

CHEMICAL IMAGING OF PARTICLES

with the PHI *nanoTOF*

OVERVIEW

A unique advantage of time-of-flight secondary ion mass spectrometry (TOF-SIMS) is the ability to obtain chemical and molecular information at a spatial resolution well below the micron scale. Chemical imaging is a key asset in TOF-SIMS analysis because it is very often desirable to associate particular chemistries with specific phases or physical features of the probed specimen. It is also advantageous to understand the dispersion of a chemical additive or surfactant, or its distribution over a large field-of-view.

Rough surfaces present a challenge in TOF-SIMS imaging due to the effects of topography on the kinetic energies and trajectories of secondary ions. These effects are commonly referred to as topographic contrast. The principal obstacle encountered when analyzing a rough conducting surface concerns the trajectories of secondary ions which are driven from the optical axis of the mass spectrometer by the local electric field gradient. The ion optics of the PHI *nanoTOF*'s TRIFT analyzer are optimized for imaging topographically rough conductors in that the optical design provides an intrinsically large solid angle-of-collection.

In this Note, we demonstrate the use of the PHI *nanoTOF* to extract chemical information associated with a randomly-oriented sample of rough, conducting particles. The sample is comprised

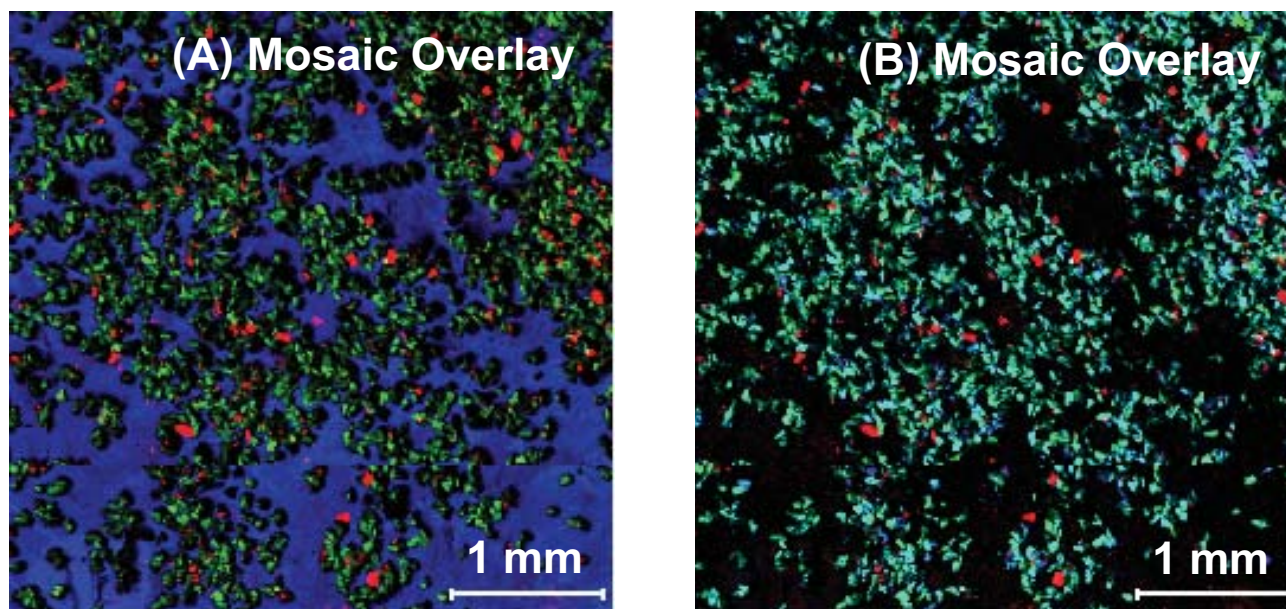


Figure 1: Color overlay images expose the distribution of mineral components within the ore particle specimen and may be used to identify areas for further analysis. (A) 4 mm FOV overlay of Si^+ (28 m/z, red), Cu^+ (63 m/z, green) and In^+ (115 m/z, blue). (B) 4 mm FOV overlay of Si^+ (28 m/z, red), Cu^+ (63 m/z, green) and Fe^+ (56 m/z, blue).

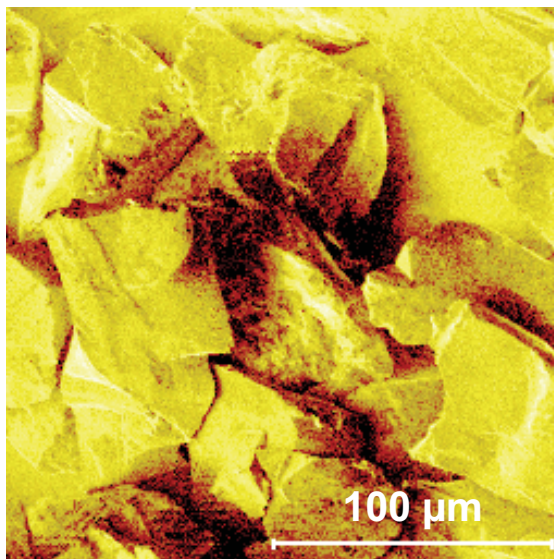


Figure 2: A total ion image (+SIMS, log scale) of the mineral ore particles in a 200 μm FOV demonstrates that the TRIFT analyzer efficiently collects secondary ions from every part of the sample that is probed by the analytical ion beam.

of chalcopyrite (CuFeS_2) mineral ore and quartz (SiO_2) particles having sizes in the range of approximately 30 μm to 100 μm . The particles have been treated with an organic surfactant, diisobutyl dithiophosphate (DTP), that is used for floatation separation of ore particles. The treated particles were fixed onto an Indium foil substrate for TOF-SIMS imaging. The salient features of the TRIFT mass spectrometer are utilized to distinguish the chemistries associated with different phases of the mineral particles.

EXPERIMENTAL

An unbunched 30 keV Au^+ primary ion beam was used to acquire images of the mineral particles in both the positive and the negative secondary ion polarities. Raw data stream files were collected to allow further post-acquisition evaluation (i.e. retrospective analysis) of the data. The mosaic (large area) images are comprised of 16 tiles x 16 tiles, each having a 250 μm x 250 μm field-of-view, for a total imaged area of 4 mm x 4 mm. Mosaic and standard (200 μm x 200 μm field-of-view) images were collected operating the Au^+ primary ion beam at DC currents of 1.5 nA and 0.5 nA, respectively, and a digital raster of 256 pixels x 256 pixels. The total acquisition times were 343 minutes for the mosaic image, and 3 minutes in each secondary ion polarity for the standard images.

RESULTS

Color overlays of the mineral particle mosaic (large area) images are presented in Figure 1. Hundreds of particles, as well as the In foil substrate, may be observed in these mosaic images. There is a significant quantity of data contained in this single raw data file from which the overlaid images were generated. Additionally, interesting clusters of particles may be identified in these images for further imaging and chemical analysis. A single 200 μm x 200 μm field-of-view, acquired in the positive secondary ion polarity, that reveals the topographic structure of several mineral particles is rendered in Figure 2. This image highlights the topography of the sample and the capability of the TRIFT mass spectrometer to collect secondary ions from every part of the sample that is probed by the primary ion beam. This characteristic of the TRIFT analyzer arises from an intrinsically large solid angle-of-collection. The analytical advantages of the TRIFT's imaging characteristics include; (a) reduced analysis time because all of the important chemical information is gathered in a single acquisition, and (b) the ability to determine the dispersion of certain chemistries or to correlate specific chemistries with morphological phases.

Variations in the intensity of an image that are related to sample topography, or roughness, is referred to as topographic contrast. Topographic contrast in TOF-SIMS images arises from three principal sources; the primary ion beam is shadowed from probing certain areas of the sample, the secondary ion sputter yield varies as the incidence angle of the primary ions varies across the sample, and the

collection efficiency of the analyzer changes as a function of angle of the secondary ions from the primary optical axis of the analyzer (i.e. solid angle-of-collection). The first two factors are physical constraints that can not be avoided, but the solid angle-of-collection is a matter of analyzer design.

The difficulty associated with achieving uniform secondary ion detection across a topographically rough conductor is illustrated in Figure 3. The illustration shows that the extraction field lines are distorted around the topographical features of the sample and the secondary ions are deflected by the contours of the distorted electric field. Secondary ions that depart the sides of the particle and the particle/substrate interface are accelerated from the optical axis of the analyzer. In order to compensate for these effects of topography, an efficient imaging mass analyzer must have a large solid angle-of-collection. Reflectron-based TOF-SIMS analyzers have a very limited solid angle-of-collection; a 4° half angle is specified in reference [1]. The TRIFT analyzer possesses a solid angle-of-collection that is sufficient to image the vertical sidewall of a focused ion beam-milled trench (an effective 90° half angle).

Overlay images of elemental secondary ions from the mineral particle sample are provided in Figure 4. The color overlays, which are composed of images from both the negative and the positive secondary ion polarities, reveal the inhomogeneity of phases that is present in this sample. In particular, these images show that there are phases of iron and copper ores, but neither of these phases are pure. Furthermore, while both phases contain oxygen and sulfur, oxygen and sulfur have higher concentrations in the iron- and copper-rich phases, respectively. Such observations concerning the spatial variation of chemistry may be made with confidence because the TRIFT mass spectrometer minimizes the ill effects of topography.

Region-of-interest (ROI) spectra were acquired from the predominantly iron-rich and copper-rich phases of the mineral particles. The regions-of-interest from which mass spectra were extracted, and the resulting mass spectra, are given in Figure 5. It is possible to extract mass spectra from defined portions of an image because the full mass spectrum of each image pixel is saved in the raw data stream file; so, the ROI is simply the designation of a set of image pixels for which a mass spectrum is displayed. The mass spectra are scaled to emphasize the 200 – 2,000 m/z region. The noteworthy peaks in each mass spectrum, those labeled with the nominal mass, are metal-organic complexes of iron and copper with diisobutyl dithiophosphate (DTP). While the composition of each peak is not disclosed here, it is remarkable that the mass spectra of each mineral phase has a unique set of fingerprint peaks.

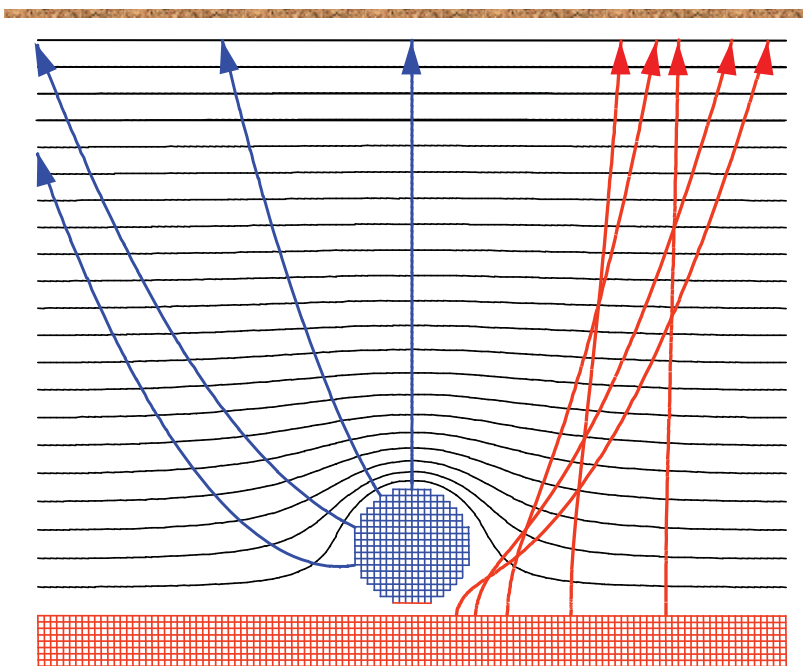


Figure 3: The importance of the TRIFT analyzer's large solid-angle-of-collection is illustrated in this simulation of the extraction field in the vicinity of a $\sim 40 \mu\text{m}$ particle on a flat substrate (e.g. Si). The field lines follow the contour of the conducting particle resulting in distortion of the extraction field along the sides of the particle and at the particle/substrate interface. The trajectories of the secondary ions are driven from the optical axis of the analyzer.

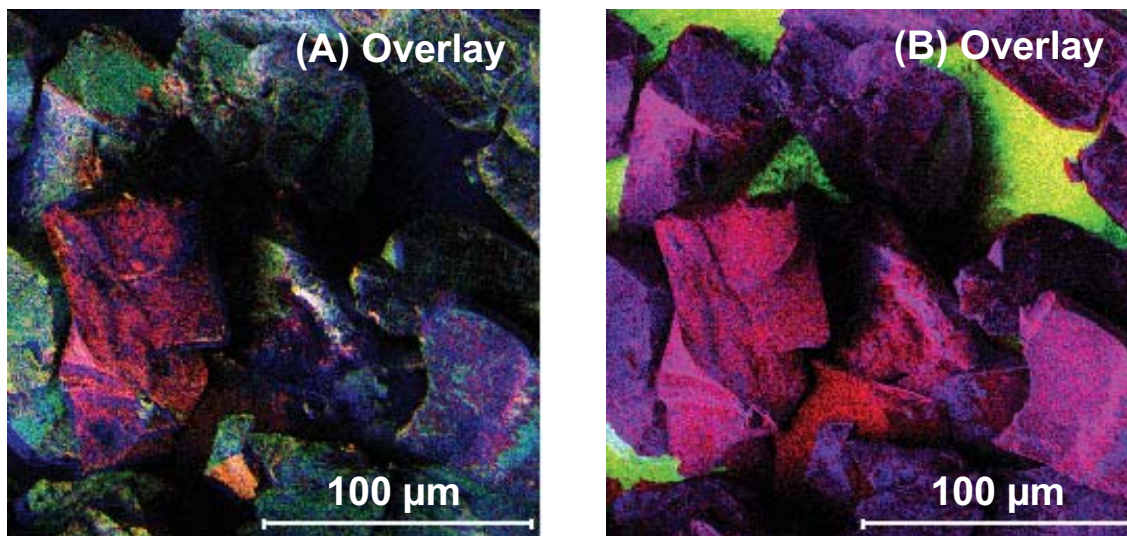


Figure 4: The mineral phases of each ore particle are exposed by the color overlay of chemical images. (A) 200 μm FOV overlay of Fe^+ (56 m/z, red), Cu^+ (63 m/z, green) and S (32 m/z, blue). (B) 200 μm FOV overlay of O^- (16 m/z, red), In^+ (115 m/z, green) and S (32 m/z, blue).

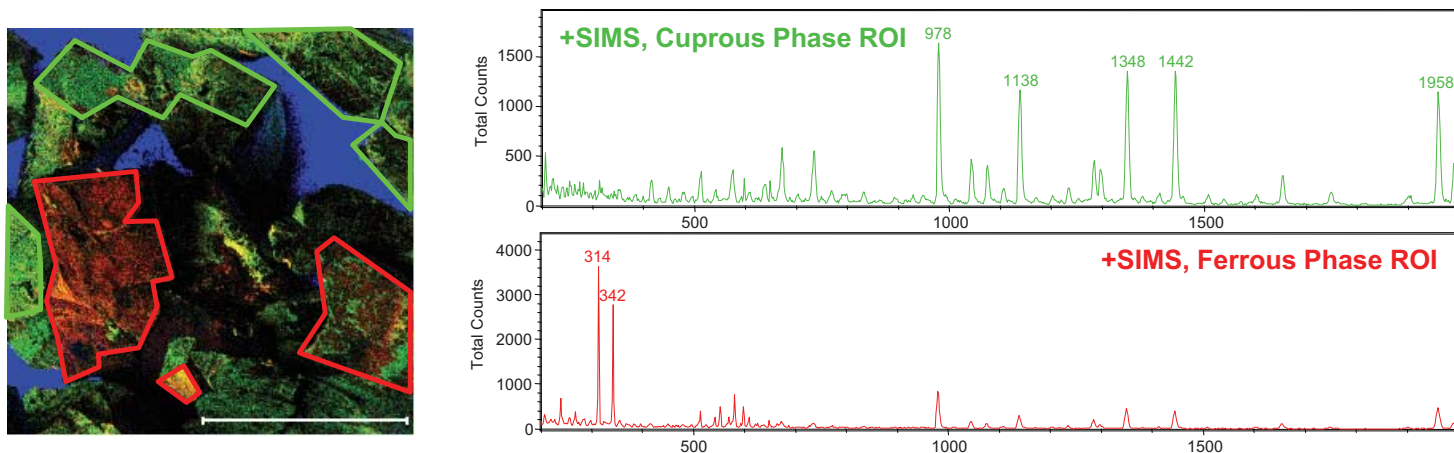


Figure 5: Mass spectra from the regions-of-interest reveal a unique set of metal-organic peaks associated with each mineral phase of the ore particles. LEFT: 200 μm FOV overlay of Fe^+ (56 m/z, red), Cu^+ (63 m/z, green) and In^+ (115 m/z, blue). RIGHT: Mass spectra from the ROIs indicated on the color overlay image.

CONCLUSION

The PHI *nanoTOF* is a practical tool for chemical imaging and analysis of topographically rough, conducting specimens due to the large solid-angle-of-collection design of the TRIFT analyzer. Essential characteristics of the TRIFT analyzer were demonstrated by imaging the mineral phases of an ore particle sample and identifying the distinctive metal-organic complexes formed between an organic surfactant and each mineral phase.

ACKNOWLEDGEMENTS & REFERENCES

We would like to thank Professor William Skinner of the Ian Wark Research Institute at the University of South Australia for providing the mineral sample.

[1] J.L.S. Lee, I.S. Gilmore, I.W. Fletcher, M.P.Seah, Topography and Field Effects in the Quantitative Analysis of Conductive Surfaces Using TOF-SIMS, *Appl. Surf. Sci.* (2008), doi: 10.1016/j.apsusc.2008.05.164.

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