The Chang’e-5 Lunar Samples Stimulate the Development of Microanalysis Techniques

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People dreamed of touching the moon for a long time, but it was not until the 1950-1960s that this was attempted. One of the major milestones towards this dream was the Apollo 11 mission, which was the first crewed lunar landing whose mission objective was to collect samples and return to earth. In the next seven years, five subsequent Apollo missions and three Luna missions took place. Approximately 382 kg of lunar samples were collected during these missions, which has significantly enhanced our understanding of the chemical features, physical processes, and geological evolution of the moon. There is no disputing the fact that the first extraterrestrial samples brought to earth through the Apollo 11 mission ushered in a new era in planetary science.

Forty-four years after the Apollo and Luna missions returned with the lunar samples, Chang’e-5 (CE-5), China’s first lunar sample return mission, returned with 1,731 g of lunar samples from Mons Rümker in northeastern Oceanus Procellarum.1,2 This landing site was located at an appreciable distance away from the Apollo-Luna sampling sites in low-latitude regions of the moon. The first wave of studies revealed that the samples brought by the CE-5 mission contained a new type of differentiated lunar basaltic rock with a Pb-Pb isochron age of approximately 2.0 Ga and originated from a non-KREEP dry mantle source.3-6 KREEP is a chemical signature of many Apollo 12 and 14 lunar samples, relatively enriched in potassium (K), rare earth elements (REE),...
phosphor (P), and other incompatible elements. These CE-5 lunar samples provide a unique opportunity to study the evolution of the moon and the surface processes on airless bodies.1, 7

Moreover, the CE-5 mission is just the beginning. China is gearing up to launch a series of new space missions in the next ten years with varied mission objectives including returning to earth with samples from the South Pole-Aitken Basin of the Moon, asteroids, and Mars.8 From a global perspective, the National Aeronautics and Space Administration (NASA) has also announced the ARTEMIS program, intending to land on the moon again in this decade, with the mission objective of returning with new lunar samples. Furthermore, the NASA and the European Space Agency (ESA) plan to return with the first Martian sample as early as 2031. Because of continual efforts and deepening international cooperation on sample return missions, we are entering a new golden era of planetary science.9 New extraterrestrial samples would significantly promote the development of advanced curation and analytical techniques as expensive missions would only return with a highly limited number of samples.10, 11

Confucius said, “If a craftsman wants to do good work, he must first sharpen his tools.” Because extraterrestrial samples such as the CE-5 lunar samples are precious, non-destructive analyses and microanalyses are always preferred. For this reason, we organized two special issues, Microanalytical Techniques for Extraterrestrial Samples - Part I and Part II, to present some advanced and powerful microscopic and spectromicroscopic techniques to study the CE-5 lunar samples and other extraterrestrial samples. Contributions to the current special issue include (1) a non-destructive study of natural color and the 3D morphology of a lunar meteorite and lunar soil simulant using a high dynamic range, color structured illumination microscope (HDR-C-SIM);12 (2) improvement of atomic force microscopy (AFM) analytical technique for the accurate measurement of adhesion force in micro-sized lunar dust grains;13 (3) development of Micro-X-ray diffraction (µXRD) methods for in situ identification of glass and minerals in extraterrestrial samples;14 (4) development of analytical methods for the precise measurement of major and trace elements and Fe3+/ΣFe in geological samples using electron probe microanalysis (EPMA);15, 16 (5) study of the valence states of iron-bearing phases in CE-5 lunar soil using advanced transmission electron microscopy (TEM) techniques;17 (6) in situ Rb-Sr dating of lunar meteorites using laser ablation multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS);18 (7) development of analytical techniques for the determination of water content in geological samples using secondary ion mass spectrometry (SIMS) and nanoscale SIMS (NanoSIMS);19 (8) development of the analytical method to measure the water content of a zircon hydrogen isotope using SIMS and the optimization of reference standards;20 (9) a dedicated review of recent progress and selected applications of synchrotron-based scanning transmission X-ray microscopy (STXM).21

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

Optical sectioning structured illumination microscopy (OS-SIM) is a state-of-the-art three-dimensional technique that uses fringe illumination patterns to modulate the in-focus and out-of-focus information of the specimens. Because of the sharp decrease in the modulation, in-focus information can be calculated. OS-SIM has the highest imaging speed among the above-mentioned methods, and it ensures an axial resolution which is as good as that of confocal laser scanning microscopy. Another advantage of OS-SIM is its ability to obtain natural color, which allows for high-magnification color micrographs. OS-SIM has been increasingly used to study various insectology, materialogy, and geology samples. In Reconstructing the Color 3D Tomography of Lunar Samples, Zhao et al.12 present a high dynamic range, color structured illumination microscope (HDR-C-SIM) for recording the 3D tomography of lunar soil simulants and their natural color in a time-efficient manner. The system has the advantages of high sensitivity, low thermal damage, and high-speed three-dimensional imaging capabilities, which are demonstrated by the fine details and color 3D tomography of the lunar meteorite and the lunar soil simulant. This method is expected to provide a new and powerful tool for visually presenting the geological evolution of the moon.

Atomic force microscopy (AFM) is a powerful technique for measuring the microphysical properties of lunar grains. The lunar dust adhesion force is an essential factor that harms spacecrafts and astronauts, and is the key to understanding the migration of lunar dust and revealing the cause of lunar horizon glow (LHG) phenomena. As a microphysical property of the interface, the adhesion force is difficult to measure accurately because of the surface adsorption of gas molecules. To measure the adhesion force of CE-5 lunar samples grains accurately, Jin et al.13 proposed an improved AFM method that can eliminate the effect of surface adsorption based on experimental measurements of the adhesion force between a silica ball and silica wafer under different environmental pressures and temperatures. At a temperature of 200 °C and environmental pressure of less than 2.4 × 10⁻⁴ Pa, the adhesion force changes sufficiently, indicating that the effect of surface adsorption is eliminated effectively. In such cases, the adhesion force can be measured accurately using AFM. This improved method provides an effective technique for measuring CE-5 lunar samples.

Glass and amorphous state materials are vital components of lunar regolith and contain considerable geological evolution information. However, it is often challenging to distinguish glass from crystals based on morphology and elemental composition, especially in complex extraterrestrial samples that have been
Electron Probe Microanalysis (EPMA) can efficiently determine the major elements of various materials from earth and other planetary samples with a high spatial resolution (1–5 μm), low cost, and high detection limits of up to a few hundred μg/g. Recent advances in EPMA have enabled the measurement of trace elements. In High-precision Measurement of Trace Level Na, K, P, S, Cr, and Ni in Lunar Glass Using Electron Probe Microanalysis, Zhang et al. proposed an optimized method to determine trace-level elements (Na, K, P, S, Cr, and Ni) in lunar glass. The authors used a 20 kV accelerating voltage, 100 nA beam current, 10 μm beam diameter, linear background mode, large-area analytical crystals, and an aggregate counting strategy to lower the detection limits and improve the accuracy and precision of these trace elements in lunar glass. The detection limits (3σ) for Na, K, P, S, Cr, and Ni were lowered to 17–96 ppm, and the accuracies of these elements were better than ± 10% (2σ). This method can fully exploit the advantages of the non-destructive nature, high spatial resolution, high precision, and accuracy of EPMA, and opens a new perspective into the study of geochemical processes involving lunar glass.

Another advantage of the EPMA technique is the Fe\(^{3+}/\Sigma\)Fe ratio. However, for a long time, there was no optimized method for simultaneously determining the major and trace elements and the Fe\(^{3+}/\Sigma\)Fe ratio within a single run. In Simultaneous In-Situ Determination of Major, Trace Elements and Fe\(^{3+}/\Sigma\)Fe in Spinel Using EPMA, Jia et al. first developed a high-precision EPMA method that can simultaneously determine major and trace elements together with Fe\(^{3+}/\Sigma\)Fe ratio in spinel, an important mineral sensitive to petrologic and geochemical processes and the redox state. The authors first set up a set of spinel standards for major and trace elements and Fe\(^{3+}/\Sigma\)Fe analyses. Then, they constructed an optimized EPMA method under double beam conditions (200 nA for trace elements and 60 nA for major elements) with an acceleration voltage of 25 kV and used a secondary standard calibration method to determine the Fe\(^{3+}/\Sigma\)Fe ratio of spinel. The detection limits for trace elements were 16–55 μg/g (3σ), and the estimated accuracies for the major and trace elements were within ± 2% and ± 6% (1σ), respectively. The accuracy of the Fe\(^{3+}/\Sigma\)Fe ratio in spinel was within ± 0.04 (2σ). This method provides robust and precise data on spinel for small, precious, and rare terrestrial or extraterrestrial samples (e.g., spinel in lunar and martian samples), which can be used to understand the formation and evolution of rocky planets.

Nanophase iron (np-Fe\(^3\)), a major product of space weathering, is important for understanding the modification of iron during the formation and evolution of lunar soils and notably alters the reflectance, absorption intensity, and continuum slope of the UV-VIS-NIR spectra of lunar soils. In In situ Investigation of the Valence States of Iron-bearing Phases in Chang’e-5 Lunar Soil using FIB, AES, and TEM-EELS Techniques, Mo et al. conducted in situ nanoscale valence analysis of iron-bearing phases in Chang’e-5 lunar soil by combining focused ion beam (FIB) microscopy, Auger electron spectroscopy (AES), and transmission electron microscopy-electron energy loss spectroscopy (TEM-EELS) techniques. The results reveal both metallic and ferric iron in the amorphous matrix of Chang’e-5 lunar soil, which provides new insights into space weathering processes (e.g., disproportionation reaction of Fe\(^{2+}\)) at the loading site.

Geochronological investigation is fundamental to revealing the stories of extraterrestrial samples, commonly achieved by U-Pb dating. Tiny sizes or the lack of relevant accessory minerals (e.g., zircon) usually impede the in situ U-Pb dating of extraterrestrial samples. In in situ Rb-Sr Dating of Lunar Meteorites Using Laser Ablation MC-ICP-MS, Zhang et al. developed an analytical procedure on LA-MC-ICP-MS and a new data reduction strategy for in situ Rb-Sr dating on rock-forming phases (e.g., plagioclase, pyroxene and glass). The robustness of the method was demonstrated by the isochron ages obtained for two lunar meteorites, which are in good agreement with previously reported U-Pb dating results. The method presented should have broad applicability for the Rb-Sr isochron dating of extraterrestrial samples.

Geochemical investigation can provide important clues to the structures, nature, and evolution of earth and moon. High spatial resolution analytical methods with a low background are crucial for quantifying the water content in nominally anhydrous minerals such as olivine. For secondary ion mass spectrometry (SIMS) studies, primary beams with high currents are utilized to achieve a low background. However, a high current also results in a low spatial resolution. Even though NanoSIMS is designed to measure high spatial resolution, the spatial resolution is maintained at values greater than 10 μm for water content analysis in order to maintain a low water background of less than 10 ppm. The work presented by Li et al. optimized the analytical settings for water content measurement in olivine using NanoSIMS and achieved a high spatial resolution of ~6 μm (i.e., a factor of ~2 better than the
It is notable that each contribution to these two special issues maintained a detailed focus on a particular technology or a specific field. Unlocking as much information as possible from each targeted sample is critical and essential because these extraterrestrial samples are precious and limited in quantity. Therefore, we call for a correlative characterization by linking existing laboratory-based instruments to establish rich multimodal and multiscale correlated datasets for mapping the local structure, mineralogy, chemistry, crystallography, and isotope geochemistry, as well as the local mechanical and magnetic performance across length scales.\textsuperscript{11}

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Notes
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REFERENCES


