Atomic Spectroscopy

Editorial

Microanalysis Techniques Guarantee Long-term Research on Chang’e-5 Lunar Samples

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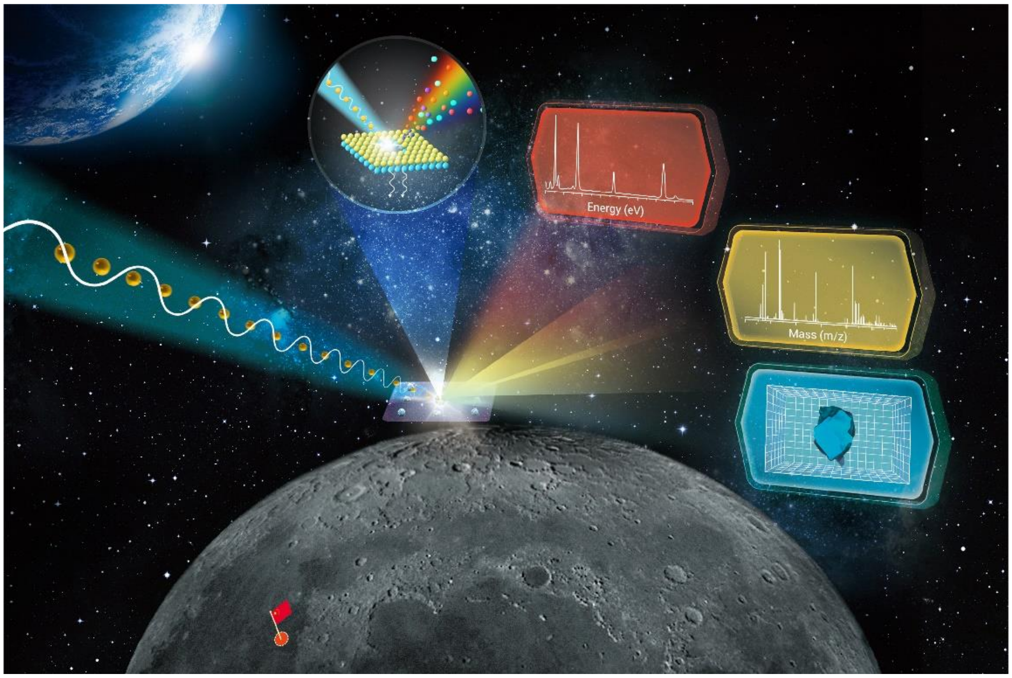
Received: *August 15, 2021;* ***Revised:*** *August 30, 2022;* ***Accepted:*** *August 31, 2022;* ***Available online:*** *August 31, 2022.*

DOI: 10.46770/AS.2022.025



Humans have successfully returned samples from the Moon ten times. Sample return missions have two advantages. First, we can carry out high-resolution and high-precision measurements of returned samples using state-of-the-art technologies in the laboratory. Second, the returned samples can support ongoing research for decades or centuries. The same sample can continuously “tell new stories” with the advancement of technology.

On July 12, 2021, the allocation of the first batch of Chang'e-5 (CE-5) lunar samples quickly ignited a research bonanza for lunar and planetary sciences in China. State-of-the-art microanalysis techniques have played important roles in both scientific research[1−15] and the artistic creation[16] of lunar samples. For example, the combination of micro-X-ray fluorescence (µXRF), 3D X-ray microscopy (XRM), and scanning electron microscopy (SEM) has supported the rapid screening and positioning of Zr-bearing minerals for U-Pb dating.[17] The high spatial resolution U-Pb dating method[18] by secondary ion mass spectrometry (SIMS) makes it possible to determine the crystallization age of tiny (< 5 µm) Zr-bearing minerals in CE-5 basalt.[7] The Sr-Nd isotopic methods[19−21] using laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) obtained key evidence for the non-KREEP origin of CE-5 basalt.[10] The water abundance and hydrogen isotope analytical method[22] using NanoSIMS has helped estimate the water abundance of the parent magma of CE-5 basalt.[4]

Despite the remarkable achievements, only a few samples have been studied. Up till now, four batches of CE-5 samples (53.626 g) have been distributed nationwide, accounting for only 3.1% of all samples (1731 g). Most of the samples are still well stored, which can support long-term research. Undoubtedly, more advanced microanalytical techniques (*e.g.*, Cs-corrected transmission electron microscopy, synchrotron-based microspectroscopy, and atom probe tomography) will provide structural, mineralogical, magnetic, chemical and isotopic information down to atomic scales in the future, which continue to provide more critical evidence for a better understanding of the evolution of the Moon and its space environment. Definitely, one could continue to discover new "stories" from the CE-5 lunar samples by using the right microanalytical approaches.

In any case, the fine grain size of CE-5 lunar soil samples and a desire for high precision data pose considerable challenges to any bulk analytical technique, but stimulate the development and application of advanced microscopic and spectromicroscopic methods.[23] Good science needs advanced technology. For this purpose, we organized two special issues (*Microanalytical Techniques for Extraterrestrial Samples - Part I and Part II*) to present the principle and applications of various microanalysis techniques in the CE-5 lunar soil samples, and other extraterrestrial samples. The first part (*Part I*) was published in February 25, 2022 (Atomic Spectroscopy, 2022, 43(1), 1−98.).

"Sharpening tools" never stop. Contributions to the current special issue (*Part II*) include (1) three- dimensional analyses by electron tomography;[24] (2) ilmenite quantification by micro X-ray fluorescence;[25] (3) bulk composition analyses of small particles by energy dispersive X- ray spectroscopy mapping[26] and high-resolution X-ray microcomputed tomography;[27] (4) trace element analyses by instrumental neutron activation analysis;[28] (5) high-resolution Cl isotope analyses by NanoSIMS[29] and high-precision C isotope analyses by SIMS;[30] (6) combined separation for high-precision iron, calcium, and magnesium isotope analyses;[31] (7) measurements of thermal-induced alterations by in situ TEM heating;[32] and (8) identification of lunar highland clasts in CE-5 breccias by TIMA-SEM-EPMA.[33]

Below, we summarize each of the contributions to this special:

Although the electron tomography (ET) technique has promoted the in-depth investigation of biological molecules in structural biology and the analysis of material structures on the atomic scale in physical sciences, it has not been widely used by the Earth and planetary science community. In "Three-dimensional Analyses of Geological Materials on Nanoscale by Electron Tomography", Xian *et al.*[24] verified the applicability of ET-related techniques (*e.g.*, morphological ET, spectroscopy ET, and atomic ET) in research related to the Earth and planetary science through several representative cases. Their results demonstrated that 1) ET can be used to observe the 3D morphology of mineral grains and 3D distributions of the chemical components of the Earth and planetary materials; 2) ET coupled with spectroscopy, including electron energy loss spectroscopy and energy dispersive spectroscopy, is an effective technique for studying the 3D distribution of elements and their various oxidation states in geological materials; 3) atomic ET can be used to identify the 3D structure of lattice-bound trace elements; thus, it serves as a promising method for investigating the precise occurrence of critical metals dispersed in host minerals.

Ilmenite ($FeTiO_3$) is an early crystallization product of lunar magma and is the most abundant oxide mineral in lunar mare basalts. It is an important lunar resource that is mainly used for He and O_2 production, but also as a source of Fe. In "Non-destructive Identification and Quantification of Ilmenite from a Single Particle of the Chang'E-5 Lunar Soil Sample", Zhang & Li[25] developed a correlative micro-X-ray fluorescence (µXRF) and three-dimensional X-ray microscopy (3D XRM) approach to non-destructively identify and quantify ilmenite from micro-sized single particles in CE-5 lunar soil samples. Their study selected two typical Ti-rich particles from the CE-5 lunar soil samples with a scanning µXRF measurement. The SEM observations indicated that both particles contain tiny ilmenite grains, but different other major minerals. Ilmenite grains within these two different particles were then visualized and quantified with 3D XRM analyses. They further demonstrated that ilmenite mass fractions estimated from the 3D XRM technique are similar to those obtained using µXRF quantification. This study, therefore, provides a new non-destructive strategy for rapid ilmenite identification and quantification from single particles of CE-5 soil samples or other precious extraterrestrial samples.

The major element composition analysis of lunar mare basalt bulk rock is crucial for understanding the thermochemical evolution of the lunar interior. In "Quantitative Analysis of Bulk Composition of Small-Size Lunar Samples Using Energy Dispersive X-Ray Spectroscopy", Yuan *et al.*[26] developed a non-destructive technique to determine the bulk composition (comprising SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O, and K_2O) of rare lunar samples with a small size (mostly < 3 mm) using scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) mapping techniques. A set of certified reference materials were used to calibrate the spectrometer; the precision and accuracy of the EDS analyses were verified using silicate glass and mineral reference materials. The accuracy of the method was confirmed by analysis of a lunar meteorite sample (NWA4734), and the results were comparable to the reference values. This non-destructive and quantitative analysis method can support research on the bulk compositions of CE-5 lunar samples and can be applied to research on terrestrial and extraterrestrial samples at the micron- to centimeter scale.

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 “Mineral Heterogeneity of Lunar Sub-milligram Basaltic Clasts and Its Effect on the Production Rates of Cosmogenic Nuclides”, Zhang *et al.*[27] established a new non-destructive method for determining the chemical composition of small mineralogically heterogeneous lunar basaltic clasts (< 1 mg) using high-resolution XRM. The volume of the individual mineral grains in each clast was obtained *via* XRM and combined with the chemical composition and density of the minerals to estimate their bulk chemical compositions. The calculated chemical compositions were ultimately used to determine cosmogenic nuclide production rates. By applying this method to five CE-5 basaltic clasts, they demonstrated that the chemical compositions of lunar regolith clastic samples (basalts) were different and the maximum variations of P21 (the production rate of cosmogenic ^{21}Ne) and P38 (the production rate of cosmogenic ^{38}Ar) among the five basaltic clasts were in the range of 18–20%. This method significantly minimized the uncertainties in the production rate calculations caused by the mineral heterogeneity of the sub-milligram samples and would result in more reliable CRE ages when applied routinely.

The multi-elemental composition of lunar meteorites or lunar returned soil could help understand the history of the Moon. Non-destructive analytical techniques are ideal for analyzing such rare and precious samples. In “Determination of the Multi-elemental Composition of Lunar Meteorites Using Instrumental Neutron Activation Analysis”, Yao *et al.*[28] developed an instrumental neutron activation analysis (INAA) method for non-destructive analysis of multi-elemental composition in lunar meteorites (Northwest Africa (NWA) 4734 and NWA 11111). The INAA results of NWA 4734 and NWA 11111 are consistent with the previously reported data obtained by inductively coupled plasma-mass spectrometry analysis within analytical uncertainties. Since the INAA analysis is non-destructive, it can be widely applied to trace element measurements for extraterrestrial samples.

Chlorine (Cl), a highly active element, is utilized to investigate many planetary processes, such as magmatic degassing, element mobility, and ore formation. In “High Precision and Resolution Chlorine Isotopic Analysis of Apatite Using NanoSIMS”, Hao *et al.*[29] reports a high analytical precision method that measures the Cl isotopic composition of apatite using CAMECA NanoSIMS 50L with FC detectors. To optimize the instrument configuration, factors of depth effect, shot noise (Poisson error) and Johnson–Nyquist (JN) noise, affecting internal analytical precision in FC detector mode, were assessed. The Cl isotopic analytical accuracy has been improved to < 0.1‰ (1SD) with ~5-10μm spatial resolutions. This technique can widely be applied to tiny apatite-group minerals in extraterrestrial samples.

Insights into the core-formation process of planets can be gained by understanding how carbon isotopes fractionate between different carbon-bearing minerals. In *“In Situ* SIMS Carbon Isotopic Analysis of Carbon-bearing Minerals in Nantan and Aletai Iron Meteorites: Implications on Genesis”, Li *et al.*[30] carried out an integrated study based on petrography and *in situ* secondary ion mass spectroscopy (SIMS) for the analysis of carbon isotopes (δ^{13}C) in Nantan and Aletai iron meteorites. They found that the δ^{13}C values of -14.80 ± 2.31‰ for haxonite in Aletai IIIE-an iron meteorite, some graphite grains in the nodule mantle (GNM; δ^{13}C value as low as -14.65‰) and all graphite grains in the nodule rim (GNR; δ^{13}C = -12.65 ± 2.90‰) are more depleted in ^{13}C than those in the nodule core (GNC; δ^{13}C = -7.17 ± 2.42‰), and the carbon isotopic fractionation (Δ^{13}C = 6.9 ± 2.7 ‰) between coexisting GNR (δ^{13}C = -12.65 ± 2.90‰) and cohenite (δ^{13}C = -19.60 ± 2.59‰). This study supports the previous understanding that the early differentiation of Earth could have led to positive carbon isotopic fractionation between graphite/diamond in the mantle and metallic melt sinking to the core.

Iron (Fe), calcium (Ca) and magnesium (Mg) are major elements of the Moon. Their isotopes show considerable variations among lunar samples, which record key information about the evolution and differentiation processes of the planet. Iron, Ca and Mg isotope data of lunar samples were usually reported independently. This consumed more precious samples and impeded tracing key evolution and differentiation processes by multiple isotopes, given the potential heterogeneity among lunar samples.[1,5,10] In “Combined Separation of Iron, Calcium, and Magnesium from Composite Lunar Samples for High-precision Isotope Analyses”, Sun *et al.*[31] reported a combined procedure able to quantitatively separate Fe, Ca and Mg from single splits of sample solutions, allowing us to obtain combined high precision δ^{56}Fe, $\delta^{44/42}$Ca and δ^{26}Mg dataset for precious lunar and other extra-terrestrial samples.

Impact-induced thermal modifications frequently occur in the solar system, and the microstructures of extraterrestrial samples can reveal the thermal-induced alterations that have occurred to their parent bodies. In “Thermal-Induced Alterations in Lunar Soil Grains Revealed via in Situ TEM Heating”, Li *et al.*[32] proposed a new method to systematically understand the chemical and microstructural changes in the CE-5 soil grains resulting from thermal-induced alterations, which combined a dual-beam system and transmission electron microscopy (TEM) techniques, with in situ TEM heating. Their results showed that the nanophase iron (np-Fe^0) particles, which appeared in both Fe-rich pigeonite and Fe-poor olivine, as well as the np-Fe^0 content and morphology, varied with increasing heating time (0 – 90 min) at 800 °C, which indicated that the formation mechanism of np-Fe^0 particles varied in different matrices. The authors claimed this method can reveal the thermal-induced alterations in celestial bodies and can be applied effectively for studying the formation of microscopic features in extraterrestrial bodies.

In "First Location and Characterization of Lunar Highland Clasts in Chang'E 5 Breccias Using TIMA-SEM-EPMA", Sheng *et al.*[33] developed combined techniques with Tescan Integrated Mineral Analysis (TIMA), Scanning Electron Microscopy (SEM), and Electron Probe Microanalysis (EPMA) to identify the mineralogy and chemical information in four lunar highland clasts from the breccias (CE5C0800YJYX132GP) returned by the CE-5 mission. Their results show that the chemical compositions of plagioclases (An 93.9–97.6) and mafic minerals (Fo 71.4–87.9 for olivine and Mg$^{\#}$ for pyroxene) in these clasts are remarkably distinct from the more abundant mare basalts in the CE-5 landing site. The authors also find that the anorthositic clasts are more magnesian than the Apollo ferroan anorthosites (FANs) but are similar to the magnesian anorthosites (MANs) commonly found in lunar highland meteorites. Future studies on more highland materials in the CE-5 samples may provide new insights into the early lunar crustal reworking and crust-mantle interaction.

Finally, we appreciate all the authors for contributing to the special issues *Microanalytical Techniques for Extraterrestrial Samples - Part I and Part II*. Although it contains 20 studies, it cannot cover all the state-of-the-art microanalysis methods. The development of microanalytical techniques and the study of CE-5 samples is ongoing. We welcome more studies on precious samples from the moon, the Mars, and other extraterrestrial bodies with various microscopic and microspectroscopic approaches.

AUTHOR INFORMATION

Wei Yang is a professor at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), operating a NanoSIMS laboratory. He received his B.S. (2001) and Ph.D. (2007) degrees in geochemistry from the University of Science and Technology of China. After completing his Ph.D., he came to IGGCAS for post-doctoral research and joined the comparative planetary science group as an associate professor in 2011. His main interest in the past decade was Mg isotope geochemistry and its application in tracing the deep carbon cycle. He is currently working on instrumentation developments on secondary ion mass spectrometry and its application in Earth and planetary sciences, the formation and evolution of the Moon based on the exploration data and returned samples of the Chinese Lunar Exploration Program. He has published over 70 peer-reviewed scientific papers in ISI-indexed journals.

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Notes

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