Quantitative WDS Analysis of a Contact Metamorphosed Calc-Silicate Rock

Key Words
FESEM, Mineral Phase, Minerals, Wavelength Dispersive Spectroscopy (WDS)

Introduction

Rocks are not simple materials but are an agglomeration of different chemical compounds or minerals. The formation mechanism and environment can determine the type, shape and distribution of minerals in the agglomerate. Understanding the chemical compositions of the minerals in metamorphic rocks is vital to determining the types of mineral and their textural evolution. In a prior Note, the mineral identification and distribution were determined using Energy Dispersive Spectroscopy (EDS). In this Note, Wavelength Dispersive Spectroscopy (WDS) is used to quantitatively measure the elemental composition of each of the identified minerals.

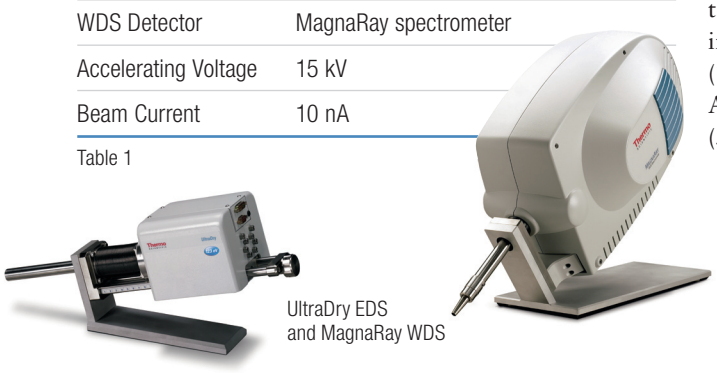
NORAN System 7
X-ray microanalysis system

Experimental

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

Sample	Contact Metamorphosed Calc-Silicate
EDS Analyzer	NORAN System 7
EDS Detector	UltraDry 10 mm² Silicon drift detector
WDS Detector	MagnaRay spectrometer
Accelerating Voltage	15 kV
Beam Current	10 nA

Table 1



UltraDry EDS
and MagnaRay WDS

Quantitative Analysis

NORAN System 7 provides the option to collect EDS-only quantitative data, quantitative EDS plus WDS data, or quantitative WDS-only data, all using known composition standards. For this contact metamorphosed calc sample, the MagnaRay WDS-only quantitative analyses were performed on the five major mineral phases found by EDS phase analysis.

Elemental X-ray intensity reference measurements were collected from commercially available known mineral standards. Out of the 53 potential standards that could be chosen, standards were selected based on the similarity of the measured EDS compositions and the tabulated standards compositions of the elements of interest. The final standards used for quantification were (1) Diposide for O, Mg, Ca and Si, (2) Biotite for K and Al, (3) Hematite for Fe, (4) Marcasite for S, and (5) Barite for Ba. In addition, a diffractor in the WDS

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spectrometer must be chosen for each elemental line. For many lines, there is only a single diffractor available (Mg-K on TAP, S-K on PET, Fe-K on LIF), but other lines have more flexibility, especially for very high and low energy X-ray lines (O-K on NiC or TAP, Al-K on TAP or PET, Si-K on TAP or PET, K-K on PET or LIF, Ca-K on PET or LIF, and Ba-L on PET or LIF). The usual diffraction selections for these lines are to use the diffractor with the lowest energy range (O-K on NiC, Al-K on TAP, Si-K on TAP, K-K on PET, Ca-K on PET, and Ba-L on PET).

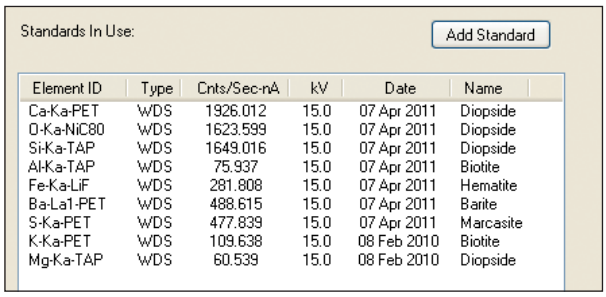

Figure 1

The quantification routine requires the measurement of the net X-ray intensities for each of these standards. This requires the measurement of both the peak intensity and the background intensity. NORAN System 7 collects the background intensity at both a lower and a higher energy location and interpolates the background for the peak energy. In this way, the background energies do not need to be equally spaced away from the peak intensity, permitting more flexibility for the operator. Once the diffractors are selected for the elements, the background energy locations of each element should be evaluated to verify that its energy does not coincide or overlap with the energy of another peak. The default energy table under the Standards radio button on the WDS Setup tab provided with the software does an adequate job at the energy selection, but high precision quantification work typically requires slight energy adjustments by the analyst.

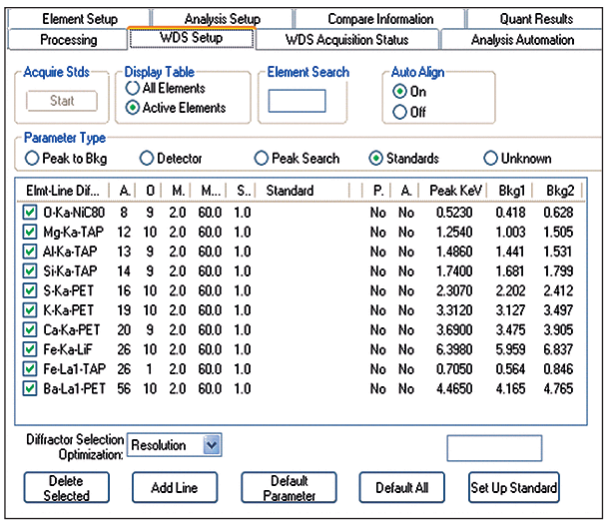

Figure 2

When multi-elemental standards are used for quantification, the standard must be setup in the software by inputting the composition of every element in the standard. For ease of acquisition of the WDS intensities, the stage location is also stored for unattended acquisition.

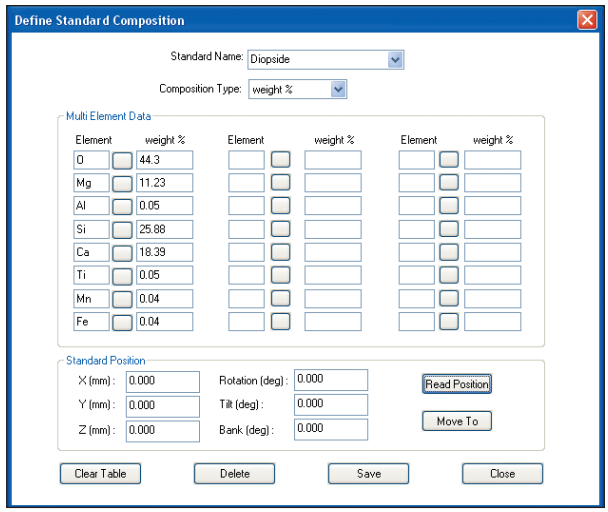

Figure 3

After all standard compositions have been input, each elemental line must select a suitable standard from the potential list of standards that contain that element. Some elements may only have a single standard, such as Barite for Ba-L, but others may have a variety to choose from, such as most of the mineral standards for O-K.

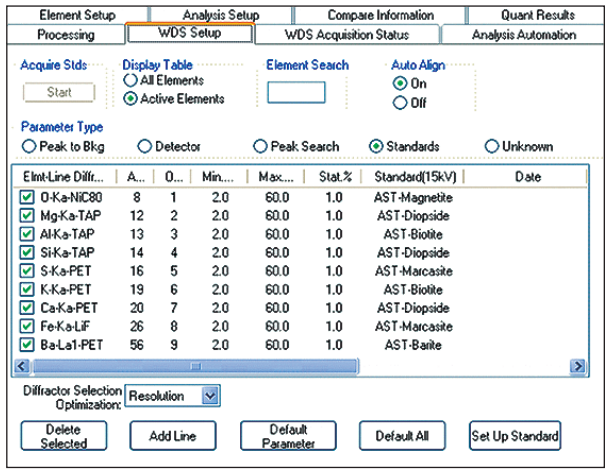

Figure 4

Since the highest precision compositions require the highest precision intensities, auto alignment of the spectrometer for each standard is the preferred method of acquisition. When the acquisition of all of the standards is begun by pressing the standards "Start" button, the stage moves to the stored stage location for the first standard in the list, reads the beam current from the Faraday cup (either stage mounted or column mounted), then aligns the WDS spectrometer for the elemental line of interest to the maximum intensity. The alignment acquisition time is adjusted to obtain a precise alignment. The peak intensity is measured until termination based on the time or precision desired, then the intensity at each of the low and high energy background intensities are collected for half of the peak collection time. When complete, the WDS Acquisition Status tab will display all of the WDS information and the values will be stored in the standard file. The system will collect all of the elemental lines for each standard before moving the stage to the next standard in the list and repeating the acquisition procedure.

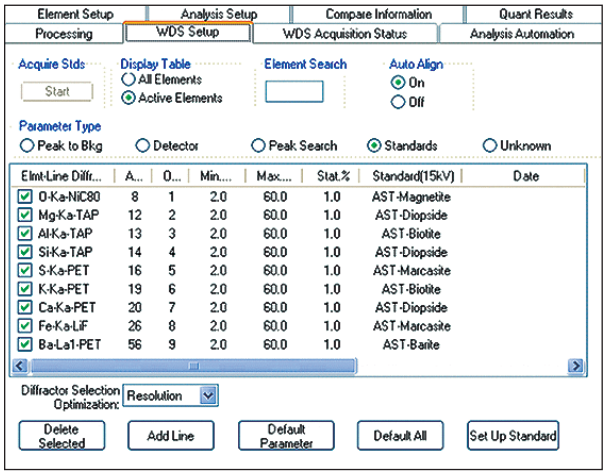

Figure 5

Collection of WDS quantification values is not much more involved than collection for EDS full-standards quantification. Standards need to be selected in the Standards tab (Figure 6 and 7), the Auto Quant On option needs to be enabled on the Processing tab (Figure 8), the matrix correction method needs to be changed to "… with Standards" on the Analysis Setup tab (Figure 9), and the "Acquire WDS" option needs to be selected on the EDS tab of the Acquisition Properties (Figure 10).

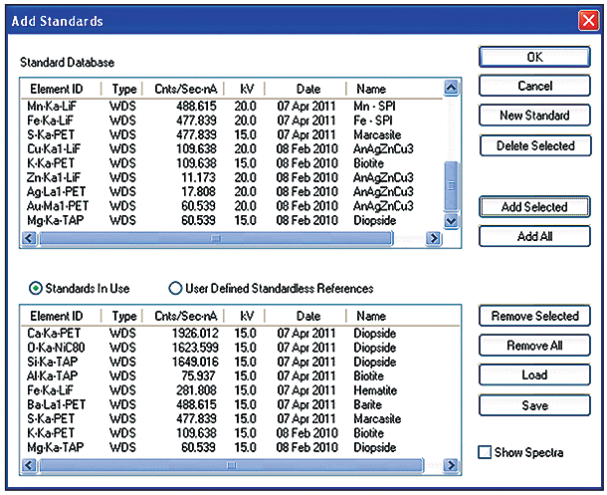

Figure 6

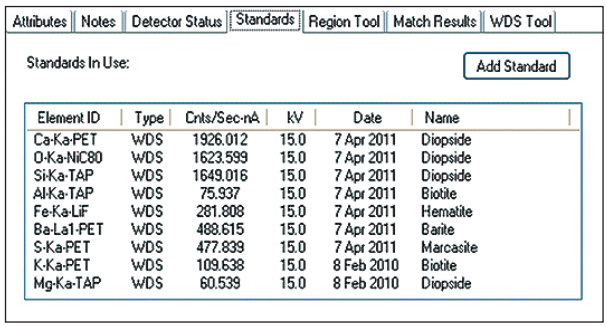

Figure 7

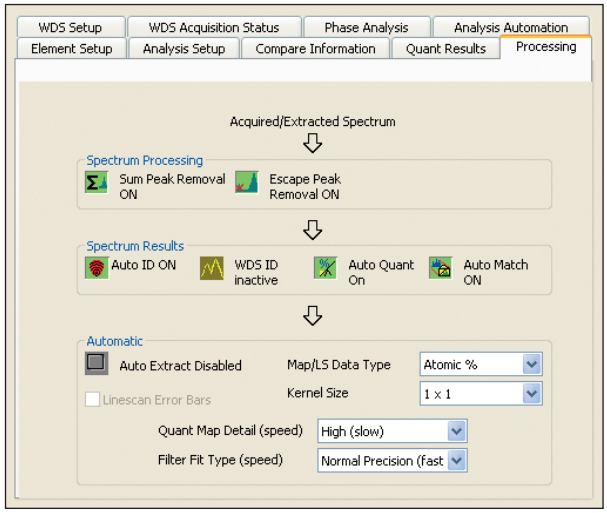

Figure 8

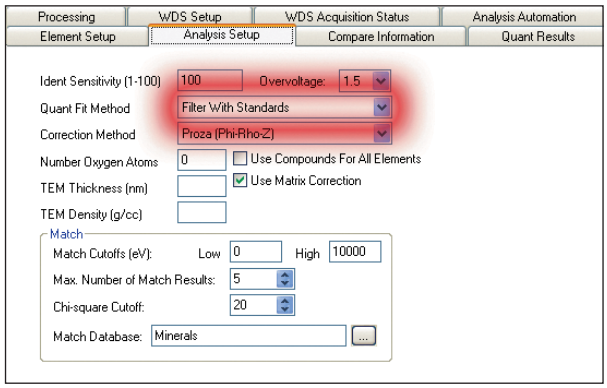

Figure 9

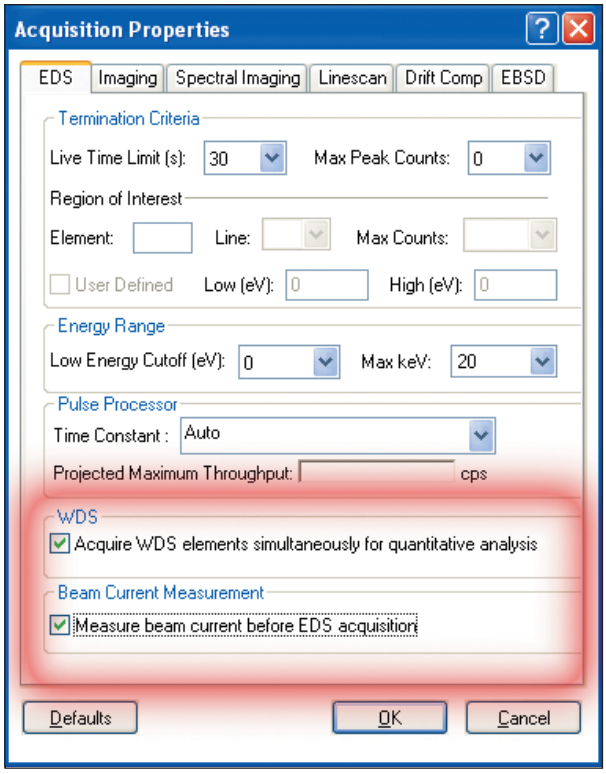

Figure 10

When the unknown material is present in the SEM image, a simple Start of the EDS acquisition will also begin the WDS quantification process. The seamless integration of the WDS control in the EDS control software makes WDS acquisitions very easy. The beam current will be measured first. If the alignment option is selected, then it will be preformed. Acquisition of the peak and background intensities will be collected to termination defined by either the time or precision for all of the elements in the standards list. The WDS intensities will be displayed in the WDS Acquisition Status tab. The quantification values will be displayed in the Quant Results tab. The WDS intensities and the resultant quantification values will be saved in the EDS EMSA file. If stage automation is performed to collect acquisitions from many locations on the sample, the stage will move to each point and collect the data in succession without user input. If desired, which is typical, the beam voltage of the SEM can also be turned off at the conclusion of the complete Automation acquisition.

Table 2 shows the WDS quantitative data collected from the minerals in the calc-silicate sample. The weight percent and atomic percent elemental data shows strong agreement with the values expected from mineral stoichiometries. The phlogopite wt% totals are low as expected for a hydrous mineral (inability to measure H content with X-rays).

Wt%	Phlogopite	Phlogopite	Phlogopite	Phlogopite	Diopside	Diopside	Diopside	Diopside	Pyrite	Pyrite	Barite	Barite	Hematite
O	45.97	45.92	45.46	46.17	45.89	45.39	45.72	45.35	0.00	0.00	27.46	27.52	32.39
Mg	13.83	14.50	13.84	13.92	9.02	9.17	9.12	8.93	0.00	0.00	0.00	0.00	0.01
Al	10.62	10.80	10.17	10.26	3.46	3.68	3.33	3.73	0.00	0.00	0.00	0.00	0.01
Si	17.85	17.41	17.17	17.10	22.91	22.81	22.12	22.64	0.00	0.00	0.00	0.00	0
S	0.01	0.00	0.02	0.00	0.00	0.02	0.01	0.00	53.19	52.57	13.67	13.11	0.1
K	8.69	8.89	8.59	8.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Ca	0.02	0.02	0.01	0.01	18.25	18.31	17.78	18.37	0.00	0.00	0.00	0.00	0
Fe	1.43	1.58	1.50	1.50	0.93	1.01	0.88	1.36	48.91	49.28	0.00	0.00	66.58
Ba	0.26	0.46	0.31	0.36	0.15	0.11	0.14	0.22	0.00	0.00	58.75	58.23	0.01
Total	**98.68**	**99.58**	**97.07**	**97.86**	**100.61**	**100.50**	**99.10**	**100.60**	**102.10**	**101.85**	**99.88**	**98.86**	**99.11**
Atom%	**Phlogopite**	**Phlogopite**	**Phlogopite**	**Phlogopite**	**Diopside**	**Diopside**	**Diopside**	**Diopside**	**Pyrite**	**Pyrite**	**Barite**	**Barite**	**Hematite**
O	60.85	60.46	61.13	61.45	61.60	61.15	62.06	61.20	0.00	0.00	66.75	67.36	62.79
Mg	12.05	12.57	12.25	12.20	7.97	8.13	8.15	7.94	0.00	0.00	0.00	0.00	0.01
Al	8.34	8.44	8.11	8.10	2.76	2.94	2.68	2.99	0.00	0.00	0.00	0.00	0.06
Si	13.46	13.06	13.15	12.97	17.52	17.51	17.11	17.41	0.00	0.00	0.00	0.00	0.01
S	0.01	0.00	0.01	0.00	0.00	0.02	0.01	0.00	66.67	66.17	16.60	16.02	0.09
K	4.71	4.79	4.73	4.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Ca	0.01	0.01	0.01	0.01	9.78	9.85	9.63	9.90	0.00	0.00	0.00	0.00	0.01
Fe	0.54	0.60	0.58	0.57	0.36	0.39	0.34	0.53	33.33	33.83	0.00	0.00	37.01
Ba	0.04	0.07	0.05	0.06	0.02	0.02	0.02	0.03	0.00	0.00	16.65	16.61	0.01
Total	**100.01**	**100.00**	**100.02**	**100.01**	**100.01**	**100.01**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**99.99**	**100.00**

Table 2

Conclusion

The NORAN System 7 system with seamless integration of UltraDry EDS and MagnaRay WDS detectors can be used to rapidly determine the quantitative compositions of mineral phases in a geological sample. This particular dataset can be used to help interpret the mineralogical and textural evolution of this calc-silicate rock during contact metamorphism.

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