

Validation of fuzzy logic method for automated mass spectral classification for mineral imaging

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Received 3 January 2006; accepted 26 March 2006

Available online 18 May 2006

Abstract

Imaging mass spectrometry requires the acquisition and interpretation of hundreds to thousands of individual spectra in order to map the mineral phases within heterogeneous geometries. A fuzzy logic inference engine (FLIE) was developed to automate data interpretation. To evaluate the strengths and limitations of FLIE, the chemical images obtained using FLIE were compared with those developed using two chemometric methods: principle component analysis (PCA) and cluster analysis (K-Means). Two heterogeneous geometries, a low-grade chalcopyrite ore and basalt, were imaged using a laser-desorption Fourier transform mass spectrometer. Similar mineral distribution patterns in the chalcopyrite ore sample were obtained by the three data analysis methods with most of the differences occurring at the interfaces between mineral phases. PCA missed one minor mineral phase in the chalcopyrite ore sample and did not clearly differentiate among the mineral classes of the basalt. K-Means cluster analysis differentiated among the various mineral phases in both samples, but improperly grouped some spectra in the chalcopyrite sample that only contained unanticipated high mass peaks. Unlike the chemometric methods, FLIE was able to classify spectra as unknowns for those spectra that fell below the confidence level threshold. A nearest neighbor approach, included in FLIE, was used to classify the unknowns to form a visually complete image; however, the unknowns identified by FLIE can be informative because they highlight potential problems or overlooked results. In conclusion, this study validated the fuzzy logic-based approach used in our laboratory and revealed some limitations in the three techniques that were evaluated.

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PACS: 07.05.Mh; 82.80.Nj; 91.67.Gy

Keywords: Chemical imaging; Mineral; Fuzzy logic; Principal component analysis; Cluster analysis; Laser desorption Fourier transform mass spectrometry

1. Introduction

Imaging mass spectrometry of minerals is of interest for both terrestrial geological studies and extra terrestrial exploration. Imaging mass spectrometry has been used to examine minerals [1,2], extra terrestrial mineral analogues [3], and fossilized bacterial biofilms [4]. The technique has been used to map bacterial colonization patterns on basalt [5], the polycyclic aromatic hydrocarbon constituents of meteorites [6], the sulfur

isotope ratios of pyrite grains in gold ores [7], and to detect specific constituents or absorbates on minerals [8,9].

Automated interpretation of mass spectra from minerals is critical for analyzing the large number of spectra generated by chemical imaging techniques. Chemometric methods are being developed and evaluated that are applicable to spectral interpretation and chemical imaging of minerals [10–12]. For example, principle components analysis (PCA) has been used to extract chemically meaningful information for mapping mass spectral data [13] and discriminating among spectral groups [14,15]. PCA can decompose a collection of data with correlated measurements into a new set of uncorrelated (i.e., orthogonal) variables that can reduce over 100 variables to systems with less than 10 principle components [10]. Another chemometric technique, statistical cluster analysis, seeks to

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identify homogeneous subgroups within a population and has been used to characterize synthetic substances [12] and ambient aerosol particles [16].

Spectra from the mineral separates have been analyzed with a software package, referred to as CORICO (ICONography of CORrelations) [17], that used multi-correlation calculations to identify mineral phases. Engrand et al. [3] used spectra from a time of flight secondary ion mass spectrometer (TOF-SIMS) to test how well the CORICO software discriminated between samples of olivine and pyroxene, which are common extraterrestrial mineral types. Olivine and pyroxene samples were chosen because they have very similar chemical compositions, yet different crystalline structures. The CORICO software successfully differentiated between the mineral separates using both major and minor spectral peaks.

Imaging of mineral phases in the heterogeneous geomatrix, basalt, was performed by Ingram et al. [1] using TOF-SIMS instrument. To handle the large amounts of data, a neural network referred to as SIMageS was developed to classify regions of interest. PCA was used to assist in determining ions of interest (IOI). Monochrome images of ~ 10 IOI were exported from the data system and imported into SIMageS, which used a generalized learning vector quantization algorithm [18]. After SIMageS identified areas of interest, spectra from these coordinates were then retrieved from the data system.

In support of an automated imaging laser desorption Fourier transform mass spectrometer (LD-FTMS) [19], Scott and co-workers [20,21] developed a fuzzy logic inference engine (FLIE) for automated spectral analysis and data interpretation. Fuzzy logic was selected as the basis for spectral identification and classification because fuzzy logic has been used to capture the linguistic description of human decision processes often used to describe mass spectra [22]. The purpose of this study was to compare the use of FLIE with two chemometric methods, PCA and K-Means statistical clustering, for the interpretation of chemical spectra used in the mapping of mineral phases in heterogeneous geomatrices. Surfaces of a low-grade chalcopyrite ore and a basalt sample were analyzed by an imaging LD-FTMS. The mineral mass spectra were then classified by FLIE, PCA, and K-Means methods and compiled into chemical imaging maps.

2. Experimental

2.1. Mineral samples and standards

Chalcopyrite samples were collected from an Arizona iron–copper sulfate mine (Miami, AZ). The basalt sample was collected in the Snake River Plain, from the Idaho National Laboratory site. Mineral standards and NIST trace metal standards (NIST 660, Gaithersburg, MD) with known concentrations were used to evaluate relative detection sensitivities of mineral cations.

2.2. Sample preparation

Relatively flat areas in chalcopyrite and basalt samples were selected and cut into ~ 15 mm \times 15 mm pieces using a slow-rate

saw (Lu6x-130, Lonnie Inc., Phoenix, AZ) without contacting the analysis surface. Cut pieces were washed with distilled water and methanol to eliminate any inorganic and organic contaminations introduced during sample preparation. Samples were affixed to the surface of a 19 mm diameter stainless steel probe tip using double-sided sticky tape (3M, St. Paul, MN). The analyzed sample surface was untouched and maintained its natural variations in surface topography, which in the case of the basalt sample included surface-exposed vesicles.

2.3. Instrumentation and parameters

Spectra were obtained using a Fourier transform mass spectrometer (FTMS) [21] equipped with a 7 T Oxford (Oxford, England) superconducting magnet, a 2-in. cubic cell, and an Odyssey control and data acquisition system (Finnigan FT/MS, Bremen, Germany) (Fig. 1). A Nd:YAG laser (Continuum, Santa Clara, CA) operating at 355 nm with a 6 ns pulse width was used for desorption/ionization using a laser fluence of 1×10^8 W/cm² for ~ 6 μ m diameter. The sample was located ~ 0.5 cm from the front trap plate. During the ionization event, the potential on the front and rear trap plates was maintained at 0 V. After ionization, a trapping potential of 2 V was applied to both front and rear trap plates and maintained until the quench event at the end of the sequence. A delay of 0.5 s was imposed prior to application of a chirp excitation over the range of 50–800 kHz with a sweep rate of 360 Hz/ μ s. The ions were detected in direct mode using 64 K data points. Pressure during analysis was less than 2×10^{-9} Torr. All spectra were collected from single laser shots. The raster patterns for the laser shots for the chalcopyrite and basalt samples were rectangular and hexagonal closest packed, respectively. Using an automated process [19] the raw data were baseline corrected, Hamming apodized, zero filled, and Fourier transformed to produce the mass spectra from which peak lists were generated for transfer to FLIE and the chemometric software. In this study, only positive ions were used for spectral identification.

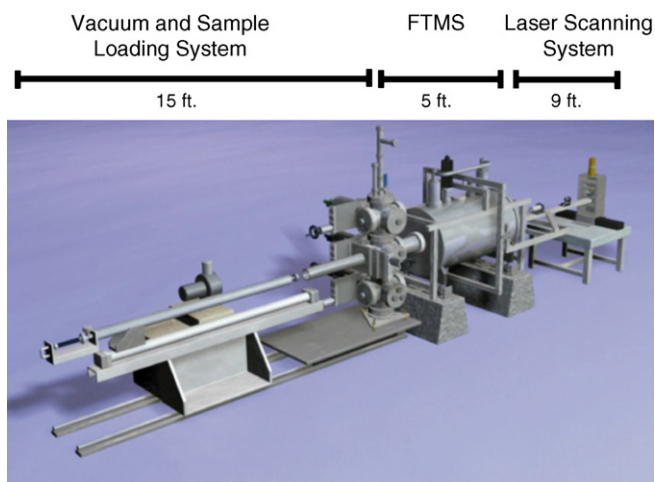


Fig. 1. Three-dimensional rendering of the imaging LD-FTMS system with a 3-in. diameter sample probe bar.

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