

Nanoscale Mineralogical Characterization of Terrestrial and Extraterrestrial Samples by Transmission Electron Microscopy: A Review

Jieqi Xing, Haiyang Xian, Yiping Yang, Qingze Chen, Jiaxin Xi, Shan Li, Hongping He, and Jianxi Zhu*



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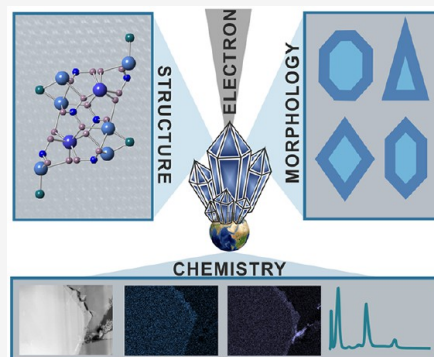
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ABSTRACT: Nanoscale minerals (i.e., nanominerals and mineral nanoparticles) in terrestrial and extraterrestrial materials are difficult to characterize because of their small particle sizes, high surface energy, and/or poor crystallization. Transmission electron microscopy (TEM) is a powerful analytical platform for the characterization of minerals at the nano and even atomic scales, and it can determine their morphology through imaging, derive structural information using multiple electron-diffraction techniques, and investigate chemical compositions. Since the 1990s, the application of TEM to the characterization of nanoscale minerals has developed rapidly into a core technique in nanoscale Earth and planetary science (NEPS). This review introduces a brief history and the general principles of TEM, considers detailed methods of preparing specimens for nanoscale mineralogical characterization by TEM, and emphasizes the contributions of TEM to multiple NEPS research fields in recent decades. These contributions are considered from the perspective of nanoscale mineralogical studies of morphology, structure, and chemistry in complex geological materials. Finally, the work provides an outlook on current opportunities to apply TEM methods to nanoscale mineralogical study. This review aims to provide common and practical TEM methods to NEPS researchers and to support the use of TEM for a wide range of applications in nanoscale mineralogy to promote NEPS development.



KEYWORDS: nanoscale mineralogy, transmission electron microscopy, nanoscale earth and planetary science, geological material, focused ion beam

1. INTRODUCTION

Rocky celestial bodies (e.g., Earth, the Moon, Mars, and asteroids) consist mainly of minerals, which exhibit an extraordinary diversity of physical and chemical properties.¹ Most physical and chemical processes on these bodies are either influenced or fully driven by the properties of their constituent minerals and are themselves recorded in the minerals.^{2–5} Hochella et al. revealed that the properties of minerals become increasingly complicated as their particle size decreases, typically to the nanoscale.⁶ Nanoscale minerals (i.e., nanominerals and mineral nanoparticles)¹ and various physical and chemical reactions of minerals at the nanoscale are thought to be ubiquitous in the hydrosphere,⁷ pedosphere,⁸ biosphere,⁹ atmosphere,¹⁰ the solid Earth, and extraterrestrial bodies.¹¹ The characterization of nanoscale minerals in complex geological materials is thus crucial for the development of nanoscale Earth and planetary science (NEPS). However, traditional characterization methods [e.g., X-ray diffraction (XRD) and electron probe microanalysis (EPMA)] cannot accurately characterize the structure and chemical properties of nanoscale minerals (e.g., clay minerals and ferrihydrite), which restricts the study of NEPS.

Various new advanced nanoscale analysis techniques, such as transmission electron microscopy (TEM), atom probe tomography (APT), and atomic force microscopy (AFM), have led to substantial progress in nanoscale mineralogy in recent decades. In particular, TEM has enabled accurate determination of the two-dimensional (2D) and three-dimensional (3D) morphology, structure, chemistry (including chemical valence state), and even magnetic and thermal properties of nanoscale minerals within inhomogeneous and scarce samples.^{12–15} However, compared with its use in other fields (e.g., material science, physics, chemistry, and biology), owing to the complexity of geological materials (e.g., inhomogeneity and complex microstructures), TEM is used relatively infrequently in NEPS (Figure 1). Developments of

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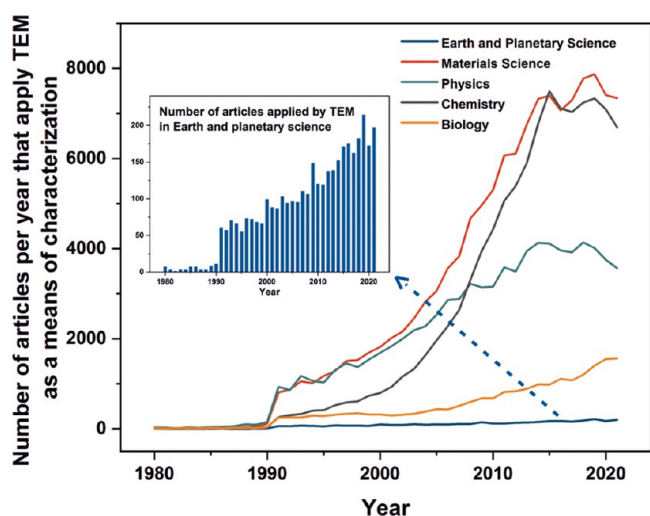


Figure 1. Number of articles applying TEM characterization in materials science, physics, chemistry, biology, and Earth and planetary science by year from 1972 to 2021. The inset bar graph gives details for Earth and planetary science. In contrast to its wide use in material science, physics, chemistry, and biology, TEM is relatively less frequently used in Earth and planetary science, mainly because of the complexity of geological samples. However, since the 1990s, TEM has seen greatly increased use in Earth and planetary science owing to the wide use of field emission guns. In addition, the applications of TEM in all fields except biology show a significant decrease in 2020 and 2021, which may be caused by the global COVID-19 crisis.

TEM in recent decades have started to change this: for example, improved sample preparation techniques, reduced electron beam damage, and combinations of multiple techniques have enabled the increasing use of TEM in NEPS studies to characterize geological samples (e.g., rocks, meteorites, and fossils) down to the nano and atomic scale (Figure 1). Several reviews have considered the contributions of TEM to geosciences from various angles. Wirth¹⁶ covered some applications of TEM to geoscience, focusing on dual-beam focused-ion-beam (FIB) combined with TEM. Li et al.^{17,18} and Nieto et al.¹⁹ reviewed the historical development of TEM, including numerous examples from the fields of Earth and planetary science. Nanoscale mineralogical characterization represents the key to NEPS and is therefore the focus of this review. This work provides a brief overview of the general historical development and common principles of TEM and describes various practical methods of preparing geological and mineralogical specimens for nanoscale characterization by TEM (including schematics of the steps required). In addition, some representative examples of recent applications of TEM in NEPS (e.g., space weathering, biomineralization, crystal growth, phase transformation, high-pressure mineralogy, and the occurrence states of elements) are shown with reference to nanomineralogical research (e.g., morphology, structure, and chemistry). Finally, the prospects for several new TEM techniques are considered for application to nanomineralogy in NEPS, including *in situ* TEM, micro-crystal electron diffraction (micro-ED), and atomic electron tomography (AET).

2. BRIEF OVERVIEW OF TEM

The wave-like characteristics of electrons were first theorized by Louis de Broglie in 1925.²⁰ According to the Abbe resolution limit theory, electron microscopy offers a much

higher spatial resolution than optical microscopy, as electrons have a much smaller wavelength than visible light and X-rays.²⁰ In the 1930s, Ernst Ruska and Max Knoll built the first electron microscope in Berlin.¹⁹ In the following decades, limitations due to specimen thickness, beam damage, resolution, and contamination were gradually overcome.²⁰ In addition, the development of high-voltage technology increased the resolving power of TEM by decreasing the electrons' wavelength. In the 1970s, the spatial resolution was increased to allow for direct observation of mineral structures, which was a significant watershed in the application of TEM to nanomineralogical research.¹⁹ The maturation of the technique since the 1980s has led to electron microscopes and ion milling machines becoming commonplace in universities and being widely used in mineralogical research.¹⁹ Scanning electron microscopy (SEM) has been incorporated into TEM to localize chemical signals with high spatial resolution. The resulting scanning TEM (STEM) is the basis of many types of positional elemental analysis. Since the 1990s, the wide use of field emission guns (e.g., cold field emission and Schottky thermal field emission) has increased the imaging capability and spatial resolution of chemical analyses in STEM mode and represents a breakthrough in the applicability of high-resolution TEM in NEPS (see Figure 1).¹⁹ Aberration correction further improved the spatial resolution of TEM,²¹ allowing mineralogists to study the occurrence and fine structure of minerals on the atomic scale.²² Over the past 20 years, the spatial resolution of material characterization has improved gradually to below 50 pm.²³

However, implementation of high spatial resolution usually requires a high-energy electron beam and a long image-acquisition time, which could lead to the electron beam damaging the geological sample to some extent. Protecting the sample during TEM observation requires the low-voltage TEM and cryo-TEM techniques developed in recent decades. For example, the application of ptychography in TEM has further improved spatial resolution, even in low-voltage mode: Jiang et al. developed a highly sensitive electron microscope pixel-array detector, which can record all transmitted electrons for complete ptychographic reconstruction, and achieved a record spatial resolution of 0.39 Å using STEM at 80 keV (lower voltage mode).²⁴ This technique has great potential applicability to the characterization of geological materials. In addition to the improvements of TEM's spatial resolution, improvements of sample preparation techniques are also essential for effective nanoscale mineralogical characterization. For example, in recent decades, dual-beam FIB-SEM has become indispensable to NEPS, greatly increasing the use of TEM in the geosciences.^{12,16,25}

3. TEM SPECIMEN PREPARATION

A TEM specimen needs to be electronically transparent, usually less than ~100 nm thick, and stable under electron irradiation;¹ good electrical conductivity is also generally required.²⁰ As conventional TEM uses electromagnetic lenses to focus the electron beam, magnetic materials can permanently adhere to the lenses, irreparably damaging the system. Therefore, any sample containing magnetic material must be immobilized, for example, by using an oyster grid and FIB method.^{26,27} In addition, terrestrial and extraterrestrial samples are complicated, so contamination during their preparation must be minimized and can be removed by

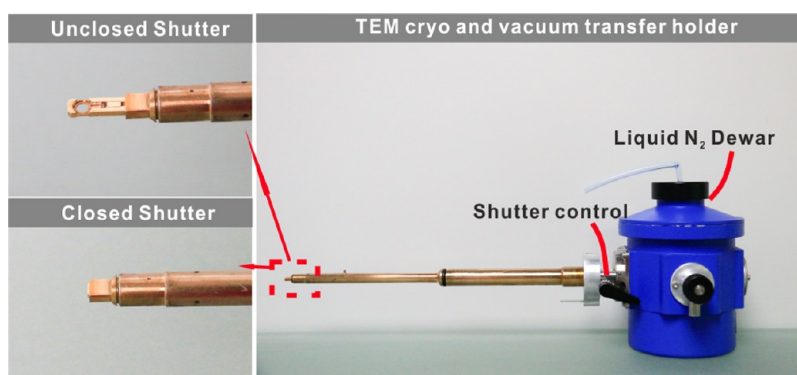


Figure 2. Photographs of a cryo-vacuum transfer TEM holder.

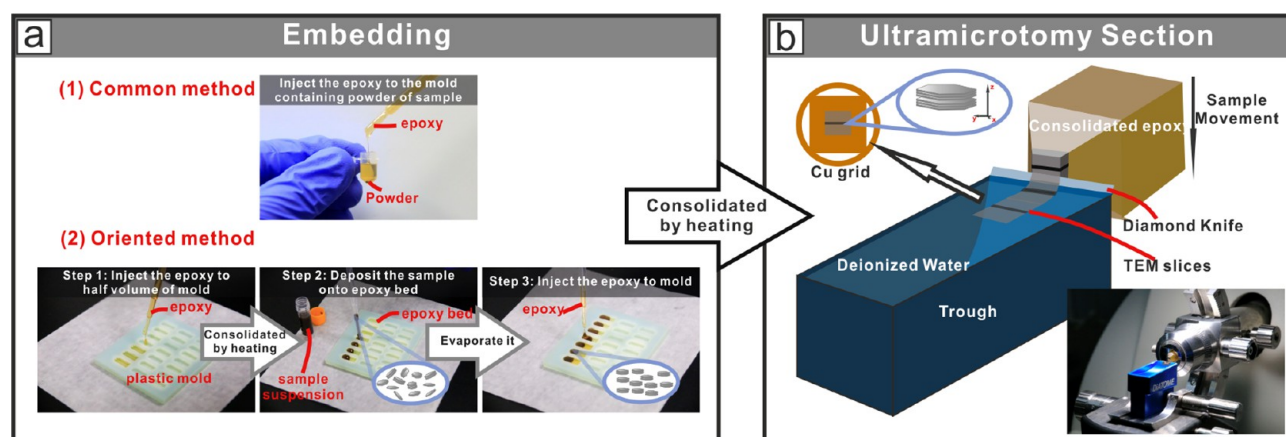


Figure 3. Schematic of the steps for ultramicrotomy of a specimen for TEM including (1) embedding (common or oriented for two-dimensional materials such as clay minerals) and (2) the ultramicrotomy processes. Step 1—embedding: there are two main methods for embedding the sample in epoxy, the common method and the oriented method. Step 2—ultramicrotomy: samples embedded in epoxy are cut into TEM slice sections (~ 20 – 100 nm; 75 nm is recommended).

plasma cleaning. The following four methods are commonly used to prepare TEM specimens from geological samples.

3.1. Powder Deposition after Dispersion. **3.1.1. Terrestrial Samples.** Some nanoscale samples are electronically transparent in themselves or at their edges. It is very important for the bulk sample to be ground into powder, suspended in an inert liquid (usually 99.99% ethanol or deionized water), and dispersed ultrasonically. The suspension is then deposited onto a supporting grid with amorphous and holey carbon film. This method could lose the original mineral contact relationships of the complex geological samples.

3.1.2. Extraterrestrial Samples. Extraterrestrial samples from airless and rocky celestial bodies (e.g., the Moon and asteroids) can react chemically with terrestrial contaminants (e.g., O_2 and water vapor), which may change their surface condition. To avoid exposure to the atmosphere, these samples are usually stored and prepared in glove boxes.^{28,29} A TEM vacuum transfer holder can be used to avoid contact between samples and the atmosphere during transfer.

The transfer holder assists the transfer of a specimen from a sample preparation station (e.g., glovebox or vacuum chamber) into the electron microscope under a controlled atmosphere (e.g., nitrogen) or under a vacuum by using a retractable vacuum shutter (Figure 2). In addition, unlike terrestrial samples that are dispersed in liquids, it is feasible for extraterrestrial samples to be sprinkled directly on a supporting grid with carbon film.

3.2. Ultramicrotomy. Ultramicrotomy is the physical cutting of a sample into films.^{30–32} The sample powder (including common and oriented samples; Figure 3) needs to be embedded in epoxy in a particular container. The epoxy is then sintered in a vacuum oven to consolidate it and minimize its porosity. The temperature and duration of heating are important to the hardness of the epoxy (80 °C for 6 h is appropriate). The consolidated epoxy may subsequently deform if it is too soft or break if it is too hard; therefore, films suitable for TEM characterization may not be obtained. Ultramicrotomy is conducted by moving the specimen past a diamond knife blade. The cut films then float on water or other inert liquid before collection on a holey carbon-coated supporting grid. Figure 3 shows the embedding processes and a schematic of ultramicrotomy. This method can in practice obtain homogeneous thin slices with a clean surface of the sample, which is essential to TEM characterization. In addition, this method (i.e., the oriented method in Figure 3a) has become mainstream for preparing samples of two-dimensional mineral materials (e.g., clay minerals) for characterization by TEM because it can easily prepare TEM slices that allow for the viewing of two-dimensional minerals along the $[00l]$ direction.

3.3. Ion Milling. Ion milling involves bombarding a sample with high-energy ions or neutral atoms (e.g., Ar and He) to create regions thin enough (less than ~ 100 nm) for TEM observation.²⁰ This method is suitable for solid bulk samples

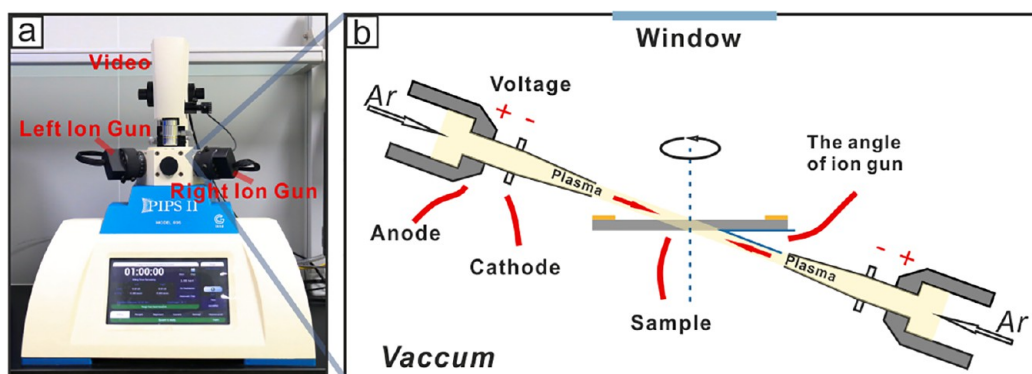


Figure 4. (a) Image of Gatan 695 PIPS II equipment and (b) schematic of ion milling.

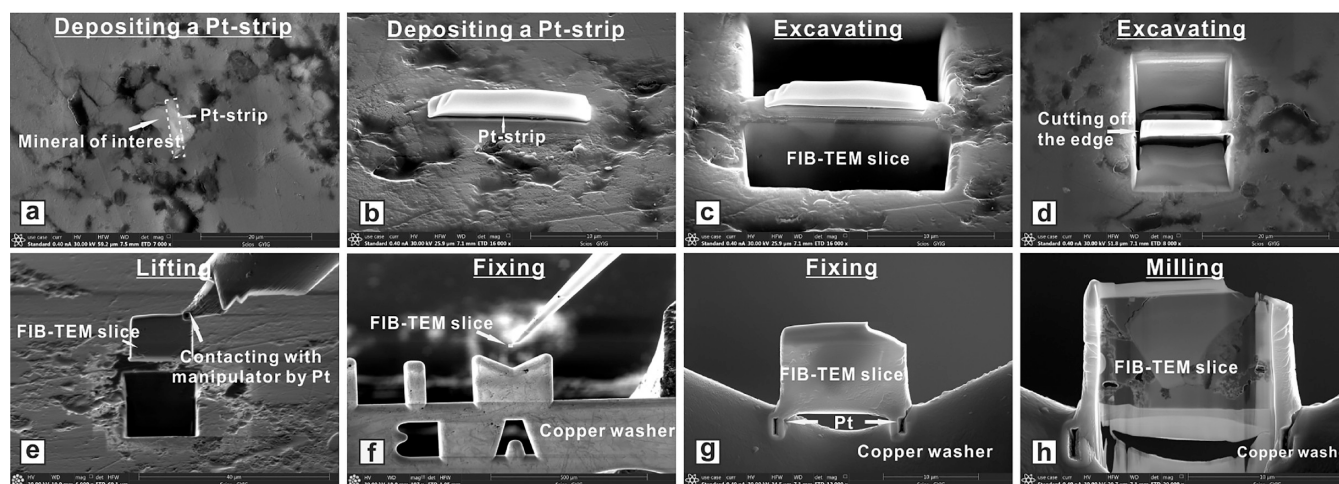


Figure 5. Procedures for FIB-TEM specimen preparation. (a and b) Pt strip is deposited to fix the selected area and protect it from the Ga beam. (c and d) Trenches on both sides are bombarded using a sloping Ga beam until the lower part of the sample is cut off. (e–g) Sample is fixed on the half-moon support washer by contacting the Pt. (h) Ga ion milling then achieves electron-transparent thickness (less than ~ 100 nm).

such as rock and metal.³³ Before ion milling, a sample usually requires mechanical milling (e.g., by using a Leica EM TXP). The mechanically milled chip is then ion milled (e.g., using a Gatan 695 PIPS II) while being rotated between two opposing ion guns (Figure 4). This method can maintain to some extent the contact relationship of minerals in a geological bulk sample and can produce a much larger thin area for TEM characterization than the latter FIB method (which is applicable to bulk samples with simple mineral assemblage relationships). In practice, however, the success rate of this method is low, and its ability to prepare site-specific specimen preparation is inferior to that of the FIB method, preventing it from becoming the prevailing method of preparing samples for TEM in NEPS.

3.4. Focused-Ion Beam (FIB). In recent decades, FIB has become the most important TEM specimen preparation method in NEPS.^{12,16,25} Dual-beam FIB-SEM is a robust instrument for precise site-specific specimen preparation and a powerful analytical platform at the microscale, and it thus provides a key link between microscale and nanoscale geoscience. Dual-beam SEM means using an ion milling gun (Ga ion beam) for cutting and SEM (electron beam) for characterization; it can prepare homogeneous thin slices for TEM with a high success rate. Figure 5 shows the basic procedures for lift-out site-specific TEM specimen preparation using FIB. However, unlike the ultramicrotomy method, the milling process can contaminate the specimen through the

sputtering of nanoparticles from the support washer. Therefore, if Cu is an element of interest in the data, a Cu support washer is not recommended. The plasma cleaner is helpful to reduce surface contamination.

4. TEM-BASED TECHNOLOGIES

TEM characterizes a specimen using various detectors to collect many kinds of ionizing radiation signals generated by the interaction between electrons and a specimen (Figure 6). Figure 6 shows the incident high-energy electrons as a nearly parallel beam in TEM mode and as a converging beam in STEM mode. The incident electrons in TEM mode comprise a nearly parallel beam, whereas in STEM mode they arrive as a convergent beam (i.e., electron probe) focused on the specimen's surface to scan it precisely (Figure 6). After the high-energy incident electron beam interacts with the specimen, there is a direct beam and a scattered beam (the direction and/or energy of the electrons changes). The bright-field (BF) detector picks up the direct beam to form a BF image. Dark-field (DF) detectors pick up scattered electron (elastically scattered electron) beams to form DF images; e.g., ADF and HAADF (or Z-contrast) images. The scattering is either elastic (only the direction of the electrons changes) or inelastic (both direction and energy change). Elastic scattering is the basis of various electron diffraction patterns such as selected-area electron diffraction (SAED), nanobeam electron diffraction

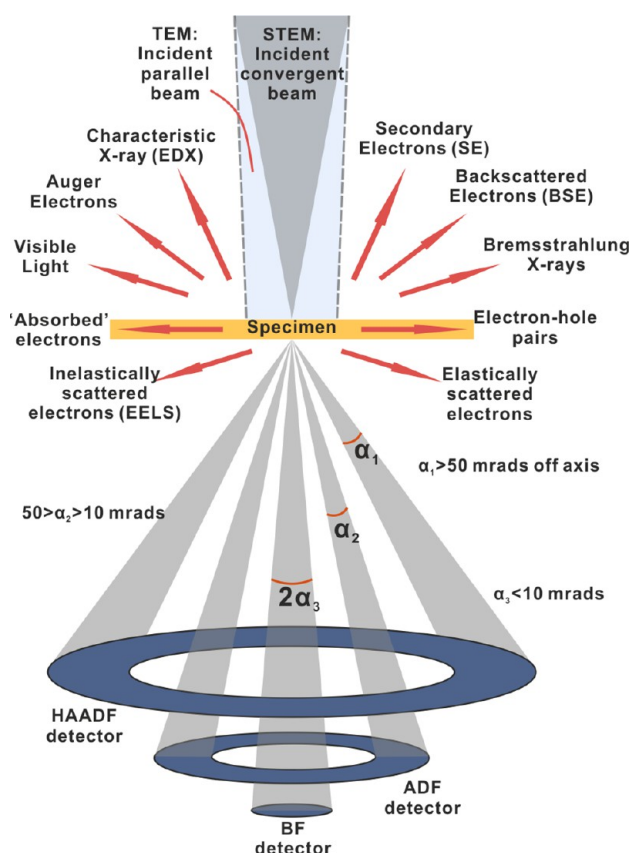


Figure 6. Secondary signals from the interaction of a high-energy beam of electrons with a TEM specimen and schematic of annular dark-field (ADF), high-angle ADF (HAADF), and bright-field (BF) detection in TEM and STEM modes. Most of the signals can be detected in various configurations of TEM. The depicted signal directions are merely indicative and not accurate. The ranges of electron scattering angles gathered by each detector are shown.

(NBD), and convergent beam electron diffraction (CBED), whereas inelastically scattered electrons and other signals (such as characteristic X-rays) are mainly used for chemical analyses such as energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). In practice, the electromagnetic lens is imperfect with many defects including spherical aberration, chromatic aberration, and astigmatism. Aberration-corrected TEM involves introducing spherical aberration-corrected electron optics to TEM.^{34,35} Spherical aberration is compensated by combining a converging lens (spherical aberration corrector) with an appropriate diverging lens (Urban, 2008). The spatial resolution of aberration-corrected TEM is more than twice that of conventional TEM without a spherical aberration corrector.

In general, TEM provides analysis at the highest spatial resolution and with a strong ability to analyze nanoscale mineral structure, but its capability for elemental chemical analysis is insufficient for NEPS due to its poor ability to analyze trace elements and missing ability to analyze isotopes. Therefore, microscale laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and submicroscale secondary ion mass spectrometry (SIMS) are usually used in combination with TEM in Earth and planetary science.

4.1. TEM Imaging. TEM can obtain BF and DF images, which are planar graphs representing the projection of a specimen in a certain direction and are the main tools for

characterizing the morphology of nanoscale minerals. The images are black and white, so the contrasts are important, and they are mainly divided into amplitude contrast (mass and/or thickness contrast) related to morphology and phase contrast related to mineral structure, which is represented by the “lattice fringe”. HRTEM records a combination of amplitude and phase contrast, making it an important tool for morphological and structural characterization of nanoscale minerals.

4.2. Electron Diffraction. At the macro and micro scale, XRD and various spectroscopic techniques (e.g., Raman, infrared spectroscopy, and X-ray absorption spectroscopy) are typically used for mineral identification and crystal structure research. Nanoscale mineral structure research by TEM has been greatly aided by various electron diffraction methods (e.g., SAED, NBD, and CBED), HRTEM with fast Fourier transform pattern (FFT), and HAADF-STEM (Z-contrast). In general, TEM diffraction patterns are regular “spots”, disks, or rings, which contain structural information about characteristics such as mineral phases and crystal orientations.²⁰ The difference among the three diffraction methods is mainly the range of their analysis area (SAED > CBED > NBD). HRTEM images contain amplitude contrast and phase contrast, so the FFT pattern of HRTEM is similar to the electron diffraction pattern, which can also reflect a mineral’s structural information. High resolution HAADF-STEM (Z-contrast) images can visually display the atomic arrangement of the specimen and obtain an FFT pattern, which is usually photographed using aberration-corrected TEM because it requires very high resolution and stable instrumentation.^{35–37}

4.3. TEM–EDS. EDS is the preferred technique for most chemical analyses in TEM and is also commonly configured on SEM. EDS can analyze almost all elements (atomic number >3) in the periodic table and can obtain information in one spectrum on most of the elements in a specimen. STEM–EDS mapping studies of complex geological samples can reveal their elemental distributions, which can guide subsequent detailed mineralogical research. Qualitative analysis of major elements by EDS is reliable, but overlapping peaks (the energy resolution is ~125 eV) may lead to misjudgment. In general, EDS mostly provides semiquantitative elemental analysis. However, correct quantitative data using a standard sample with similar thickness and chemical composition to the specimen allows for the quantitative chemical composition of the specimen to be obtained reliably (with ~0.1% error). EDS is mainly used to analyze major elements; its detection limit of ~1000 ppm hinders the analysis of trace elements. This has been an obstacle to comparative studies of key metals in Earth and planetary science.

4.4. TEM–EELS. EELS has advantages in quantitative, valence, and trace element analyses and can analyze almost all elements, even hydrogen. Its energy resolution is less than 1 eV, making it more accurate than EDS. STEM–EELS can detect contents of transition metals and lanthanides down to 10 ppm in powdered glass with high electron beam stability. The thickness of the specimen is critical for EELS analysis, with thinner specimens providing more comprehensive information. EELS can provide fine details about a specimen’s chemical, crystallographic, and electronic structure. Core-loss spectra show detailed intensity variations; i.e., the energy-loss near-edge structure (ELNES) and the extended energy-loss fine structure (EXELFS). In practice, the thinner the electron

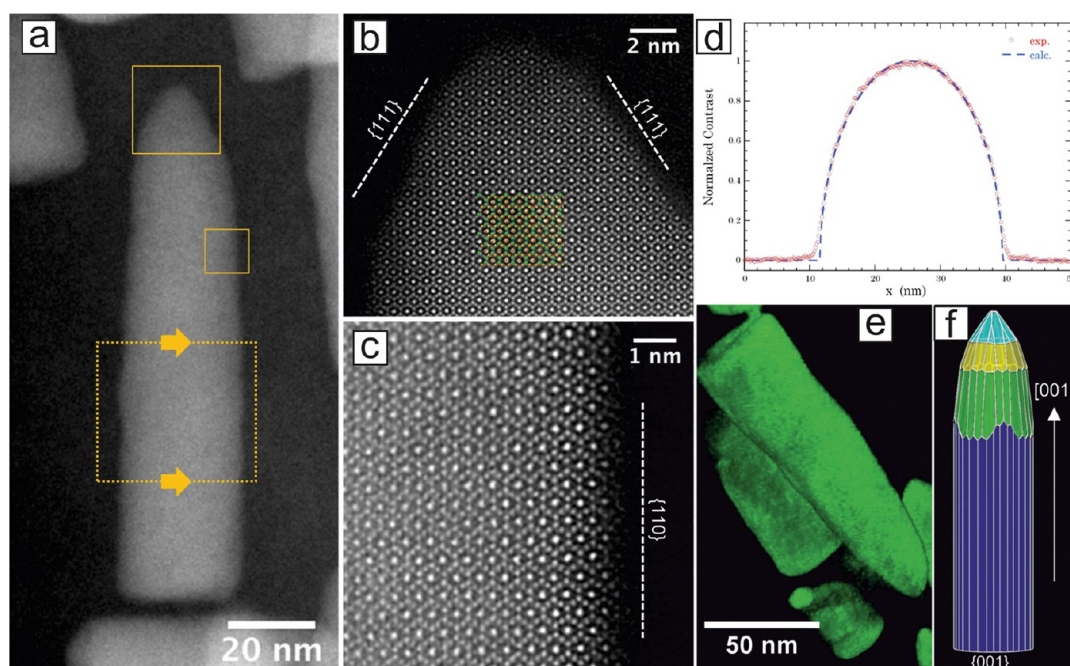


Figure 7. Atomic structure and 3D morphology of WYHR-1 magnetosomal crystals. (a) HAADF-STEM image of a mature WYHR-1 magnetosomal crystal. (b and c) Atomic structure of the top and side of the same particle indicated by the solid yellow boxes. (d) Normalized contrast profile across the yellow dashed box in (a). (e) 3D tomographic reconstruction image of WYHR-1 magnetite particles. (f) Morphological model for WYHR-1 magnetosomal magnetite. Reproduced from ref 40. Copyright 2020 John Wiley and Sons.

beam-stabilized sample, the better the quality of the EELS results, which requires high-quality sample preparation.

4.5. Atomic-Resolution HAADF-STEM (Z-contrast) Images. In STEM mode, high-angle scattered electrons are collected using a HAADF detector in aberration-corrected TEM. High-resolution aberration-corrected HAADF-STEM images can generally reveal the atomic arrangements and trace elements substituted within crystal lattices at deep sub-Ångström resolution, which is almost the highest spatial resolution achievable by TEM. Combined with EDS and EELS, HAADF-STEM imaging is widely applied to the study of elemental occurrences in nanoscale minerals. For example, Utsunomiya et al. used atomic-resolution HAADF-STEM to study the nanoscale occurrence of Pb in an Archean zircon, identifying two states of Pb: a nanoscale patch in the zircon structure and Pb concentrated in the amorphous domain created by fission fragmentation damage.³⁸ In practice, this requires the sample to have high electron-beam stability to support long-time high-energy convergent-beam scanning. Therefore, the analysis of many geological samples sensitive to electron beams (e.g., clay minerals) may need the help of cryo-TEM or a cryo holder to obtain high-quality atomic-resolution HAADF-STEM images.

5. MINERAL MORPHOLOGY AT THE NANOSCALE

Natural minerals generally occur as crystalline solids (although exceptions include amorphous minerals such as opal, agate, and ferrihydrite) with a definite chemical composition and a highly ordered atomic arrangement. Under ideal conditions, minerals spontaneously form regular crystalline polyhedra. As natural environments are diverse and constantly changing, the mineral crystals formed in them are not ideal regular polyhedra. Mineral morphology is controlled by chemical composition and mineral structure, which can be influenced by geological environments. Research in recent decades has

shown that records of many geological processes are captured in nanoscale minerals (e.g., magnetosomal magnetite and nanophase iron).^{39,40} However, the SEM and EPMA techniques commonly used in microscale geoscience cannot identify minerals with submicroscale and nanoscale (i.e., less than 100 nm) particle sizes. Therefore, TEM is the best way to characterize these minerals (after preparation by ultra-microtomy or FIB).

5.1. Nanoscale Biomineralization. Microfossils are important evidence of the evolution of life and biological activity, and TEM allows for their study at the nanoscale. This is an exciting research area that has already gained recognition and offers much scope for new findings.^{4,41–43} For example, biomineralization involves the interaction of minerals and microorganisms and is a widespread process. In recent decades, some research has shown that magnetite produced by magnetotactic bacteria (MTB) is a natural single-domain magnetic nanocrystal that can provide useful paleo-environmental information, as its morphology is associated with the environment in which the MTB groups lived.^{27,40,44,45} For example, Li et al. used BF-TEM, HRTEM, HAADF-STEM, and 3D visualization (tomographic reconstruction imaging) to study the chain assembly and crystal growth patterns of bullet-shaped magnetosomes (Figure 7) and the relationship between bacterial phylogeny and magnetosomal magnetite morphology.^{40,45,46} The establishment of the relationship between magnetosome morphology and the bacterial living environment would become an important tool for the study of various paleo-environments.

5.2. Space Weathering. Rocky and airless celestial bodies (e.g., the Moon, mercury, and asteroids) are exposed almost directly to the harsh space environment that includes galactic cosmic rays, solar energetic particles, solar-wind particles, and meteorite and micrometeorite impacts.^{47,48} Materials on the surfaces of the bodies are gradually altered by a variety of

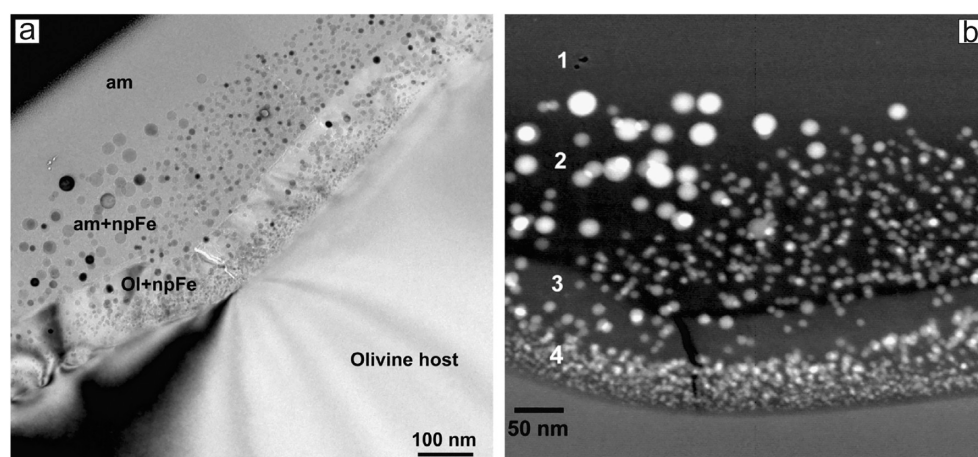


Figure 8. BF-TEM and HAADF-STEM images of an area of olivine irradiated by laser alteration showing four distinct sublayers. (1) am = amorphous silicate matrix. (2) am + npFe = amorphous silicate matrix with nanophase iron. (3 and 4) Ol + npFe = crystalline olivine with finely dispersed nanophase iron. Reproduced from ref 52. Copyright 2020 Elsevier.

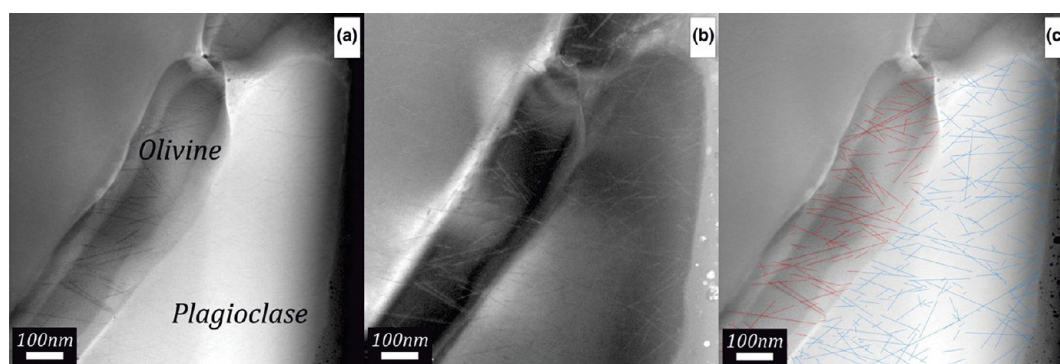


Figure 9. TEM images of solar energetic particle tracks in both olivine and plagioclase prepared using an FIB specimen from a lunar sample (Apollo 16 sample 64455). (a) BF-TEM image. (b) DF-STEM image. (c) BF-TEM image with tracks in olivine highlighted red and those in plagioclase in blue. Reproduced from ref 51. Copyright 2021 John Wiley and Sons.

physical and chemical processes in the complex environment of space, with no atmospheric protection. The combined products (e.g., nanoscale minerals and amorphous materials) of space weathering processes can be related to their location in the solar system (through conditions such as the speed and flux of impact radiation and temperature), the type of surface (i.e., composition of the host), and the duration of surface exposure to the space environment.⁴⁷ The processes affecting the surfaces of bodies occur at the nanoscale, so TEM combined with FIB has become indispensable in the characterization of lunar soils retrieved from the Moon or delivered by lunar meteorites⁴⁹ and other experimental samples having undergone space weathering.⁵⁰ For example, TEM imaging has revealed nanoparticles such as nanophase metallic iron (npFe⁰), amorphous rims, solar energetic particle tracks on mineral surfaces, and impact melts.⁵¹ The space weathering simulation experiment suggested that their weathered layers would be different (~450 nm in olivine and 100–250 nm in pyroxene), as would any spherical npFe⁰ in amorphous rims (Figure 8).⁵²

In addition, previous research has identified three major radiation sources (solar wind, solar energetic particles, and galactic cosmic rays) with different energies that can affect regolith minerals at different depth scales.⁵¹ For example, solar energetic particles can affect a few millimeters of regolith mineral, whereas galactic cosmic rays can penetrate to depths

of centimeters to meters.⁵¹ Measurements of track densities have been widely used to estimate the surface exposure ages of rock and minerals on the lunar surface. The measurements by chemical etching and SEM imaging are limited to densities of $\sim 10^9$ cm⁻². However, nanoscale observation of tracks in minerals and accurate measurement of higher track densities requires TEM. For example, Keller et al. used TEM to precisely calibrate the production rate of solar energetic particle tracks in lunar samples (Apollo 16 sample 64455; Figure 9), with potentially interfering observations of defects and grain boundaries being easily distinguished from energetic tracks.⁵¹

6. MINERAL STRUCTURE AT THE NANOSCALE

The processes of formation and evolution in minerals are complex, especially in extreme environments (e.g., under the impacts and irradiation of space), which usually have mineral structural changes at the nanoscale. Electron diffraction results from TEM can effectively identify nanoscale mineral phases in terrestrial and extraterrestrial samples, thus providing important information about crystal growth and phase transformations.

6.1. Crystal Growth and Phase Transformations. The theory of crystal nucleation and growth is the basis of mineralogy. Classical crystal growth models include layer-by-layer growth (i.e., Kossel–Stranski two-dimensional nucleation

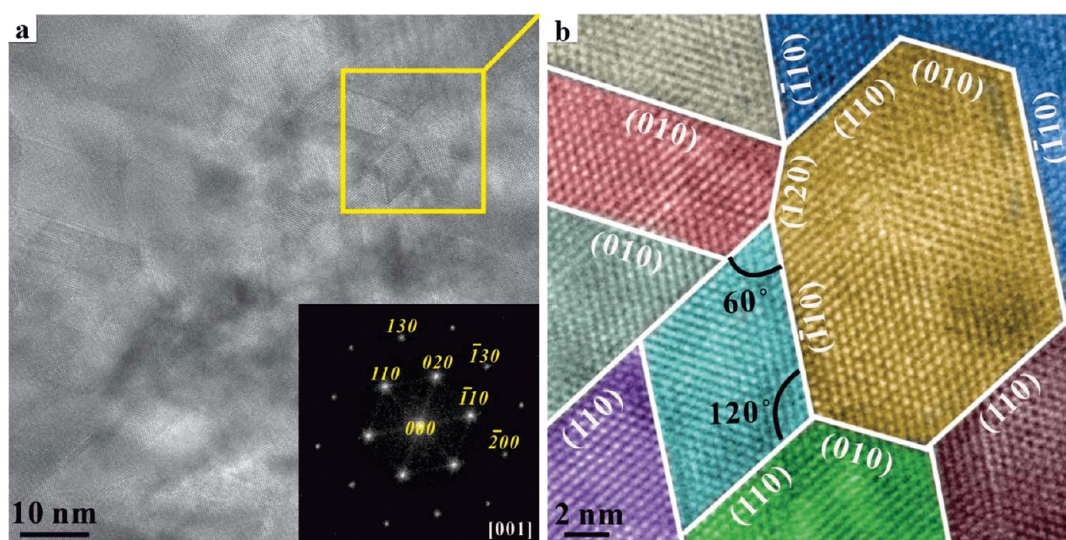


Figure 10. HRTEM image of synthetic fluorophlogopite from a melt. (a) Synthetic fluorophlogopite comprises domains of nanoparticles with parallel crystallographic orientation. (b) Oriented attachment between different nanoparticles. Reproduced from ref 59. Copyright 2021 Mineralogical Society of America.

growth) and spiral growth mechanism.⁵³ The application of TEM in recent decades has gradually increased research of nonclassical models of crystal growth such as crystallization of particle attachment (CPA) and amorphous transformation.^{54–57} Thus, CPA has been found to occur in supergenic geological processes,⁵⁸ high-temperature (e.g., melt) mineralization,⁵⁹ and hydrothermal fluid mineralization of shallow crust,²⁶ suggesting that nonclassical crystal models may occur extensively in various geological processes. Analyzing electron diffraction in TEM has become a mainstream tool for accurately characterizing mineral structures at the nanoscale in the above processes. For example, a recent TEM study of the crystal growth mechanism of phyllosilicate minerals and natural and synthetic micas showed the initial formation of multi-ion clusters (nucleation), which then self-assembled to form nanoscale flakes that ultimately became domains in larger crystallites by oriented attachment (Figure 10).⁵⁹ In addition, methods of researching mineral growth and phase transition have gradually moved toward *in situ* TEM observations (e.g., *in situ* liquid TEM), which have provided direct evidence of mineral growth patterns.⁶⁰ For example, researchers have performed TEM using a fluid cell to directly observe the oriented attachment of iron oxyhydroxide nanoparticles⁶¹ and Pt₃Fe nanorods in solution.⁵⁶

6.2. High-Pressure Mineralogy. High-pressure minerals (naturally occurring crystalline phases) have a stable field that does not extend to ambient pressure, and their structure reflects a significant change in chemical bonding character compared with that at ambient pressure.⁶² Such minerals usually form under ultrahigh-pressure conditions (e.g., meteorite impacts and in planetary interiors). Mineralogists have tried to find high-pressure minerals in meteorite impact craters and extraterrestrial samples (e.g., meteorites and samples returned by spacecraft) to understand hypervelocity impacts during the evolution of the solar system and the structure and dynamics of the inner Earth.⁶³ However, some high-pressure minerals are nanoscale and distributed heterogeneously on the microscale, so nanoscale mineral characterization technology (e.g., TEM) is critical to their identification and study. TEM–SAED combined with FIB techniques has

greatly aided the study of high-pressure mineralogy in past decades.^{63–66} For example, it has been determined that the pressure and temperature of impact (25–45 GPa and 800–900 °C) at the Xiuyan impact crater in China were sufficient to decompose ankerite [Ca(Fe²⁺, Mg)(CO₃)₂] and form nanoscale diamond in the absence of another reductant,⁶⁷ and maohokite, which is a new nanoscale postspinel polymorph of MgFe₂O₄, was formed by shocked genesis.⁶⁸ Chen et al. suggested that diamond is the dominant form of carbon in the lower mantle and maohokite is an important constituent mineral of the lower mantle.⁶⁷ In addition, many high-pressure minerals (e.g., ringwoodite, majorite, akimotoite, lingunite, tuite, xieite, and hemleyite) were identified in shocked meteorites, which often show nanoscale microstructures (e.g., planar defects) that can be characterized by TEM.^{69–75} For example, recent nanoscale mineralogical observations of the defects (stacking faults) and crystal structure analyses of olivine, ringwoodite, and wadsleyite have indicated that shear mechanisms promote polymorphic transformations and the occurrence of an intermediate spineloid structure (named poirierite by the Commission on New Minerals and Mineral Names of the International Mineralogical Association).⁷⁶ Previous studies^{77–79} of airless extraterrestrial bodies (e.g., the Moon) have shown that the large number of impact craters of different sizes on their surfaces indicate that the conditions for hypervelocity impacts are capable of forming high-pressure mineral phases and impact melts, which require further investigation using TEM.^{80–82}

7. NANOSCALE MINERAL CHEMISTRY

In recent years, compositional analyses (e.g., EDS and EELS) using TEM have been widely applied in studies of nanoscale elemental occurrence. Especially important is the study of critical metals such as Au, rare earth elements (REEs), Co, Ni, Mn, Li, and platinum group elements (PGEs), which have unique physical and chemical properties and are critical in cutting-edge industries such as new energy, information technology, and aerospace.^{83–85} STEM imaging combined with high-resolution chemical analyses (e.g., EDS and EELS) can intuitively show the occurrence states and distributions of

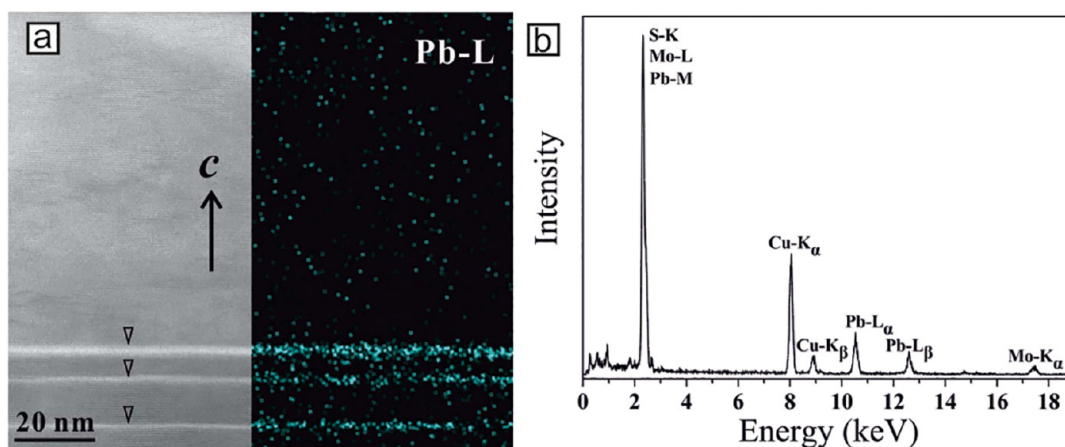


Figure 11. Nanoscale features of Pb-bearing molybdenite. (a) HAADF-STEM image (left) showing ~ 1 nm wide bright bands in the Pb-bearing zones of molybdenite and an EDS elemental map of the Pb-L line of the target Pb-bearing zones (right). (b) EDS results collected from the Pb-enriched area in (a). Reproduced from ref 86. Copyright 2022 Mineralogical Society of America.

elements at the nanoscale (Figure 11).⁸⁶ However, critical metals are usually dispersed in geological materials at low contents, and TEM cannot easily characterize elemental distributions at the microscale or identify low-content elements. Therefore, it is essential to combine TEM with EMPA, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and secondary ion mass spectrometry (SIMS) to study elemental occurrences in geological samples.

7.1. “Invisible” Au in Carlin-Type Au Deposits. Despite the first Carlin-type deposit (White Caps, Nevada) being discovered in 1917, this type of gold deposit was neglected by geologists until the discovery of the Carlin deposit in 1961.⁸⁷ Further examples were subsequently discovered worldwide (e.g., in China in the 1980s), and they currently account for $\sim 8\%$ of annual worldwide gold production.⁸⁸ In a Carlin-type Au deposit, Au is almost undetectable using optical microscopy and SEM. To understand the genesis of a Carlin-type Au deposit and the occurrence of Au, a variety of nanoscale analytical methods (particularly TEM) have been used to investigate Au occurrence in arsenopyrite or arsenian pyrite.^{89–91} Previous TEM observations have identified isolated Au nanoparticles in arsenian pyrite, which has been reported to be abundant in Carlin-type deposits in Nevada.⁹⁰ In addition, recent research using SEM-FIB and TEM has suggested that ionic Au in the crystal lattice of arsenian pyrite is likely dominant in Carlin-type deposits from Getchell and Cortez Hills, Nevada, USA, and Shuiyindong and Jinfeng, Guizhou Province, China; it also revealed that some Au nanoparticles in arsenian pyrite likely evolved from Au¹⁺ during an annealing process.⁸⁹ In summary, studies have indicated that “invisible” Au occurs mainly as ionic Au¹⁺ or Au⁰ nanoparticles in arsenian pyrite in a Carlin-type deposit, although other occurrence states have also been found; e.g., Au hosted in nanoscale dislocations⁹² and Au occurring as diffuse atoms within arsenian pyrite.⁹³

7.2. Rare Earth Elements in Marine Sediments. REEs are crucial for emerging technologies because of their physical and chemical properties, and marine sediments and sedimentary phosphorites have been regarded as REEs resources.^{94–96} Fe–Mn (oxyhydr)oxides (e.g., Fe–Mn nodules and crust) and Ca-phosphate (e.g., apatite) have been considered important carriers of REEs and modulators of their enrich-

ment.^{97–99} For example, a recent study used HRTEM and extended XAFS spectroscopy to identify the transformation of phyllosulfates to todorokite and found that the transformation of phyllosulfates to todorokite can affect the distribution of critical metals.¹⁰⁰ In addition, investigation of hydroxyapatite in deep-sea mud using HAADF-STEM and EDS has revealed the substitution of REEs in the hydroxyapatite crystal lattice.¹⁰¹ For samples stabilized using an electron beam, chemical mapping at atomic resolution using EDS and EELS offers nearly perfect visual evidence.¹³ This seems difficult to achieve in geological samples, which have insufficient electron beam stability to sustain long-term scanning with a high-energy electron beam. However, cryo-TEM or cryo-TEM holders are widely used in biological fields to study samples such as volatile molecules that are sensitive to electron beams.¹⁰² This may aid the study of electron-beam-sensitive samples (e.g., Fe–Mn (oxyhydr)oxides, hydroxyapatite, and clay minerals).

8. SUMMARY

In recent decades, TEM, with its high spatial resolution and compatibility with a variety of structural and chemical analysis techniques, has become the most commonly used analysis platform for nanoscale mineralogical characterization in Earth and planetary science. TEM’s widespread adoption is also attributed to the continuous improvement of TEM specimen preparation technology (e.g., ultramicrotomy and FIB method). In general, unlike the samples analyzed in materials science, physics, chemistry, and biology, geological samples are usually heterogeneous at the microscale. However, TEM cannot be useful for microscale and macroscale characterization, which may result in TEM analysis alone possibly being one-sided. Therefore, in the field of Earth and planetary science, it is recommended that macroscale bulk analysis and microscale and nanoscale characterization should be combined to achieve comprehensive analysis. In addition, various microscopic (e.g., SEM and EMPA) and microspectroscopic techniques including those based on lasers, X-rays (e.g., micro XRF and synchrotron-based STXM), and ion-mass-spectrometry (e.g., SIMS and NanoSIMS) are sometimes used together for the comprehensive analysis (e.g., trace element and isotope geochemistry) of complicated or precious geological samples. Besides, preparing a sample for TEM and executing the

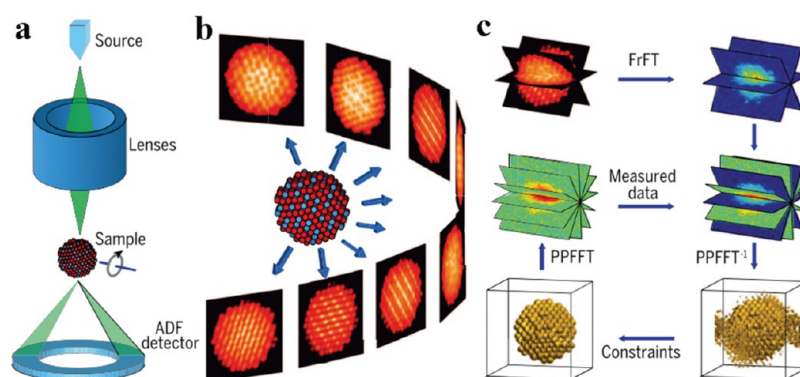


Figure 12. Schematic layout of AET. Reproduced from ref 110 Copyright 2016 the American Association for the Advancement of Science.

characterization might introduce amorphous damage or sputtering contamination, which requires researchers to make judgments and apply methods (e.g., plasma cleaning and using a cryo-TEM holder) to reduce these interferences.

9. OUTLOOK

9.1. *In Situ* TEM Characterization. Various *in situ* TEM techniques have been developed to characterize the dynamic processes of physical and chemical reactions in materials at the nanoscale. These include *in situ* heating TEM,¹⁰³ *in situ* liquid cell TEM,^{56,61} environmental TEM that allows gases to contact samples,¹⁰⁴ and cryo-TEM for samples sensitive to an electron beam.¹⁰⁵ The thermal behavior of natural gold nanoparticles in pyrite has thus been observed directly using *in situ* heating TEM, which revealed that thermal stability is dependent on the particle size and on the surrounding host mineral.¹⁰³ In addition, the oriented attachment processes of iron oxyhydroxide nanoparticles have been directly observed using *in situ* liquid cell TEM; the process is important to the alignment process and mechanism of oriented attachment.⁶¹ Cryo-TEM can also prevent the loss of volatile compounds from specimens.¹⁰² Therefore, in NEPS, cryo-TEM offers clear advantages to the characterization of samples that are sensitive to an electron beam, such as clay minerals.

9.2. Microcrystal Electron Diffraction (MicroED). Single-crystal XRD and crystal structure refinement are important tools in macroscale mineralogy. Researchers can identify individual atoms and assign their positions in the crystal by analyzing XRD data. However, nanoscale minerals are too small for powder or micro XRD. Two research teams (one in the United States and the other in Switzerland and Germany) have improved diffraction techniques by replacing X-rays with electron beams.^{106,107} Using cryo-TEM, electron beams were fired at nanocrystals on a rotating stage and the diffraction pattern was collected using slight continuous rotation, similar to high-resolution nanocrystal structure computed tomography scanning. This technology is usually called microED.^{107,108} Although it has attracted extensive attention for its rapid determination of microcrystalline structures of molecular compounds in biology,¹⁰⁹ this technique is also of great significance to the study of nanomineralogical structures apparently.

9.3. Atomic Electron Tomography (AET). AET has enabled 3D determination of crystal defects and potentially disordered systems at atomic resolution.¹¹⁰ Particularly important is its application to determining the 3D atomic structures of amorphous solids.^{111,112} Figure 12 gives an

overview of AET.¹¹⁰ Amorphous solids are widely distributed in terrestrial and extraterrestrial samples such as obsidian, opal, agate, and various glasses formed by meteorite impacts in lunar soils and various mineral precursors (e.g., ferrihydrite). These materials remain poorly understood because they are difficult to characterize. The application of AET to nanoscale mineralogy in NEPS would be sensational.

AUTHOR INFORMATION

Corresponding Author

Jianxi Zhu – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China; orcid.org/0000-0002-9002-4457; Email: zhujx@gig.ac.cn

Authors

Jieqi Xing – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Haiyang Xian – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China; orcid.org/0000-0002-8602-3750

Yiping Yang – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China

Qingze Chen – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence

in *Deep Earth Science*, Guangzhou 510640, China;

orcid.org/0000-0003-2103-2338

Jiaxin Xi – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Shan Li – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China

Hongping He – CAS Key Laboratory of Mineralogy and Metallogeny and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, P. R. China; CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsearthspacechem.2c00278>

Notes

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