



# Solutes in Seasonal Snow

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# Overview

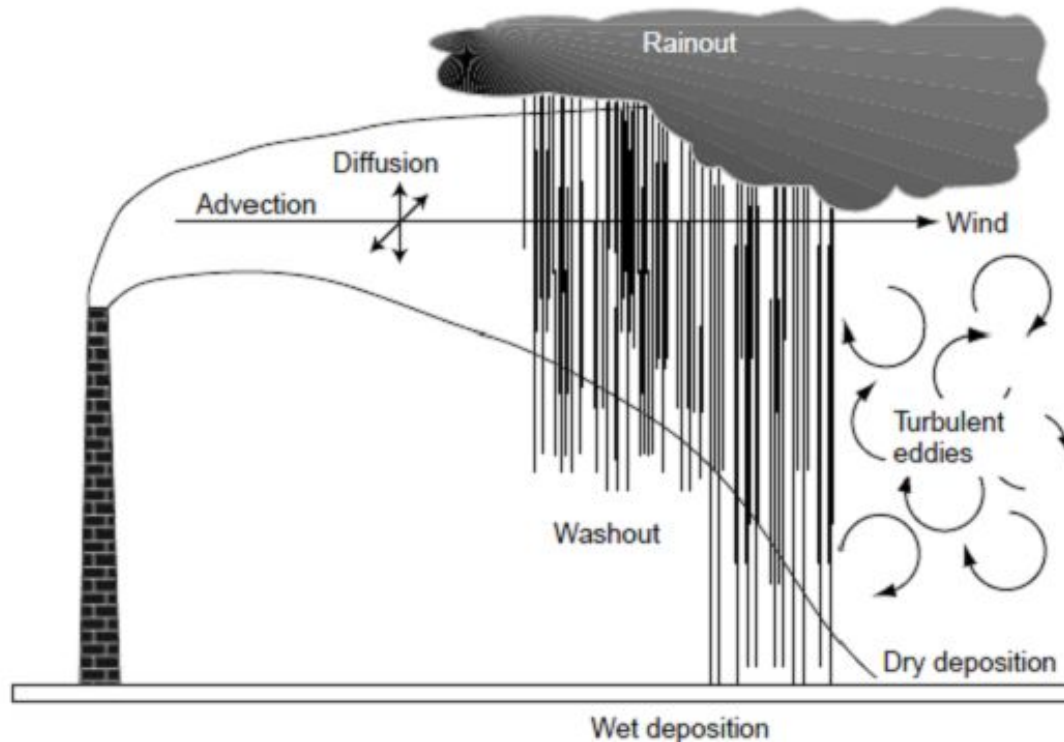


- Deposition of solutes on snow
  - Wet deposition
  - Dry deposition
- Solute dynamics within snowpack
  - Snow metamorphism in wet, dry snowpacks
  - Solute movement through snowpack
- Meltwater/runoff
  - Solute transportation case study



# Deposition of solutes on snow

# Solute deposition



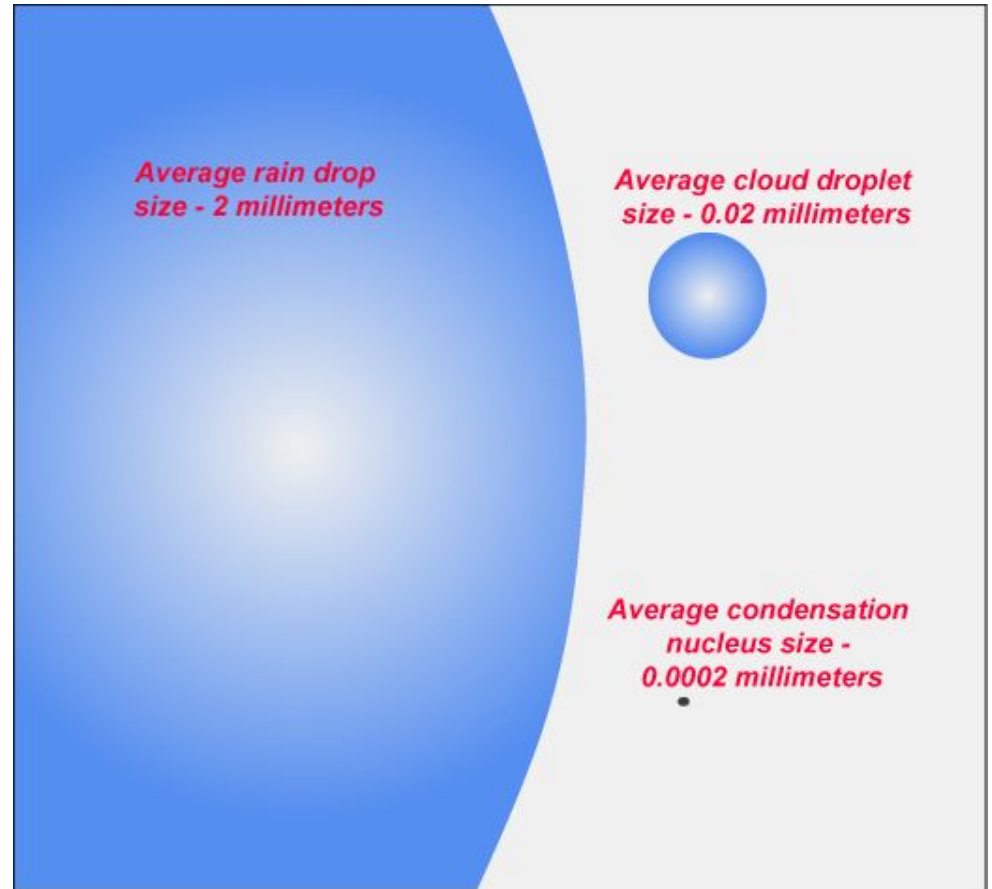
# Wet deposition of gases

- Processes in which atmospheric chemicals are accumulated in rain, snow, or fog droplets and are subsequently deposited onto Earth's surface.
  - When incorporation of chemicals into water droplets occurs within a cloud, the process is called **rainout**.
  - When incorporation occurs beneath a cloud, as precipitation falls through the air toward Earth's surface, the process is called **washout**.
- At equilibrium,  $C_{\text{water}} = C_{\text{air}}/H$ , where C = concentration, and H = Henry's constant (which is different for different species)
- Chemical equilibrium may generally be assumed if the rain forms in contact with the air (rainout) or travels through at least several tens of meters in contact with an air mass (washout).

All: (Hemond and Fechner, 2015)

## Cloud condensation nuclei (CCN)

- Without CCN, water wouldn't typically condense until  $\sim -13$  to  $-20^{\circ}\text{C}$
- In above freezing temperatures the air would have to be supersaturated to around 400% before the droplets could form
- Average CCNs are 1/100th the size of average cloud droplets



# Wet deposition of particles



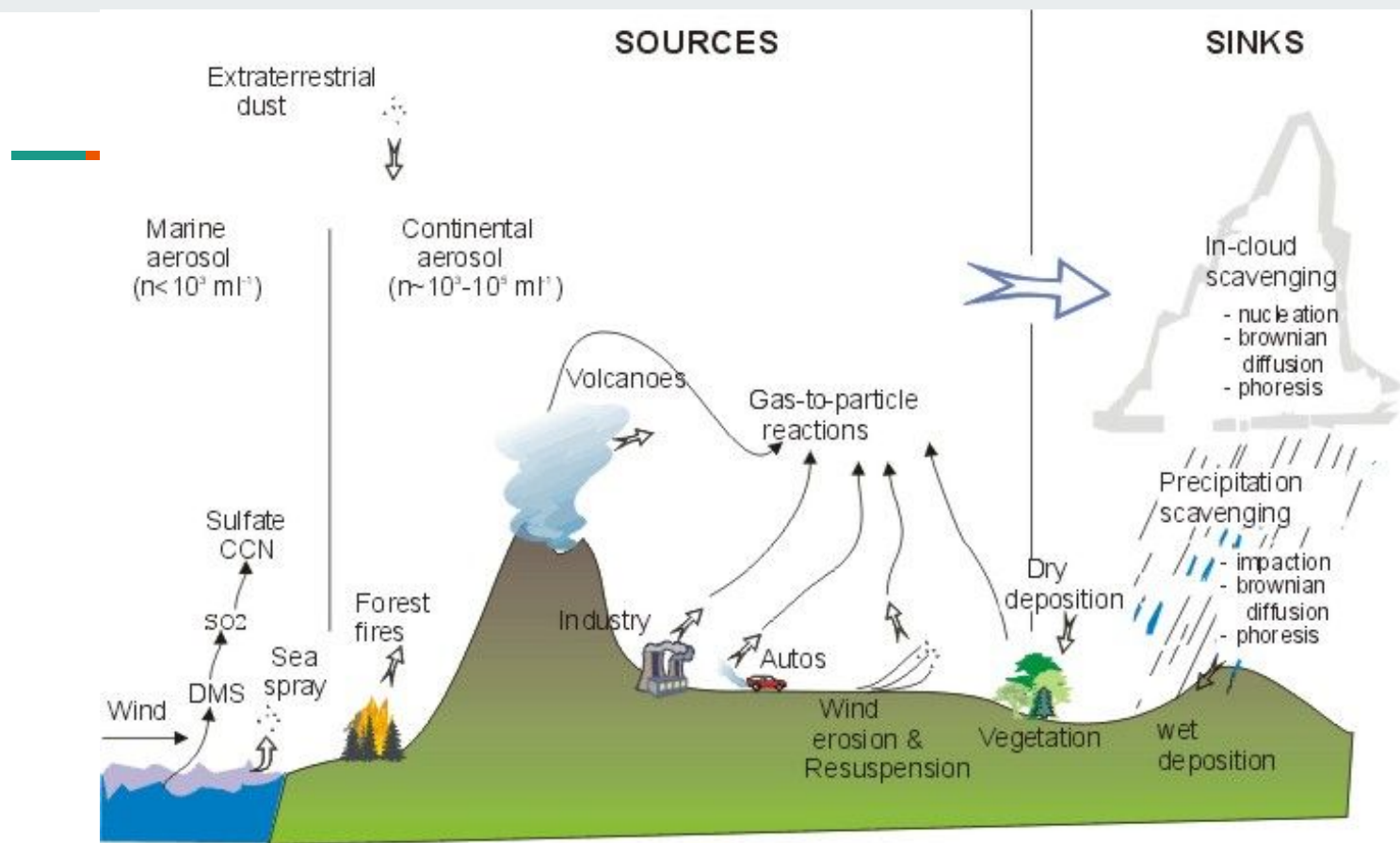
- If nucleation sites were absent, water droplets would not form unless the air temperature were significantly below the dew point (Hemond and Fechner, 2015)
- The removal rate of particles by rainout is typically higher than the removal rate by dry deposition (Hemond and Fechner, 2015)
- Particles, unlike gases, do not partition between air and water in a consistent and thermodynamically predictable way (Hemond and Fechner, 2015)
- Fine particles that consist of water-soluble, hygroscopic substances are more likely to act as CCNs. (Pacyna 2008)
- Results of various studies conclude that the primary source of CCNs in marine air is sulfate aerosol. (Pacyna 2008)

# Dry deposition



- Occurs in dry weather through such processes as **settling**, **impaction**, and **adsorption**.
- Important **atmospheric parameters** include wind speed, humidity, stability, and temperature.
- Important **surface parameters** include friction velocity, roughness height, and zero-plane displacement.
- Important **particle parameters** include the size, shape, density, reactivity, hygroscopicity, and solubility of particles.







# **Solute dynamics within snowpack**

# Snow metamorphism



- Rate at which solubles removed from snowpack depends on:
  - atmospheric conditions of deposition
  - **degree, type of metamorphism within snow**
- In snowpack:
  - grain size increases
  - rounding
  - surface area of snow decreases
- Most impurities not accepted into crystal lattice as recrystallization occurs
  - Ammonia, fluoride salts most readily accepted
- As recrystallization occurs, smaller particles evaporate, snow grains steadily purified → **Impurities concentrated on grain surfaces**
- Rate at which solubles removed depends on atmospheric conditions of deposition and degree, type of metamorphism within snow

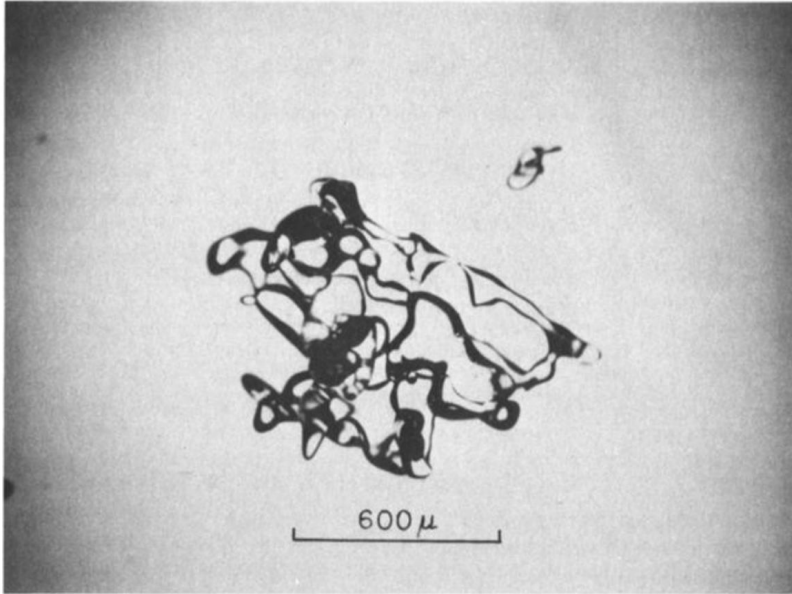
# Metamorphism in dry snowpack



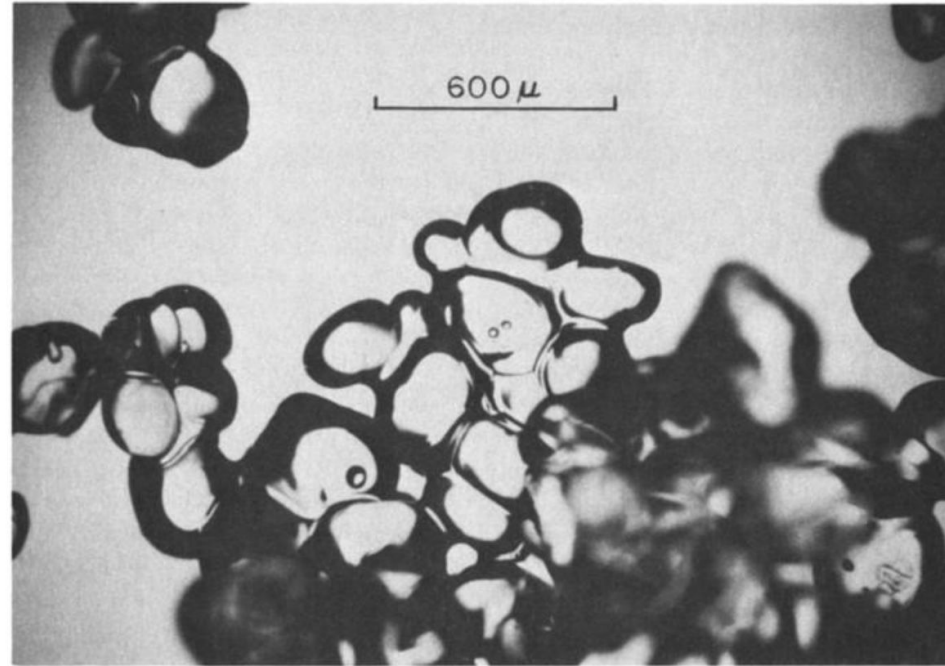
- Vapor pressure, temperature gradients drive grain growth
  - High growth rate → faceted grains (kinetic growth form)
  - Low growth rate → rounded grains (equilibrium growth form)
- Both grain growth forms lead to segregation of solutes on snow grains
  - Surfaces losing mass: solutes accumulate on grain surface by distillation
  - Surfaces gaining mass: solutes accumulate on grain surface because they aren't incorporated into crystal lattice
- Impurity concentration on grain surface
  - Impurity depletion in grain interior
  - Rate of solute removal from interior depends on diffusion rates, ice solubility (dependent on chemical species)

# Snow crystal grain changes

Wet snow grains (during melting)



Dry snow grain (pre-melt)



# Metamorphism in wet snowpack



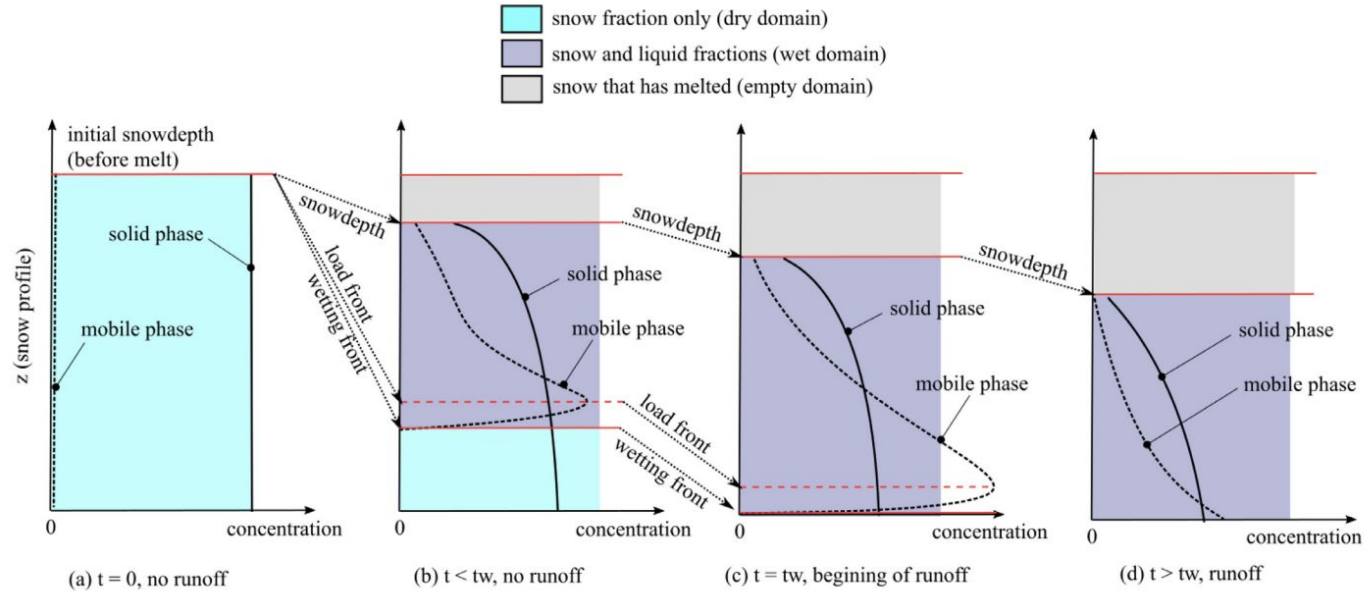
- When liquid first enters snowpack, some freezes (to increase snow temp to allow melting) and rest held by capillary attraction
- 'Wetting front' propagates downward as far as moisture availability allows
- Presence of liquid in snowpack accelerates partitioning processes (heat, mass more efficiently transported)
- Degree to which solute kept in ice grain crystal during metamorphic processes depends on solubility of ion or gas within ice (species)
- Mean reactions in snowpack:
  - Partitioning between liquid, solid, gas phases
  - Oxidation, reduction (unlikely)
  - Particulate dissolution (unlikely)

# Impurity mixing with meltwater through snow



- Molecular diffusion due to local concentration gradients
  - Spreads impurities throughout snowpack, either picks up or releases impurities depending on surrounding concentrations
- Mechanical dispersion from velocity variation in flowing liquids
  - Increases with speed of water
  - Dependent on geometry of pore space
- Relationship between mechanical forces described by Peclet number
  - $Pe = vd/D$
- $v$  = velocity of flowing water,  $d$ =grain size,  $D$ =coefficient of molecular diffusion

# Moisture in snowpack, melt-freeze cycles



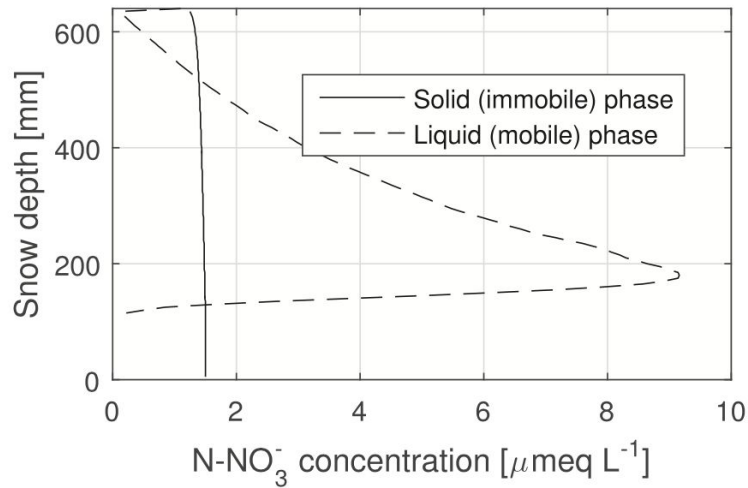
- As melt-freeze cycles occur, solutes further cleaned from particles, more available for runoff



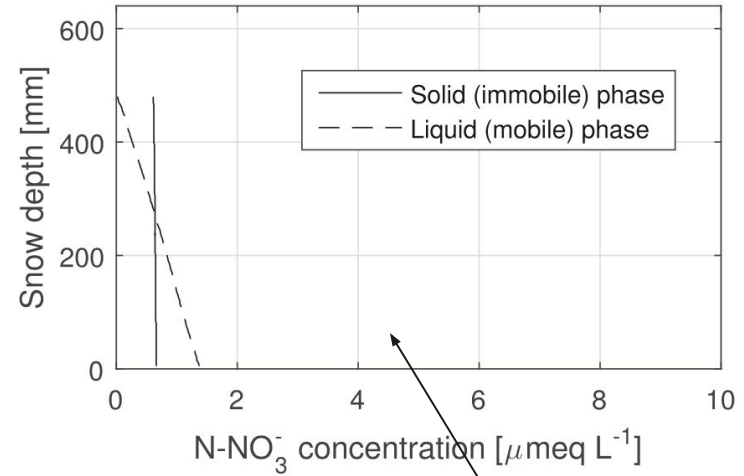
# Solid and mobile phases before and after ion load (wetting front) reaches snowpack bottom

D. Costa et al.

(a) Before the ion load front reaches the snowpack bottom



(b) After the ion load front reaches the snowpack bottom



Costa et al.

Most solutes depleted



# Solutes in snow meltwater

# Solute snowmelt dynamics

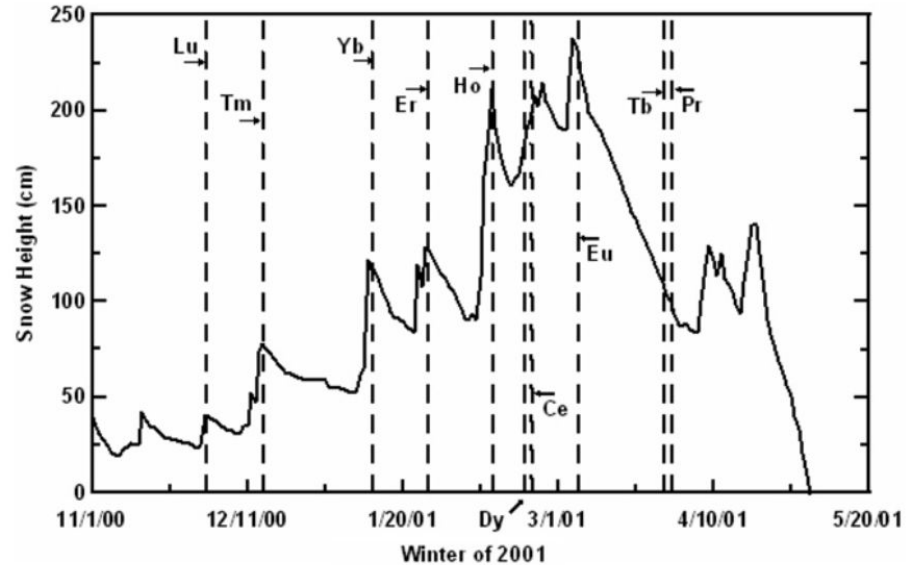
- Seasonal snowmelt affects the chemistry of lakes and streams.
- Rapid release of pollutants, “Ionic Pulses”, can dramatically change water system chemistry.
- **What controls solute redistribution and transport throughout the entire winter season?**



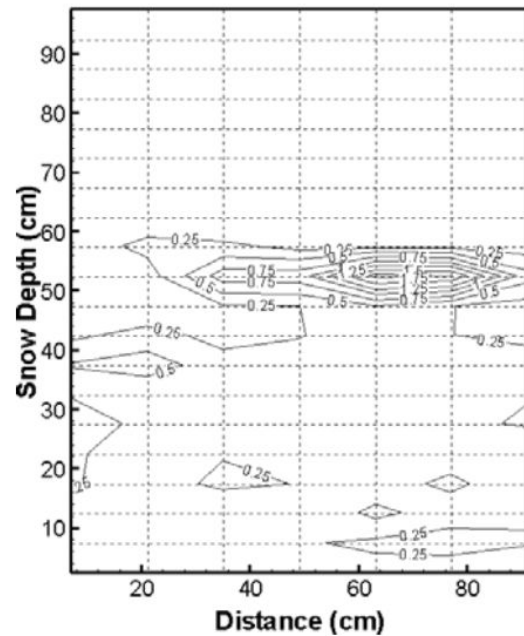
# Methods

- Central Sierra Nevadas
- Nov. 1, 2000 to May 31, 2001
- REE tracers added to plot snow surface after each major storm.
  - Large signal to noise ratio
- Sampled fresh snow, snow profiles, snowmelt for natural and artificial tracers.

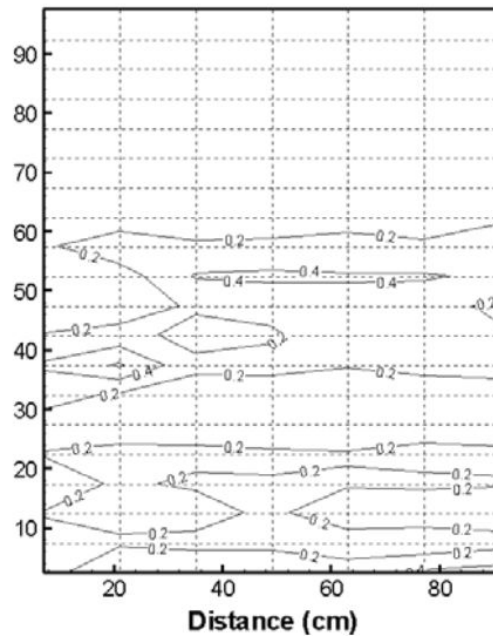
## Rare Earth Elements (REE)



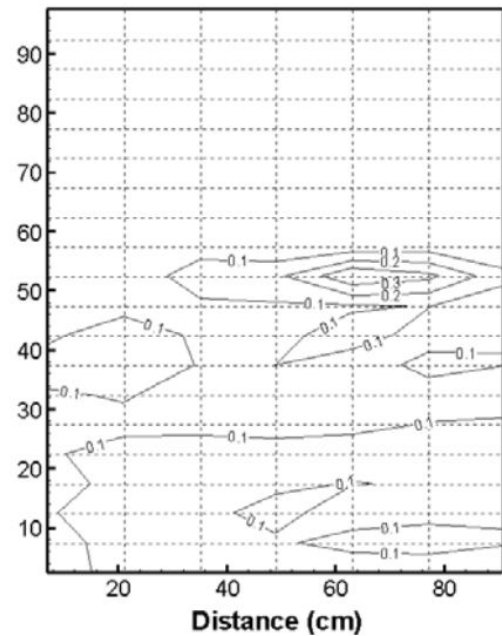
**(g) Chloride**



**(h) Nitrate**

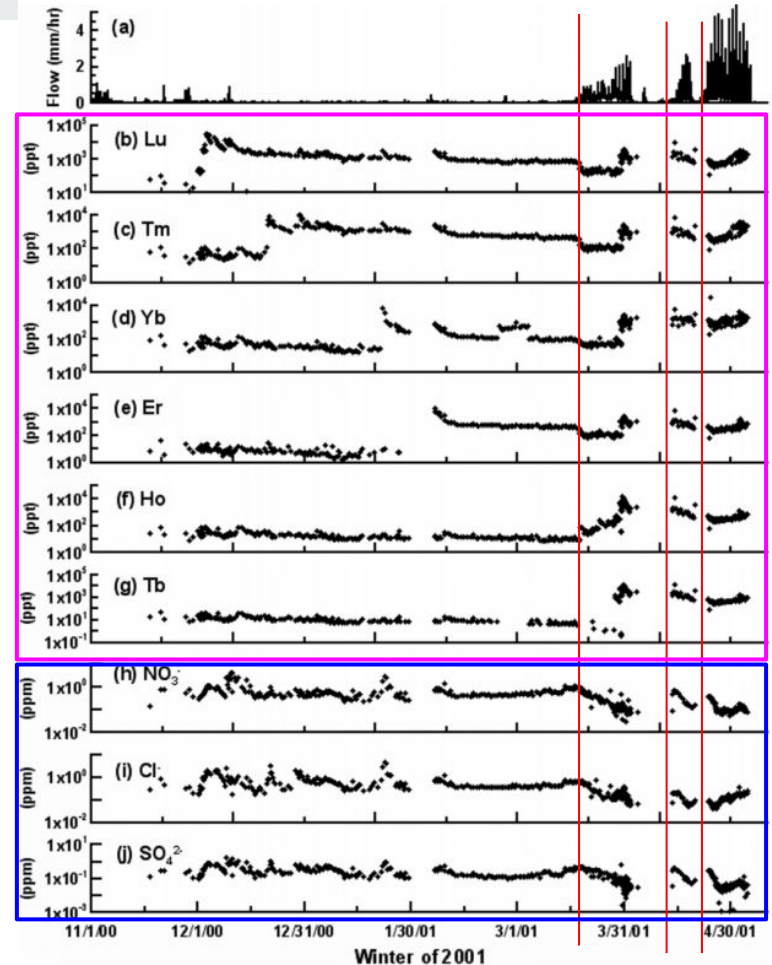


**(i) Sulfate**



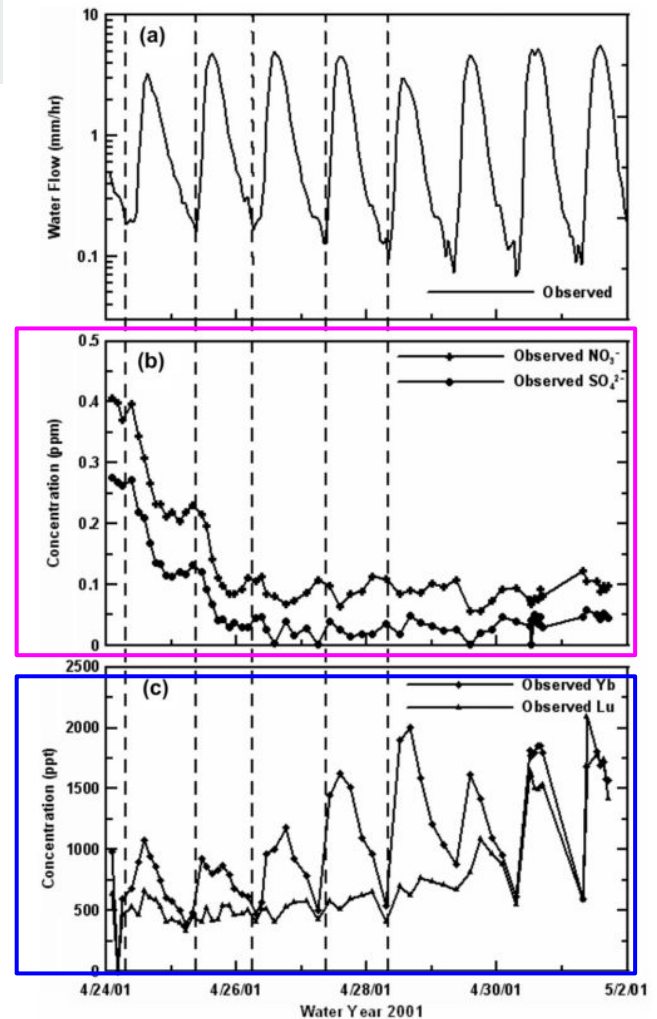
# Melt water results

- Log scale
- Max concentration of solutes in meltwater much higher than new snow or profile.
  - Sulfate: ns=0.3, sp=0.4, sm=1.8 ppm
- Major melt events had peaks in solute concentration, which tailed off exponentially (ionic pulses).
  - Enriched pores (flushed)
- REE increased with flow.
  - Located in pores accessed by high flow



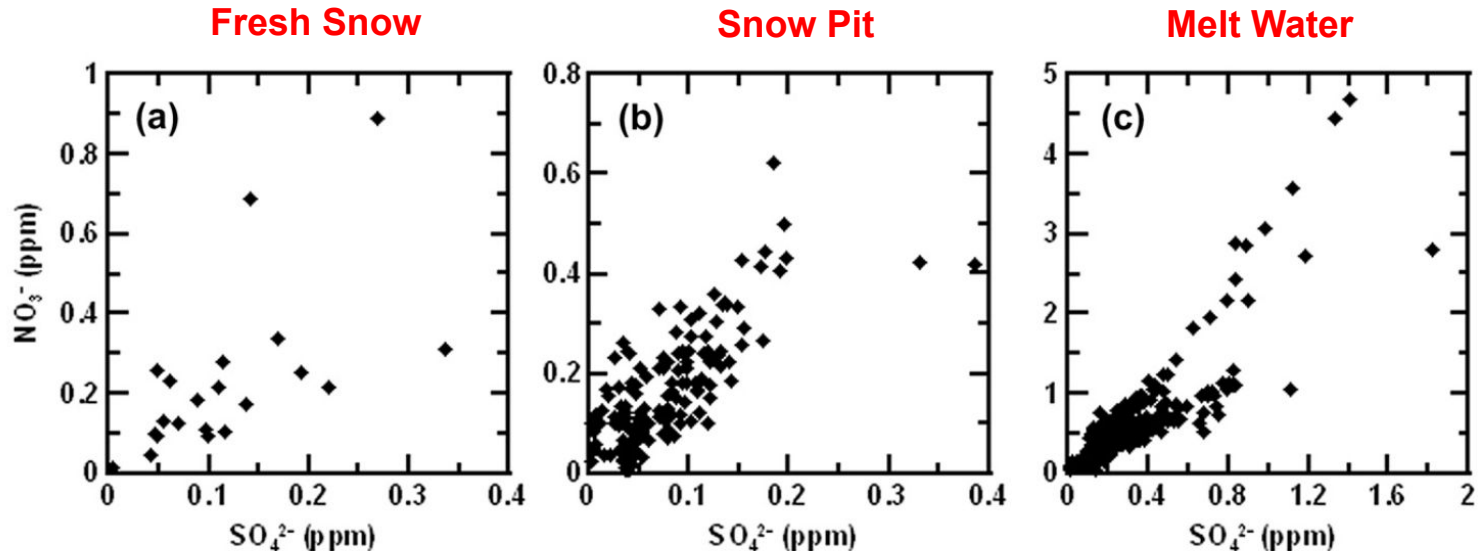
# Diurnal signals

- REE concentration peaked in afternoon.
  - Channels with tracers activated during high flow.
- Solute concentration showed negative relation with melt volume.
  - Likely due to being diluted from increased flow.



# Sulfate vs Nitrate across processes

- Correlation increased between sulfates and nitrates shows similar processes.
  - Elution and redistributed similar
- Snow metamorphism leaves pore water with high solute concentrations.





# Solute Snowmelt Dynamics Summary



- Observed redistribution of solutes in the snow
  - Suggested by increasing covariation of  $\text{NO}_3^-$  and  $\text{SO}_2^-$ 
    - new snow->snow profile->snowmelt
- High solute concentrations associated with major melting episodes
  - Solute concentration decreased exponentially over episodes
  - Released in 3 ionic pulses
- Diurnal variation of water flow caused fluctuation of solutes
  - Diluted during day time

# Conclusions

- Deposition of solutes on snow
  - Wet deposition takes place in 2 parts: rainout (within cloud) and washout (post-cloud)
  - Dry deposition occurs in the absence precipitation due to settling, impaction, and adsorption
- Solute dynamics within snowpack
  - During metamorphosis, solutes transported from inside snow grain to grain surface
  - Meltwater transports solutes through snowpack via diffusion, mechanical processes
  - Melt-freeze cycles increase solutes available for transport
- Solutes in melt water
  - Solute species can undergo complex redistribution
  - Ionic pulses are real (important to understand for downstream chemistry)
  - Diurnal dynamics can exist, but may not be straightforward

# REFERENCES

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