Identification of the $K_2Ca_6Si_4O_{15}$ ternary phase in ashes of biomass mixtures

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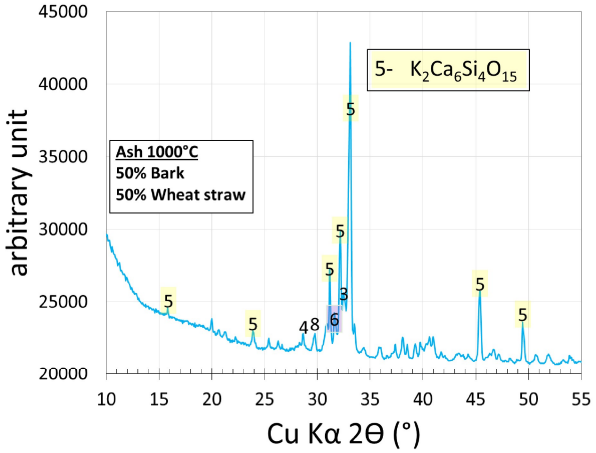

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- Introduction
- Biomass selection
- Methods
- Results
- Conclusions

Introduction

Context of the study:

Increasing demand for wood pellets in combustion processes
→ Enlarge the market to other biomass feedstock such as agricultural or forestry residues

Wood

Ash content : ~ 1%

Ash main components : SiO_2-CaO-K_2O

Agricultural waste Fuel

Ash content : 2-15%

Ash main components : SiO_2-CaO-K_2O + P_2O_5-MgO

Cl, S and N higher content than in wood

Use in combustion problematic:

- Fooling => Cleaning
- Particles => Filter
- NOX => Dedicated treatment
- Ash melting and slagging => Additive

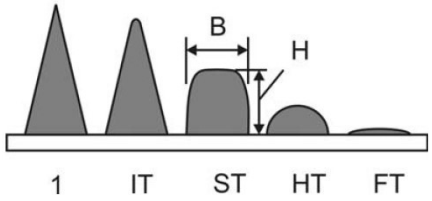
Proposed solution: blend biomass

Introduction

Context of the study:

Classical methods used in Industrie to blend

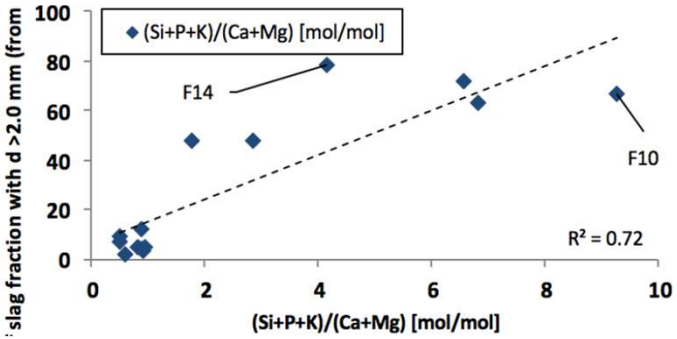
Ash melting test



Expensive
Reproducibility
Necessity for each biomass and for each mixture.

…

Fuel indexes



Easy to use but empirical approach,

Proposed method:

Physico-chemical predictive tools assuming thermodynamic equilibrium is reached

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2 biomasses selected with criteria

- Agricultural or forestry residues
- Large amount available
- Adapted for biomass transformation
- One main inorganic element (**Ca** or **Si** or **K**)

Wheat straw

Oak Bark

		Wheat straw	Oak bark
% db	Ash 550°C	6,30	8,40
%	SiO_2	**33,7**	12,2
%	CaO	6,5	**42,6**
%	K_2O	**27,4**	3,7
%	P_2O_5	2,4	0,9
%	Al_2O_3	0,1	1,7
%	MgO	1,2	1,4
%	Fe_2O_3	0,2	0,6
%	SO_3	2,7	0,7
%	CO_2	17,2	36,3
%	Na_2O	0,4	0,2
%	MnO_2	0,1	1,3

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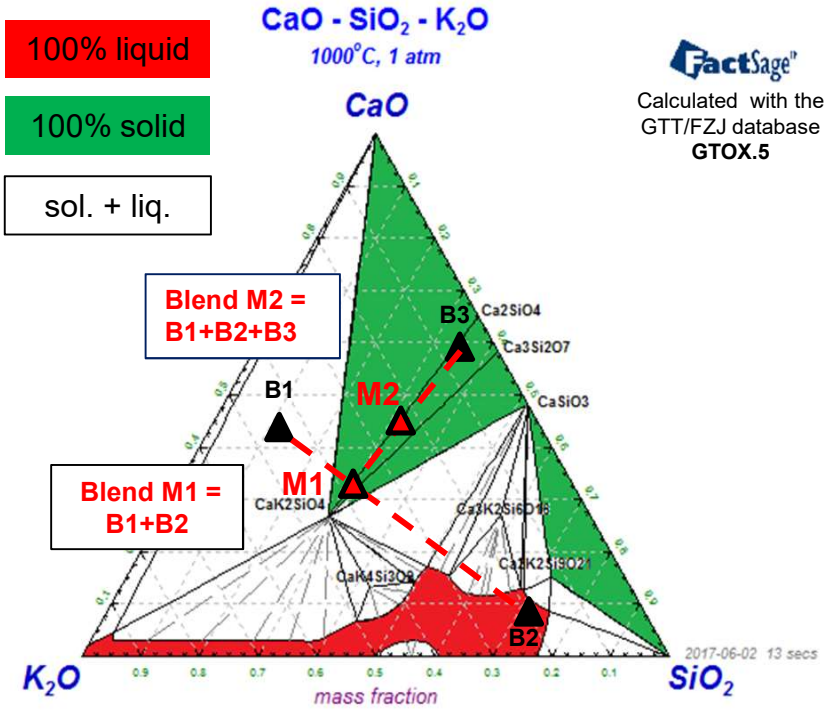
METHODS: Physico-chemical predictive tools

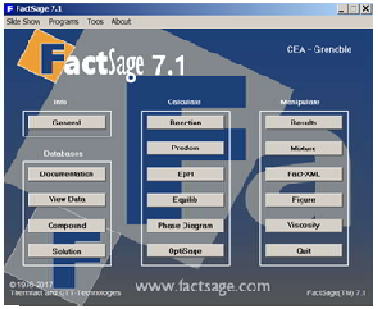
1- Simplified approach by phase diagram

- 3 major oxides of most biomass ashes are CaO, SiO_2 and K_2O
- Give a first estimation of the occurrence of liquid at a given temperature (De Fusco et al. 2016)
- Blend in high melting point compounds area (solid area in green)



2- Factsage approach with

- 3 databases (FactPS, GTOX oxides, FTSalt)
- 15 elements CHONSClCaSiPMgNaAlFeMn and atmosphere (air)

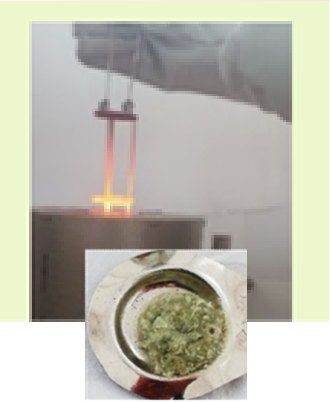


L. De Fusco, F. Defoort presented in Venice 2016 6th international symposium on energy from biomass and waste 14-17/11/2016

METHODS: Experimental approach

Compressed ash chips → favour chemical reactivity

Lab scale
Ash test
6h 1000°C
annealing/quench
XRD SEM-EDX



Compressed biomass pellets → reality

Lab scale
Pellet test
1h 1000°C
XRD

Pilot test
Boiler
XRD

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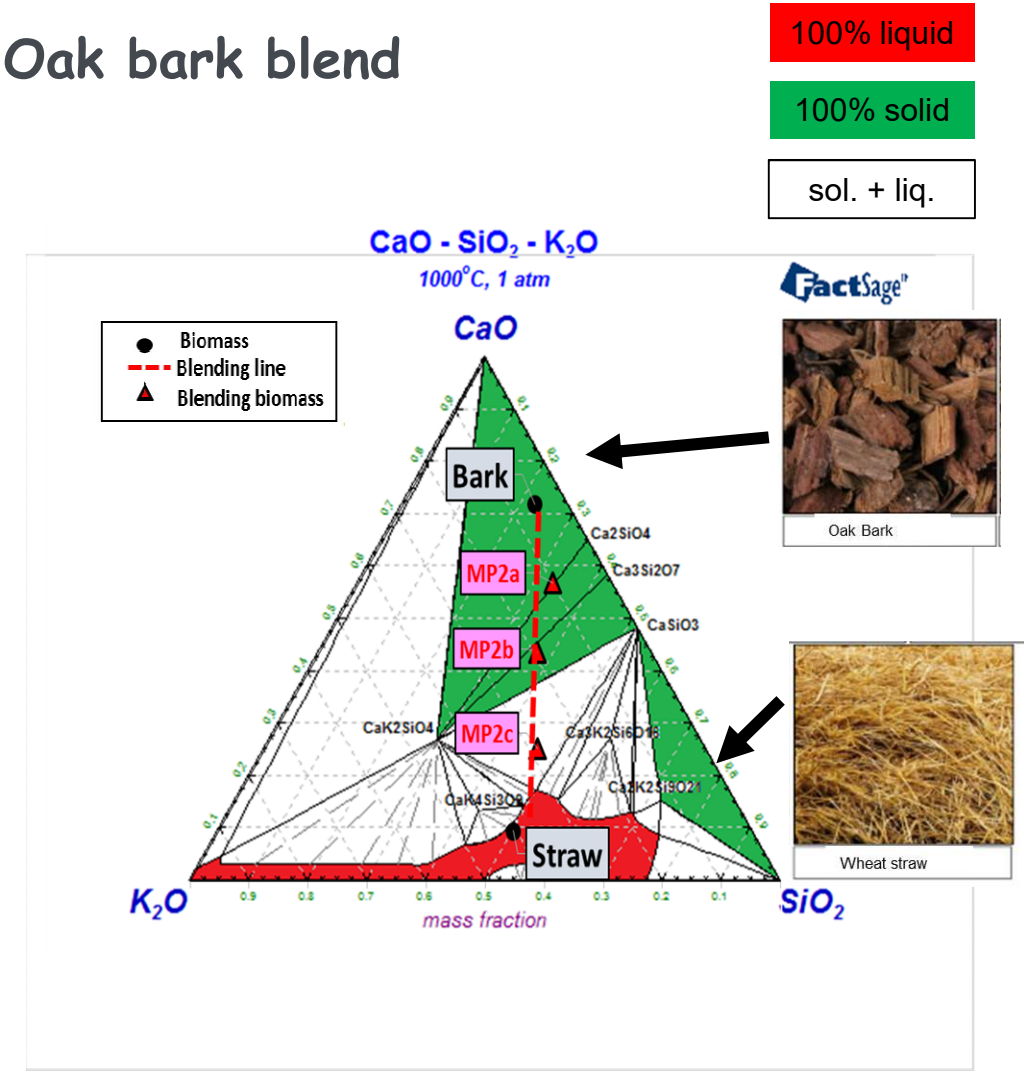
RESULTS: prediction by phase diagram

Wheat straw / Oak bark blend

Biomass mass fraction (wt% d.b.)	Oak bark	
Oak bark	100%	Solid
MP2a	80%	Solid
MP2b	50%	Solid
MP2c	20%	Solid+Liquid
Wheat straw	0%	Liquid

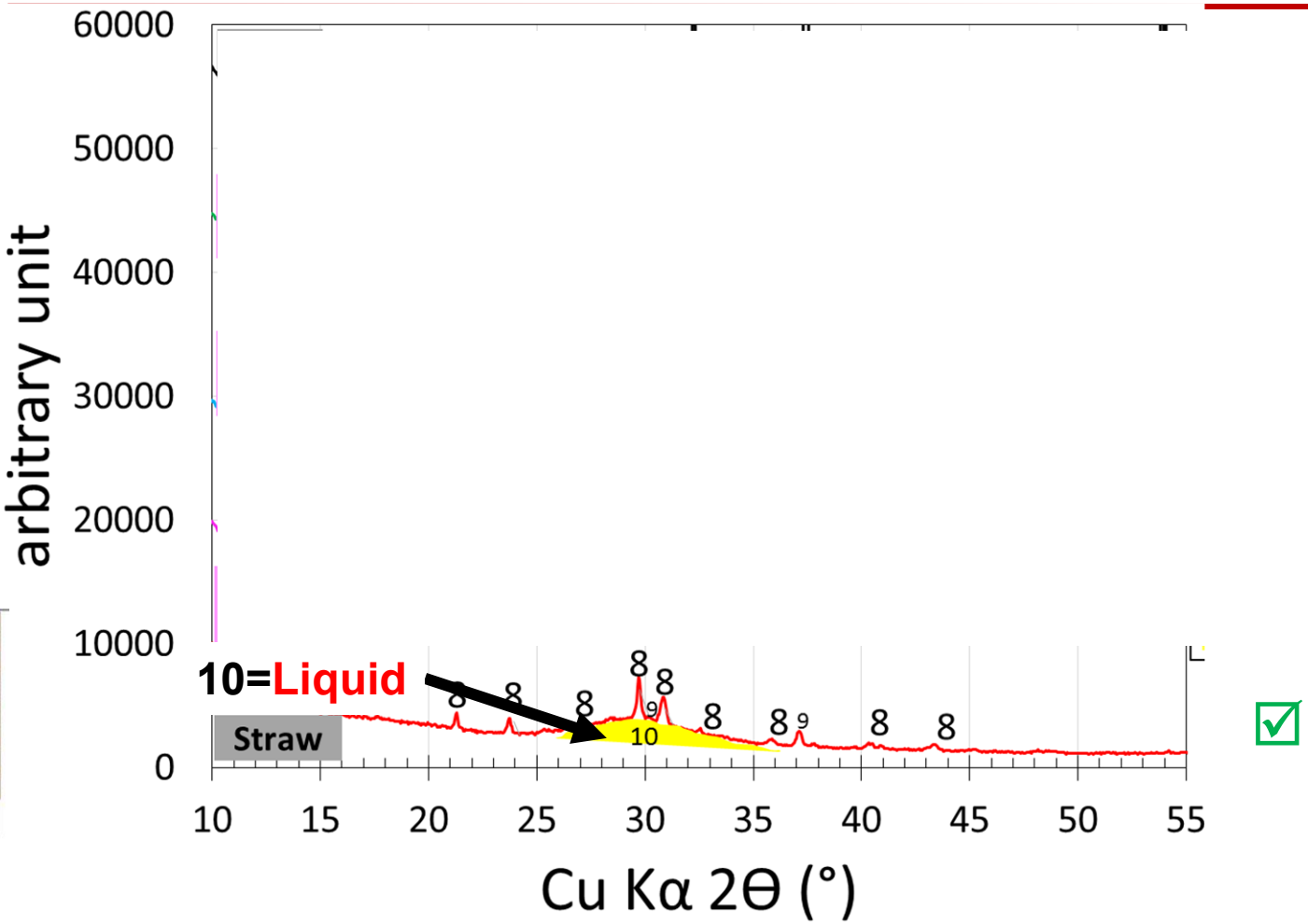


RESULTS: prediction by Factsage

Wheat straw / Oak bark blend

→Apparition of new solid phases in blend not existing in single biomass ($CaSiO_3$, $Ca_3Si_2O_7$)

RESULTS: experiments → XRD



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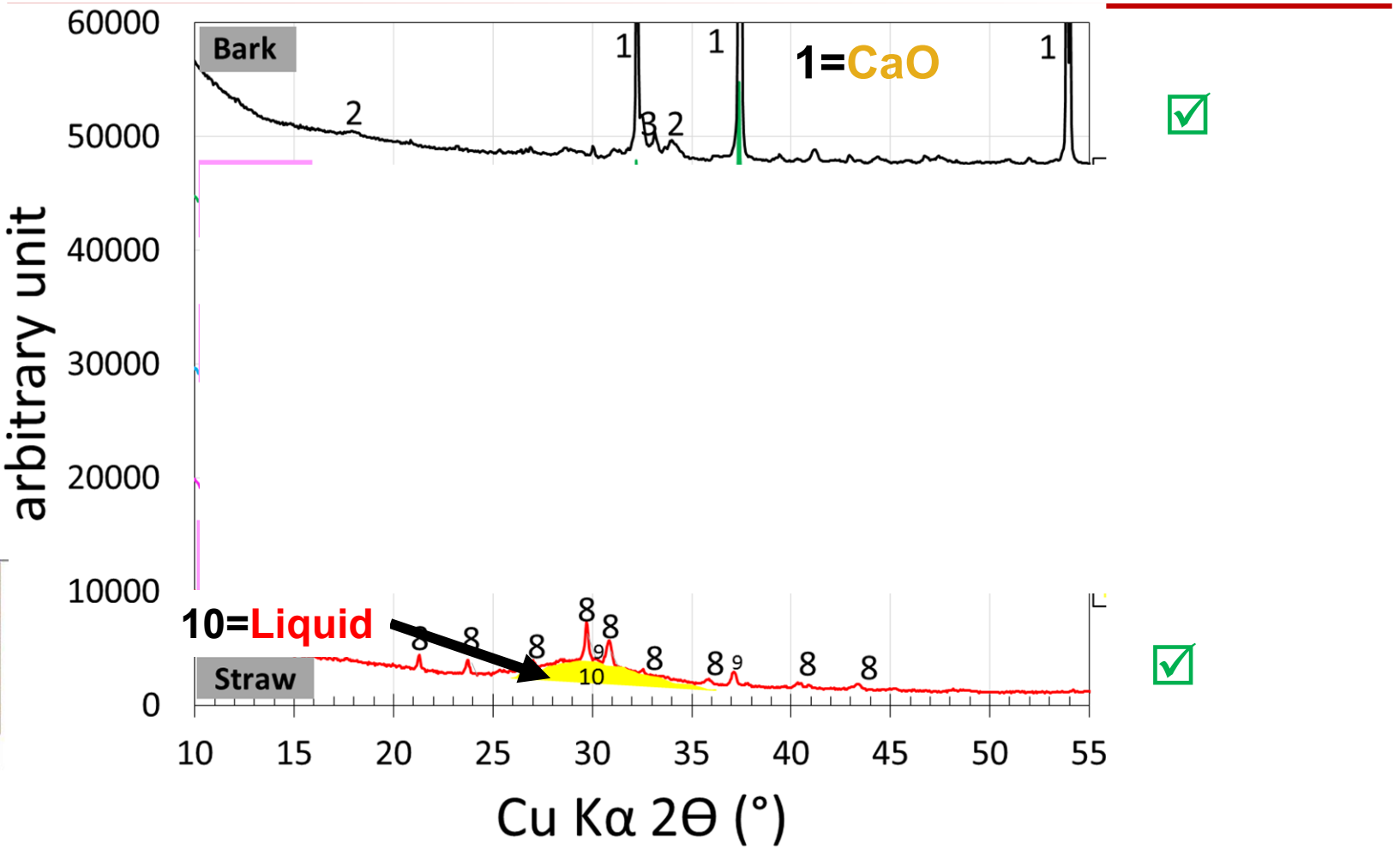
RESULTS: experiments → XRD

Oak Bark

Wheat straw



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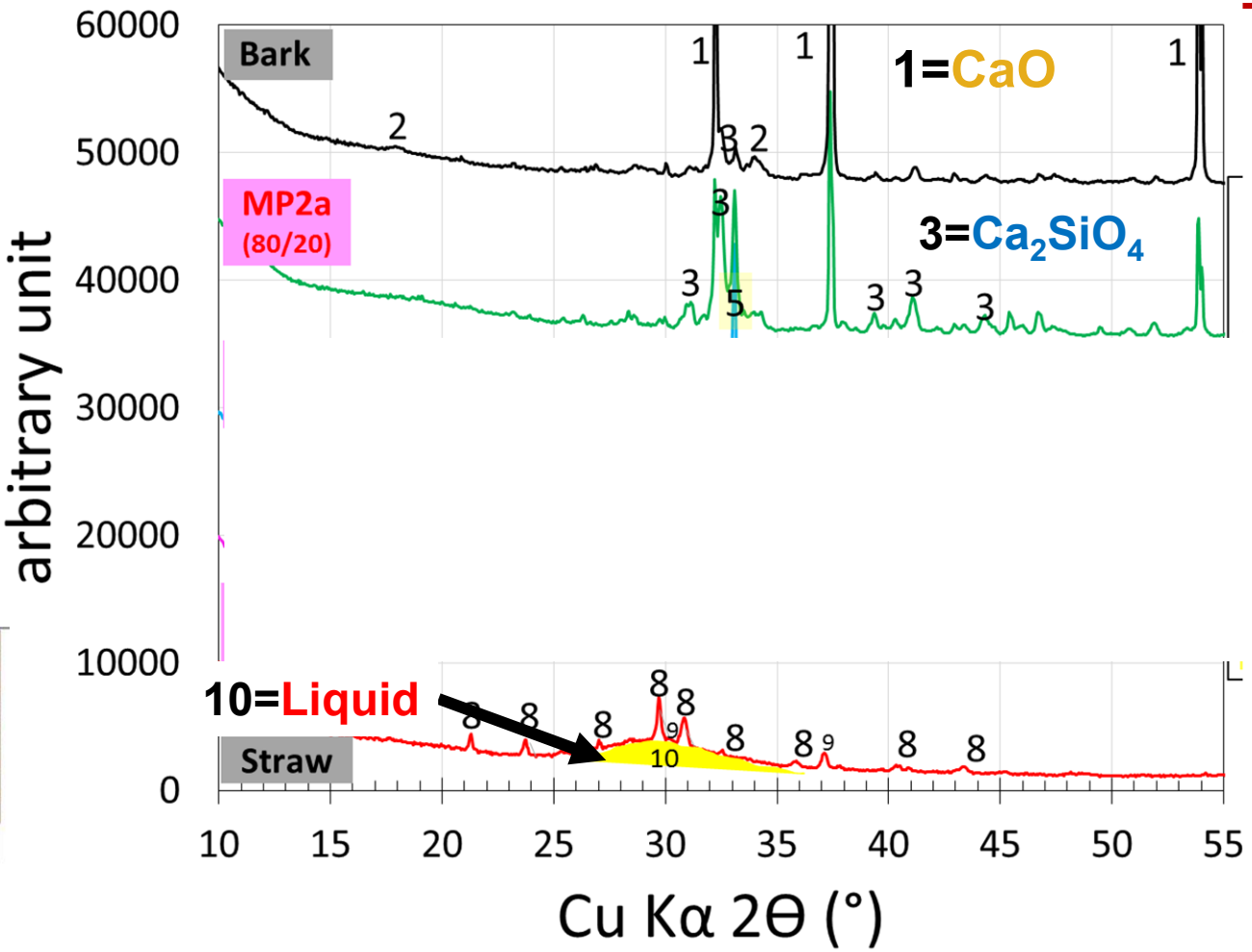
RESULTS: experiments → XRD

Oak Bark

Wheat straw



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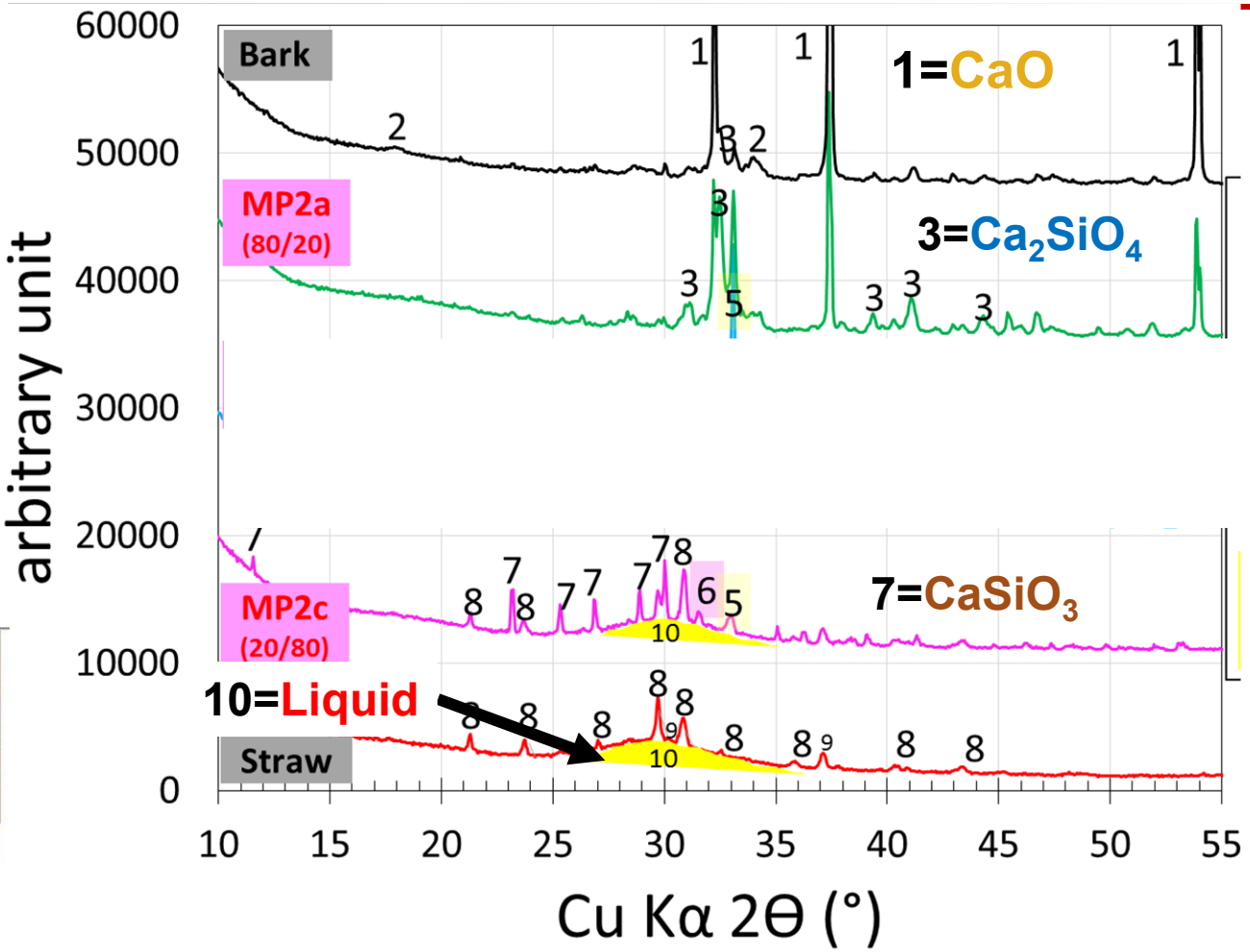
RESULTS: experiments → XRD

Oak Bark

Wheat straw



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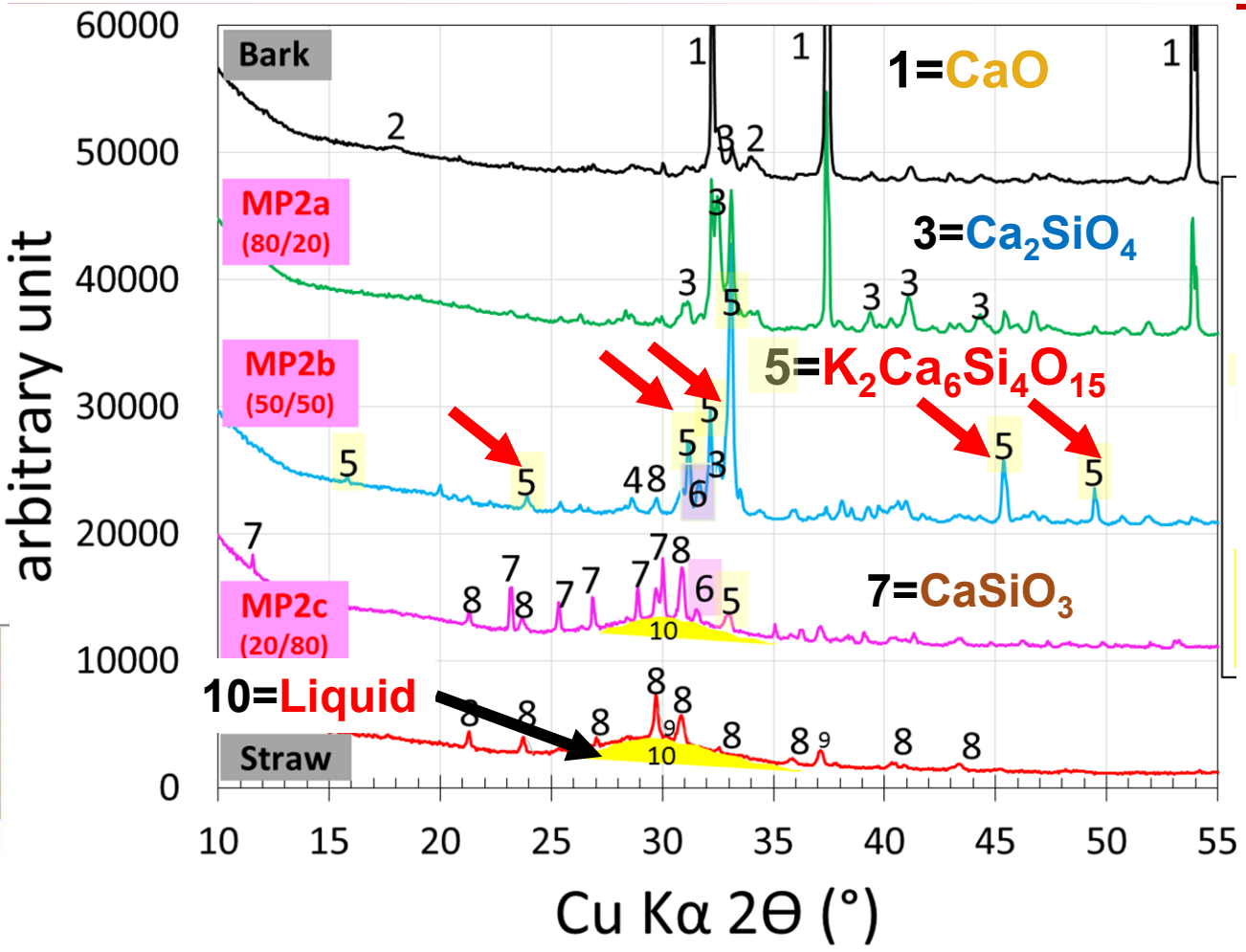
RESULTS: experiments → XRD

Oak Bark

Wheat straw



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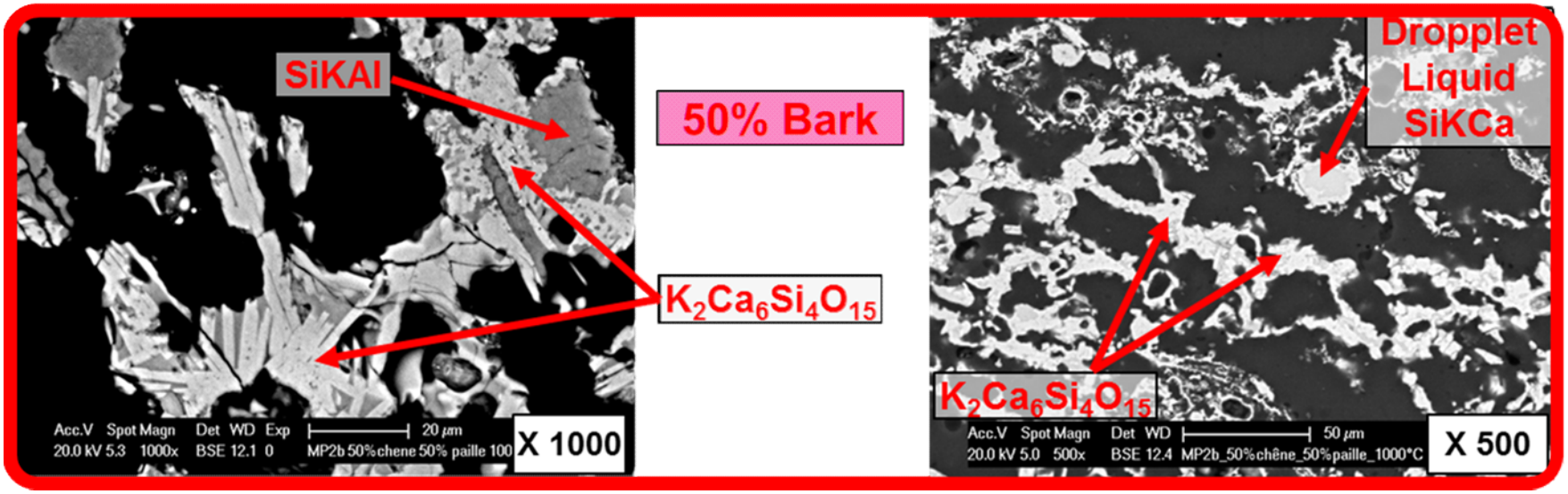
RESULTS: experiments → SEM-EDS



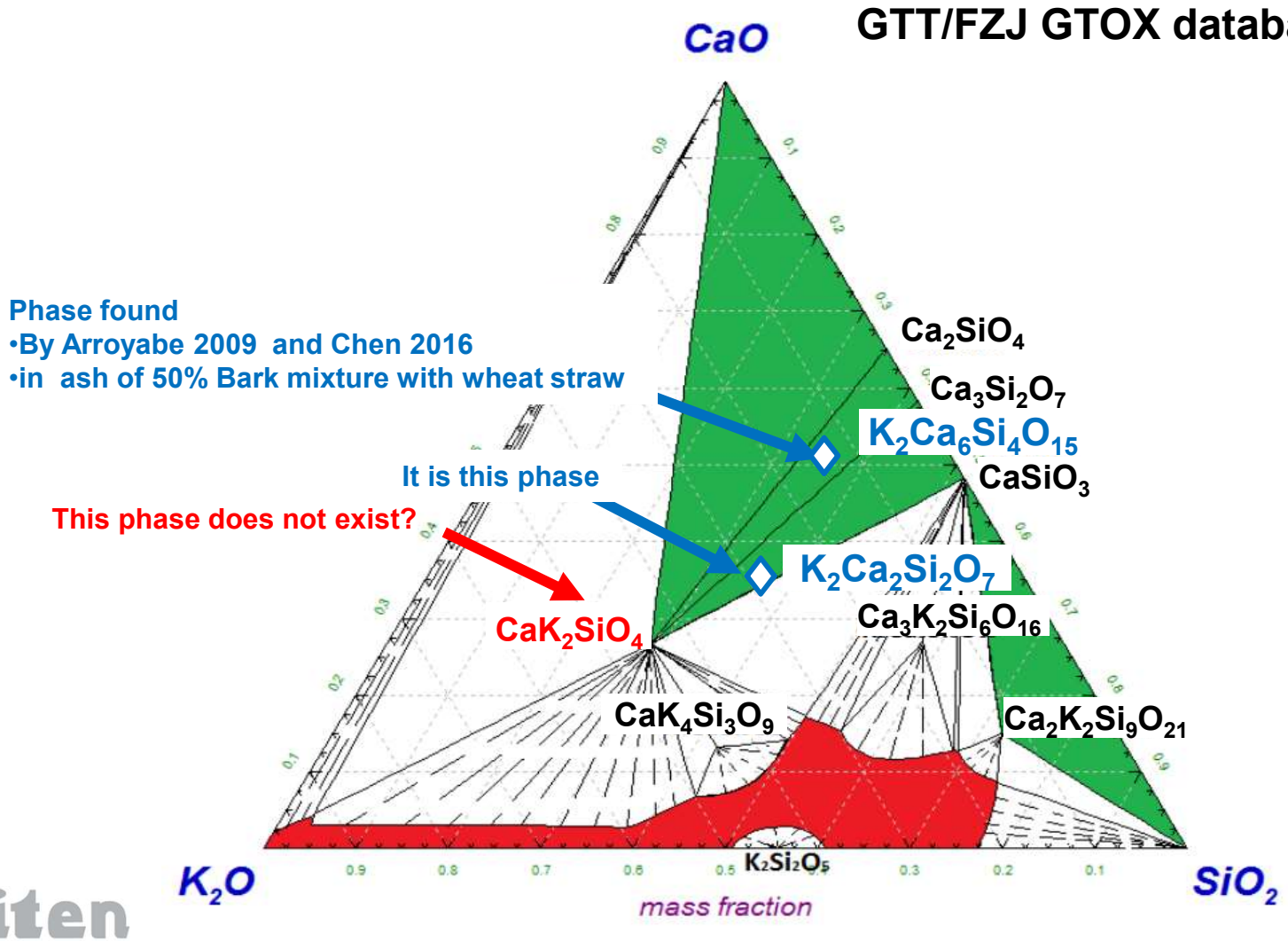
Good agreement with XRD

Discussions

Where is this ternary $K_2Ca_6Si_4O_{15}$ phase in the phase diagram?

1000°C, 1 atm

GTT/FZJ GTOX database



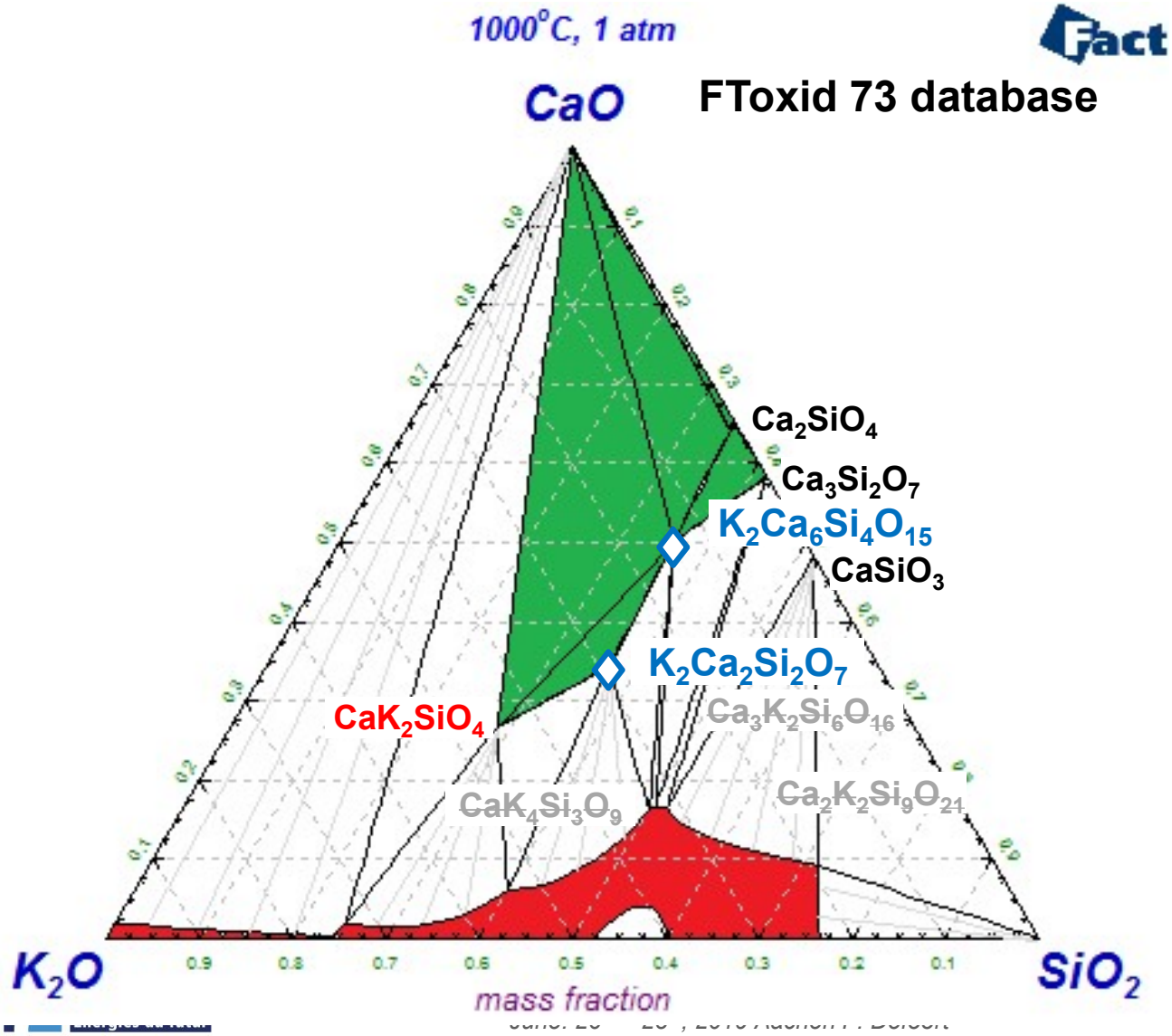
Phase found
- By Arroyabe 2009 and Chen 2016
- in ash of 50% Bark mixture with wheat straw

It is this phase

This phase does not exist?

Discussions

Where is this **ternary $K_2Ca_6Si_4O_{15}$** phase in the phase diagram?



Conclusions about $K_2Ca_6Si_4O_{15}$

- **Not observed by the 1930 studies related to the CaO-SiO_2-K_2O system (Morey)**
- **Observed**
  - By Arroyabe in 2009 (crystal structure) → exist in XRD database
  - By Chen in 2016 in a phase equilibria study (melting point >1150°C)
- **Not clearly observed yet in biomass ash → First time clearly observed in this study**
- **Many new ternary phases observed by XRD studies for several applications (magma studies, fertilizers, etc) linked with carbonates**
- **Very recently included in Ftoxid 73 database along with several ternary compounds like GTT/FZJulich/GTOX database**
  - But only estimated thermodynamic data !
  - Need reliable data from experiments (calorimetry, DSC, etc) or calculations (ab initio) to determine $\Delta H°_f(298K)$, $S°_f(298K)$, $C_p(T)$
    - **Projects ongoing:**
    - **France (OPALHE project with Simap Grenoble)**
    - **Germany (FZ Julich), Austria (U of Innsbruck)**

Thank you for your attention !
Any questions ?

The French Carnot Institute is thanked for the financial support of this study (Palissandre project)
Benoît Fer is thanked for its work during its intership