Mineral Heterogeneity of Lunar Sub-milligram Basaltic Clasts and Its Effect on the Production Rates of Cosmogenic Nuclides

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ABSTRACT: Precise determination of the chemical composition of lunar samples is crucial for obtaining cosmogenic noble gas production rates and reliable cosmic ray exposure (CRE) ages. In this study, we established a new non-destructive method for determining the chemical composition of small mineralogically heterogeneous lunar basaltic clasts (<1 mg) using high-resolution X-ray microcomputed tomography (μCT). The volume of the individual mineral grains in each clast was obtained via μCT and combined with the chemical composition and density of the minerals to estimate the bulk chemical composition of each sample. The calculated chemical compositions were ultimately used to determine cosmogenic nuclide production rates. We used the lunar mare simulant sample (LMS-1) to evaluate the uncertainty of our method on the calculation of production rates of cosmogenic Ne (#Ne, #Ne, and #Ne) and Ar (#Ar and #Ar) (4% and 5% were adopted as suggested values, respectively). By applying this method to five Chang’E-5 basaltic clasts, we demonstrated that the chemical compositions of lunar regolith clastic samples (basalts) were different and the maximum variations of P (#Ne) (the production rate of cosmogenic #Ne) and P (#Ar) (the production rate of cosmogenic #Ar) among the five basaltic clasts were in the range of 18–20%. Therefore, the average chemical composition cannot be used to represent a single grain. In our study, mineral heterogeneity influenced the theoretical production rate of cosmogenic noble gas. Furthermore, the maximum cosmogenic #Ne production rate deviation from the average value reached 18.4% (~2 g/cm²). Our method significantly minimized the uncertainties in the production rate calculations caused by the mineral heterogeneity of the sub-milligram samples and when applied routinely would result in more reliable CRE ages.

INTRODUCTION

The Chang’E-5 (CE-5) spacecraft successfully landed in the mid-latitude region of the northeastern Oceanus Procellarum (43.06° N, 51.92° W) of the Moon on December 2, 2020, and returned with 1731 g of lunar regolith samples on December 17, 2020. Studying this material has great significance in understanding lunar thermal evolution and impact history.1 The CE-5 regolith samples represent materials ejected from several craters that have likely experienced a complex history at the lunar surface, including a variable exposure to cosmic rays. The cosmic ray exposure (CRE) age of lunar regolith can be used to define the formation time of craters2–4 and better constrain lunar impact history.

The CRE ages are calculated from the concentration of cosmogenic noble gas nuclides that are produced by spallation...
reactions on target elements exposed to galactic cosmic rays (GCR) and solar cosmic rays (SCR). The CRE ages are strongly dependent on the theoretical nuclide production rates that are governed by chemical composition.56 Thus, the concentrations of the target elements responsible for producing the respective nuclides must be precisely determined. Recent studies have shown that mineral heterogeneity in sub-milligram-sized samples of medium-to-coarse-grained regolith samples leads to differences in the concentration of target elements between fragments of the same basalt.5,8 Consequently, reliable CRE ages of lunar regolith and meteorites7,10 require precise determination of the chemical composition of the single grain used for measuring the CRE age.

To date, the most commonly used non-destructive methods involve obtaining the modal mineral abundance using back-scattered electrons (BSE) and energy-dispersive X-ray spectroscopy (EDS) on the surface of lunar regolith clasts.11 Based on the results of these studies, it is assumed that the mineral proportions in the analyzed areas represent those within the mass of the grain. The mass proportion of each mineral was used to calculate the bulk composition. However, the assumptions on which this approach is based are not valid, especially for mineralogically heterogeneous samples, i.e., the proportion of the mineral in the cut section depends on its spatial distribution in each grain. In addition, the procedures required to undertake this work can affect the noble gas isotope analysis. For instance, fixing samples in epoxy can lead to irreversible adsorption of atmospheric gases and increase the background contribution in a noble gas mass spectrometer as a reactive organic interference.12,13

In this study, we aimed at resolving these issues using X-ray microcomputed tomography (μCT) to obtain the volume proportions of individual mineral grains within single small (milligram-to-hundred micrograms) clasts. This can be combined with the established mineral chemistry and density determinations to estimate the chemical composition of single clasts, which would later be used to calculate cosmogenic nuclide production rates.

The feasibility of this method is preliminarily evaluated using standard materials and the influence of mineral heterogeneity in basaltic clasts on the cosmogenic nuclide production rate is systematically discussed within the method error. This method can reduce the uncertainty associated with mineral heterogeneity in single clasts and improve the reliability of CRE ages based on the determination of cosmogenic noble gas production rates.

**MATERIALS AND METHODS**

**Standard.** The standard material used in this study, i.e. the lunar mare simulant sample LMS-1 (hereinafter referred to as LMS-1), helped confirm the feasibility of our proposed method. LMS-1 was developed by CLASS Exolith Lab (Orlando, USA). It is a high-fidelity, mineral-based simulant whose composition represents a generic or average mare location on the Moon. Its mineralogy and bulk chemical compositions are well known (CLASS Exolith Lab online website: sciences.ucf.edu/class/exolithlab/) and the mineral species were confirmed using X-ray diffraction (XRD).14

**Sample.** Five basaltic clasts (hereinafter referred to as clasts #2, #3, #8, #16, and #18) were hand-picked from a single CE-5 soil sample (CE5C0400YJFM00406, ~2000 mg) taken from the lunar surface and allocated by the China National Space Administration. The crystallization age of this soil sample and implications of lunar history was recently reported by Li et al. and Tian et al.15,16 Their preliminary studies of the bulk rock chemical and isotopic compositions revealed that the landing site of CE-5 may not contain any additional exogenous material and the source of the soil samples is similar. This is consistent with the spectral analysis results reported by Qian et al.17 As a result, we have assumed that the five basaltic clasts were locally derived, excluding the possibility that exogenous basalt has a significant chemical composition difference in mineral facies.

**X-ray fluorescence (XRF) spectrometry.** We redetermined the bulk chemical composition of LMS-1. The major element abundances of LMS-1 were obtained via XRF spectrometry on fused glass discs using a PANalytical AXIOS Minerals instrument. The PANalytical AXIOS Minerals instrument is equipped with a Rh anode X-ray tube operated at an excitation power of 4 kW. It is a sequential instrument, operating under vacuum, with a single goniometer measuring channels covering the complete elemental measurement range from F to U (atomic numbers: 9 – 92) in the concentration range from 1.0 ppm to few % level. A detailed description of the glass disc preparation and calibration is available in the literature.18,19

**Electron probe microanalysis (EPMA).** The chemical compositions of the anorthite, enstatite, olivine, and ilmenite grains in the LMS-1 were determined using EPMA in a JEOL JXA-8230 instrument. The concentrations of Si, Al, Na, K, Ti, Mn, Ca, Mg, Fe, and P were determined. The microanalyzer was operated at an accelerating voltage of 15 kV and beam current of 20 nA, and 1-10 μm beam sizes with an analysis error of <1%. American SPI standard was used for the measurement, and all data were corrected for ZAF; i.e., effects of atomic number (Z-stopping power, back-scattering factor, and X-ray production power), absorption (A), and fluorescence (F).

**Mineral volume determination using X-ray microcomputed tomography (μCT).** High-resolution X-ray μCT is a reliable non-destructive technique for mineral segmentation analysis to determine the volume of minerals.20-22 X-rays passing through an object are detected using a series of detectors that measure the
degree attenuation of the signal. A set of X-ray intensity measurements made by all sensors for a given object position and scanner geometry is called a view or projection. The main goal of X-ray μCT is to obtain precise data on a particular object in a specific range of angular directions and then use the generated data to create a cross-sectional image of the object along that plane (for example, the slice in Fig. 1). The grayscale in this type of image reflects the relatively linear X-ray attenuation coefficient, which is a function of the density, atomic number, and X-ray energy. A complete three-dimensional (3D) volume of data can be obtained by collecting a stack of consecutive slices.\(^{23,24}\)

Based on the above principle, the volumes of pyroxene, plagioclase, olivine, and ilmenite in each studied sample were analyzed using a HeliScan MicroCT. Each sample was placed in a glass tube with a diameter of 3 mm. The voltage and current of the X-ray tube were set to 80 kV and 100 μA, respectively, detector exposure time was 0.030 s, and scanning accuracy was 0.8 μm. The size of the basaltic clasts used in this study exceeded 100 μm. We suggest that the volume analysis error of the single grayscale part in the clast is <1%.

**Calculation of chemical composition.** The volume, chemistry, and density of the main minerals in the samples were considered.

**Volume.** We obtained 3D grayscale resolution images from X-ray μCT for the different mineral components (Fig. 1). Minerals were identified based on their different grayscale in the 3D images, i.e., the same type of mineral is characterized by a similar grayscale. Segmentation and classification were performed to obtain the volume of the 3D images and similar grayscale units, the combination of which represents the volume of a particular mineral (V), i.e., the volume of each mineral in each sample.

**Chemistry:** LMS-1. We used the average chemical compositions of the anorthite, enstatite, olivine, and ilmenite grains obtained from the EPMA results (Table 1). Noticeably, in all EPMA results, in the absence of calibration for Fe\(^{3+}\), we considered all Fe to be Fe\(^{2+}\) and the chemical composition of ilmenite was determined using the ilmenite grains in the basaltic clasts.

**CE-5 basaltic clasts:** We compared the mineral data published by Che et al.\(^{11}\) and Tian et al.\(^{11,16}\) with our own. Considering that the average chemical composition of minerals on larger basaltic clasts is more representative, we adopted the mineral chemical data published by Che et al.\(^{11}\) In addition, we used the chemical compositions of the minerals in CE5-B1 and CE5-B2 (defined by Che et al.\(^{11}\)) as representative of the coarse-grained and fine-
grained samples; for samples #2 and #16, we used the EPMA data of CE5-B1, and for samples #3, #8, and #18, we used the EPMA results of CE5-B2.

Density: We used the reference mineral species in the CE-5 lunar soil, as determined by XRD and EPMA. More than 90% of the feldspar consists of bytownite and the pyroxene primarily consists of augite and some pigeonite. We used the typical mineral species as representative of the total mineral types, and the established density to determine the following mineral densities:

\[ \rho_{\text{Bytownite}} = 3.71 \text{ g/cm}^3 \]
\[ \rho_{\text{Anorthite}} = 3.73 \text{ g/cm}^3 \]
\[ \rho_{\text{Augite}} = 3.4 \text{ g/cm}^3 \]
\[ \rho_{\text{Fayalite}} = 3.3 \text{ g/cm}^3 \]
\[ \rho_{\text{Ferrom Enstatite}} = 4.72 \text{ g/cm}^2 \]

Considering that the Fo abundances (40-60) of the CE-5 olivine, densities of endmembers (\( P_{\text{Olivine}} = 4.39 \text{ g/cm}^3 \)) and densities of olivine (3.27 g/cm^3) showed significant variations, we recalculated the densities based on the average Fo abundances (LMS-1, Fo abundance = 78; CE-5, Fo abundance = 50). We found that the olivine density of LMS-1 is \( \rho_{\text{Olivine}} = 3.52 \text{ g/cm}^3 \), and that of the CE-5 basaltic clasts is \( \rho_{\text{Olivine}} = 3.83 \text{ g/cm}^3 \).

Based on these conditions, the following formulas were used to estimate the bulk element in each sample:

\[ M_i = \rho_i \times V_i \]
\[ M_{\text{total}} = \sum M_i \]
\[ M_{i,j} = M_i \times \omega_j \]
\[ M_{i,j,\text{total}} = \sum M_{i,j} \]
\[ \omega_{\text{total}} = M_{i,j,\text{total}} / M_{\text{total}} \]

where \( M \) is the mass of the mineral or oxide content, \( \omega \) represents the weight percentage, \( i \) corresponds to anorthite, enstatite, olivine, or ilmenite, and \( j \) corresponds to SiO2, TiO2, Al2O3, FeO, MnO, MgO, CaO, Na2O, K2O, Cr2O3, P2O5, NiO, Total.

### RESULTS

#### Chemical composition of LMS-1

We normalized all oxide contents to elemental contents to remove the effect of the different atomic masses of FeO and Fe2O3 on the weight percentages, and compared the deviation of the chemical composition calculated using this method and the results of the XRF analysis. The recalculated results are given in Table 2, which indicate a deviation of all elements relative to the XRF analysis results.

#### Chemical composition of CE-5 basaltic clasts

We applied our proposed method to determine the chemical composition of each basaltic clasts and calculated the production rates.

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**Table 1. Average chemical composition (wt.%) of the minerals in LMS-1 determined using EPMA**

<table>
<thead>
<tr>
<th></th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Cr2O3</th>
<th>P2O5</th>
<th>NiO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthite</td>
<td>48.55</td>
<td>0.02</td>
<td>32.47</td>
<td>0.47</td>
<td>0.00</td>
<td>0.03</td>
<td>15.64</td>
<td>2.31</td>
<td>0.06</td>
<td>0.00</td>
<td>0.02</td>
<td>nd</td>
<td>99.56</td>
</tr>
<tr>
<td>(n=25) 1σ</td>
<td>0.54</td>
<td>0.01</td>
<td>0.77</td>
<td>0.07</td>
<td>0.01</td>
<td>0.01</td>
<td>0.67</td>
<td>0.19</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>-</td>
<td>1.92</td>
</tr>
<tr>
<td>Enstatite</td>
<td>55.88</td>
<td>0.11</td>
<td>1.41</td>
<td>10.55</td>
<td>0.22</td>
<td>29.56</td>
<td>1.57</td>
<td>nd</td>
<td>nd</td>
<td>0.55</td>
<td>nd</td>
<td>0.08</td>
<td>99.94</td>
</tr>
<tr>
<td>(n=50) 1σ</td>
<td>0.25</td>
<td>0.03</td>
<td>0.17</td>
<td>0.55</td>
<td>0.01</td>
<td>0.01</td>
<td>0.68</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>nd</td>
<td>2.71</td>
</tr>
<tr>
<td>Olivine</td>
<td>38.91</td>
<td>0.16</td>
<td>0.03</td>
<td>20.59</td>
<td>0.29</td>
<td>0.39</td>
<td>0.06</td>
<td>nd</td>
<td>nd</td>
<td>0.02</td>
<td>0.08</td>
<td>0.11</td>
<td>100.12</td>
</tr>
<tr>
<td>(n=20) 1σ</td>
<td>0.42</td>
<td>0.08</td>
<td>0.01</td>
<td>1.95</td>
<td>0.04</td>
<td>1.65</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>nd</td>
<td>62.93</td>
<td>0.59</td>
<td>30.05</td>
<td>1.25</td>
<td>0.33</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.06</td>
<td>nd</td>
<td>0.00</td>
<td>95.22</td>
</tr>
<tr>
<td>(n=9)   1σ</td>
<td>1.69</td>
<td>0.38</td>
<td>1.75</td>
<td>0.80</td>
<td>0.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>0.00</td>
<td>2.50</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2. Chemical composition (wt.%) of LMS-1 after removal of O and Ni**

<table>
<thead>
<tr>
<th></th>
<th>XRF</th>
<th>Calculated</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>43.0287</td>
<td>42.2367</td>
<td>1.8750</td>
</tr>
<tr>
<td>Ti</td>
<td>3.1500</td>
<td>3.4568</td>
<td>8.8742</td>
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<tr>
<td>Al</td>
<td>14.9055</td>
<td>12.7931</td>
<td>16.5116</td>
</tr>
<tr>
<td>Fe</td>
<td>9.0951</td>
<td>11.6580</td>
<td>15.0367</td>
</tr>
<tr>
<td>Mn</td>
<td>2.4234</td>
<td>2.5671</td>
<td>5.1857</td>
</tr>
<tr>
<td>Mg</td>
<td>16.6901</td>
<td>16.7324</td>
<td>0.2524</td>
</tr>
<tr>
<td>Ca</td>
<td>10.2622</td>
<td>9.0591</td>
<td>13.2802</td>
</tr>
<tr>
<td>Na</td>
<td>1.4137</td>
<td>2.5733</td>
<td>45.0625</td>
</tr>
<tr>
<td>K</td>
<td>0.0417</td>
<td>0.8666</td>
<td>70.1206</td>
</tr>
<tr>
<td>Cr</td>
<td>0.3540</td>
<td>0.2242</td>
<td>57.8932</td>
</tr>
<tr>
<td>P</td>
<td>0.0055</td>
<td>0.1430</td>
<td>96.1206</td>
</tr>
</tbody>
</table>

---

We applied our proposed method to determine the chemical composition of each basaltic clasts and calculated the production rates.
clast. The grain sizes of the five basaltic clasts were distributed on the micron scale. Usually, clasts consist of several single minerals, which are dominated by pyroxene and feldspar, with olivine and ilmenite as additional components (Table 3 and Fig. 2). Most of our samples were too small (hundreds of micrometers) to determine their texture (e.g., aphanitic, porphyritic, poikilitic, and equigranular). We simply divided the five grains into two categories: fine-grained (#2 $\&$ #16) and coarse-grained (#3, #8, and #18). The classification method we used is based on CE5-B1 and CE5-B2 samples, where CE5-B1 is fine-grained ($\leq$1 mm long) with radiating elongated crystals of plagioclase and ilmenite, and CE5-B2 is coarse-grained ($\geq$2 mm long). The corresponding chemical compositions of each basaltic clast are listed in Table 4 and shown in Fig. 3 by normalizing the average chemical compositions using the data of the 16 basaltic clasts reported by Tian et al. 

**Table 3. Summary of the average chemical composition (wt.%) of the minerals in CE5-B1 and CE5-B2 from literature determined using EPMA**

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Cr$_2$O$_3$</th>
<th>P$_2$O$_5$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE5-B1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>48.87</td>
<td>0.09</td>
<td>31.61</td>
<td>0.87</td>
<td>0.01</td>
<td>0.20</td>
<td>16.02</td>
<td>1.13</td>
<td>0.17</td>
<td>0.00</td>
<td>0.02</td>
<td>98.99</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>46.59</td>
<td>1.94</td>
<td>2.59</td>
<td>27.04</td>
<td>0.40</td>
<td>6.90</td>
<td>12.83</td>
<td>0.03</td>
<td>0.00</td>
<td>0.26</td>
<td>0.02</td>
<td>98.60</td>
</tr>
<tr>
<td>Olivine</td>
<td>31.84</td>
<td>0.33</td>
<td>0.01</td>
<td>53.19</td>
<td>0.56</td>
<td>12.30</td>
<td>0.43</td>
<td>0.00</td>
<td>0.00</td>
<td>0.05</td>
<td>0.11</td>
<td>98.83</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.06</td>
<td>51.90</td>
<td>nd</td>
<td>45.99</td>
<td>0.38</td>
<td>0.21</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>98.54</td>
</tr>
<tr>
<td>CE5-B2</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>49.03</td>
<td>0.08</td>
<td>31.73</td>
<td>0.79</td>
<td>0.02</td>
<td>0.10</td>
<td>15.69</td>
<td>1.47</td>
<td>0.22</td>
<td>0.00</td>
<td>0.02</td>
<td>99.14</td>
</tr>
<tr>
<td>Pyroxene</td>
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<td>1.40</td>
<td>1.70</td>
<td>25.87</td>
<td>0.41</td>
<td>7.56</td>
<td>13.73</td>
<td>0.03</td>
<td>0.00</td>
<td>0.18</td>
<td>0.02</td>
<td>98.73</td>
</tr>
<tr>
<td>Olivine</td>
<td>30.92</td>
<td>0.24</td>
<td>0.01</td>
<td>58.17</td>
<td>0.65</td>
<td>8.26</td>
<td>0.52</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.12</td>
<td>98.90</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.02</td>
<td>52.50</td>
<td>nd</td>
<td>45.61</td>
<td>0.38</td>
<td>0.35</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>98.87</td>
</tr>
</tbody>
</table>

*The average chemical composition was obtained from literature.

**Table 4. Chemical composition (wt.%) of five basaltic clasts calculated using the method developed in this study**

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Cr$_2$O$_3$</th>
<th>P$_2$O$_5$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>40.96</td>
<td>8.83</td>
<td>9.49</td>
<td>23.64</td>
<td>0.31</td>
<td>4.34</td>
<td>11.92</td>
<td>0.30</td>
<td>0.04</td>
<td>0.16</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>43.46</td>
<td>0.97</td>
<td>10.75</td>
<td>27.83</td>
<td>0.36</td>
<td>5.44</td>
<td>10.52</td>
<td>0.48</td>
<td>0.07</td>
<td>0.08</td>
<td>0.05</td>
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Production rate of CE-5 basaltic clasts. To evaluate the impact of chemical composition heterogeneity in these samples on production rates, we determined the production rate of cosmogenic $^{21}$Ne (P$_{21}$Ne) and $^{38}$Ar (P$_{38}$Ar) in Table 5 based on the chemical composition of the basaltic clasts reported in Table 4 and the 2-s exposure model of Hohenberg. The results are presented in Figs. 4 and 5. The abundances of Na, Mg, Al, Si, Ca, and Fe are the target elements for the production rate of cosmogenic $^{21}$Ne, whereas $^{38}$Ar is produced by spallation involving K, Ca, Ti, and Fe. Based on the differences in the chemical compositions of each sample, the predicted cosmogenic production rates of the Ne isotopes ($^{20}$Ne, $^{21}$Ne, and $^{22}$Ne) at different depths (0–500 g/cm$^2$) of each sample were calculated. To further illustrate the effect of heterogeneity on the predicted cosmogenic Ne production rates, we plotted a Ne three-isotope diagram, i.e., $^{20}$Ne/$^{22}$Ne vs. $^{21}$Ne/$^{22}$Ne (Fig. 6).
The effects of chemical/mineral heterogeneity can be clearly observed. The difference is most pronounced at the surface (0 g/cm²) of the different single grains, and the difference decreases with an increase in the shielding depth. Furthermore, there is a difference of ~17% and 20% for 20Ne/22Ne and 21Ne/22Ne, respectively, between #8 and #16. Instead, the Ne isotope ratios of samples #2 and #3 are similar at different shielding depths with an increase in the shielding depth. Furthermore, there is a difference of ~17% and 20% for 20Ne/22Ne and 21Ne/22Ne, respectively, between #8 and #16. Instead, the Ne isotope ratios of samples #2 and #3 are similar at different shielding depths with good correlation, even though their P38 values are different.

**DISCUSSION**

**Assessment of LMS-1.** Using the method, we established in this study to estimate the chemical composition of single clasts, we obtained the chemical composition of LMS-1. Compared with the XRF analysis, we determined the deviations of the two methods (Table 2). The most evident element deviations are observed for...
Na, K, Cr, and P (>40%), which are low abundance in the minerals (<1%). The other elements deviate by < 20%. The deviations in Na, K, Cr, and P in the calculations reflect the shortcomings of this method; therefore, our method is not as reliable and accurate as the XRF results. The method we established is mainly based on the distinction of the main mineral phases combined with the average chemical composition of each mineral phase, ignoring the estimation of accessory minerals. This may be the main factor leading to the differences observed for low-abundance elements. The observed deviations in Fe (15.03%), Al (16.51%), Ti (8.87%), and Ca (13.28%) might have been caused by the slight difference in the mineral compositions of the samples used for XRF analysis and X-ray μCT analysis in this work. However, they were both taken from LMS-1 (which was well mixed and believed to represent the bulk material). In addition, the same type of minerals has different chemical compositions, and the average chemical composition used for the calculations only represents an approximation, resulting in additional variations. Here, we attempt to specifically consider the analytical errors associated with X-ray μCT and errors in mineral boundary selection for the calculation of mineral volumes. However, LMS-1 is a powder sample containing millions of grains of different sizes, making it difficult to estimate the errors of each grain.

Precise determination of the chemical composition of the samples is critical for the calculation of noble gas production rates and CRE ages. To calculate the production rates of the isotopes of Ne (PNe) and Ar (40Ar, 39Ar) (PAr), we used both the chemical compositions determined by XRF and X-ray μCT. The deviations of each production rate at the same depth for Ne were less than 3.82% and less than 4.72% for Ar. We decided to use 4% and 5% as the upper limit of uncertainty for calculating PNe and PAr, respectively. The uncertainty was integrated with the analytical error of EPMA, analytical error of X-ray μCT, uncertainty in the identification of minerals, and error of mineral density.

**Heterogeneities in chemical compositions.** Deviations in element abundances between the five basaltic clasts were clearly observed (listed in Table 4 and shown in Fig. 3). The maximum deviation of TiO2 in different basaltic clasts is 91.98% between samples #3 and #16. With the exception of SiO2 (14.83%) and CaO (18.11%), the deviations of Al2O3 (57.44%), FeO (23.82%), MnO (21.36%), MgO (25.59%), and Na2O (73.57%) are greater than 20%. All the oxides mentioned above are significantly higher than the uncertainty of the method established in this study. Typically, similar trends can also be observed in the different basaltic clast sections on elemental mapping analyzed by EDS.16 Cautiously, K2O (73.65%), Cr2O3 (58.58%), and P2O5 (64.57%) also have significant deviations, but it cannot be ruled out whether it is caused by the uncertainty of the method.

The internal chemical compositions are heterogeneous, considering coarse- and fine-grained basaltic clasts. The average chemical composition of the basalt in the CE-5 regolith may not be representative of a single basaltic clast, which is less than one milligram in weight. Given the above experimental and calculation results, there is no reliable evidence to prove that these five basaltic clasts have similar chemical properties. Thus, we concluded that they are unique and chemically heterogeneous.

**Influence on production rate.** We have already verified the error of this method for Ne (<4%) and Ar (<5%) with LMS-1; therefore, it is reasonable to believe that the production rate bias in different clasts is mainly caused by the heterogeneity of the mineral composition rather than by the method itself. The variation in the mineral composition of different basaltic clasts significantly affects the bulk chemical composition of the single grains, which also affects the determination of production rates for cosmogenic noble gas nuclides based on specific target elements (Figs. 4 and 5). Generally, the maximum deviation of PAr between different basaltic clasts is 18.29%, which is smaller than that of PNe (20.7%), and the production rate variations for different shielding depths have similar trends. Moreover, the maximum deviation is observed at different depths for P21 (at ~1 g/cm²) and P38 (at ~225 g/cm²). However, direct variation is most significant at shallow depths (those close to 0 g/cm²). Assuming a similar shielding depth for different samples, the maximum deviation of P21 or P38 ranges between 18% and 20%. This is also verified by assuming a similar shielding depth for single samples, and the difference in their chemical compositions causes an error of up to ~20% for the production rates.

With increasing shielding depth, P38 and P21 display similar trends, characterized by an initial steep decrease, followed by a slight increase within the range of 5–10 g/cm² until reaching a plateau at ~50 g/cm². A gentle decrease is observed up to ~500 g/cm². The disparity controlled by the shielding depth can reach up to two orders of magnitude. However, chemical heterogeneity still controls the theoretical spallation production rate ratio curves26 on the Ne three-isotope plot (Fig. 6) used to estimate the shielding depth of each grain.

By comparing P21, P38, and the predicted model correlations determined using the average chemical compositions found in the literature with the five basaltic clasts measured in this study, we notice a clear deviation. In most cases, we observe that P21, calculated using the average chemical composition, is higher than that calculated using the chemical composition of a single CE-5 basaltic clast, whereas P38 is lower. These results confirm that it is crucial to evaluate the chemical composition of each clast to determine P21 or P38 instead of choosing the average chemical composition. If we only consider theoretical noble gas production rates, the P21 maximum variation of #16 from the average value can reach 18.4% (at ~2 g/cm²), and the maximum deviation range
for all the clasts at different depths (0–500 g/cm²) is 14.8–18.4%, which is more significant than the model prediction error (10%). In other words, by calculating the chemical composition of the sub-milligram grains, the maximal variation in the production rates can be estimated; instead, only the superposition error in the measurement process needs to be considered. For Pss, the maximum deviation range for different depths (0–500 g/cm²) is 13.5–16.1%, similar to P21. However, the uncertainty itself is greater than the value of P21 and it is difficult to determine the shielding depth (sometimes the deviation caused by depth estimation is greater than the deviation caused by the chemical heterogeneity of the sample); therefore, the calculation of the chemical composition of the individual sample may not be as significant as that of Ne, but is still suitable for the calibration of aliquots (different fragments of a sample). Here, we could not precisely determine the shielding depth for our samples because of our inability to establish a mixing line between cosmogenic endmembers and trapped endmembers in the Ne three-isotope plot obtained by step extraction analyses.27

To summarize, we demonstrated that sample chemical/mineral heterogeneity in different clasts needs to be considered. The variability in the target elements for the production rate of cosmogenic noble gases has a significant effect on the modeled production rates.

Assessment of accessory minerals and olivine. Because of the accuracy of μCT (Heliscan MicroCT, the theoretical scanning accuracy is 0.8 μm) and the similarity of the mineral density, it becomes challenging to make precise statistics on the presence of accessory minerals such as apatite and spinel. Therefore, we only considered the main minerals in the basaltic clasts (pyroxene, feldspar, olivine, and ilmenite) using 3D images to estimate the volume of each mineral. We found that this introduced considerable uncertainty in estimating K, Cr, and P, but it does not affect the calculation of the production rates of Ne and Ar, as only K is a target element in the production of cosmogenic 39Ar and it has no effect on the determination of the 38Ne production rates based on the model of Hohenberg.5 In addition, the main target element for the production of cosmogenic 39Ar is Ca instead of K. If we apply the model of Leya et al.,6 none of the above elements are considered in the calculations of the Ne and Ar production rates. Generally, the uncertainty resulting from not considering accessory minerals is not the major source of variation in the calculation of production rates.

Variations in olivine density depend on its Fo abundances. However, some olivine has conspicuous deviations in Fo abundance from the rim to the core,16 which are more prominent in different basaltic clasts. The grayscale is mainly controlled by density; hence, the lower the Fo abundance, the greater the density and the brighter the gray color on the image (Fig. 1). The volume and density of olivine will affect the maximum uncertainty of our method. The complexity of olivine in the lunar soil and variations in Fo abundances were considered,16,25 and we chose the average value as a representative of the average olivine density. The grayscale of the pyroxene and olivine are similar when the density of pyroxene is within a similar range to olivine (close to endmember Fo35.8 g/cm³), causing part of the pyroxene to be falsely counted as olivine. However, this is not significant because the volume of olivine accounts for a relatively small proportion in most of our samples, except sample #3 which contains 24.75% olivine in bulk volume. Olivine is mainly composed of SiO₂, FeO, and MgO. The contributions of Si, Fe, and Mg from olivine remain limited compared to the entire basaltic clasts, as Fe, Mg, and Si in basaltic clasts are mainly controlled by pyroxene. If we assume that sample #3 (contains a higher abundance of olivine), part of the pyroxene is counted as olivine in the statistics, leading to miscalculations. The results show that the largest deviations are for FeO (35.1%), followed by SiO₂ (10.3%), and MgO (5.3%). However, the above assumption is an extreme case and the cosmogenic production rate of Ne isotopes is mainly controlled by Si and Fe, and to a relatively smaller extent by Mg.7 We recalculated P21 and P38 using the chemical composition obtained after removing the olivine; the maximum deviation of these elements will eventually reduce P21 by 5.84% at a depth of ~5 g/cm², and P38 by ~25% at all depths. Under normal circumstances, the density of olivine is greater than that of pyroxene, and there is no overall statistical error. However, as described above, the possible error caused by the incorrect estimation of the volume of olivine is negligible, considering the actual deviation between each individual grain.

Possible applications of this method. Although this method has already been tested on sub-milligram basaltic clasts in this study, it has not been compared with other lunar samples. The mineralogical composition of igneous rock clasts (such as anorthosite and gabbro) is relatively simple and almost without interference from exogenous components. Therefore, we speculated that this method is applicable. However, this method may not be suitable for complex samples with diverse mineral compositions, such as breccia or agglutinates. These sample types formed by meteorite impact events may suffer from different degrees of volatilization, which might cause a change in the chemical composition of the glass components.28–30 as the average composition of glass is still an essential parameter that needs to be taken into account in the calculation, the expected chemical composition of breccia or agglutinates may introduce a significant error that is difficult to quantify. Therefore, we recommend that this method be used only to calculate the chemical composition of samples with a relatively single mineral composition and low glass content (<1%) to calibrate the cosmogenic noble gas production rates.
CONCLUSIONS

Prior to noble gas analysis, non-destructive determination of the chemical composition of heterogeneous clasts in sub-milligram lunar particles is crucial. In this study, we applied X-ray µCT to five Chang’E-5 lunar basaltic clasts to determine the volume proportions of individual mineral grains. By combining the mineral compositions and densities, we explored a new method to calculate the chemical composition of the bulk sample. We used LMS-1 to evaluate the uncertainty of our method for the calculation of Ne and Ar production rates, which were estimated to be 4% and 5%, respectively. Subsequently, the method was applied to five Chang’E-5 basaltic clasts and revealed significant variations among the different grains; the P21 maximum deviation from the average value reached 18.4% (at ~2 g/cm2), more significant than the model prediction error (10%). The variations of P21 and P38 among different samples were compared, the maximum deviation of P21 and P38 among different samples was 20%. In addition, the chemical/mineral heterogeneity of the samples significantly changed the shape of the theoretical spallation production rate curves, which would affect the precise determination of a Ne-GCR endmember value for the calculation of CRE ages. For future work on sub-milligram lunar regolith samples, we recommend considering the method proposed in this paper to re-examine their individual chemical composition. To some extent, this method quantifies the uncertainty of the mineral heterogeneity.

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Notes

The authors declare no competing financial interest.

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