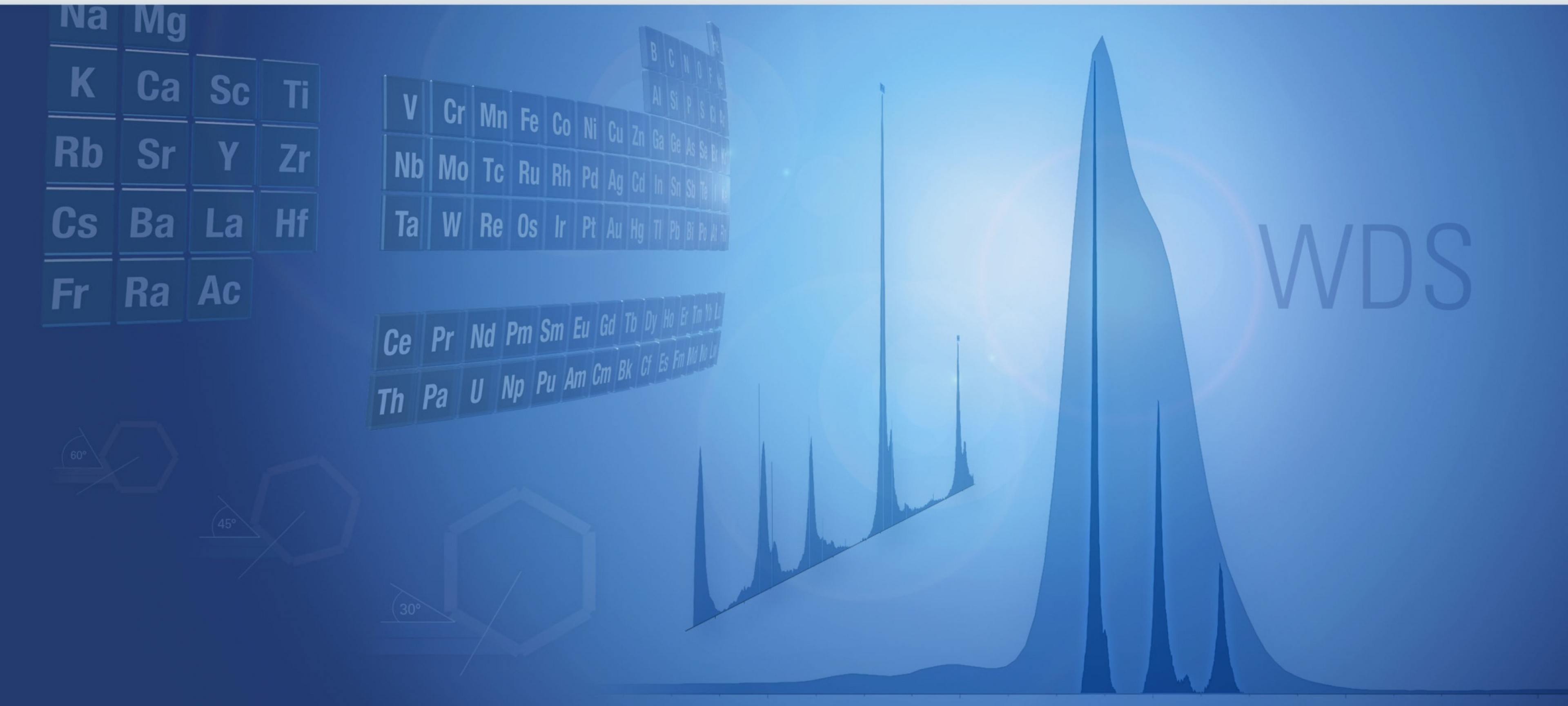
Advanced elemental analysis of geological samples using QUANTAX WDS for SEM

Bruker Nano Analytics, Berlin, Germany
Webinar, April 25, 2019



Presenter

Dr. Michael Abratis

Sr. Application Scientist WDS,
Bruker Nano Analytics, Berlin, Germany

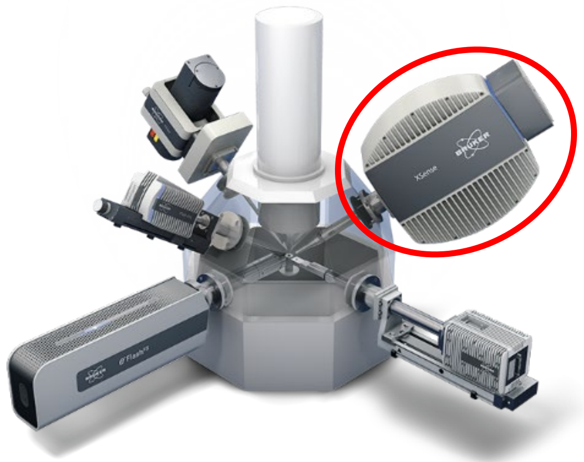
Advanced elemental analysis of geological samples using QUANTAX WDS for SEM

OUTLINE:

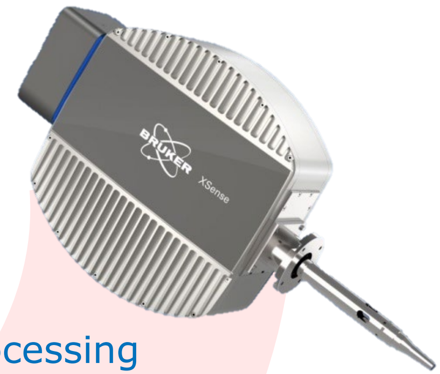
- QUANTAX WDS – the principles
- Full quantitative analysis with QUANTAX WDS
- Advanced applications showing
    - trace element determination
    - high spectral resolution
    - trace element determination requiring high spectral resolution

QUANTAX WDS
System Components

QUANTAX WDS: integral part of the QUANTAX family



XSense™ WD spectrometer

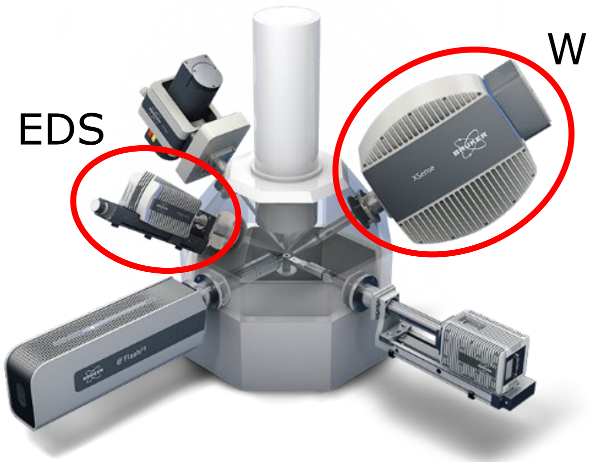


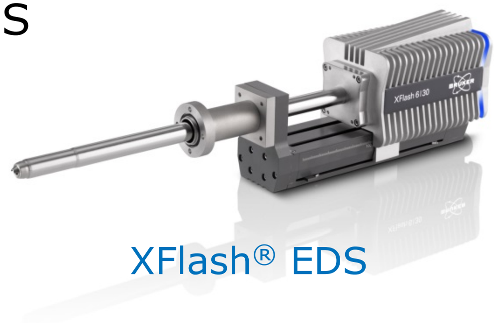
Signal processing unit SVE 6

ESPRIT 2

Spectrometer comparison
Advantages of WDS over EDS

QUANTAX WDS: integral part of the QUANTAX family





XFlash® EDS

XSense WDS

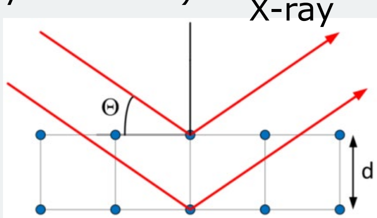
Compared with EDS the WDS shows:

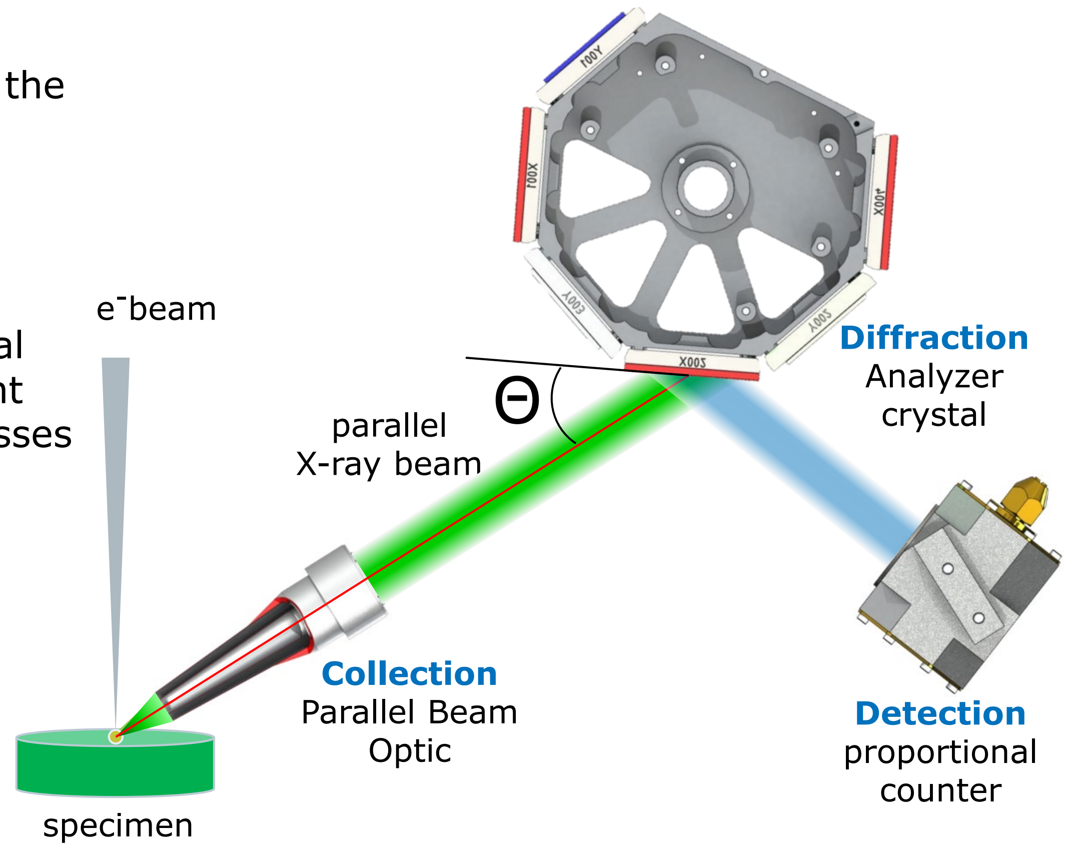
- substantially higher spectral resolution (typically 4 – 20 eV FWHM)
- enhanced P/B-ratios, i.e. lower detection limits
- outstanding sensitivity for light elements including Be, B

WDS is an ideal technique to complement EDS in demanding applications

XSense WD Spectrometer
Setup and Working Principle

- Parallel Beam Optic (PBO) transforms X-rays diverging from the sample into a parallel beam
- Polychromatic beam undergoes Bragg diffraction at flat analyzer crystal
- Angle Θ between beam and crystal surface and crystal lattice constant $2d$ determines the energy that passes through to the detector
- X-ray detection by a flow proportional counter





Bragg equation: $n\lambda = 2d\sin(\theta)$

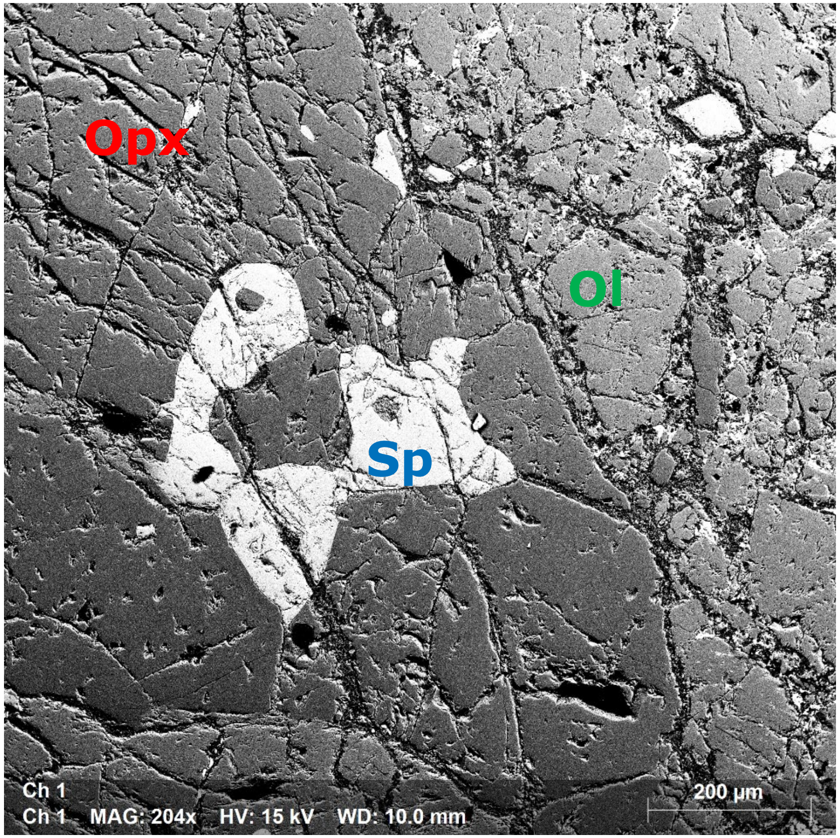
Application of QUANTAX WDS
Analyzing peridotite

Peridotite (ultramafic rock)

- Olivine (Ol)
- Orthopyroxene (Opx)
- Spinel (Sp)
- Clinopyroxene

Full quantitative mineral analysis by WDS on SEM

Sample courtesy of Prof. Giancarlo Capitani, University of Milano, Italy



BSE image of peridotite

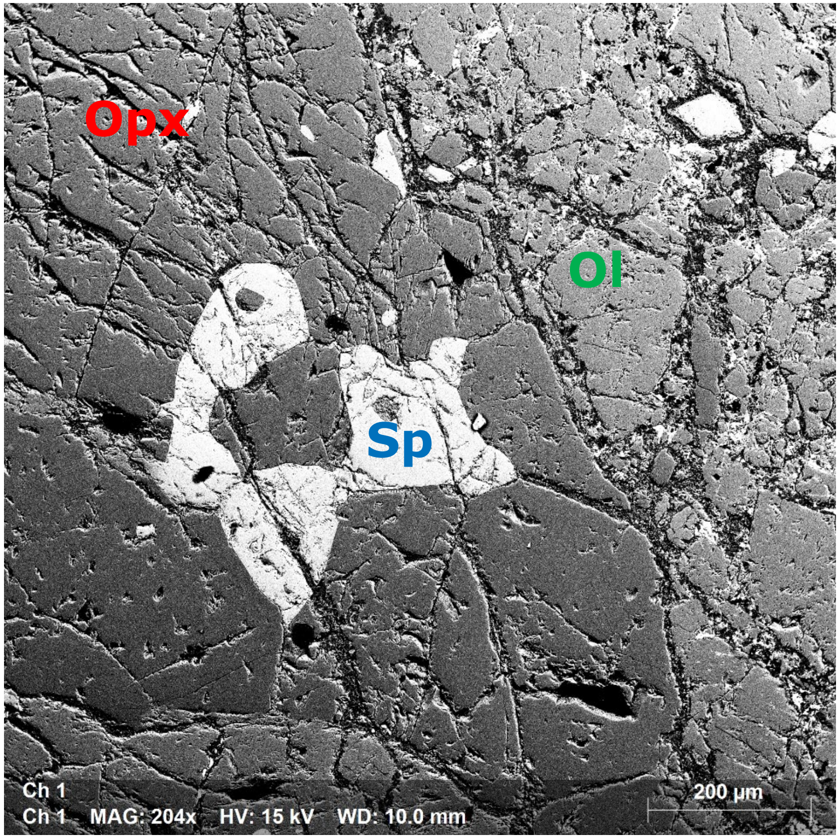
Full quantitative analysis by WDS
Olivine, pyroxene and spinel in peridotite

WDS standards and settings

Element	X-ray line	Diffractor	Standard	Peak time
Mg	Ka	TAP	Olivine	30 s
Al	Ka	TAP	Pyrope	30 s
Si	Ka	PET	Diopside	30 (60) s
Ca	Ka	PET	Diopside	60 s
Ti	LI	BRML80	Rutile	30 s
Cr	LI	BRML30	Cr_2O_3	30 s
Mn	La	TAP	Rhodonite	30 s
Fe[1,2]	La	TAP	Olivine	30 s
Fe[3]	La	TAP	Almandine	30 s
Ni	La	TAP	Ni_2Si	60 s
Zn	La	TAP	Willemite	60 s

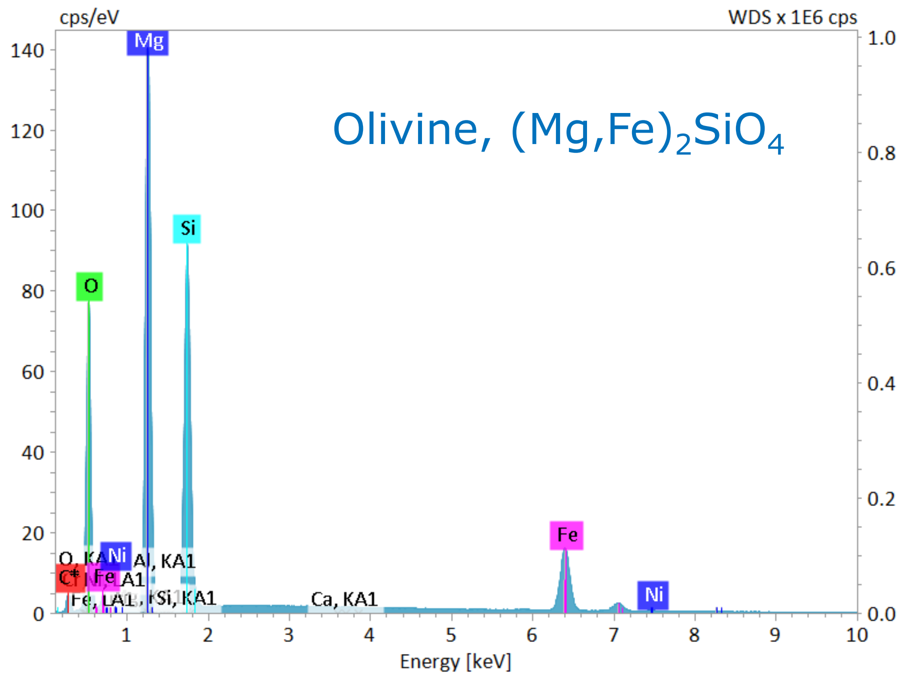
1: Olivine, 2: OPX, 3: Spinel

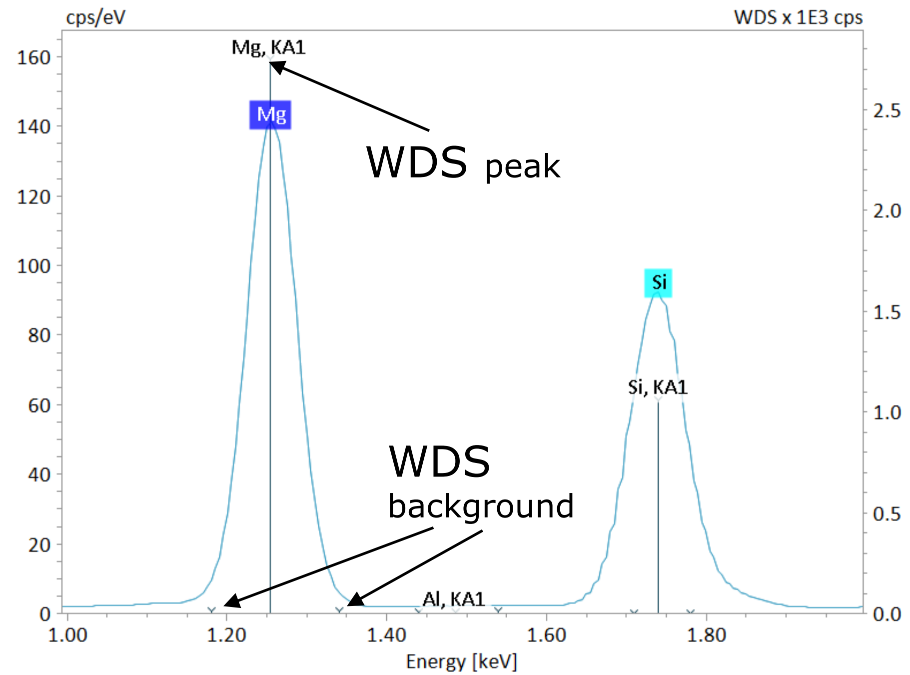
20 kV, 20 nA



BSE image of peridotite

Comprehensive spectrum by EDS
Selective P/B measurements by WDS





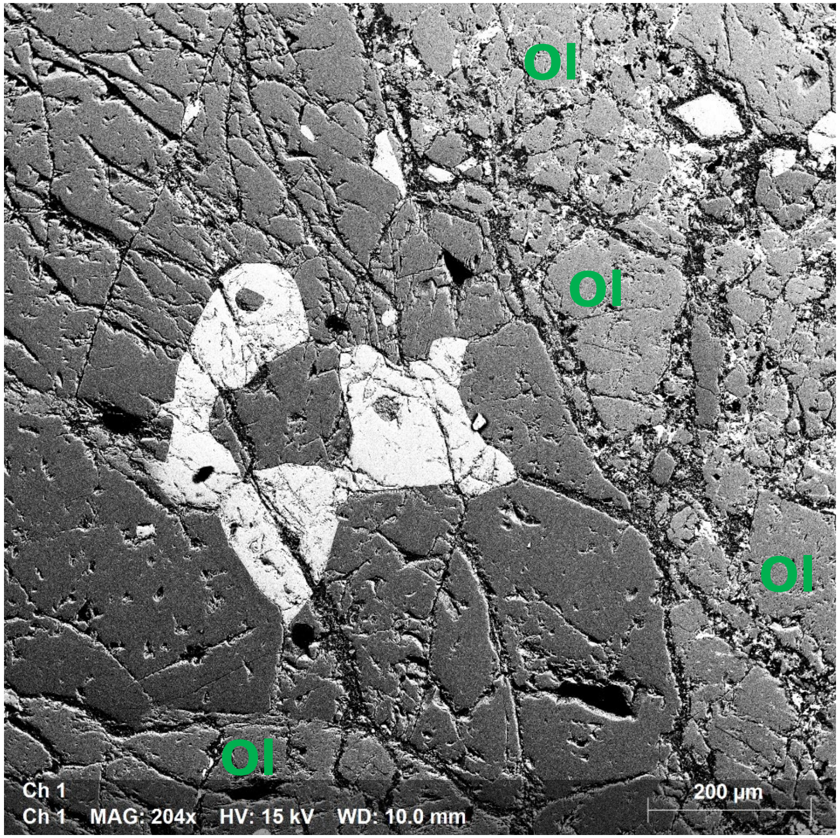
EDS spectrum indicates elements

WDS P/B for quantification

Full quantitative analysis by WDS
Olivine in peridotite

Stoichiometric concentrations in %

Spec-trum	MgO	SiO_2	FeO	NiO	Sum
N1_ 1	47.57	38.25	15.61	0.24	101.67
N1_ 3	45.35	37.73	15.56	0.28	98.92
N1_ 4	47.13	37.99	15.17	0.24	100.53
N1_ 6	45.93	37.82	15.02	0.26	99.03
N1_ 7	46.88	37.71	14.71	0.31	99.61
N1_ 8	49.00	38.24	14.71	0.25	102.20
N1_ 13	46.46	37.69	14.99	0.27	99.40
N1_ 14	47.48	37.87	15.24	0.27	100.86
N1_ 15	47.50	37.92	15.10	0.26	100.77
N1_ 27	46.06	37.83	15.93	0.30	100.12
Mean	**46.94**	**37.90**	**15.20**	**0.27**	**100.31**
Sigma	**1.04**	**0.20**	**0.39**	**0.02**	**1.10**
Sigma Mean	**0.33**	**0.06**	**0.12**	**0.01**	**0.35**

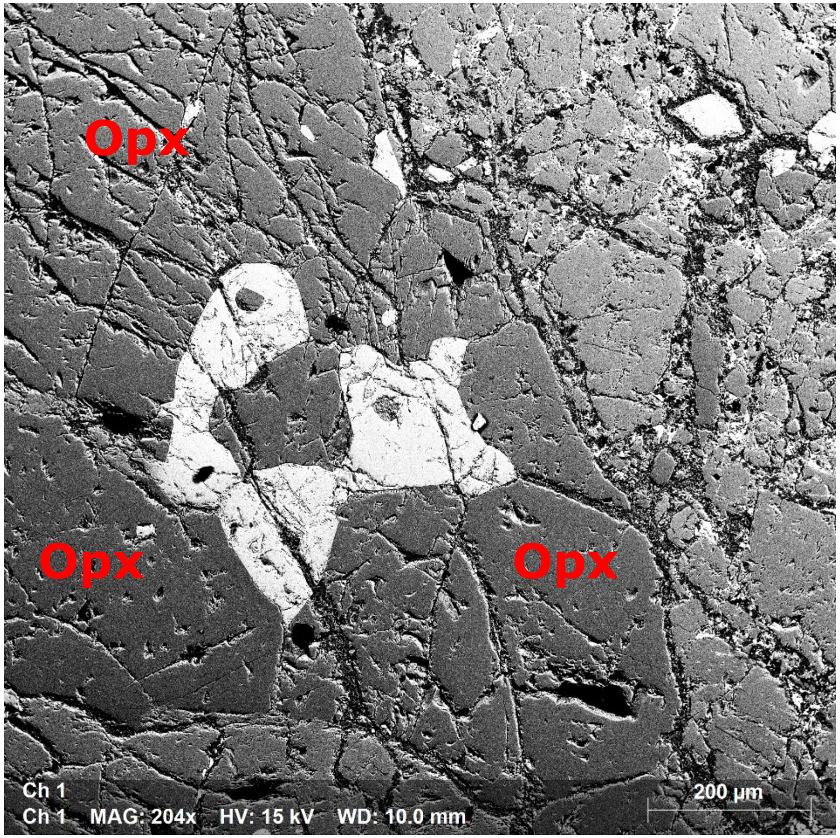


BSE image of peridotite

Full quantitative analysis by WDS
Orthopyroxene in peridotite

Stoichiometric concentrations in %

Spec-trum	MgO	Al_2O_3	SiO_2	FeO	CaO	Sum
10	33.63	1.94	54.27	11.78	0.31	101.94
11	32.46	1.73	54.15	9.93	0.27	98.53
12	31.70	1.77	53.57	10.14	0.31	97.49
13	32.01	1.85	53.55	10.66	0.27	98.35
15	31.91	1.24	54.58	11.52	0.27	99.50
16	31.83	1.57	53.66	11.76	0.21	99.03
17	31.79	1.69	55.06	11.69	0.24	100.47
19	31.14	1.45	53.82	11.38	0.34	98.14
20	31.95	1.83	54.00	11.59	0.26	99.64
21	32.13	1.58	53.96	10.96	0.27	98.90
22	33.55	1.75	54.41	11.42	0.30	101.43
Mean	**32.19**	**1.67**	**54.09**	**11.17**	**0.28**	**99.40**
Sigma	**0.76**	**0.20**	**0.46**	**0.66**	**0.04**	**1.39**
Sigma Mean	**0.23**	**0.06**	**0.14**	**0.20**	**0.01**	**0.42**



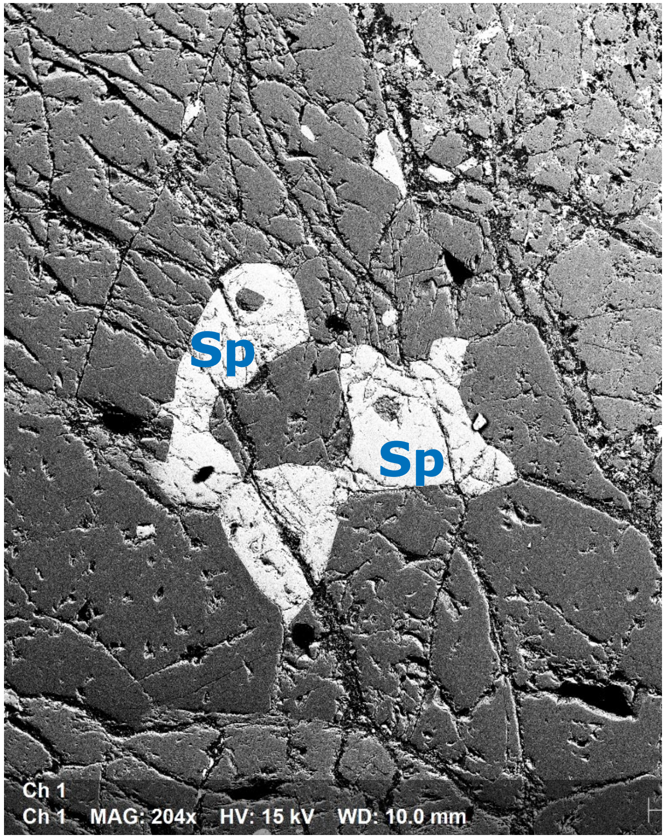
BSE image of peridotite

Full quantitative analysis by WDS
Spinel in peridotite

Stoichiometric concentrations in %

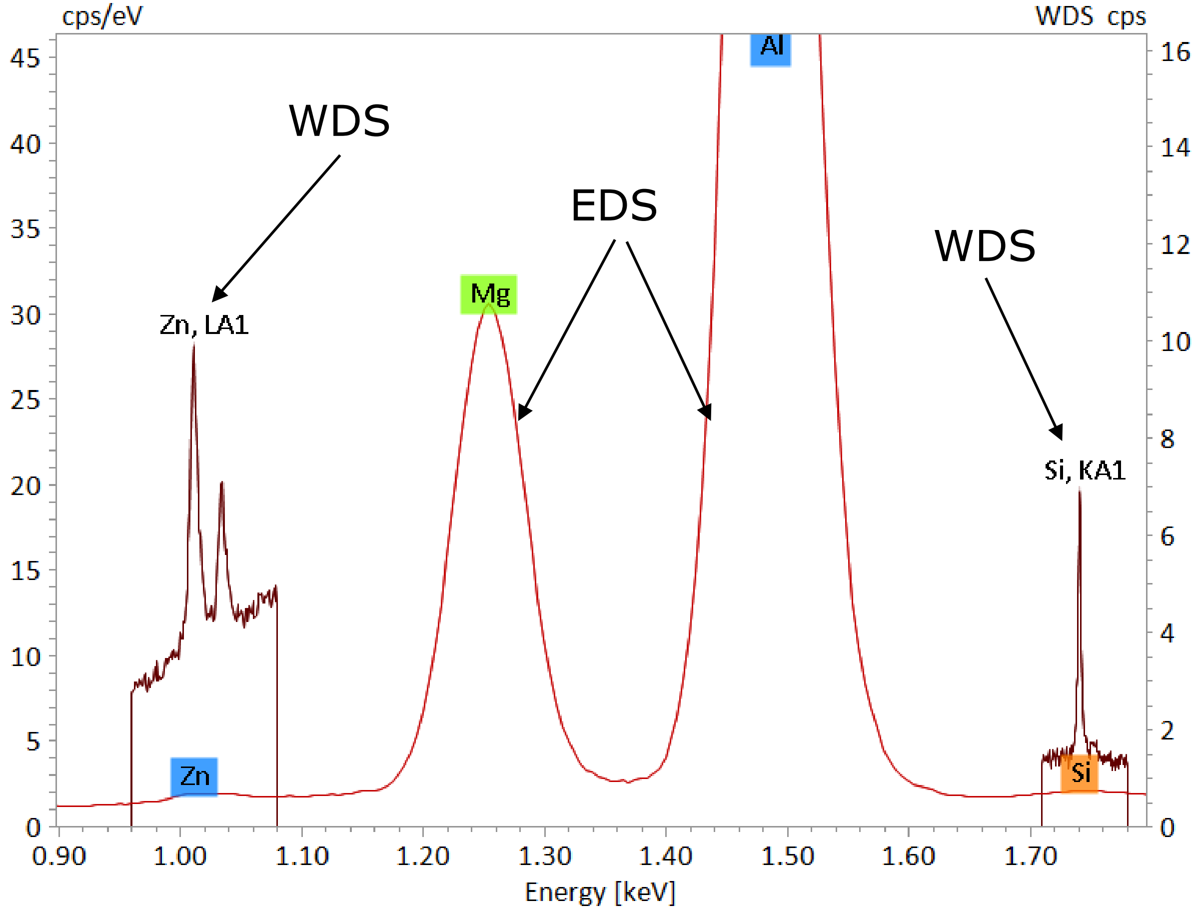
Spectrum	MgO	Al_2O_3	FeO	Cr_2O_3	TiO_2	MnO	Sum
1	13.21	42.88	24.79	13.35	3.22	1.31	98.76
2	13.23	42.42	25.43	13.85	3.51	0.57	99.00
3	13.52	42.93	25.33	14.11	3.48	1.18	100.54
4	12.88	41.33	25.16	13.70	3.27	1.01	97.36
5	12.14	39.51	25.58	14.34	3.42	0.83	95.81
7	12.35	43.03	27.32	12.97	3.32	0.74	99.73
8	13.01	42.12	27.16	14.32	3.53	0.72	100.85
Mean	**12.90**	**42.03**	**25.82**	**13.81**	**3.39**	**0.91**	**98.86**
Sigma	**0.50**	**1.26**	**1.00**	**0.51**	**0.12**	**0.27**	**1.79**
Sigma Mean	**0.19**	**0.48**	**0.38**	**0.19**	**0.05**	**0.10**	**0.68**

Low totals: missing elements?

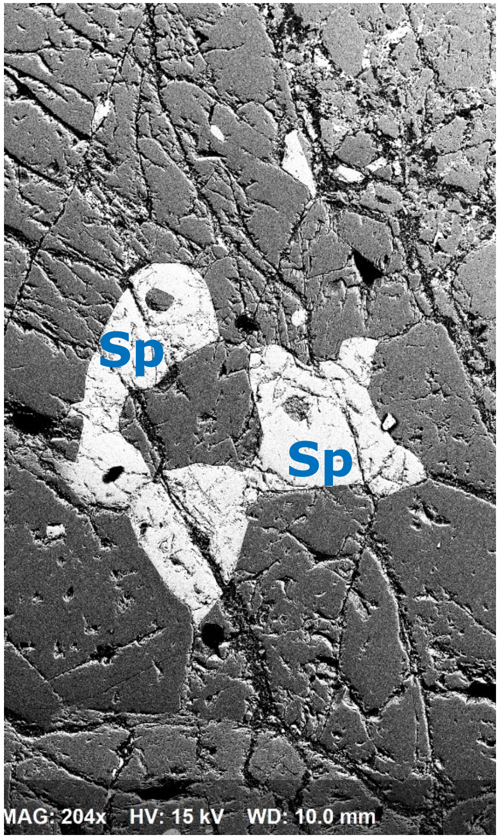


BSE image of peridotite

Spinel in peridotite
Trace element detection by WDS



WDS energy range scans for Si and Zn

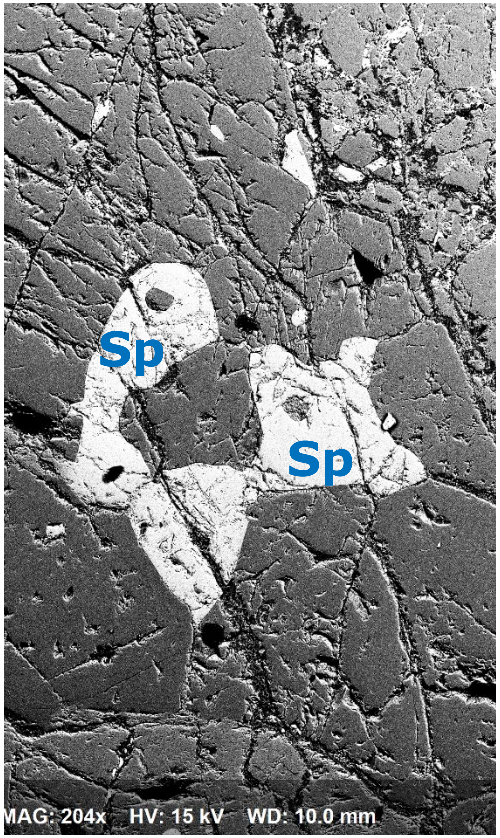


BSE image of peridotite

Full quantitative analysis by WDS
Spinel in peridotite

Stoichiometric concentrations in %

Spectrum	MgO	Al_2O_3	SiO_2	FeO	Cr_2O_3	TiO_2	MnO	NiO	ZnO	Sum
1	13.21	42.88	0.03	24.79	13.35	3.22	1.31	0.18	0.38	99.35
2	13.23	42.42	0.05	25.43	13.85	3.51	0.57	0.10	0.39	99.54
3	13.52	42.93	0.04	25.33	14.11	3.48	1.18	0.08	0.47	101.13
4	12.88	41.33	0.03	25.16	13.70	3.27	1.01	0.05	0.39	97.83
5	12.14	39.51	0.10	25.58	14.34	3.42	0.83	0.14	0.40	96.45
7	12.35	43.03	0.04	27.32	12.97	3.32	0.74	0.02	0.48	100.27
8	13.01	42.12	0.05	27.16	14.32	3.53	0.72	0.08	0.50	101.48
Mean	**12.90**	**42.03**	**0.05**	**25.82**	**13.81**	**3.39**	**0.91**	**0.09**	**0.43**	**99.44**
Sigma	**0.50**	**1.26**	**0.03**	**1.00**	**0.51**	**0.12**	**0.27**	**0.05**	**0.05**	**1.79**
Sigma Mean	**0.19**	**0.48**	**0.01**	**0.38**	**0.19**	**0.05**	**0.10**	**0.02**	**0.02**	**0.68**



BSE image of peridotite

QUANTAX WDS

Resolving common overlaps in EDS microanalysis

Element and line	Interferences with	Δ eV	Samples or applications where the overlaps are found
Cu-L	Na-Kα	18	Biological samples (grid)
As-L	Na-Kα	79	Biological samples (stain or fixative)
Ag-L	Cl-Kα	10	Biological samples (stain or fixative)
Ru-L	S-Kα	54	Biological samples (stain or fixative)
Os-M	Al-Kα	5	Biological samples (stain or fixative)
U-M	K-Kα	22	Biological samples (stain or fixative)
Sr-Lα	Si-Kα	31	Silicates (feldspars in particular)
Y-Lβ	P-Kα	18	Phosphates
Y-Lβ	Zr-Lα	46	Silicates (zircon), oxides (zirconia)
S-Kα,β	Mo-Lα; Pb-Mα	14; 38	Minerals, lubricants, sulfides, sulfates
Ti-Kβ	V-Kα	20	Steels, Fe-Ti oxides
V-Kβ	Cr-Kα	13	Steels
Cr-Kβ	Mn-Kα	47	Steels
Mn-Kβ	Fe-Kα	87	Steels
Fe-Kβ	Co-Kα	128	Steels, magnetic alloys
Co-Kβ	Ni-Kα	169	Steels, hard surfacing alloys
W-Mα,β	Si-Kα,β	35	Semiconductor processing
Ta-Mα,β	Si-Kα,β	27	Semiconductor processing
Ti-Kα	Ba-Lα	45	Optoelectronics, silicates
As-Kα	Pb-Lα	8	Pigments

Overlaps known from biological, geological and material sciences and industries

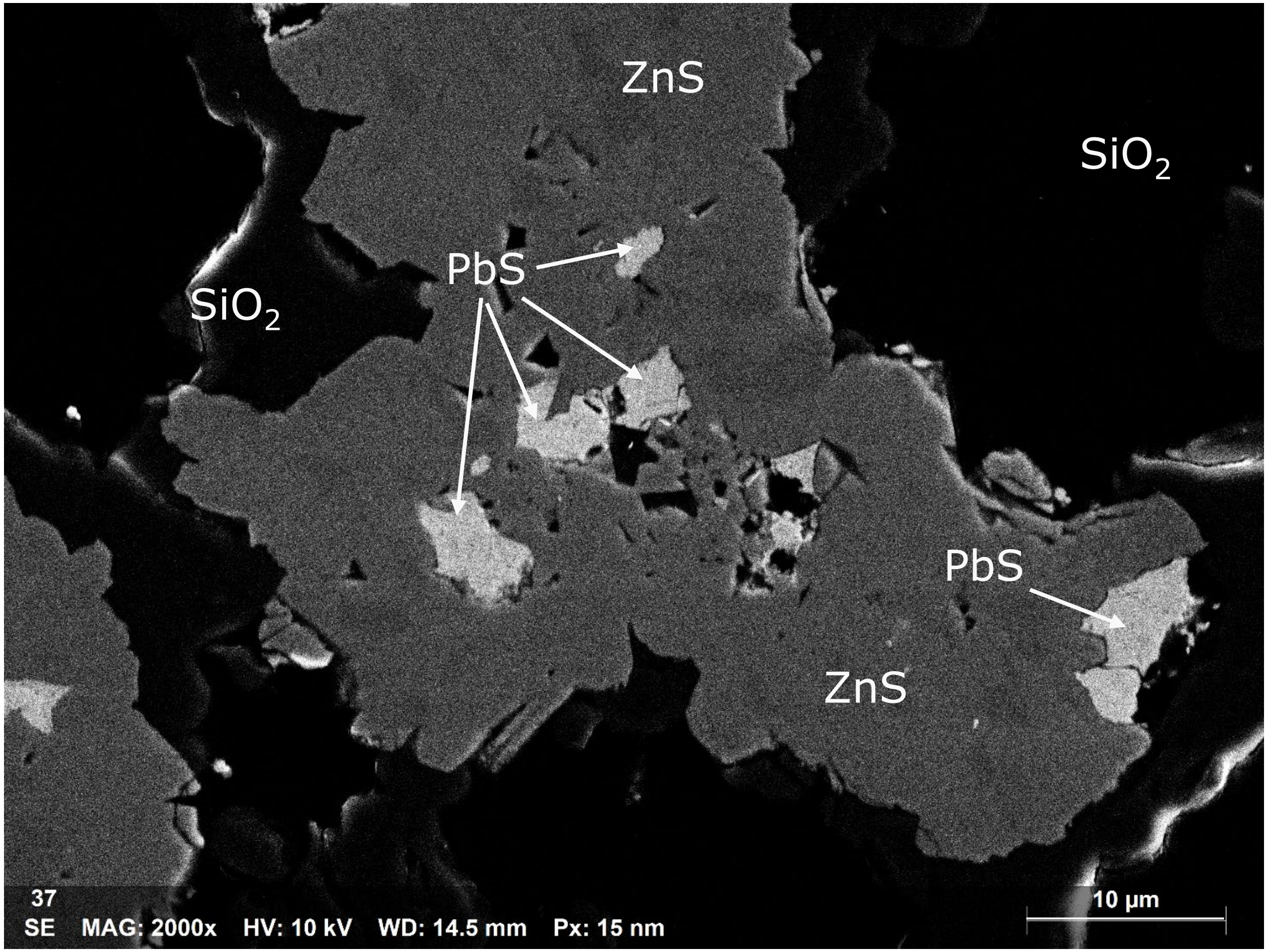
Modified after Goldstein et al. (2007). Scanning Electron Microscopy and X-Ray Microanalysis. Springer

QUANTAX WDS and EDS

Comparison of WDS and EDS resolution

Element	Atomic No.	X-ray line	Energy [keV]	FWHM EDS [eV]	WDS diffractor	FWHM WDS [eV]	Resolution improvement
Si	14	Kα	1.740	75	PET	3.6	21x
P	15	Kα	2.014	77	PET	5	15x
S	16	Kα	2.307	85	PET	7	12x
Y	39	Lα	1.922	82	PET	6.5	13x
Zr	40	Lα	2.042	83	PET	7.2	12x
Mo	42	Lα	2.293	87	PET	9.5	9x
Ta	73	Mα	1.712	71	PET	6	12x
W	74	Mα	1.775	74	PET	6.4	12x
Hg	80	Mα	2.195	80	PET	9	9x
Pb	82	Mα	2.345	91	PET	12	8x

Galena in sulfide deposits
Spectral and spatial resolution matter!



Micro-grains of galena (PbS) besides other minerals

A small analytical volume is crucial!

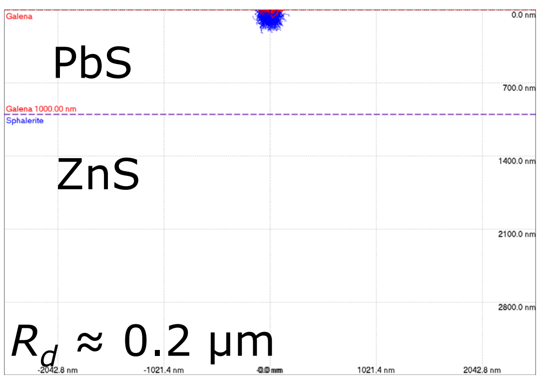
Sulfide-bearing rock from active submarine hydrothermal field at Tonga island arc (SO192/2)

Sample curtesy of Dr. Manuel Keith, GeoZentrum Nordbayern, Erlangen, Germany

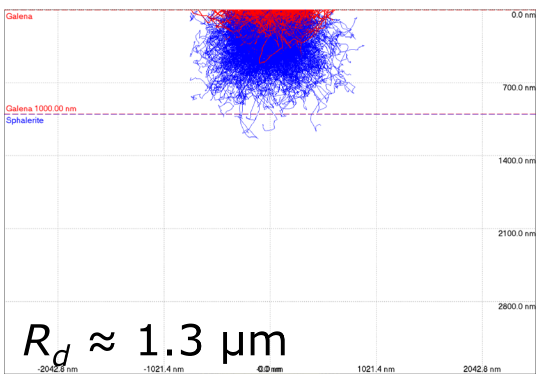
Galena in sulfide deposits
Effect of HV on spatial resolution

- Monte Carlo electron-trajectory simulations of interaction volume in galena as function of primary beam energy

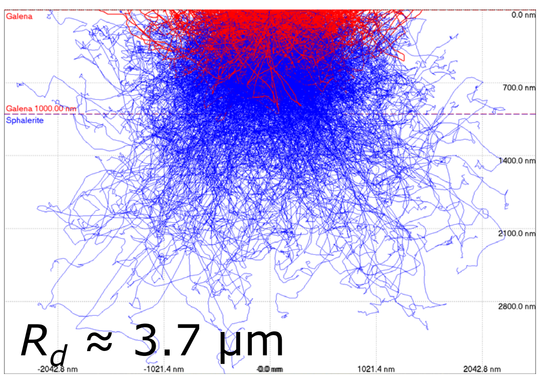
EHT = 5 kV



EHT = 15 kV



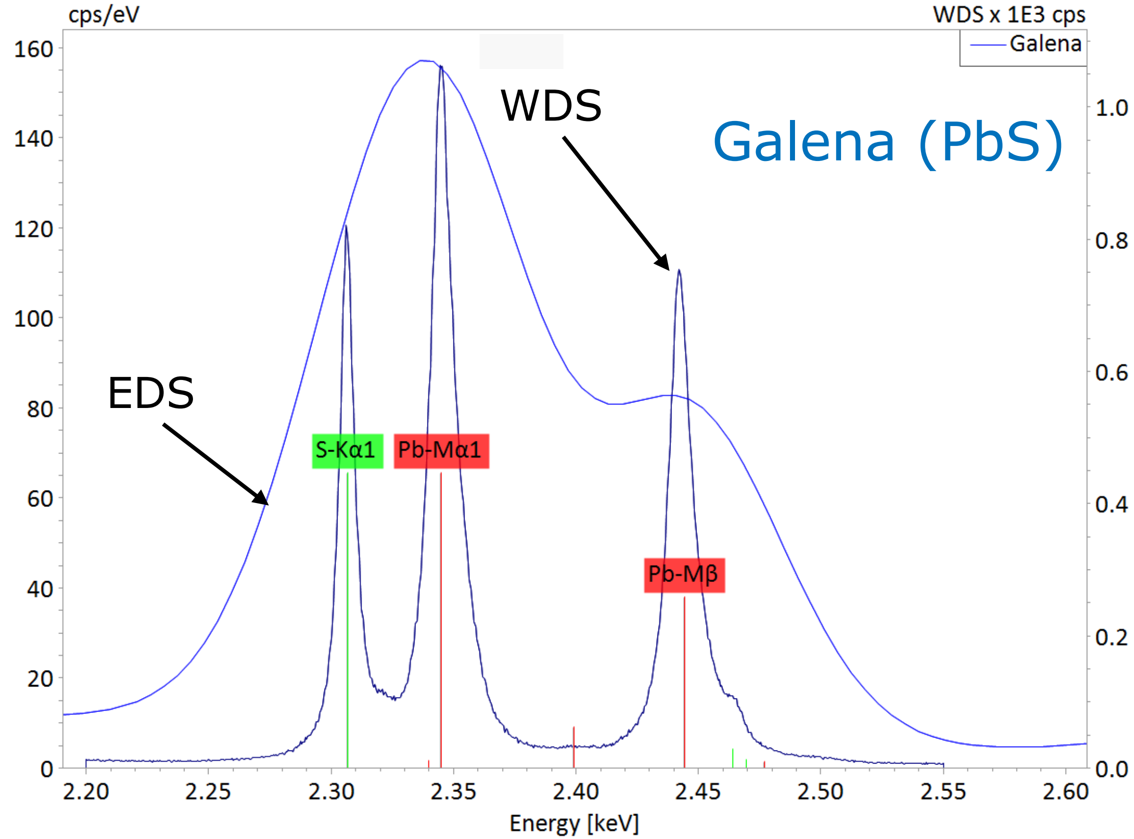
EHT = 25 kV



Casino v.2.5.1

→ With higher primary electron energy penetration depth is increasing and spatial resolution of the analysis is decreasing

Galena in sulfide deposits
Spectral resolution of WDS vs. EDS



Δ S-Kα – Pb-Mα: 38 eV

WDS resolves the individual peaks of S and Pb in the X-ray spectrum

Element line	FWHM EDS [eV][1]	FWHM WDS [eV][2]
S-Kα	85	6.0
Pb-Mα	91	11.9

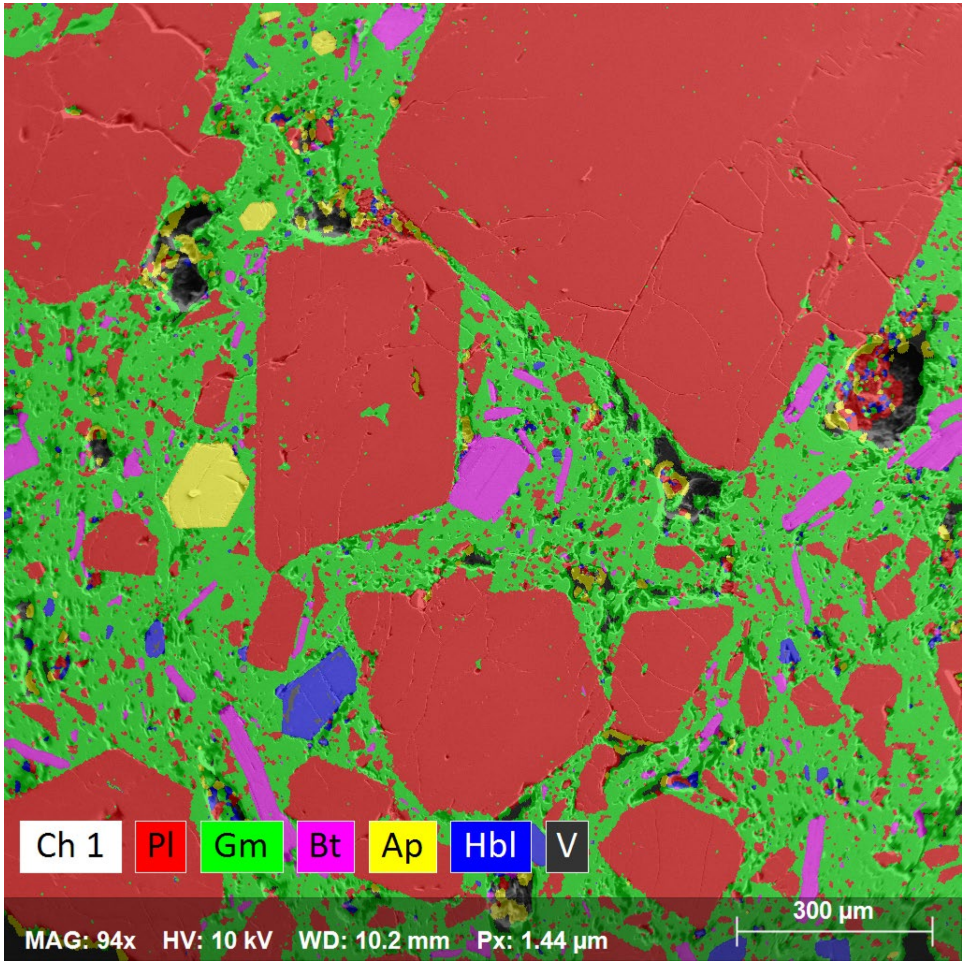
1 = determined on XFlash 6|30 using peak fitting for α and β line separation

2 = determined with a PET and XSense

Galena in sulfide deposits
Quantitative results by QUANTAX WDS

	Mass %			Normalized mass %		Atomic mass %	
Spectrum	**S**	**Pb**	**Sum**	**S**	**Pb**	**S**	**Pb**
Spectrum 1	13.41	86.04	99.46	13.49	86.51	50.19	49.81
Spectrum 2	13.14	85.30	98.43	13.35	86.65	49.88	50.12
Spectrum 3	13.30	85.44	98.74	13.47	86.53	50.14	49.86
Spectrum 4	13.46	86.35	99.81	13.48	86.52	50.18	49.82
Spectrum 5	13.35	85.49	98.84	13.51	86.49	50.23	49.77
Spectrum 6	13.40	86.06	99.46	13.47	86.53	50.15	49.85
Spectrum 7	13.51	85.32	98.84	13.67	86.33	50.57	49.43
Spectrum 8	13.29	86.59	99.88	13.31	86.69	49.79	50.21
Spectrum 9	13.36	85.96	99.32	13.45	86.55	50.10	49.90
Spectrum 10	13.45	85.70	99.16	13.57	86.43	50.35	49.65
Mean (n=10)	**13.37**	**85.83**	**99.19**	**13.48**	**86.52**	**50.16**	**49.84**
Sigma	**0.11**	**0.45**	**0.48**	**0.10**	**0.10**	**0.22**	**0.22**
SigmaMean	**0.03**	**0.14**	**0.15**	**0.03**	**0.03**	**0.07**	**0.07**

Trace element Sr in plagioclase
High resolution and sensitivity required!



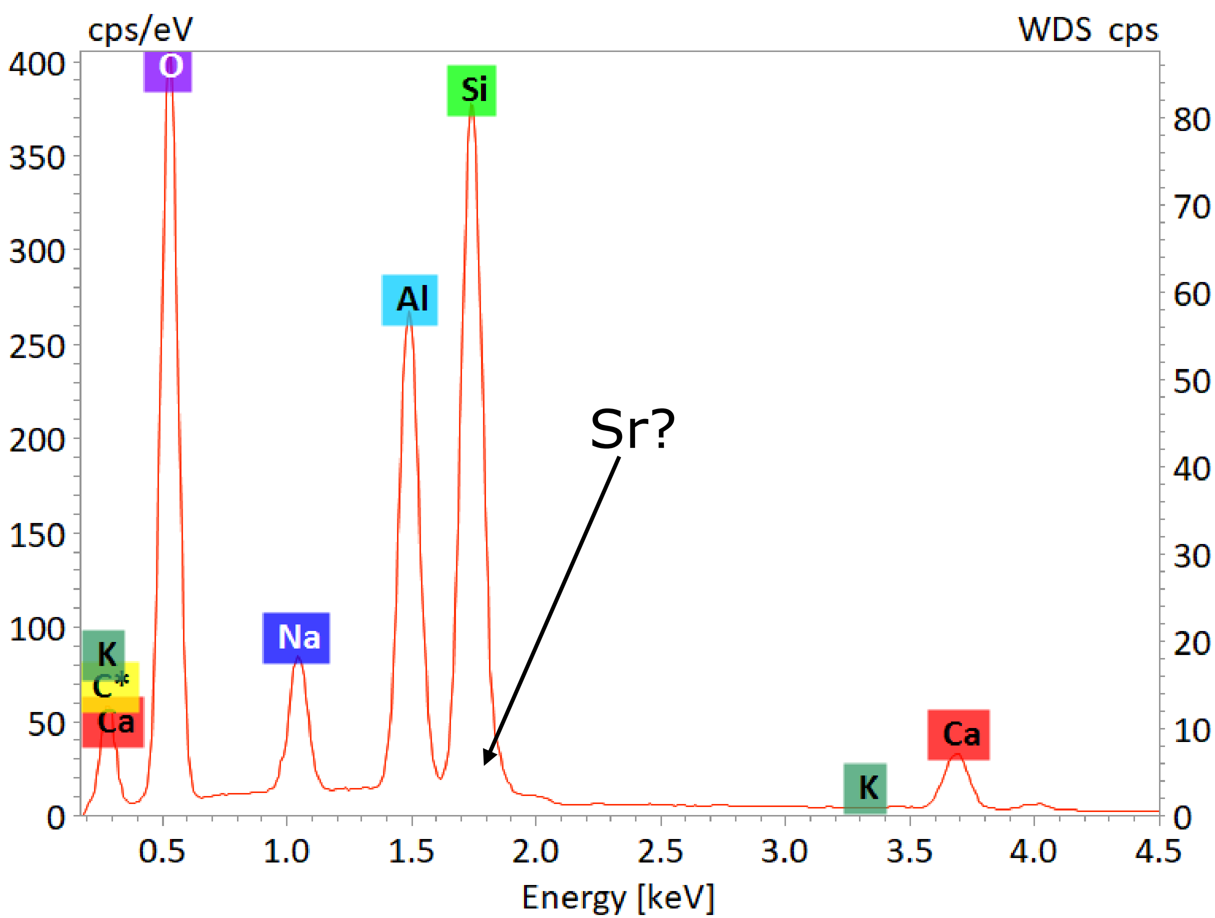
EDS phase map

Plagioclase is the major mineral phase in this volcanic rock

Trachyte from Savo in the Solomon Islands (SW Pacific)

Sample curtesy of Dr. Daniel Smith, University of Leicester, UK

Trace element Sr in plagioclase
EDS spectrum

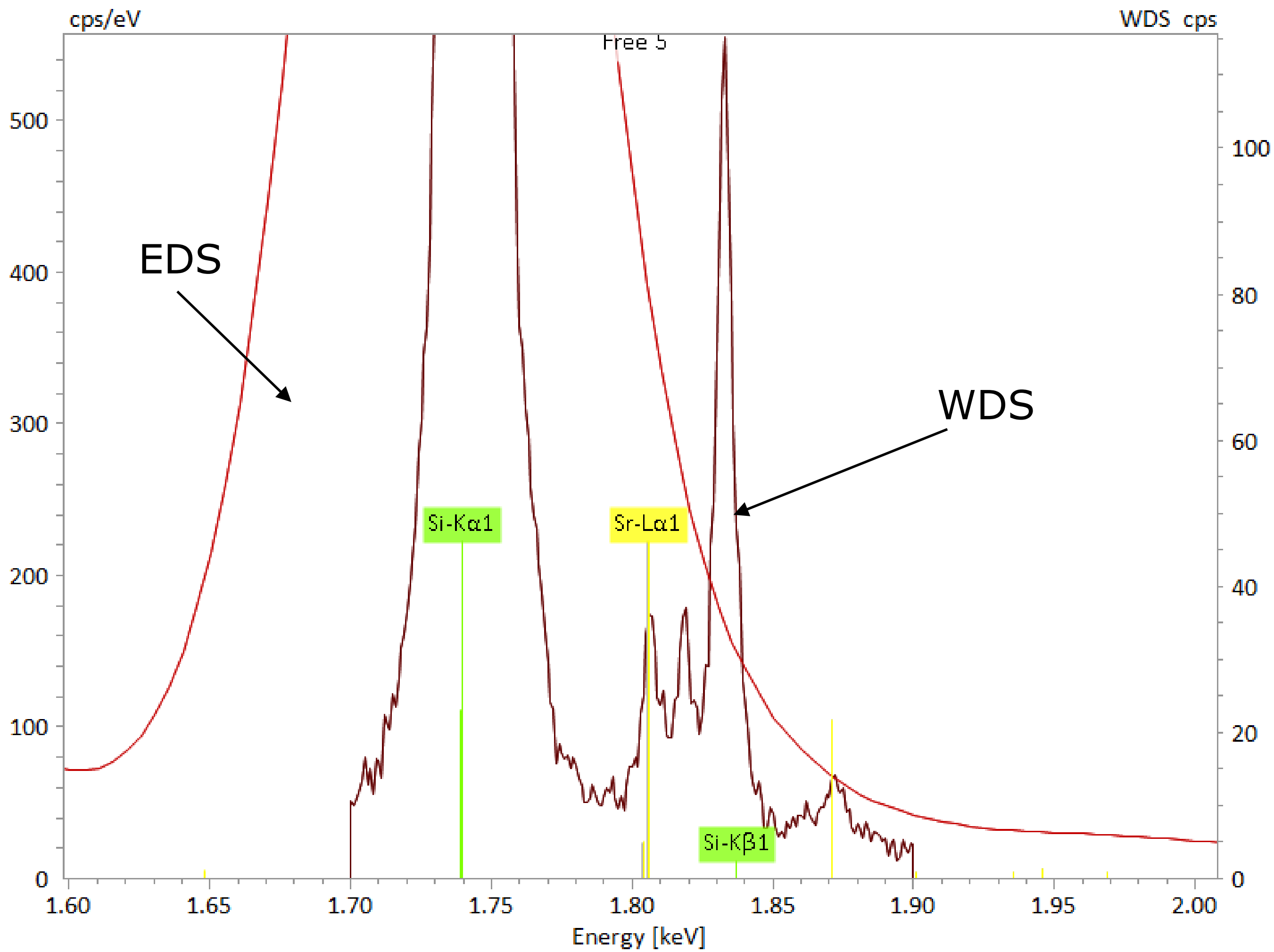


Sr may be a trace element in plagioclase

Difficult to determine by EDS

EDS spectrum of an oligoclase

Trace element Sr in plagioclase
Spectral resolution of WDS vs. EDS

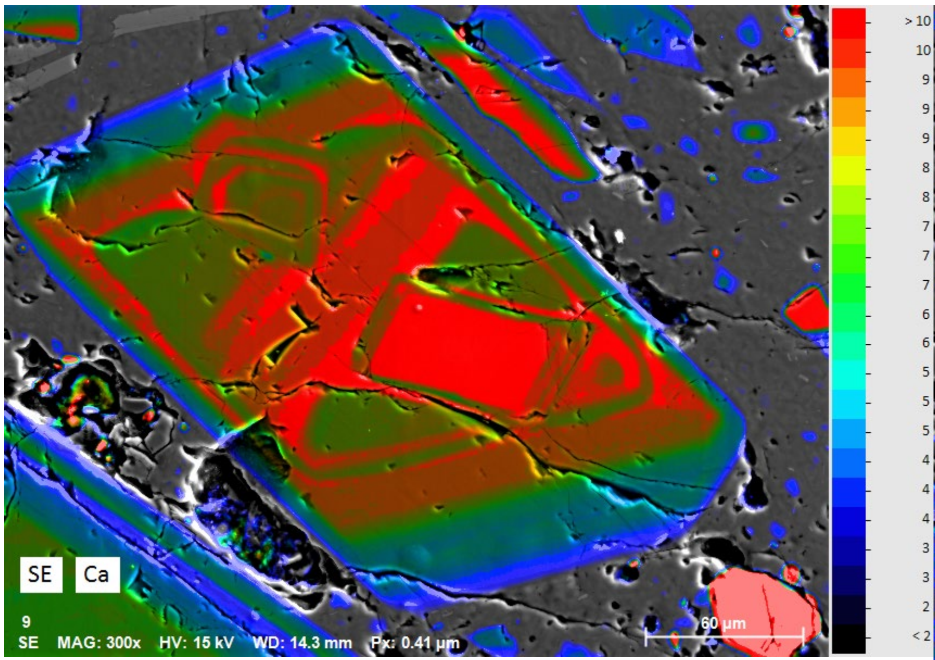


Resolution:
FWHM Si-Kα
EDS: 70 eV
WDS: 3.5 eV

Consequence:
WDS can detect very small Sr-L peaks in plagioclase

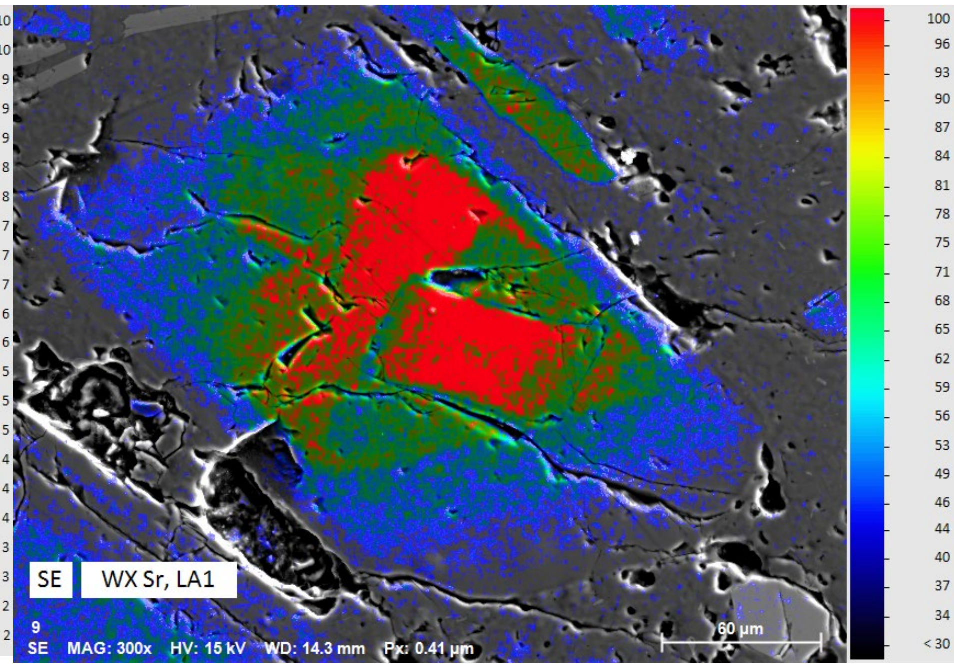
Trace element Sr in plagioclase
Combined mapping by EDS & WDS

EDS



Major element Ca

WDS



Trace element Sr

Combining EDS and WDS provides comprehensive information

Summary of todays Webinar
QUANTAX WDS

- Principles of PB WDS on SEM
- High spectral resolution
- Major to trace element determination
- Qualitative and quantitative analyses
  - Objects (points)
  - Profiles
  - Mapping
- Can be used alone or in combination with EDS
- A powerful tool for analyzing geological samples

Q&A

Are There Any Questions?

Please type in the questions you might have

in the Q&A box and press *Send*.

Innovation with Integrity