Observations of chemical composition in frost flower growth process and their implication in aerosol production and bromide activation chemistry

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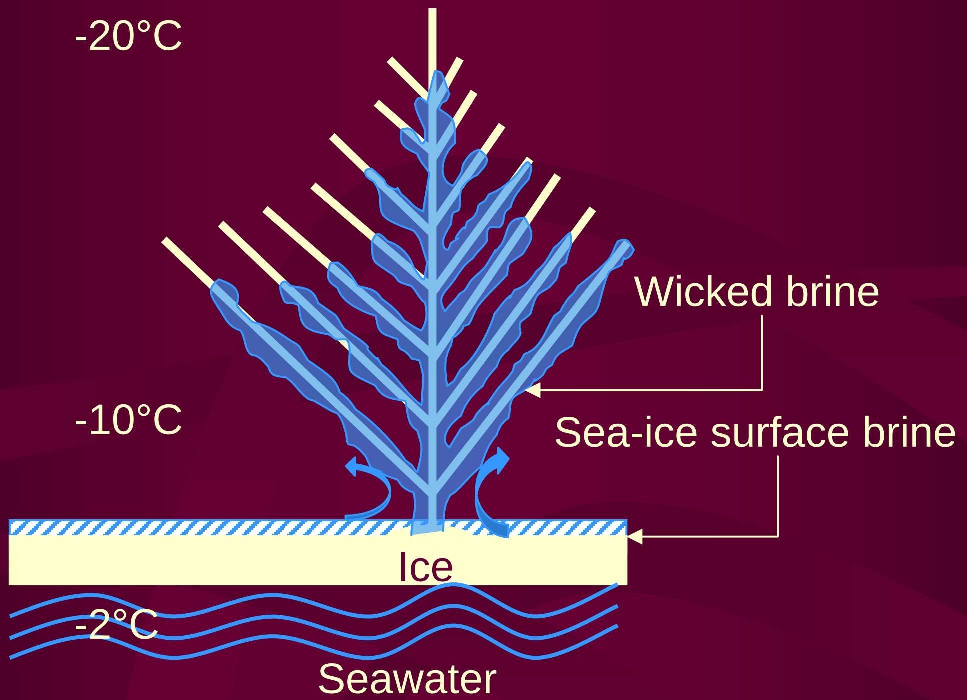
Why do we care about frost flowers and how they relate to our research main topic?

- Bromide activation chemistry has been linked to mercury deposition in the Arctic in the springtime.
- Bromide comes from sea salt from the ocean, but how the sea salt got into the atmosphere is not understood yet.
- Possible atmospheric sea salt sources could be ocean spray, frost flowers (FF) and wind blown snow.
- Is believed that FF contribute to most of the sea-salt aerosol.

What are frost flowers?

- FF are ice crystals that grow in new forming ice and are highly concentrated in sea salt.

How frost flowers form?

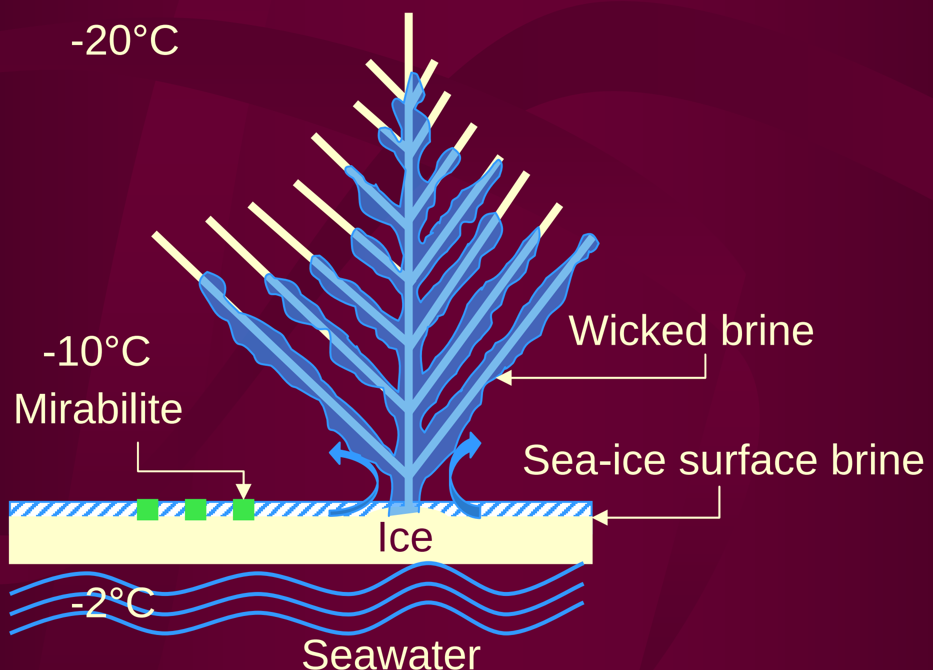


1. As sea water freezes salts are pushed out off the ice crystal
2. Water evaporates creating a water vapor layer (1-3cm) just above the surface that is supersaturated in respect to ice.
3. Then the brine between the crystals is drawn by capillary forces

Rankin et al. 2002

Frost flower implication in aerosol production

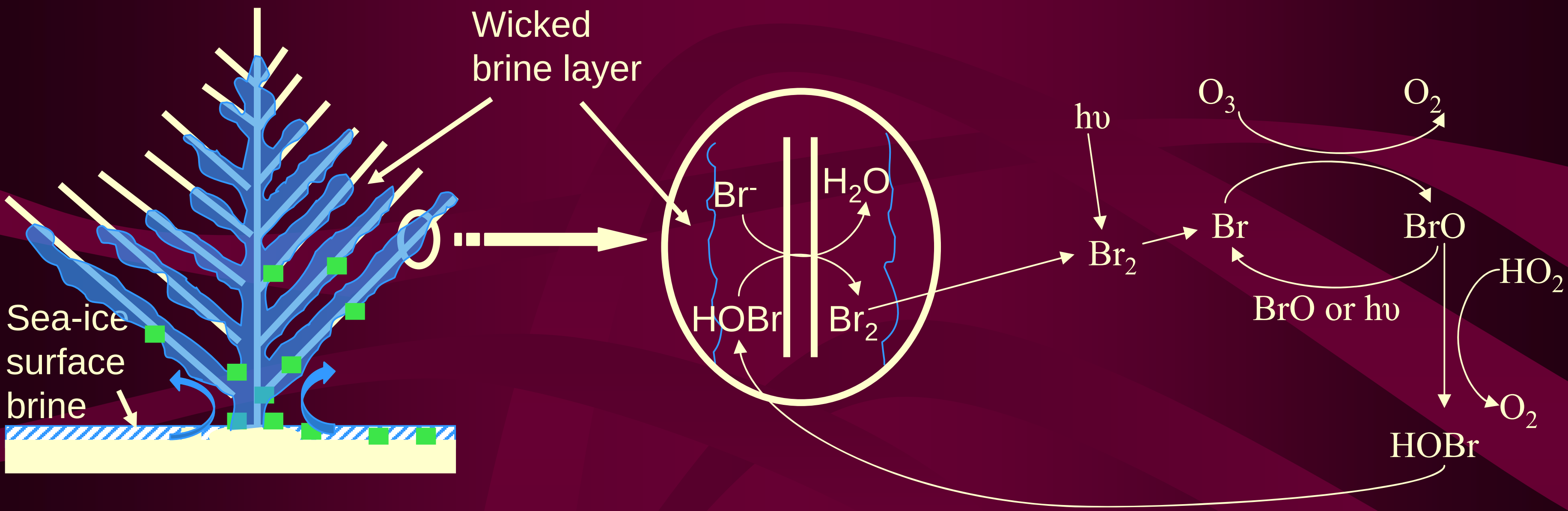
- The primary evidence that FF are a source of sea-salt aerosol is that SO_4^{2-} is depleted in both FF and aerosols, [Rankin et al. 2000].
- $Na_2SO_4 \cdot 10H_2O$ (mirabilite) precipitates at -8°C, very common temperature in frost flower formation.
  - FF are depleted in SO_4^{2-} because of mirabilite precipitation



Frost flower implication in bromide activation chemistry

- Chemical models indicate that gas-phase bromine forms when Br^- reacts with HOBr releasing Br_2 that is photolyzed to produce bromine atoms [Fan and Jacob, 1992; Tan and McConnell et al. 1992; McConnell 1996].
- FF could participate in Br^- activation by HOBr directly reacting with Br^- present in the frost flower structure or indirectly by producing aerosols that will contain Br^- and react with HOBr later on.

Frost flower implication in bromide activation chemistry



- According to this mechanism Br^- should be depleted in FF.

Objectives

- Present conceptual model of FF growth and chemical fractionation in FF growth
- Show chemical analysis of FF and sub parts of FF at various life stages of their growth
- Show how the chemical analysis reinforces the conceptual model
- Consider how the chemical analysis relates to aerosol production and bromide activation.

Enhancement factors and salinity

- Enhancement factor (Ef) gives us information on modifications in the sample compared to seawater.

Enhancement factor:

$$Ef = \frac{\left(\frac{[Ion]}{[Cl^-]}\right)_{Sample}}{\left(\frac{[Ion]}{[Cl^-]}\right)_{SeaWater}}$$

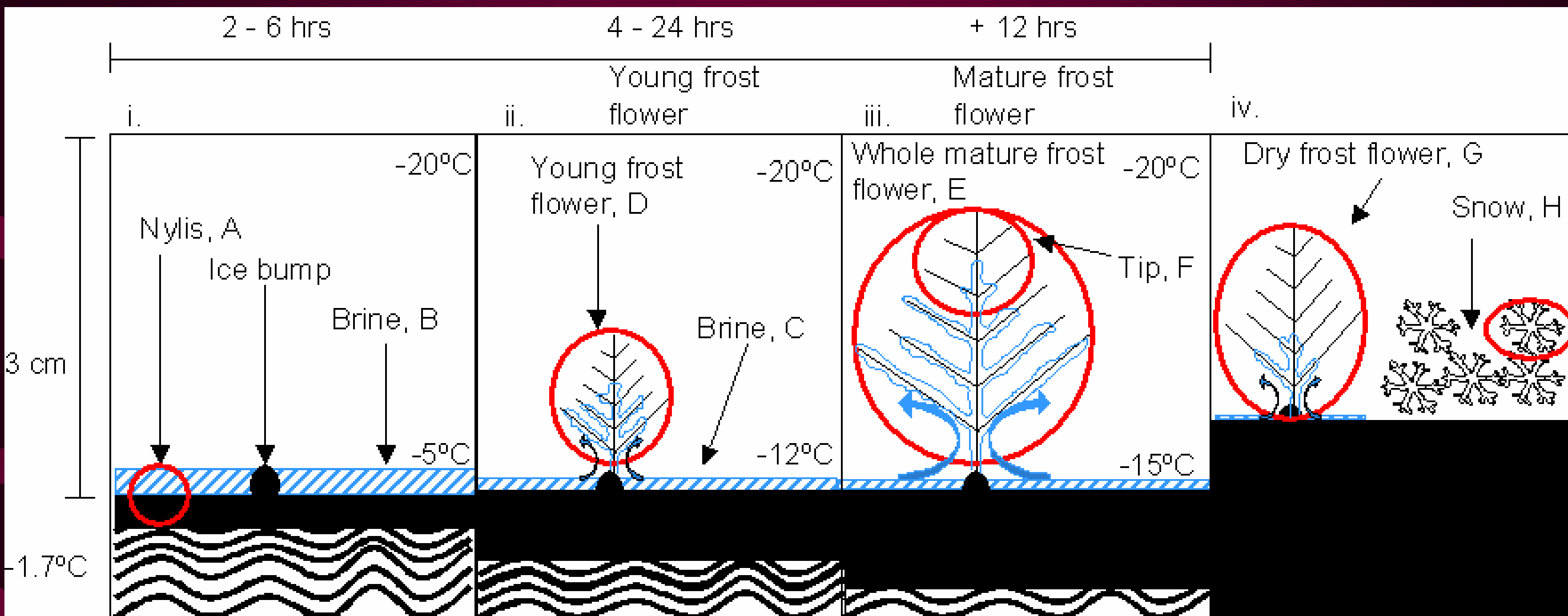
- $Ef < 1$ → Depletion
- $Ef = 1$ → Unmodified
- $Ef > 1$ → Enhancement

- Salinity (S) is to have an idea of total ionic content in the sample.

$$S_{Sample} = \frac{[Cl^-]_{Sample}}{[Cl^-]_{Seawater}} \times S_{Seawater}$$

Seawater S = 35 PSU and $[Cl^-]_{Seawater} = 0.558$ mol/L

Conceptual model of frost flower growth process



Sulfate

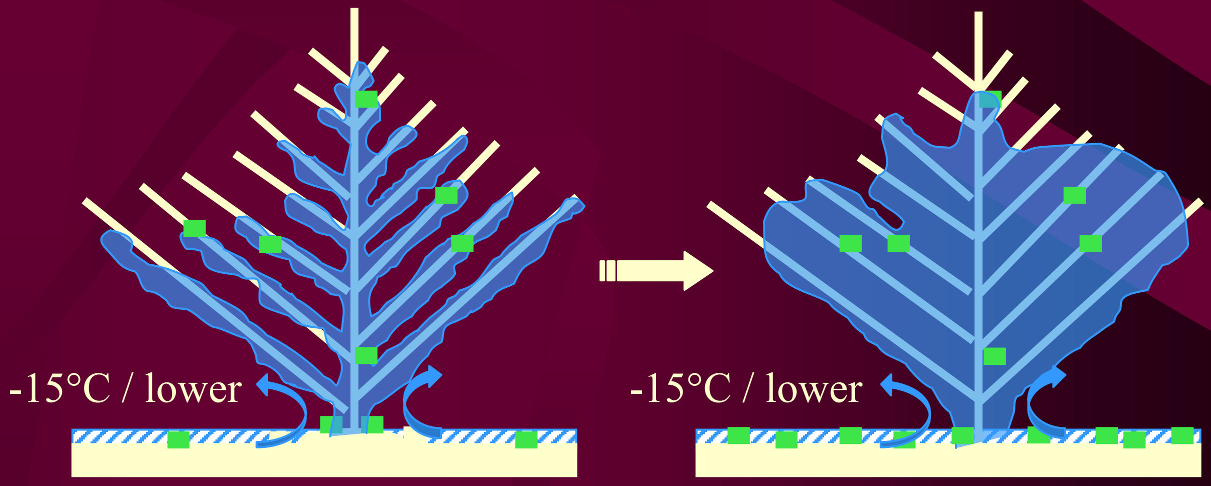
- SO_4^{2-} Efs are variable from sample to sample and even in the same sample type.

Sample	Description	Salinity (PSU)	Ef Br^- (± 0.03)	Ef SO_4^{2-} (± 0.04)
	Standard ocean water	35	1.00	1.00
A	Briny wet ice, very early growth stage	16	0.98	1.03
		23	0.98	1.03
		Variable low	Comparable to unity	Comparable to unity
B	Brine on early growth stage	34	0.96	1.02
		37	0.96	1.01
		Comparable to ocean water	Small depletion	Comparable to unity
C	Brine on young frost flower stage	78	0.96	1.04
		67	0.97	1.05
		Variable high	Mostly comparable to unity	Comparable to unity
D	Young whole frost flower	48	0.97	1.08
		45	0.97	1.08
		79	0.98	1.12
		85	0.97	1.05
		98	0.98	0.88
		93	0.98	0.96
		Variable high	Comparable to unity	Variable enhanced and depleted
E	Mature whole frost flower	105	0.98	0.35
		83	0.98	0.35
		93	0.98	0.97
		57	0.98	1.43
		22	0.96	0.98
		23	0.96	0.92
		20	0.96	0.92
		16	0.96	0.99
		93	0.97	0.94
		105	0.98	0.82
		Variable high and low	Comparable to unity	Variable enhanced and depleted
F	Mature frost flower tip	14	0.97	0.89
		17	0.97	0.78
		Low	Comparable to unity	Variable depleted
G	Mature dry whole frost flower	16	0.98	0.91
		25	0.97	0.80
		Variable low	Comparable to unity	Variable depleted
H	Surface hoar close to flowers	2	0.30	0.66
		2	0.56	0.66
		Low	Variable depleted	Depleted

Mature frost flower tips SO_4^{2-} discussion

- Mature FF tips have low salinity values and are depleted in SO_4^{2-}.
- Wicked brine takes longer to arrive to the tips
  - Sample could be diluted if there is more ice skeleton FF structure than wicked brine
  - Mirabilite precipitation most occur in other parts of the FF or on the sea-ice surface brine.

S (PSU)	SO_4^{2-} Ef
14	0.89
17	0.78



SO_4^{2-} conclusion

- Wind blown brine droplets leave attached to the FF mirabilite precipitate resulting in enhancement of SO_4^{2-}.
- Depletion in SO_4^{2-} occurs because mirabilite precipitates before the brine is wicked.
- SO_4^{2-} fate in FF is highly correlated to temperature changes.

Bromide

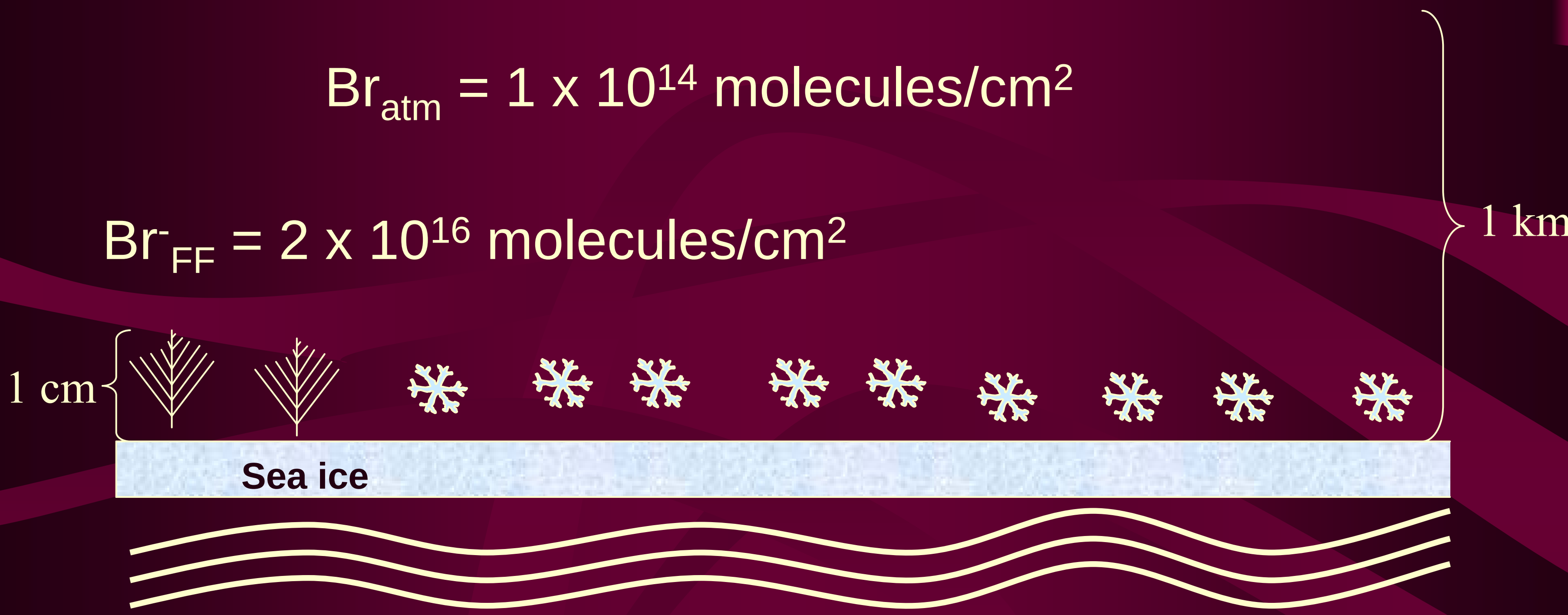
- While SO_4^{2-} is variable and provides information on aerosol formation Br^- does not seem to have much of a story.
- Only the snow sample was depleted in Br^-

Sample	Description	Salinity (PSU)	Ef Br^- (± 0.03)	Ef SO_4^{2-} (± 0.04)
	Standard ocean water	35	1.00	1.00
A	Briny wet ice, very early growth stage	16 23	0.98 0.98	1.03 1.03
		Variable low	Comparable to unity	Comparable to unity
B	Brine on early growth stage	34 37	0.96 0.96	1.02 1.01
		Comparable to ocean water	Small depletion	Comparable to unity
C	Brine on young frost flower stage	78 67	0.96 0.97	1.04 1.05
		Variable high	Mostly comparable to unity	Comparable to unity
D	Young whole frost flower	48 45 79 85 98 93	0.97 0.97 0.98 0.97 0.98 0.98	1.08 1.08 1.12 1.05 0.88 0.96
		Variable high	Comparable to unity	Variable enhanced and depleted
E	Mature whole frost flower	105 83 93 57 22 23 20 16 93 105	0.98 0.98 0.98 0.98 0.96 0.96 0.96 0.96 0.97 0.98	0.35 0.35 0.97 1.43 0.98 0.92 0.92 0.99 0.94 0.82
		Variable high and low	Comparable to unity	Variable enhanced and depleted
F	Mature frost flower tip	14 17	0.97 0.97	0.89 0.78
		Low	Comparable to unity	Variable depleted
G	Mature dry whole frost flower	16 25	0.98 0.97	0.91 0.80
		Variable low	Comparable to unity	Variable depleted
H	Surface hoar close to flowers	2 2	0.30 0.56	0.66 0.66
		Low	Variable depleted	Depleted

Bromide budget

$Br_{atm} = 1 \times 10^{14}$ molecules/cm^2

$Br^-_{FF} = 2 \times 10^{16}$ molecules/cm^2

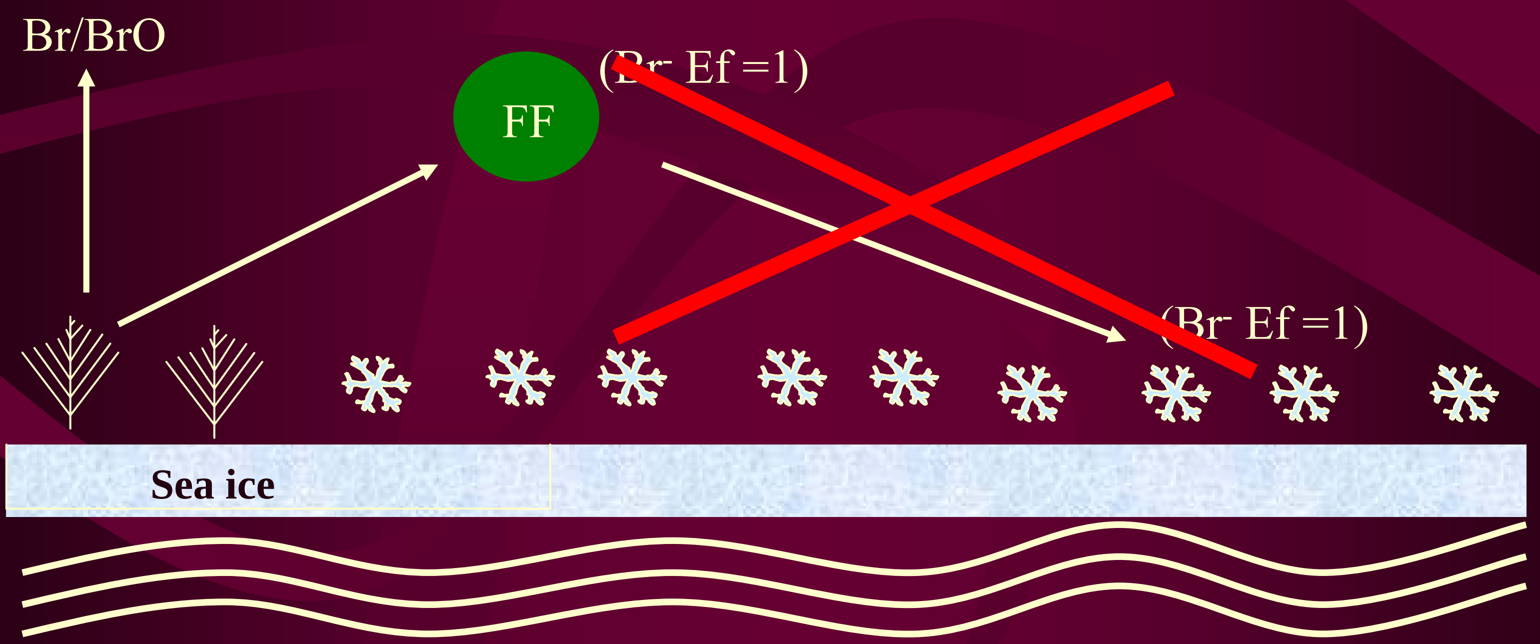


- If depletion in Br- occurs in FF we will not see it, because there is so much Br- that a small modification (0.5%) is not detectable.

Role of FF in Bromide Activation

However, if all activation occurred on FF, and FF are not depleted in Br^-, no snow would be found that was depleted in bromide.

Because we see snow that is depleted in bromide, there must be some activation subsequent to frost flowers formation.



Future work

- Compare the results from this FF study to aerosol chemical data to support our conclusions.
- Use the knowledge gain in this research on FF growth process to better understand the relation between rich-BrO air masses and potential FF areas.

Acknowledgments

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Questions?