Correlative microscopy and machine learning – new tools for material characterization

Harald Fitzek[1], Ruth Schmidt[1,2], Manfred Nachtnebel[1], Johannes Rattenberger[1], Armin Zankel[1,2], Ferdinand Hofer[1,2] and Hartmuth Schröttner[1,2]

1. Graz Centre for Electron Microscopy (ZFE), Steyrergasse 17, 8010 Graz, Austria
2. Institute of Electron Microscopy and Nanoanalysis (FELMI), Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

Introduction

The correlation of different microscopic techniques has seen increased interest in recent years due to the possibility of combining the strengths of multiple techniques. In addition to the practical challenges with regard to sample preparation, instrument design and the need for operators experienced in multiple techniques, unique data treatment challenges arise when combining data sets with different resolutions and contrast mechanisms. Using Raman-SEM-EDS as an example correlative technique we are discussing two approaches for correlative microscopy and data treatment thereof on the example specimen of a WO_3-WS_2 powder and a volcanic rock. The aim of both approaches is to translate microscopic images (or mappings) into quantified data. The first approach puts the focus on getting the most information out of minimal experimental effort (WO_3-WS_2 powder). The second approach puts the focus on maximal analytical quality (volcanic rock).

WO_3-WS_2 powder – intuitive & fast approach

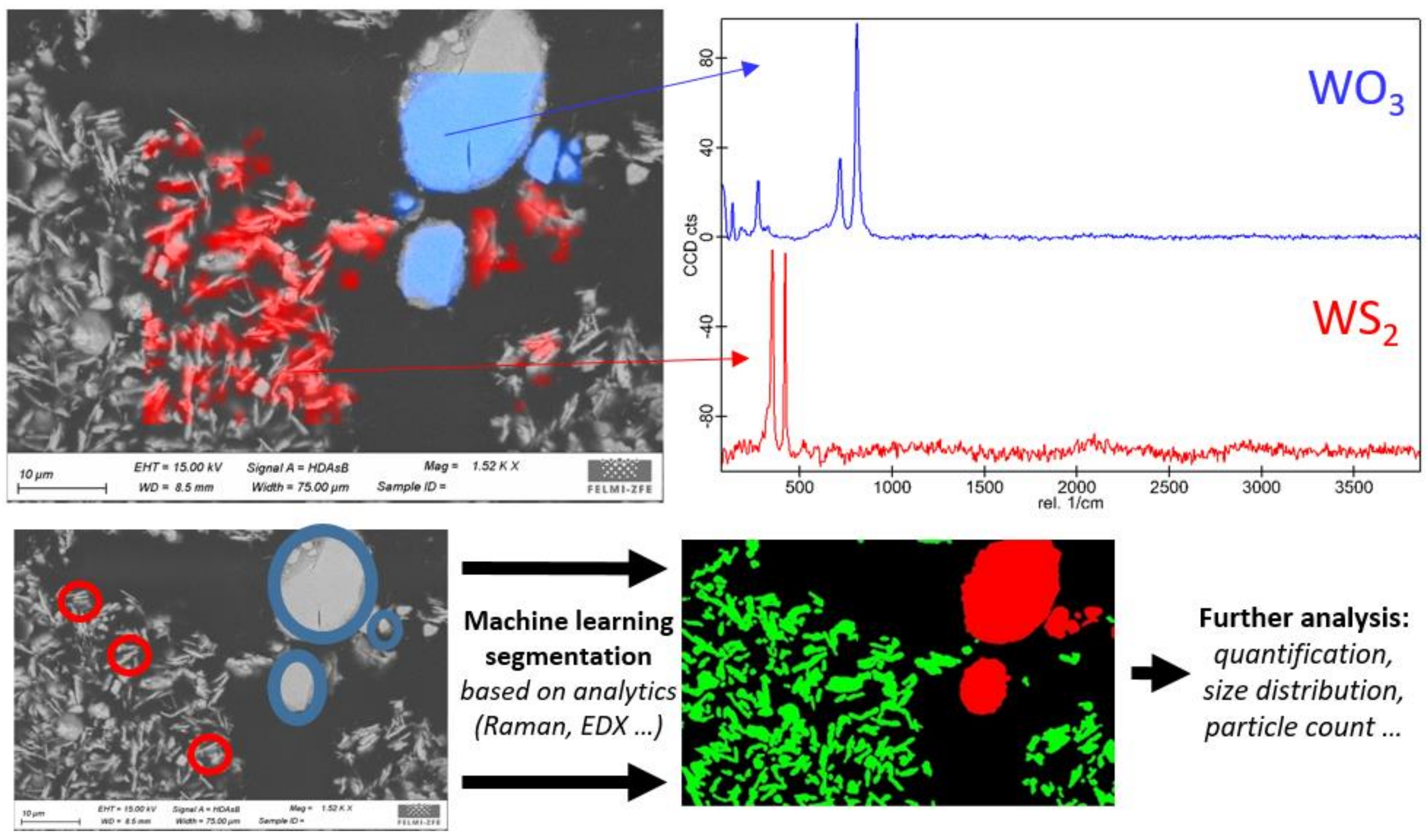


Fig. 1: Summary of the "intuitive" approach. (Top) After getting a first impression of the sample (by SEM images) a small region that contains all interesting structures is chosen and a quick analysis using the analytic technique (Raman) is done. (Bottom) Given the clear distinction between different phases based on contrast and shape a machine learning segmentation is trained that can generate quantitative data from SEM images.

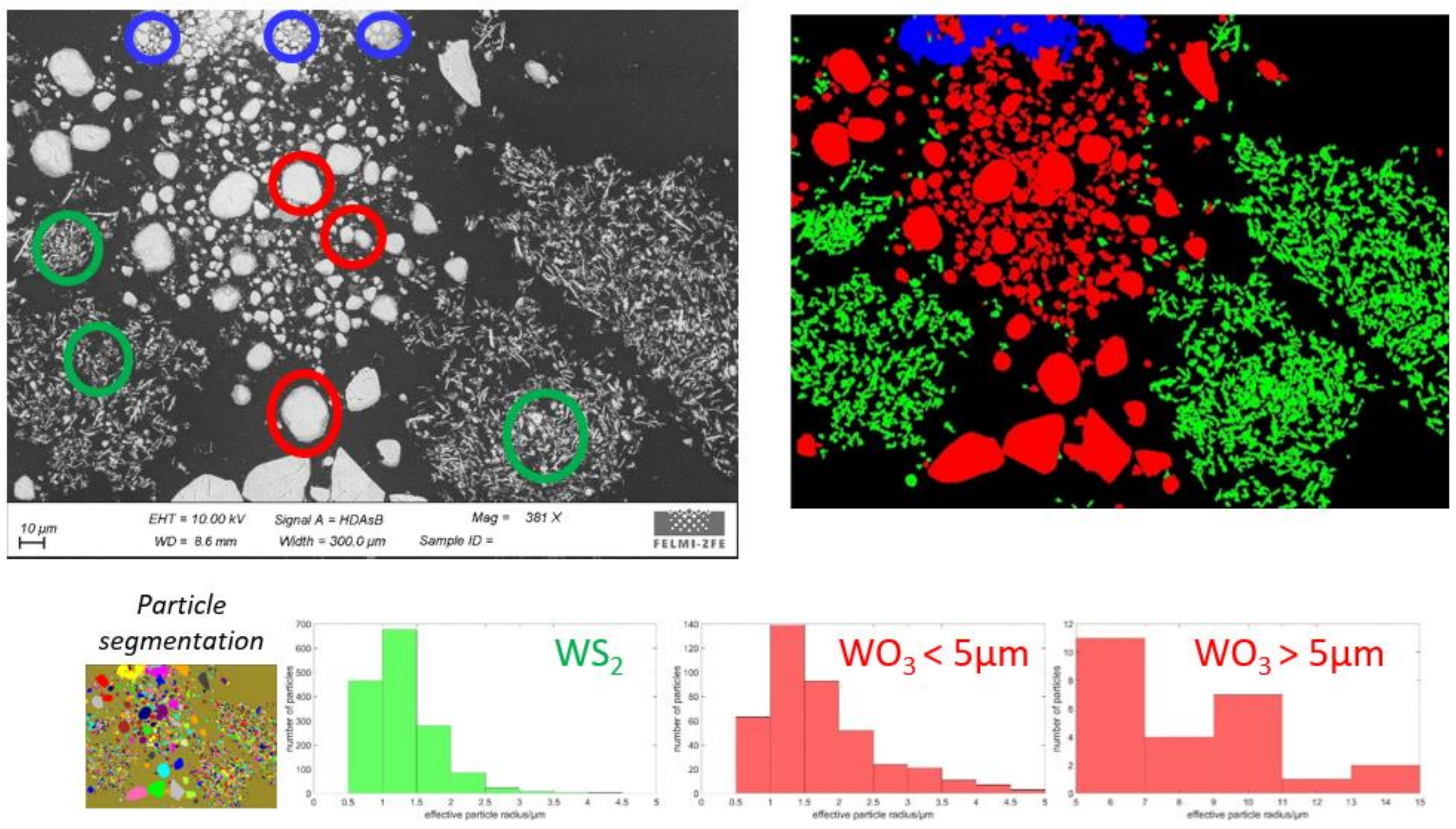


Fig. 2: Quantitative analysis of a large SEM image based on the random forest classifier generated in Fig.1. (Top) Original SEM image and classifier results. Note that the WO_3 phase was subdivided into a coarse and fine phase to improve the classification. (Bottom) Particle segmentation based on the results shown at the top, with histograms of the particle size distribution.

Table 1: Quantitative evaluation of the SEM image shown in Fig. 2.

Composition	Surface area / %	# of particles	<eff. radius>/µm
WO_3	49	429	2.1
WS_2	44	1547	1.3
Fine WO_3	7	-	-

Volcanic rock – maximal analytical quality approach

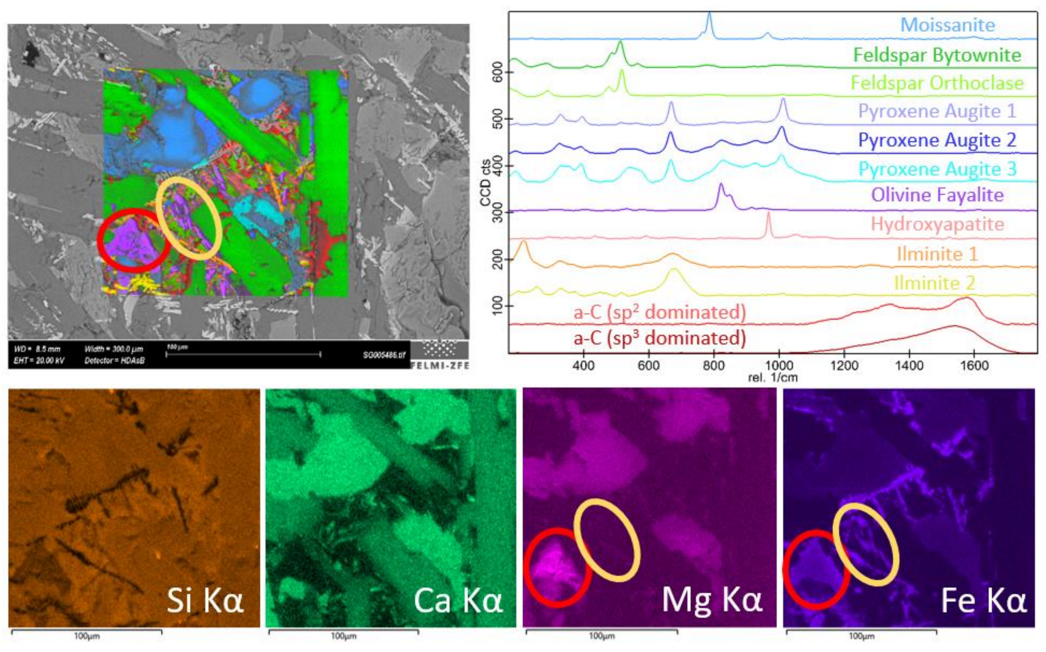


Fig. 3: Correlative SEM-EDS-Raman mappings measured on a volcanic rock. (Top) Overlay of the Raman mapping with the BSE image. (Bottom) Selected elemental distribution from the EDS mapping. The markings denote an elemental variation within the Olivine phase that requires both EDS and Raman to be interpreted correctly.

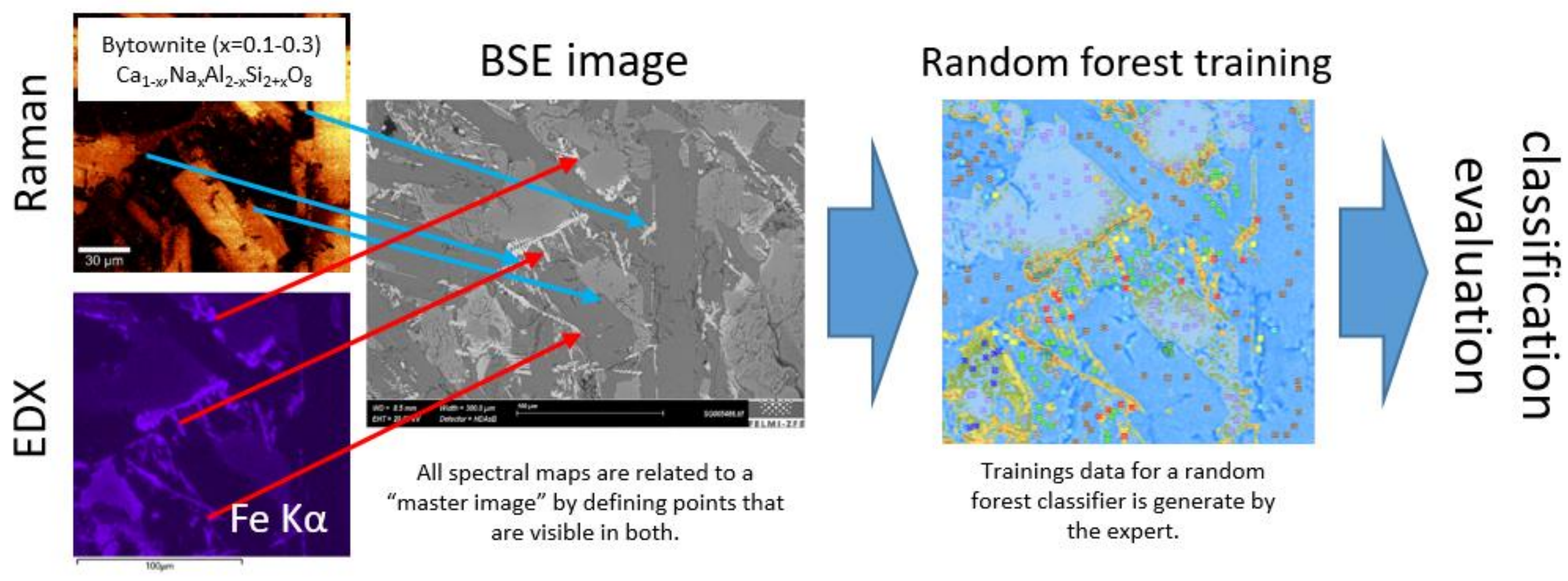
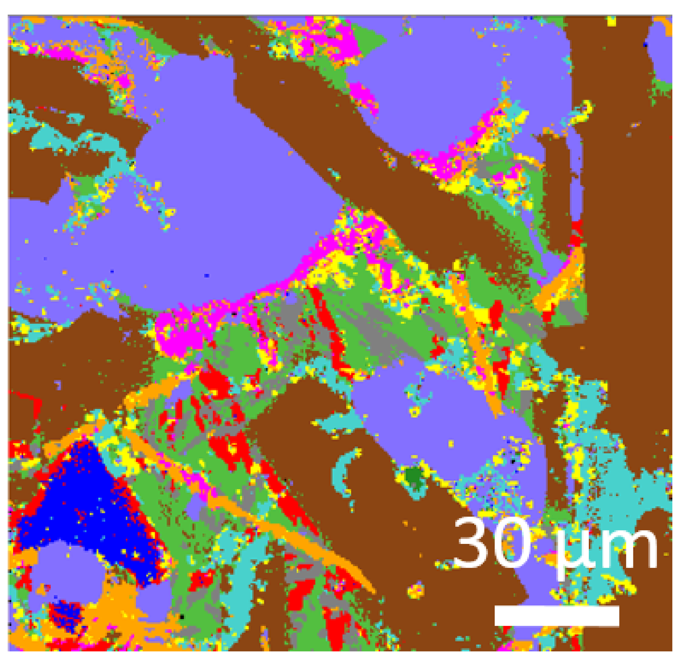


Fig. 4: Schematic of the data combination and treatment process. (Left) Raman, EDS and SEM data is spatially correlated by marking positions in the Raman and EDS mapping that are also visible in the BSE image. Everything is then interpolated to the resolution of the BSE image in order to generate a "super spectral image" that contains Raman, EDS and SEM information in each pixel. (Right) A random forest classifier is trained by manually marking positions of each of the 11 phases found and used to evaluate the entire data set.

Random forest classification (combined EDS-Raman-BSE-SE)



Phase	Composition	Area-%	Remark
Feldspar Bytownite	$Ca_{1-x}Na_xAl_{2-x}Si_{2+x}O_8$	34.8	Good in both EDS/Raman; used for map-alignment
Pyroxene Augite	$(Ca,Mg,Fe)\ Si_2O_6$	26.0	Raman interpretation improved by EDS
Feldspar Sanidine	$Na_xK_{1-x}AlSi_3O_8$	10.1	Raman interpretation improved by EDS
Amorphous C (sp3)	C	7.3	From sample preparation mostly in holes (SE helped)
Ilmenite	$FeTiO_3$	5.4	Pure Raman mapping improved by EDS/BSE
Hydroxyapatite	$Ca_5(PO_4)_3(OH)$	4.0	-OH only detectable by Raman
Amorphous C (sp2)	C	3.8	Only detectable by Raman
Olivine Fayalite	Fe_2SiO_4	3.4	Combined EDS/Raman necessary for good map
Ferrotitanium	Fe_xTi_{1-x}	2.6	Only detectable by EDS
Olivine Fe-Mg mixed	$Fe_{2-x}Mg_xSiO_4$	2.4	Combined EDS/Raman necessary for good map
Moissanite	SiC	0.2	Particle from sample preparation

Fig. 5: Results of the combined analysis of SEM-EDS-Raman on the volcanic rock sample. (Left) Random forest classification of all 11 phases. (Right) Summary of the benefit of the correlation and quantification of the area-% of each phase. Further and finer analysis, especially of the crystal structures with a variating composition, is possible from this data. We would like to point the interested colleagues to our own work on algorithms [1] and the Chelyabinsk meteorite [2], as well as a recent extensive review on the subject [3].

Literature

[1] S. Bitrus, H. Fitzek, R. Eugen, J. Rattenberger and D. Entner, *Ultramicroscopy* in press

[2] H. Fitzek, A. Zankel, M. Dienstleder, J. Rattenberger, H. Schröttner and F. Hofer, *Micron* 153, 103177, (2022)

[3] T. Ando, S. P. Bhamidimarri, N. Brending, H. Colin-York, L. Collinson, N. De Jonge, P. J. de Pablo, E. Debroye, C. Eggeling, C. Franck, M. Fritzsche, H. Gerritsen, B.N.G. Giepmans, K. Grunewald, J. Hofkens, J. P. Hoogenboom, K. P. F. Janssen, R. Kaufmann, J. Klumperman, … G. Zifarelli,. *J. Phys. D* 51(44), (2018)

Acknowledgements

The authors are deeply grateful to "HRSM-Projekt ELMINet Graz" (BMBWF), the "TIMELY" project (BMDW & ACR; PN: SP-2020-02) and the "Innovative Materialcharakterisierung" project (BMDW & ACR; PN: SP2016-002-006) for financial support.

Contact

harald.fitzek@felmi-zfe.at
www.felmi-zfe.at