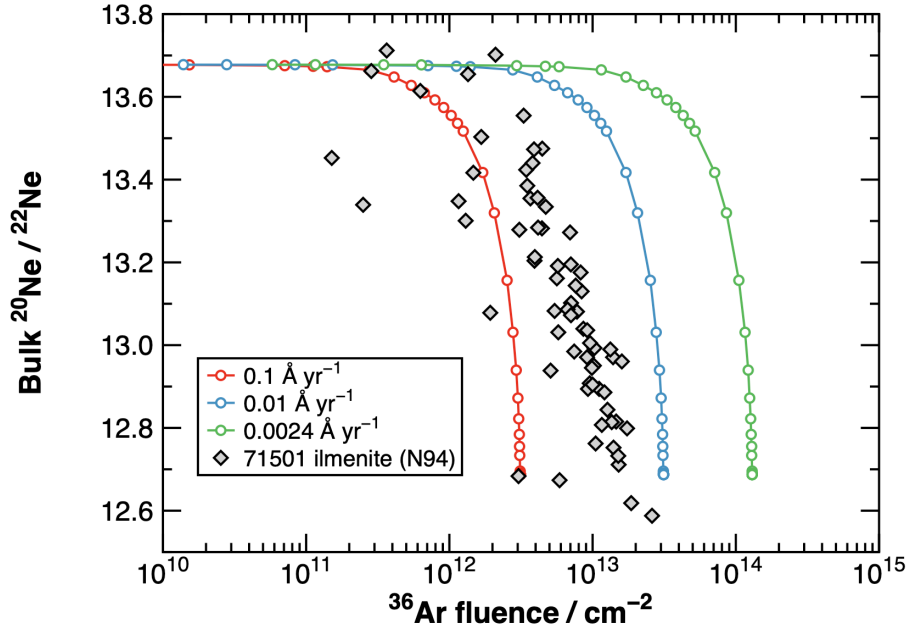


Figure 4.12: A comparison of the modeled and single grain analysis results of ^{36}Ar fluences versus bulk $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. The modeled results are shown based on three sputter rates. The single grain dataset of 71501 ilmenite (N94) is from Nichols et al. (1994). The fluences of single grain data set are calculated based on the mass and ^{36}Ar concentration by assuming spherical grain shape. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are corrected for cosmogenic components according to $(^{20}\text{Ne}/^{22}\text{Ne})_{\text{cos}} = 0.85$ and $(^{21}\text{Ne}/^{22}\text{Ne})_{\text{cos}} = 0.92$ based on Nichols et al. (1994).

4.4.3 Discrepancy of noble gas characteristics between modeled and actual lunar samples

In the preceding two sections, it was shown that the bulk compositions of the $^{20}\text{Ne}/^{22}\text{Ne}$, $^{36}\text{Ar}/^{84}\text{Kr}$, and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios, as well as the depth profiles of $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{36}\text{Ar}/^{84}\text{Kr}$ ratios, observed in 71501 ilmenite are broadly consistent with the modeled signatures produced by sputtering of several tens of nanometers. The sputtering rate was estimated to be on the order of $\sim 0.01 \text{ Å yr}^{-1}$. However, a discrepancy remains between the modeled noble gas characteristics and those observed in lunar samples. This discrepancy can be interpreted as indicating the amount of sputtering per implanted ^{36}Ar is higher in the

actual lunar soils than in the model. This ratio R can be described as follows

$$R = \frac{\Phi_M \times s}{\Phi_{36\text{Ar}} \times \beta_{36\text{Ar}}} \quad (4.9)$$

where Φ_M is the flux of sputtering-inducing particles. Because the ratio $\Phi_M/\Phi_{36\text{Ar}}$ could be regarded as constant in the SW, the quantity that effectively controls R is $s/\beta_{36\text{Ar}}$. To explore the cause of the discrepancy, several factors that could influence the relationship between sputtering, implantation, and noble gas retention are examined.

The model assumes a smooth lunar surface, whereas the actual lunar regolith is composed of irregularly shaped grains, clasts, and fines. As a result, individual grains experience a wide range of incidence angle for SW ions. Qualitatively, increasing incidence angle decreases the trapping efficiencies ($\beta_{36\text{Ar}}$; Fig. 4.3a). In contrast, larger incidence angles are known to increase the sputtering yield (s), peaking at $\sim 70^\circ$ – 80° (e.g., Brötzner et al. 2025). Thus, larger incidence angles may increase R , and conversely, smaller incidence angles can decrease it. A quantitative evaluation of this balance would require detailed settings of the complex morphology of the regolith layer, and such modelling is beyond the scope of this study. Nevertheless, if SW irradiation occurs preferentially at larger incidence angles than those assumed for a smooth sphere, this effect could act to increase R and may therefore contribute to the discrepancy.

An additional surface-eroding process that increase apparent sputtering rate s is another possible mechanism for raising R . Micro-flaking induced by SW-irradiation damage is one such candidate. However, the thickness removed in a flaking event is random and not systematically linked to the depth distribution of implanted noble gases. Consequently, such processes cannot reproduce the trend in which surface compositions approach the SW values, as expected from the sputtering-implantation equilibrium discussed in Section 4.3.2.

In this study, the SRIM results of $\beta_{36\text{Ar}}$ was used, but in actual lunar materials, it may be lower. SRIM treats the target as amorphous and resets the state after each implanted ion, whereas real lunar materials accumulate SW particles and develop a progressively thickening SW-damaged rim (Keller et al. 2021). How such irradiation damage affects $\beta_{36\text{Ar}}$ remains unknown at present, but it is noted here as a potential factor that could

increase R .

The discussion so far has implicitly assumed that ^{36}Ar is not lost from ilmenite by any process other than sputtering. Even if the estimate of R is accurate, the discrepancy could be resolved if ^{36}Ar has been lost through non-sputtering mechanisms. One possible loss mechanism is defect-mediated effusive loss, similar to that observed for He and Ne. As shown in **Chapter 3**, effusive loss of He and Ne occurs even at ^{36}Ar fluences of $2\text{--}3 \times 10^{12} \text{ cm}^{-2}$, indicating that irradiation over such durations is sufficient to generate defect networks. Therefore, defect-mediated effusive loss of Ar cannot be ruled out. However, if ^{36}Ar were lost in this way, ^{84}Kr and ^{132}Xe would also need to be lost in proportions that preserve both the $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios. Furthermore, once significant effusive loss occurs, the evolution of noble gas compositions would no longer follow the implantation-sputtering evolution described in the present model. For these reasons, while Ar loss remains a possibility, it does not yet provide a full explanation.

Furthermore, the estimation of sputter rates itself may involve uncertainties. Fluence calculations from previous study and sputtering estimates assume uniform irradiation onto the entire grain surface, whereas actual lunar materials may have experienced asymmetric irradiation depending on their orientation and micro-topography.

As a summary, these considerations highlight that exposure durations inferred from ^{36}Ar may not simply represent the true near-surface residence time of lunar grains. Further work will be required to clarify how SEP-track exposure ages and noble gas-derived exposure durations correspond to one another.

4.5 Conclusions

In this chapter, SW noble gas depth profiles in Apollo 17 ilmenite were simulated using SRIM. The evolution of both depth profiles and bulk compositions under surface sputtering was modeled.

The present model indicates that, in particular, noble gas compositions of the topmost surface approach to the SW-like value, which is calculated by the irradiated SW composition and the trapping efficiencies of each isotope. The modeled depth profiles and bulk compositions successfully reproduce the observed $^{20}\text{Ne}/^{22}\text{Ne}$, $^{36}\text{Ar}/^{84}\text{Kr}$, and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios, as well as depth profiles of $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{36}\text{Ar}/^{84}\text{Kr}$ ratios, reported for the Apollo 17 soil 71501, assuming sputtering of several tens of nanometers.

From the maximum ^{36}Ar fluence in 71501 ilmenite grains and the modeled fluences, the upper limit of the sputter rate is constrained to be $0.01 \text{ \AA yr}^{-1}$. Because noble gas signatures deviate from linearity after $\sim 10 \text{ nm}$ of sputtering and reach equilibrium after $\sim 100 \text{ nm}$, the duration over which SW noble gas compositions can be used as a faithful snapshot of surface exposure is limited to at most $< 10 \text{ kyr}$.

Even when adopting a sputter rate of $0.01 \text{ \AA yr}^{-1}$, the modeled relationship between ^{36}Ar fluence and the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio does not reproduce the observed single-grain data. Several possible causes of this discrepancy were evaluated, but no single mechanism fully resolves it.

Overall, this study demonstrates that SW noble gas signatures evolve over time and eventually reach a sputtering-implantation equilibrium. Given the difficulty of correcting for the associated timescales, caution is required when interpreting SW noble gas signatures in irradiated materials.

Chapter 5

Summary of the Thesis

Chapter 2 establishes a simultaneous in situ analytical method for the five noble gas isotopes, ^4He , ^{20}Ne , ^{22}Ne , ^{36}Ar , and ^{40}Ar using ToF-SNMS. The detection limits were confirmed to be sufficiently low for measuring solar wind derived noble gases in lunar materials. The analytical precision and stability were shown to be adequate for resolving the typical grain-to-grain variations of $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios in lunar samples, as well as the depth-dependent variations of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio. Furthermore, depth profiling of noble gases in olivine, a representative silicate mineral, was demonstrated with detection limits comparable to those achieved for ilmenite, except for ^{40}Ar due to high calcium abundance.

These results represent an advancement, as they provide a new quantitative depth scale for studying solar noble gases not only in lunar ilmenite but also in other SW-irradiated materials. The method enables not only the visualization of noble gas depth profiles but also nanoscale investigations of elemental and isotopic fractionation processes occurring near the material's surface.

Using this novel method, nanoscale noble gas depth profiles were obtained for the Apollo 17 soil sample 71501 in **Chapter 3**. Quantitative depth profiles of elemental and isotopic ratios were successfully measured. Remarkably, the noble gas concentrations and the $^4\text{He}/^{20}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios obtained from the small analyzed area were comparable to the mean values of ilmenite grain separates measured by previous bulk

measurements. This demonstrates that the “bulk” data from conventional noble gas analyses effectively reflect the noble gas signatures within only the uppermost ~ 100 nm of the grains.

For the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio, a gradual decrease toward isotopically heavier values with increasing depth was observed, revealing the presence of the conventional “SEP component” around 50 nm. This finding provides strong additional support that the isotopically heavy Ne observed in lunar samples represents fractionated solar wind (fSW), rather than a true SEP contribution, thereby further refuting the historical SEP hypothesis.

The measured noble gas depth profiles were broadly reproduced by ion-implantation simulations. Therefore, at least ^4He , ^{20}Ne , and ^{22}Ne must have been lost from ilmenite while preserving the general shapes of their depth distributions. The dominant process responsible for this loss is most likely defect-mediated effusion.

The agreement between the measured and simulated depth profiles provides strong support for previous interpretations of noble gas fractionation based on numerical simulations. Building on this consistency, a unified modeling approach was developed that combines ion implantation with surface sputtering to collectively explain the observed noble gas concentrations, isotopic ratios, and elemental ratios (**Chapter 4**).

It was found that sputtering of several tens of nanometers can coherently reproduce the compositions and depth profiles of the $^{20}\text{Ne}/^{22}\text{Ne}$ isotopic ratio and the elemental ratios $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ of 71501 ilmenite. This implies that, if sputtering indeed occurs on the lunar surface, i) solar-wind-derived Ar–Xe in lunar ilmenite are not significantly lost by processes other than backscattering and surface sputtering; ii) effusive loss of Ne does not measurably fractionate the neon isotopic ratios; and iii) most ilmenite grains in 71501 have not reached implantation–sputtering equilibrium, but instead experienced sputtering of several tens of nanometers, resulting in only a few percent loss of noble gases.

The sputtering timescale was also estimated, yielding an upper limit of $<0.01 \text{ Å yr}^{-1}$. However, this value cannot reproduce the observed relationship between ^{36}Ar fluences and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. This mismatch likely reflects differences between the simplified model assumptions and the actual nature of SW irradiation and sputtering on the lunar

surface, but no single controlling factor could be identified. Therefore, further investigation of the sputtering timescale is essential for advancing our understanding of noble gas fractionation in lunar and other extraterrestrial materials. This could contribute to our understanding of lunar or planetary exosphere.

Overall, this study focused on SW noble gases implanted in lunar ilmenite and demonstrated, using a newly developed nanoscale depth-profiling technique, that noble gases are clearly fractionated depending on depth within the uppermost tens of nanometers of lunar grains. Numerical simulations further confirmed that such nanoscale fractionation patterns can be reproduced by ion-implantation models.

Although this study was limited to noble gas depth profiles in lunar ilmenite, extending similar analyses to other lunar minerals will deepen our understanding of mineral-dependent trapping and fractionation of SW noble gases. Such knowledge is directly relevant to reconstructing the irradiation history of extraterrestrial materials and may also contribute to future lunar exploration, particularly in the context of utilizing SW-derived materials as potential resources.

Furthermore, extending noble gas imaging in meteorites beyond ^4He to measure elemental and isotopic ratios will enable more robust interpretations of regolith gardening processes, including evaluation of noble gas loss degrees. If materials that preferentially concentrate noble gases exist, in situ analyses based on noble gas elemental and isotopic ratios may also allow identification of specific noble gas components and their carrier phases.

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