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Mineral transformations in biomass combustion

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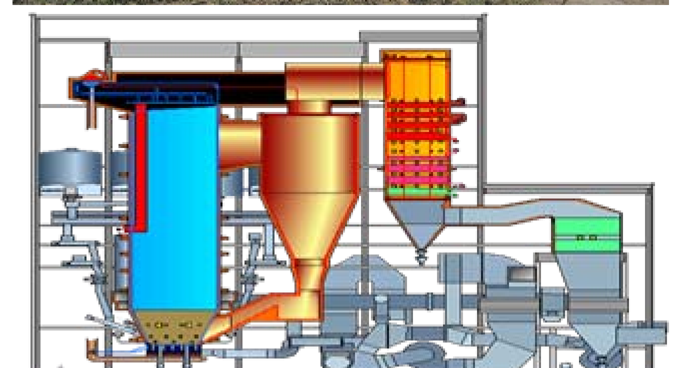
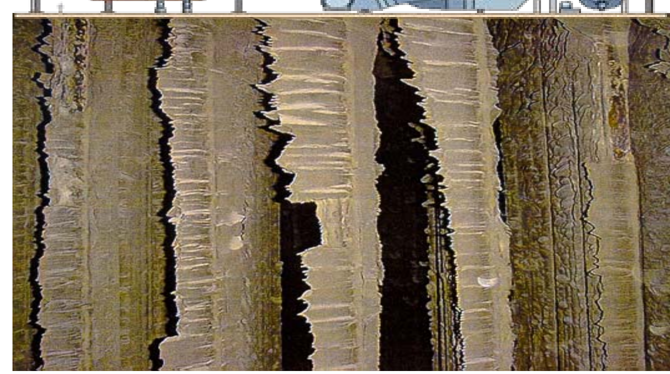
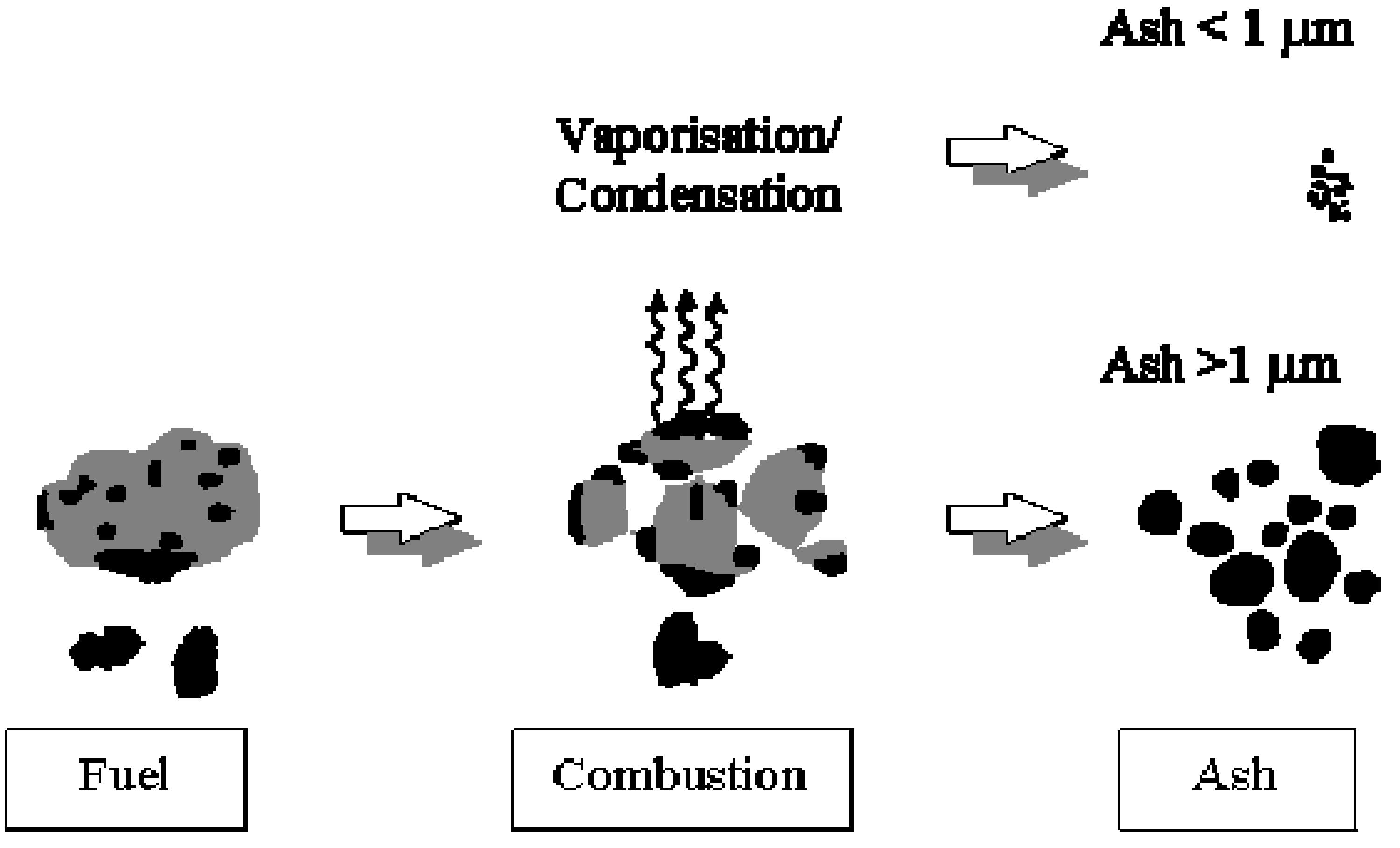
Introduction and Background

- Biomass in Scandinavia includes logging residue (tree top and branches)
- Utilized in large-scale FBC with simultatious power production
- Ash-related problems in large-scale units: fouling, slagging and corrosion of furnace equipment.

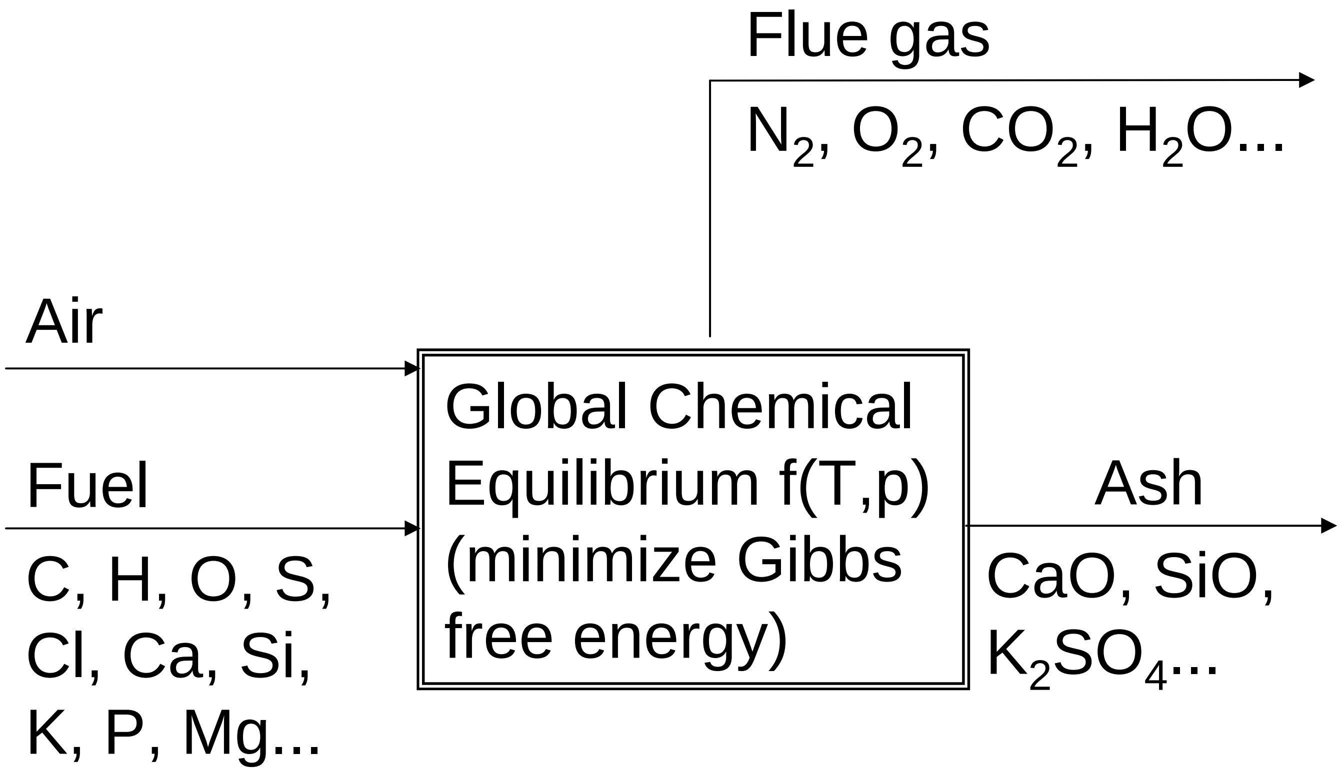




Ash formation mechanisms



Equilibrium modelling



Mineral transformation/Ash formation

- Hypothesis 1: Global equilibrium
  - ash species predicted by global equilibrium
  - homogeneous fuel and indefinite reaction time
- Hypothesis 2: Locally global equilibrium
  - global equilibrium for each fuel particle
  - inhomogeneous fuel and indefinite reaction time
- Hypothesis 3: No equilibrium reached
  - ash-forming matter transforms slowly
  - inhomogeneous fuels and limited reaction time

Objectives

- Model the equilibrium ash chemistry of individual fuel particles
- Validate the results experimentally by measuring the ash chemistry after ashing
- Determine the chemical forms of the ash-forming matter by low temperature ashing
- Discuss the transformation of fuel minerals to equilibrium ash species

Method

Modelling:

- Multiphase Chemical Equillibrium Calculation
- Phases present at chemical equillibrium

Measuring:

- Ashing in laboratory oven at 1000°C, 4 h
  - SEM-EDXA
  - PXRD
- Low-temperature ashing
  - PXRD

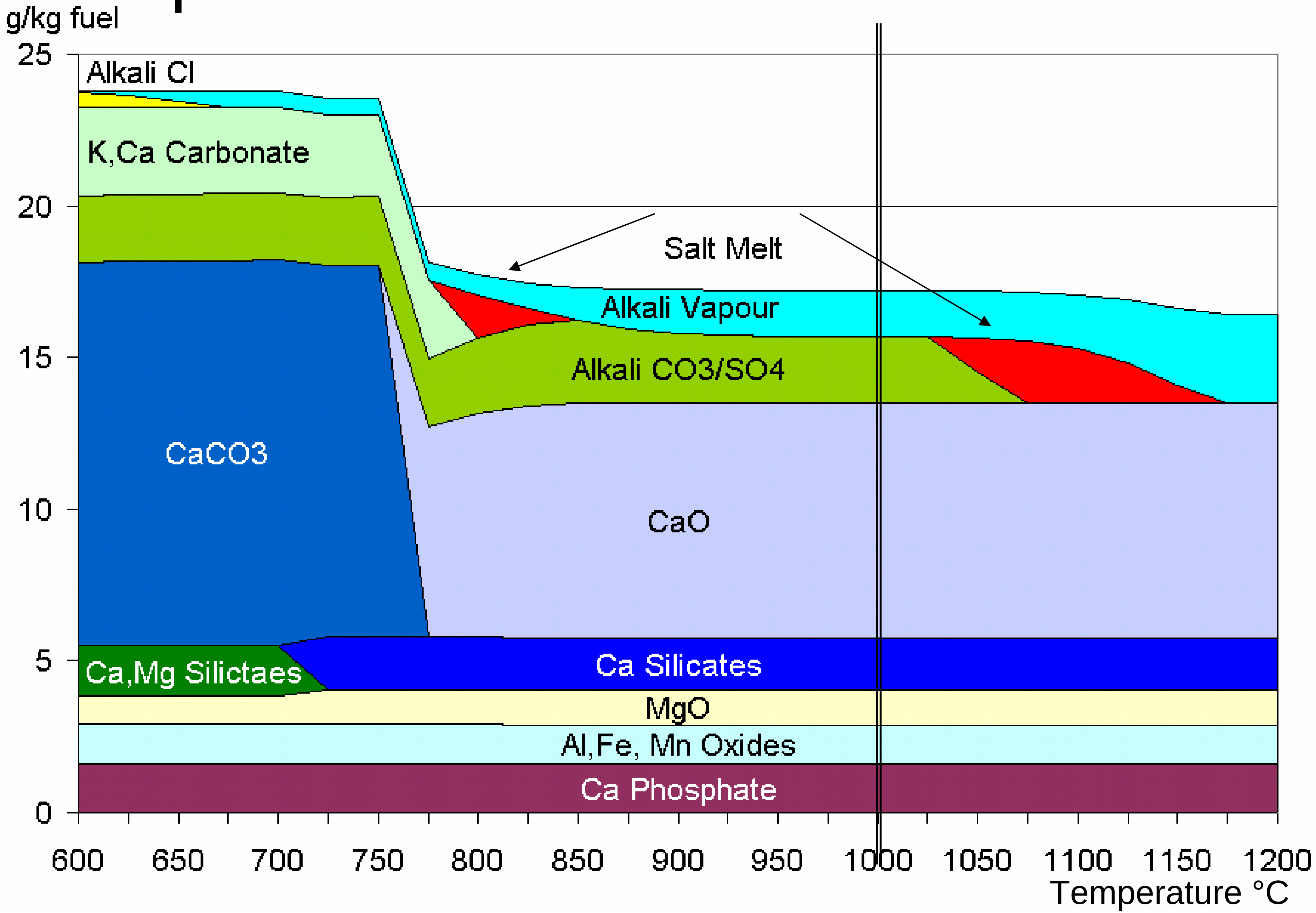
Three samples of Spruce:

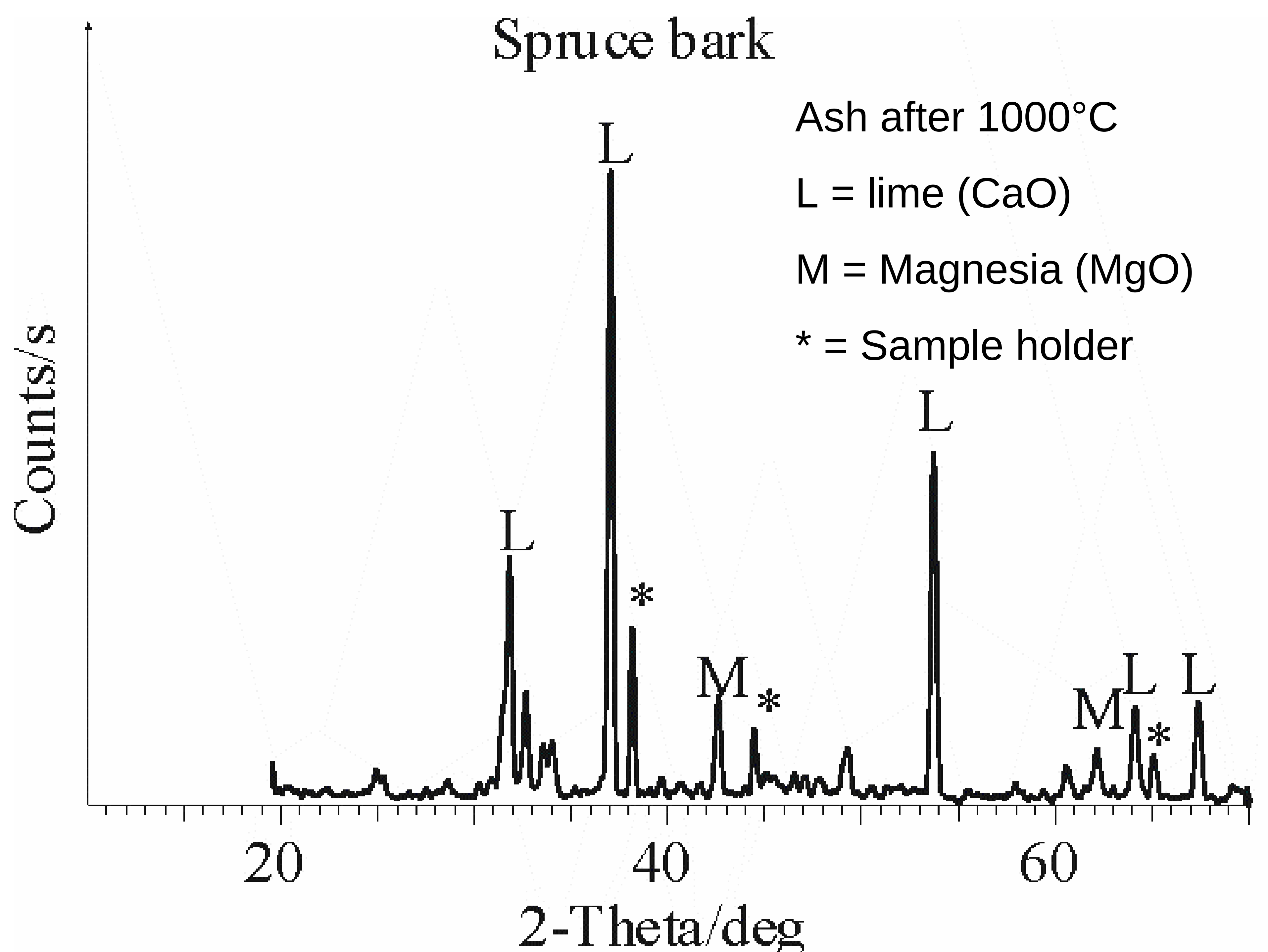
bark, needles and shoots

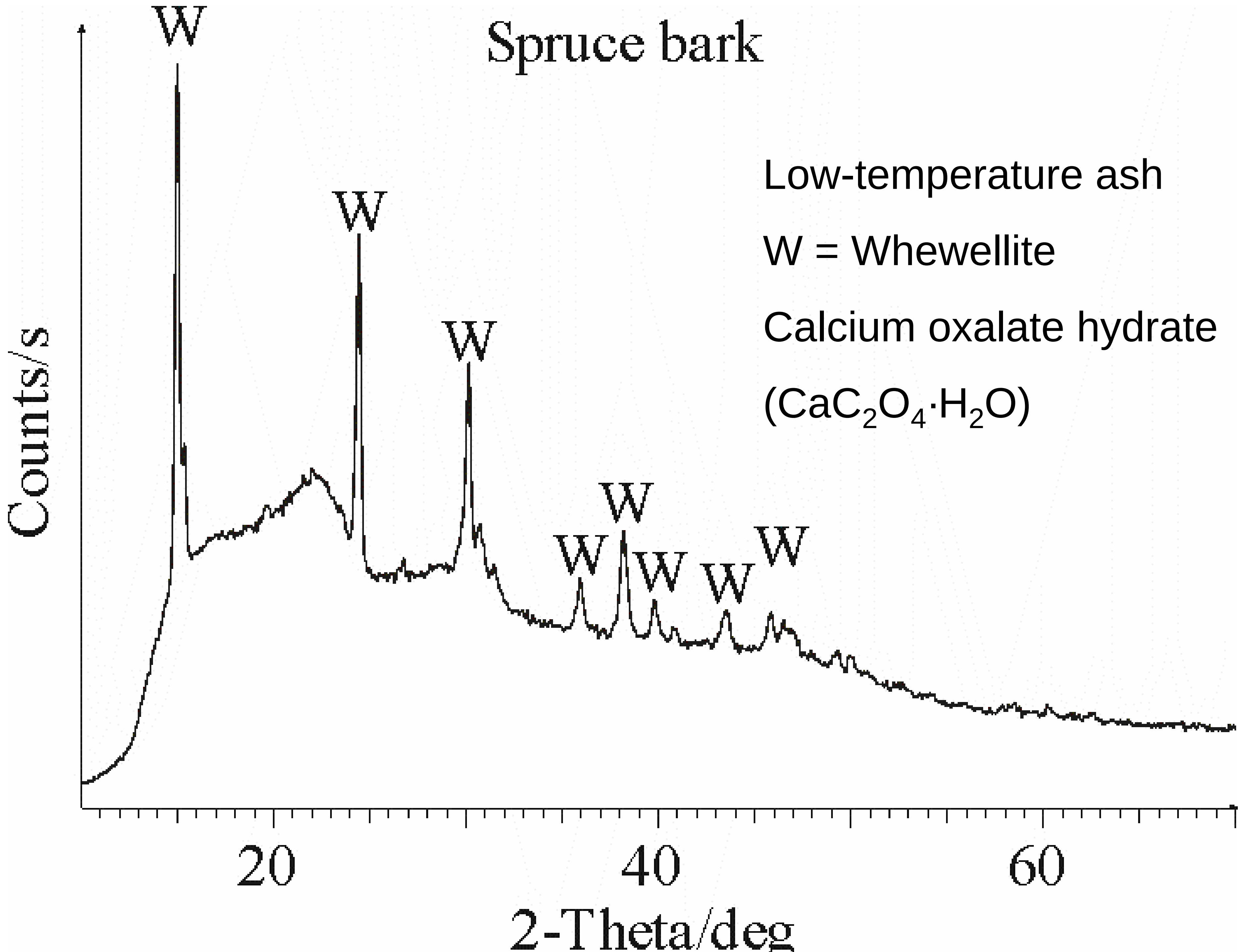
Contents of ash-forming elements

mg/kg D.S.	Bark	Needles	Shoots
Si	171	6640	300
Ca	8350	8030	1670
Mg	865	1050	907
Mn	714	1390	245
K	2030	4270	14600
P	452	1540	3830
S	367	704	1320
Cl	260	504	1090

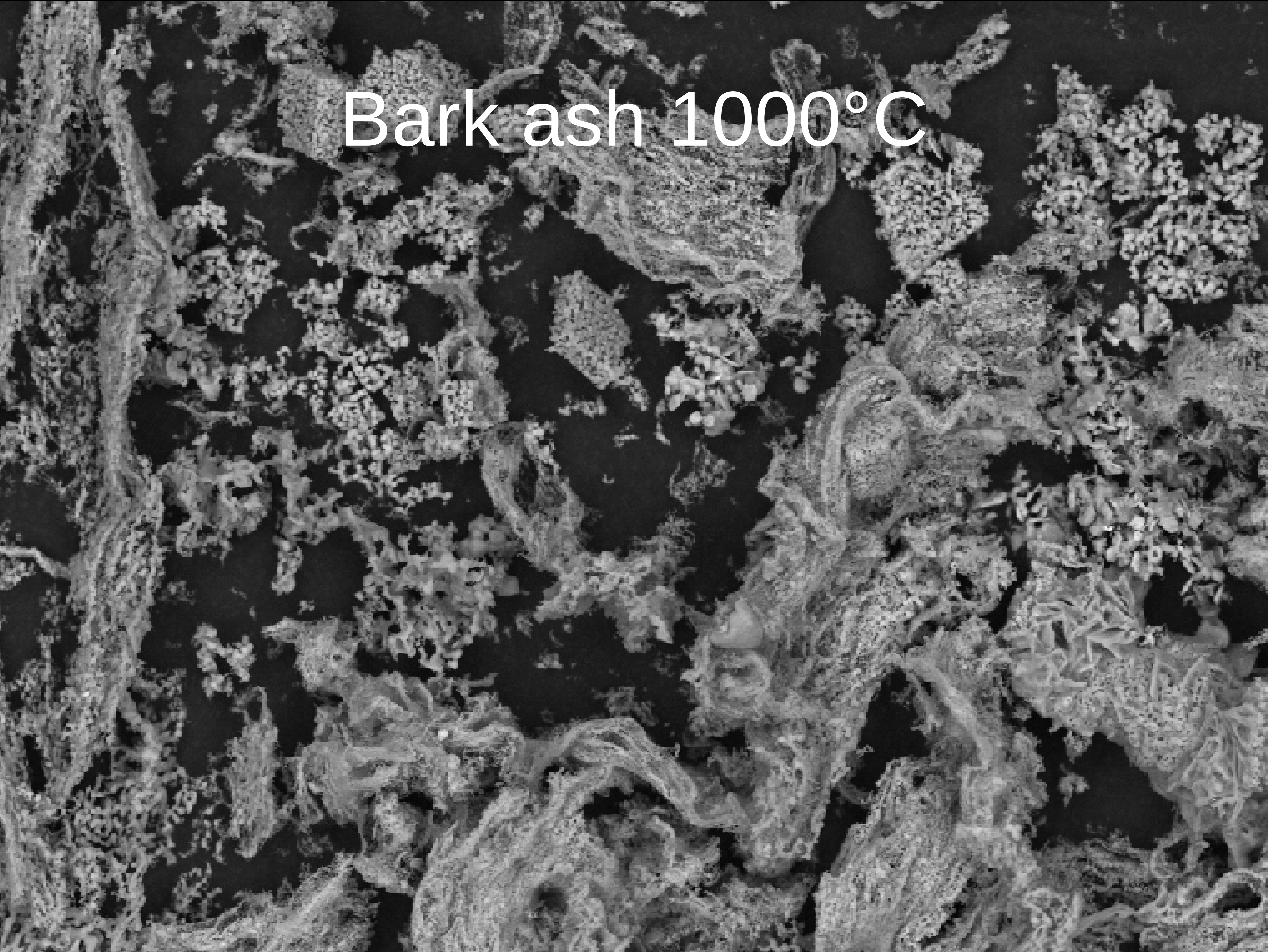
Equilibrium bark ash 600 - 1200°C

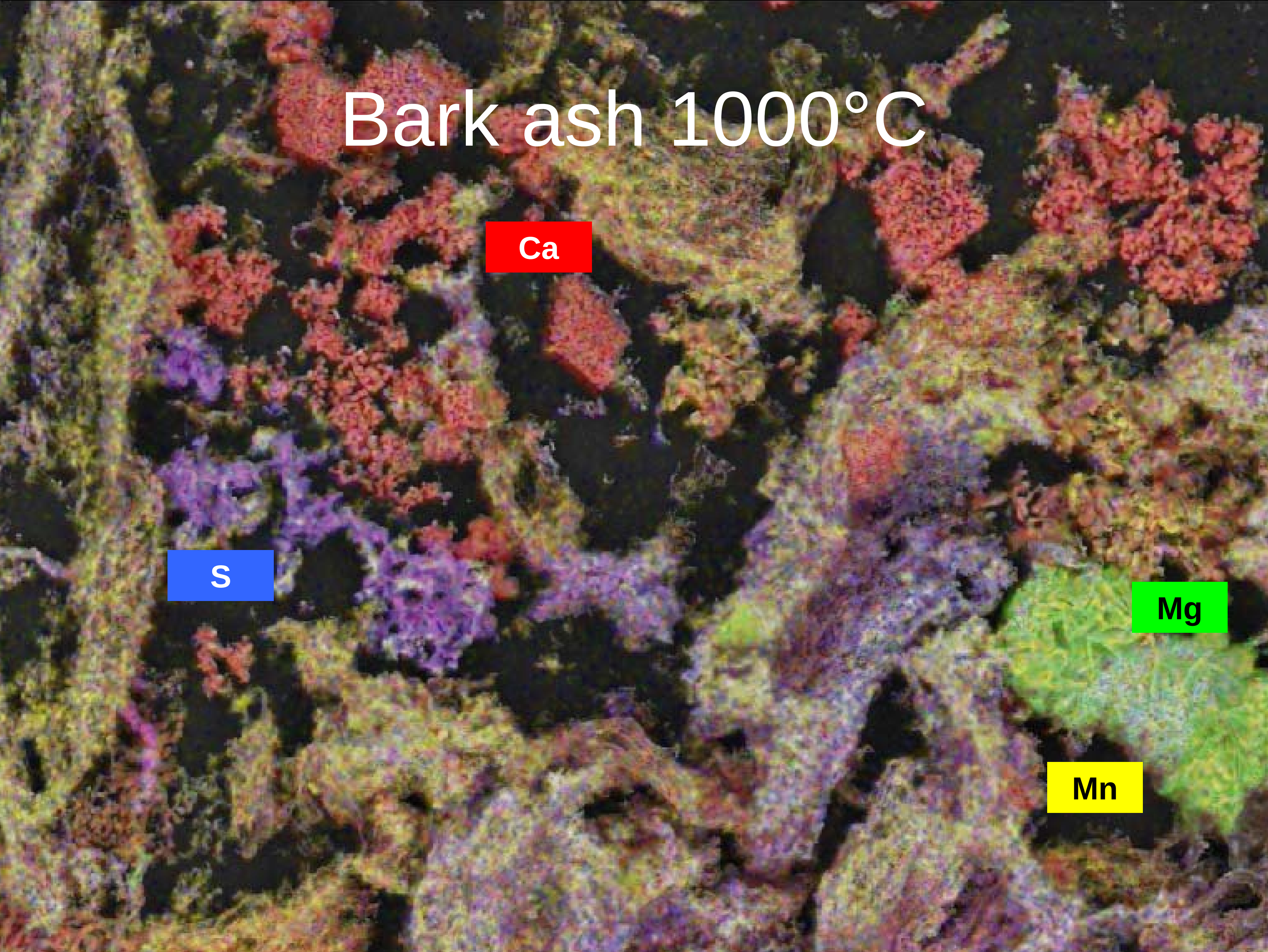


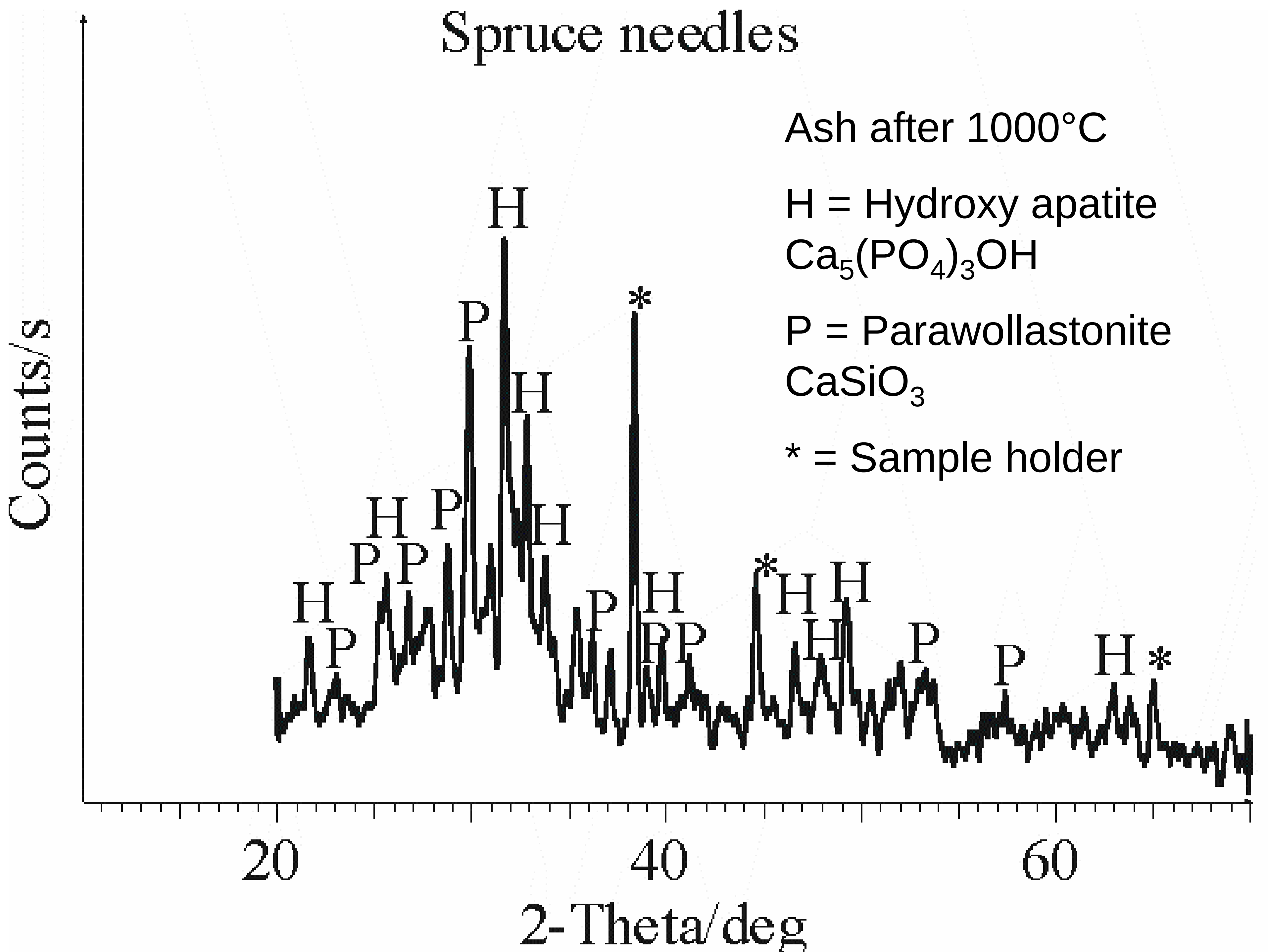

Spruce bark
Ash after 1000°C
L = lime (CaO)
M = Magnesia (MgO)
* = Sample holder
L
L
*
M
*
L
M
L
*
L
Counts/s
20
40
60
2-Theta/deg



Spruce bark
Low-temperature ash
W = Whewellite
Calcium oxalate hydrate
($CaC_2O_4 \cdot H_2O$)
W
W
W
W
W
W
W
W
Counts/s
20
40
60
2-Theta/deg


Bark ash 1000°C

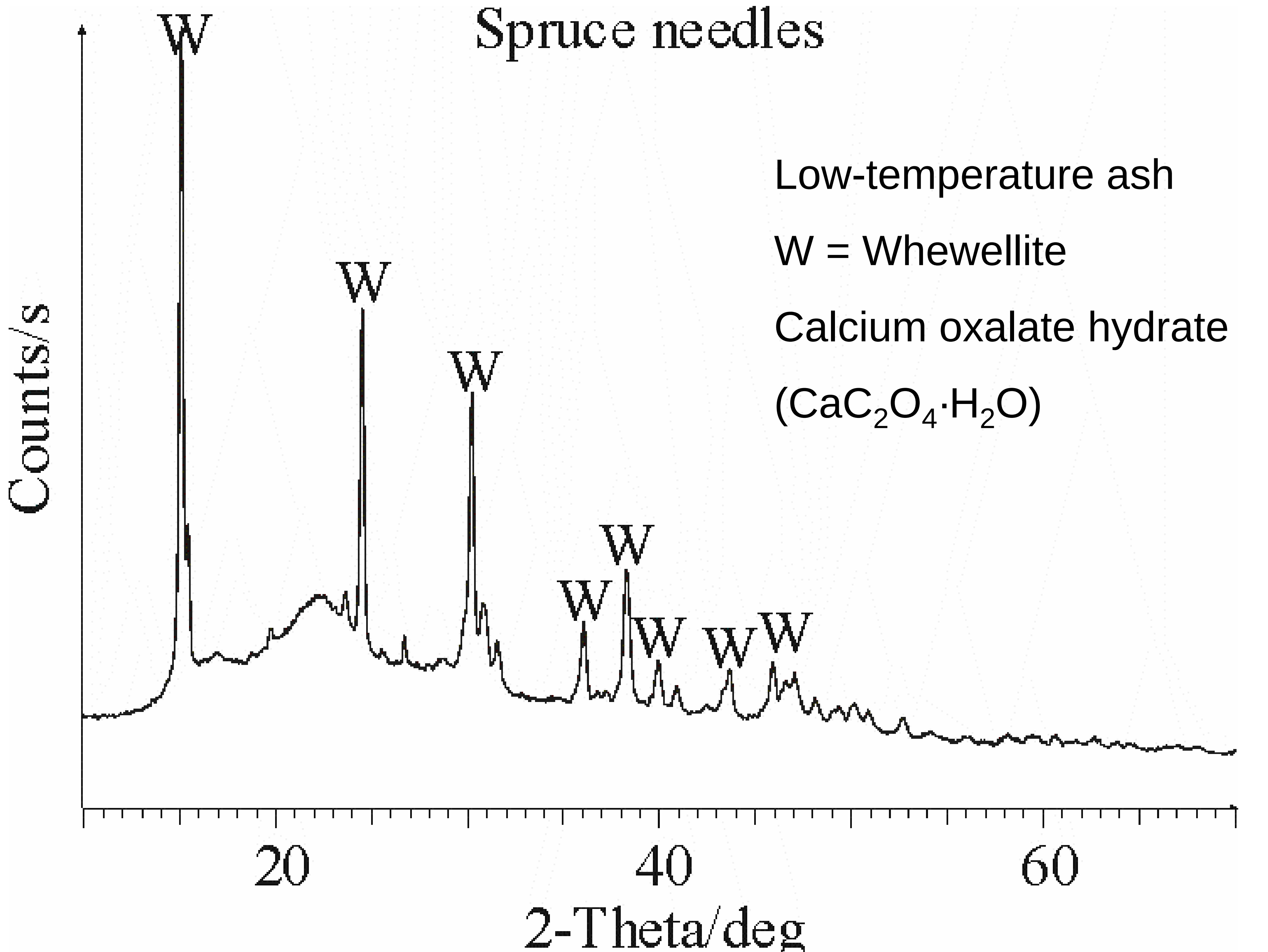

Bark ash 1000°C
Ca
S
Mg
Mn

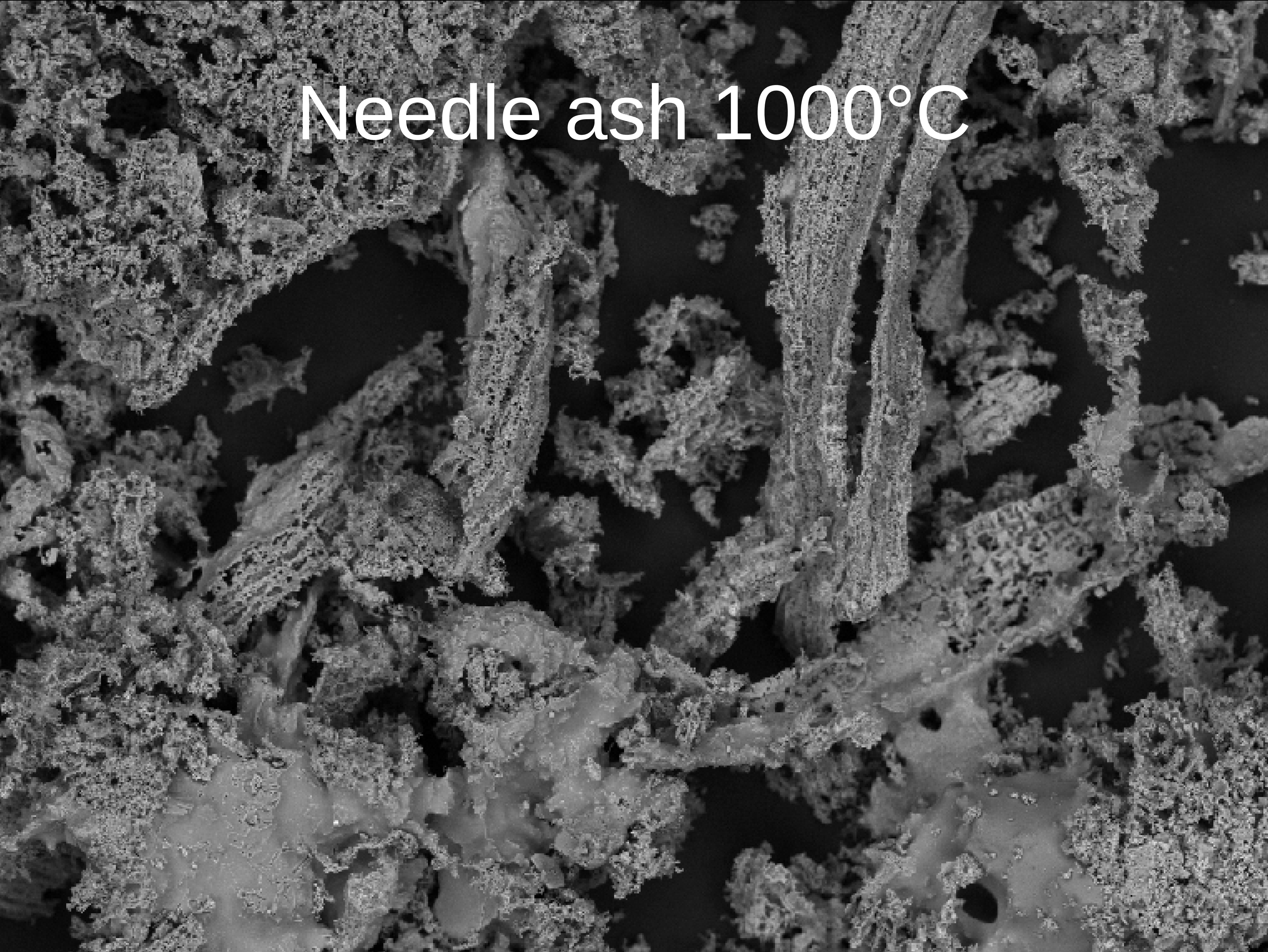


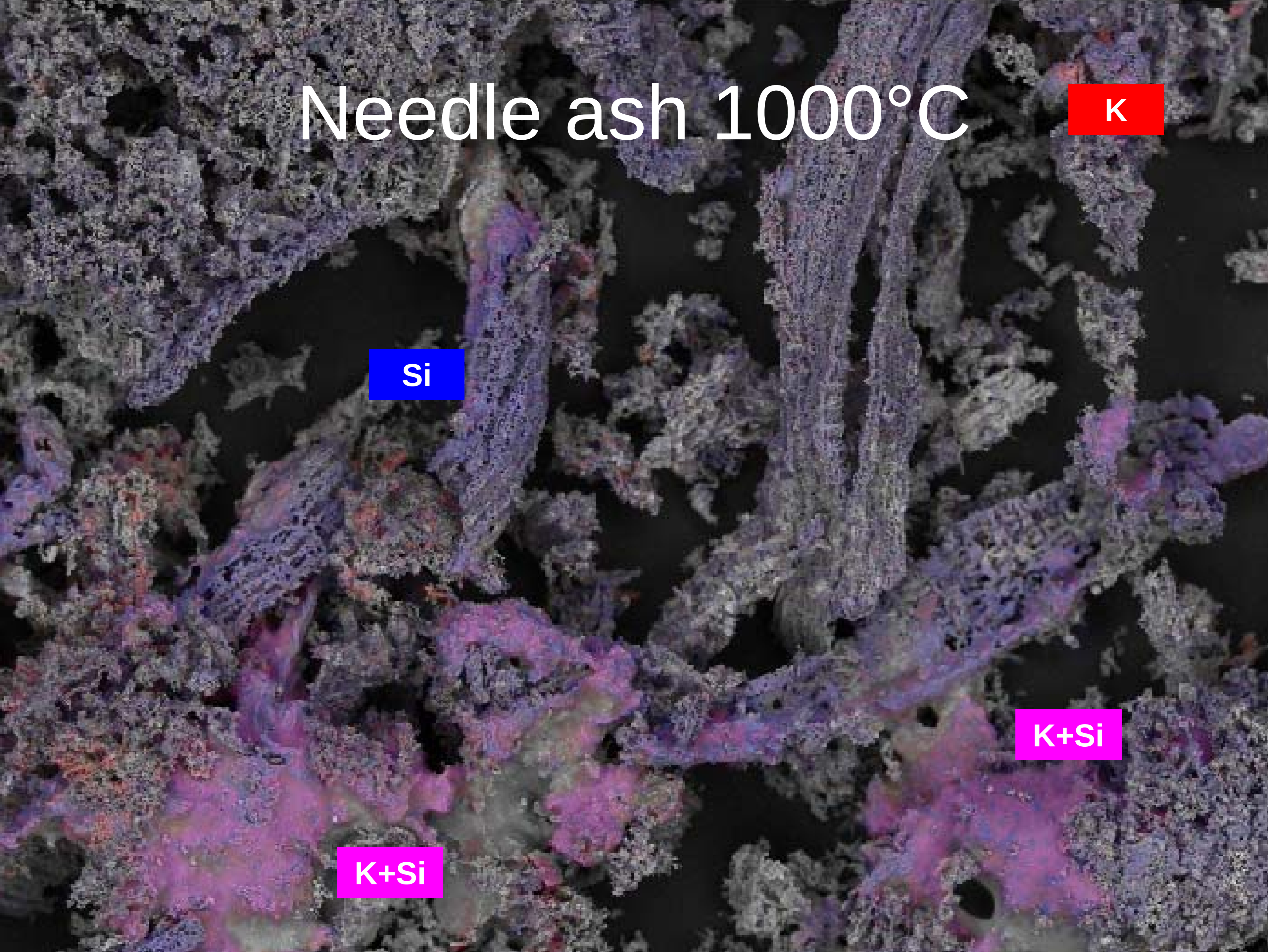
Spruce needles
Ash after 1000°C
H = Hydroxy apatite
$Ca_5(PO_4)_3OH$
P = Parawollastonite
$CaSiO_3$
* = Sample holder
Counts/s
20
40
60
2-Theta/deg

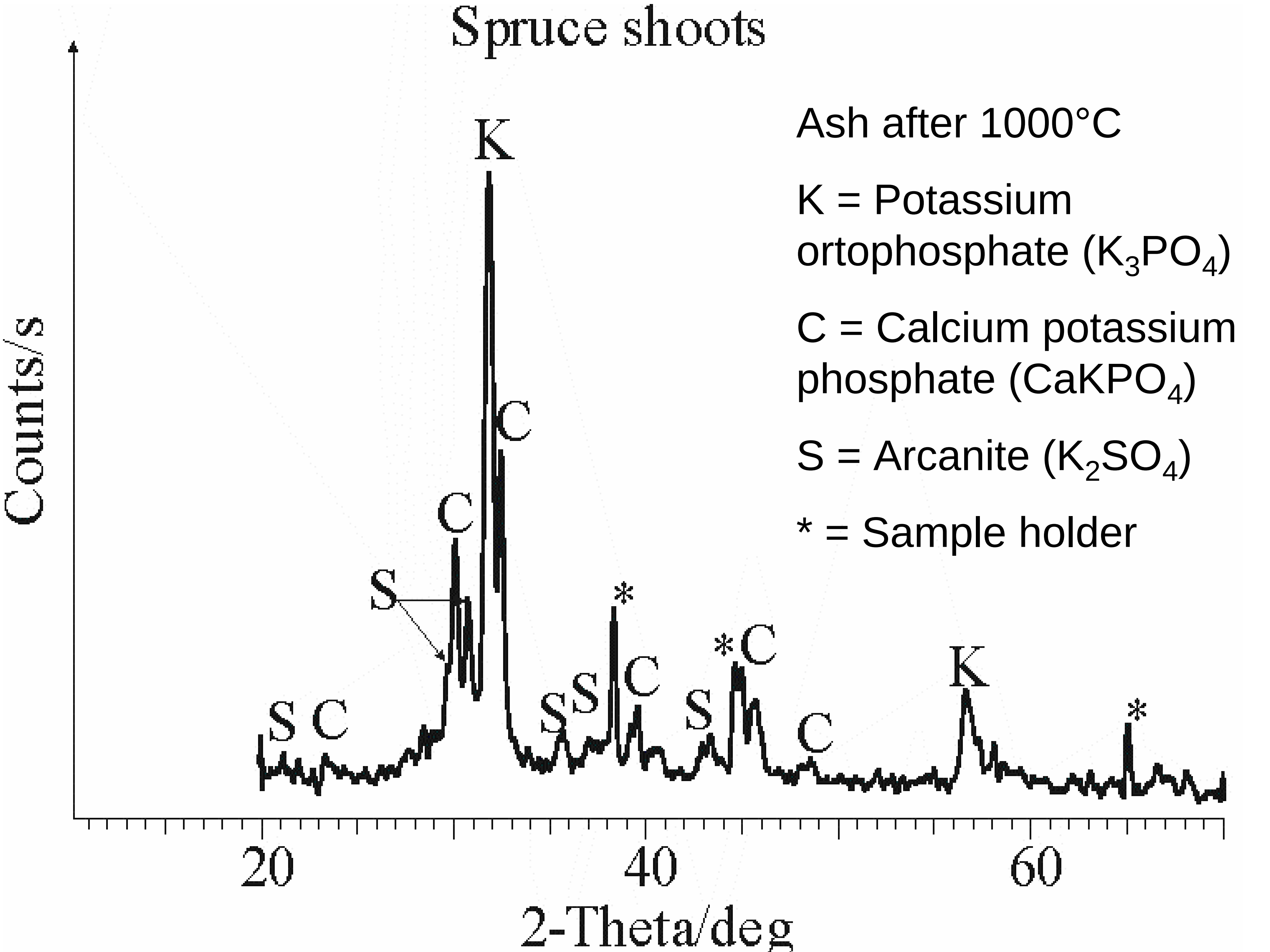
Needle equilibrium ash (g/kg fuel)

$(K,Na)_2(CO_3,SO_4)(ss)$	3.23
of which is K_2SO_4	*99%*
$Ca_5(PO_4)_3OH\ (s)$	8.33
$(Ca,Mg,Fe)SiO_3(ss)$	8.89
of which is $CaSiO_3$	*98%*
$CaMgSi_2O_6(s)$	8.94
Oxide/Silicate Melt	7.39
of which is SiO_2	*62%*
of which is K_2O	*35%*


Spruce needles
Low-temperature ash
W = Whewellite
Calcium oxalate hydrate
($CaC_2O_4 \cdot H_2O$)
W
W
W
W
W
W
W
W
Counts/s
20
40
60
2-Theta/deg

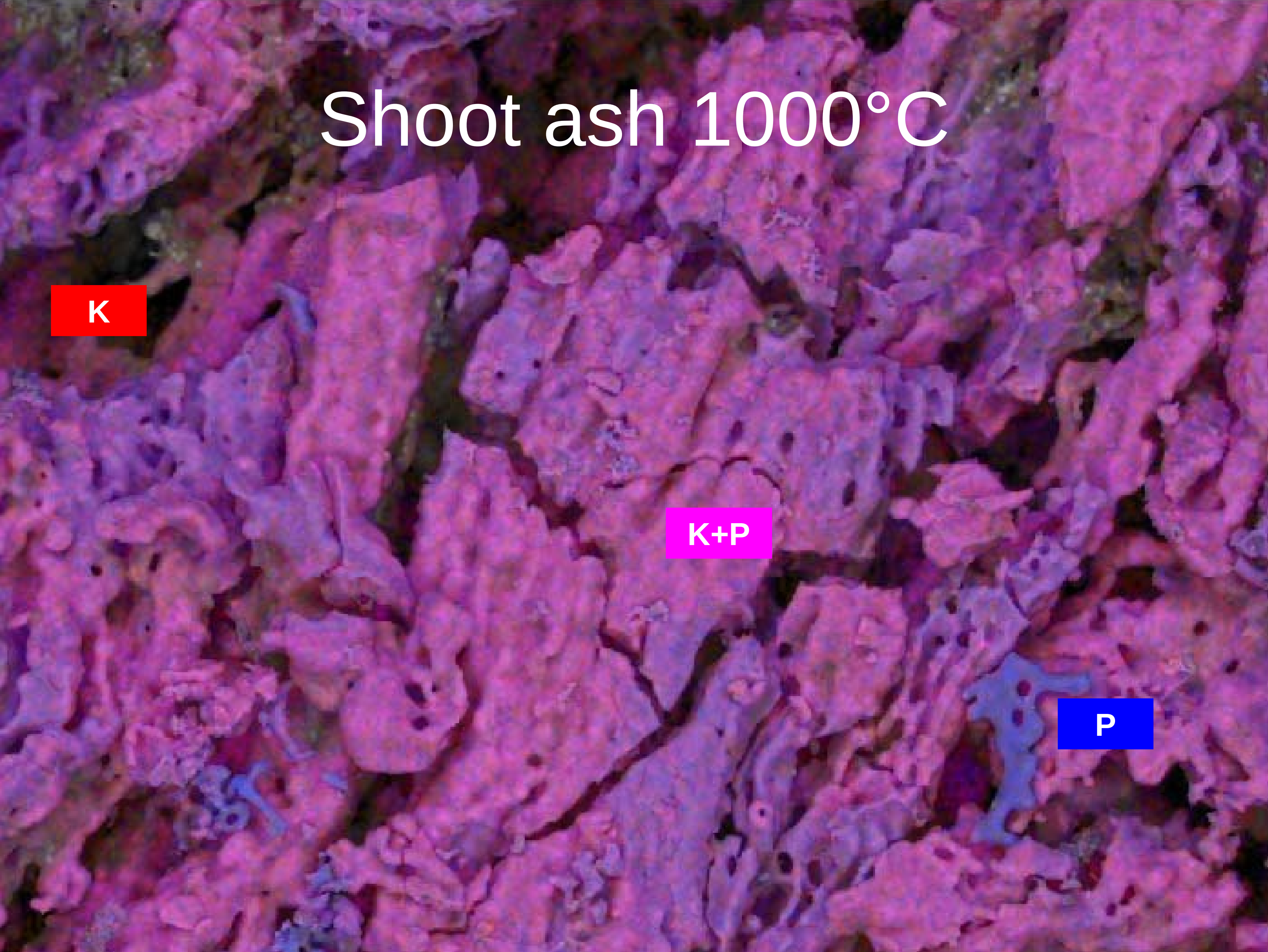

Needle ash 1000°C

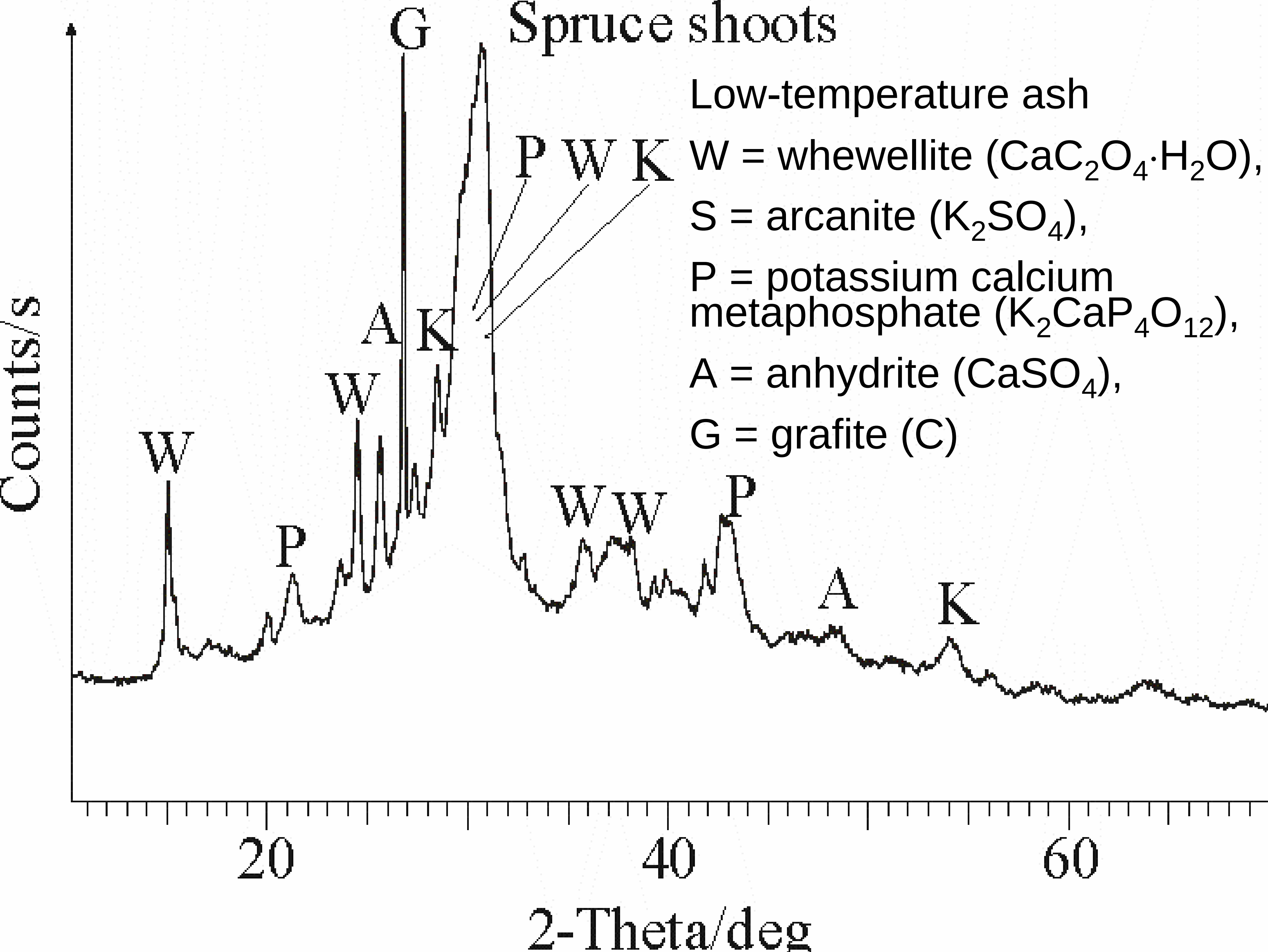

Needle ash 1000°C
K
Si
K+Si
K+Si


Spruce shoots
Ash after 1000°C
K = Potassium ortophosphate (K_3PO_4)
C = Calcium potassium phosphate ($CaKPO_4$)
S = Arcanite (K_2SO_4)
* = Sample holder
Counts/s
2-Theta/deg
20
40
60
K
C
S
*

Shoot equilibrium ash (g/kg fuel)

$(K,Na)_2(CO_3,SO_4)(ss)$	4.23
of which is K_2SO_4	*99%*
$Ca_5(PO_4)_3OH\ (s)$	4.19
$K_3PO_4\ (s)$	20.94
$(Ca,Mg,Mn,Fe)O(ss)$	0.73
of which is MgO	*86%*
of which is MnO	*14%*
$Mn_3O_4(s)$	0.23
$Mg_2SiO_4(s)$	1.50


Shoot ash 1000°C
K
K+P
P


Spruce shoots
Low-temperature ash
W = whewellite ($CaC_2O_4 \cdot H_2O$),
S = arcanite (K_2SO_4),
P = potassium calcium metaphosphate ($K_2CaP_4O_{12}$),
A = anhydrite ($CaSO_4$),
G = grafite (C)
G
P W K
A K
W
W
P
W W
P
A
K
Counts/s
20
40
60
2-Theta/deg

Conclusions

- Single particle ash chemistry modelled
- Equilibrium phases detected in 1000°C ash
- Whewellite found in low-temperature ashes
- Originally weddellite: $CaC_2O_4 \cdot 2H_2O(s)$, that transforms differently depending on surrounding and form following main species:
  - In bark: CaO (lime)
  - In needles: $CaSiO_3$ (wollastonite) and
  - In shoots: $CaKPO_4$.

Acknowledgements

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