EDS Phase Mapping of a Contact Metamorphosed Calc-Silicate Rock

Key Words

COMPASS, Energy Dispersive Spectroscopy (EDS), FESEM, Mineral Phases, Minerals, Multivariate Statistical Analysis (MSA)

Introduction

Rocks are not simple materials but are an agglomeration of different chemical compounds. The formation mechanism and environment can determine the type, shape and distribution of minerals in the agglomerate. Understanding the spatial distribution and chemical compositions of minerals in these rocks is vital to determine the mineral and textural development and history. This Note shows analyses of Energy Dispersive Spectroscopy (EDS) acquisitions to rapidly locate and identify sub-millimeter scale mineral phases in the sample.

Experimental

A thin section of contact metamorphosed Leadville Limestone from Colorado, USA was sectioned, polished, mounted to a glass slide, and final polished to transparency. It was examined in a FESEM without carbon coating using the Thermo Scientific[™] NORAN[™] System 7 with a fully integrated Thermo Scientific[™] UltraDry[™] EDS detector. The analytical conditions are shown in Table 1.

Sample	Contact Metamorphosed Calc-Silicate
EDS Analyzer	NORAN System 7
EDS Detector	UltraDry 10 mm ² silicon drift detector
Accelerating Voltage	15 kV
Beam Current	10 nA
Magnification (for spectral imaging)	$450 \times$ and $4300 \times$
Mapping Resolution	512 × 384
Table 1	

UltraDry silicon drift X-ray detector



X-ray microanalysis system

Images were collected in the SEM using secondary electrons. EDS Spectral Imaging (SI) mapping acquisitions were performed to collect the distribution of all of the elements in the map analysis region. Spectral Imaging is a technique that collects every X-ray from each pixel location in a scanned region of a map and stores them into a spectrum for each pixel. In this manner, a 3D histogram of X-ray intensities is stored for the dimensions (x, y, Energy). From this 3D histogram, spectra can be extracted for selected regions in the x-y image plane and elemental X-ray maps can be extracted for any elemental lines along the energy axis.



A primary benefit to Spectral Imaging data acquisitions is the ability to perform Multivariate Statistical Analyses (MSA) on the whole 3D histogram. MSA uses only the 3D data set as an input and analyzes all of the contained spectra in a self-consistent manner, comparing the spectra at each pixel to the spectra at every other pixel, looking for similarities and differences. When two pixels have a statistically similar shape (elemental ratios), they are grouped into a common map. When two spectra have statistically different shapes (elemental ratios), the pixels are stored in separate maps. The final result is a series of spectrum-map pairs of the unique chemical materials in the analysis area. These analyses do not rely on the experience level of the analyst to select any data inputs, like elements of interest, but uses only the X-ray intensities within the 3D SI histogram to find common spectral shapes. Because each mineral has a unique spectral shape, each mineral will be found and located at its acquisition location in the scanned region. From these map and spectral results, complete mineralogical phase distributions will be determined. Thermo Scientific™ COMPASS[™] is the software option for the NORAN System 7 that provides this capability.

Results

Spectral Imaging Acquisition

The secondary electron image (Figure 1) of the sample area reveals a number of different phases with interesting phase boundary contrasts. However, it should be noted that intensity and contrast in the electron image is determined by the secondary electron emission of the sample, but is only indirectly related to the composition of the region. Two areas with similar secondary electron intensities can possess very different compositions. This means that not all of the minerals present in the electron image may be distinguished from other neighboring minerals. Only EDS chemical analyses can provide unique mineral distributions.



Figure 1

The cumulative spectrum from all of the scanned pixels in the SI acquisition is the primary starting data result for most analyses. The peak identification of this spectrum indicates that there are a number of elements to be investigated beginning with the expected O, Mg, Al, Si, K, and Ca, and also the slightly less likely C (probably from beam contamination), S, Fe, and Ba. Note that the intensity of peaks in this spectrum depends on the composition of the minerals analyzed, but also depends on the area fraction of the mineral phases. Large area regions, like the mid-gray that dominates the electron image, will provide an over abundance of X-ray intensity, and a small mineral particle which contributes to the spectrum from only a few pixels may not contribute enough elemental intensity in a peak to be observed.





Traditional Elemental Mapping

From the peak identification of this spectrum, elemental X-ray count maps can be extracted for display and analysis by pressing the "Extract Map Images" toolbar button. The extracted elemental maps show contrast indicative of the existence of different minerals in the sample. Unfortunately, all of the intensity in these count maps is not due solely to the characteristic X-rays of the element of interest but has some contribution from background X-rays in the spectrum. Analysis of these maps could lead to incorrect interpretation if this background intensity is not removed. Quantitative elemental mapping is the method used to display the correct elemental distributions in maps.





Quantitative Elemental Mapping

Quantitative elemental mapping uses the same routines as quantitative spectral processing for composition measurements to convert X-ray counts into meaningful composition values. The needed corrections are background intensity removal, peak deconvolution (for overlapped peaks), and matrix corrections for significant density or X-ray absorption edge effects.

Quantitative elemental mapping is performed by selecting option on the Processing tab in the lower left pane of NORAN System 7 software. The first option is to select the type of quantification output, i.e., Atomic %. The kernel size can be automatically set or manually set to a value most useful for the intensity of X-ray data in the 3D data histogram, in this case 1×1 . The last options define the quality and precision balanced against computation time. The preferred methods for most sample analyses are "High" Detail and "Normal Precision" Fit Type. Simply press the "Extract Map Images" toolbar button and the quantification processing will occur.





When these corrections are applied to the maps on a pixel-by-pixel basis, the true elemental distributions are observed. For many samples, there may be huge differences in the contrast of many elemental maps. For this sample, the primary change is a slight modification of the background intensities of the maps.

However, as an analyst, you are interested in the distribution of the minerals in the sample, not elements. If each mineral had a single unique element, then identification and localization of the corresponding mineral could be performed. But many elements exist in more than one mineral (especially Si, Al, and O) and isolation of unique minerals by single elements is not always possible.

Manual Phase Mapping

A simplistic method of mineral identification is performed when the user selects a set of three elemental maps and overlaps them to look for unique color formation. This technique requires that each elemental map color is changed so that each is a primary color in





the color spectrum, i.e., Red, Green, or Blue (RGB). In this sample the analyst must select three important elements from the list of nine potential elements, which leads to 84 potential combinations. An example using Al, Si and Fe is shown in Figure 6.

Each unique color indicates a potential unique mineral. There are unique colors for at least the red, green, and blue colors based on these three elements. But some of the green and blue regions may be combinations of other minerals containing other elements that cannot be included in this simple model. In addition, there are pixels which contain no color at all, meaning that other elemental combinations are required to determine the final solution.



Figure 6

Selection of the best elemental maps for each combination requires much experience and time as there may be many combinations to perform. For simple samples with only a few elements, this technique may have merit. For complex geological analyses with at least six elements, a better technique would be more useful.



Automated Phase Mapping

Collecting a spectrum at every pixel in the sample with Spectral Imaging provides a platform for a multivariate statistical analysis that determines the distribution of the chemical phases across the sample. This well established routine is licensed to Thermo Fisher Scientific from Sandia National labs (Sandia, NM USA) and is marketed as the COMPASS option for the NORAN System 7. The first step in the analysis is to simply press the "View Compass Data" toolbar button then the "Extract Map Images" toolbar button. The resultant map-spectrum pairs are displayed, as shown in Figure 7, in under a minute.

A more visually appealing result is to convert these results into binary phase maps which are then used to extract spectra from the 3D SI histogram. A preliminary step is to automatically assign a mineral name to the results by using the Match option of the NORAN System 7 software. The Match user-defined database must be populated with a spectrum for each phase that is expected in the sample and enable the Match option to be used for the phase analysis. The spectra are added by clicking the Match Database "..." button on the Analysis Setup tab (see the bottom of Figure 8a) and loading each spectrum in the Database Manager dialog shown in Figure 8b. Creation of a special database for the current project is usually helpful.

Processing WDS Setup WDS Acquisition Status Analysis Automation Element Setup Analysis Setup Compare Information Quant Results Ident Sensitivity (1-100) 100 Overvoltage 1.5 Filter With Standards Quant Fit Method Ŧ Proza (Phi-Rho-Z) Correction Method Use Compounds For All Elements Number Oxygen Atoms 0 Use Matrix Correction TEM Thickness (nm) TEM Density (g/cc) Match 150 10000 Match Cutoffs (eV): High Low * Max. Number of Match Results: 5 * 500 Chi-square Cutoff: Match Database: Diopside



						- New Match File	
Name		kV	Date	Label	<u>_</u>	New Matchinie	
Barite		15.0	09 Sep 2009	Barite	E	Import	From Spectru
Diopsidic pyroxer	ne	15.0	09 Sep 2009	Diopsidic pyroxene			E 601
Hematite		15.0	09 Sep 2009	Hematite		Manual	From LSV
Phlogopite		15.0	09 Sep 2009	Phlogopite			
Pyrite		15.0	09 Sep 2009	Pyrite		Del	ete
Quartz		15.0	09 Sep 2009	Quartz	*	Add To F) at a hanse
•				P		Addition	Jalabase
Current Database:	Diopside			Create Database		Delete D	atabase
Currently in Databa	ise:						
Name		kV	Date	Label	*		
Barite		15.0	09 Sep 2009	Barite	=		
		15.0	09 Sep 2009	Diopsidic pyroxene			
Diopsidic pyroxer	ie .						
Diopsidic pyroxer Hematite	ie.	15.0	09 Sep 2009	Hematite			
Diopsidic pyroxer Hematite Phlogopite	ie.	15.0 15.0	09 Sep 2009 09 Sep 2009	Hematite Phlogopite			

Figure 8b

Enabling the Match capabilities requires selecting the Auto Match option on the Processing tab shown in Figure 9.



Phase results are produced by clicking the Auto button on the Phase toolbar. Phase maps will be displayed that are binary colored and labeled with the title from the match spectrum that best fits the phase spectrum. All of the phase maps are automatically overlaid on to the electron image for ease of interpretation. The phase maps (Figure 10) collected at $450 \times$ magnification reveals six distinct chemical phases; quartz (SiO₂), phlogopite (K₂Mg₆[Si₆Al₂O₂₀](OH)₄), diopside (CaMgSi₂O₆), barite (BaSO₄), pyrite (FeS₂) and hematite (Fe₂O₃).

Figure 10

The individual mineral phase maps and associated spectra are also shown in Figure 11. Diopside and phlogopite form the calc-silicate matrix of the sample. The barite occurs as an inclusion within a large phlogopite grain. The barite grain also contains an inclusion of pyrite with what appears to be a reaction texture between the pyrite and barite composed of hematite.

Figure 11

A detailed acquisition at a magnification of 4300× concentrating on the pyrite inclusion and barite interface (Figure 12) shows the reaction texture more clearly.

Figure 12

Figure 12 clearly shows that the hematite is growing into the pyrite predominantly from the prior barite-pyrite interface.

The total acquisition and analysis time for this dataset was less than four minutes.

Phase Mapping During Acquisition

If desired, this method of phase mapping can be performed as the data is being collected. The user adjusts the settings as described above before starting the SI acquisition, then just acquires the electron image and press the Start button to collect the SI data set. As the acquisition proceeds, the COMPASS and match routines are performed, and phase maps and spectra are displayed instead of the traditional elemental maps. In this way, data analysis and interpretation are occurring during the acquisition with no loss of time by the analyst.

Under the analytical conditions shown on Table 1 (page 1) this match routine took less than one minute to collect the data and unambiguously determine the presence of these six phases.

Conclusion

The NORAN System 7 microanalysis system with COMPASS and Match software and UltraDry EDS detector can be used to rapidly determine the distribution and compositions of mineral phases in a geological sample. The results can be used to help interpret the mineralogical and textural evolution of this calc-silicate rock during contact metamorphism.

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