Effects of Li, Ca, Fe, and B on $NaAlSiO_4$ nepheline crystallization in high level waste glasses

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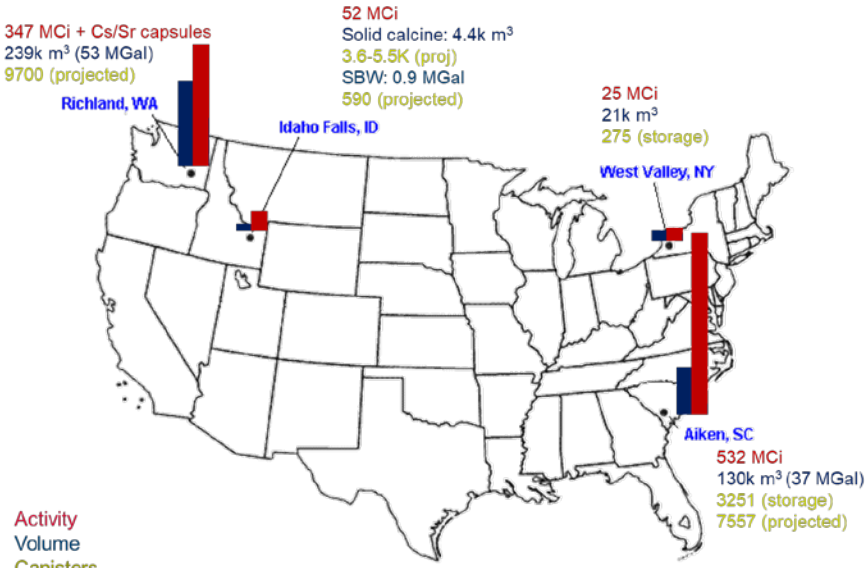
Glass Wasteforms

Sydney, Australia

Oct 31, 2017

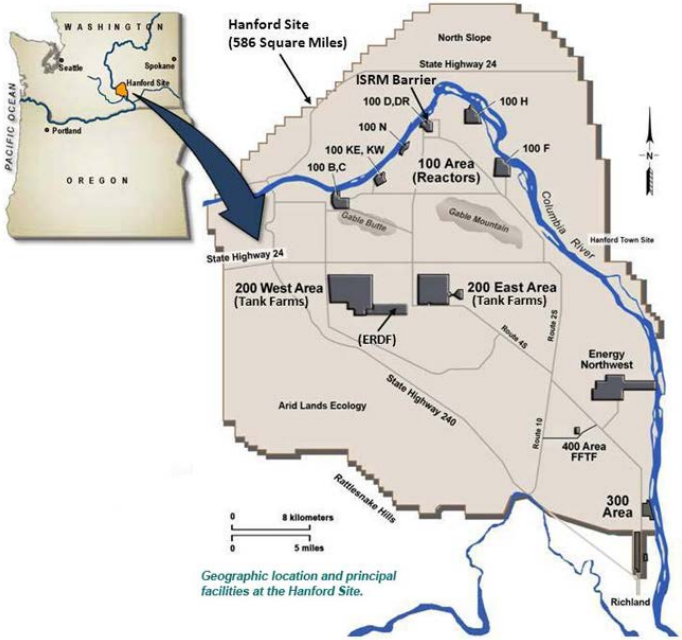
Motivation

US HLW



Numbers as of Sept 2011 (Blue Ribbon Commission)

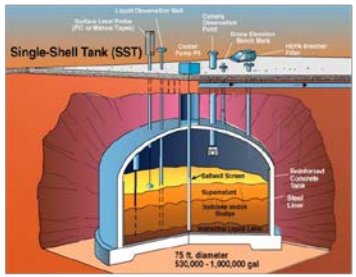
Hanford site



Geographic location and principal facilities at the Hanford Site.

Hanford Tanks

56 million gallons of mixed radioactive waste



www.ecy.wa.gov

- 1943-1964: **149** single-shell tanks (67 presumed to have leaked)
- 1968-1986: **28** double-shell tanks (1 leaking, waste contained within annulus)

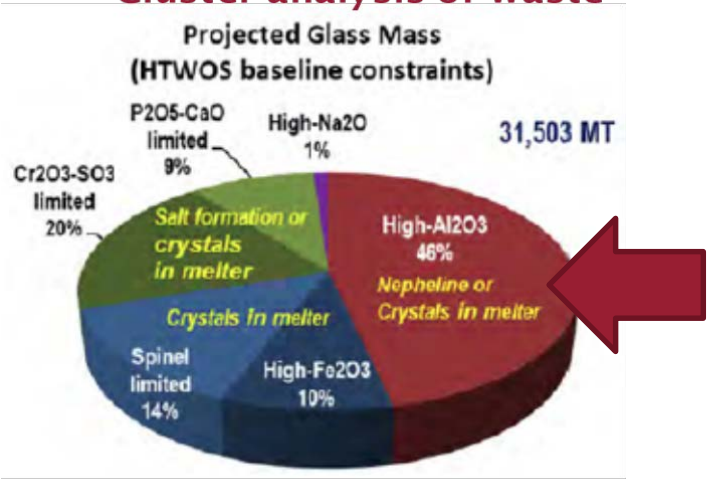
Supernatant

Saltcake

Sludge

Courtesy, A. Kruger, DOE-ORP
www.hanford.gov

Cluster analysis of waste

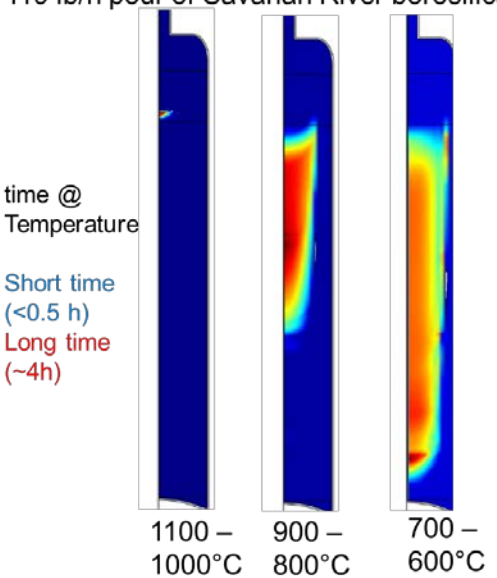


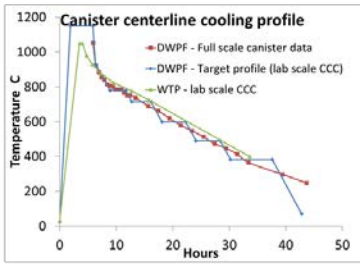
Kim et al, PNNL-20774 (2011)

The Nepheline problem

Canister centerline cooling

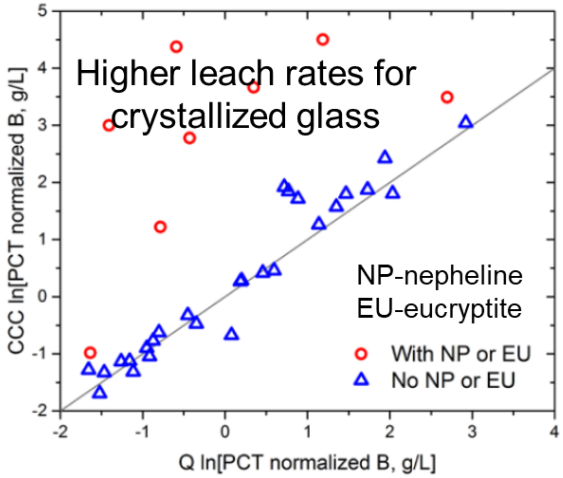
119 lb/h pour of Savanah River borosilicate, T_m=1150 °C into HLW canister





Amoroso et al, SRNL-STI-2011-00546
Rodriguez et al, PNNL-20184 (2011)

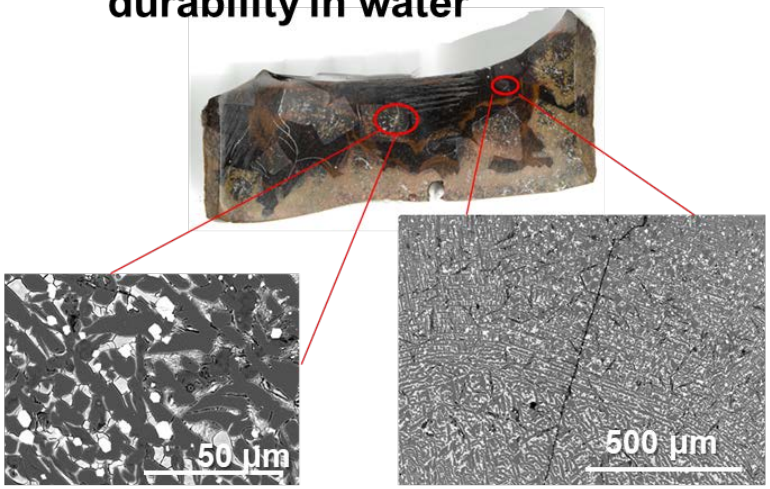
Increased leach rate



Kroll et al, Ceram Trans 260, 159 (2016)

Large crystals in some cases

Nepheline ($NaAlSiO_4$)
[or Eucryptite ($LiAlSiO_4$)]
crystallizes →
residual glass low chemical durability in water



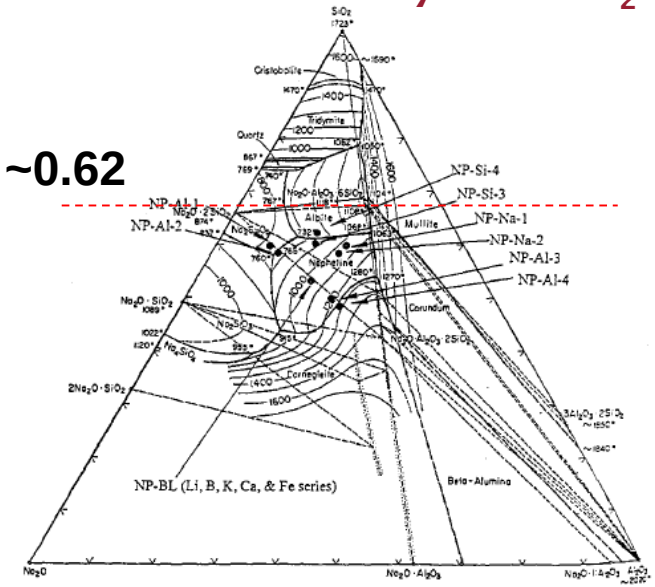
Nepheline
Spinel, & other

Dendritic structure

Marcial et al, Proc MRS 1744, 85 (2015)

Previous work on nepheline formation

Normalized ternary and SiO_2

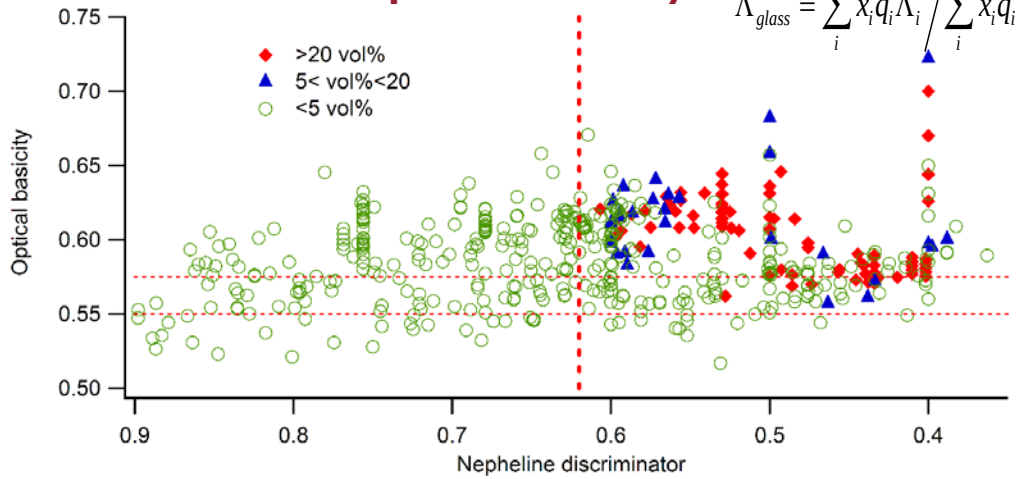


Li et al, *Cer Trans* 87, 279 (1998)

$ND = SiO_2/(SiO_2+Al_2O_3+Na_2O) > 0.62$

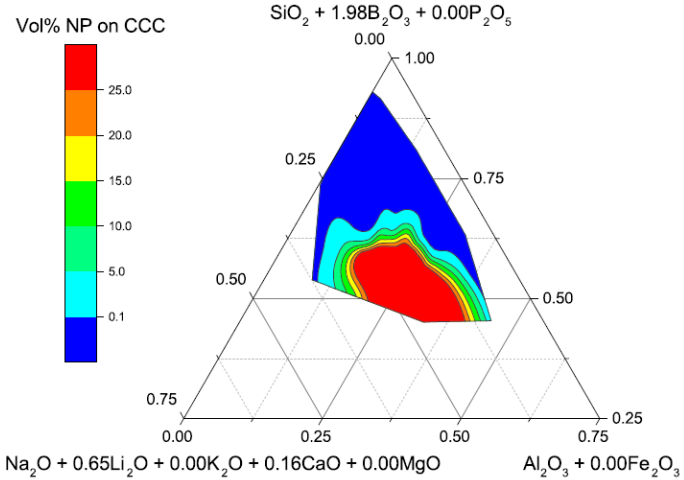
Optical Basicity

$$\Lambda_{glass} = \sum_i x_i q_i \Lambda_i \Big/ \sum_i x_i q_i$$



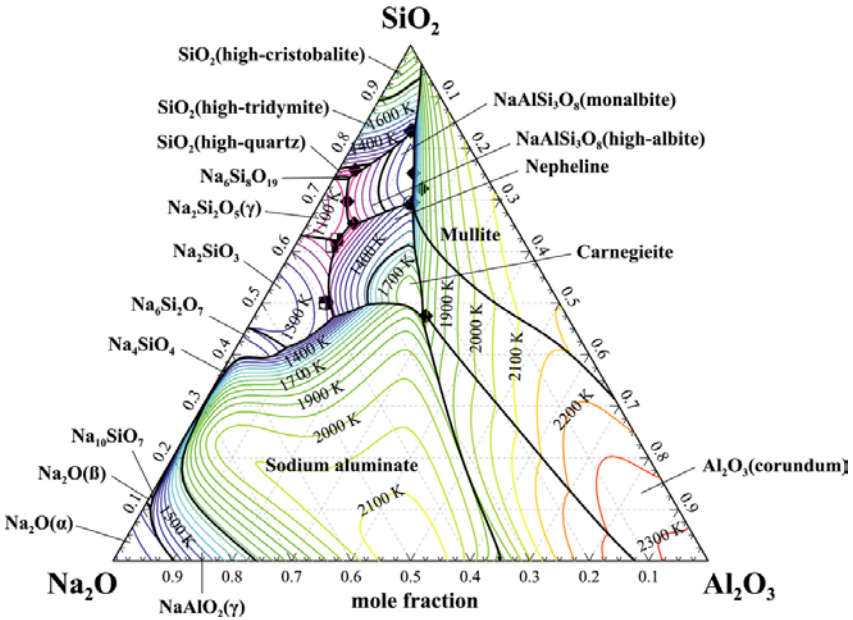
McCloy et al, *IJAGS* 2, 201 (2011)

Neural network and quantification



Vienna et al, *IJAGS* 8, 143 (2016)

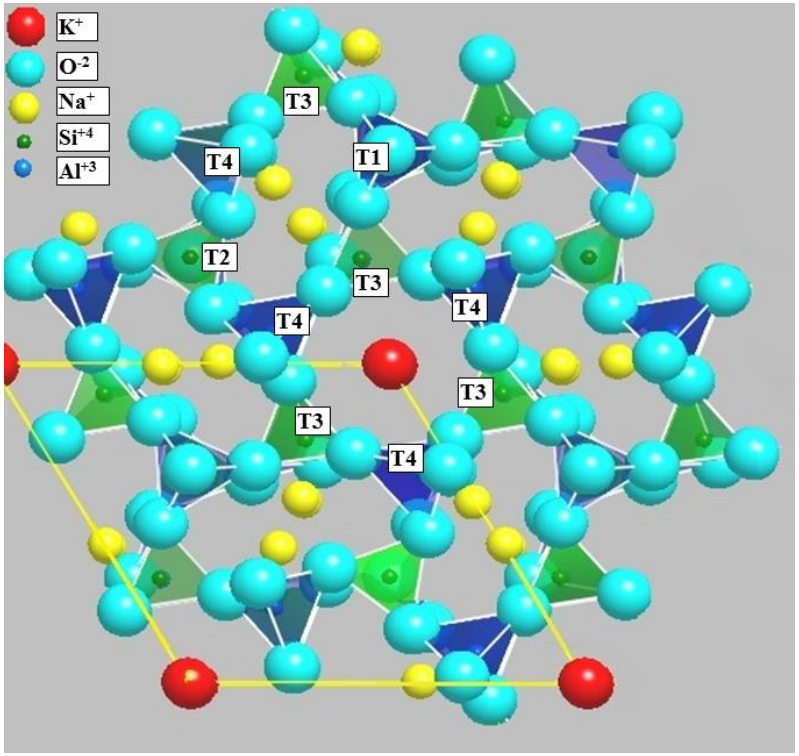
Thermodynamic



Utlak & Besmann, *JACERS* in press (2017)

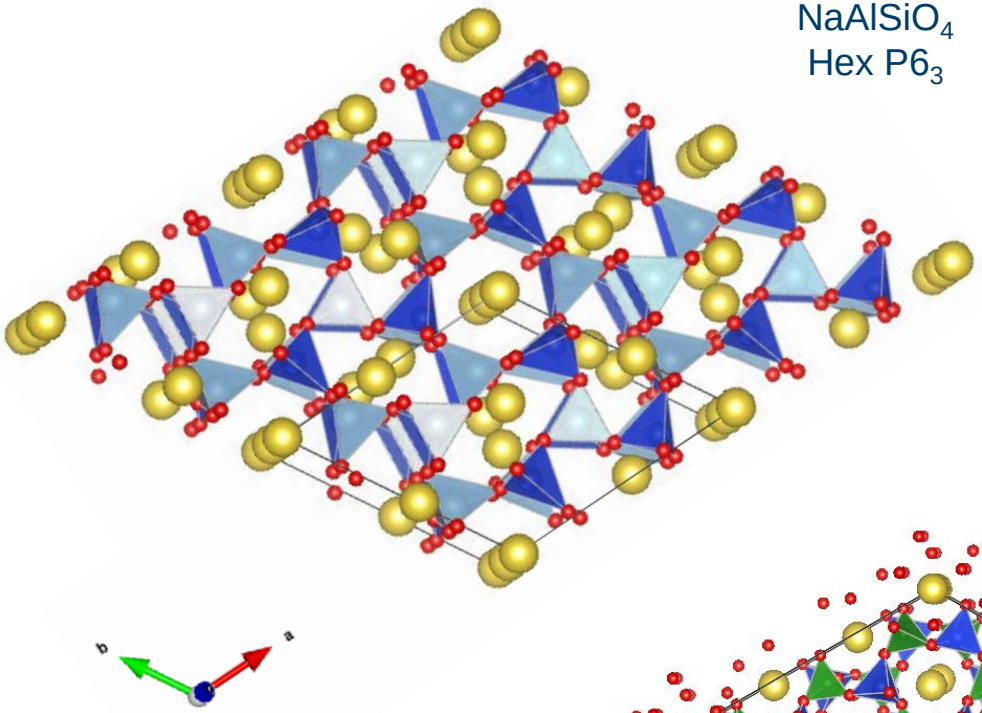
Overview

- Crystallography – nepheline & related minerals
- Composition from complex waste glasses
- Effect of different cooling conditions
- Glass composition effects
  - Al/B
  - Al/Fe
  - Na/Ca
  - Na/Li

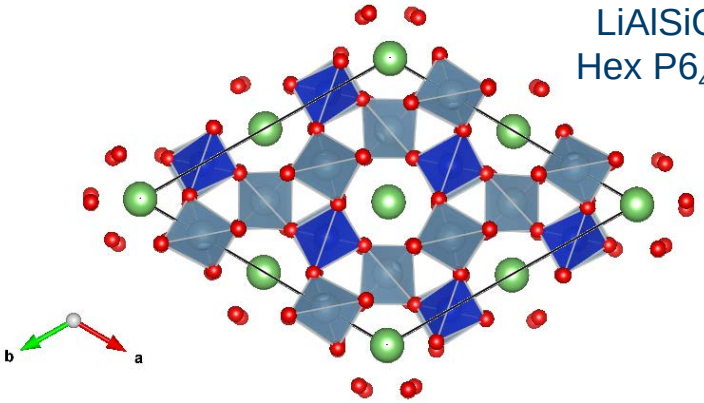


Crystallography: (A,AE)(Al,B,Fe)SiO_4

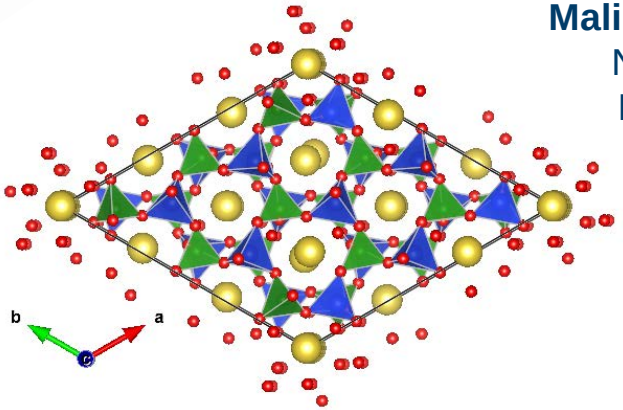
Nepheline (NE)
$NaAlSiO_4$
Hex $P6_3$



Eucryptite (EU)
$LiAlSiO_4$
Hex $P6_422$



Malinkoite (MA)
$NaBSiO_4$
Hex $P6_3$

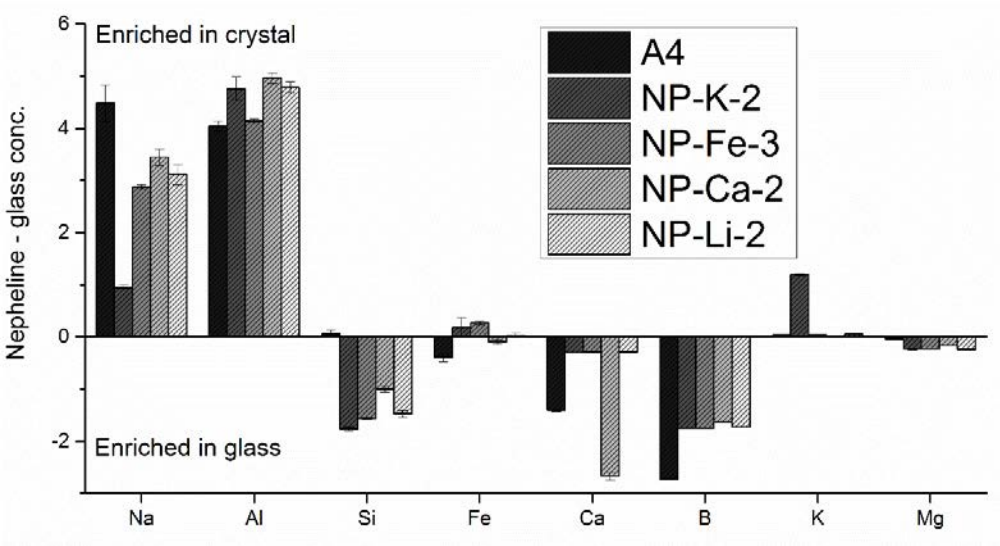


Na, Fe: no mineral
Li, Fe: no mineral
Ca, Al: Anorthite
Ca, B: Danburite

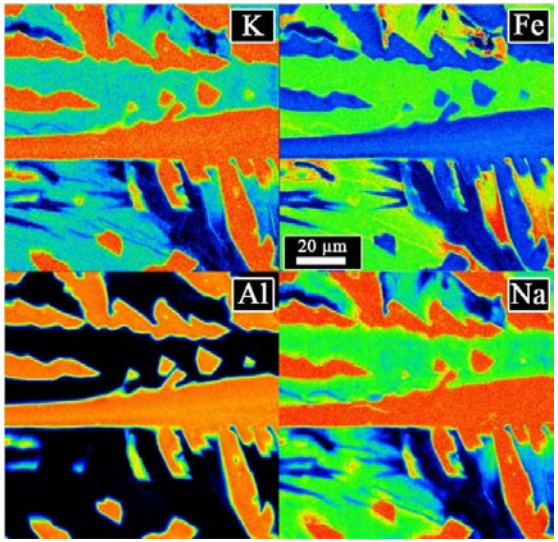
NEPHELINE: $(Na,Ca,Mg,\square)_{0.75}^{oval}(K,Na,Ca,\square)_{0.25}^{hex}(Al,Fe)SiO_4$

Nepheline in complex HLW glasses

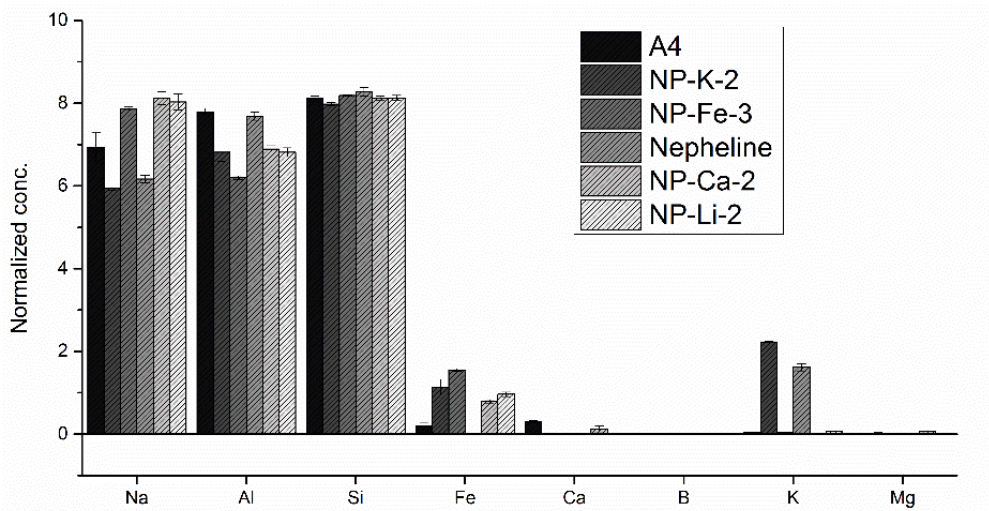
Selective partitioning



Compositional maps, NP-K-2 CCC

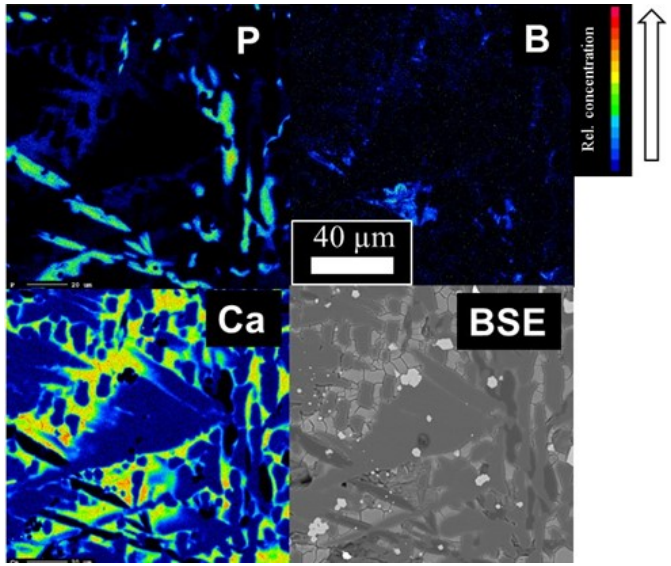


Nepheline crystal composition (WDS)



Marcial et al., Amer. Min., 101(2), 266-276 (2015).

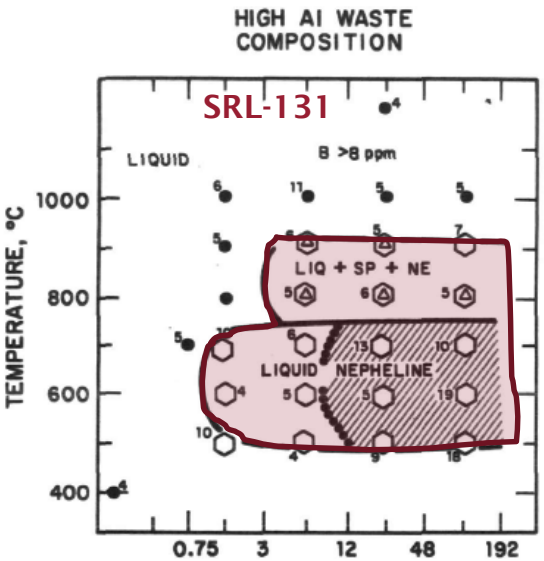
Compositional maps, A4 CCC



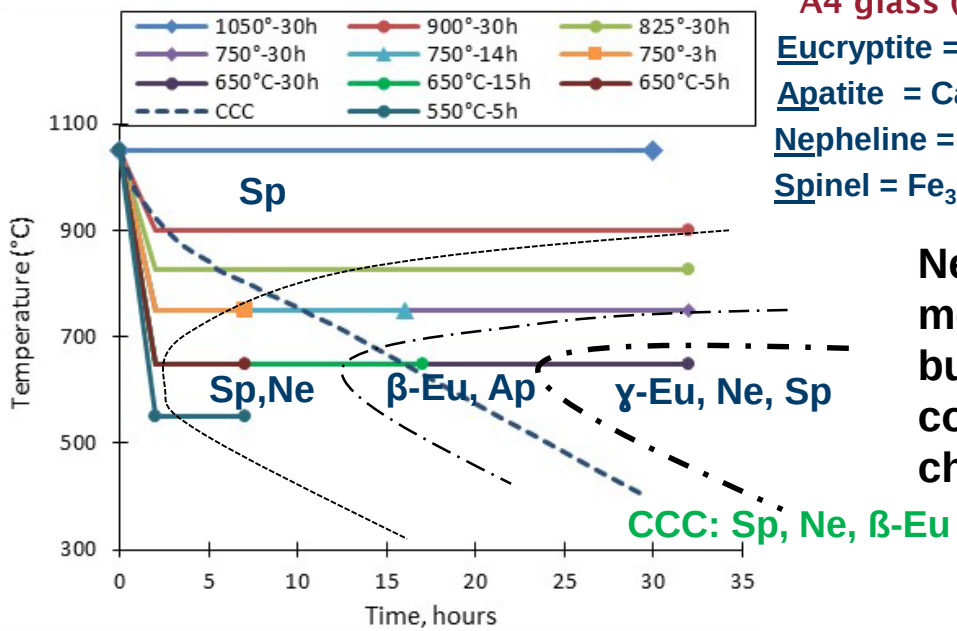
Marcial et al, Proc MRS 1744, 85 (2015)

Effect of heat treatments

Time-Temperature-Transformation



Jantzen et al., Proc. Mat. Res. Soc., 44 (1985).



A4 glass (high Li)

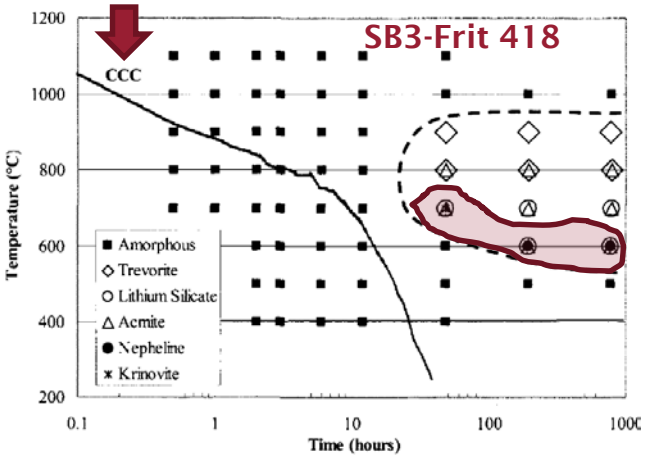
Eucryptite = $LiAlSiO_4$

Apatite = $Ca_5(PO_4)_3(OH)$

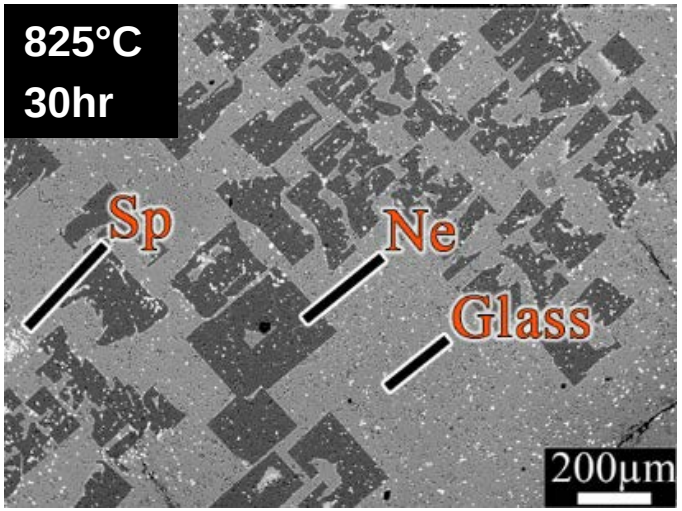
Nepheline = $NaAlSiO_4$

Spinel = Fe_3O_4

Nepheline morphology but NOT composition changes



Billings et al, *Adv Mat Sci ENT* 222, 51 (2010)

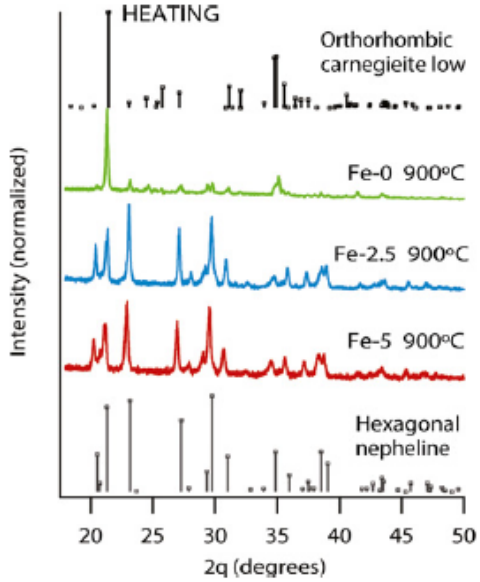


Euhedral nepheline

Marcial et al., Proc. Mat. Res. Soc., 1744 (2015).

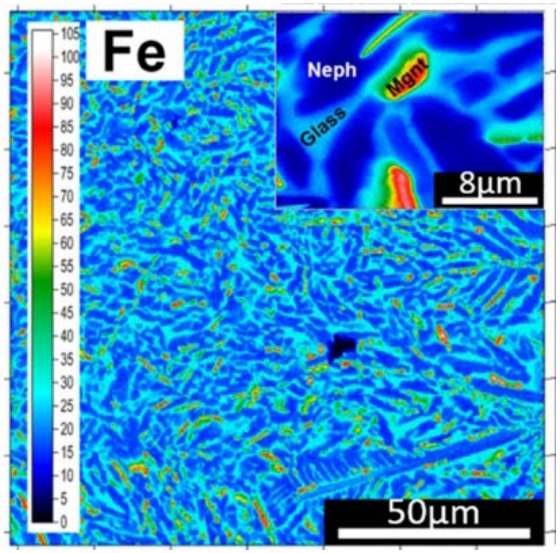
Effect of Al/Fe: $NaAl_{1-x}Fe_xSiO_4$

Fe favors bulk nucleation of Neph over surface nucleation of Carneg

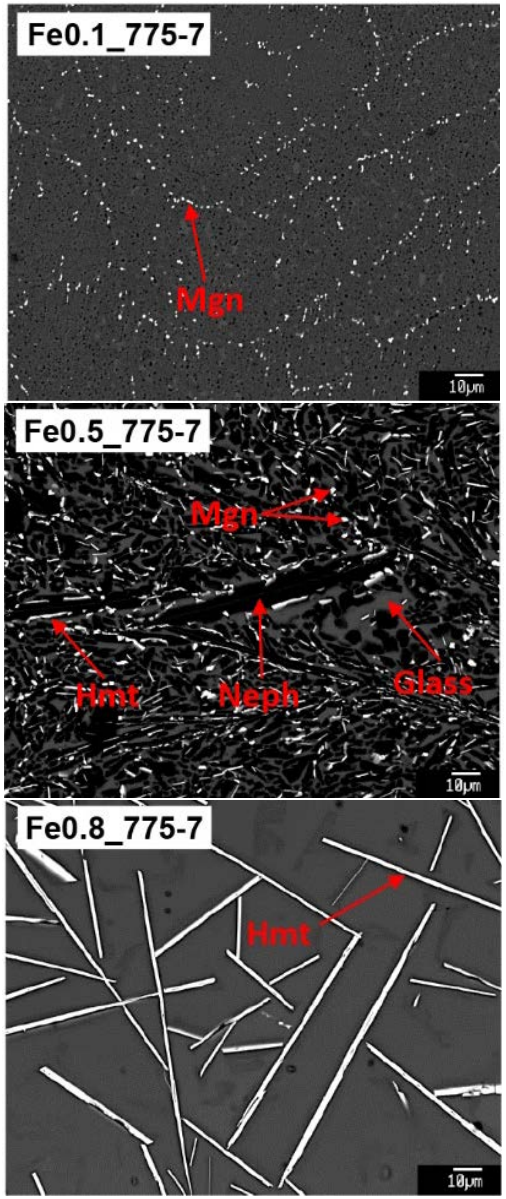


Shaharyar et al., *JACERS 99*, 2306 (2016)

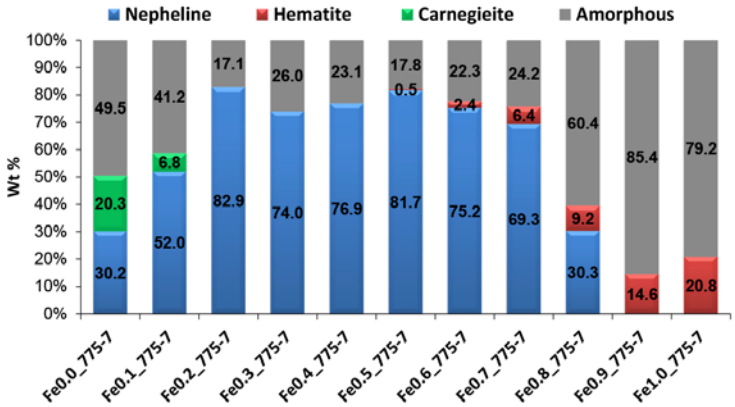
Fe substitutes on Al site at least x=0.37



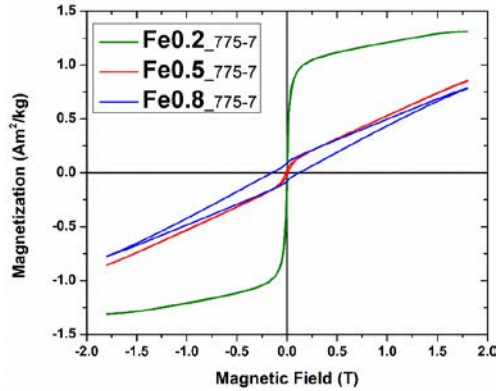
Ne and Fe-oxides



Highest Fe: no Neph



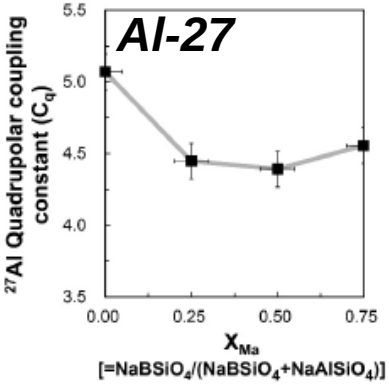
Magnetic Meas.



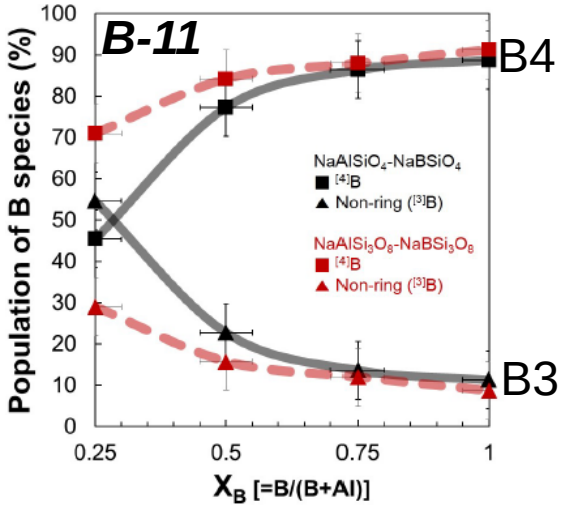
Ahmadzadeh et al., *J Geophys Res Sol Ear* 122, 2504 (2017)

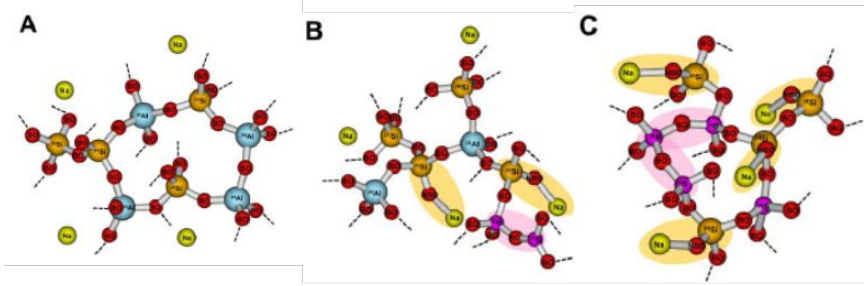
Effect of Al/B: $NaAl_{1-x}B_xSiO_4$ glass structure

↑B → **ordered around Al**



↑B → (Malink or B-albite) **B4↑ & B3↓**

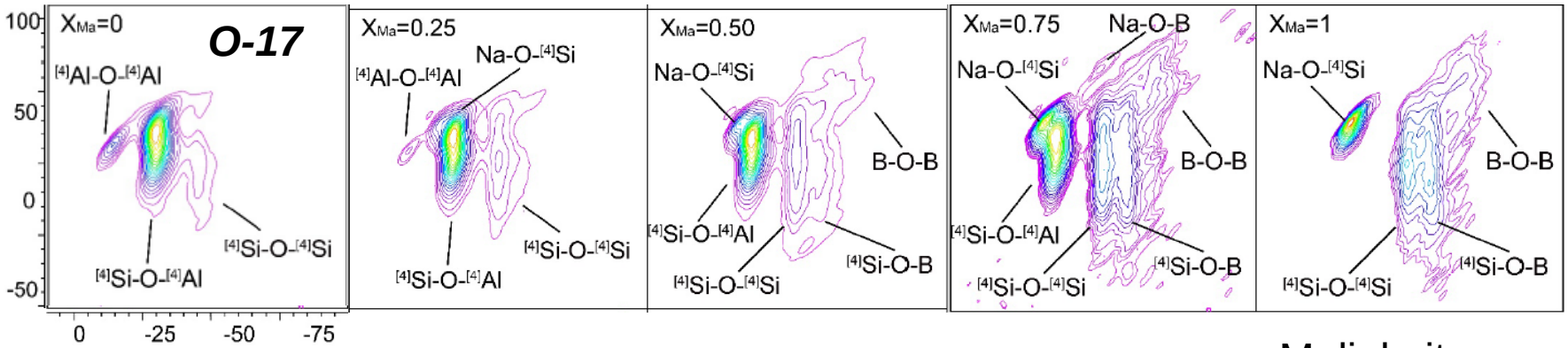




$NaAlSiO_4$ intermediate $NaBSiO_4$

Na-O-Si B-Ø-B

↑B → **Na-O-Si (NBO on Si) formed** not Na-O-B (NBO on B)

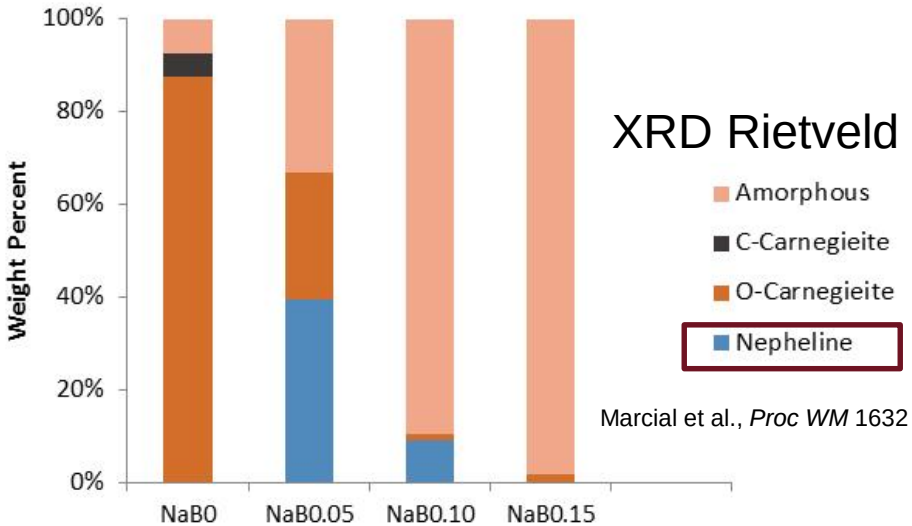


Nepheline Malinkoite

Lee, MS thesis, Seoul Natl Univ, 2017

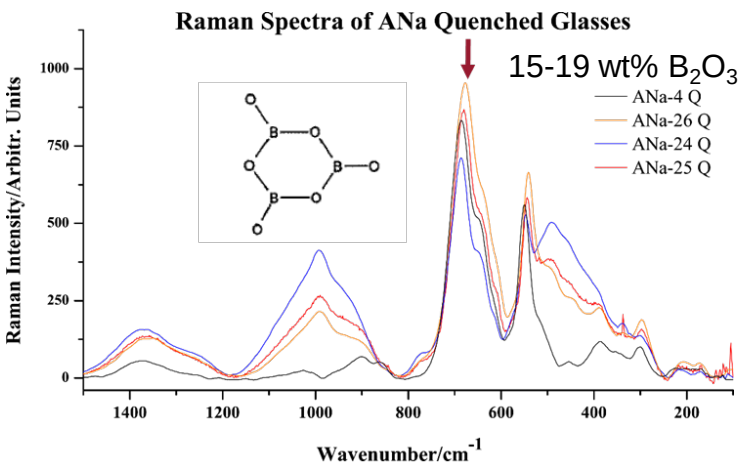
Effect of Al/B: Nepheline crystallization

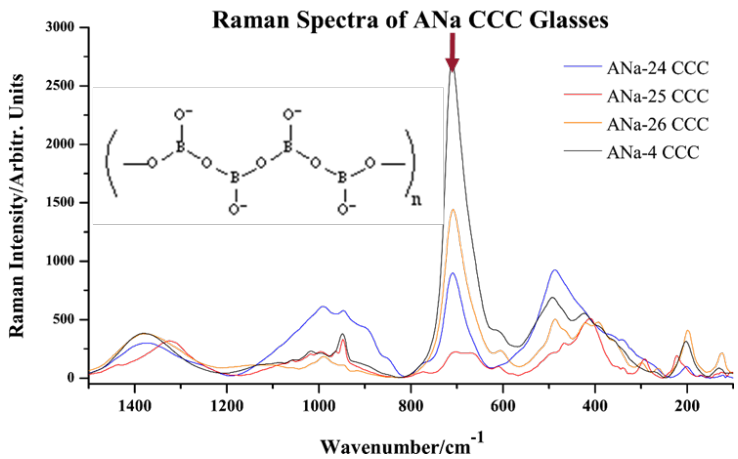
Low B in $NaAl_{1-x}B_xSiO_4$ allows Nepheline to form



Marcial et al., *Proc WM* 1632 (2016)

Some compositions with Si~B~Al (molar) crystallize a lot of Nepheline; changes ring to chain metaborates

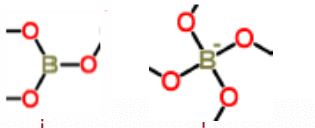


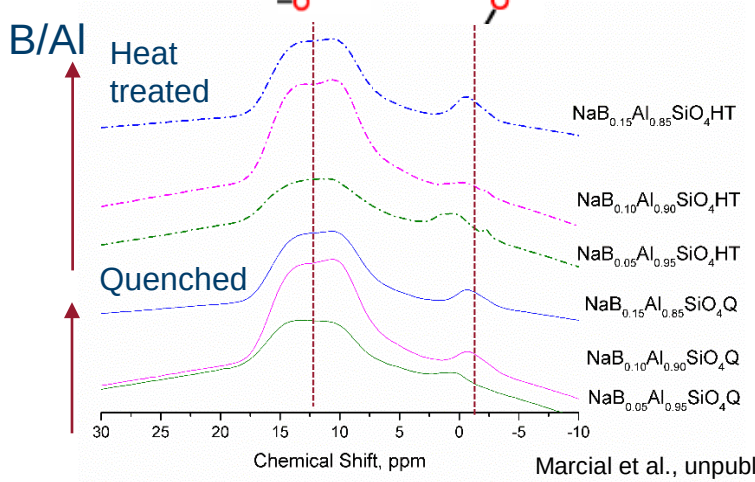


McCloy et al, *JNCS* 409, 149 (2015)

Change in B4/B3 when Nepheline crystallizes

B-11 MAS NMR

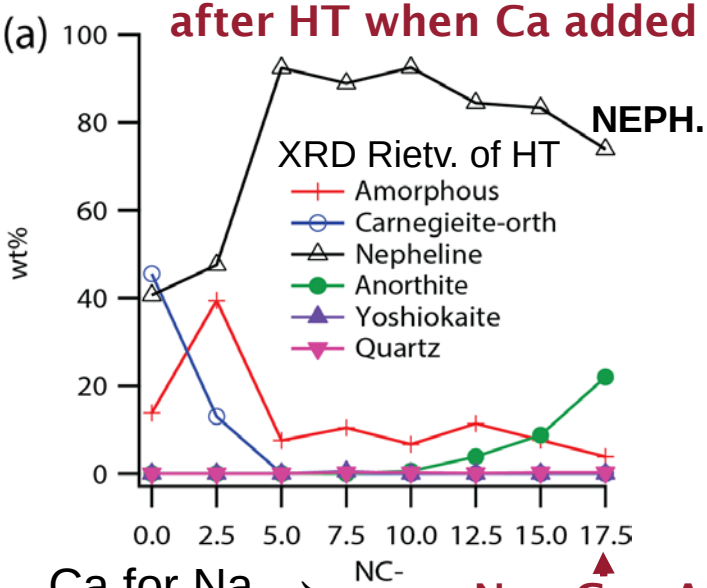




Marcial et al., unpublished data

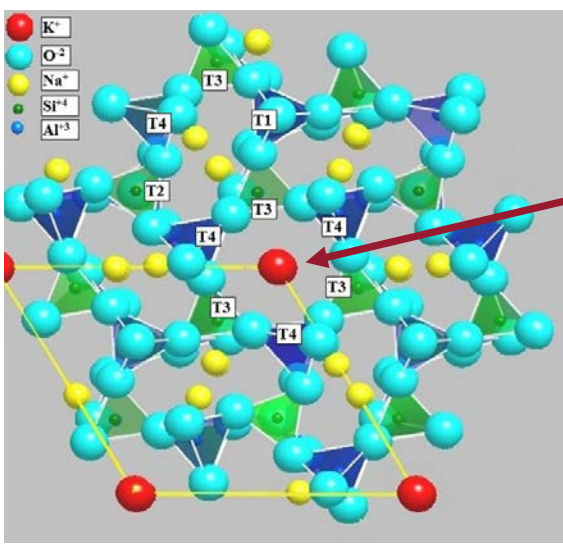
Effect of Na/Ca: Nepheline crystallization

Large amounts of Neph after HT when Ca added



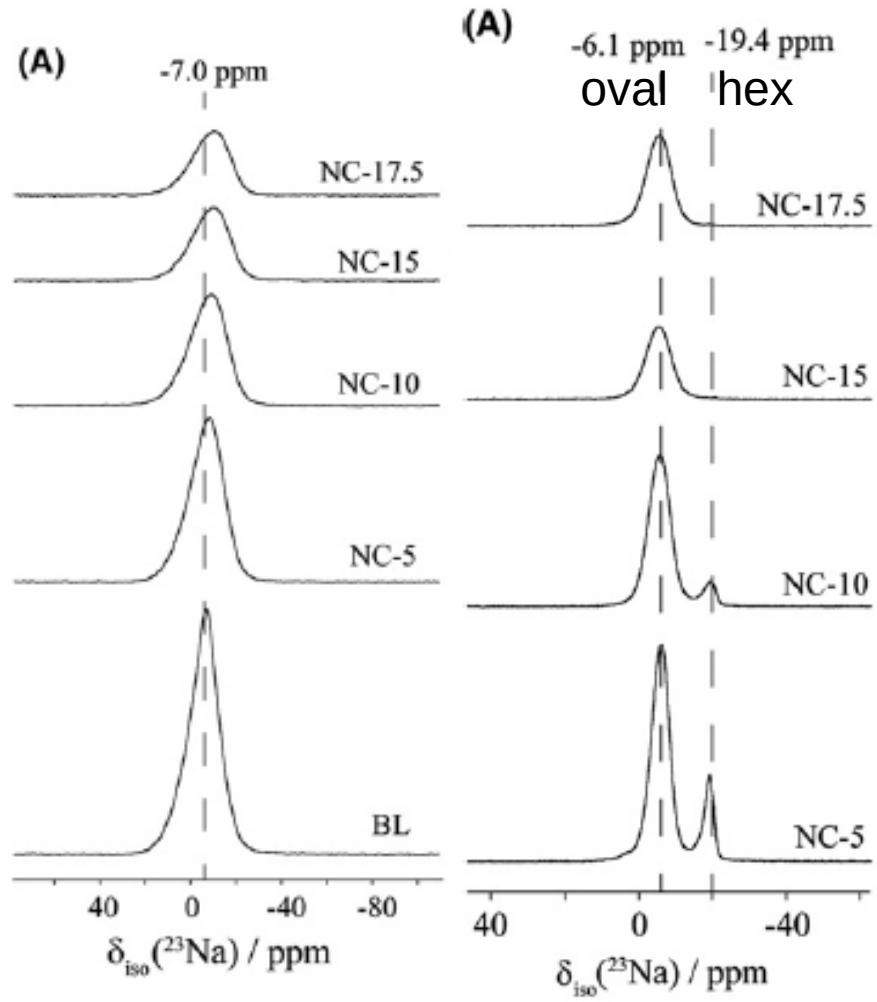
Ca for Na →

$Na_{0.3}Ca_{0.7}AlSiO_4$



Ca

Na-23 in $Na_{1-x}Ca_xAlSiO_4$;
↑Ca, Na-O bond lengthen;
Ca goes into Neph Hex channel

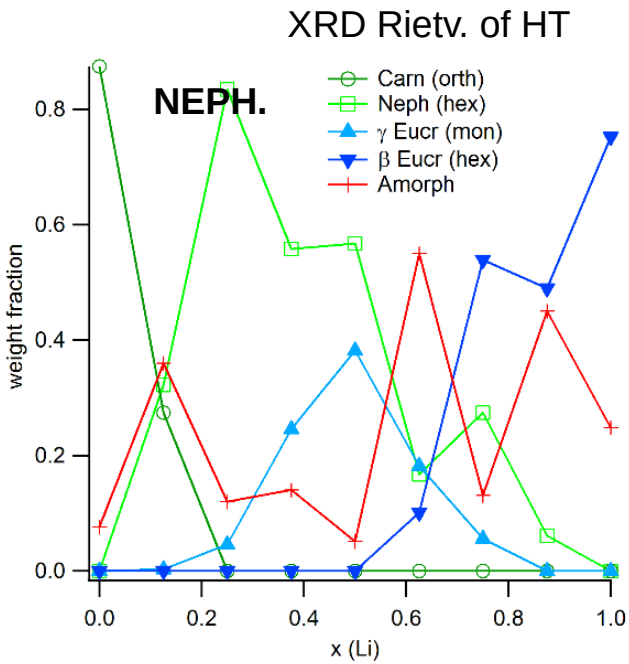


Deshkar et al, *JACERS* 100, 2859 (2017)

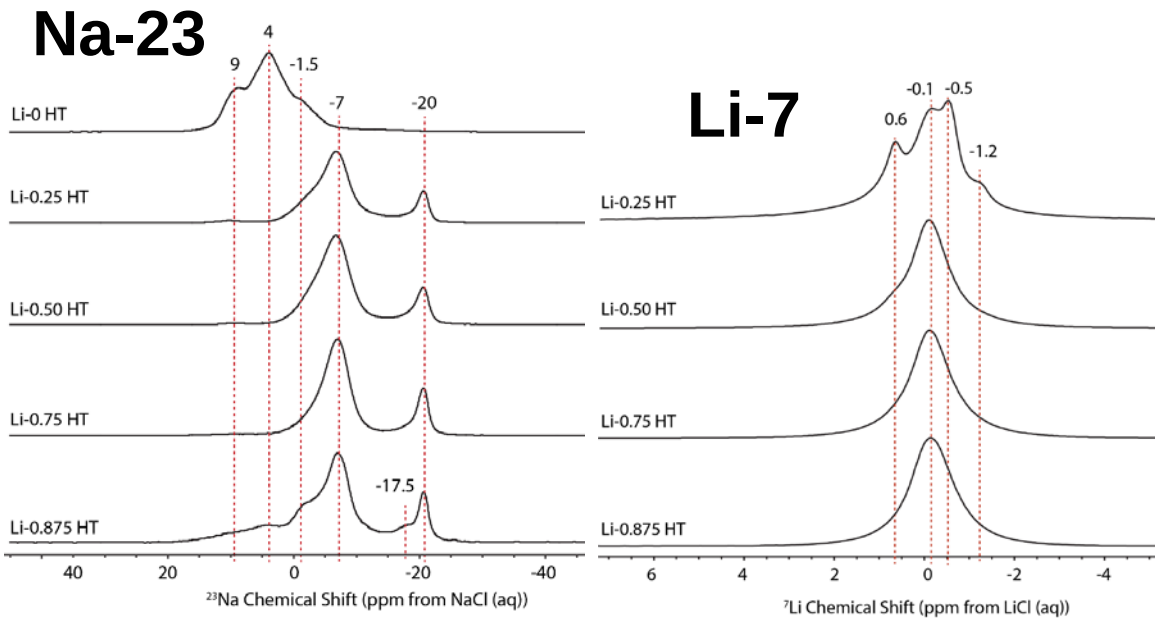
Effect of Na/Li: Nepheline crystallization

$Na_{1-x}Li_xAlSiO_4$

Neph max at low Li
Eucr phases at mid/high Li



No Li: Na→Orth Carneg
Low Li: Li→Neph; complex Li environ.
Mid Li: Na env ~ Neph; Li env ~ γ Eucr
High Li: Na→Eucr; complex Na environ.



Marcial et al., submitted

Implications

- Glasses & crystallized glasses should be studied
  - NMR, Raman, EPMA, XRD, magnetic methods, Mössbauer
- Cooling conditions strongly influence amounts of nepheline, in some cases phases and/or compositions
- Fe, Ca, and likely Li go into nepheline; B does NOT go in
- High Fe and B generally suppress nepheline
- Li and Ca have more complex effects

Future

- Quantify amount of Ca that can go into nepheline
- Further defined the change in B with crystallization
- Explore any role of Ti and of combined effects
- Role of alkali/AE coordination on crystallization tendency
- Recommend composition adjustments to avoid crystallization
- In-situ synchrotron crystallization experiments

Collaborators

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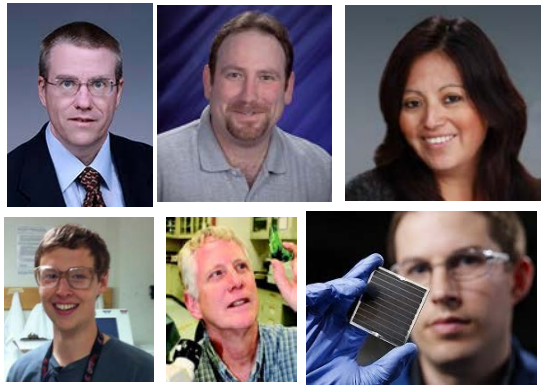

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Thanks!