Spectro-Spatial phase analysis applied to S.E.M. mappings of building materials *Concepts & Cases of application*

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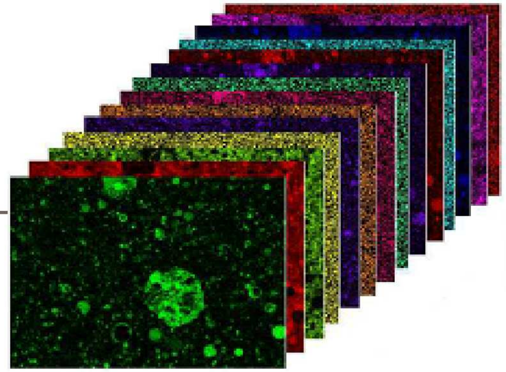
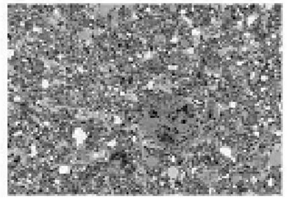
LafargeHolcim

12/ 05 / 2016

This presentation is about…

- Cement / building materials microstructures
- How satellite IA techniques helped us in microstructure understanding
  - HYPER/MULTI–spectral image analysis
- Phase Clustering…..
- An 'industrial' point of view…
  - related to the ue of SEM in order to resolve a key question
- X-Ray mapping
  - An easy method to localize main chemical elements
  - Now (very) fast !!
  - Most of time (90% ?), simply using it for visualization…(ex: where is the sulfur ?)

LafargeHolcim: a new group at a glance

90
countries

2,500
operations

32.6
billion CHF net sales

115,000
employees

Listed on the Swiss stock exchange SIX and Euronext

All figures on Pro Forma basis, for the year ended December 31, 2014.

More than 180 years of experience … and over 125 in R&D

R&D

- **1833** — Lafarge founded in Ardèche, France
- **1864** — Lafarge contributes to construction of Suez Canal
- **1887** — Lafarge sets up the world's first cement research laboratory
- **1912** — Holcim founded in Holderbank, Switzerland
- **1920–1945** — Holcim invests in cement companies in Europe and beyond
- **1945–1960** — Holcim invests in North and Latin America
- **1970–1990** — Holcim continues expansion
- **1980** — Lafarge develops high-performance concretes
- **1990** — Lafarge Research center established
- **2001** — Name of the group changed from Holderbank to Holcim — Lafarge acquires Blue Circle
- **2008** — Lafarge acquires Orascom Cement
- **2015** — Merger of Holcim and Lafarge

Optical Microscopy

First SEM

Le Chatelier PhD

LafargeHolcim


A story borned not so far away !
AVIGNON
Le Teil plant (Ardèche) - Now

Direct CO_2 emissions in Cement Manufacture (critical issue)

In 2014 total world annual production of cement was about 4000 millions T.

CO_2 from Limestone calcination	**≈ 510 kg/t clinker**
(fairly constant from plant to plant)	**+**
CO_2 from fuel combustion	**≈ 315 kg/t clinker**
(larger variations from plant to plant)	**=**
Direct CO_2 emissions for clinker	**≈ 825 kg/t clinker**
	x
Global average PC clinker content in "cementitious materials," due to addition of fillers and SCMs	**75%**
	=
Direct CO_2 emissions for cementitious materials	**≈ 620 kg/t cement**

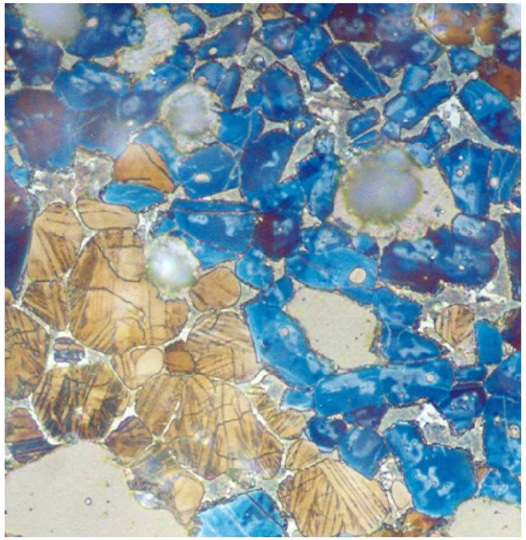
.62 t/CO_2 X 4 billions T. of cement = 2 billions T. of CO2 *(per year)*

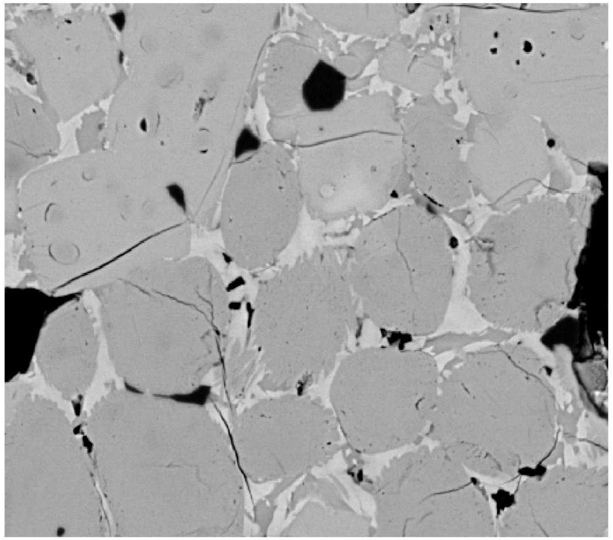
A reminder: What is cement (OPC) ?

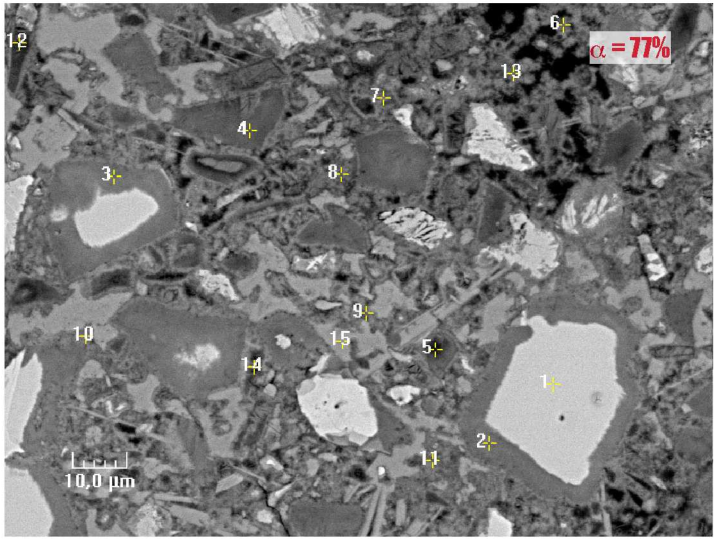
= powder of 4 mineral phases (clinker) and gypsum which react with water

 = 

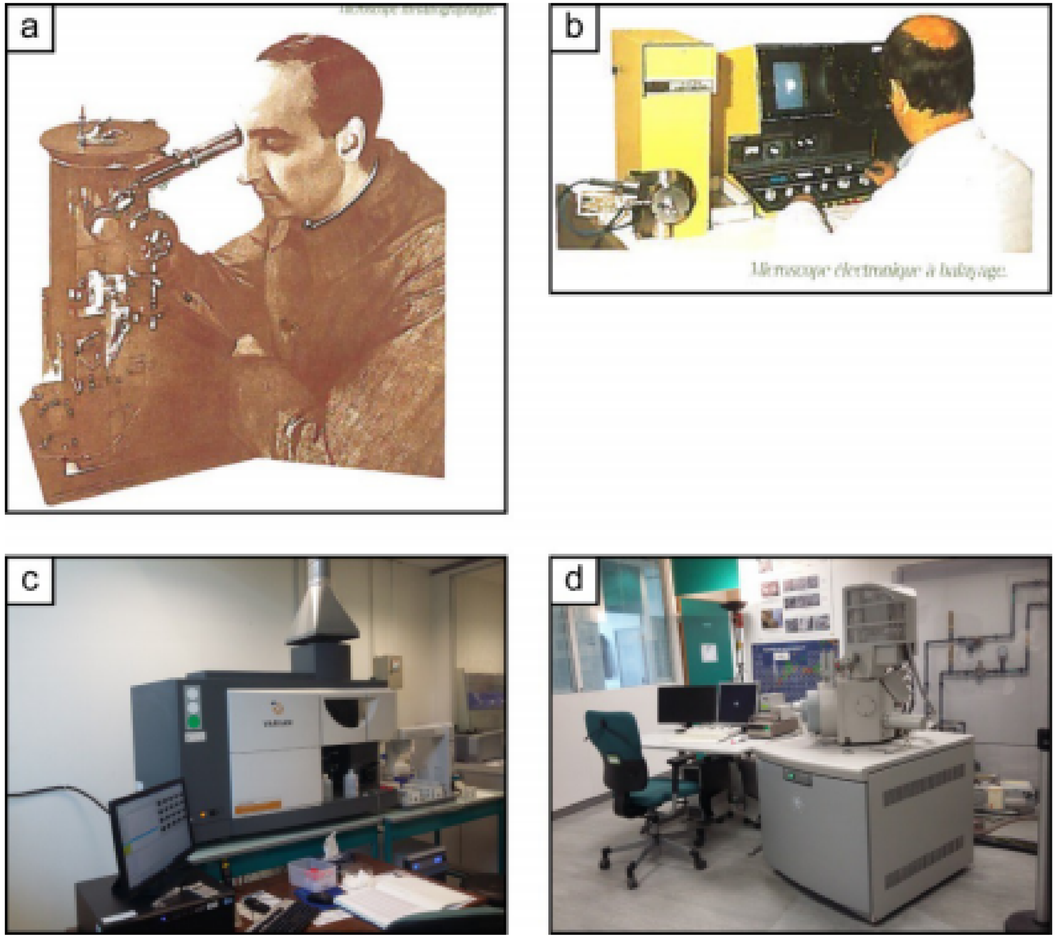
+  +  (Concrete)

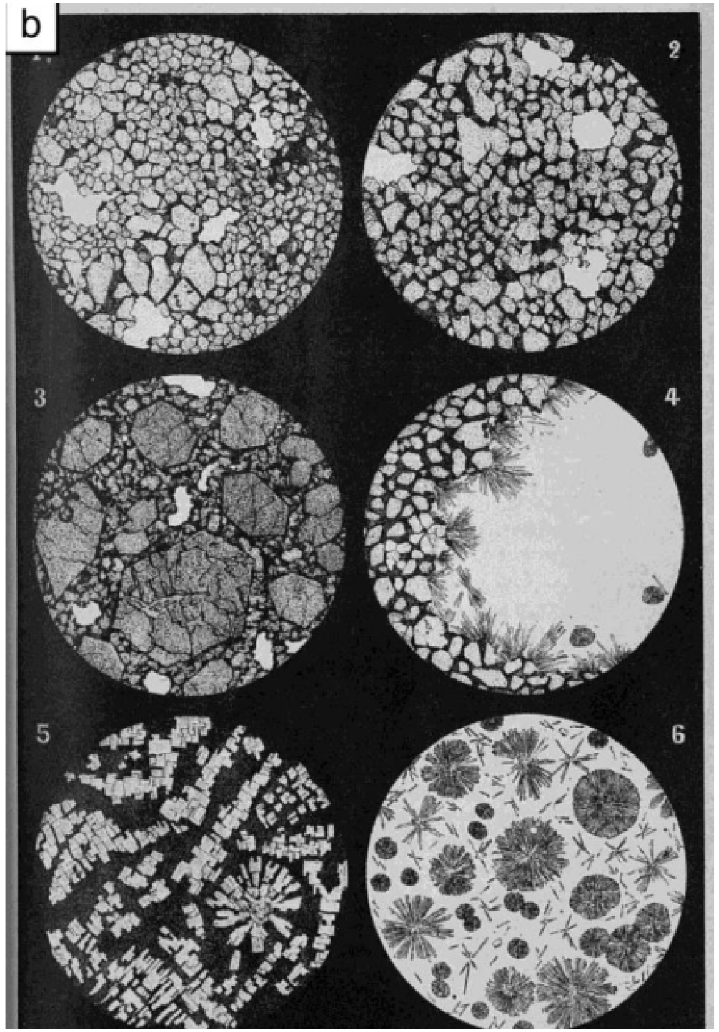




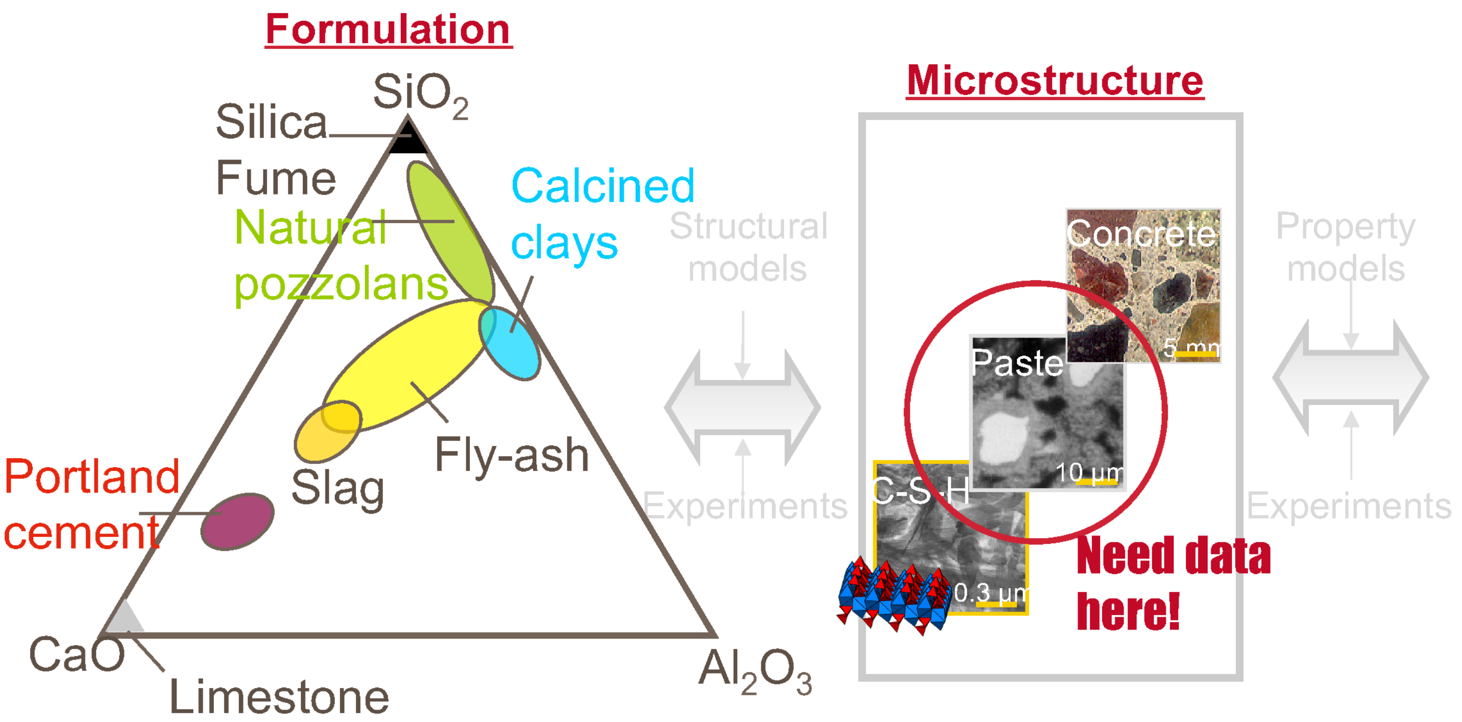


Imaging & SEM uses is a long story in cement industry





How to reduce OPC in concrete keeping durable prop. ?



Properties

Rheology
Strength
Creep, Shrinkage
Modulus
Acoustic
Thermal
Permeability
Durability

The successful use of SCMs requires that we master the formulation-microstructure-property link

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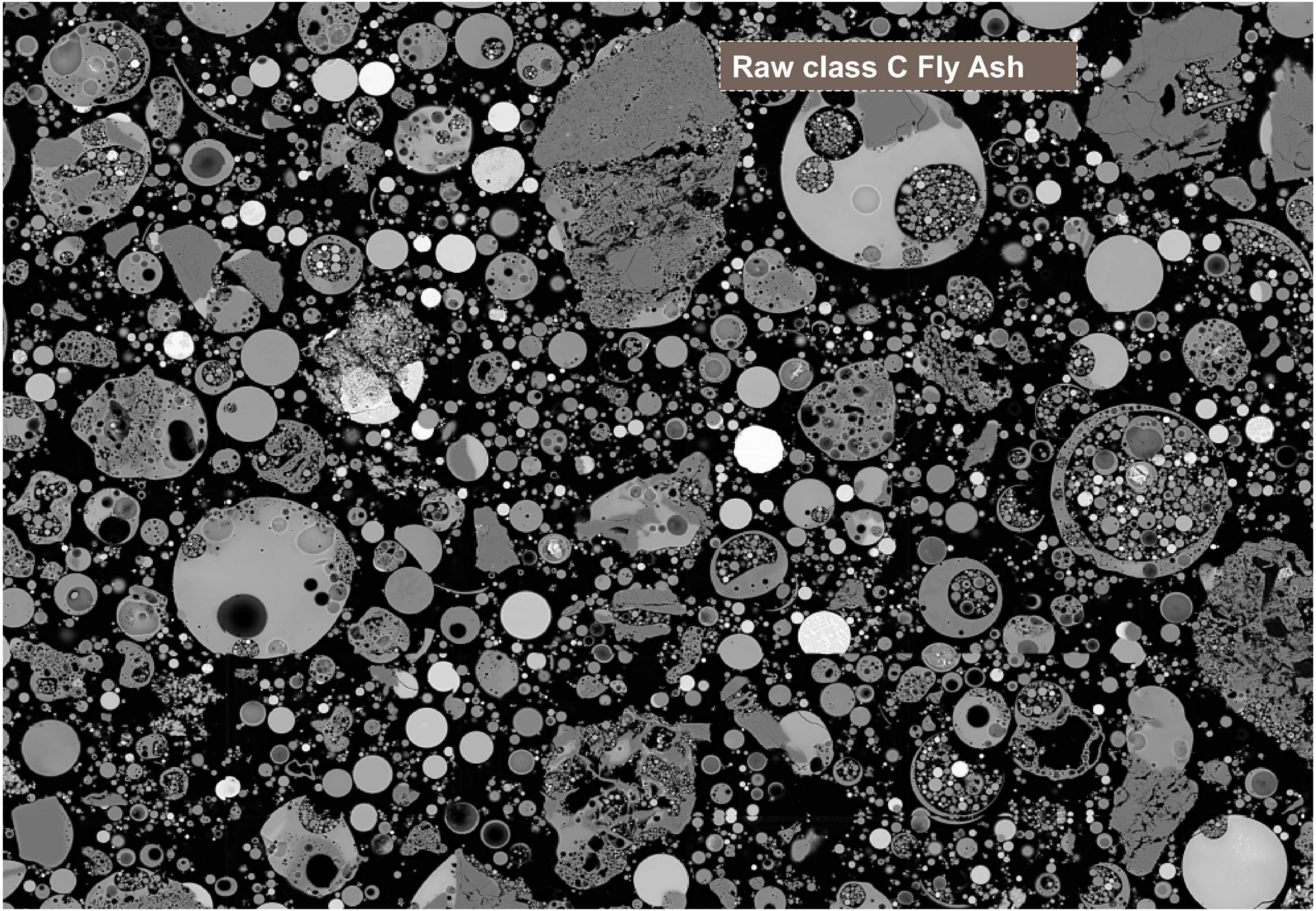
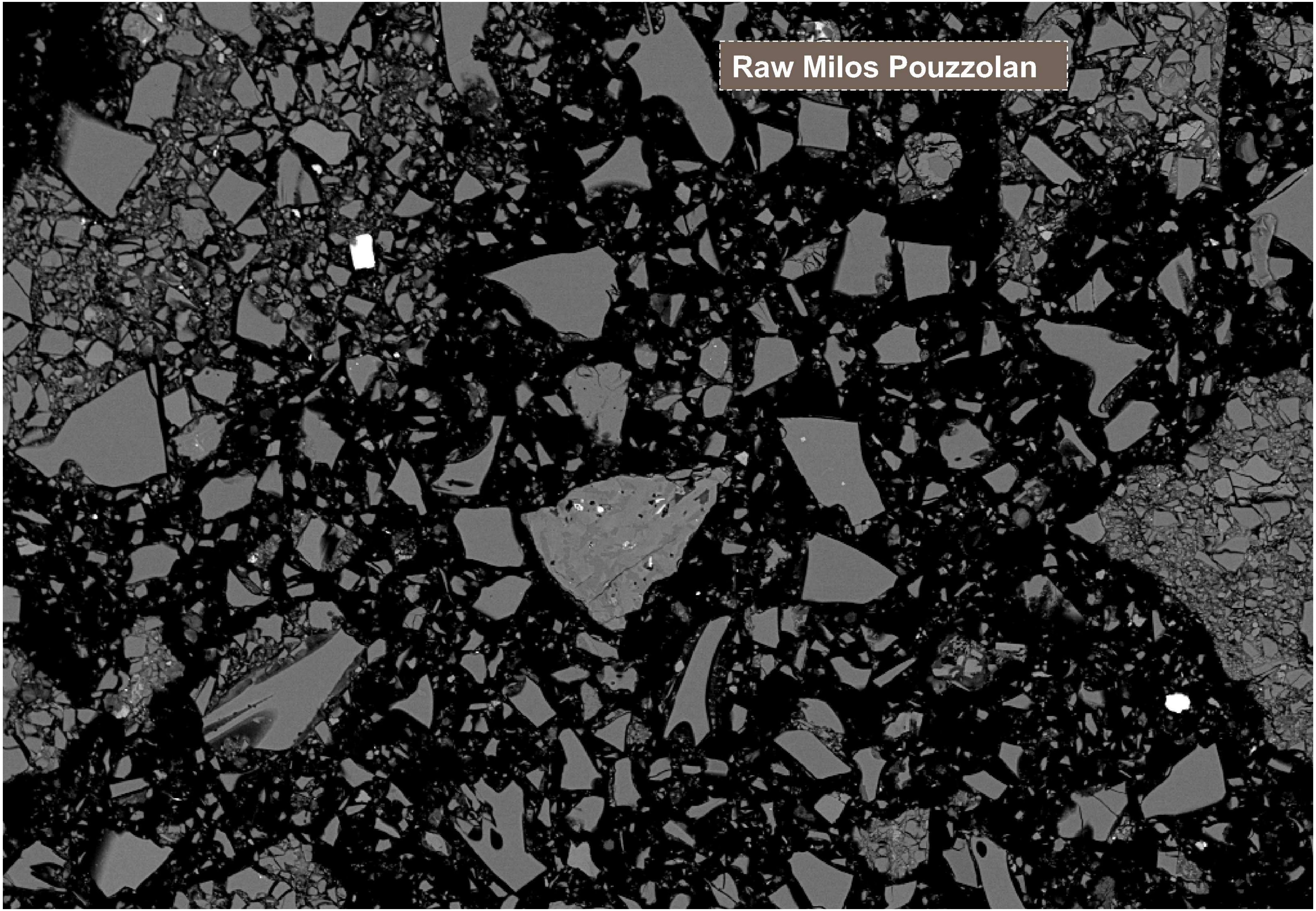
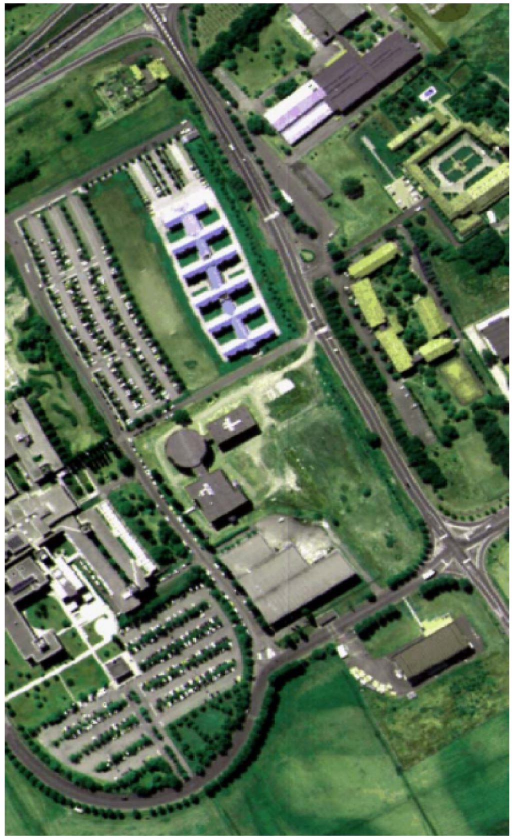

Raw class C Fly Ash


Raw Milos Pouzzolan

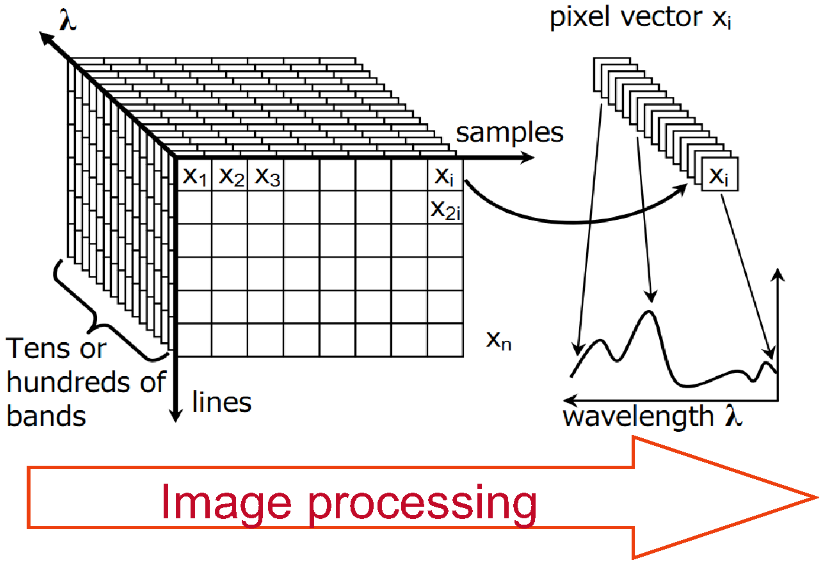

65OPC/25FA/10LF
What we want is to measure phase fraction of materials !

What can we learn from hyperspectral satellite imaging?

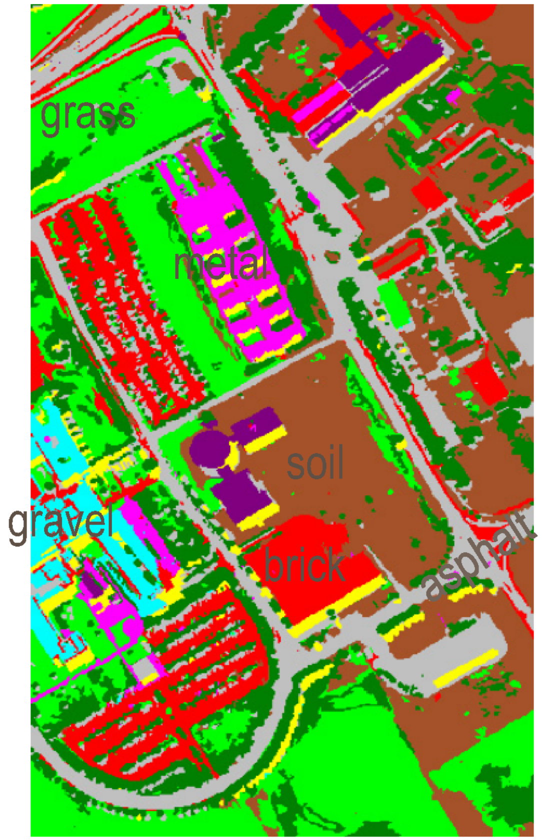
Hypespectral image of Univ Pavia, Italy



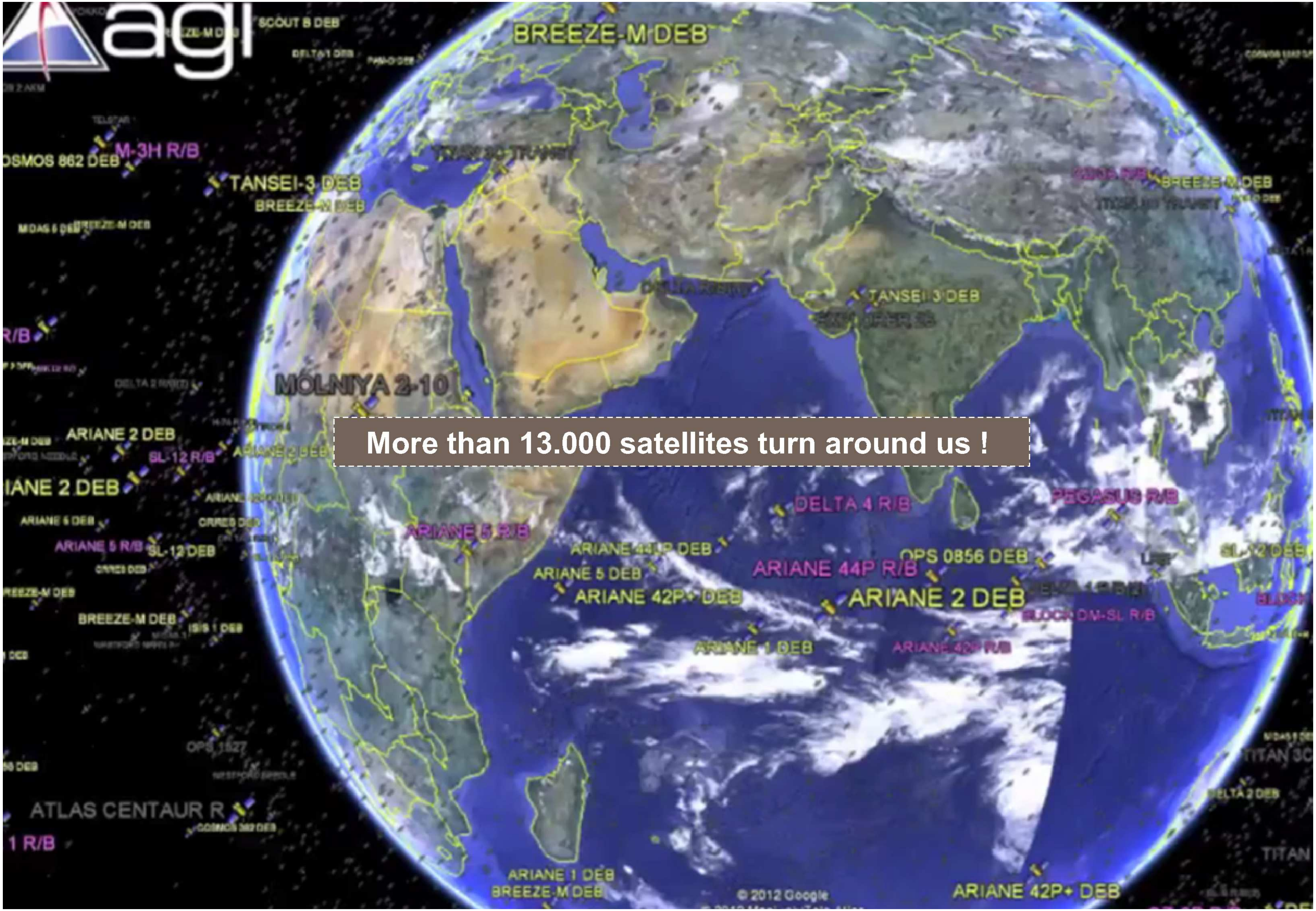
Each pixel is a vector containing a reflectance spectrum. (This is a lot of data!)



Advanced algorithms use spectral + spatial info to classify objects

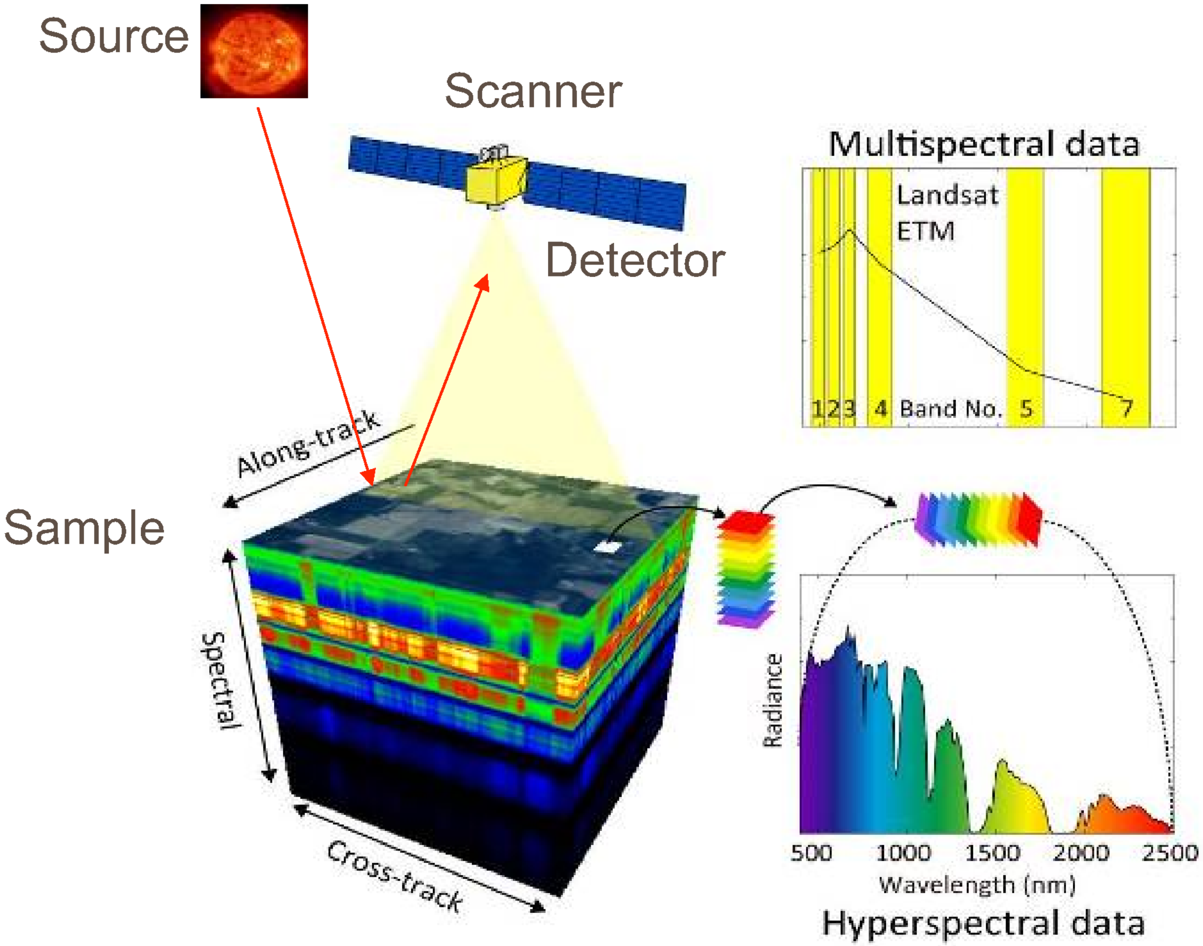


From Y. Tarabalka PhD, Univ Grenoble, 2010



More than 13.000 satellites turn around us !

Could satellite imaging tools inspire us for Building Materials ?



Think about this :

- → 3000 channels + (x,y) position

⇒3002 octets/pixel

⇒629.146 ko (614Mo) if 2000x2000 pixels for 1 image

- Suppose 1pixel=5m resolution

⇒1image = 100 km²

- Paris = 2845 km²

⇒30 images & 17 To of Data !

- USA = 10.000.000 km²=6000 To

huge quantity of Data !

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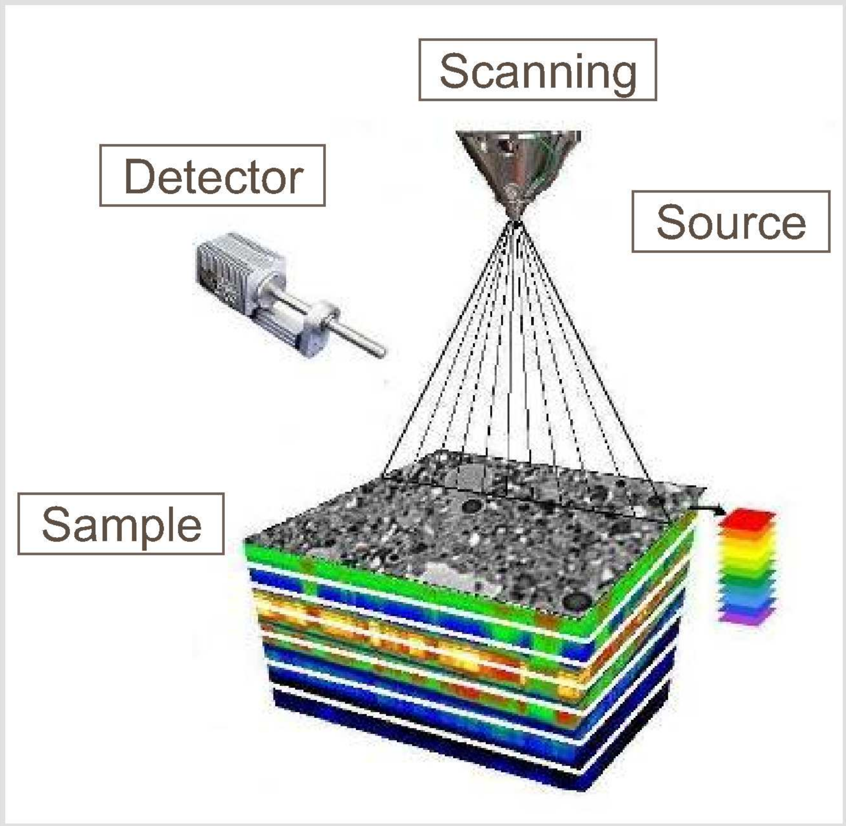
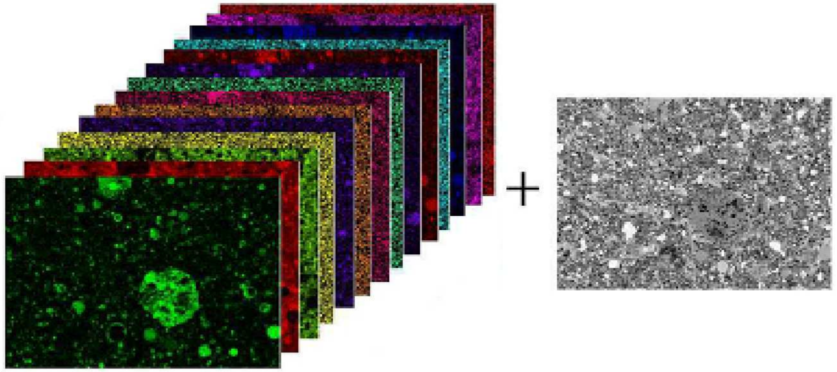
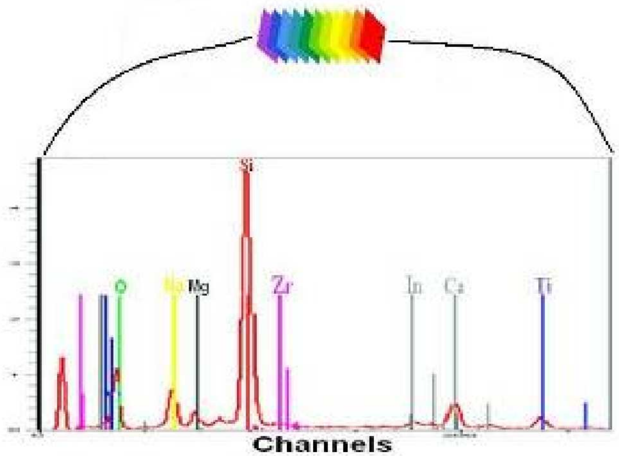
Multispectral means a few channels



Scanning Electron Microscope

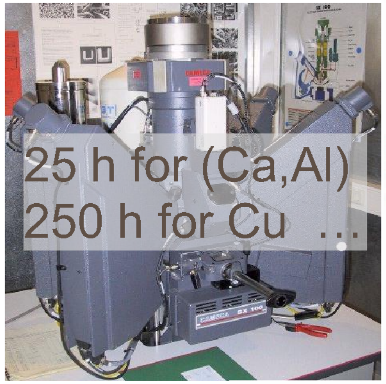


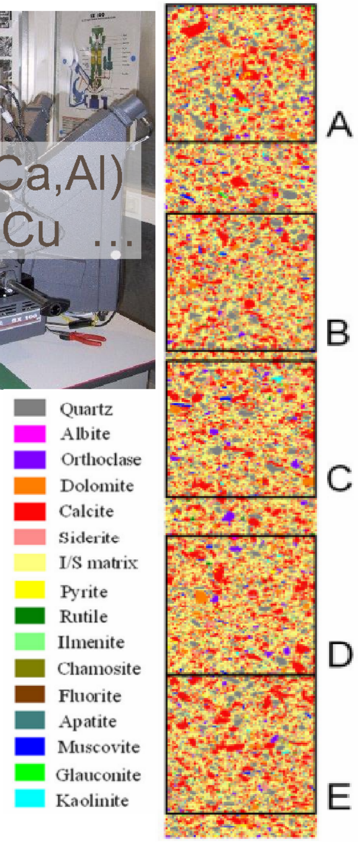


The more simplest way to do phase clustering

How to get phase Id. And clustering from our S.E.M. datasets ?

- By thresholding the grey-level histogram *(ImageJ®, FiJi®)*
  - *Observe your sample in optical microscope before SEM !*
- Full quantitative mappings
  - *If you have (lot of) time and don't need large analyzed area*
- Unsupervised classification *(K-Means, ME, Clara, etc…)*
  - *Let's the computer decide for you !*
- By combining BSE image and a selected elemental map
  - *A 'mask' is used to cluster a specific signature*
- Supervised classification ← **The solution we've chosen**
  - *Welcome to the jungle ! Complex field of knowledge but it gives the best robustness !*





*Robinet, J-C., 2008. Minéralogie, porosité et diffusion des solutés dans l'argilite du callovo-oxfordien de Bure (Meuse/ Haute-Marne, France) de l'échelle centimétrique à micrométrique, Thèse de l'université de Poitiers, France

Some free and commercial tools (non exhaustive)

- ImageJ® / FiJi ® - '*Weka*'
- Multispec®
- And all others clustering Algo in the internet ….
  - Python
  - Matlab, etc…

free

- Phase Cluster Analysis including in EDS soft.
- ENVIE® free soft.
- 'Royce Rolls' = M.L.A. *(Mineral Liberation Analysis)*

commercial

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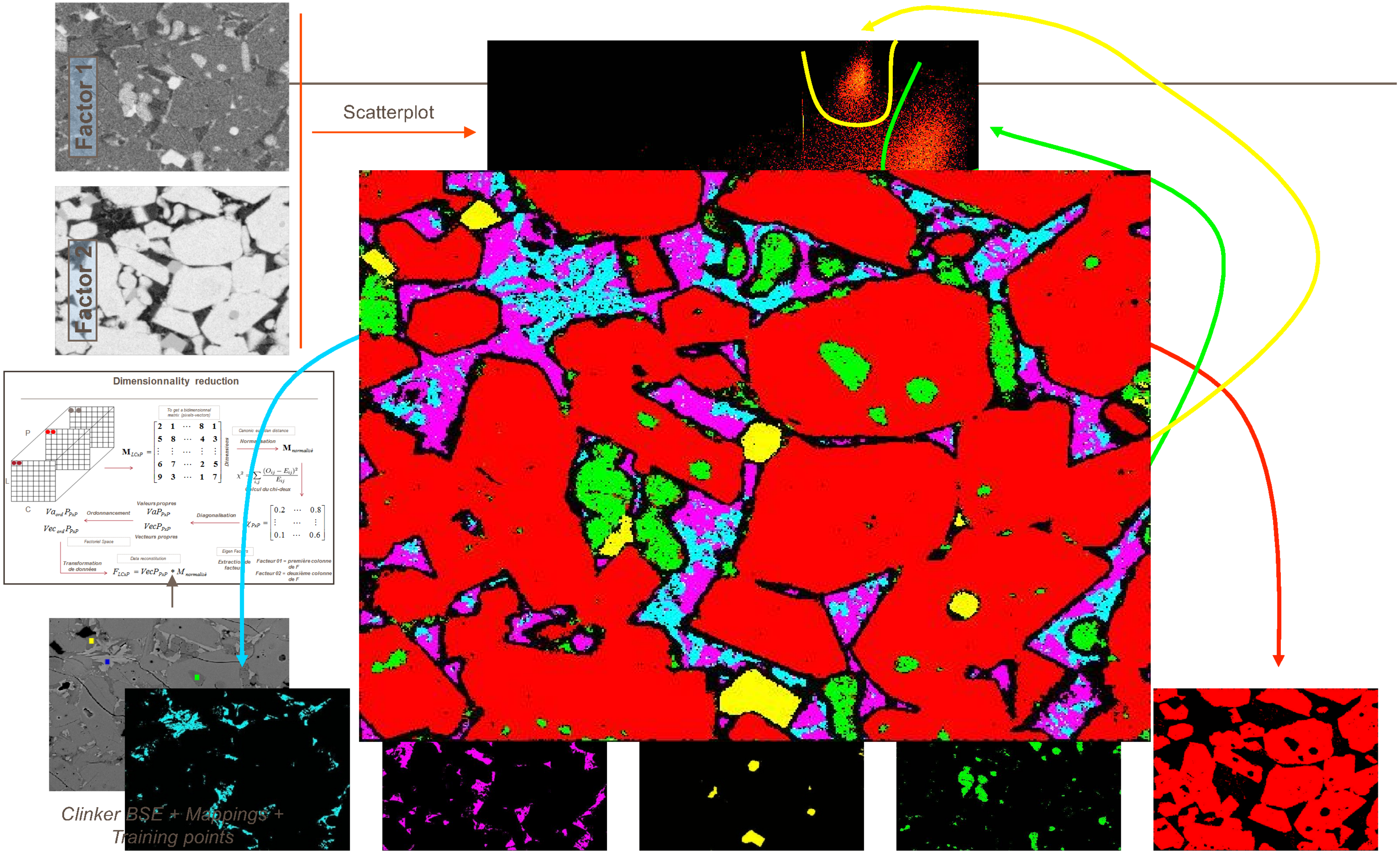
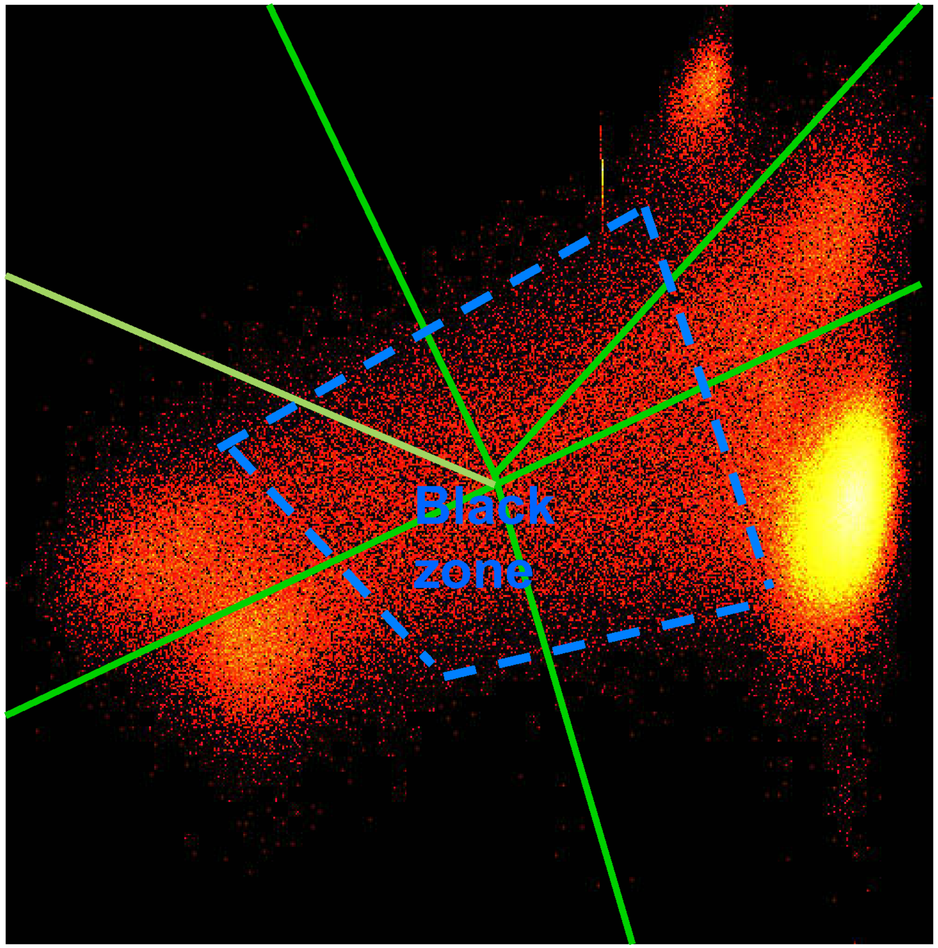
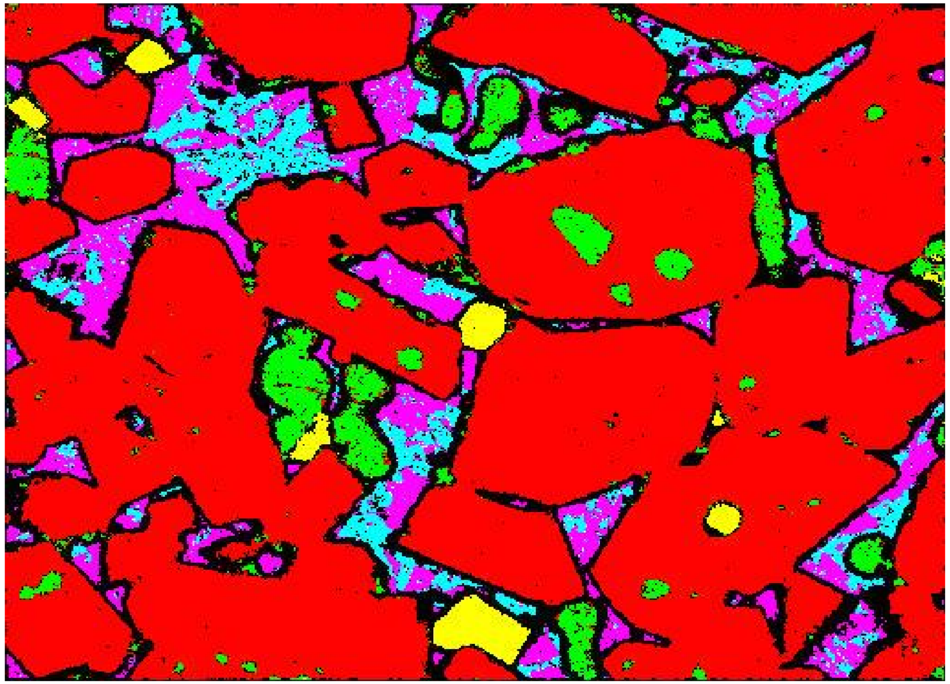
Let’s apply PCA *(‘easily’)* with SEM clinker data

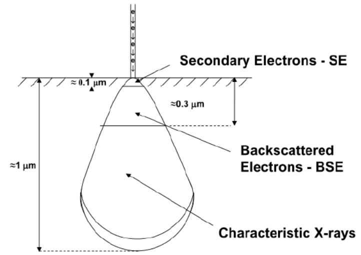


C4AF ***C3A*** ***MgO*** ***Belite*** ***Alite***

What happened near the interface of phases ?







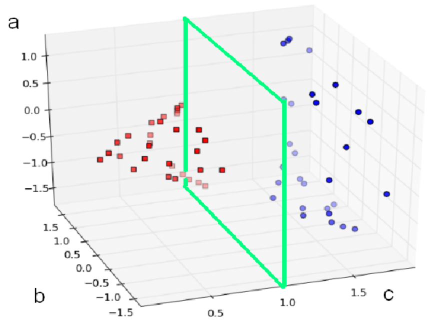
Let’s have a look on ‘Clustering’ applied to building materials

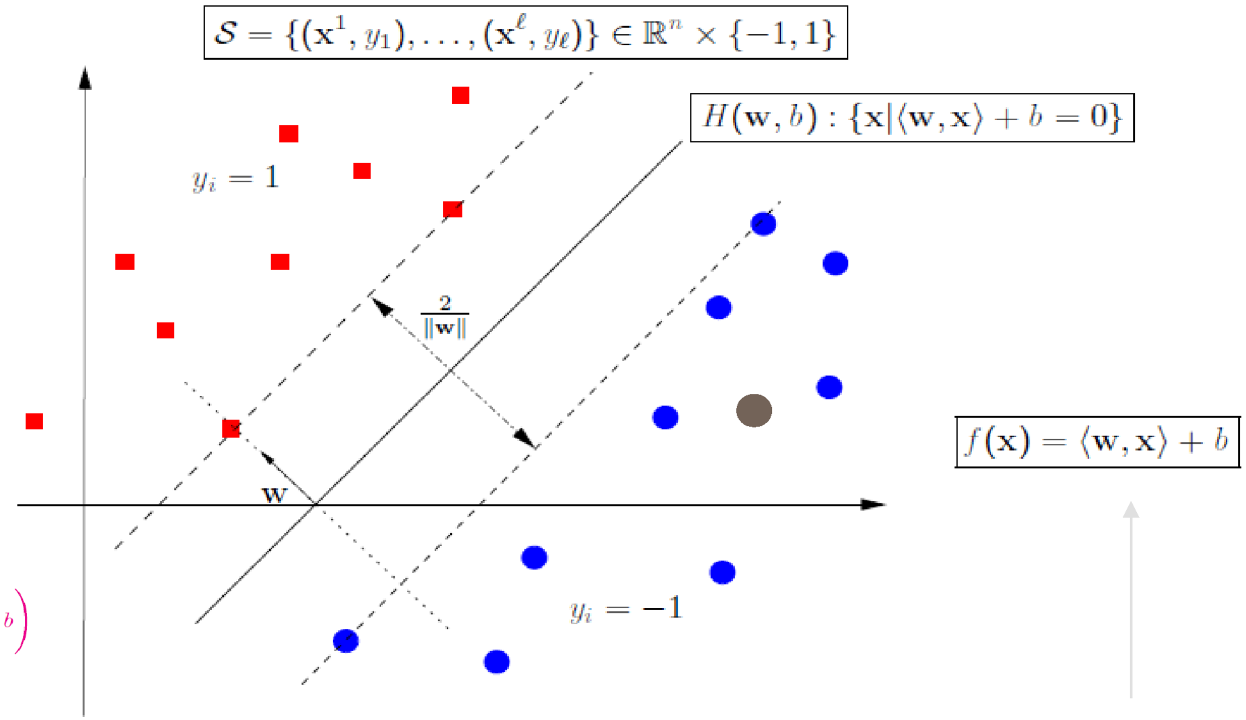
- **1994**: D.P. Bentz & P Stutzman (NIST) combined BSE & X-Ray maps for cement Quant.
- **1997**: Bonnet et al. (Mines Nancy) used PCA as a tool for clustering (rocks)
- **2003**: D.P. Bentz & P Stutzman (NIST) introduced pixel-wize classification
  - Using EDS quantitative maps, applied on clinkers & OPC
- **2003:** Pret et al. (Univ. Poitiers) used WDS quanti mapings for clustering
- **2009**: Kocaba et al. (EPFL) used Mg mapping to measure HD of slag
- **2010**: Ben Haha et al. found a grey level way to quantity fly ashes
- **2010**: Chancey et al. (Austin) used Maps & Multispec® to quantify phases in Anh-FA
- **2013**: Meulenyzer (Lafarge) introduced supervised classification using non quanti mappings of blended pastes
- **2015**: Durdinsky et al. (EPFL) used EDX quantitative maps as input for clustering
- **2015**: Munch et al. (EMPA) combined supervised classification and quanti EDS

<u>Choosing a classifier</u>: Support Vector Machines (SVM) as a tool to transform hyper-multispectral data into linearly separated set of pixels

Optimal separating hyperplane [Vapnik-98]:

- Minimize training errors over $\mathcal{S}$
- Maximize the margin $\Longleftrightarrow$ minimize $||\mathbf{w}||^2$





Decision: $g(\mathbf{x}) = \text{sgn}\,(f\,(\mathbf{x})) = \text{sgn}\left(\sum_{i=1}^{\ell} \alpha_i y_i \langle \mathbf{x}^i, \mathbf{x} \rangle + b\right)$

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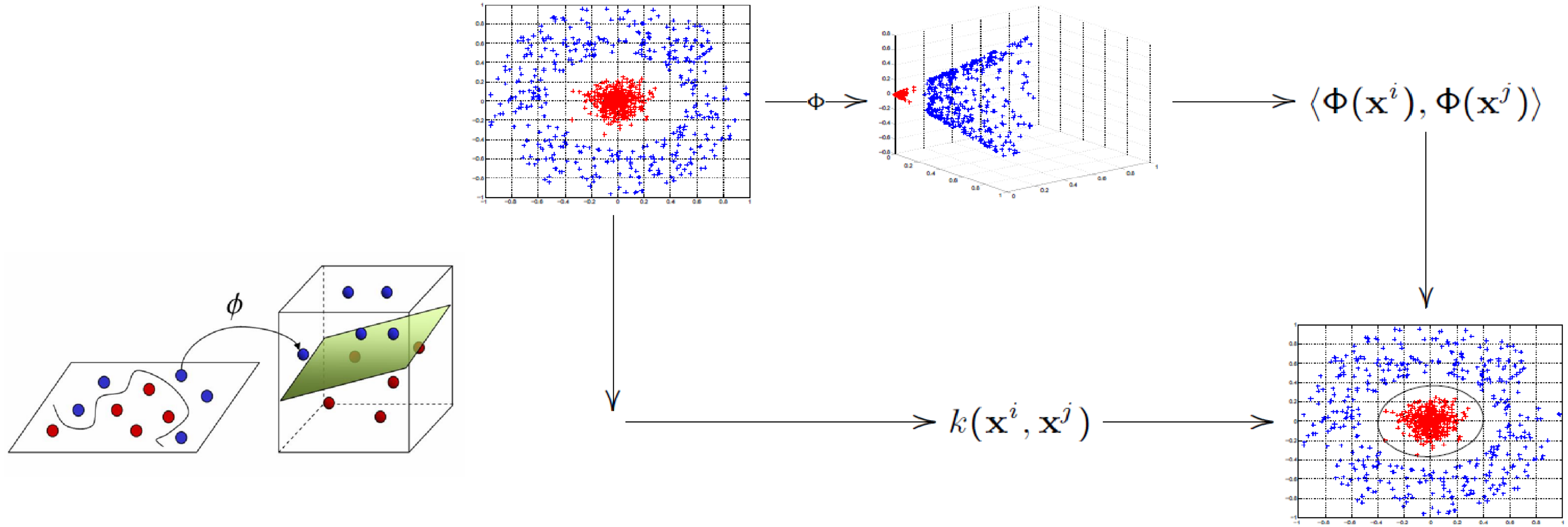
No need to know dimension of working space !

Kernel methods: Use kernel function k (positive semi-definite)

$$k(\mathbf{x}^i, \mathbf{x}^j) = \langle \Phi(\mathbf{x}^i), \Phi(\mathbf{x}^j) \rangle_{\mathcal{H}}$$

Fauvel et al., 2007*



Some kernels:

- Polynomial kernel: $k(\mathbf{x}^i, \mathbf{x}^j) = \left(\langle \mathbf{x}^i, \mathbf{x}^j \rangle + q\right)^p$
- Gaussian kernel: $k(\mathbf{x}^i, \mathbf{x}^j) = \exp\left(-\frac{\|\mathbf{x}^i - \mathbf{x}^j\|^2}{\gamma^2}\right)$

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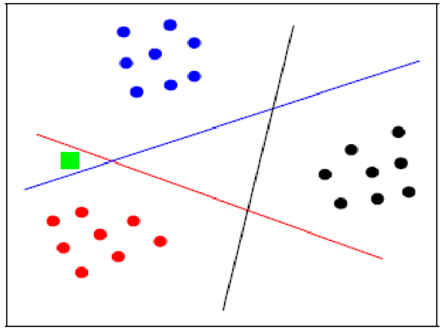
** Mathieu Fauvel, Jocelyn Chanussot, Jon Atli Benediktsson, Johannes R. Sveinsson: Spectral and spatial classification of hyperspectral data using SVMs and morphological profiles. IGARSS 2007: 4834-4837*

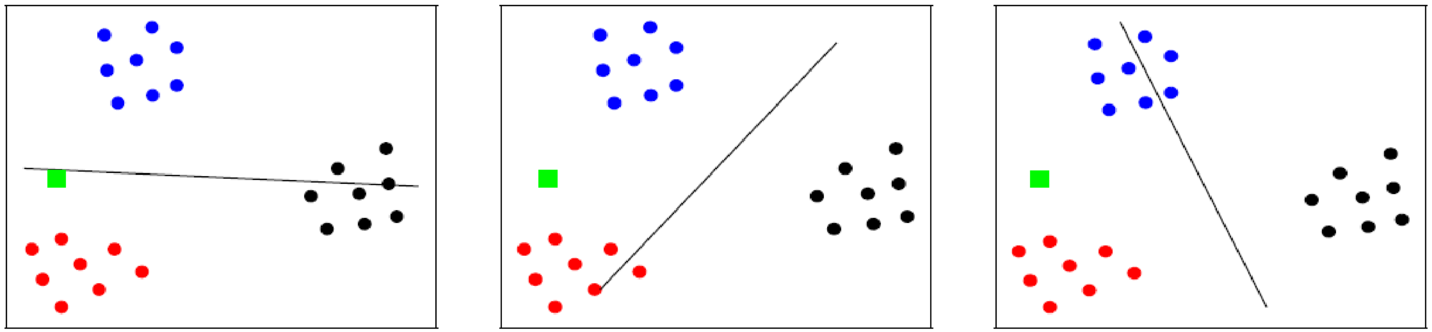
How to separate data in a multiclass problem ?

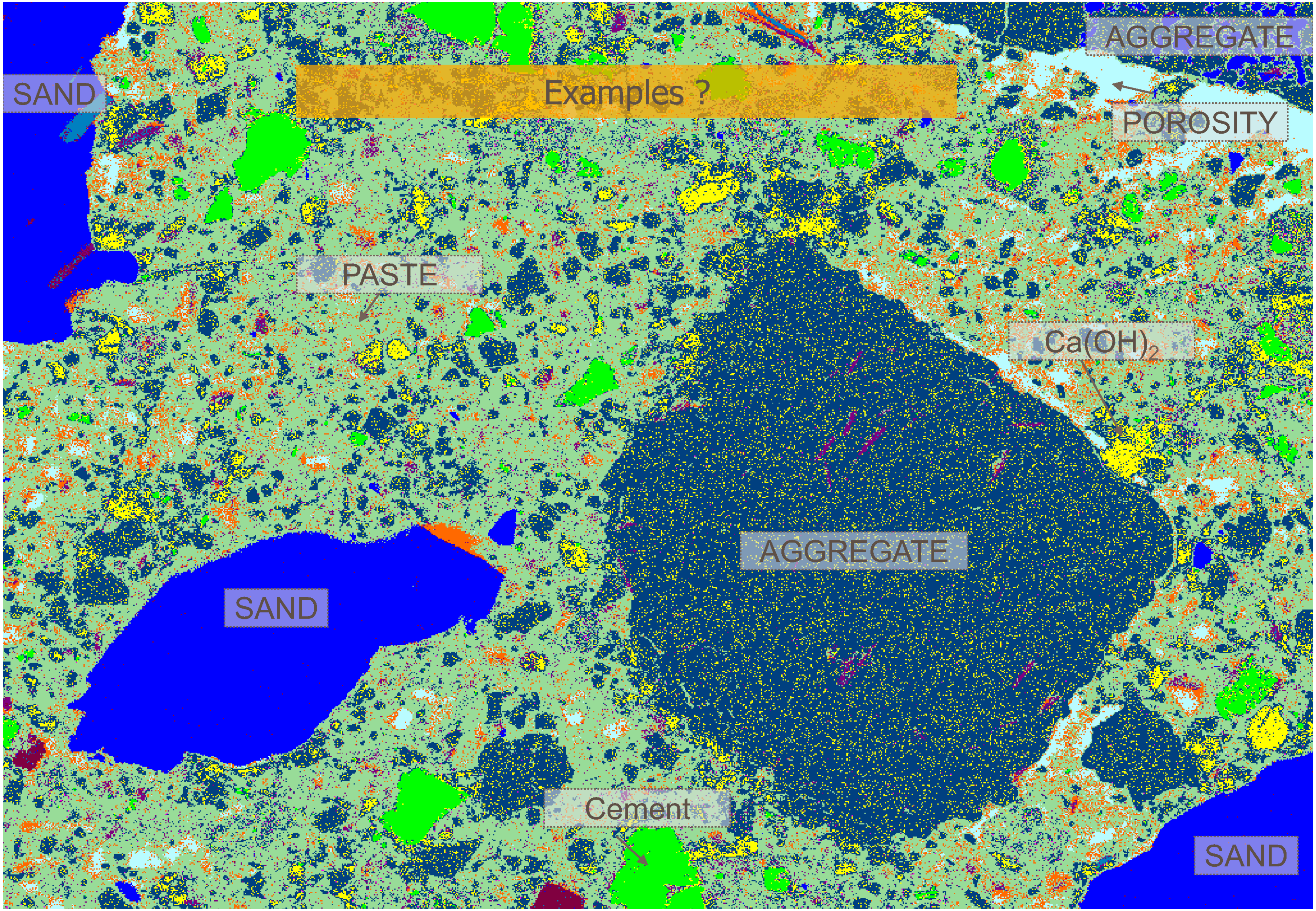
Multiclass problem: m classes

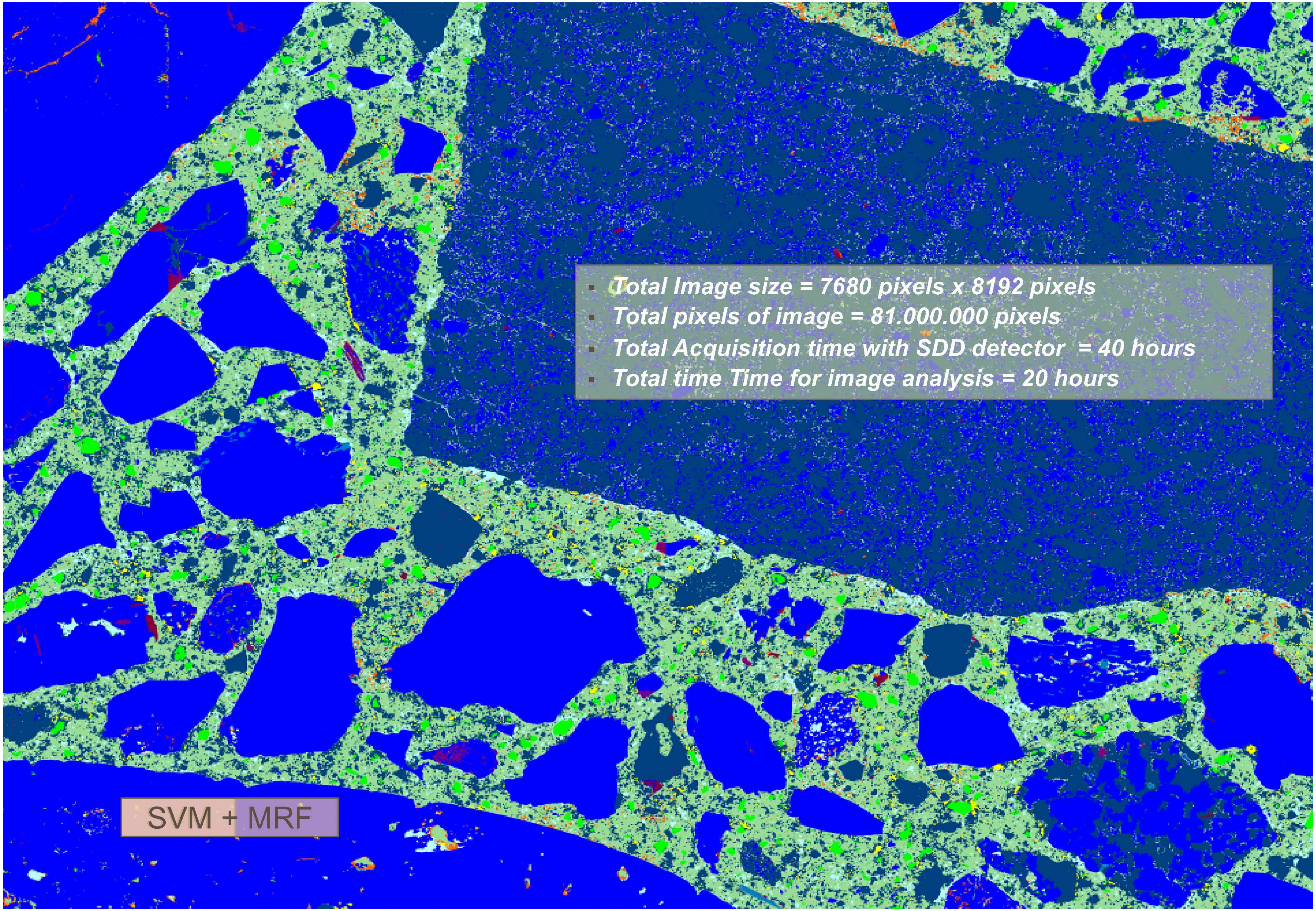
1. One versus All: m binary classifiers

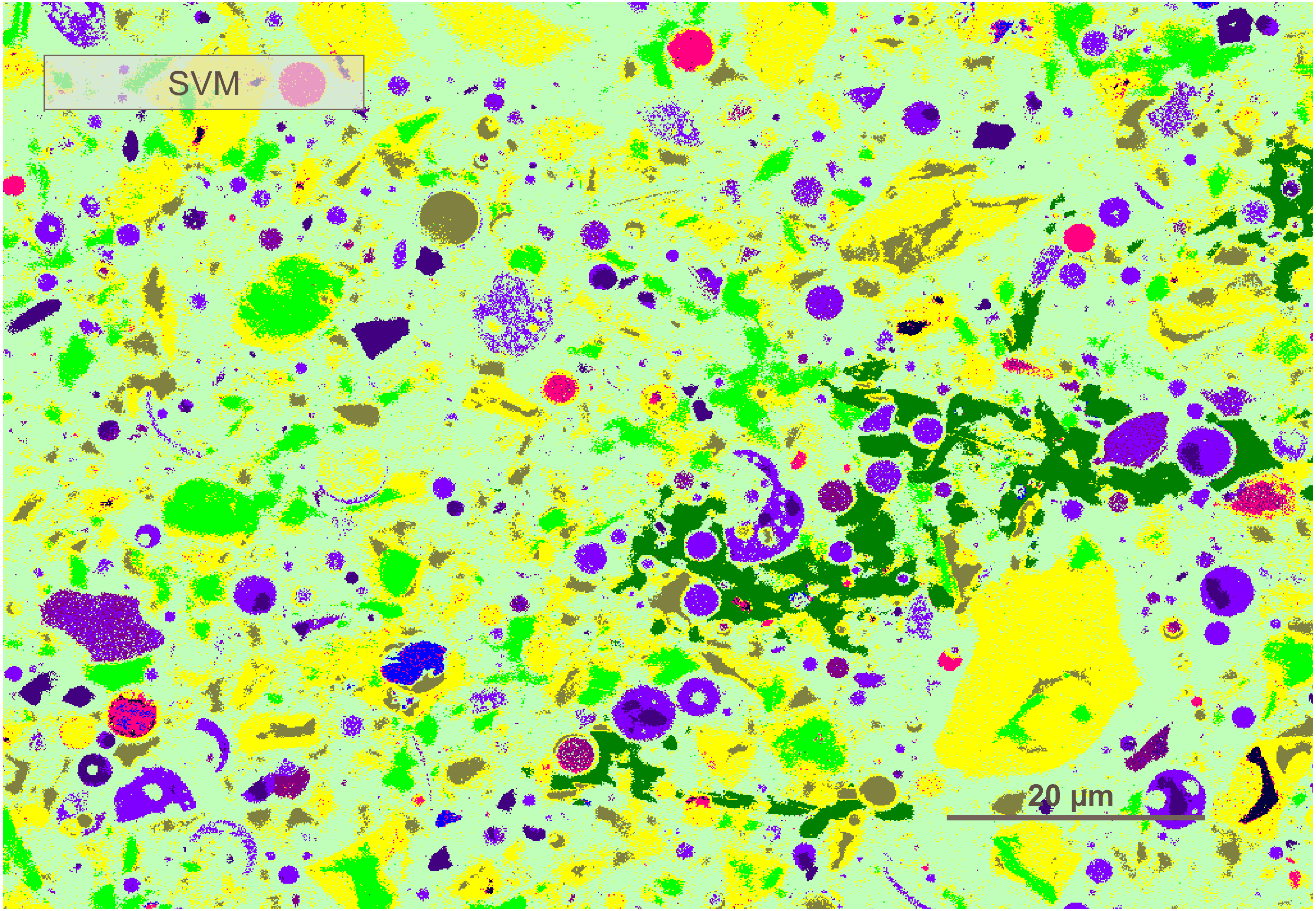


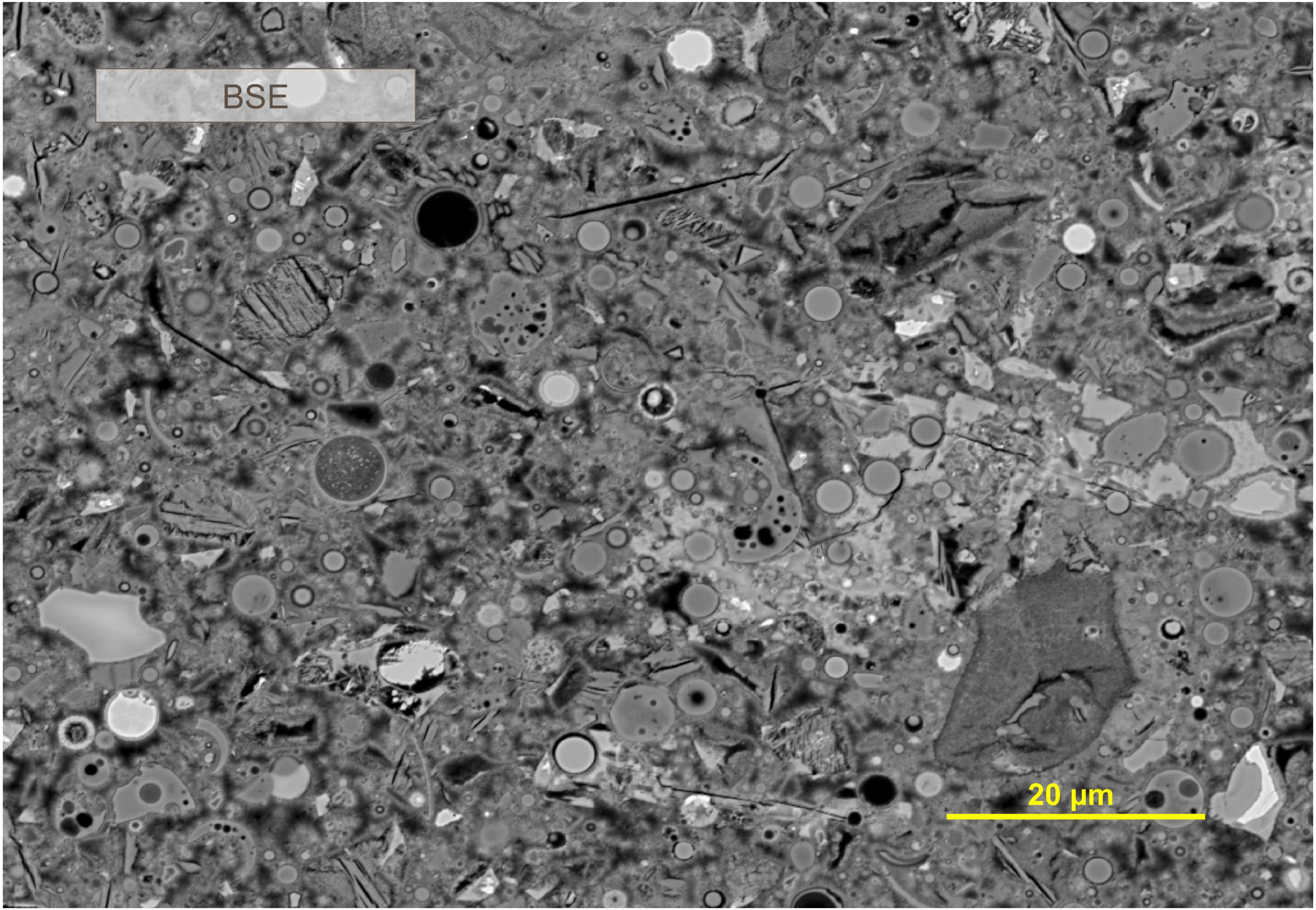
2. One versus One: m(m-1)/2 classifiers




Examples ?
SAND
AGGREGATE
POROSITY
PASTE
Ca(OH)2
AGGREGATE
SAND
Cement
SAND


Total Image size = 7680 pixels x 8192 pixels
Total pixels of image = 81.000.000 pixels
Total Acquisition time with SDD detector = 40 hours
Total time Time for image analysis = 20 hours
SVM + MRF


SVM
20 μm

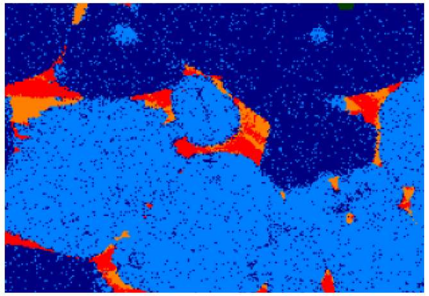

BSE
20 µm

Filtering ?

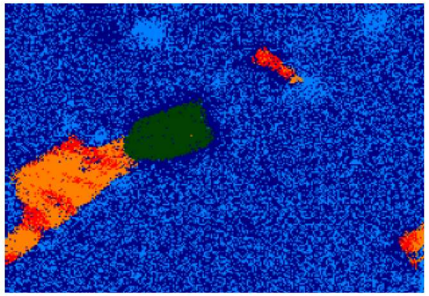
Need to incorporate information from the spatial domain

M.R.F.

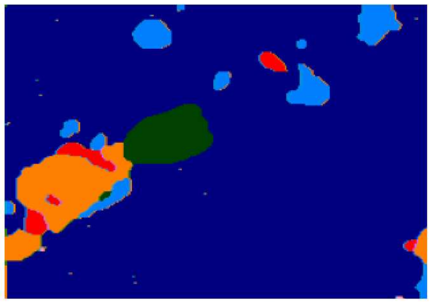
Boggle effect



Clinker with alite / belite

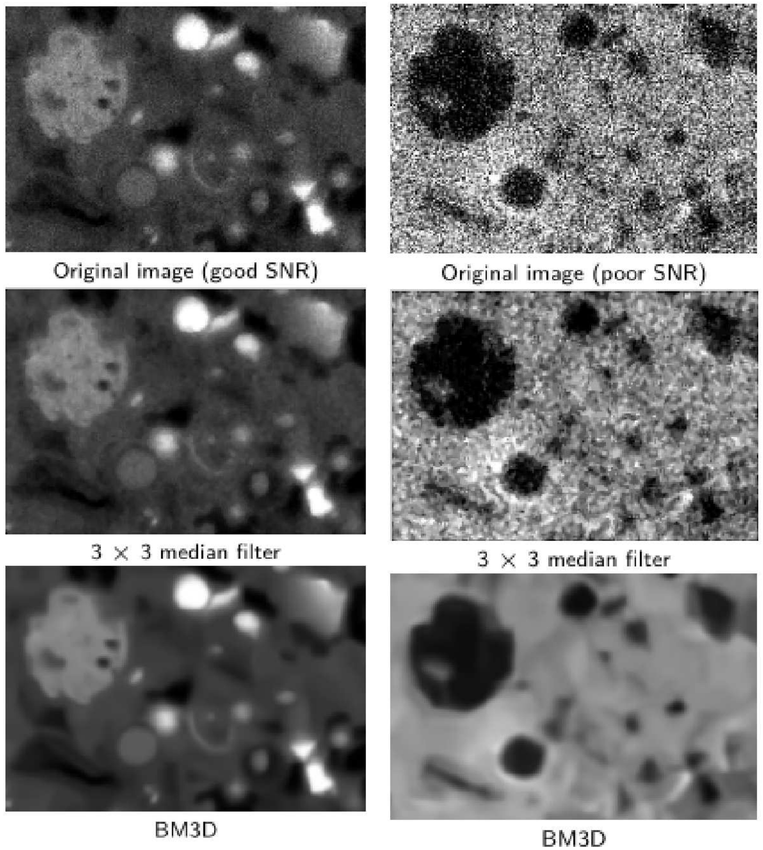


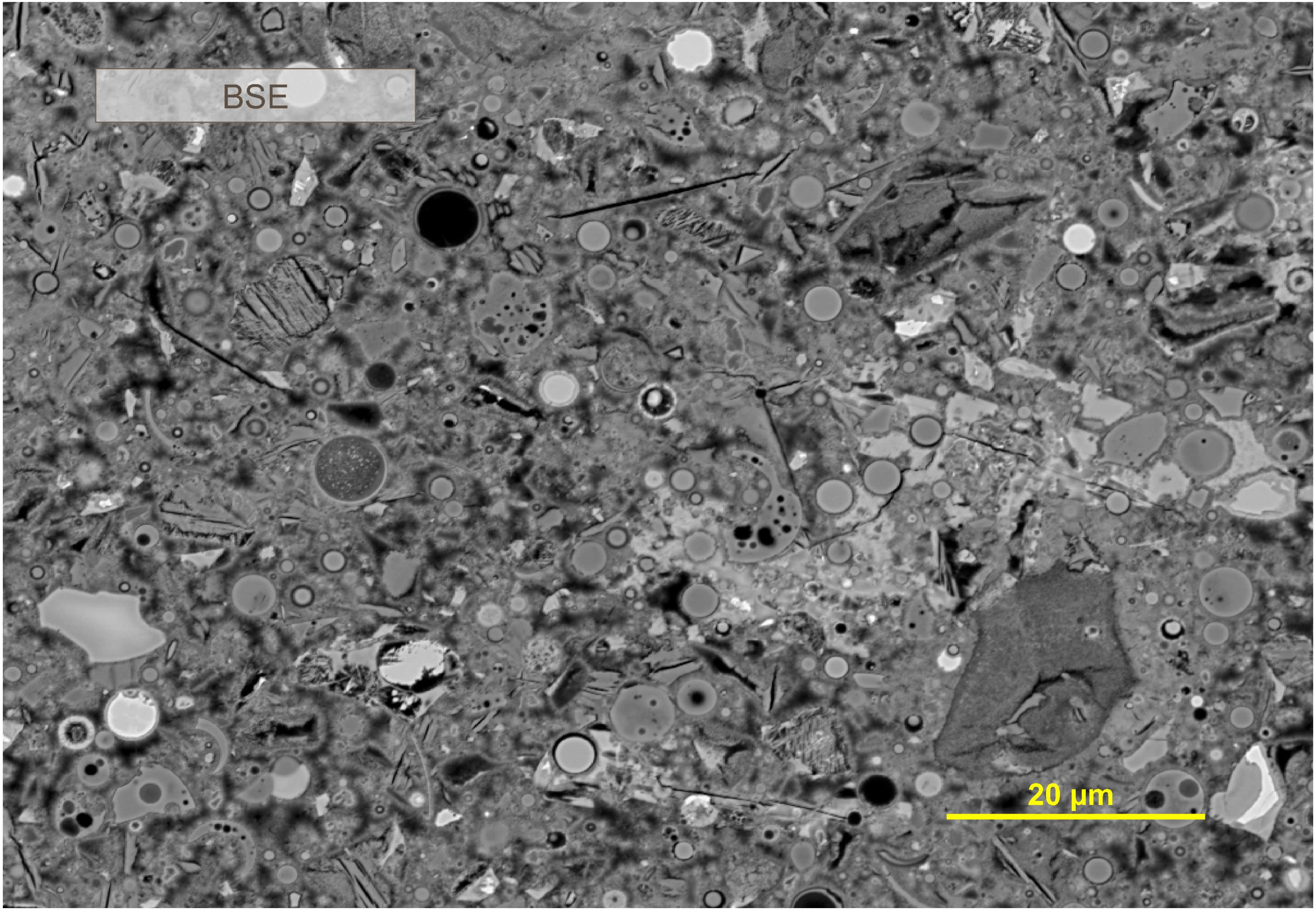
Clinker with alite (SVM)

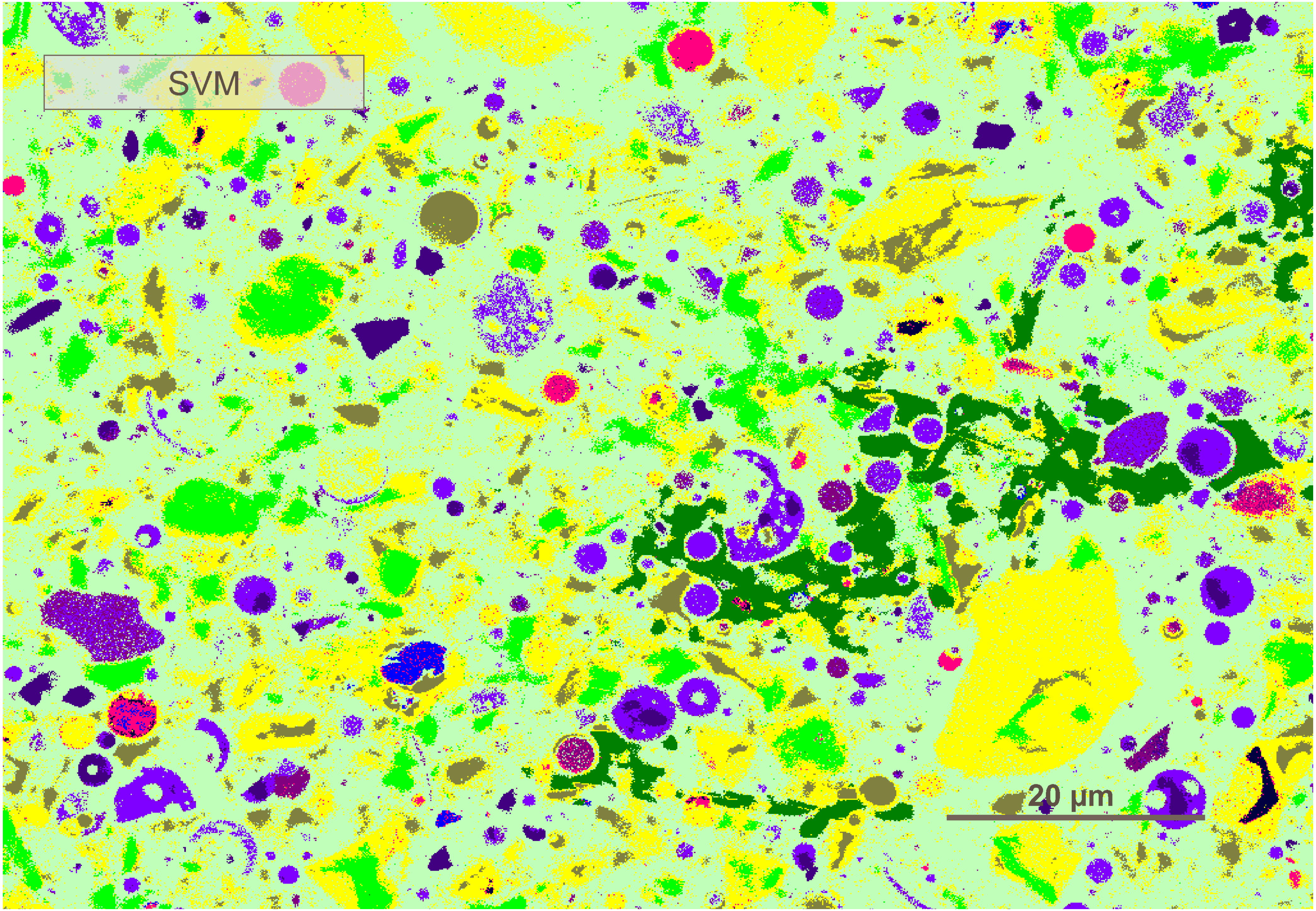


Clinker with alite (SVM + MRF)

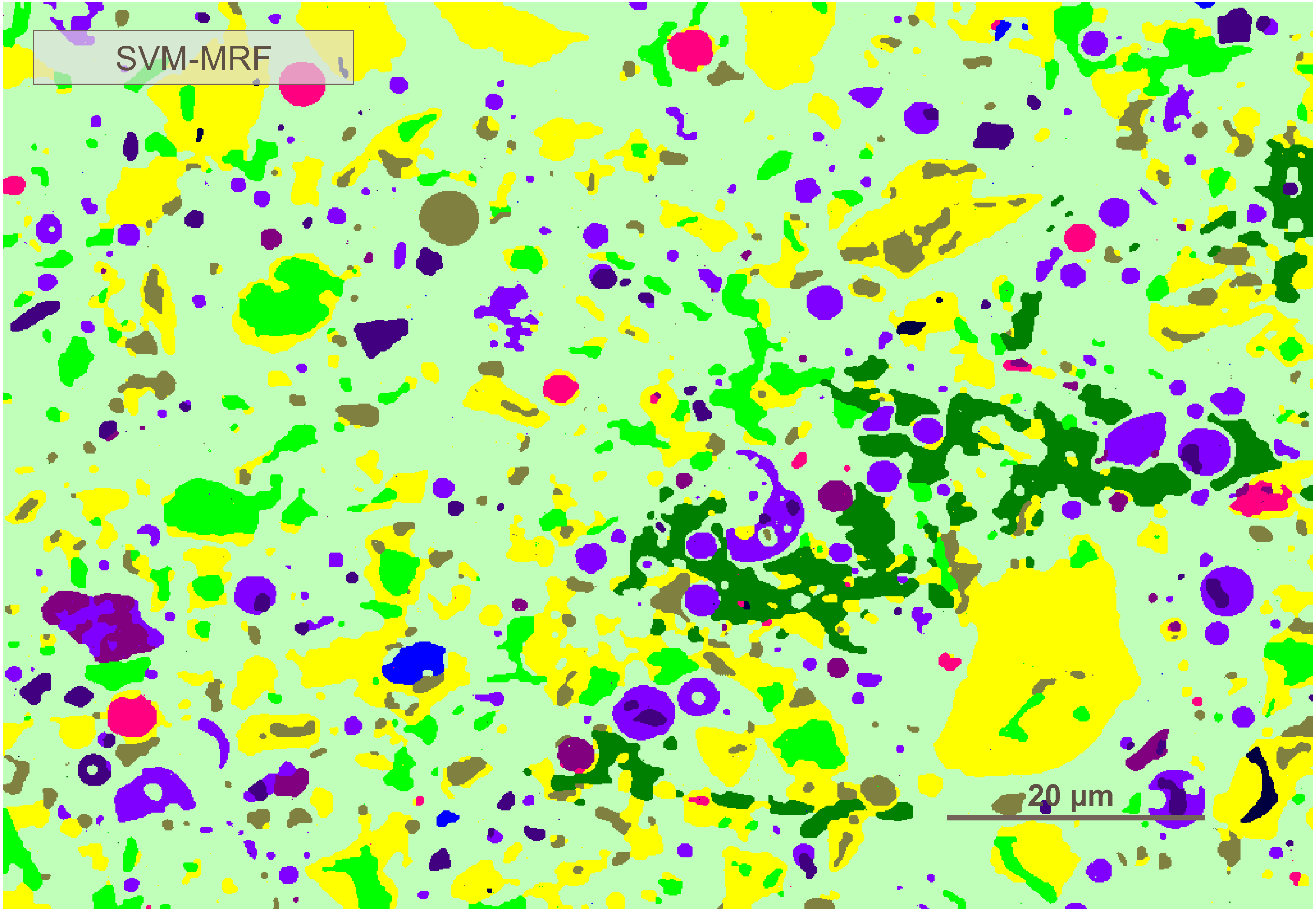
BM3D



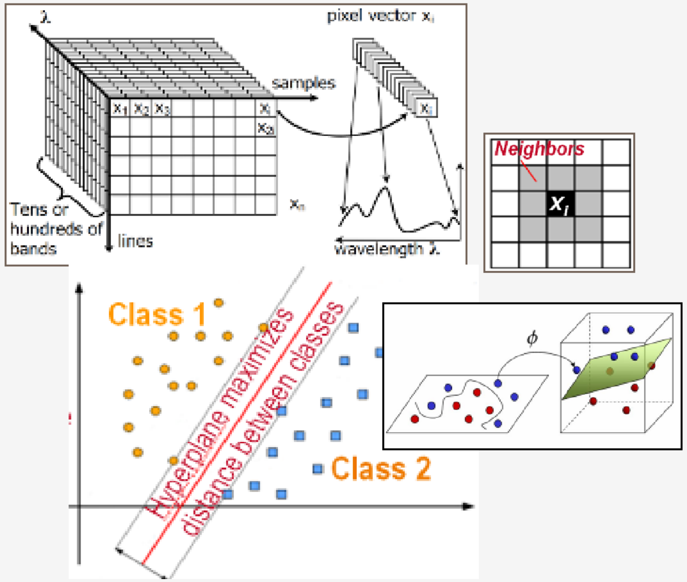

BSE
20 µm



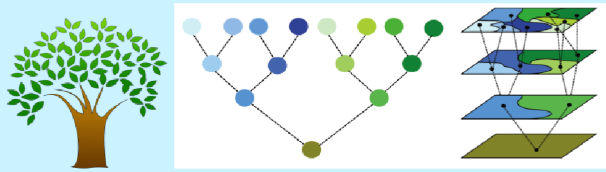
SVM
20 µm

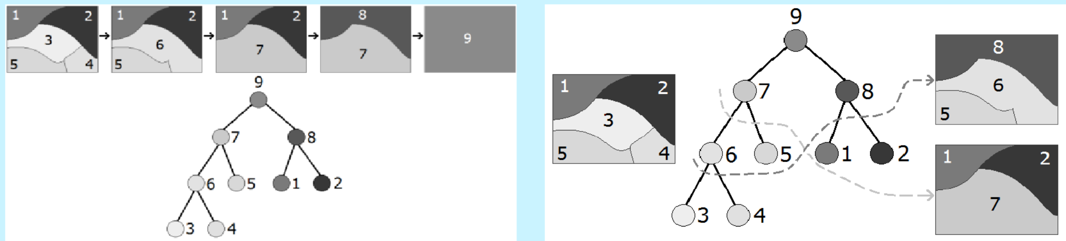

SVM-MRF
20 µm

Supervised classification: a classifier, a filtering process and an idea to improve final results

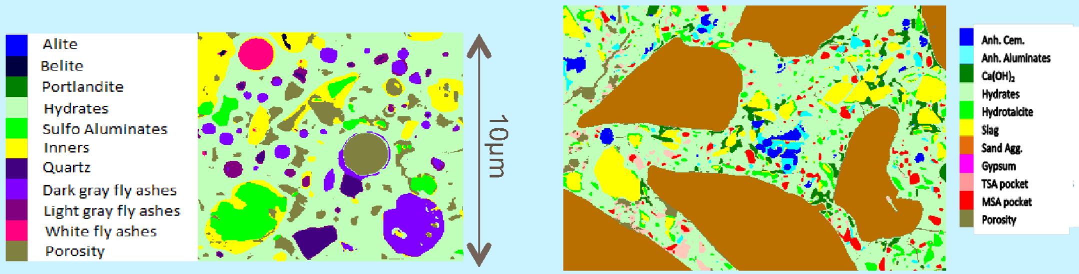


- **Multispect. image (= BSE+X-Ray Maps) is dimensionally reduced**
- **Expert assign some of chosen pixel to a known class → SVM is performing on training data set (= a class has now a specified signature)**
- **SVM is performed on the entire dataset →each new unknown pixel is assigned to a class according its probability of belonging**
- **A filter is applied in order to get more spatiality in images (alone pixels)**
- **Final result is the classified image : all classes are now separated**

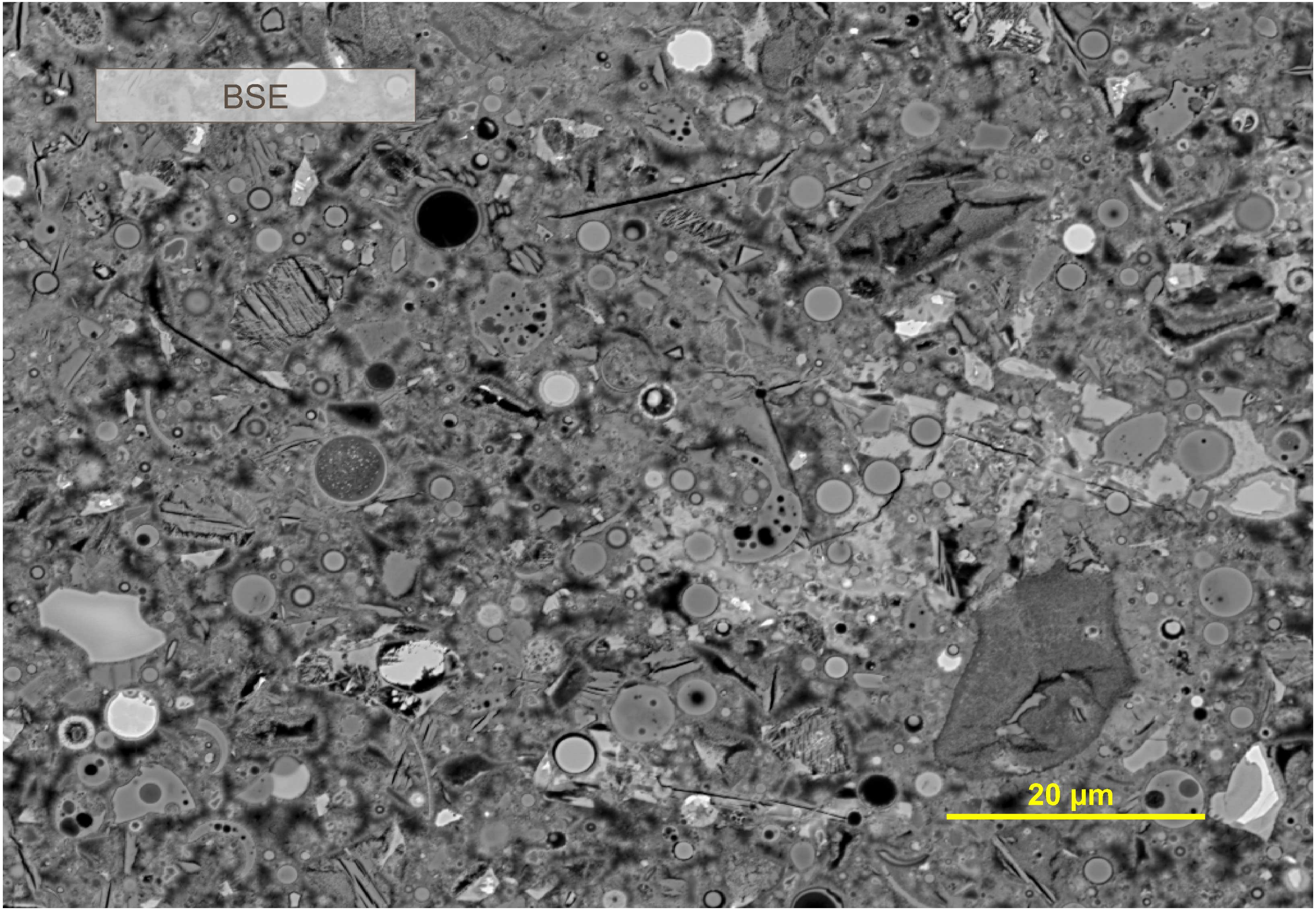


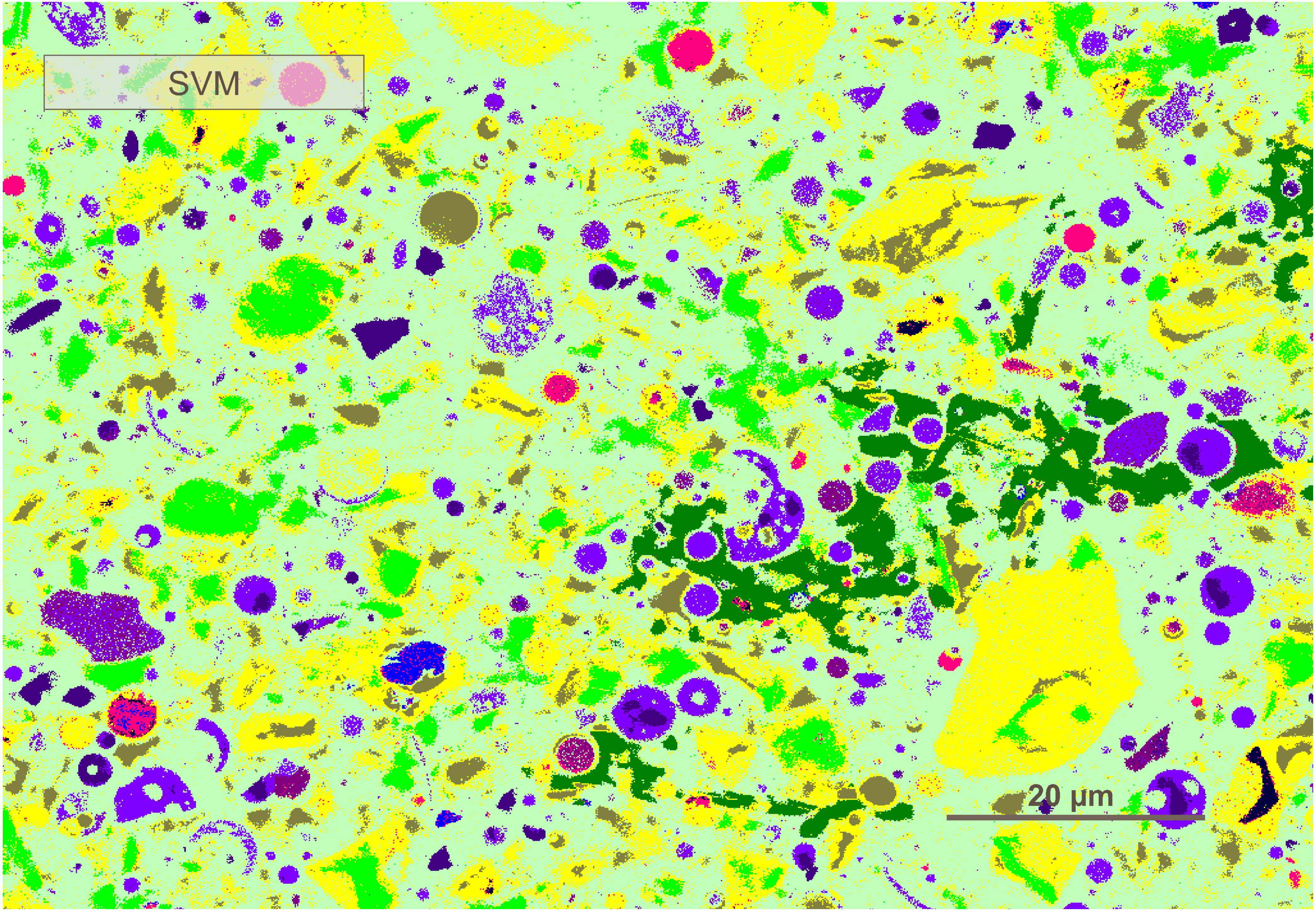


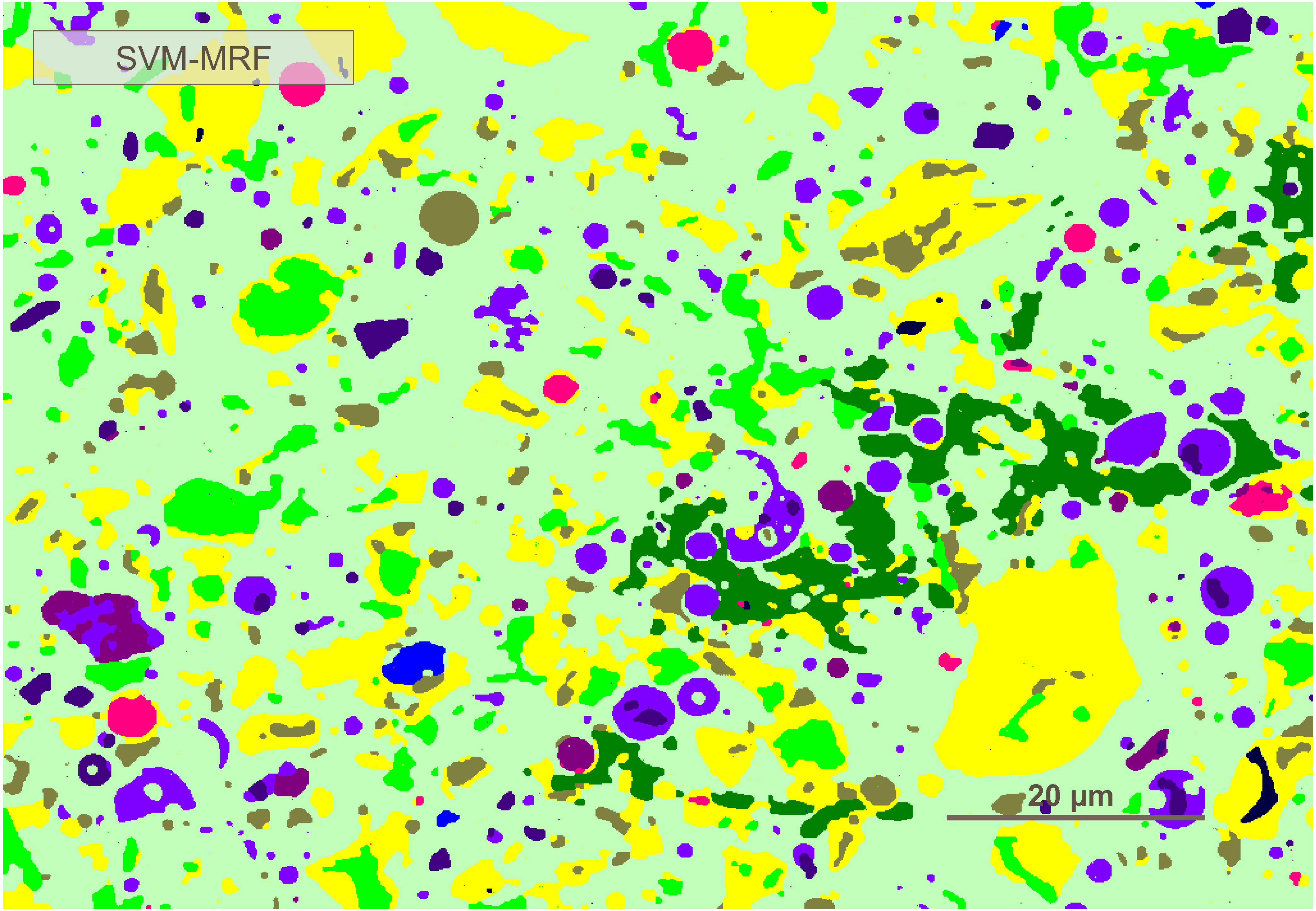
- **BPTs are a region-based hierarchical representation of an image** *[Salembier & Garrido, 2000]*
- **A BPT is built using denoised data using initial SVM partition**
- **An user can interact with classification using pruning process keeping only certain nodes of the tree. A new class can e.g. be created. Then the modified training set provide new classified image**

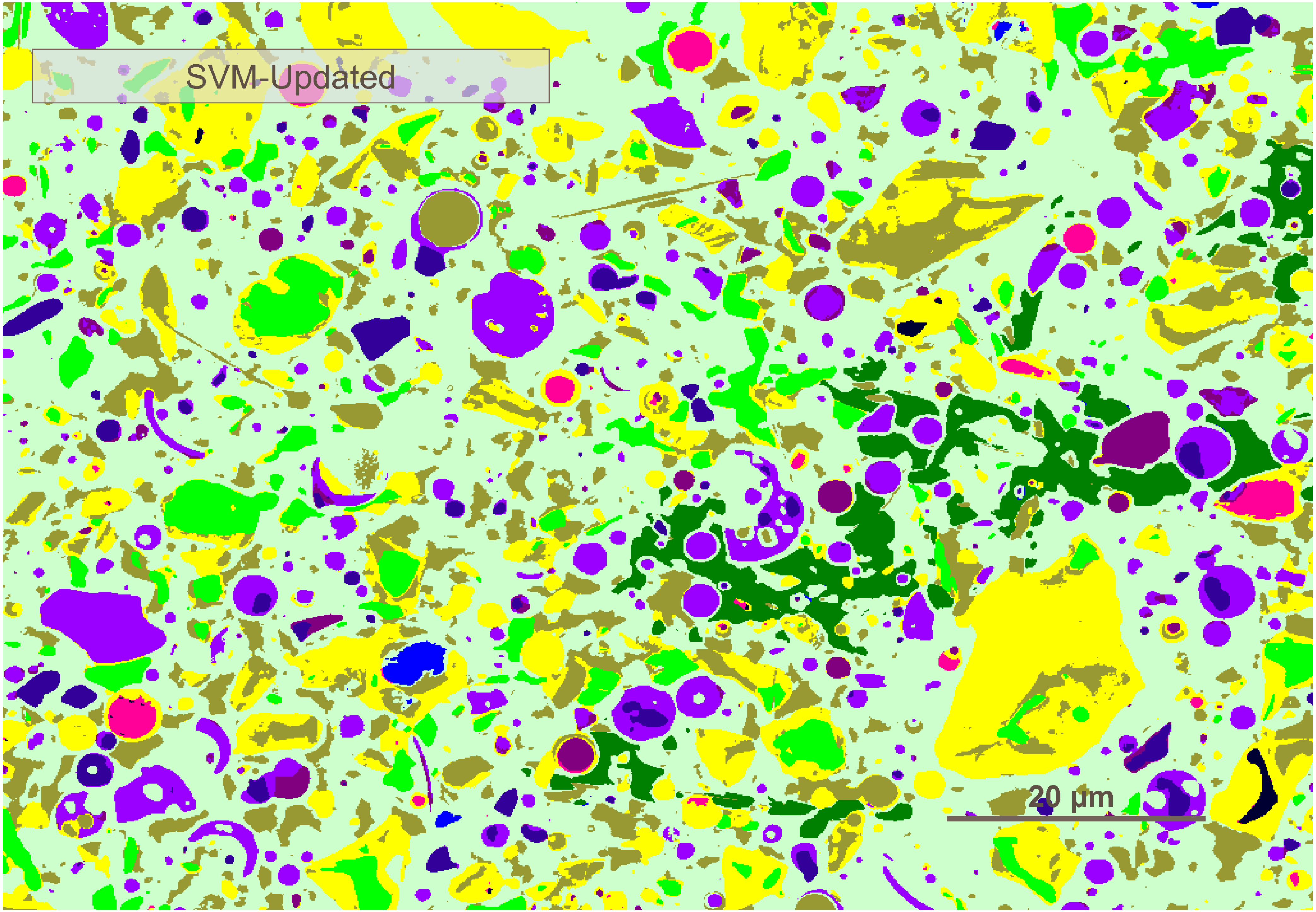


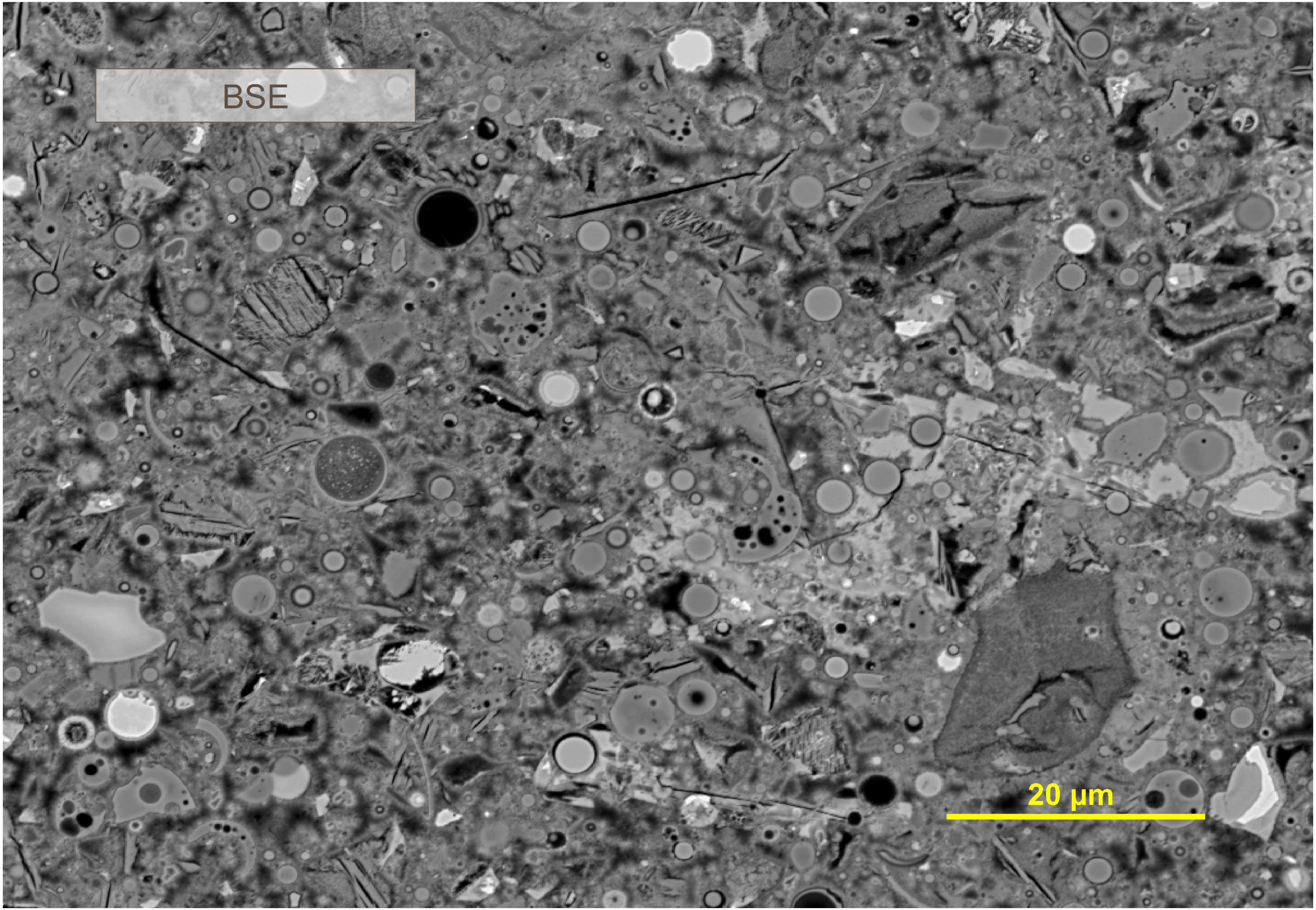
L. Drumetz ; M. Dalla Mura ; S. Meulenyzer ; S. Lombard ; J. Chanussot; ***Semi-automatic classification of cementitious materials using scanning electron microscope images.*** Proc. SPIE 9534, Twelfth International Conference on Quality Control by Artificial Vision 2015, 953403 (April 30, 2015) doi:10.1117/12.2182762.


BSE
20 µm


SVM
20 µm


SVM-MRF
20 µm

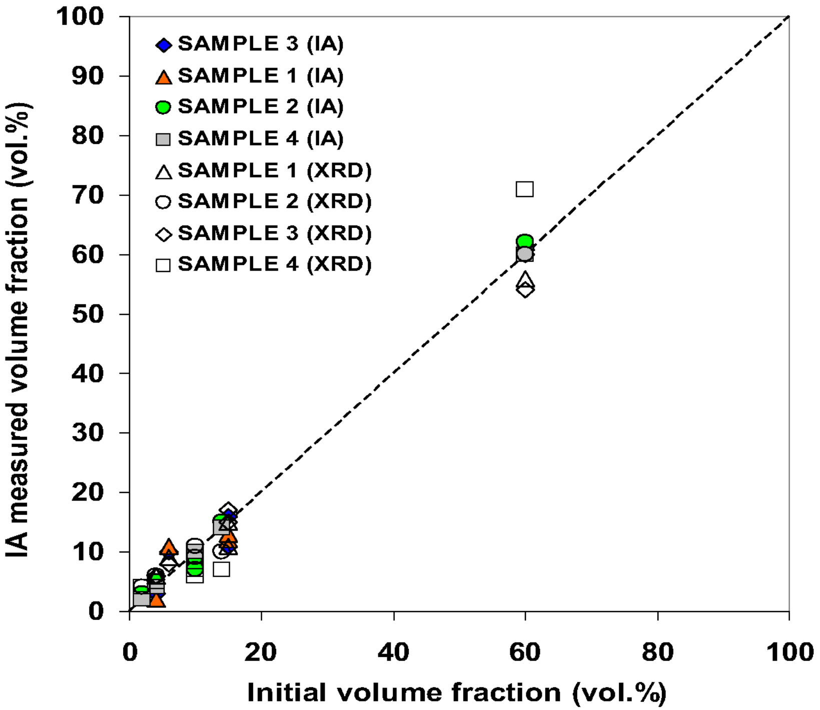

SVM-Updated
20 µm

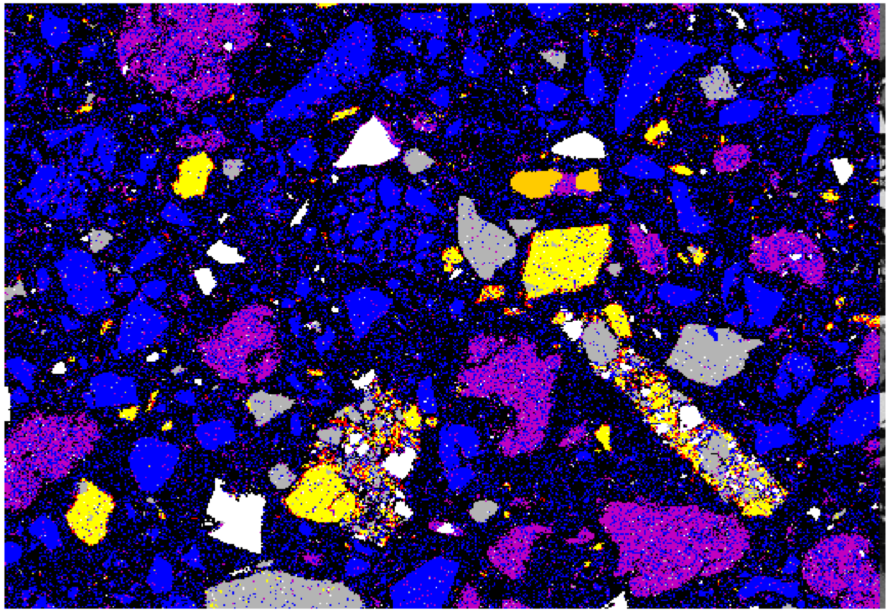

BSE
20 µm

CASE 1: Measuring the amorphous fraction of Pouzz.

- Artificial mixing :

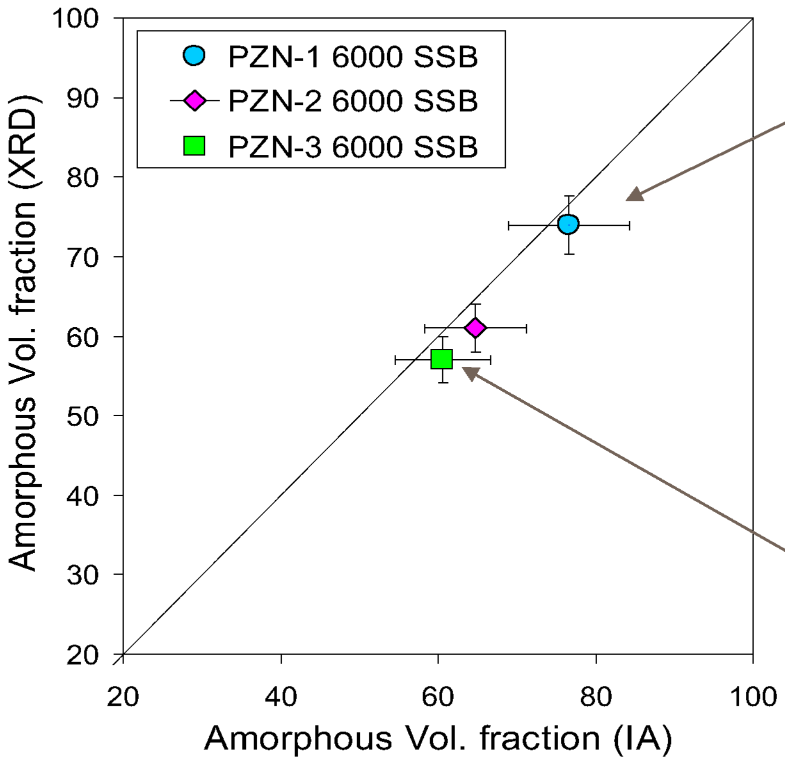
	Glass	Feldspar	augite	clay	dolomite	calcite	quartz	forsterite	magnesite	Edenite	titanite	Magnetite
PZN1	76.8	8.7	0.3	1.1	6	3.5	2.3	-	-	1.3	-	-
PZN2	53.1	14.3	8.1	2.8	-	2	0.2	16.9	--	0.2	-	2.3
PZN3	47	32.1	5.2	1.3	-	0.4	-	9.4	1.4	0.3	1.4	1.5
PZN4	64.5	26.8	0.1	5.6	-	0.5	2.2	-	-	-	-	0.28

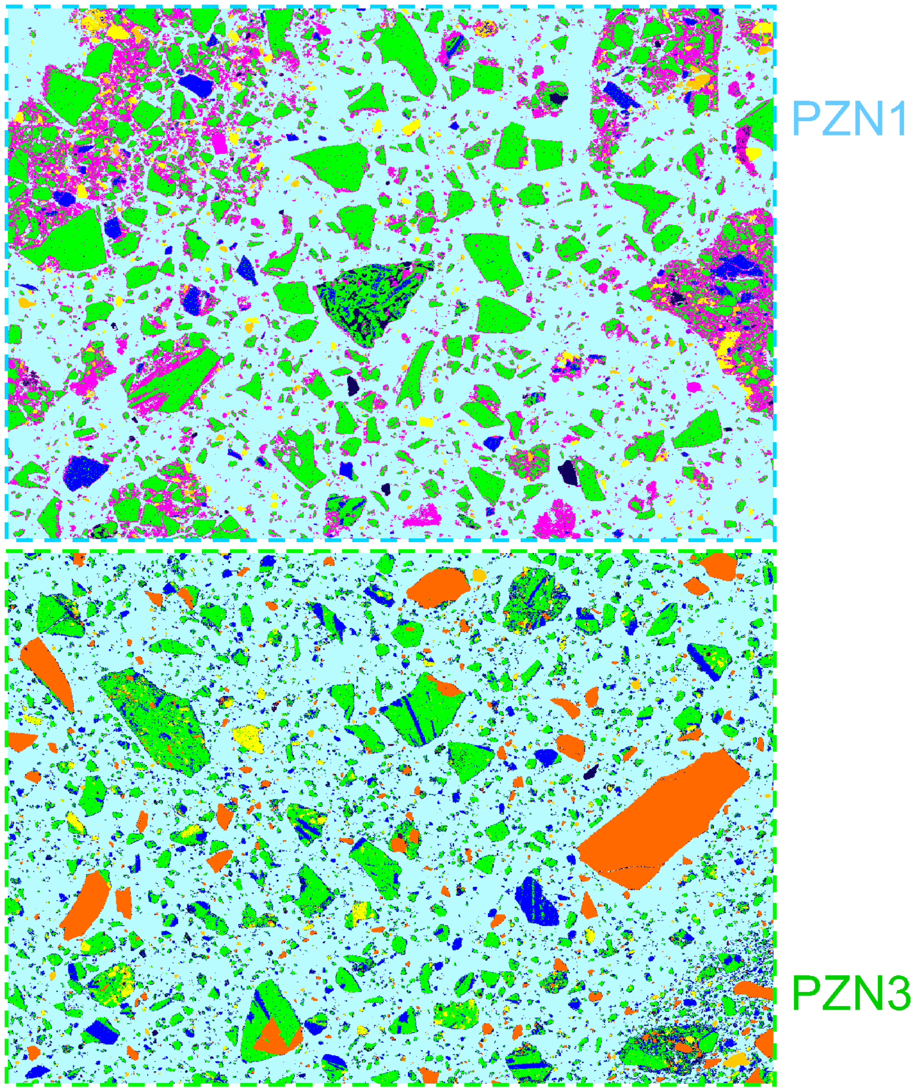




CASE 1: Measuring the amorphous fraction of rocks

- Natural pouzzolana :





Amorphous

CASE 2: Validating SVM-MRF-BPT on reference mix design

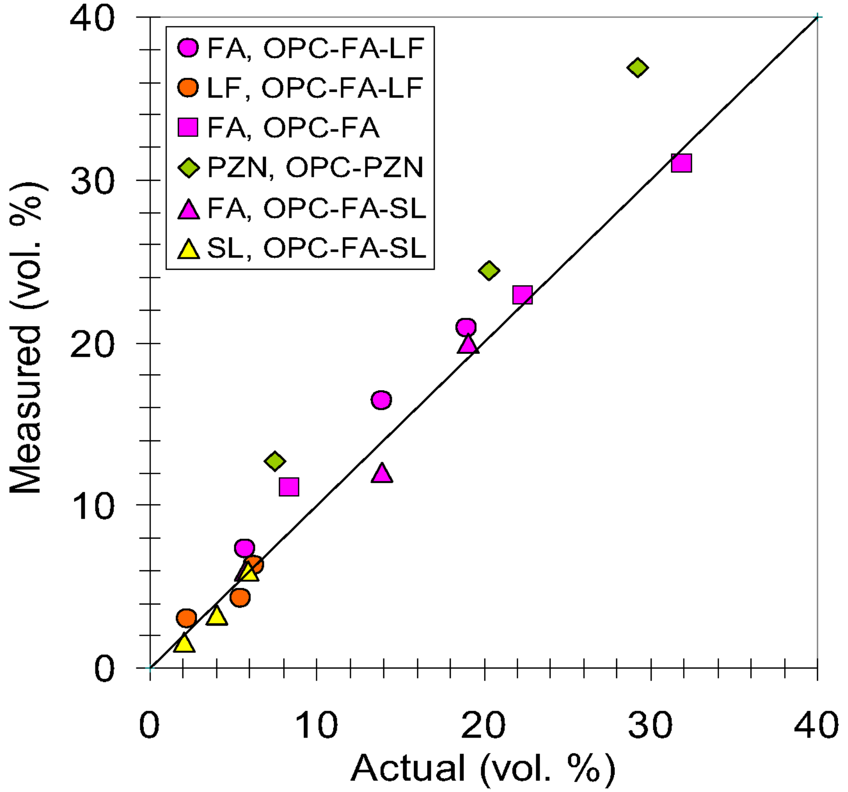
- 1d-stopped blended pastes:

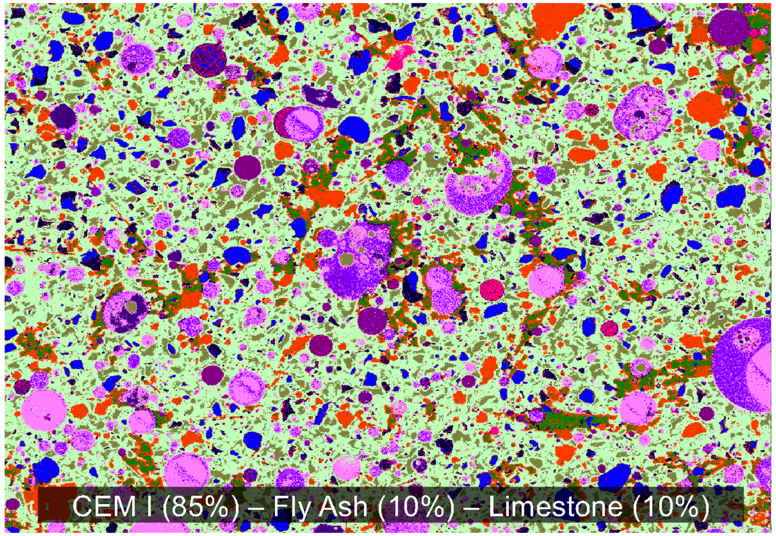
	System	Series	Sample designation	Micronized-OPC (20µm)	Fly Ash	Limestone Filler	Slag	Pozzolan
1 day	Binary	1	µOPC-FA1-1	38	62	-	-	-
			µOPC-FA1-2	58	42			
			µOPC-FA1-3	85	15			
		2	µOPC-PZN-1	38	-	-	-	62
			µOPC-PZN-2	58				42
			µOPC-PZN-3	85				15
	Ternary	3	µOPC-FA1-LF-1	50	35	15	-	-
			µOPC-FA1-LF-2	65	25	10		
			µOPC-FA1-LF-3	85	10	05		
		4	µOPC-FA1-SLAG-1	50	35	-	15	-
			µOPC-FA1-SLAG-2	65	25		10	
			µOPC-FA1-SLAG-3	85	10		05	

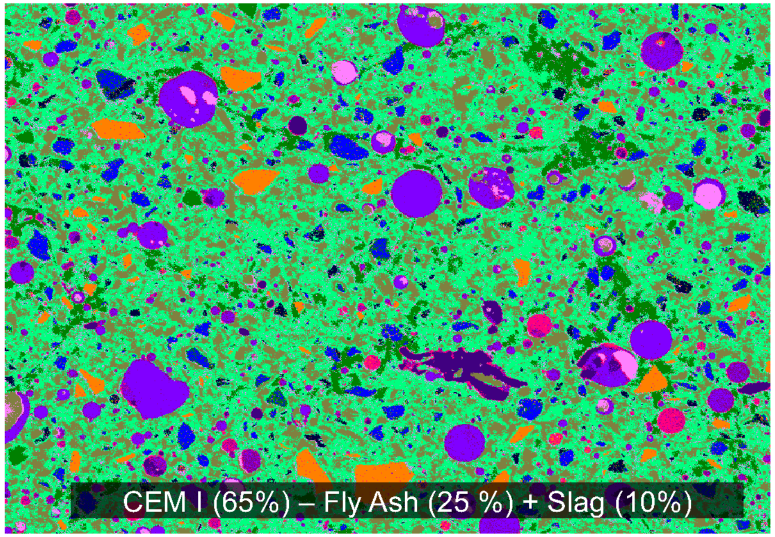
- 91 d stopped mature pastes:

	Sample designation	Regular-OPC	Slag	Fly Ash	PZN1	PZN2	PZN3
91 d	OPC	100					
	OPC-SLAG	55	45				
	OPC-FA1	55		45			
	OPC-PZN1	55			45		
	OPC-PZN2	55				45	
	OPC-PZN3	55					45
	OPC-SLAG-FA1	55	10	35			

CASE 2: 1d-stopped blended pastes

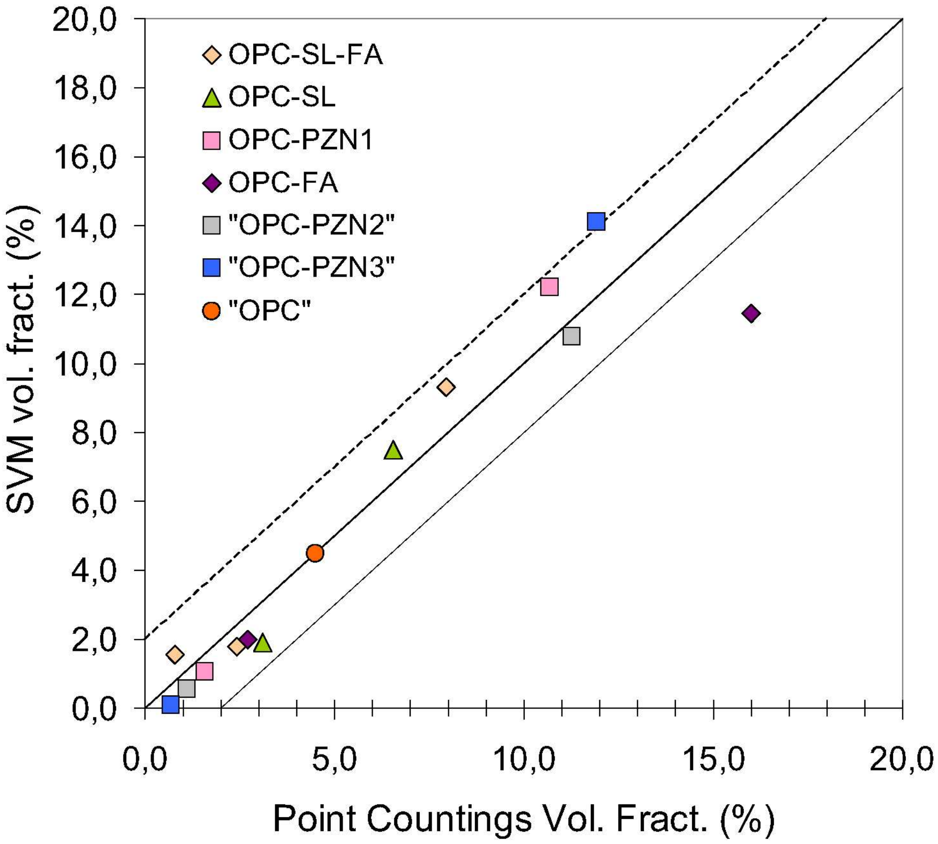


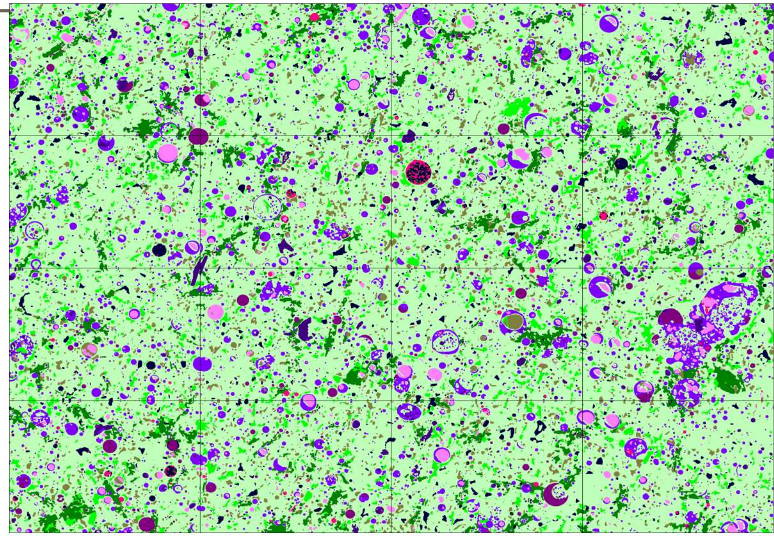


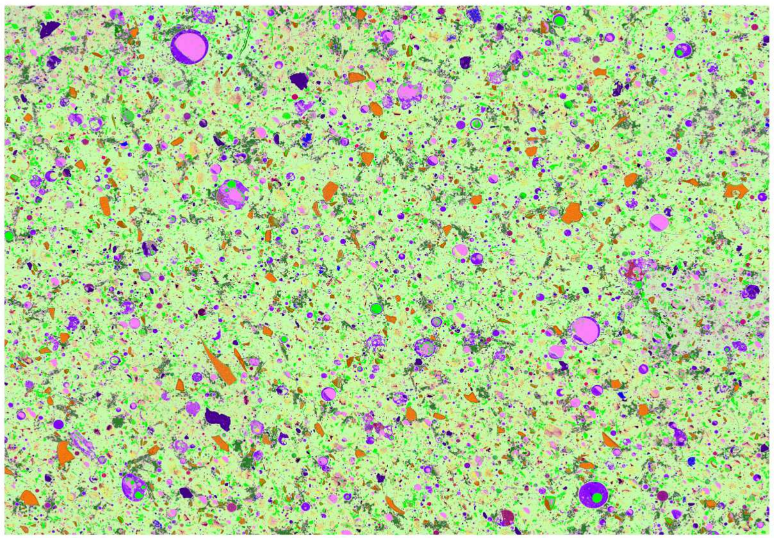


Method shows excellent results on fly-ash, limestone, slag. Discrepancy on pozzolan due to clay impurities.

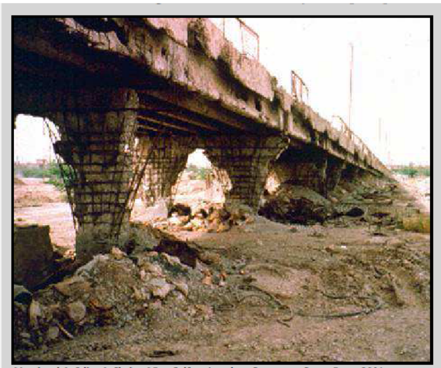
CASE 2: 91d-stopped mature blended pastes







CASE 3: Connecting binders formulation to sulfate resistance


Marchand, J., Odler, I., Skalny, J.P., « Sulfate Attack on Concrete », Spoon Press, 2001

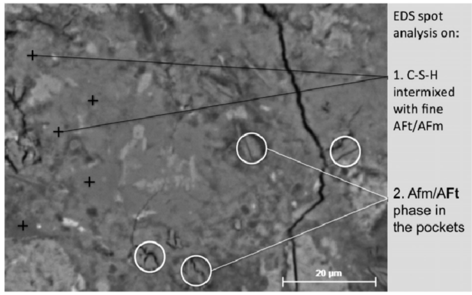
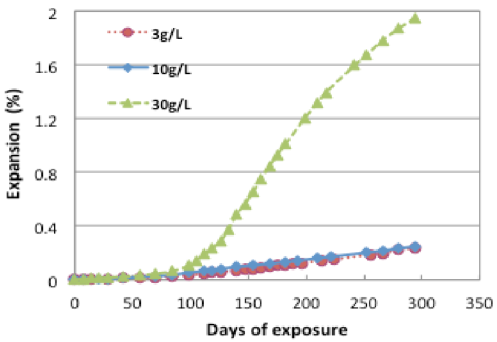


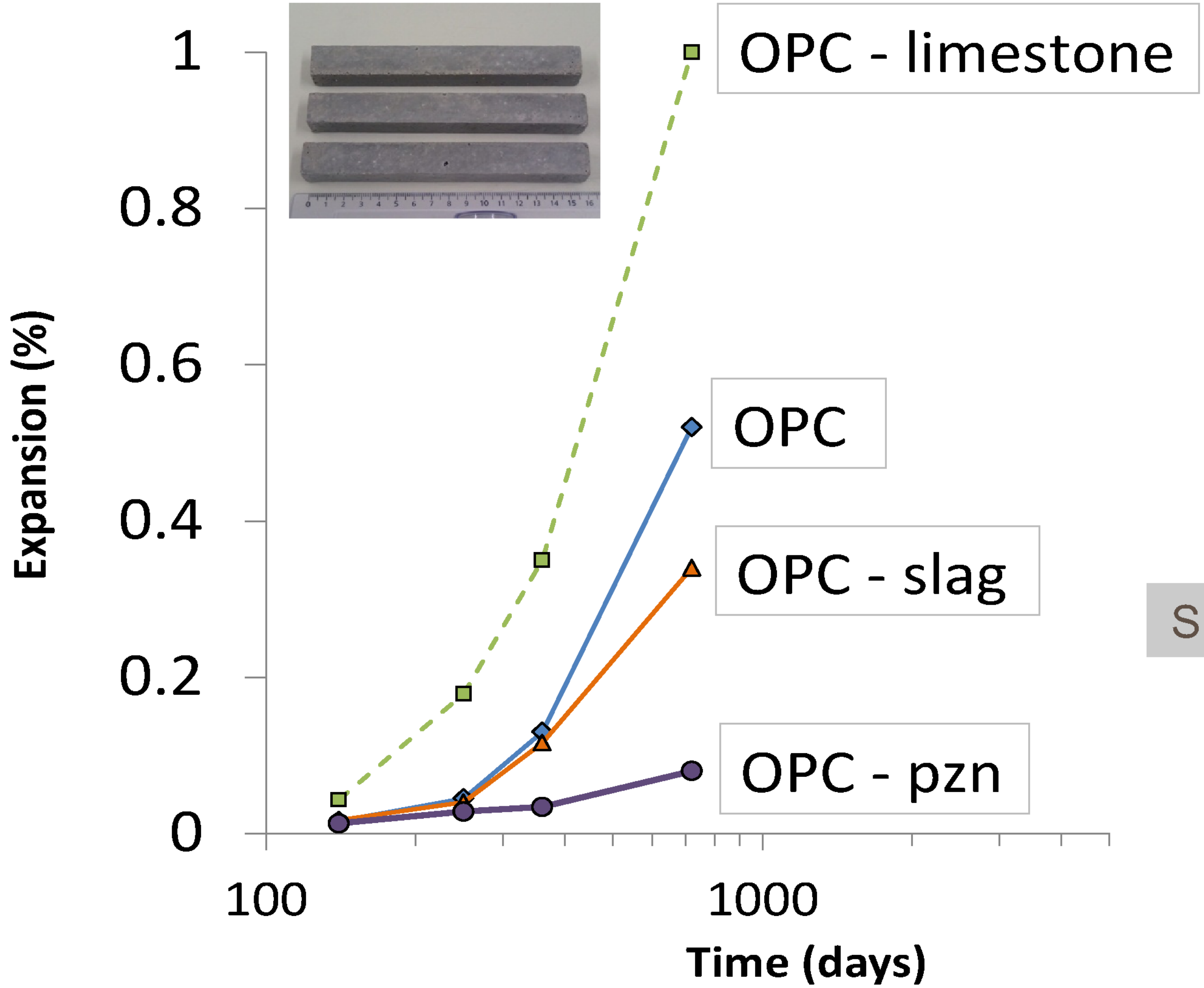
Fig. 2. Example of EDS spot analysis on C-S-H and AFm/AFt phases in the pocket for PC samples.

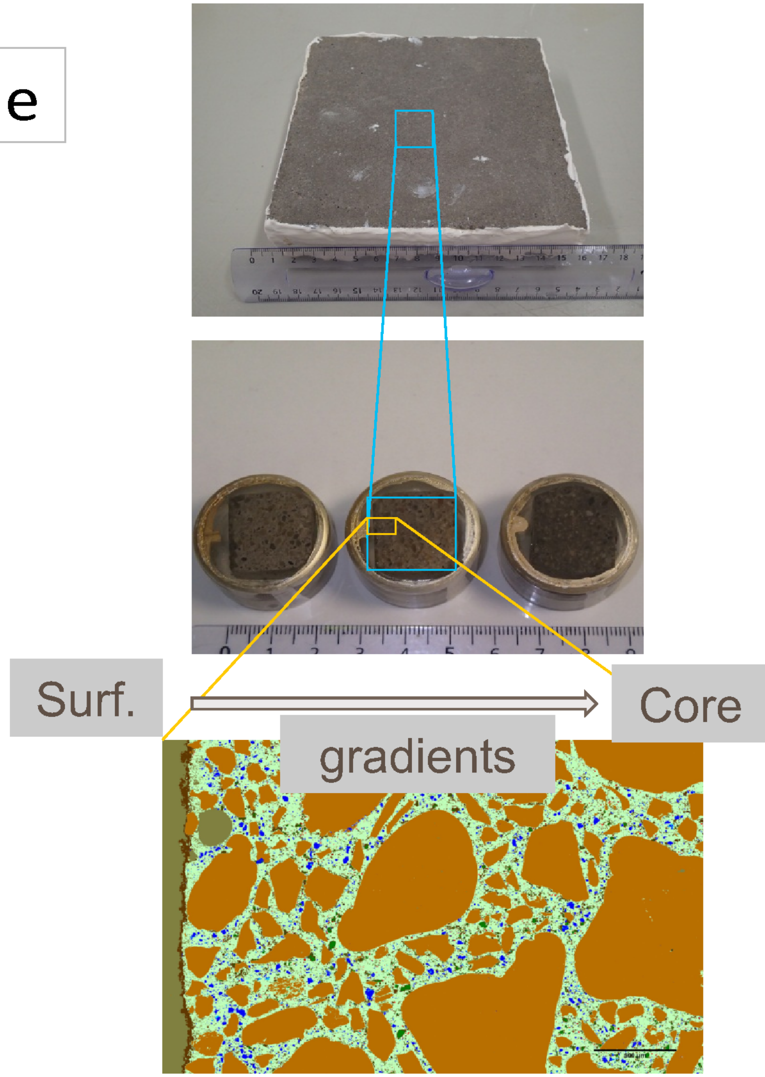


[Yu & Scrivener, 2013]

- Mechanisms understanding is needed to produce new binders or new concretes
- It is widely recognized that Ettringite and (probably) Gypsum (sulfate containing phases) cause damage due to expansion
- Recent studies (e.g. Scrivener, 2013) have shown that pocket of MSA could act as a buffer
- Recent IA development (like supervised spectral classification, *Meulenyzer, EMABM 2013*) have shown potential to quantify these pockets
- We've taken opportunity to study 4 mortars through industrial project
  - **OPC**
  - **OPC-Limestone Filler**
  - **OPC-Slag**
  - **OPC-Pzn**

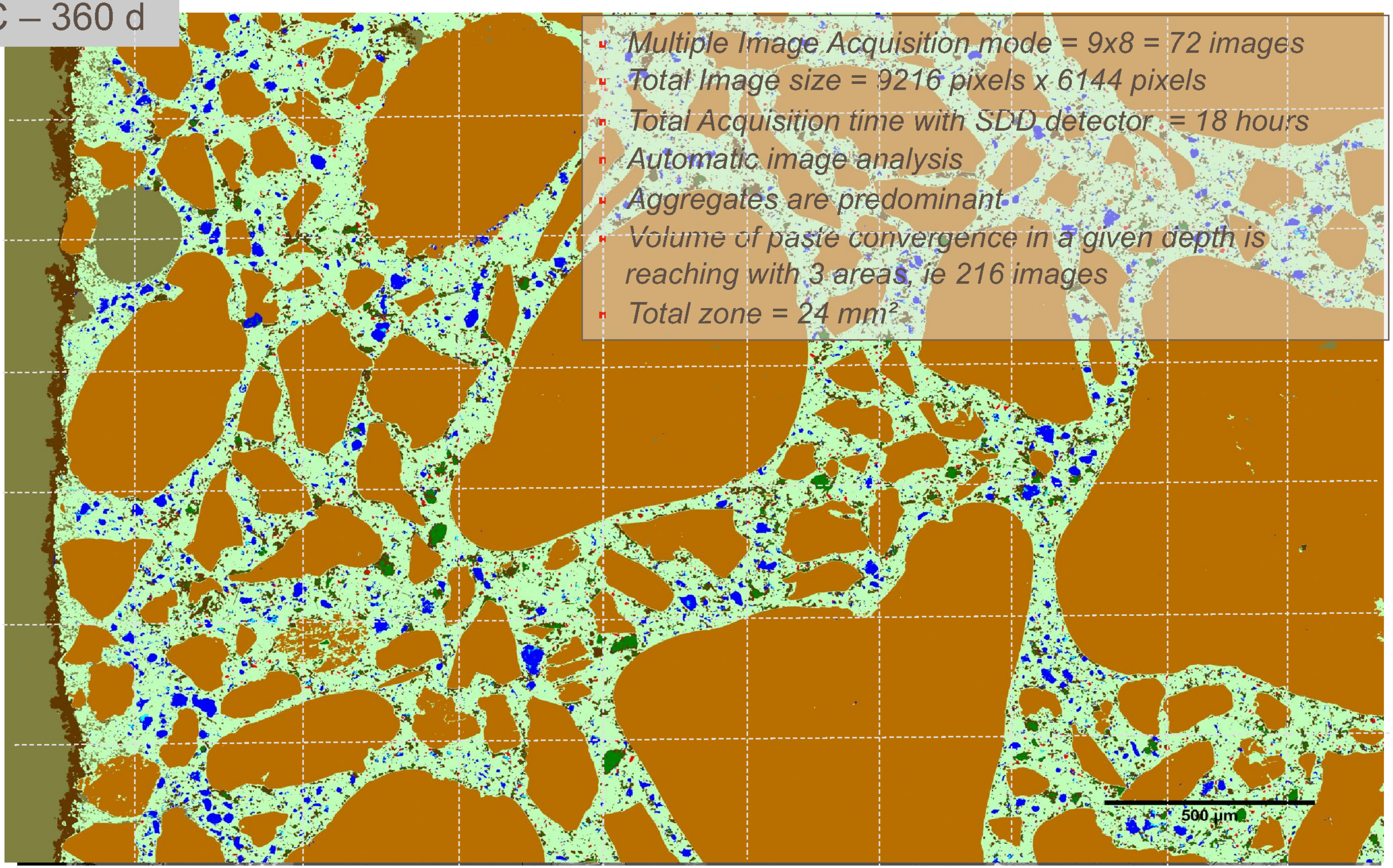
Expansion strongly depends on binder composition





What are good conditions to be representative ?

OPC – 360 d



- *Multiple Image Acquisition mode = 9x8 = 72 images*
- *Total Image size = 9216 pixels x 6144 pixels*
- *Total Acquisition time with SDD detector = 18 hours*
- *Automatic image analysis*
- *Aggregates are predominant*
- *Volume of paste convergence in a given depth is reaching with 3 areas, ie 216 images*
- *Total zone = 24 mm²*

Huge Image acquisition program…

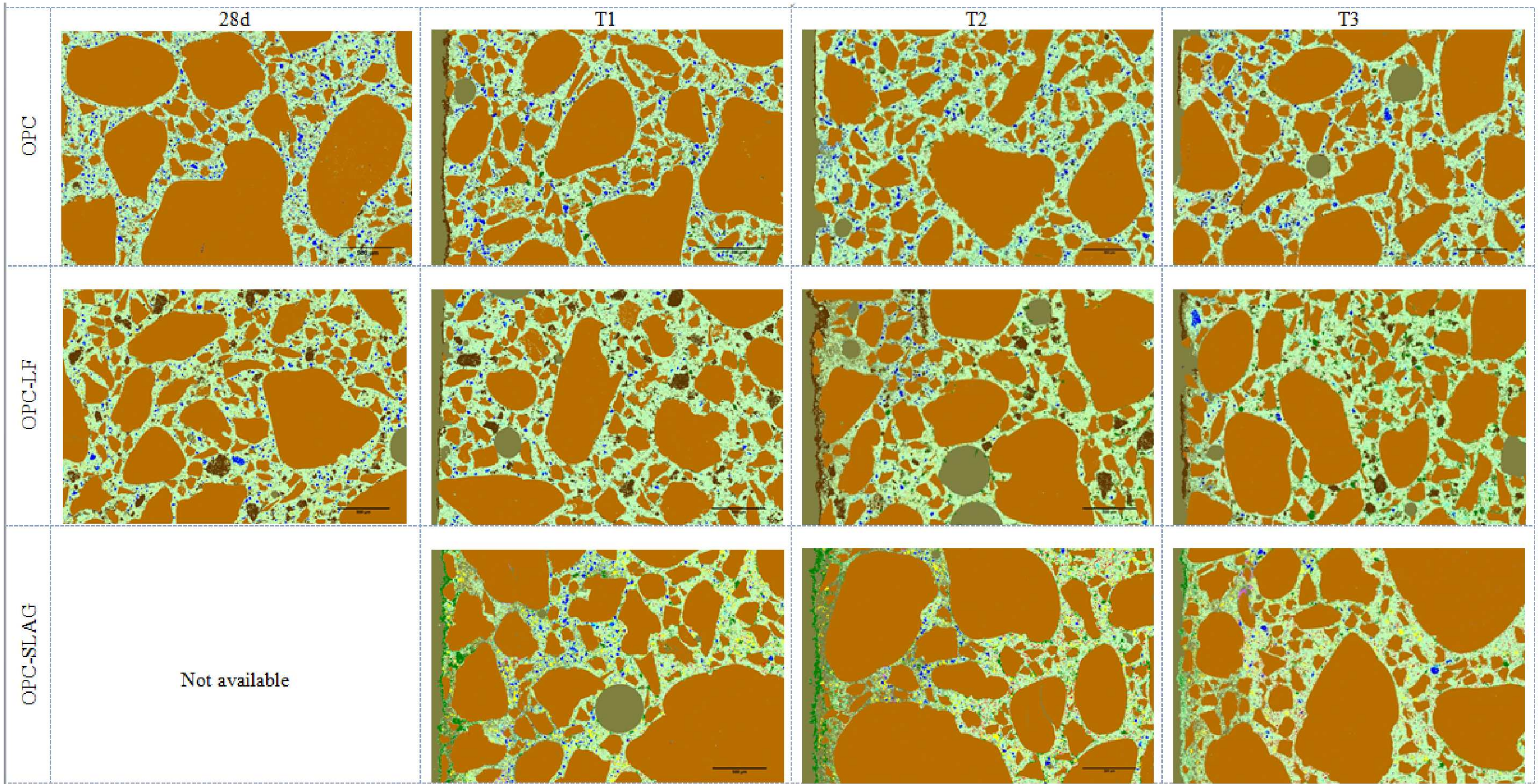
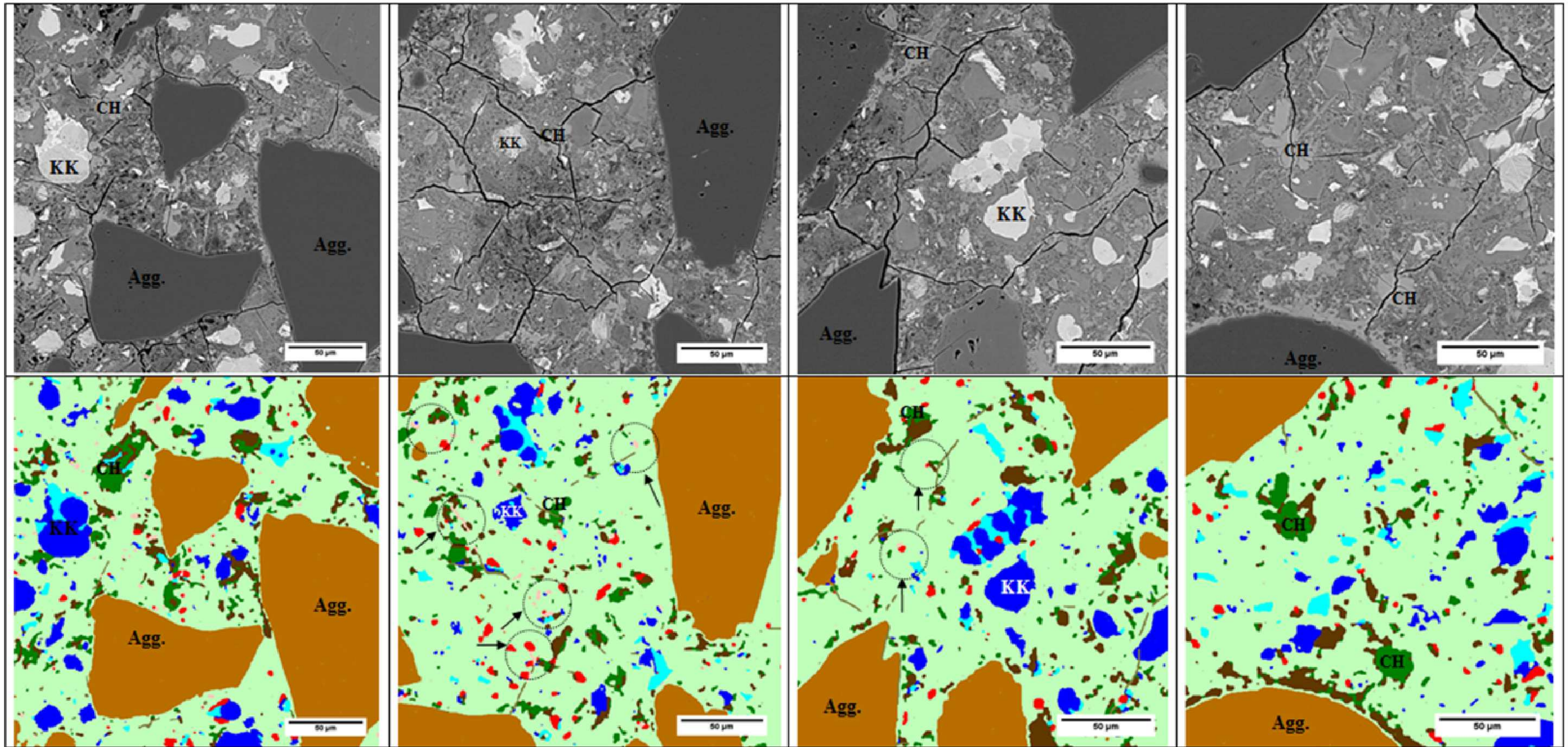


Figure 5: Classified images of OPC, OPC-LF (Limstone Filler) and OPC-Slag at 28, 250, 350 and 720 days, corresponding to previous BSE images (Figure 3).
Scale bar is 0.5 mm. The code of colors are: Sand (Orange), Porosity (light brawn), Porlandite and/or calcite in OPc and OPC-Slag mortars (dark green), 'Outers' (light green), C3S C2S silicates (light and dark blue), Slag (Yellow), monosulfoaluminates grains (red), trisulfoaluminate coarser phases (rose), limestone filler (dark brawn).

OPC T2 (1-year) local gradient evolution

3.3.1 Microstructural évolution of OPC-T2 mortar

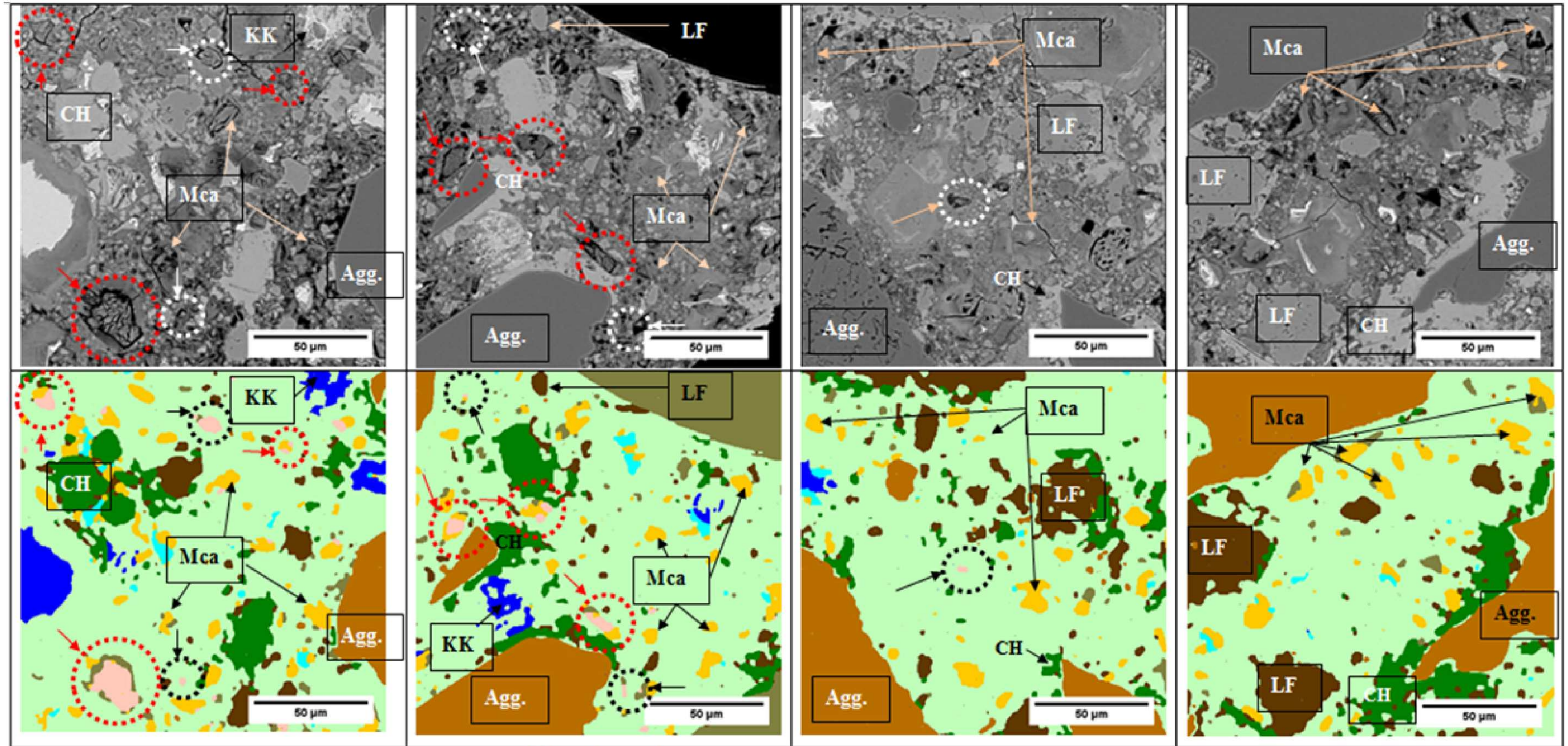


Near the surface *HFW =160 µm* *Msa grains seem coexisted with Tsa grains.*	*1.25 mm from surface* *HFW =160 µm* *As sulfate concentration is smaller than in the surface. TSA are found (pink) but seem more 'thinner' than in the surface.*	*1.98 mm from surface* *HFW =160 µm* *TSA (pink color) starts to appear (pointed circle) in place where monosulfoaluminate grains (red) have been dissolved...*	*2.84 mm from surface* *HFW =160 µm* *Sulfates haven't penetrated yet. Red grains are monosulfoaluminate (confirmed by EDS). No TSA grains.*

Figure 7: Microstructural phase evolution at local scale from surface (left) to core of mortar (OPC). KK=clinker; Agg.=Aggregates; CH=portlandite;

OPC-LF T2 (1 year) local gradient evolution

3.3.2 Microstructural évolution of OPC–Limestone filler–T2 mortar

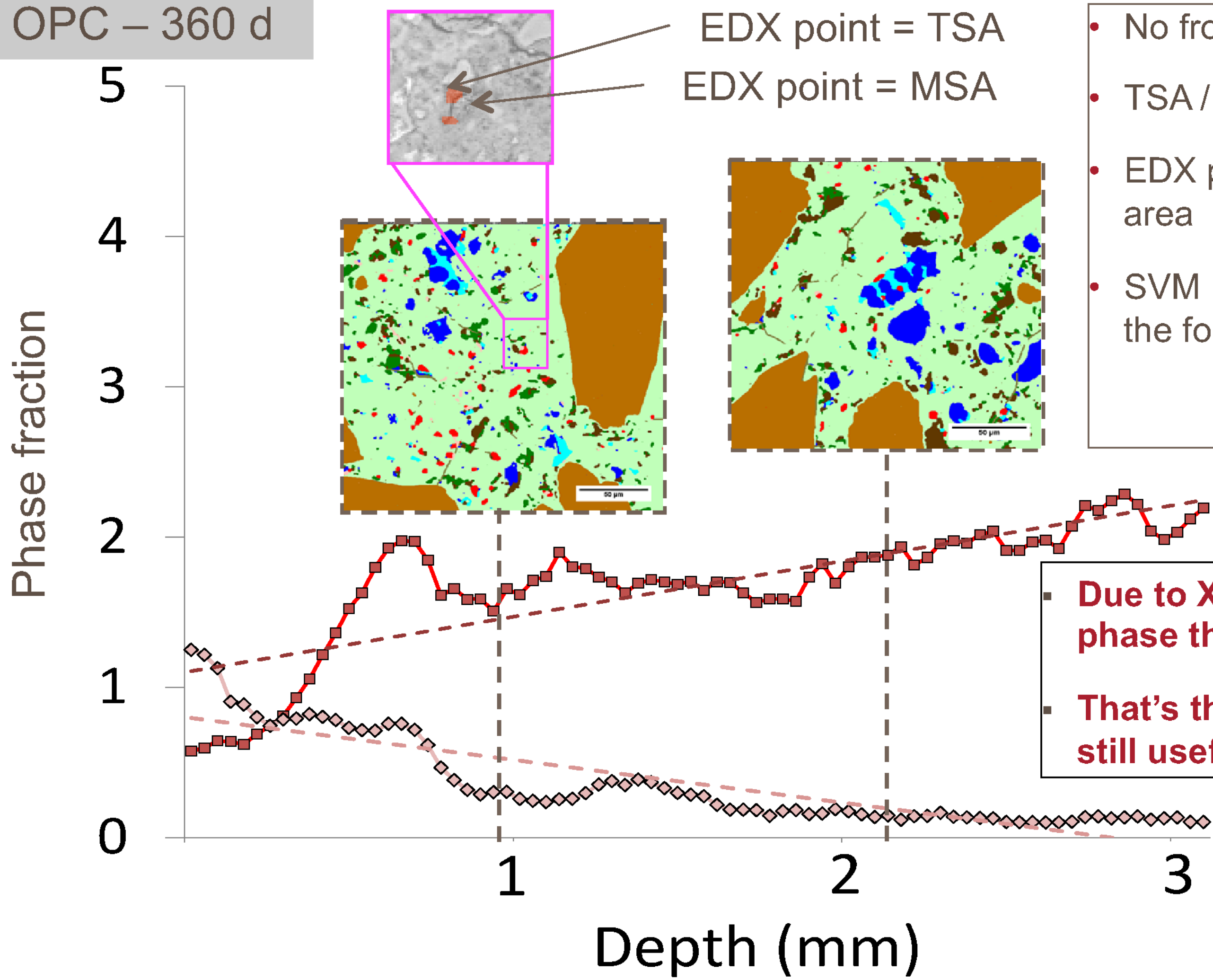


0.87 mm from surface *HFW=160µm* *'Massive' TSA grains can be found. Also many TSA grains are in formation.*	*1.25 mm from surface* *HFW =160 µm* *As sulfate concentration is higher more TSA are found. Some Mca grains seem going to be 'transformed' in TSA (red circles)…*	*1.98 mm from surface* *HFW =160 µm* *TSA starts to appear (pointed circle) in place where Mca grains have been dissolved…*	*2.84 mm from surface* *HFW =160 µm* *Sulfates haven't penetrated yet. No TSA grains.*

Figure 8: Microstructural phase evolution at local scale from surface (left) to core of mortar (OPC-LF). KK=clinker; Agg.=Aggregates; CH=portlandite; LF=Limestone Filler; Mca= Monocarboaluminate

MSA / TSA Pockets gradients get quantified

OPC – 360 d

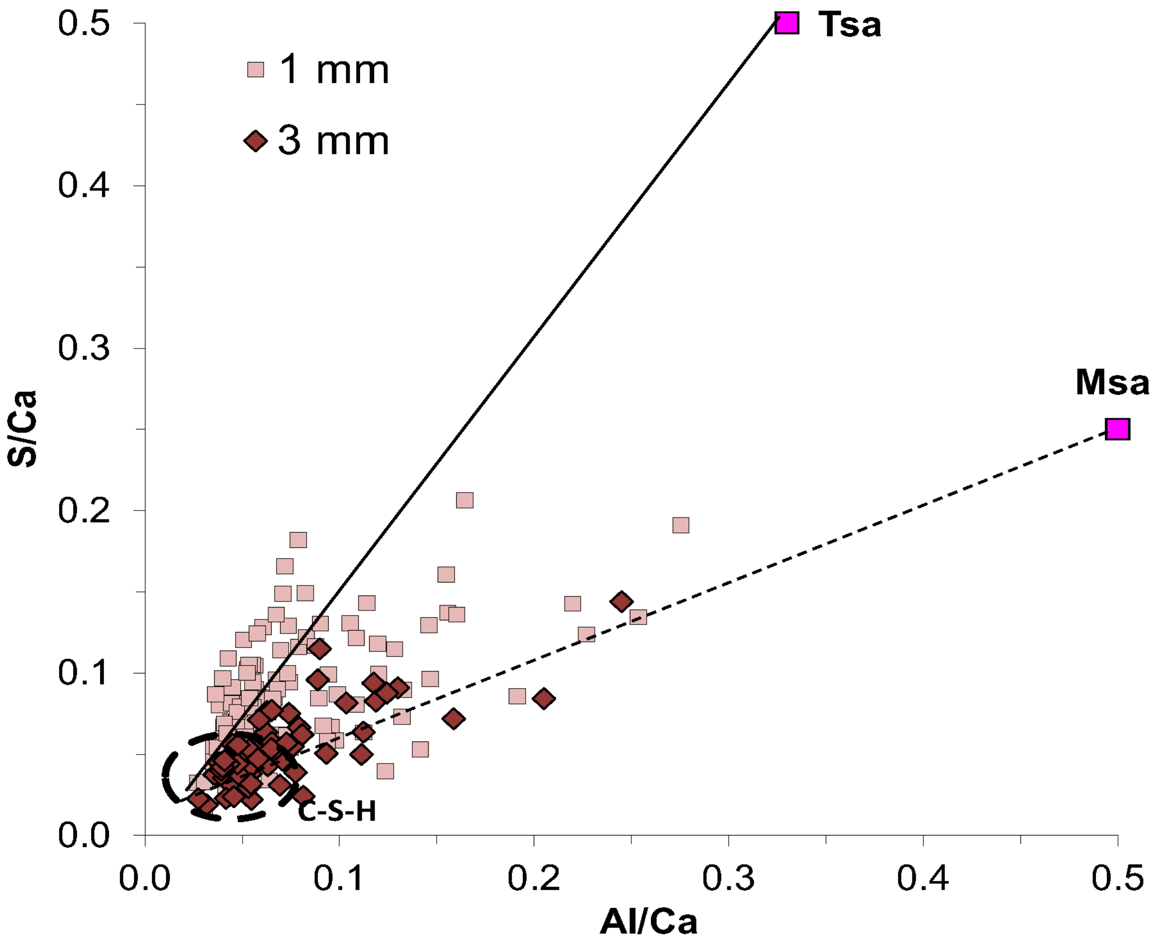


- No front in that case, surprising
- TSA / MSA pockets are sometimes coexisting
- EDX points confirm both MSA / TSA in a same area
- SVM IA gave us ‘macro’ vision of TSA / MSA, in the form of pocket

- **Due to X-Ray maps, we are limiting by size of phase that could be detected, ie few µm**
- **That’s the reason why EDX analyses in CSH are still useful and complementary**

EDX on CSH show evolution from MSA to TSA

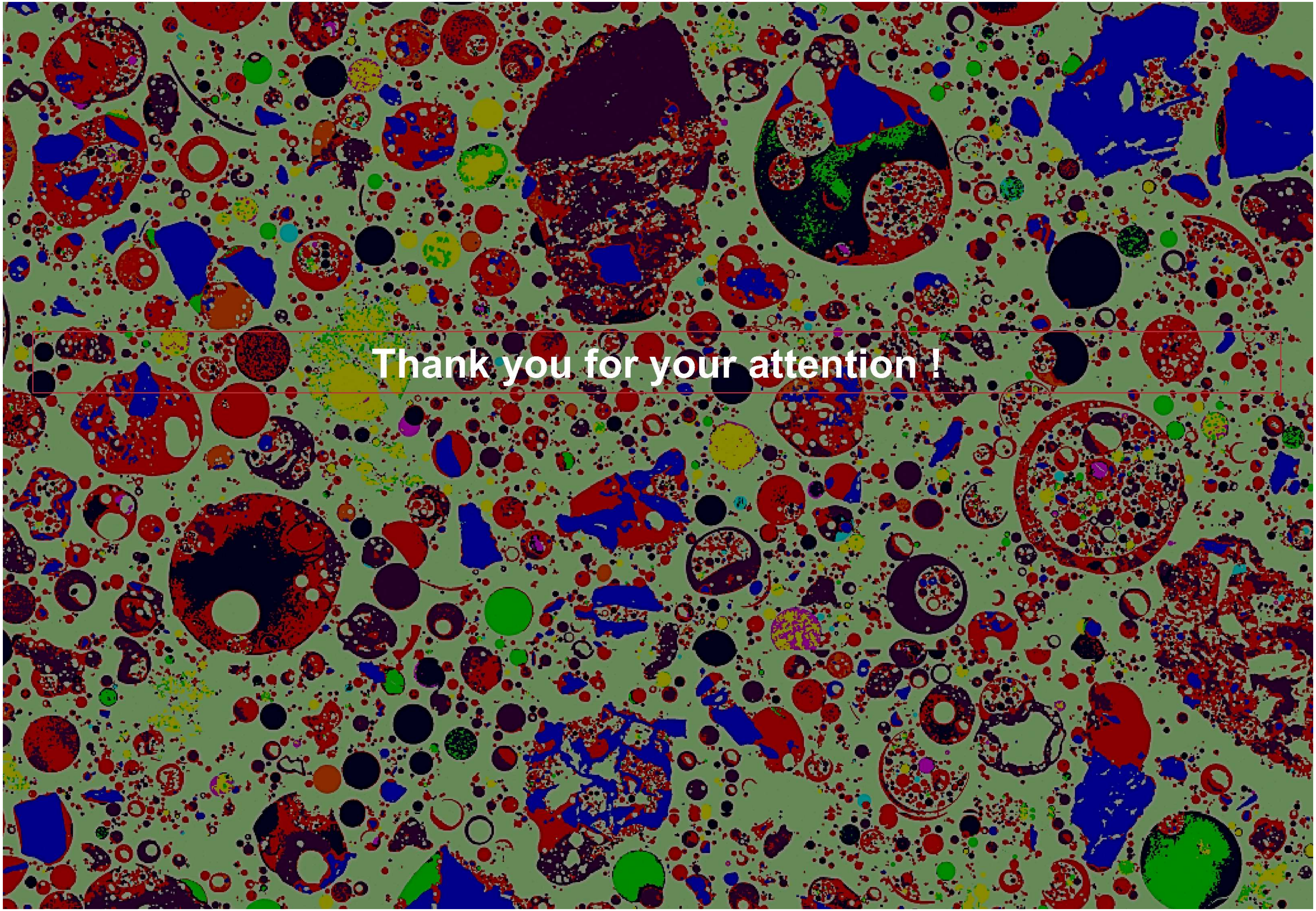
OPC – 360 d



- Classical EDX quantifications have been operated in function of depth
- In theory, pocket of Msa should have a buffering effect with sulfates before creating TSA in CSH (smallest pores…)
- IA combined to EDX clearly show that both phenomena seem coexist…

Concluding remarks

- Classification techniques allow us to quantify with robustness noisy but fast Mappings of elements
  - Especially supervised IA
  - But you are encouraged to play with the technique which will resolve your problem !
- Demonstrated the first application of the SVM-MRF classification on SEM multispectral image datasets of blended cement and blended cement paste
- Good agreement with known values and those measured by XRD Rietveld for selected SCMs & natural pozzolans
- Good results were obtained in hydrated blended cement paste


Thank you for your attention !