

SUPPLEMENTARY MATERIAL

For

Isotopic fractionation during ice growth by riming and its effect on
the d-excess of precipitation

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Atmospheric Chemistry and Physics

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25 **Table S1 (A-F).** Dates/times for which concurrent radar and isotope data were available. Daily averages of MDV were calculated for Summit and Dumont d’Urville. Averaging times were daily or sub-daily at Ny-Ålesund and Andenes, and 25- or 30-min at Cazadero and Rio Claro.

A. SUMMIT, Greenland

Date	Date	Date	Date	Date	Date	Date	Date
20130117	20140226	20120514	20120723	20120803	20140821	20130915	20131012
20140101	20140228	20120516	20120724	20120804	20140823	20130919	20131013
20140104	20130318	20120525	20120725	20120806	20110901	20130920	20131015
20140106	20130322	20120526	20120726	20120807	20110905	20130922	20131016
20140107	20130327	20120527	20120728	20120808	20110906	20130924	20111103
20140108	20140307	20120528	20120729	20120809	20110914	20130925	20111105
20140109	20140311	20120529	20120730	20120810	20110915	20130926	20111106
20140110	20140312	20120530	20130709	20120811	20110916	20130929	20121127
20140111	20140324	20140502	20130710	20120814	20110917	20111001	20131104
20140112	20140326	20140503	20130711	20120815	20110918	20111002	20131107
20140118	20140330	20140508	20130716	20120822	20110919	20111003	20131108
20140119	20120409	20140519	20130721	20120823	20110920	20111004	20131110
20140120	20120410	20140521	20130726	20120824	20110921	20111005	20131111
20140121	20120411	20140522	20130727	20120825	20110922	20111009	20131112
20140122	20120412	20120606	20130728	20120827	20110923	20111010	20131119
20140123	20120413	20120615	20130730	20120831	20110924	20111012	20131120
20140124	20120414	20120616	20140726	20130801	20120906	20111013	20131125
20140125	20120415	20120617	20140727	20130802	20120907	20111014	20131126
20140127	20120416	20120618	20140729	20130803	20120912	20111015	20131127
20140128	20120425	20120619	20140730	20130805	20120913	20111016	20131129
20140129	20120426	20120620	20140731	20130806	20120914	20111018	20131130
20140130	20120428	20120621	20110811	20130807	20120915	20111019	20121213
20140131	20120430	20120625	20110812	20130809	20120920	20111020	20131209
20130201	20140403	20120626	20110814	20130814	20120922	20111021	20131210
20130208	20140406	20120627	20110815	20130815	20120925	20111022	20131214
20140203	20140413	20120628	20110817	20130816	20130901	20111027	20131216
20140205	20140425	20120630	20110818	20130817	20130902	20111029	20131217
20140206	20120501	20110726	20110822	20130818	20130903	20121001	20131221
20140213	20120503	20110727	20110826	20130819	20130904	20121004	20131223
20140214	20120504	20110728	20110827	20130820	20130905	20121005	20131225

A. (continued)

Date	Date	Date	Date	Date	Date	Date	Date
20140216	20120505	20120701	20110828	20130822	20130906	20121026	20131227
20140218	20120506	20120702	20110829	20130824	20130907	20121027	
20140219	20120507	20120703	20110830	20130825	20130908	20131001	
20140221	20120510	20120704	20110831	20130826	20130909	20131008	
20140222	20120511	20120707	20120801	20140811	20130913	20131009	
20140223	20120512	20120708	20120802	20140819	20130914	20131010	

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B. Dumont d'Urville

Date	Date	Date	Date	Date	Date	Date
1/27/19	5/29/19	1/13/20	4/14/20			
2/6/27/19	2/6/2/19	3/12/19	14/18/2019	5/12/206/19	5/29/19	6/2/19
3/427/19/19	7/4923/19	1/7/20	1/13/20	1/18/20	2/16/20	5/443/2/20
4/18/19	7/23/19	3/2/20	8/28/20			
3/17/20	4/14/20	5/6/1912/20	1/75/14/20	3/478/28/20	9/10/20	

C. Ny-Ålesund, Svalbard (Norway)

Date	Type	Date	Type	Date	Type	Date	Averaging Time
4/28/17	RAIN (daily)	Rain	SNOW (daily)	5/16/18	Rain	2/2/18	Snow
6/27/17	Rain	5/23/18	Rain	5/19/17	Snow		
6/28/17	Rain	5/24/18	Rain	5/21/17	Snow		
6/29/17	Rain	7/8/18	Rain	5/26/17	Snow		
7/54/28/1	Rain	6/29/17	7/95/16/	Rain	4/23/16	3/1/20	Snow
7/14	9/28/15	7/65/17	Rain	7/19/18	Rain	11/24/16	3/3/20
6/25/14	9/29/15	7/65/17	Rain	7/19/18	Rain	11/24/16	3/3/20
7/1/14	1/24/16	7/76/17	Rain	7/12/18	Rain	12/20/16	3/5/20
7/11/14	7/30/16	7/86/17	Rain	7/24/18	Rain	12/22/16	3/8/20
7/13/14	8/7/16	9/22/17	Rain	7/27/18	Rain	4/26/17	3/8/20

7/19 8/8/ 40/9 Rain 8/20 Rain 4/27/17 3/13 Snow 18:00 (3/12) - 09:00 (3/13)
/14 16 7/8/ 17 7/10 1/15
/18 /16
9/4/ 8/13 40/408/7/17 Rain 1/16 8/2 Rain 3/14 Snow 20:00 (3/8) - 11:00 (3/14)
14 /16 7/12 /16 8/18 8/18 20
/18 17
1/40/ Rain 9/3/17 8/29 Rain 5/21/17 3/14 Snow 11:00 - 18:00
189/ 8/14 7/21 1/23
5/14 /16 /18 /16
9/6/ 18/1 Rain9/22/17 9/37 Rain 5/21/17 3/15 Snow 17:00 (3/14) -13:00 (3/15)
14 5/18 27/ 2/12
16 18 /16
10/2 8/28 9/23/17 8/20 2/13 5/26/17
3/14 /16 /18 /16
10/2 9/6/ SNOW 8/28 2/17 5/26/17
4/14 16 (daily) /18 /16
10/2 9/14 10/9/17 8/29 2/20 10/17/17
5/14 /16 /18 /16
6/27 9/21 10/9/17 9/3/ 3/6/ 12/20/17
/15 /16 18 16
7/2/ 10/1 10/10/17 5/9/5 Rain 9/52/18 Rain
15 9/16 /18 3/7/
16
7/24 10/2 1/10/18 5/19 4/2/
/15 0/16 /17 16
7/25 10/2 1/15/18 8/30 4/4/
/15 3/16 /14 16
8/19 6/27 4/16/18 Rain 4/8/
/15 /17 8/31 16
/14
9/12 6/28 5/5/18 4/16 4/22
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D. Andenes, Norway

Date	Averaging (start-end)	Type	Date	Averaging (start-end)	Type
2/25/20	RAIN	daily	3/1/20	2/29_16:00 - 3/1_8:00/20	snow
2/26/20	daily	snow	3/1/20	8:00 - 12:00	snow
3/8/20	daily	rain	3/2/20	3/1_16:00 - 3/2_10:00/20	snow
3/9/20	daily	rain	3/12/20	3/12/20_10:00 - 16:00	snow

~~snow~~12:00 - 16:00

E. Cazadero, California

3/21/05	22:00	22:30		14:15	14:45
	22:30	23		14:45	15:45
	23:00	23:30	1/25/10	0:15	0:45
	23:30	0:00:00		1:15	1:45

Date	Start time	End time	Date	Start time	End time
3/22/05	0:00	0:30		1:45	2:15
	0:30	1:00		3:15	3:45

	1:00	1:30	4:15	4:45
	1:30	2:00	14:45	15:15
	2:00	2:30	16:15	16:45
	2:30	3:00	16:45	17:15
	4:00	4:30	17:15	17:45
2/8/07	19:15	19:45	19:45	20:15
	19:45	20:15	20:45	21:15
	20:15	20:45	22:45	23:15

F. Rio Claro, Brazil

Date	Start	End	Date	Start	End	Date	Start	End
10/8/19	14:30	15:05	12/10/19	20:43	21:18	1/5/20	17:37	18:09
	15:05	15:45		21:18	21:53		18:09	18:49
	15:45	16:15		21:53	22:28			
	17:05	17:55		23:08	23:28			

50 **Table S2.** MASC fall velocity and corresponding d-excess of daily precipitation at Summit.

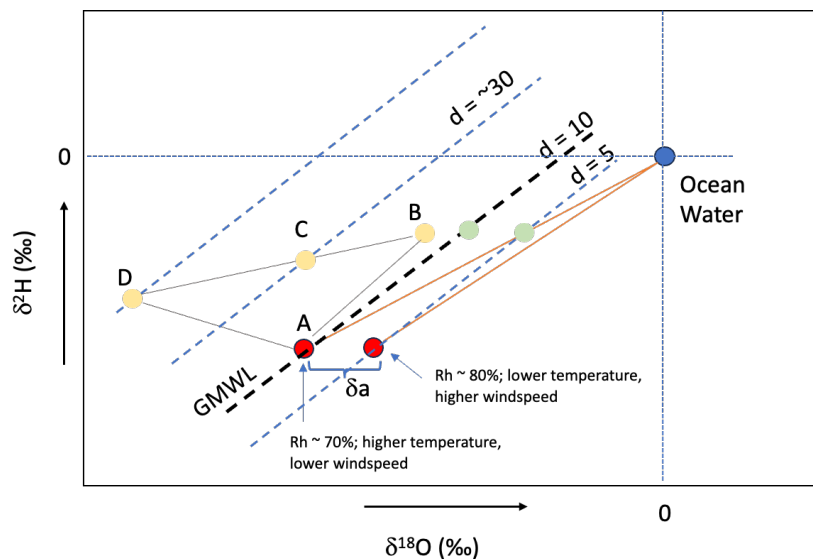
Date	Number of snowflakes observed	Average fall velocity (measured on individual particles)	d-excess (‰) (daily precipitation)
7/26/2014	93	0.81	± 12.3
7/29/2014	5	1.04	± 13.6
7/30/2014	14	0.60	± 18.5
7/31/2014	40	0.64	± 17.0
6/10/2014	13	0.74	± 9.5
6/11/2014	1	1.07	± 10.9
6/22/2014	13	1.25	± 11.7
6/25/2014	3	1.15	± 7.7
6/26/2014	11	0.98	± 6.4
6/28/2014	6	0.69	± 19.3
8/11/2014	7	0.91	± 11.3

Table S3. Parameters and their physical significance in the process-based isotope calculations.

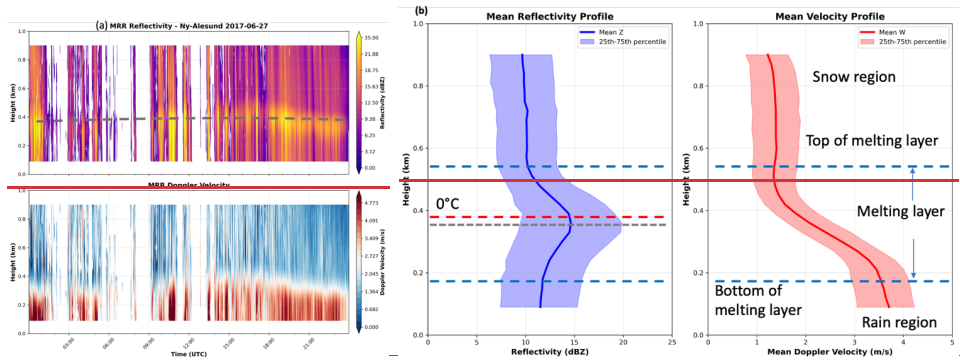
Symbol	Parameter	Units	Process	Physical role
A. SOURCE VAPOUR VAPOR ISOTOPE INPUTS				
$\delta^{18}O_v$	$\delta^{18}O$ of ambient va pou r vapor	‰	All	Sets the ^{18}O content of source va pou r vapor; controls $\delta^{18}O$ of deposited ice directly through α_{sv} . At strongly ^{18}O -depleted values ($\delta^{18}O_v < -45\text{‰}$), drives deposited ice d-excess below source va pou r vapor d-excess through the differential response of $\alpha_{sv}(^{18}O)$ and $\alpha_{sv}(D^2H)$ to depletion.
$d\text{-}excess_v$	d-excess of ambient va pou r vapor	‰	All	Transmitted to deposited ice with slope $\sim 1.13\text{‰}/\text{‰}$ — affects only $\delta D\delta^2H$ of deposited ice; $\delta^{18}O$ is insensitive to d-excess_v. Source d-excess is set by kinetic fractionation at the evaporation source (Merlivat and Jouzel, 1979).
$\delta^{18}O_c$	$\delta^{18}O$ of cloud water	‰	Wet-growth riming	Initial isotope composition of supercooled droplets accreted onto the growing particle. Controls Point A (initial rimed ice composition) and the equilibrium concentration toward which the film evolves at high LWC.
$d\text{-}excess_c$	d-excess of cloud water	‰	Wet-growth riming	d-excess of accreted cloud water; transmitted to rimed ice with attenuation factor ~ 0.5 relative to cloud water value, because film evaporation partially overwrites the cloud water signal.
B. EQUILIBRIUM FRACTIONATION FACTORS				
$\alpha_{sv}(^{18}O)$	Solid- va pou r vapor fractionation, ^{18}O	—	V apou r Vapor dep.; Diamond dust	Temperature-dependent equilibrium enrichment of ^{18}O in ice relative to va pou r vapor (Majoube, 1971: $\exp(11.839/T - 0.028224)$).
$\alpha_{sv}(D^2H)$	Solid- va pou r vapor fractionation, D	—	V apou r Vapor dep.; Diamond dust	Temperature-dependent equilibrium enrichment of D^2H in ice relative to va pou r vapor (Merlivat and Nief, 1967: $\exp(16288/T^2 - 0.0934)$).
α_{ls}	Liquid-solid fractionation	—	Dry-growth riming; Wet- growth (film)	Equilibrium enrichment of heavy isotopes in ice relative to liquid at the freezing interface. For ^{18}O : $\alpha_{ls} = 1.00291$ (O'Neil, 1968); for D^2H : $\alpha_{ls} = 1.02117$. Sole fractionation mechanism in dry-growth riming.
$\alpha_{lv}(^{18}O)$, $\alpha_{lv}(D^2H)$	Liquid- va pou r vapor	—	Wet-growth riming (film)	Controls the isotope flux from the liquid film surface to the va pou r vapor phase by evaporation. Drives the isotopic evolution of

	fractionation at 0°C		surface)	the film away from cloud water composition toward a lower d-excess asymptote.
C. KINETIC FRACTIONATION (VAPOUR VAPOR DEPOSITION AND DIAMOND DUST)				
S_i	Ice supersaturation ratio	—	Vapour Vapor dep.; Diamond dust	Dominant control on d-excess of ice forming by vapor deposition.
D/D_{iso}	Diffusivity ratio, light/heavy isotopologue	—	Vapour Vapor dep.; Diamond dust	Ratio of molecular diffusivity of H ₂ O to that of the heavy isotopologue in air: 0.9723 for H ₂ ¹⁸ O and 0.9755 for H₂¹⁸O ¹⁶ O (Merlivat, 1978). Determines the kinetic enrichment per unit supersaturation.
f	Ventilation factor	—	Vapour Vapor dep.; Diamond dust	Accounts for enhanced mass transfer due to air flow around the falling crystal ($f \leq 1$). At $f = 1$ (diffusion only) kinetic fractionation is maximum; at $f < 1$ ventilation reduces the kinetic enhancement. Typically $f \approx 0.997$ for small ice crystals.
T_c	Growth temperature	°C	Vapour Vapor dep.; Diamond dust	Controls both $\alpha_{sv}(^{18}\text{O})$ and $\alpha_{sv}(\text{D}^2\text{H})$ through their temperature-dependent exponential forms.
D. WET-GROWTH RIMING PARAMETERS				
T_a	Ambient air temperature	°C	Wet-growth riming	Primary control on d-excess of rimed ice. Controls both the evaporation rate from the film surface (through ρ_{sat} difference) and the wet/dry growth boundary.
LWC	Liquid water content	g m ⁻³	Wet-growth riming	Largest total sensitivity (~25% range). Turbulence can increase LWC above background stratiform values through adiabatic updraft condensation.
r	Particle radius	mm	Wet-growth riming	Controls both collection rate and evaporation rate. Larger particles have higher collection-to-evaporation ratio, producing less riming fractionation.
V	Relative fall speed	m s ⁻¹	Wet-growth riming	Increases collection rate and Sherwood number (enhancing both evaporation and isotope flux).

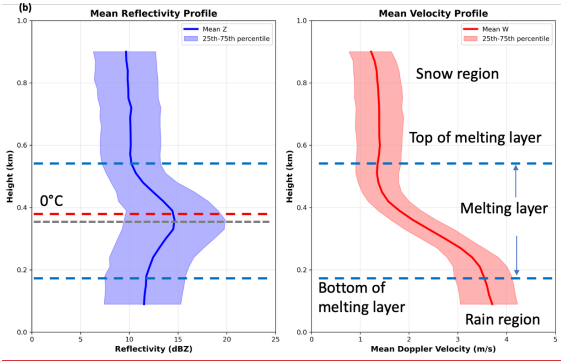
E	Collection efficiency	—	Wet-growth riming	Fraction of droplets in the swept volume that are actually collected. Typical values 0.6–0.9 for mixed-phase clouds; sensitivity is moderate and monotonic.
μ_L/e_M	Film mass / thickness	kg / μm	Wet-growth riming	Controls the timescale of film evolution but does not change the final asymptote. Typical film thickness 10– 50 <u>50</u> μm .
E. WET/DRY GROWTH BOUNDARY				
LWC_{min}	Minimum LWC for wet growth with a persistent liquid film	g m^{-3}	Riming	Defined by the heat balance. Below LWC_{min} , collected water may freeze rapidly and a persistent liquid film may not be present (dry growth); however, an intermittent film may form that can allow wet-growth. Above LWC_{min} , a persistent liquid film forms (wet growth). LWC_{min} decreases with warmer T_a and larger r ; at -10°C and $R = 1\text{mm}$, $LWC_{min} \approx 0.024 \text{ g m}^{-3}$.



FigureFig. S1. Schematic diagram showing isotopic fractionation and d-excess change in evaporation and condensation (after Merlivat and Jouzel, 1979; Jouzel and Merlivat, 1984). The global meteoric water line (GMWL) is the global average isotopic composition of precipitation ($\delta^2\text{H} = 8\delta^{18}\text{O} + 10$) with a d-excess (d) of ± 10 . The isotopic composition of water vapor (δa) from the evaporation of ocean water (blue circle) would have different d-excess values (red circles) depending upon the relative humidity, temperature and wind speed during evaporation. Condensation of water vapor in isotopic equilibrium would result in liquid water with the same d-excess as the vapor (green circles). Ice growth by deposition from a starting vapor at A would produce the solid phase (yellow circles) along the line B-D where the level of supersaturation with respect to ice increases towards D. Ice supersaturation is the ratio of ambient water pressure to vapor pressure at ice saturation. At B, the vapor pressure could be $\sim 20\%$ and at C $\sim 100\%$ greater than that at ice saturation. D represents pure diffusion where air flow is unaffected in the vicinity of ice crystals.

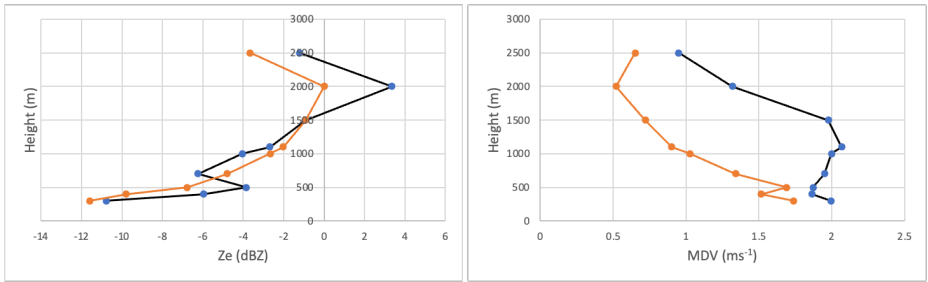


70 Figure

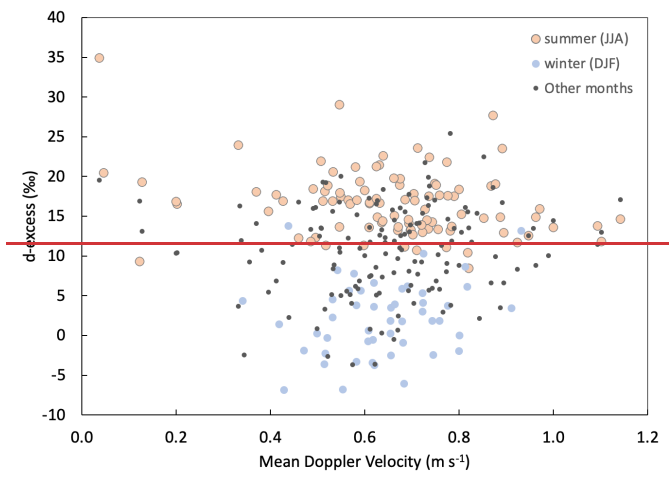


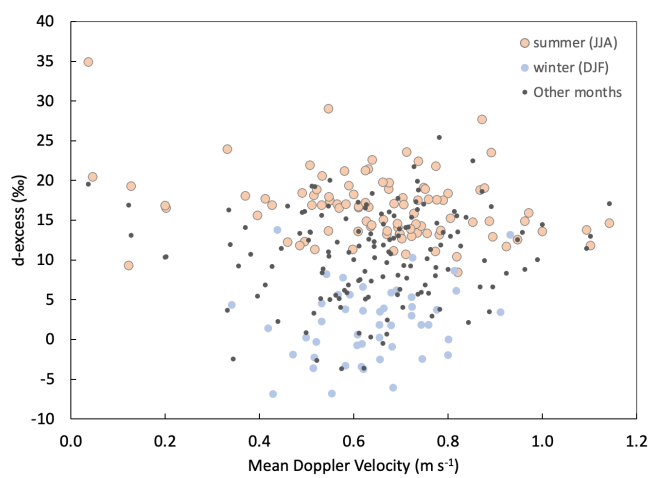
75

Fig. S2 Vertical profiles of reflectivity (Z_e) and mean Doppler velocity (MDV) for 2017-06-27 at Ny-Ålesund from a micro-rain radar. The left panel shows the variations with time. The right panel shows daily average values with the shaded areas showing the variability as 25th and 75th percentiles. The dashed red line shows the 0°C isotherm, the dashed grey line shows the peak in reflectivity marking the bright band, and the dashed blue lines show the top and bottom of the melting layer.



80 **FigureFig.** S3 – Typical profiles of reflectivity and MDV at Dumont d’Urville for 1/28/2019 (blue) and 3/3/2019 (brown/orange) when snowfall likely was sublimated at lower altitudes as indicated by a substantial decrease in Ze below ~1 km.





Figure

Fig. S4 – Summit d-excess and MDV for all months showing that the summer (JJA) and winter (DJF) encompass the range of values in the other months.

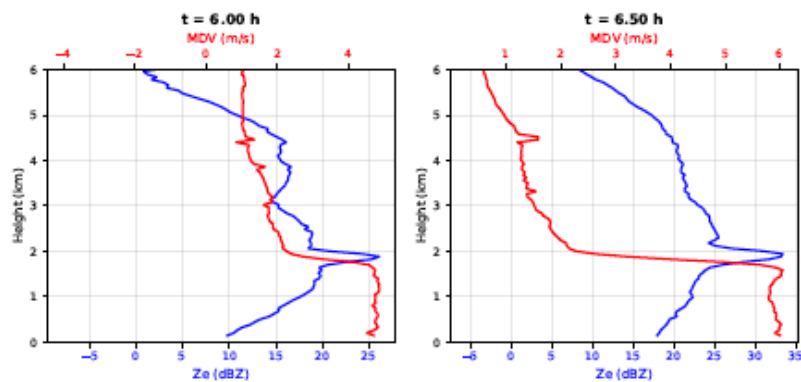
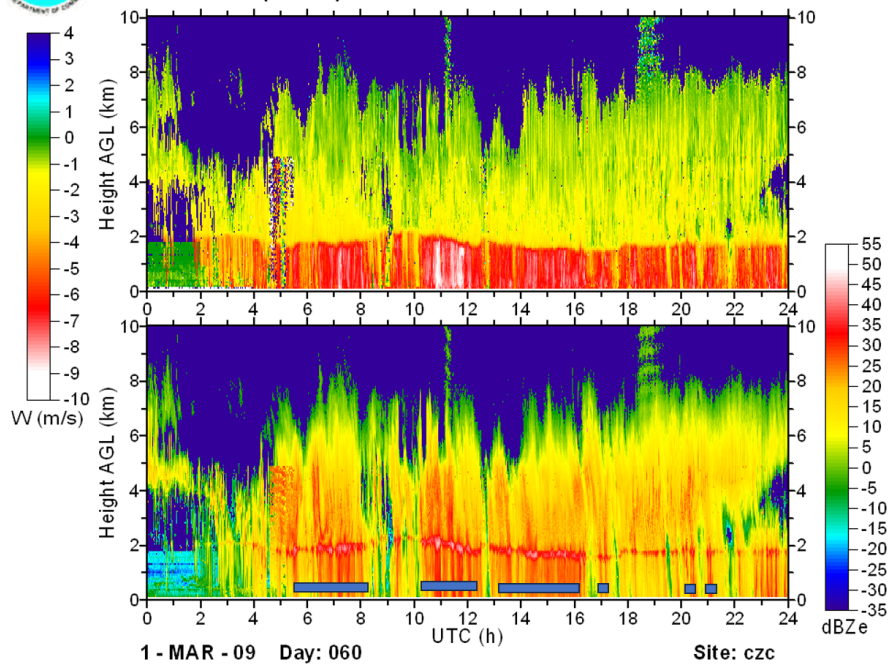


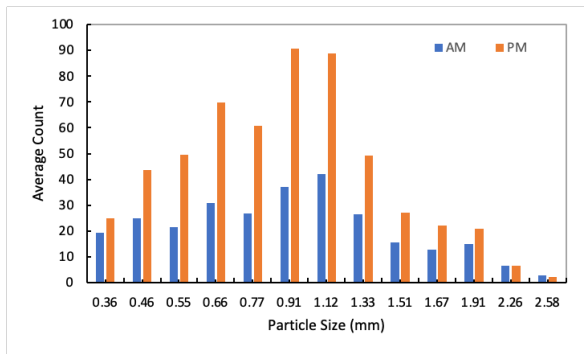
Figure S5 – Typical vertical profiles of reflectivity (Ze) and MDV at Cazadero, California indicating potential sub-cloud evaporation (decreasing Ze below ~1.5 km) on 1 March 2009. Time intervals: left panel: 05:45 to 06:15 hr; right panel: 06:15 to 06:45 hr (also see Fig. S13 below).



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Water Cycle Branch
S-band (3-GHz) Radar Studies -- Combined Mode



FigureFig. S6 – Time-height profiles of MDV (top) and reflectivity (bottom) for the 1 March 2009 event at Cazadero. Note that the MDVs are shown with a reversed scale and increasingly negative values indicate a greater fall velocity. The horizontal blue rectangles in the lower panel show the time where MDV was averaged for 30 min intervals corresponding to isotope samples.



FigureFig. S7 – Particle size distribution in Cazadero precipitation on 1 March 2009 recorded with a disdrometer. Note the smaller size in the morning that may indicate sub-cloud evaporation. (Data provided by A. White, email communication, 13 August 2023).

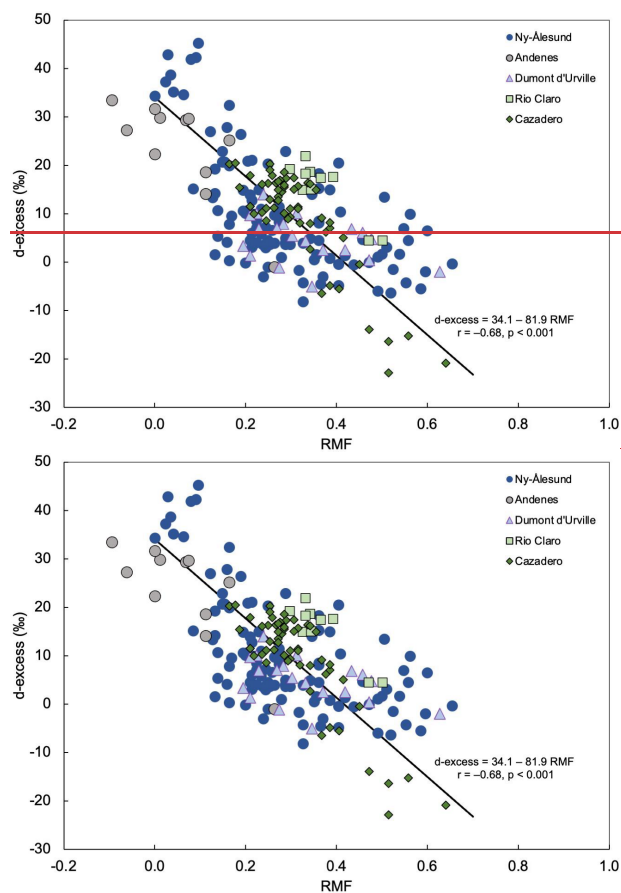


Fig. S8. Scatter plot of d-excess and rimed mass fraction (RMF) at Ny-Ålesund, Andenes, Dumont d'Urville, Cazadero and Rio Claro. Data for Summit are not shown because riming was only partially responsible for d-excess variations. The RMF values were obtained using the method of Kneifel and Moiseev (2020). The solid black line is the best fit line for

standardized total least squares regression of data from all locations, excluding samples with negative values of RMF.

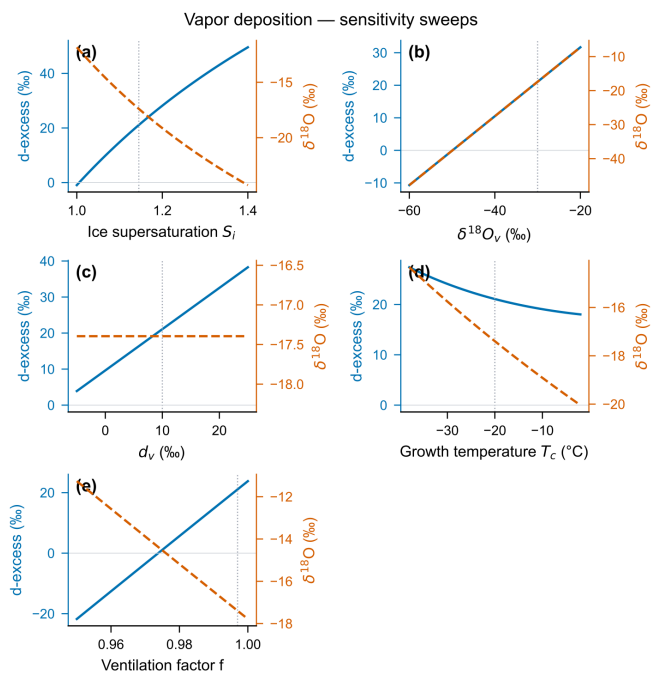


Fig. S9 Sensitivity of calculated d-excess of vapor deposition end-member to various parameters ($\delta^{18}O_v = -30\text{‰}$, $d_v = +10\text{‰}$, $T_c = -20^\circ\text{C}$, $S_i = 1.145$, $f = 0.997$).

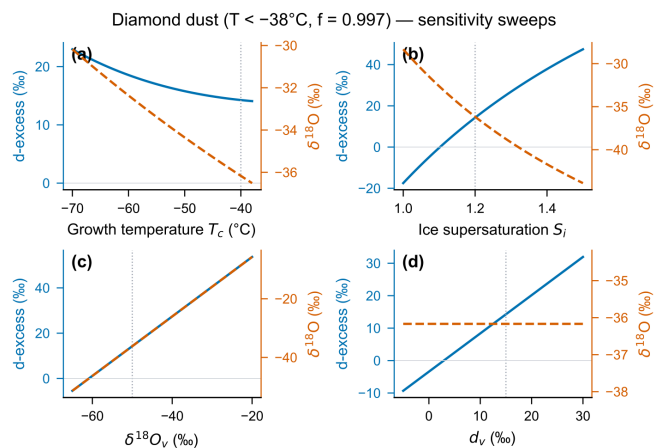


Fig. S10 Sensitivity of calculated d-excess of diamond dust end-member to various parameters ($\delta^{18}\text{O}_v = -50\text{‰}$, $d_v = +15\text{‰}$,
125 $T_c = -40^{\circ}\text{C}$, $S_i = 1.2$, $f = 0.997$).

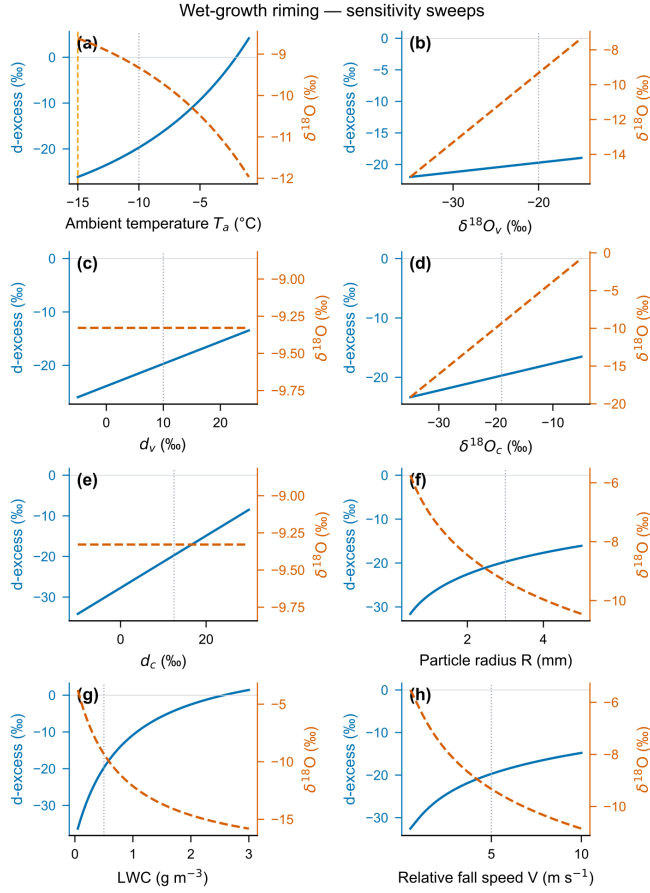


Fig. S11 Sensitivity of calculated d-excess of wet-growth riming end-member to various parameters ($\delta^{18}\text{O}_v = -20\text{‰}$, $\delta^{18}\text{O}_c = -190\text{‰}$, $d_c = +12.5\text{‰}$, $T_a = -10^\circ\text{C}$, $r = 3\text{ mm}$, $V = 5.0$, $\text{LWC} = 0.5\text{ g m}^{-3}$, $E = 0.8$).

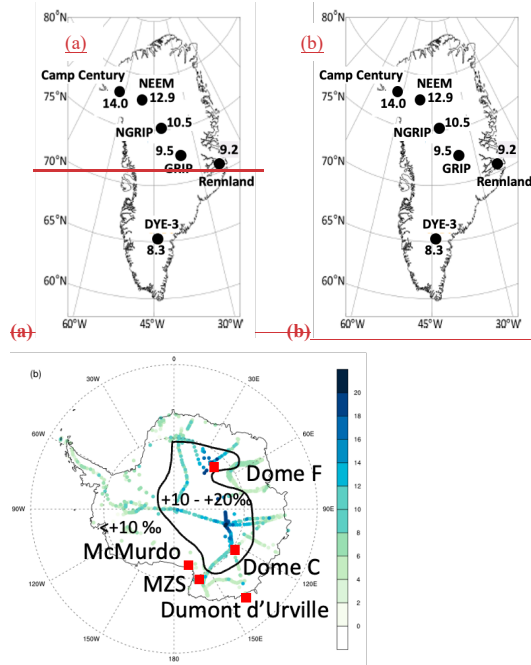
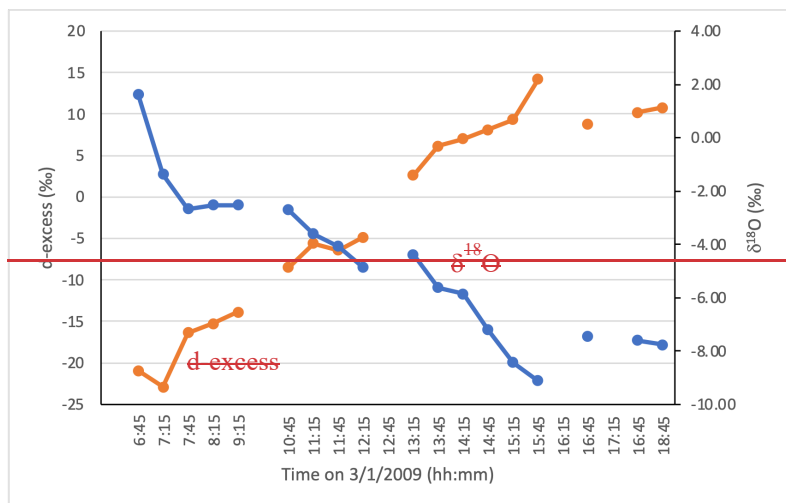


Fig. S12. Spatial variations of d-excess in surface snow. (a) Greenland: the base map was obtained from Rasmussen et al. (2023). The numbers show surface snow d-excess value at the north-south locations marked with black circles. (b) Antarctica: the base map with small colored circles showing measured d-excess values of surface snow was obtained from Wang et al. (2022). Red circles mark the locations of various research stations (MZS is Mario Zucchelli station). The thick black curve approximately traces the boundary between d-excess values less than or greater than +10‰.



145 **Figure**

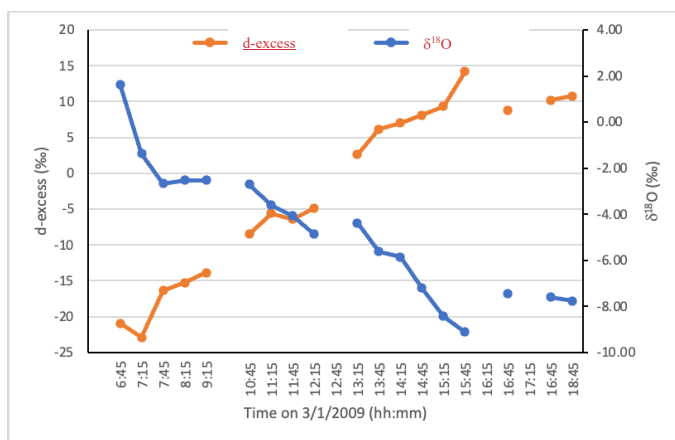


Fig. S13. Temporal variations of d-excess and δ¹⁸O from 5:45 hr to 18:45 hr in Cazadero precipitation on 1 March 2009.