



# Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport – Phase 2

Roland Balint, Tor Laurén, Emil Vainio, Markus Engblom

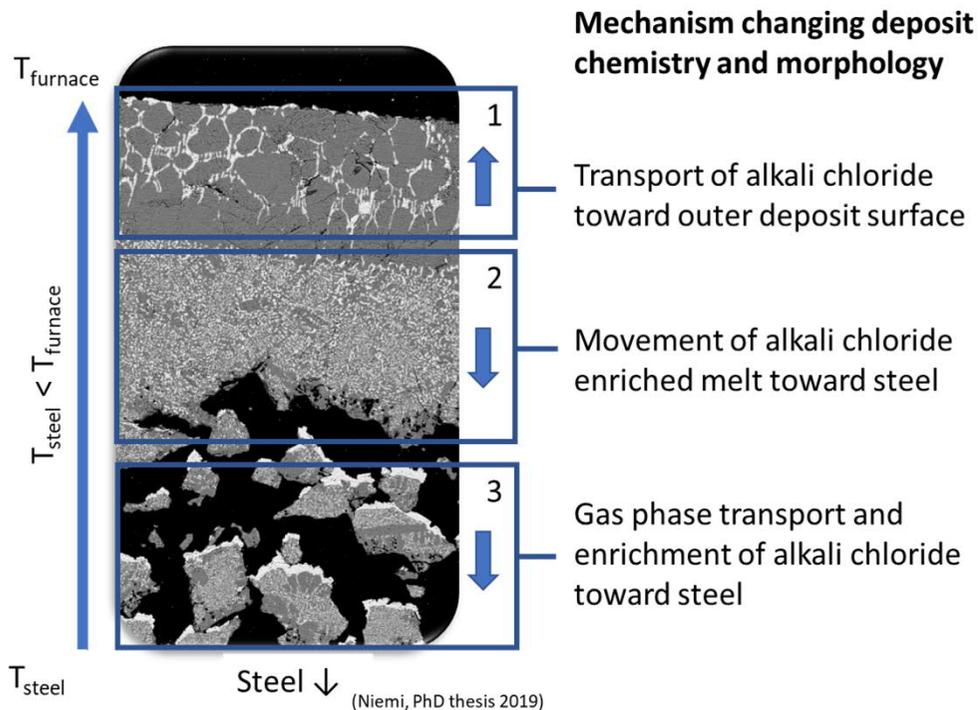
SKY LTR 30.11.2021

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# Mechanisms that change deposit morphology and chemistry with time and due to temperature gradient

*Laboratory deposit exposed to temperature gradient*

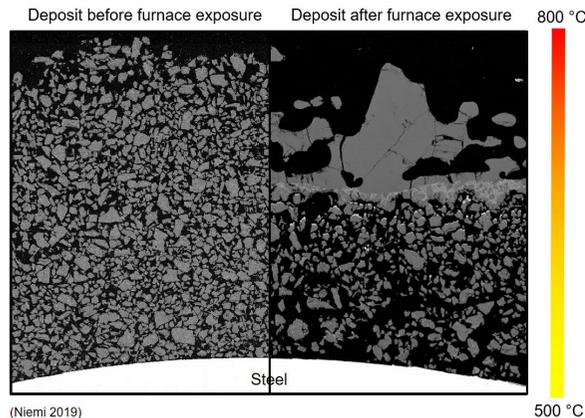
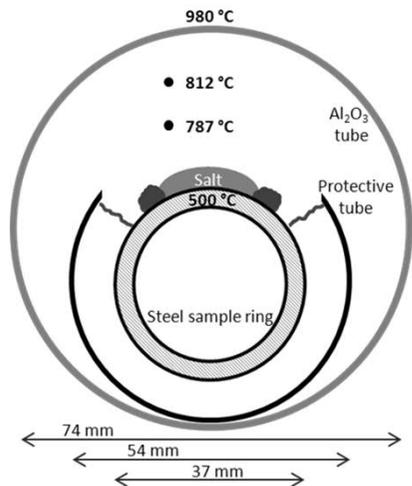
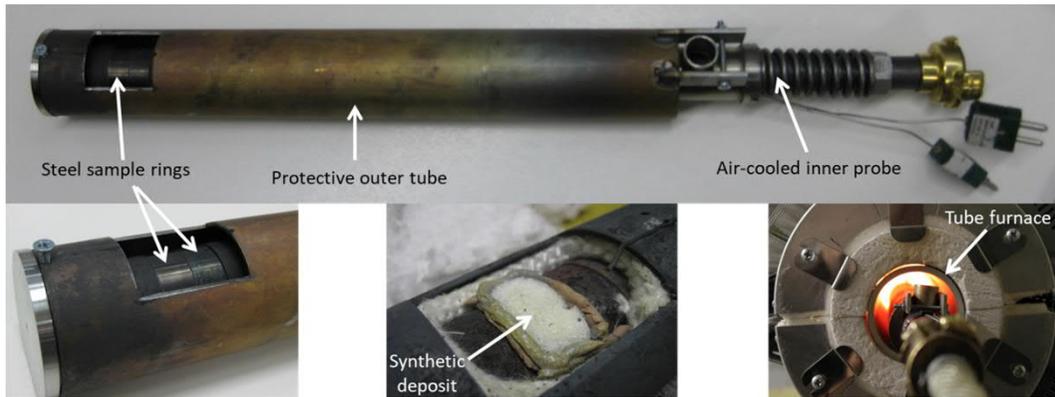


These mechanisms are observed in Brazilian superheater deposits

**The gas phase alkali chloride transport is observed in SKY project probe samples as well as SH deposit samples from the same Finnish boiler.**

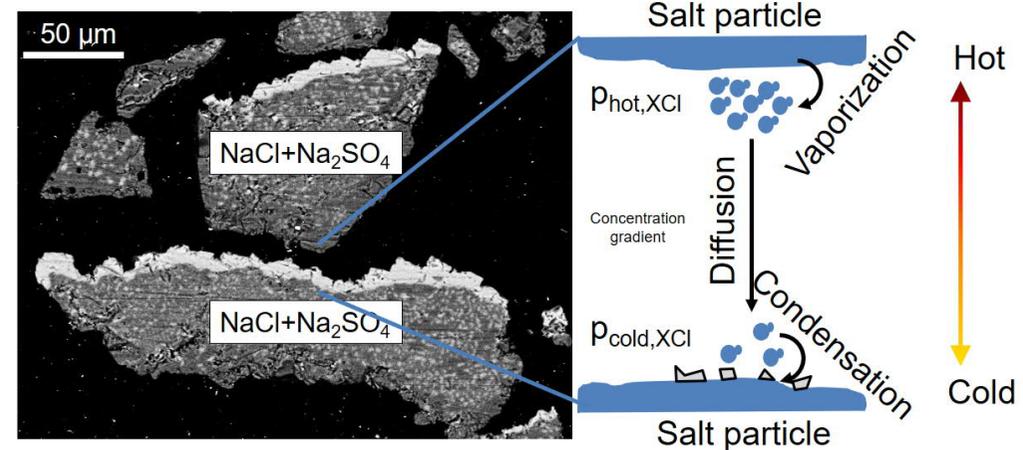
(Gas phase alkali chloride transport also seen in Brazilian deposits)

# Gas phase transport and enrichment of alkali chlorides toward steel



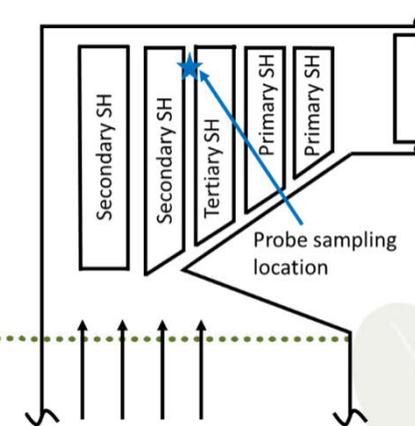
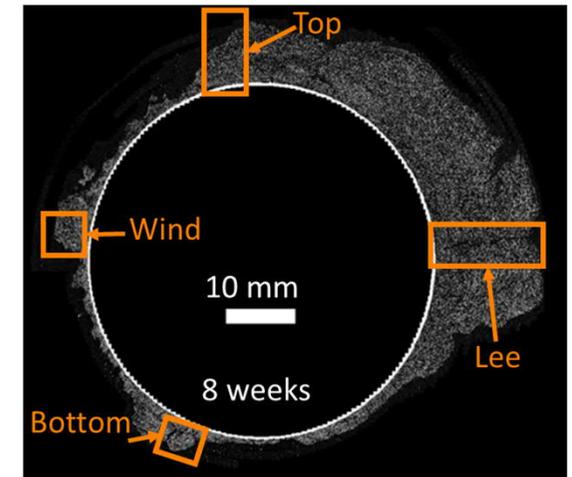
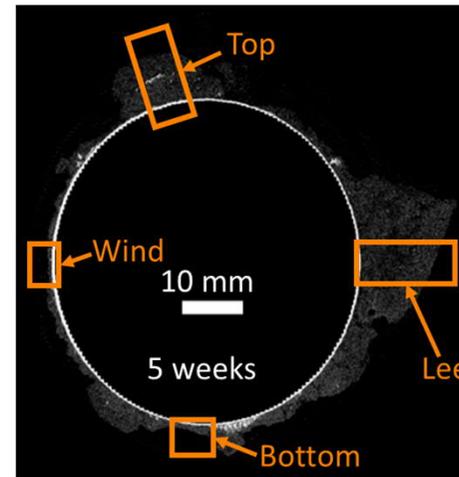
(Niemi 2019)

- Temperature gradient induced concentration diffusion
- Moves alkali chlorides toward steel resulting in alkali chloride enrichment toward and onto onto steel



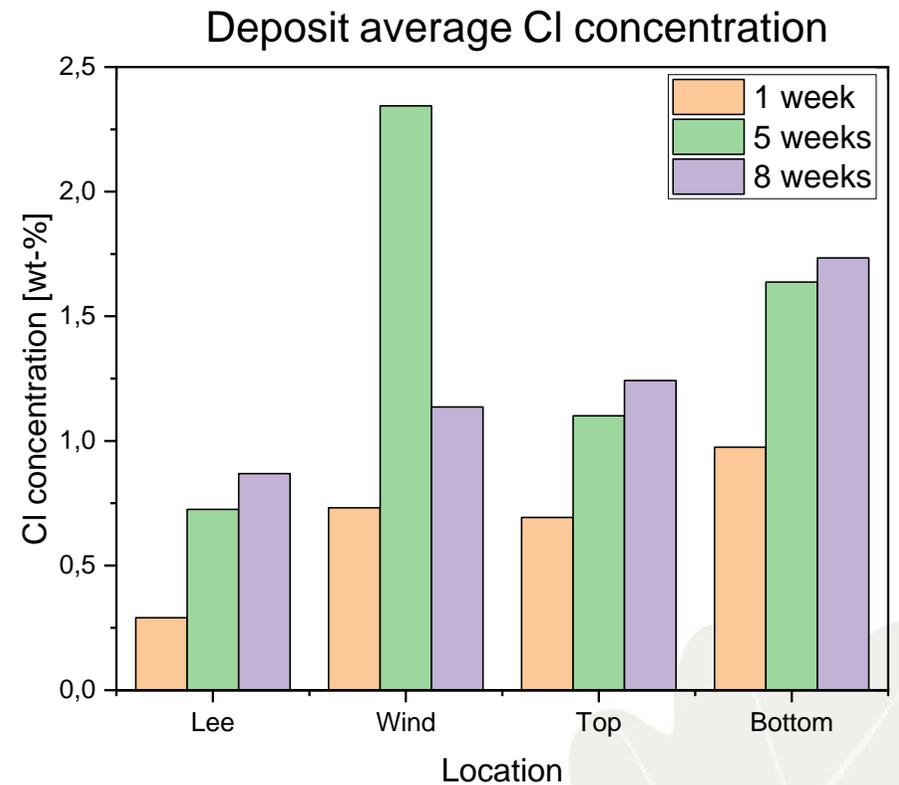
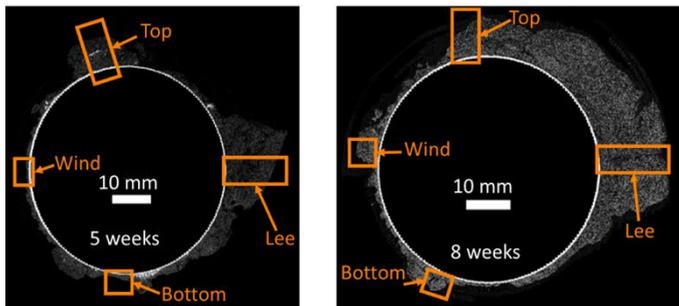
# Probe measurements

- Phase 1
  - 1 week measurement
- Phase 2
  - 5 and 8 week measurements



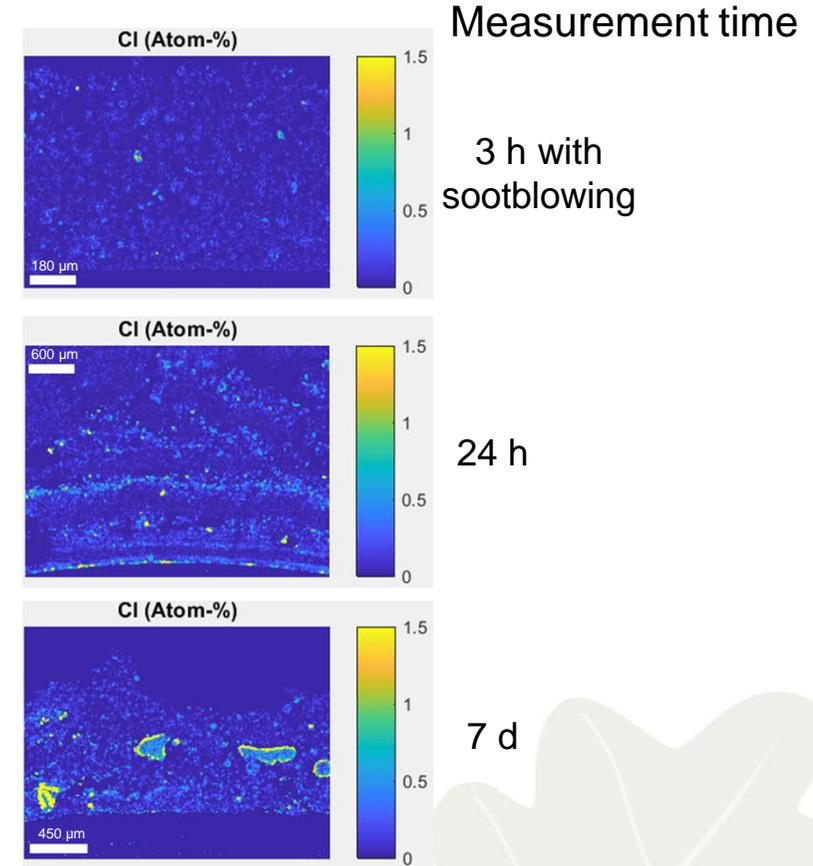
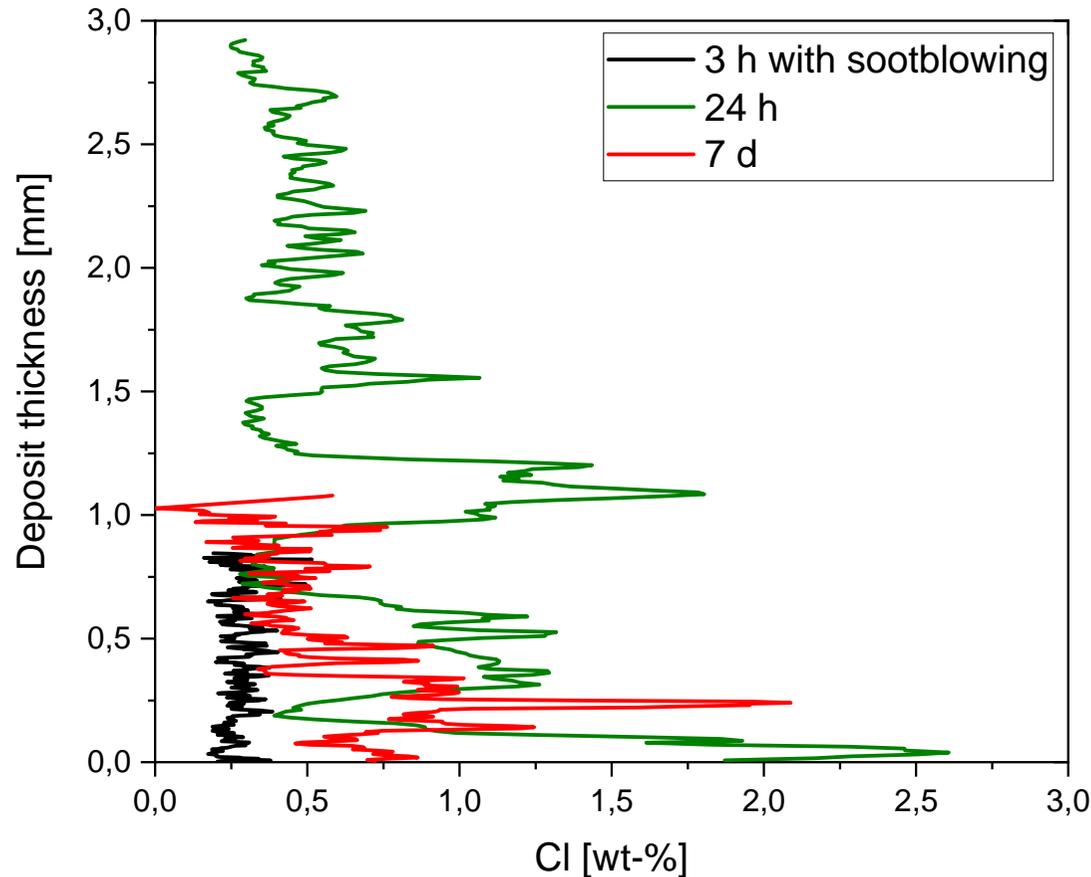
# Probe measurements - Results

- Deposit chloride concentration increases with time



1 week measurement is from Phase 1

# Phase 1 probe measurements

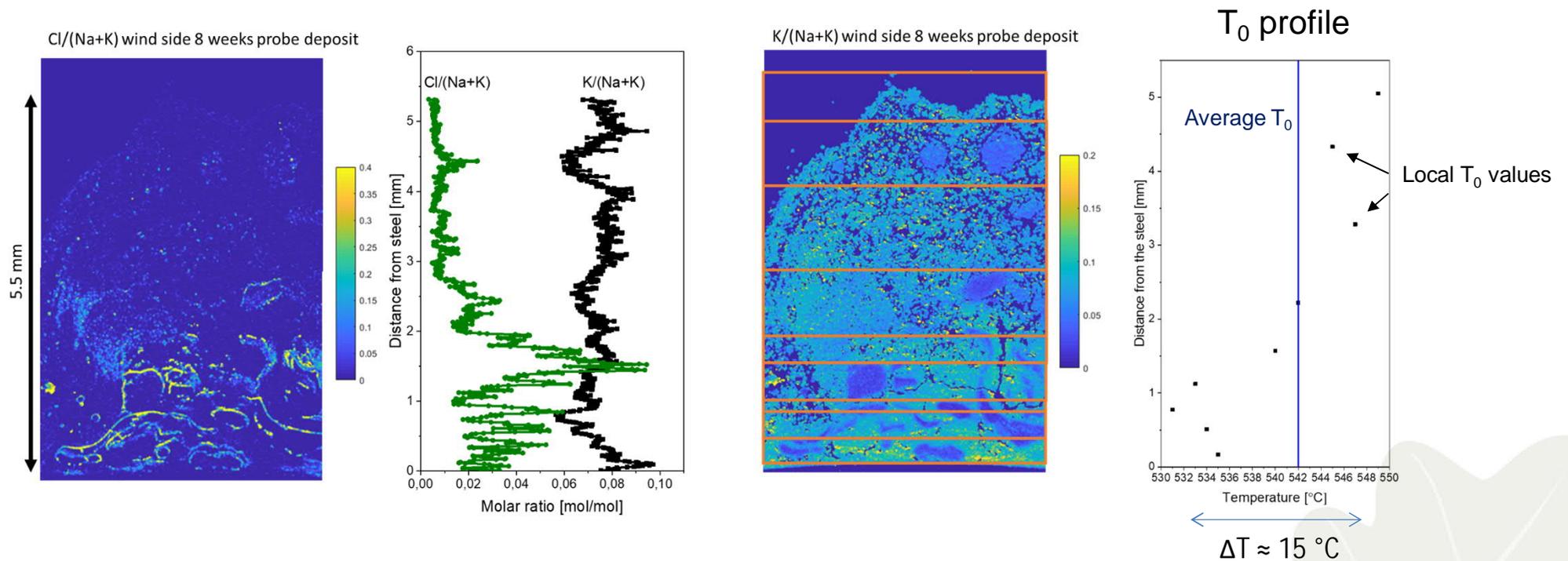


Samples from vind side

The profiles are calculated from maps on right by averaging over the horizontal plane

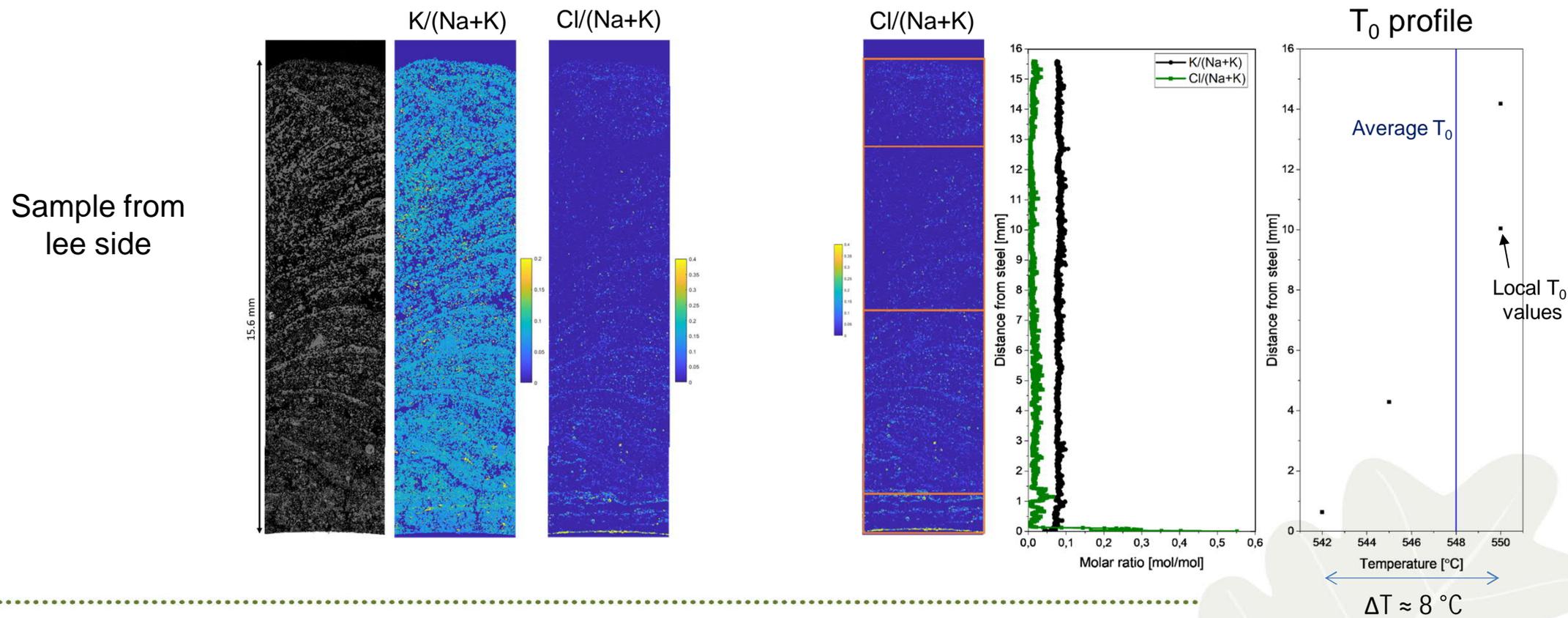
# Phase 2 probe results – Deposit $T_0$ profiles

- Deposit local  $T_0$  is lower toward steel



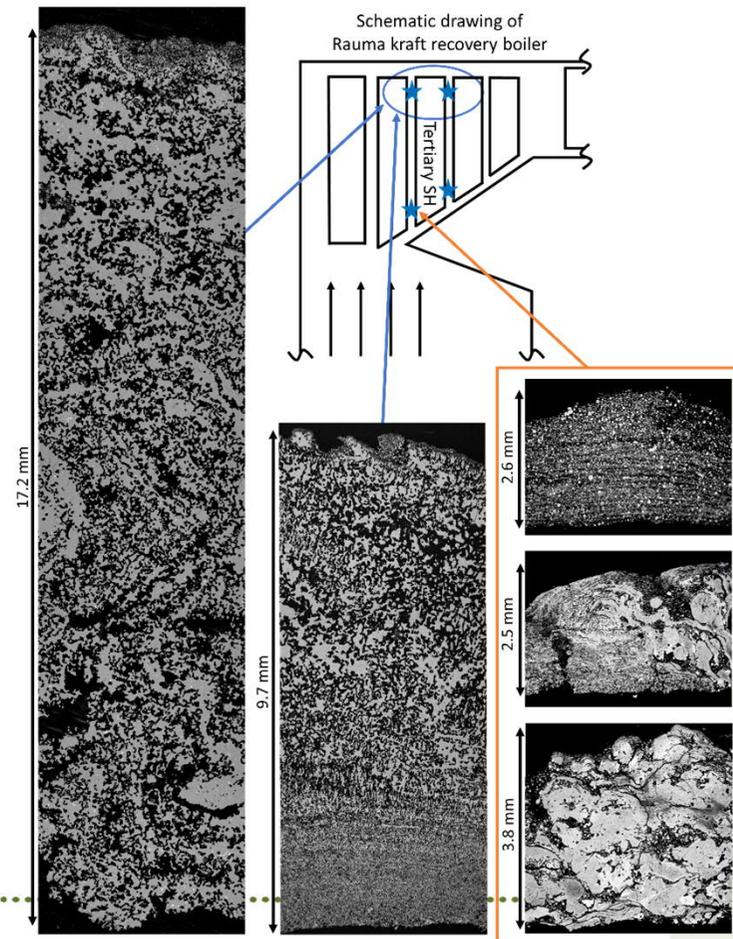
# Phase 2 probe results – Deposit $T_0$ profiles

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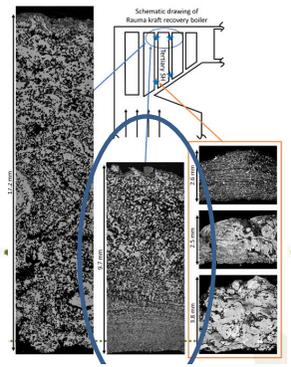
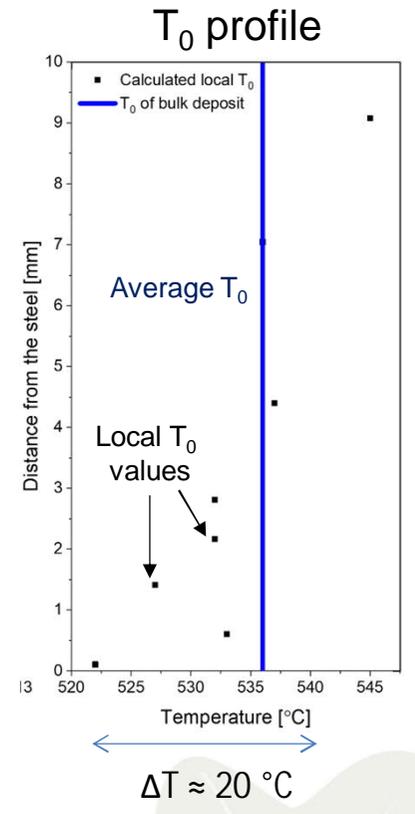
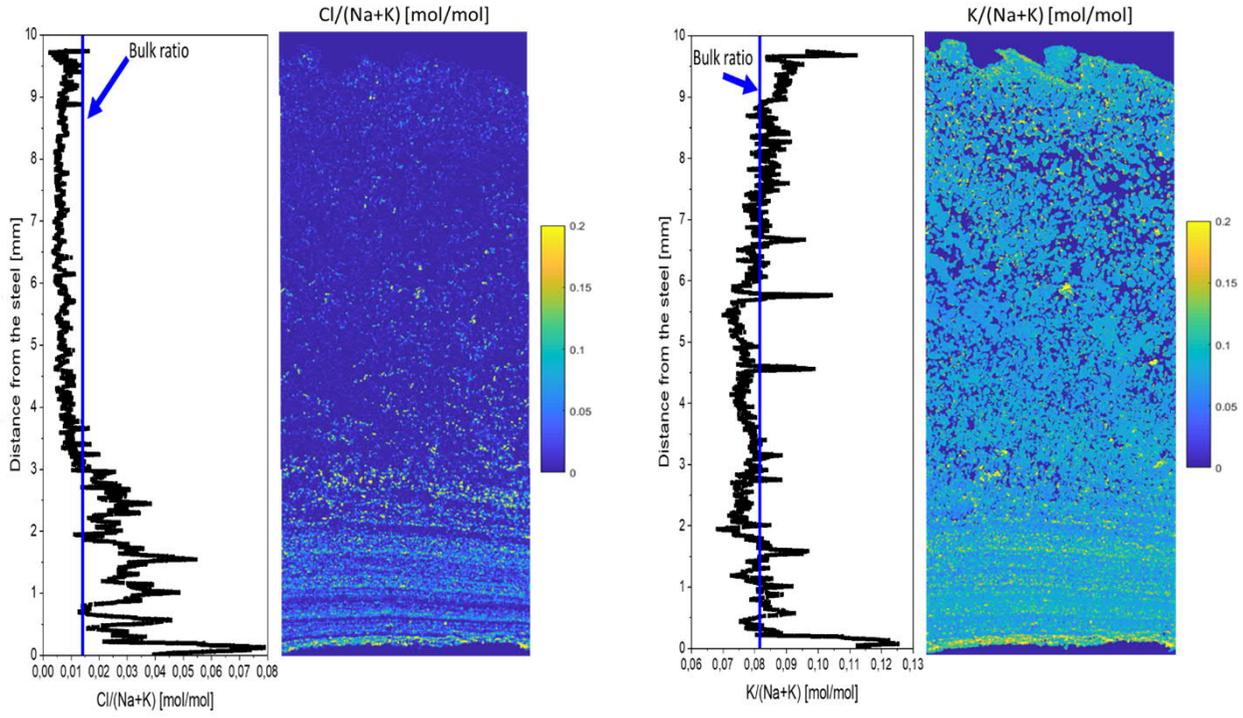
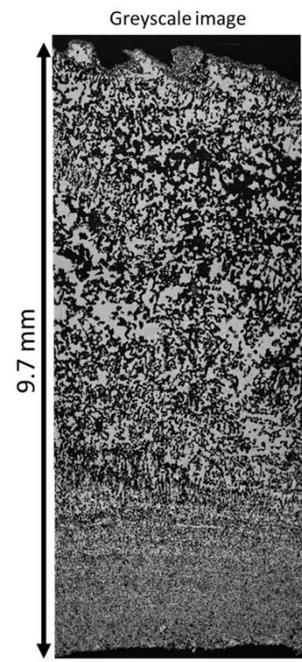


# Superheater deposit samples

- In addition to probe samples, deposit samples have been obtained from superheaters
- Superheater samples "only" 1 month old
- Similar observations as with probe samples ("Type 1 deposit")
  - Cl enrichment toward/onto steel
  - Local  $T_0$  lower toward steel
- In addition, in some probe and SH deposits, a Cl depleted region close to steel observed ("Type 2 deposit")
  - Possibly due to sulfation

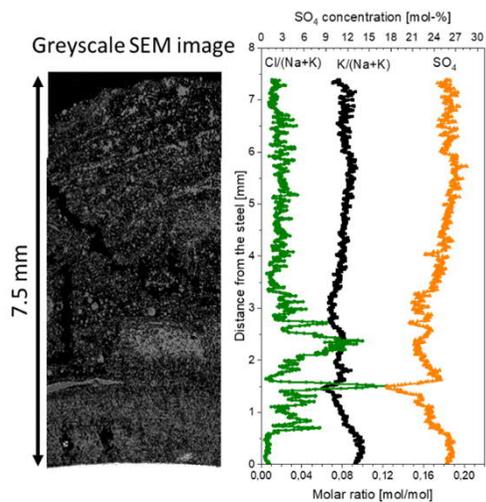


# Superheater deposit samples ("Type 1")

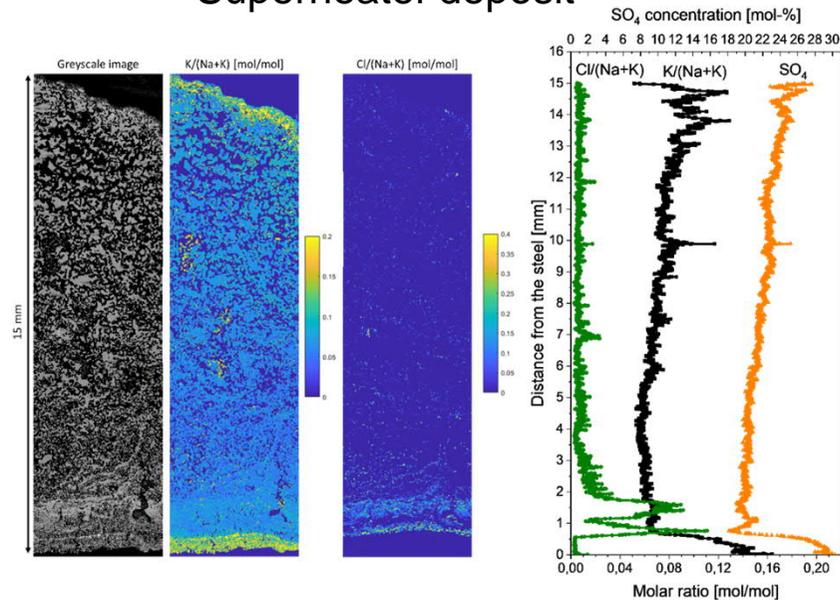


# Deposit samples ("Type 2")

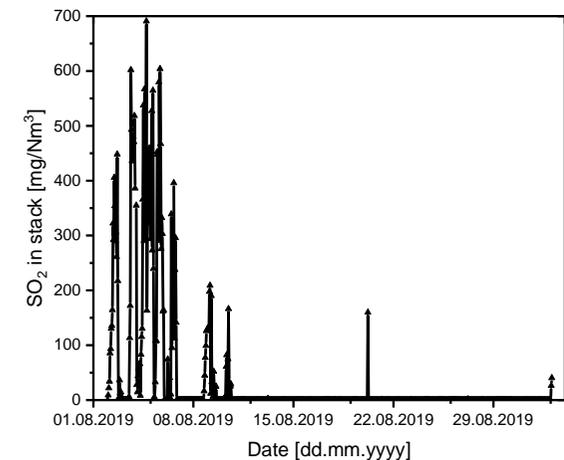
8 week probe deposit



Superheater deposit



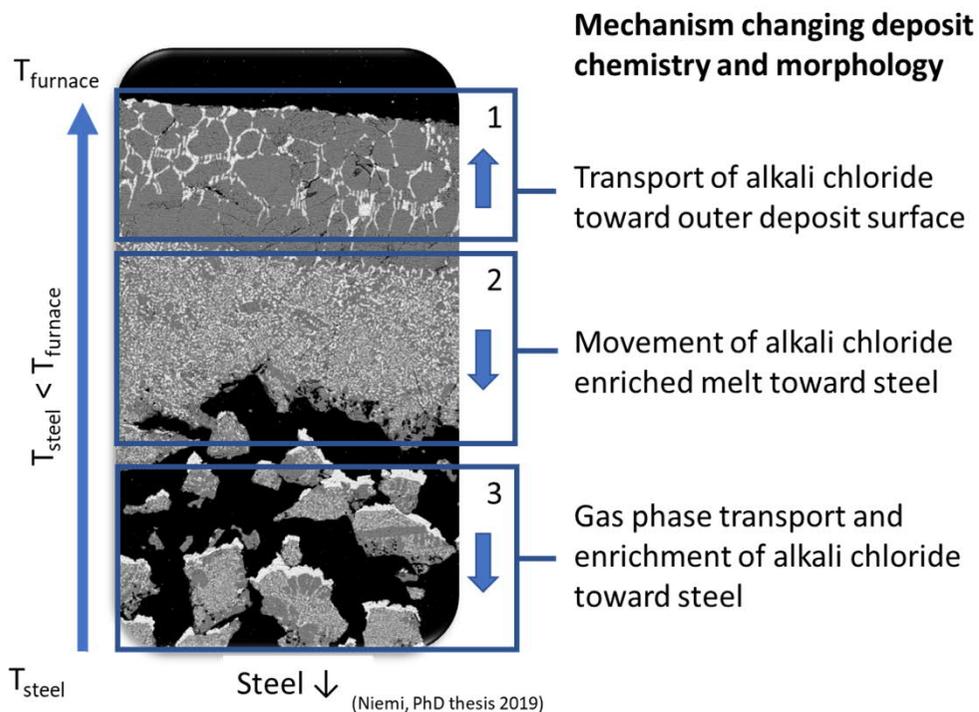
Stack SO<sub>2</sub> during time when superheater deposit in boiler



- In some probe and SH deposits, a Cl depleted region close to steel observed ("Type 2 deposit")
  - Possibly due to sulfation
- Further work needed to understand better

# Mechanisms that change deposit morphology and chemistry with time and due to temperature gradient

*Laboratory deposit exposed to temperature gradient*



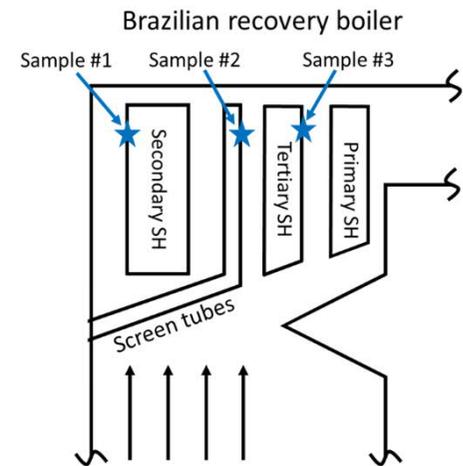
**These mechanisms are observed in Brazilian superheater deposits**

The gas phase alkali chloride transport is observed in SKY project probe samples as well as SH deposit samples from the same Finnish boiler.

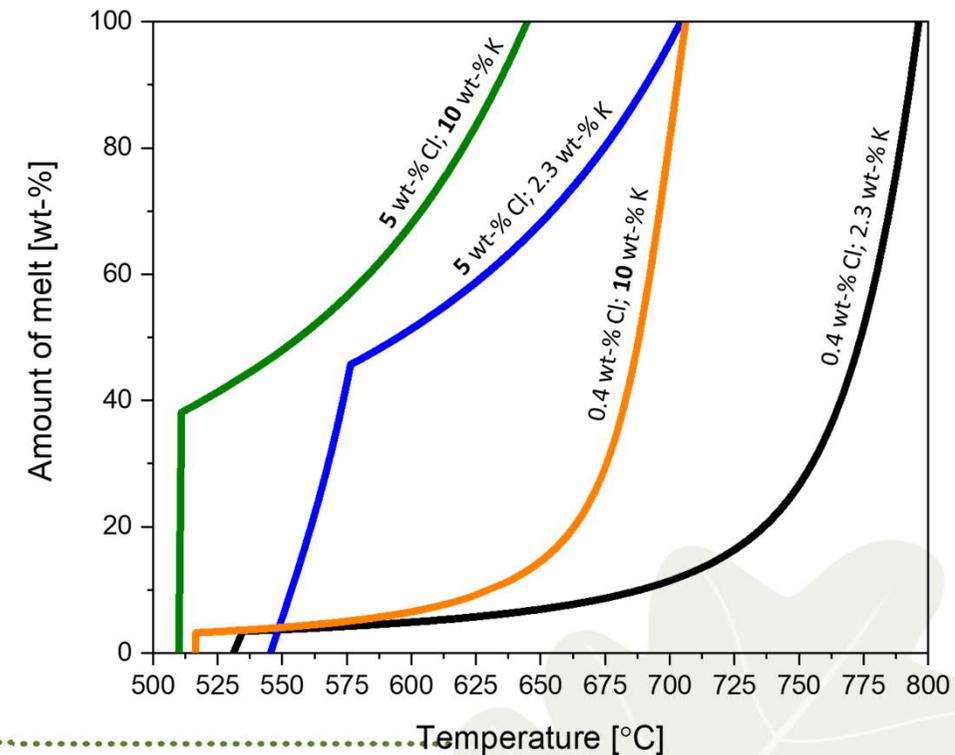
(Gas phase alkali chloride transport also seen in Brazilian deposits)

# Brazilian superheater deposits

- Brazilian liquor/deposits higher in Cl
- More melt formed at temperatures relevant for SH region
- The melt that forms has a lower  $T_0$  than the original bulk deposit
- The low- $T_0$  melt moves toward the steel



Compound [wt-%]	Brazilian deposits	Finnish deposits
Na	34.4	31.6
K	3.4	4.9
Cl	4.4	0.7
SO <sub>4</sub>	37.5	48.9
CO <sub>3</sub>	20.3	13.9



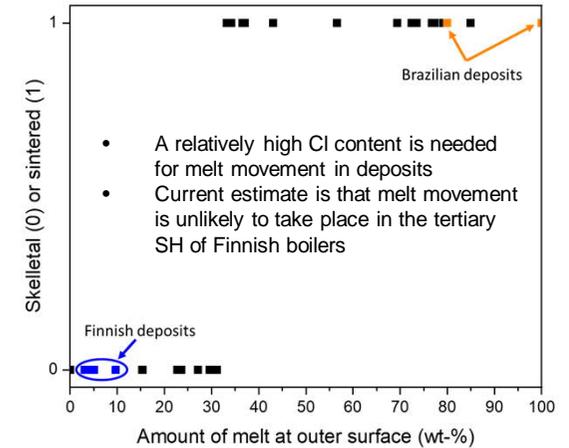
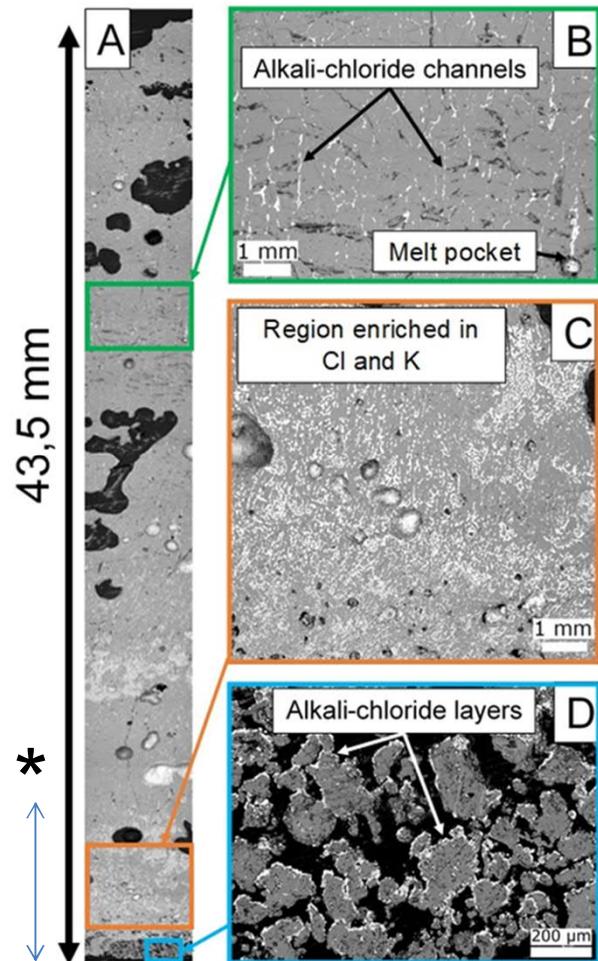
# Brazilian superheater deposits

Deposit aging mechanism

Temperature gradient zone melting transporting alkali chloride toward outer surface of deposit

Movement of K and Cl enriched melt toward steel

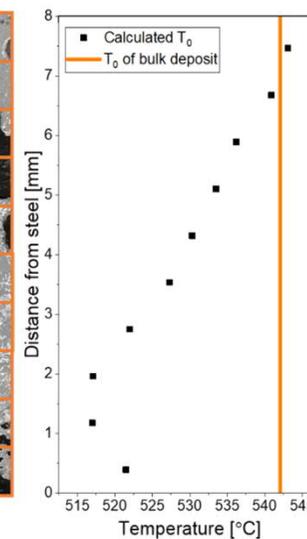
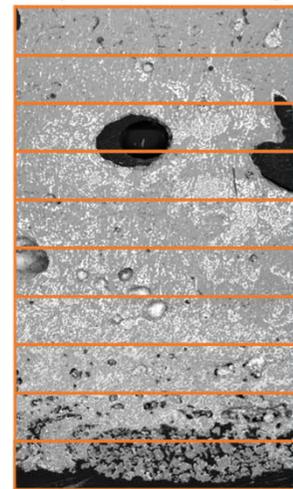
Diffusional gas phase transport and enrichment of alkali chloride toward steel



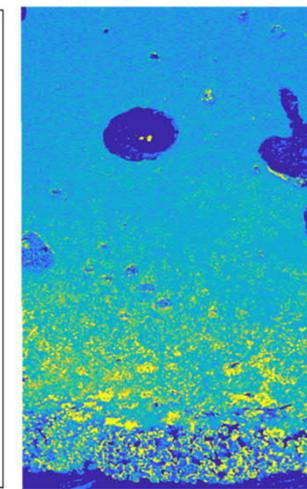
Melt with low  $T_0$  moves toward steel

\*

Greyscale cross-sectional image



K/(K+Na) ratio [mol/mol]



# Rauma probe and SH deposits - Conclusions

- 5 and 8 week probe measurements successfully carried out
- Deposit chlorine content increases with time
- Chlorine enrichment toward steel
- Local  $T_0$  within deposit (up to  $\sim 15$  °C) lower toward steel as compared to  $T_0$  at outer parts of the deposit
  - Increased risk of corrosion