Chapter 2
Micro-Mineralogical Investigative Techniques

This chapter gives a summary of techniques used in the investigations of minerals, particularly the fine-grained minerals in the Suizhou meteorite. For the various techniques summarized by Edward C.T. Chao and Xiande Xie in their two publications (Chao and Xie 1989, 1990), here we try to describe techniques needed and suitable for the investigation of shock-induced fine structures within minerals, as well as for identification and characterization of tiny new high-pressure polymorphs produced by shock, including optical microscopy, scanning electron microscopy (SEM) energy-dispersive X-ray analysis (EDS), electron microprobe (EPMA), Raman microprobe analysis (RMA), synchrotron radiation X-ray diffraction (SRXD), X-ray micro-diffraction (XRMD), transmission electron microscopy (TEM), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to provide examples of optimal use of the various techniques and how they complement each other.

2.1 Petrographic Microscopic Studies

The petrographic microscope is a basic tool for the use to identify minerals and petrologic type of meteorite, mineral assemblages, and structural and textural relationships and thus infer paragenesis. Petrographic microscopic study is a preliminary stage of meteorite research needed to pinpoint identification of minerals and selection of samples for detailed SEM, EDS, and micro-Raman analyses, as well as to guide other aspects of multidisciplinary investigations. One of the principal objectives of using polished thin sections (PTSs) of the Suizhou meteorite was to study the internal structures and deformation features of an impact process in minerals. Such deformational process produces effects that reflect fast strain rates generated by meteorite impact. Microscopic investigations are of great importance in the study of shock metamorphic features of olivine, pyroxene, and plagioclase in a meteorite and thus classify its shock degree. Another objective is to find shock-induced high-pressure phases in shock melt veins. Microscopic study is also important for photographic documentation of the locations of the minerals in PTS for further SEM-EDS, EPMA, and RMA.
An MPV-SP optical microscope with both transmitted and reflected lights has been used at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, for petrographic microscopic studies of both transparent and opaque minerals in the Suizhou meteorite (Fig. 2.1). The example given here is concerning the study of shock-induced deformation features in olivine of the Suizhou meteorite (Fig. 2.2).

2.2 Scanning Electron Microscopy Energy-Dispersive X-Ray Analysis

A scanning electron microscope equipped with appropriate detectors and electronics for EDX provides a capability for rapid semi-quantitative compositional analysis of individual mineral and inclusions within grains. For textural analysis, SEM extends the capability of the optical microscope with respect to depth of field.
and spatial resolution (about 2.5 nm). The three-dimensional aspect of the images obtained by SEM is of particular value for applications such as characterization of crystal morphology, porosity studies, and deformation features. Images obtained using back-scattered electrons (BSEs) show variations in intensity which highlight differences in average atomic number, thus revealing the different mineral phases present and serving as a guide for more efficient SEM-EDX and EPMA analysis.

For SEM-EDX studies of the Suizhou meteorite, a Hitachi S-3500 N scanning electron microscope equipped with a Link ISIS 300 X-ray energy-dispersive spectrometer has been used at Guangzhou Institute of Geochemistry (Fig. 2.3). In analyses, the minimum detection level for most elements for routine SEM-EDX analysis is approximately 0.1–0.2 wt%. In addition, our EDX can detect elements present in particles as small as about 1 μm. Figure 2.4 is an SEM image in back-scattered electron (BSE) mode showing a shock-induced melt vein in the Suizhou meteorite and different minerals outside the vein.

**Fig. 2.3** The Hitachi S-3500 N scanning electron microscope with a Link ISIS 300 X-ray energy-dispersive spectrometer

**Fig. 2.4** Back-scattered electron image showing a shock vein in the Suizhou meteorite (Xie et al. 2011)
2.3 Electron Probe Microanalysis

Quantitative analysis with the electron microprobe requires more elaborate sample preparation than for most SEM studies: Surface for analysis must be flat, polished, and as scratch free as possible. Thus, specimens for EPMA must be PTS or polished mounts. The outstanding advantage of EPMA is the ability to carry out in-place identification of a minute mineral or crystal in a prepared sample without having to extract the grain for study.

A Cameca SX-51 electron microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences, and a JEOL JXA-8100 electron microprobe at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (Fig. 2.5), were used for analyzing the Suizhou minerals. Minimum detection limits for our EPMA for routine analysis of most elements are of the order of 500 ppm, and the minimum area of analysis is a circle of about 3 μm in diameter. Depth of penetration of the incident electron beam into the target is about 3 μm in most Suizhou minerals. The capability for quantitative analysis of such small areas makes EPMA invaluable to us for (1) mineral identification of the Suizhou meteorite on the basis of concentration of major and minor elements present, especially in cases where the sensitivity of analysis by SEM-EDX may not be sufficient for identification (Fig. 2.6); (2) identification of phases transformed in solid state or crystallized and quenched from shock-induced melt at high pressures and temperatures; (3) determination of the chemical formula of Suizhou minerals and high-pressure polymorphs and assignments of cations to site occupancies, as in analyzing new minerals tuite and CaFe₂O₄- and CaTi₂O₄-structured polymorphs of chromite; (4) mapping of elements in different phases in the shock melt veins; and (5) study of melt-vein minerals with incorporation of additional elements from the surrounding matrix melt.

![Fig. 2.5 The JEOL JXA-8100 microprobe](image)
2.4 Raman Microprobe Analysis

With the recent development of micro-Raman techniques, the Raman microprobe is emerging as an important tool in mineralogical research. Raman spectroscopy provides detailed structural information about site symmetry, short-range and long-range bonding, and lattice vibrational properties. Macro-sampling Raman spectroscopy has been used as the main analytical method of studying the structures of silicate glasses quenched from various temperatures and pressures. The method provides critical structural information such as the mechanism of pressure densification, the angle of Si–O–Si linkages, the number of nonbridging oxygens, and the effects of ion substitution (Chao and Xie 1989, 1990; Fukukawa 1981; McMillan 1984; Mysen et al. 1982). Raman spectra are also sensitive to slight differences in the symmetry of polymorphous mineral phases and to the ordering of cations.

The coupling of a research-grade microscope to a Raman spectrometer has led to the capability of obtaining Raman spectra for micron-sized samples. A Raman microprobe can be used as a routine petrographic tool comparable to a conventional petrographic microscope. High spatial resolution and rapid measurement can be obtained with regular PTS. In addition to “fingerprinting” identification of micron-sized minerals, RMA yields sophisticated structural information of shock-metamorphosed minerals. The broadening of a Raman band in a shocked mineral may be indicative of pressure densification and changing in bonding angles. The additional band in the Raman spectrum of a shocked mineral may reflect shock-produced disorder. The changing and shifting of Raman bands may reflect the structural transformation of a shocked mineral. Therefore, obtaining this crystal chemical information for minerals in place in thin section is critical to understanding the history and the evolution process of a meteorite.

Fig. 2.6 BSE image of an apatite grain (Apt)
A Renishaw RM2000 laser Raman microprobe (Ar$^+$ laser, 514.5-nm line) in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (Fig. 2.7), and the RM1000 laser Raman microprobes (Ar$^+$ laser, 514.5-nm line) in the Beijing Institute of Nonferrous Metals as well as in the China University of Geosciences have been used for recording Raman spectra of different minerals and polymorphous phases of the Suizhou meteorite. An example of RMA application is the study of shock metamorphic features of plagioclase in Suizhou. The Raman spectrum of the new mineral tuite, the shock-induced high-pressure polymorph of whitlockite, in the Suizhou melt vein is shown in Fig. 2.8.

2.5 Synchrotron Radiation X-Ray Diffraction in Situ Analysis

Synchrotron radiation energy-dispersive X-ray diffraction (SRXRD) technique developed in the Geophysical Laboratory of the Carnegie Institution of Washington is one of the best techniques for in situ studying of micron-sized polycrystalline grains or single crystals under high pressures or at ambient conditions, as well as for studying inclusions and lamellae in minerals (Hemley 1998). This technique uses the entire energy spectrum of synchrotron radiation. The collimated polychromatic (white) X-ray beam impinges on the mineral specimen. The polychromatic diffracted beam is collimated at a fixed 2θ angle and collected by a solid-state detector which disperses the diffracted photons in the energy spectrum, and at a fixed Bragg angle 2θ, and the d-spacings are determined from the peak energies (Hemley 1998). Minute samples and samples of low diffraction intensity (low atomic number) can be studied with this technique.

SRXRD has been used for studying the fine-grained minerals and polymorphs of the Suizhou meteorite. After investigation with optical microscope, scanning SEM, EPMA, and RMA, the micron-sized target mineral grains in thin sections were
analyzed in situ by energy-dispersive X-ray diffraction using the synchrotron beamline X17C at the National Synchrotron Light Source, Brookhaven National Laboratory, USA (Fig. 2.9). The operating voltage was 2.584 GeV and the current —300 to 100 mA. X-ray beam was collimated to a size of μm 15 × 15 and was focused on the probed mineral sample in the PTS which was rotated systematically (ω = −30°−30°, χ = 0°−360°) to collect diffraction lines. Energy-dispersive X-ray diffraction (EDXD) was gathered with an intrinsic germanium detector. The X-ray diffraction data were acquired at 2θ settings of 8° and 10°, respectively.

It should be pointed out that using the advanced SRXRD technique, the authors of this book were able to obtain the X-ray diffraction patterns for the fine-grained vein matrix minerals and three shock-produced and micron-sized new minerals, namely tuite, the high-pressure polymorph of whitlockite, and two post-spinel high-pressure phases, the CaFe2O4-type and CaTi2O4-type polymorphs of chromite in the Suizhou meteorite, and the three synthetic quenched products recovered from high P-T experiments were also analyzed by synchrotron X-ray diffraction at the

**Fig. 2.8** The Raman spectrum of the high-pressure polymorph of whitlockite in Suizhou

**Fig. 2.9** The synchrotron radiation X-ray diffraction device at Brookhaven National Laboratory
X17C superconducting wiggler beamline of the National Synchrotron Light Source, Brookhaven National Laboratory, USA, for phase identification and crystal structure determination (Xie et al. 2005; Chen et al. 2003a, b) (Fig. 2.10).

The utility of synchrotron radiation techniques has exceeded the development of high-pressure mineralogy. At the same time, the techniques developed for in situ studies at high pressures and temperatures are being used to investigate microscopic inclusions such as coesite in high-pressure metamorphic rocks and deep mantle samples as inclusions in diamond (Hemley 1998). The results of our investigations added some more examples of using synchrotron radiation technique for in situ investigations of fine-grained mineral aggregates and identification of extremely small-sized new minerals embedded in the fine-grained matrix.

2.6 X-Ray Micro-Diffraction in Situ Analysis

X-ray micro-diffractometer is an effective tool for obtaining X-ray diffraction data of tiny size of minerals and materials, usually less than 1 mm, directly on thin sections or plane blocks containing the mineral or material of interest. The structure of the instrument is similar to four-circle single-crystal diffractometer, but differs in lacking the \( \chi \)-axis in the former. The RIGAKU D/Max Rapid IIR X-ray micro-diffractometer in the Central South University has been used in in situ study of some Suizhou minerals. It is mainly composed of the following parts (Fig. 2.11): (1) X-ray generator with the maximum power of 18 KW; (2) X-ray collimator tube of diameters 0.1, 0.05, 0.03, and 0.01 mm; (3) two-axis goniometer defined as the \( \phi \)-axis (vertical to the sample plane) and \( \omega \)-axis (vertical to the horizontal plane); (4) X-photon detector of high-sensitivity two-dimensional image plate or CCD setup as a cylinder with the diameter around 127.4 mm; (5) monitoring video for sample positioning with magnitude from 30 to 240; and (6) controlling software.
The diffraction effect of the sample is recorded on 2D image plate of the area \((470 \times 256)\ \text{mm}^2\) arranged in \(4700 \times 2560\) pixels. The pixel coordinates of a diffraction dot on the image are related to the incident angle \(\theta\) of X-ray and the dipping angle \(\beta\) of the normal line of the sample plane. Numerous diffraction dots with the same \(\theta\) constitute a Debye ring. Intensity integration along the Debye rings yields one-dimensional \(2\theta\)-I data similar to the pattern of powder diffraction (Fig. 2.12).

The area of the sample covered by X-ray depends upon the diameter \(d\) of collimator, and the angle \(\omega\) between incident X-ray and the sample plane and the starting \(2\theta\) in the diffraction data is close to \(\omega\). In practice, the minimum grain size required for a pure phase diffraction data is around 0.15 mm for 0.03-mm collimator and \(\omega = 20^\circ\), and around 0.25 mm for 0.05-mm collimator and \(\omega = 20^\circ\).

Various forms of samples may be accepted for X-ray micro-diffRACTometer, including polished thin section or polished block, powder, small specimen, and a single tiny grain. The minimum grain size of sample to have distinguishable diffraction lines (dots) varies with the diffraction ability expressed by K value and
the crystallinity as well as the iron contents, to say, as small as 2 microns for minerals of high K values, such as galena, or as big as 40 microns for clay minerals of low K values, such as kaolinite. The exposure time to get good results varies with the collimator diameter and the grain size of the sample, to be as short as 10 min for 0.1-mm collimator on a grain size of 0.5 mm, or to be as long as 12 h for 0.03-mm collimator on a grain size of 0.05 mm.

2.7 Transmission Electron Microscopy

Microstructures or domains in minerals are indicative of the geological environment and the processes involved in their formation and evolution. Microstructures in rock-forming minerals resulting from pressure, temperature, and composition conditions during crystallization and cooling include atomic site ordering, exsolution, and phase transitions. Fine internal structures produced by deformational processes may be characteristic of particular ranges of strain rates. However, microstructures are too small to be resolved either by optical methods or by SEM, but they can be studied using TEM. Prior to the development of thinning by ionic bombardment, samples thin enough to be transparent to electron beams could generally be produced only as dispersed small particles or flakes. Chemically thinned individual grains or surface replicas and ultramicrotome sections are prepared from bulk specimens. It was only after the advent of ion thinning that it became possible to heavily utilize TEM in geological and mineralogical studies. Another aspect using TEM is the acquisition of electron diffraction data, either SAED (selected area electron diffraction) or general area diffraction. This allows one to identify very small mineral grains while studying its substructures. TEM is particularly suitable for identification of inclusions or high-pressure polymorphs less than 5 μm in size which are difficult to extract in order to obtain XRD data, or identification of submicron-sized minerals observed optically.

A Hitachi transmission electron microscope and a JEM 2100F field-emission transmission electron microscope (Fig. 2.13) at the Wuhan University of Technology were used for studying the mineralogy and fine structures of minerals of the Suizhou meteorite. Figure 2.14 is a TEM micrograph showing the shock-induced fine-grained high-pressure polymorphs in a Suizhou melt vein.

Very recently, the focused ion beam (FIB) method has been developed for fast preparing of the TEM samples in material sciences (Zhou and Xu 2004). This technique can be used to cut thin TEM samples in different fixed locations on PTS of terrestrial or extraterrestrial rocks. One of such kinds of instruments is Seiko SMI 2200 focused ion beam system produced by the Seiko Company of Japan. There are two methods of preparing TEM samples. One is the traditional trench method. At the first stage, a specimen is cut to a 3 mm × 0.1 mm size and ion-thinned to a thickness of 20–30 μm. Then, a TEM sample of 10 μm × 5 μm with a thickness
of 0.1 μm is prepared by using the FIB system. The other is the lift-out method. At first, a carbon layer is deposited on the sample to protect the sample surface. Then, a cross section will be engraved on one side of the sample on polished thin section, and afterward, another cross section also be cut on the other side of the sample. However, the thickness of the sample is about 0.8 μm that is thicker than that required for TEM study. For further thinning, the sample holder should be tilted to 45° for cutting through the sample’s lower edge and then return the sample holder to its original position. After the sample being thinned to 0.2 μm in thickness, cut through the foil sample at two tops; thus, a suitable TEM sample is prepared. Finally, lift out the prepared sample and lay it on a carbon-coated copper grid by using a specimen transfer.
2.8 Laser Ablation ICP-MS

The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can precisely determine trace element concentrations of geological samples ranging from ultramafic to granitic and the precision and accuracy for elements with concentrations higher than 0.1 μg/g (Tu et al. 2011). In LA-ICP-MS, the sample is directly analyzed by ablating with a pulsed laser beam. The created aerosols are then transported into the core of inductively coupled argon plasma (ICP), which generates temperature of approximately 8000 °C. The plasma in ICP-MS is used to generate ions that are then introduced to the mass analyzer. These ions are then separated and collected according to their mass-to-charge ratios. The constituents of an unknown sample can then be identified and measured. ICP-MS offers extremely high sensitivity to a wide range of elements. For laser ablation, any type of solid sample can be ablated for analysis; there are no sample-size requirements and no sample preparation procedures.

Chemical analysis using laser ablation requires a smaller amount of sample (micrograms) than that required for solution nebulization (milligrams). Depending on the analytical measurement system, very small amount of sample quantities may be sufficient for this technique. In addition, focused laser beam permits spatial characterization of heterogeneity in solid samples, with typically micron resolution in terms of both lateral and depth conditions.

In the study of our Suizhou minerals, an Agilent 7500a coupled with a Resonetics RESOlution M-50 laser ablation system in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, was used to analyze about 40 trace elements for all minerals (Fig. 2.15). It consists of an excimer (193 nm) laser, a two-volume laser ablation cell, a squid smoothing device, and a computer-controlled high-precision X-Y stage. The two-volume laser ablation cell is designed to avoid cross-contamination and reduce background flushing time. The squid smoothing device can reduce statistic error induced by laser ablation pulses.

**Fig. 2.15** The Agilent 7500a ICP-MS coupled with a Resonetics RESOLution M-50 laser ablation system
The accuracy of the X-Y stage is better than 0.1 μm. Laser ablation was operated at a constant energy 60 mJ and a repetition rate of 8 Hz, with a spot diameter of 31 μm (Fig. 2.16), using external standards of NIST SRM 610, NIST SRM 661, and GOR 128 from Ding-Glass (Pearce et al. 1997; Jochum et al. 2005). The primary data used two different internal standards to calibration of $^{29}$Si in silica melt and $^{59}$Ni as the FeNi metal grains. The relative standard deviations are mostly less than 5 %, and relative standard deviations of obtained average concentrations from reference values are mostly less than 10 % (Tu et al. 2011). Data reduction was carried out using ICPMSDataCal (Liu et al. 2008).

References

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