A SEM-EDS Study of Cultural Heritage Objects with Interpretation of Constituents and Their Distribution Using PARC Data Analysis

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Abstract: Two cultural heritage objects studied with scanning electron microscopy–energy dispersive spectroscopy (EDS) are presented in this article: (1) archeological iron present in a soil sample and (2) a chip from a purple-colored area of an undisclosed 17th century painting. Novel PARC software was used to interpret the data in terms of quantitative distribution of mineral and organo-mineral phases as well as their chemical composition. The study serves to demonstrate the power of PARC rather than solving specific archeological issues. The observations on archeological iron potentially can assist in (1) studing the source of iron-metal and the style of forging, (2) learning about alteration processes of artifacts in the particular soil from which the sample originated, and (3) determining the nature of the fractures in the Fe-oxide envelope (desiccation of the sample after excavation, or as primary feature caused by volume change from oxidation). In the paint chip, 11 consecutive layers can be distinguished using the PARC software. In general, each layer consists of a carrier supporting inorganic fragments. In the basal layer the fragments are dominant; in the superimposed layers the carrier usually is. Both organic and inorganic carriers appear to be present. Organic carriers can contain typically inorganic constituents (e.g., Pb, Al), beyond the chemical spatial resolution of EDS (i.e., <1 μm).

Key words: PhAse Recognition and Characterization (PARC), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), spectral imaging (SI), silicon drift detectors, archeological iron, painting layer structure

INTRODUCTION

Microanalysis in combination with scanning electron microscopy (SEM) is a widely used technique for analysis and characterization of solid materials (Goldstein et al., 1992). Using spectral imaging (SI) techniques (i.e., X-ray spectra for each pixel in the SEM image field) and fast silicon drift detectors, quantitative phase analysis of large areas of an object can be obtained in relatively short acquisition times. We have developed PARC (PhAse Recognition and Characterization) software as a tool for automated interpretation of such spectral imaging datasets.

In general, in research applications, it is not only important which elements are present at each location (or pixel), but also which multielement *phases* are present. From the user point of view, individual phase information is required such as chemical composition, as well as area/volume percentage and spatial distribution. This information is needed (1) to characterize the microstructural state of a material and (2) to understand physical-chemical processes of phase compositional change as functions of time, and imposed conditions. The challenge is to characterize the available phases at the pixel level as accurately as possible while keeping acquisition time acceptable. The impression of the spatial distribution of phases that is needed to unravel macroscopically observable features sometimes requires the collection of SI of large areas (e.g., 5 × 20 mm) at a micron level scale. Especially in these cases the acquisition time can become prohibitive to obtain adequate data for the determination of phase distributions. The PARC software, in combination with an optimized SEM SI acquisition strategy, can meet this requirement and provide exact chemical compositions of the phases in a sample—including trace elements—and provide an overview of the spatial distribution of chemically relevant phases. Archeological artifacts are a prime example of complex heterogeneous multiphase materials with a complex history of creation, utilization, and of deterioration over time under variable ambient or catastrophic conditions. Typically large datasets over extended areas are needed to study these objects. In this article we show the power of PARC for scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS) data interpretation of two cultural heritage objects.

ANALYTICAL METHODS

Our goal for SI interpretation has been to sort every analyzed pixel according to the phase to which it belongs. The SEM instrument, detector type, and acquisition parameters determine the chemical resolution and acquisition time of a PARC analysis. For the current study we used a JEOL-7001F field emission (FE)-SEM with two silicon drift detectors and

Noran-System-7 (NS7) hardware/software and off-line PC with NS7, SI-conversion software and PARC software

Data Acquisition and Processing

The following steps are involved in the data acquisition and processing and will be discussed in the following sequence: (1) dataset acquisition requirements, (2) dataset processing requirements for PARC, and (3) PARC software.

1. *Dataset acquisition requirements.* Two important parameters need to be considered in the acquisition: (1) step size of the electron beam and (2) counting time per pixel. The selection of step size for the electron beam is based on the size of the particles and elements of interest. In general smaller particles require smaller steps and lower accelerating voltage, and light elements can be analyzed with higher spatial resolution at low accelerating voltage. The best approach is to use Monte Carlo simulation software (Gauvin & Lifshin, 2004) to select proper accelerating voltage to minimize overlapping of generated X-ray volumes. We commonly use step sizes of 0.3 μm with 8 kV, up to 1 μm with 20 kV, or even larger in the case of coarse grained phases. The image resolution is set to 512 $\times$ 384 pixels for ease of data handling with an ordinary PC or MAC

2. *Data processing requirements for PARC.* The PARC software is able to get access to the individual spectra per pixel for phase characterization by converting the SI dataset into the universal Lispix format. Making use of the open access to SI-converted datasets, we have developed our own routines for better data interpretation—in our case phase recognition in complex multiphase samples. This includes batch-processing routines to run a user-defined setup on multiple SI datasets.

3. *PARC software.* The challenge for the PARC software is the extraction of the unique phases (multielement spectra) from SI datasets without prior knowledge about the sample composition. The key issue in automated phase recognition is to classify—or group—the individual spectra into chemically consistent phases whereby simultaneously all available information is used.

   The PARC software does not look at individual elements but at complete spectra and classifies them into:

   - pure spectra from a single phase
   - mixed spectra from two or more phases that results from measurements at grain boundaries or from grains that are smaller than the excitation volume from which characteristic X-rays are emitted
   - spectra with artifacts arising from structures adjacent to cracks, which may lead to partial absorption of X-ray signals of features of interest
   - empty spectra—i.e., spectra with no detectable peaks—may arise as a result of absorption of generated X-rays when analyzing rough surfaces or pits.

The presence of mixed, artifact, and empty spectra strongly affects the efficiency to classify or group the individual spectra into chemically consistent phases. One of the

Table 1. Measurement Conditions of Cultural Heritage Samples.

	Archeological Iron Sample	Paint Chip NG6461
Accelerating voltage	15 kV	15 kV
Step size	1 μm	0.1 μm
Resolution per field	512 $\times$ 384 pixels	512 $\times$ 384 pixels
Field array	13 $\times$ 5	6 $\times$ 1
Measurement time per field	20 min	60 min

strengths of the automated phase recognition method incorporated in PARC is that it deals with mixed and empty spectra before further classification, which significantly improves the efficiency of the automated phase recognition procedure. After loading a data file, peak position and heights are determined of each pixel spectrum. Using a selective energy filter, spectra are classified into sample material spectra, mixed spectra (sample material and, for example, embedding material), and embedding material. Hereafter different phases or chemical groups within the sample material spectra are defined; the mixed spectra are added to the nearest created phases (optional) or classified as "unidentified." Embedding material spectra are allocated to a separate group. Further refinement of the phase model can be done using density plots (that is, *XY* plots of element X-ray counts), which further separates chemically similar phases provided that SI data are of sufficient quality. Longer acquisition times may be required to get more detailed phase separation, e.g., with different iron oxides, FeO, Fe_3O_4, Fe_2O_3, FeOOH.

Once a particular setup (phase model) is defined, a large number of similar SI datasets can be processed, which allows the creation of a very large image of the phase distribution within a single sample by automatically stitching multiple SI datasets. Accurate stoichiometric compositions of each of the phases can be calculated with NS7 software using the PARC-exported spectra.

PARC Application Examples

A summary is given in Table 1 of the measurement conditions for the two samples. In the first sample elements with an atomic number up to Zn (Kα X-ray energy of 8.638 keV) are of interest, and a proper choice for acceleration voltage is 15 kV. Using a higher acceleration voltage, the analytical spatial resolution deteriorates without gaining additional chemical information. Lowering the voltage decreases signal for the higher energy transition metals (Fe-Zn) requiring longer dwell time per pixel. With 15 kV the analytical spatial resolution is 1 μm. Considering the large size of the specimen, the step size 1 μm was chosen equivalent to the approximate analytical spatial resolution.

The second sample contains a wide range of elements varying from C to Pb. Two criteria have determined our choice of measurement conditions: detection of Pb Lα1 (X-ray energy 10.549 keV) and best achievable resolution of boundaries between chemical features. With the choice of
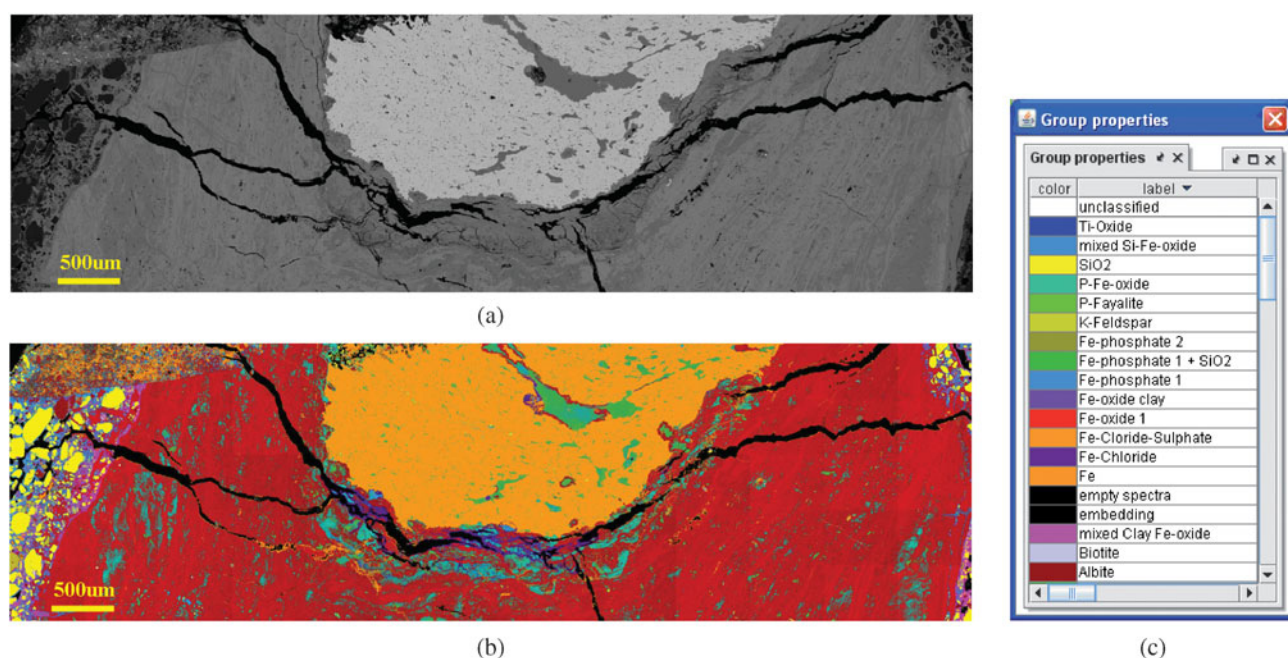
Figure 1. a: BSE image archeological iron conserved together with soil. **b:** Phase spatial distribution from archeological iron. **c:** Phase color legends.

15 kV acceleration voltage, the analytical spatial resolution is set. Depending on chemical composition and density (porosity), it varies from 0.1 μm (in Pb compounds) up to 2 μm (organic compounds). Our wish for maximum detail in chemical feature transitions made us select a step size of 0.1 μm. The small sample size in this case permitted the small step size.

Archeological Iron Conserved Together with Soil

The first example concerns a study of various methods used for conservation iron-metal nail artifacts. In this example we selected one sample only to illustrate the information that can be obtained using PARC. A backscatter electron image, PARC quantitative phase analysis, and corresponding color code are presented in Figures 1a, 1b, and 1c, respectively.

The image reveals a Fe-metal core of about 4 mm cross-sectional diameter enveloped by a Fe-oxide crust that contains sand grains at its outer rim. The iron metal is P bearing, and it contains abundant two-phase inclusions of P-fayalite (phosphor-bearing Fe_2SiO_4) with silica. The Fe-oxide envelope is veined, has open fractures, and is clearly formed as an alteration product of the Fe metal core. The oxide envelope contains two distinct Fe-phosphate phases (with 8.7 wt% and 1.1 wt% of P_2O_5) as well as two different Fe-oxides and Fe-chloride salt.

The Fe-oxide in the veins (likely hematite Fe:O = 1:1.5) has the lower oxygen content and can be separated from the ground mass (likely limonite Fe:O $\sim$ 1:2) using density plots (Fig. 2b) by interactively setting the boundary to give good correspondence between the PARC assignment (Fig. 2c) and the backscatter image (Fig. 2a). The Fe-chloride salt is only found in proximity to the metal core. The sand associated with the sample consists of large rounded quartz and small

K-feldspar ($KAlSi_3O_8$) grains and minor albite ($NaAlSi_3O_8$). Within the Fe-oxide crust, the K-feldspar has altered to clay forming intimate mixtures with the alteration products of the Fe-metal, differentiated in a clay- and an Fe-oxide rich fraction (Fig. 1c). Locally Fe-chloride-sulfate salts and open voids occur within the clay-Fe-oxide domains. In Table 2 compositions are given of a selection of detected phases of Figure 1c. Mineral names are inferred from PARC phase stoichiometry.

The apparent rinds of the quartz grains (blue-colored rims around yellow areas) represent mixed pixels toward Fe-oxide. Such blue-colored pixels also occur in the metal domain in association with the P-fayalite inclusions. It can be concluded that the P-fayalite inclusions are a distinct mineral phase based on their *phosphorous* content, and not their Fe:Si ratio. The phase "mixed Si-Fe-oxide" must have a large range of Fe:Si and can be Fe-richer or Si-richer than fayalite and could be further subdivided if desired.

The observations can assist in (1) studying the source of iron-metal and the style of forging, (2) learning about alteration processes of artifacts in the particular soil where the sample originated from, and (3) determining the nature of the fractures in the Fe-oxide envelope (desiccation of the sample after excavation, or as primary feature caused by volume change from oxidation).

Paint Chip NG6461

A chip of paint from a purple-colored area of an undisclosed 17th century painting was investigated. The chip was polished in cross section for SI measurement. A backscatter electron image and the PARC phase assignment are presented in Figures 3a and 3b, respectively. The different layers observed in the paint sample are described in Figure 3a.
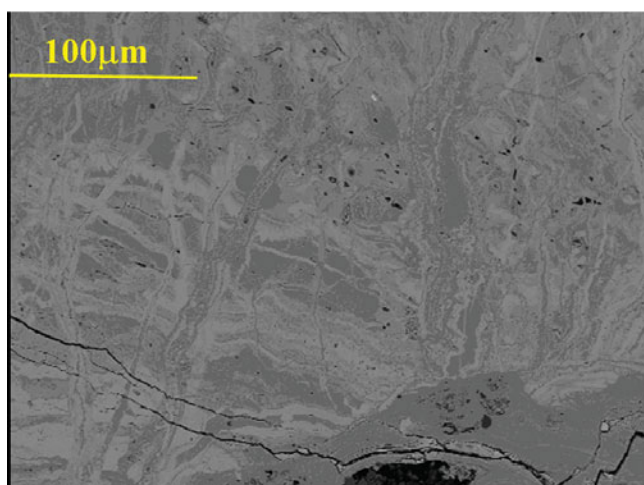
(a)
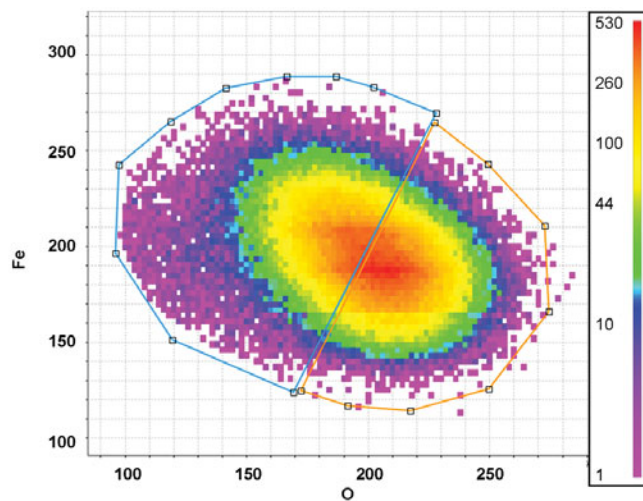
(b)
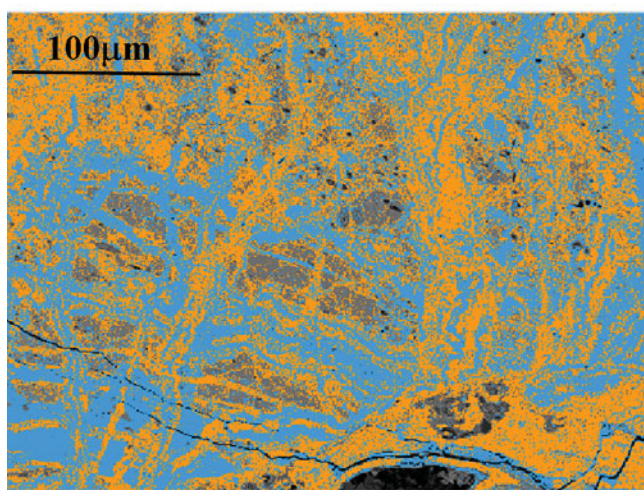
(c)

Figure 2. a: BSE image. **b:** Density plot Fe versus O. **c:** Visualization of selected Fe_2O_3 (blue) and FeOOH (orange) from the density plot.

Eleven consecutive layers can be distinguished using the PARC software. In general each layer consists of a carrier supporting inorganic fragments. In the basal layer the fragments are dominant; in the superimposed layers the carrier usually is. Both organic and inorganic carriers appear to be present. Organic carriers can contain typically inorganic constituents (e.g., Pb, Al), beyond the chemical spatial resolution of EDS (i.e., <1 μm).

Organic Carriers

Most layers contain organic carriers for which EDS elemental analysis gives no information on the molecular structure. The group assignment Organic II is fortunate and based on chemistry alone of a distinct (nearly oxygen free) and pure organic carrier that was recognized with PARC. The many organic carriers that contain other constituents are marked with "organic" in their group

Table 2. Chemical Composition of Selected PARC Phases Detected in the Archeological Iron-Soil Sample.

Phase ID	Label	Oxides (wt%)										
		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	FeO
5	Mixed Si-Fe-oxide	0.6	0.3	2.6	17.1	0.9	1.1	0.1	0.1	0.7	0	76.5
8	SiO_2	0.4	0.1	0	95.9	0	2.8	0	0	0	0	0.8
10	Mixed clay-Fe oxide	0.4	0.7	12.6	23.4	1.9	1.1	0.1	1.1	1.6	0.4	56.5
11	Albite	11.2	0	18.5	63	0.6	1.2	0	0	0.2	0	5.3
12	K-feldspar	1	0	18.3	64.3	0.6	0.9	0	13.8	0	0	1
13	P-fayalite	0.3	0.1	0.4	26.9	7.5	0.9	0	0	0	0.1	63.7
21	Biotite	0.5	9.2	20.3	33.2	0.2	0.2	0	2.9	0.2	2.6	30.7

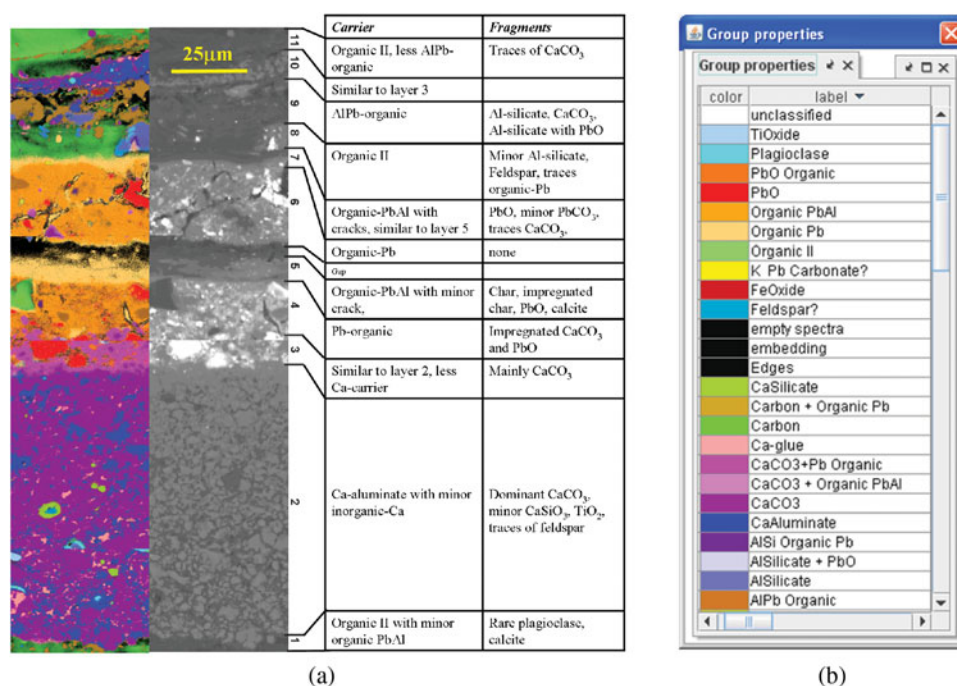| Layer	Carrier	Fragments
11, 10	Organic II, less AlPb-organic	Traces of CaCO₃
9	Similar to layer 3	
8	AlPb-organic	Al-silicate, CaCO₃, Al-silicate with PbO
7	Organic II	Minor Al-silicate, Feldspar, traces organic-Pb
6	Organic-PbAl with cracks, similar to layer 5	PbO, minor PbCO₃, traces CaCO₃,
5	Organic-Pb	none
Gap		
4	Organic-PbAl with minor crack,	Char, impregnated char, PbO, calcite
3	Pb-organic	Impregnated CaCO₃ and PbO
	Similar to layer 2, less Ca-carrier	Mainly CaCO₃
2	Ca-aluminate with minor inorganic-Ca	Dominant CaCO₃, minor CaSiO₃, TiO₂, traces of feldspar
1	Organic II with minor organic PbAl	Rare plagioclase, calcite

(a)

(b)

Figure 3. a: Phase spatial distribution (left), BSE image (middle), and layer characterization (right) of a paint chip. **b:** Phase color legends.

names, based on the presence of a carbon signal in the analysis.

Organic is used as a prefix in the group name to indicate that organics are dominantly present, and as a suffix when subordinate. Most common are the mixed organic carriers: Organic-PbAl, PbAl-organic and Organic Pb, or PbO organic. In all these mixed carriers, the Pb and Al could be present as a mixed-in oxide. Alternatively, Pb could exist as an organic compound. Locally these inorganic constituents also can be found at higher concentrations, up to almost pure, organic-free compositions (e.g., PbO, CaCO₃). We therefore could argue that the various mixed-organic carriers are indeed mixtures of organic material with very fine inorganic particles, beyond the spatial resolution of EDS. This could be resolved with high-resolution SEM imaging.

Inorganic Carriers

The basal layer contains a Ca-aluminate carrier in addition to a Ca-based inorganic carrier.

Inorganic Constituents

The inorganic fragments rarely yield analysis free of organic carrier, which complicates their identification. Standard correction procedures (Phi-Rho-Z) assume homogeneous phases and cannot be used to quantify phase mixtures. In the paint-chip case, this strongly affects the quantification of light elements such as carbon and oxygen. Since most inorganic fragments are simple compounds containing only one or two elements, no absolute distinction therefore can be made between a nature of oxide, hydroxide, or carbonate.

Major inorganic constituents identified are CaCO₃, PbO, and alumino-silicate (clay?). Minor inorganic constituents are Ca silicate ($\sim$ CaSiO₃) and Ti-oxide. Single fragments were found of carbon-char, Fe-oxide, some common silicate minerals (feldspars), and probably PbCO₃ (K-bearing).

Conclusion

The in-house developed software package PARC has been developed for the processing of multiple SI datasets to determine chemical phase distributions in large sample areas. PARC automatically classifies phases based on the presence of elements with the option of further user-selected phase refinements. Phase compositions are quantified on exported phase spectra using standard routines (ZAF, PRZ). Phase (area) proportions are derived from numbers of classified pixels. The limits of analytical spatial resolution in PARC derive directly from those inherent to SEM-X-ray microanalysis. The application of PARC is therefore just as versatile as SEM-X-ray microanalysis. This is illustrated with the two examples presented in this article.

Acknowledgment

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