Elemental mapping with a micro X-ray fluorescence spectrometer (micro-XRF): applications for geological samples

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Geological specimens are frequently heterogeneous in micron meter scale. We can utilize various high precision and high resolution instruments for microscale point analysis, however it is important to know the significance of the target point within the specimens evaluated. Thus before any microscale point analysis, the detail observation of samples is generally applied, typically using microscope and other techniques. Mappings of samples with various methods are important techniques for selection of target points. The recent mapping techniques generally provide the spatial resolutions in a range of sub-micron to tens of micron, thus analytical points can be selected with the help of the mapping data. Furthermore, the mapping data are useful to understand nature and origin of the heterogeneity in the specimens. Electron micro-probe analyzer (EPMA) and scanning electron microscope with EDS system are typically utilized to obtain the micro-scale elemental distribution patterns in the geological samples. For about 10 years, a micro X-ray fluorescence spectrometer (micro-XRF or μXRF) has been utilized for specimen description at the Geological Survey of Japan, AIST. Recently we replaced it with a new micro-XRF, Bruker M4 Tornado (Shimizu, 2015). Performance and applications of the micro-XRF are presented here.

Various mapping techniques with high spatial resolution are available, and listed as follows. The characteristics of the techniques are briefly summarized to compare to those of the micro-XRF.

Micro-scale mapping methods

(1) EPMA (Electron probe micro-analyzer)
(2) SEM (BSE and SE images) (Scanning electron microscope, Back-scattered and Secondary electron images)
(3) SEM-EDS (SEM with energy dispersive X-ray detector)
(4) SEM-EBSD (SEM with electron back scatter diffraction)
(5) SEM-CL (SEM with cathodoluminescence)
(6) SIMS (Secondary ion mass spectrometer)
(7) LA-ICP-MS (Laser ablation ICP-MS)
(8) LIBS (Laser induced breakdown spectroscopy)
(9) Micro laser Raman
(10) PIXE (Particle induced X-ray emission)
(11) SR-XRF (Synchrotron radiation XRF)
(12) Micro-XRF (μ-XRF)

The micro-scale mapping instruments use a focused primary probe to obtain signal from the specimens. EPMA and SEM utilized electron beams as primary source. The SIMS uses ion beams to spatter secondary ions from samples. Laser beams are applied as primary beams for LA-ICP-MS, LIBS, and Micro laser Raman. Proton beams and synchrotron radiation generate X-rays for PIXE and SR-XRF, respectively. Among the techniques, SIMS, LA-ICP-MS, and LIBS are destructive method, and others are non-destructive methods.

The M4 Tornado is a bench-top micro-XRF and is operated with 100 V electric power supply. X-ray tube used for the instrument has Rh target and 30 W excitation energy with maximum of 50 kV and 0.8 mA. The X-rays are focused with polycapillary lens. The diameter of the focused X-ray beams is 25 μm on the sample surface. The sample chamber can be pumped down to vacuum of 2 mbar, reducing atmospheric absorption of long wavelength X-rays, such as Na Kα. It is also possible to measure under atmospheric pressure, so wet samples and biological samples can be analyzed, though the long wavelength X-rays, i.e., light elements, are not possible to analyze in this condition. The M4 Tornado has a large sample chamber and is possible to measure sample surfaces of up to 200 mm x 160 mm. The micro-XRF analysis does not require conductive coating of the sample surface, thus minimum sample preparation is required.

The M4 Tornado has several analytical protocols, such as point analysis, line analysis, and 2D mapping. The mapping mode is most frequently used at the Geological Survey of Japan. Line analysis is also important to understand linear change of chemical composition in geological samples (De Winter and Claeys, 2016). Rock slabs and thin sections are typical samples. Elemental maps with the spatial resolution of 25 μm provide valuable information to understand general texture of the sample and inter-relationships among minerals (Flude et al., 2017). Elemental mapping of whole surface of polished thin section can be obtained within two hours. Result data file contains EDS profiles for each points, so we can generate elemental maps or phase maps after the acquisition of the data. The elemental mapping data of the thin section greatly help identification of

minerals. Furthermore, elemental images can be used to guide selection of analytical points for EPMA. In the typical mapping mode, lower detection limits of elements are in the rage of several hundred ppm. When we need to get further lower detection of elements, we use point analysis mode with longer integration time.

Various microscale analytical methods are applied for geological samples, the micro-XRF has an advantage on elemental mapping of a large area with spatial resolution of 25 μm. The minimum sample preparation required for the analysis provides efficient analytical works,

References

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