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Remarks on the deuterium excess in precipitation in cold regions

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ABSTRACT

Jouzel and Merlivat developed and used an expression for the kinetic fractionation coefficient α_k, and greatly improved the predictions of $\delta(^{18}O)$ and d, (the deuterium excess) for East Antarctica. The α_k coefficient is re-derived in terms of ambient cloud temperatures and is used to re-calculate their single-source East Antarctic simulations. While the "improved" α_k produces virtually no change in the δ's, there is a small change in predicted d's. However, no matter which α_k is used, the simulated d's are *very* sensitive to the supersaturation history of the precipitating air mass. The single-source model is run for a wide range of supersaturation histories. Averaging the resulting suite of $\delta(^{18}O)$ and d solutions gives reasonable and stable d predictions. The temperature T_s at which clouds switch from being supercooled water drops to ice crystals depends in part on the microparticle loading of the air. The value of T_s significantly influences the d's and even δ's predicted. Thus ice-core microparticles, d and δ might be "process related".

1. Introduction

Stable isotope measurements $\delta(^{18}O)$ and $\delta(D)$ from ice cores contain a wealth of information about the history of water cycle parameters e.g., (Dansgaard et al., 1973; Jouzel et al., 1982; Fisher and Alt, 1985; Robin, 1983; Langway et al., 1985). The deuterium excess $d = \delta(D) - 8\delta(^{18}O)$ has also been recognized as a rich mine of information about the position of water sources, near surface relative humidity h and the wind speeds over these sources (Johnsen et al., 1989; Fisher and Alt, 1985; Merlivat and Jouzel, 1979 and Jouzel and Merlivat, 1984). In cold regions where the condensation temperatures T are below some $T_s < 0°C$, the direct water vapour to ice crystal phase change becomes predominant in the production of precipitation. When this happens, clouds tend to become supersaturated with respect to the forming ice crystals and the isotopic fractionation process is dominated by diffusion of water vapour towards the crystals. This "kinetic" fractionation process in cold supersaturated clouds produces δ's markedly different than the vapour to ice fractionation in saturated or sub-saturated (wrt ice) environments. Jouzel and Merlivat (1984) have examined the kinetic fractionation process and developed an expression for α_k the kinetic fractionation factor that must multiply the equilibrium fractionation factor α_s.

Using plausible (supersaturation-condensation temperature) relationships and a single source model, they were able to successfully explain the high elevation part of the δ profile along the traverse from Dumont d'Urville to Vostok in East Antarctica (Jouzel and Merlivat, 1984). However, the deuterium excess predicted by the model is not stable in that even slight changes in the supersaturation history of the precipitating air mass while not effecting δ much produces large changes in d. Efforts to use their model to fit the East Antarctic d data have not been fully satisfactory. Part of the explanation for these difficulties probably lie in the assumption of a single source for the precipitating air mass, but this paper will examine the fractionation model itself and try to suggest improvements within the context of a

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single source model. A multi-source model is described elsewhere (Fisher, 1990).

When vapour changes to ice the released heat of sublimation warms the crystals (and their immediate boundary layer) above the ambient air temperature. Jouzel and Merlivat allow for this by correcting the supersaturations using a procedure from Pruppacher and Klett (1980). In order to directly use the (measured) air temperatures and supersaturations, the author re-derived α_k as a function of ambient air temperature and supersaturation. In principal the two methods should be identical. Using this "improved" α_k the author's model $T-\delta$ relationship is virtually the same as theirs and the $d-T$ relationship is only slightly changed.

Inorder to fit Antarctic d data, it was necessary for Jouzel and Merlivat to specify the supersaturation-temperature relation with extreme precision. As they admit it seems unlikely that precipitating air masses unerringly follow such supersaturation trajectories. It is more likely that what one "sees" is the result of the mixing of air masses with different supersaturation histories. By way of experiment a wide range of solutions of the single source model were added across a suite of supersaturation histories that span the full possible range of conditions that can exist in cold clouds. The average δ and d results provide a reasonable fit to the Antarctic data thus supporting the mixing idea.

2. Improving the estimate of α_k by using the ambient air temperature

Under equilibrium (non-kinetic) conditions, the progress of $\delta_{precip}=\delta_p$ for a "Rayleigh air mass" from a single source is followed by the differential equation (Merlivat and Jouzel, 1979; Fisher and Alt, 1985)

$$\frac{d\delta_p}{1+\delta_p}=\frac{\alpha_s(\alpha_s-1)\,dy+y\,d\alpha_s}{\alpha_s(y+\alpha_s y_e)} \tag{1}$$

where y is the mixing ratio of the water vapour and y_e is the mixing ratio due to cloud "storage" for droplets, which is set to 0 for $T<T_s$.

Jouzel and Merlivat (1984) have pointed out that at "cold" condensation temperatures $T<T_s$, the equilibrium fractionation process is taken over by molecular diffusion down the water vapour partial pressure gradient created by the fact that the saturation vapour pressure over ice is less than over water all else being equal. When a water vapour cloud begins to form ice crystals the crystals "environment" is one of supersaturation probably even if the cloud is not fully saturated wrt water. They show that the equilibrium fractionation coefficient α_s under these conditions should be replaced by $(\alpha_s\alpha_k)$, where α_k the kinematic fractionation coefficient is

$$\alpha_k=\frac{\mathrm{Si}}{\alpha_s\dfrac{D}{D'}(\mathrm{Si}-1)+1}, \tag{2}$$

where α_s is the appropriate equilibrium value for (vap $\rightarrow$ solid) and D and D' are the molecular diffusion coefficients for ordinary water and heavy isotope water respectively. Si is the supersaturation ratio, $\mathrm{Si}=y/y_i=e/e_i$, where y is the mixing ratio of the air mass and y_i is the mixing ratio that would be saturated wrt ice; e and e_i are their equivalents in terms of partial vapour pressures.

Jouzel Merlivat (1984) correct their assumed Si functions to allow for the $(T_{crystal}-T_{air})$ difference, but it would be helpful to change the expression for α_k so that all the variables are for the ambient air. Doing so also means the Si functions used are directly comparable to the measured values. This alternative formulation of α_k results in:

$$\alpha_k=\frac{\mathrm{Si}(T)}{\alpha_s(T)\dfrac{D}{D'}(\mathrm{Si}(T)-1)E+\gamma}. \tag{3}$$

E and γ are close to 1 and are defined below:

$$E=\frac{1}{\alpha_s(T)}\frac{\alpha_s(T)\eta+\gamma\,D'Q^*e_i(T)}{\eta+DQe_i(T)},$$

$$\gamma=(1+s)/(1+s'),$$

$$s=\frac{QD}{\eta\mathscr{L}}(\mathrm{Si}(T)-1)\,e_i(T),$$

$$s'=\frac{Q^*D}{\eta\mathscr{L}}(\mathrm{Si}(T)-1)\,e_i(T,$$

$$\eta=\frac{R^*T}{M},$$

$$\mathscr{L} = \frac{Q}{M} De_i(T) + 1,$$

$$Q = \frac{L_s^2 M}{KR^* T^2}$$

$$Q^* = Q + \left(\frac{1}{(1+\delta_p)} \frac{d\delta_p}{dT} - \frac{1}{\alpha_s} \frac{d\alpha_s}{dT} \right) \frac{L_s}{K}.$$

NB. γ is so close to 1 that it can be set to 1 with little effect. T is the ambient air temperature (K), R^* is the gas constant M, the g mole wt for ordinary water $H_2{}^{16}O = 18$ g/mole, L_s the latent heat of sublimation (vapour to ice), $e_i(T)$ saturation water vapour pressure with respect to ice, K thermal conductivity of air, D molecular diffusion coefficient of water vapour in air, D' molecular diffusion of heavy isotope water: $D'/D = D(H_2{}^{18}O)/D(H_2{}^{16}O) = 0.9723$ and $D'/D = D(H\,D^{16}O)/D(H_2{}^{16}O) = 0.9755$.

While the above expression looks complicated, it is easily evaluated during the integration of (1) and as can be seen, α_k is a function of T, the ambient cloud temperature. The complete details of the derivation are given in (Fisher, 1989).

Inorder to assess differences resulting from this slightly different formulation of α_k, the Jouzel Merlivat single source model was run using first eq. 2 and then eq. 3. Eq. 1 was integrated along the temperature-pressure trajectory given in Jouzel and Merlivat. The boundary values in each case were: start condensation temperature $T_o = -10°C$; start $\delta(^{18}O) = -15‰$; deuterium excess $d = 0‰$; temperature to shift to vapour → ice phase changes, $T_s = -10°C$. A supersaturation function taken from Jouzel and Merlivat (1984) (line #4 in their Fig. 8) is used because it gives d values in rough agreement with measured data. The solid line in Fig. 1 shows the least squares line through the δ data from the Dumont d'Urville to Vostok traverse for sites above 1000 masl. All the site temperatures have been corrected to condensation or cloud temperatures (Jouzel and Merlivat, 1984). The dashed line is the Jouzel Merlivat RMK (Rayleigh model including kinetic effect) result using eq. 2. The

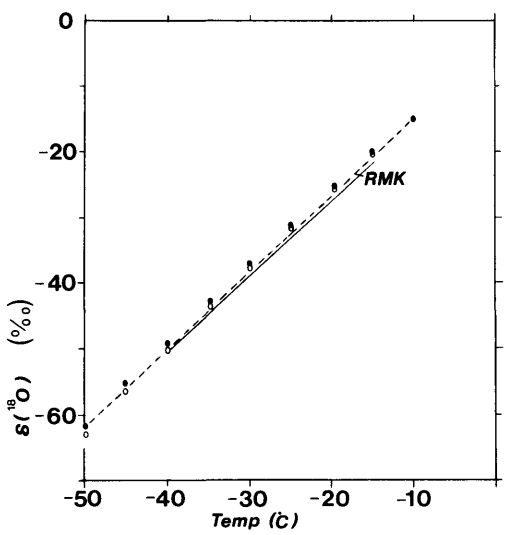

Fig. 1. $\delta(^{18}O)$ versus condensation temperature. The solid line is data from East Antarctica. The dashed line is predicted by Jouzel and Merlivat's (1984) Rayleigh single source model using equation 2. The circles are the author's predictions using equation 3. The dots are the author's version of the Jouzel and Merlivat run using their eq. (2). All runs use the same Si(T) function, namely Jouzel and Merlivat's line #4 with $T_s = -10°C$.

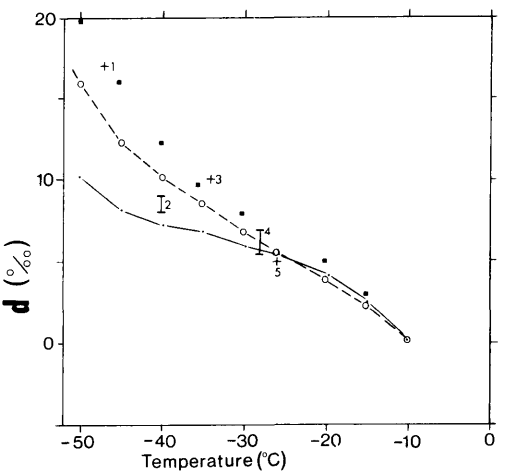

Fig. 2. Deuterium excess $d = \delta(D) - 8\delta(^{18}O)$ plotted against T the condensation temperature. The solid line is predicted using eq. (2) and the dashed line is predicted using eq. (3). These d functions come from the runs described in Fig. 1 and use the same Si(T) function. The solid squares are from the mixed single source "model" described in the text. The number points are measured values from Antarctica. 1 (Standard Light Antarctic Water), 2 (Dome C), 3 (South Pole) and 5 (Adelie Land) are referenced in Jouzel and Merlivat 1984. Number 4 (Byrd, Holocene) is inferred from (Gow 1970).

points are obtained by the author using the single source model eq. 1 with eq. 2 and the circles using eq. 3 instead of 2. The model runs using eq. 3 give nearly the same δ's as those using eq. 2, very close to the RMK result. Thus, the author's reformulation of α_k has virtually no effect on the calculated δ's.

Fig. 2 shows calculated d values using the #4 line of Jouzel and Merlivat (1984). The solid line was obtained using eq. 2. This d function is close to that calculated by Jouzel and Merlivat and what small differences there are are probably due to the author's slightly different formulae giving $\alpha_s(T)$ for D and the saturation vapour pressure. The dashed line gives the author's solution for d using eq. 3. The numbered points are d data from various Antarctic sites plotted against the sites' inferred cloud condensation temperature. It appears that using the eq. 3 form for α_k produces only a slight change in the predicted d-function. Moreover, experiments with other Si functions and eq. 3 produce $d(T)$ predictions that are just as sensitive to the chosen Si function as the original eq. 2. In fact, the $d(T)$ functions produced using eq. 3 are all close to Jouzel and Merlivat's for the same Si functions. It should be remembered that using eq. 3 means supersaturation functions are w.r.t. air temperature while using equation 2 w.r.t. crystal temperature. Thus, for example, the eq. 2 run should use Si(4) listed in (Jouzel and Merlivat, 1984 their Table 2), while the eq. 3 run, their S(4).

This alternate formulation for α_k does not alter the predicted δ's and only slightly changes the predicted d's. The over sensitivity of $d(T)$ to the input Si(T) function also remains. Multi-source models still have this problem of instability of d (Fisher, 1990).

3. The grand mixture

Jouzel and Merlivat (1984) assumed that typical supersaturation in marine air masses moving over the Antarctic is (Si =) 1.2 and thus limited the possible Si functions to the range covered by their lines #1 to #6 (Jouzel and Merlivat, 1984), which have roughly this average value. Much outside this range results in Si averages too removed from 1.2. Furthermore, and more important for them, the $d\delta/dT$ slope and d's predicted using Si's beyond the #1 to #6 range is either much too large or too small.

Fig. 3 shows some possible Si versus cloud temperature, T, functions for a cooling moist air mass. The uppermost line shows the maximum possible Si values that are obtained if the moist air is always saturated w.r.t. liquid water. The T-axis (Si = constant = 1) gives the function if the air is saturated w.r.t. ice. Jouzel and Merlivat's (1984) suggested range of possible Si functions lie in the shaded region and are straight or nearly straight lines.

First, one should point out that the Si = 1.2 measured value they quote as typical for marine air masses moving over the Antarctic (Miller and Schwerdtfeger 1972) refers specifically to "blue sky" precipitation. This kind of non-storm precipitation makes up only a fraction of the annual precipitation along most of the traverse route they are modelling. Miller and Schwerdtfeger estimate such precipitation might result in about 1 g cm^2 yr^{-1}. One might expect that during storms, higher Si values could be attained, especially in the clouds. Furthermore, considering the dynamic nature of clouds, one might expect there to be quite a range of Si across a cloud, with lower values towards the edges.

Near the Antarctic coast, the Si values can approach the maximum values, e.g., the winter Si average at Halley Bay is 1.3 (IAEA, 1969–1975).

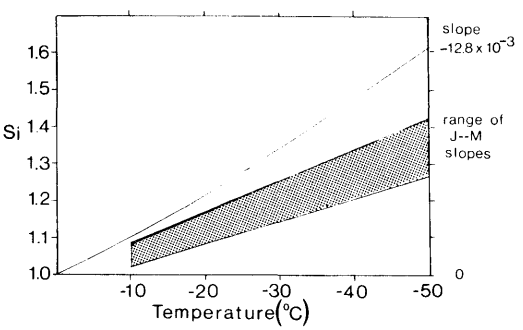

Fig. 3. The supersaturation function Si(T) versus condensation temperature. The upper line represents the maximum possible supersaturations of ice crystals in an air mass saturated w.r.t. water drops. The T axis Si(T) = 1.0 is for air masses saturated w.r.t. ice crystals. The shaded region is Jouzel and Merlivat's proposed zone of possible Si(T) functions. The linear slopes d Si/dT of the noted Si lines are given on the right side.

Thus, one can not rule out near coastal Si's well above the "allowed" range of Fig. 3.

As an experiment, the author made a suite of runs of the single source model from $T = -10$ to $-50°C$, using the above boundary conditions. Each run used a different linear Si(T) function. The entire range of possible linear Si functions was tried from Si = 1.0 to close to the maximum Si curve on Fig. 3. The Si functions were just taken as straight lines through $T = 0°C$, Si = 1.0 and characterized by their slopes. The kinetic coefficient was "turned on" at $T_s = -10°C$ in all cases, which was also the start temperature. The d's from this suite of runs are summarized in Fig. 4, where d is plotted for various temperatures as a function of the slope of the Si line used. Slope = 0 is the run that gives d's along the vertical dashed line marked A in Fig. 4 (this is the pure ice equilibrium run); the extreme slope $= -12.8 \times 10^{-3}\,C^{-1}$ run is demarked by B and represents ice crystals surrounded by vapour saturated w.r.t. water. The "allowed Si line range" from Jouzel and Merlivat is marked by the horizontal line noted as J—M and the arrows numbered 4 and 6 refer roughly to the results using their #4 and #6 Si lines. The $d\delta(^{18}O)/dT = (\delta(-10) - \delta(-50))/40$

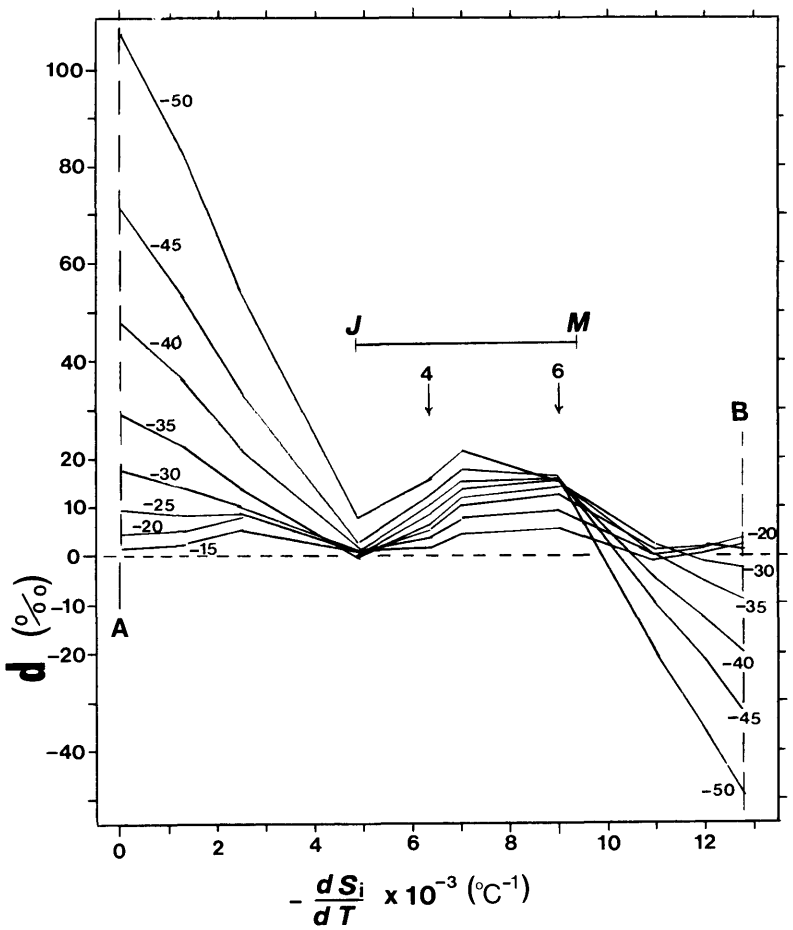

Fig. 4. The deuterium excess d versus the slope dSi/dT, of linear Si lines. Each run goes from $T = -10$ to $-50°C$ and uses a particular linear Si function and the Rayleigh single source model with eq. (3). The maximum possible Si(T) function gives d's along the vertical dashed line labeled B and the minimum Si line predicted d's are shown by dashed line A. The temperatures are indicated. Jouzel and Merlivat's zone of possible Si functions lies between J—M in the figure and their #4 and #6 lines are approximately indicated.

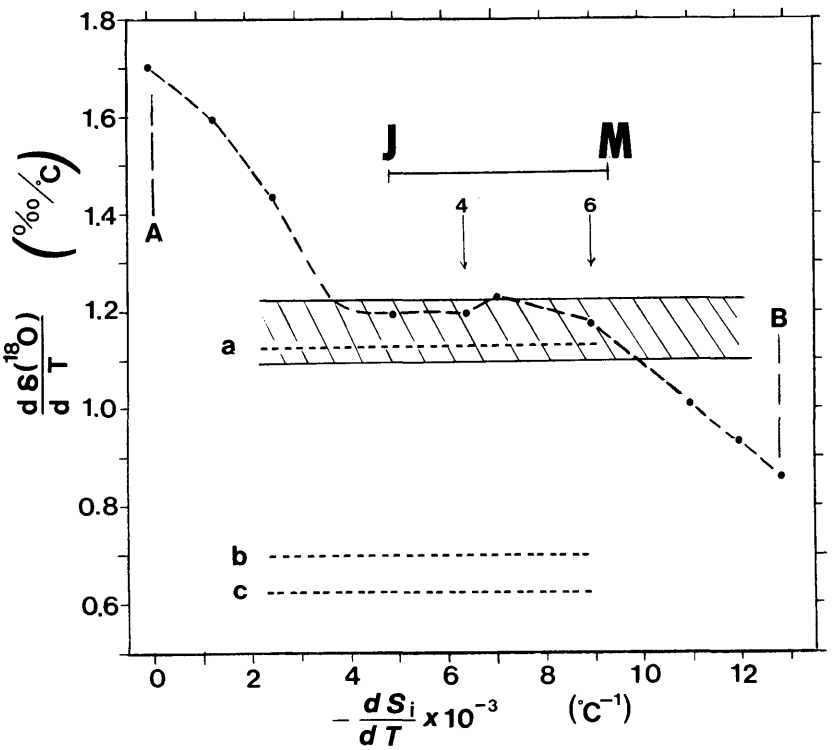

Fig. 5. The average slope $d\delta(^{18}O)/dT$ versus the slope of the linear Si function used in the runs of Fig. 4. The zone of possible linear Si functions is shown by J—M and Jouzel and Merlivat's #4 and #6 lines are roughly indicated. The Jouzel and Merlivat RMK runs give $d\delta/dT$'s in the shaded bar. The data from East Antarctica has $d\delta T/dT = a$ which falls within the shaded bar. The slope of the World $\delta(^{18}O) - T$ relationship (Dansgaard, 1964) is indicated by b and the high elevation Greenland slope (Dansgaard et al., 1973) is given by (c).

slope for the sute of runs is plotted in Fig. 5. The shaded part of Fig. 5 is the range of $d\delta/dT$ reported from RMK runs; *a* is the "measured" value for the French East Antarctic traverse, and *b* is the slope of the World $\delta(^{18}O) - T$ relationship (Dansgaard 1964), excluding sites equatorward of about 25° latitude. (c) of Fig. 5 is the high elevation Greenland slope (Dansgaard et al. 1973). Figs. 4 and 5 demonstrate why Jouzel and Merlivat want to keep the allowed Si lines slopes between J and M. Outside this range, one sees $d(T)$ curves and $d\delta(^{18}O)/dT$ slopes just not observed on the Antarctic traverse. However, as an experiment, if one "mixes" all the results of runs in the suite with equal weight, the resulting $d\delta(^{18}O)/dT$ slope falls within the shaded region of Fig. 5 and the resulting $d(T)$ curve is that shown by the squares in Fig. 2. The "mixed" result is of course just an experiment using the Rayleigh single source model, but within the formalism of the experiment, it does fit the data better that any of the single runs separately and is stable in the predicted $d(T)$. Until there is much better information about Si(T) on a seasonal and micro-met level over the Antarctic, one can not rule out mixing of some sort.

4. Below what temperature should the kinetic fractionation model be used?

In any given moist air masses' passage towards colder temperatures, the question arises "at which temperature $T_{shift} = T_s$ should one switch from (vap → water) phase changes to (vap → ice) changes?". For temperatures $> T_s$, the models assume that isotopic fractionation is an equilibrium (vap → water) process and for colder tem-

peratures it is a kinetic (non-equilibrium) (vap → ice) process. It is evident that T_s is very important in determining d and to a lesser extent δ. Jouzel and Merlivat (1984) choose $T_s = -10°C$. Other authors like Johnsen et al. (1989) use $T_s = -5°C$. At what temperature does the (vap → water) process essentially cease to be important? This must surely be the temperature below which there are no more liquid droplets in the clouds. If this is true, then T_s will depend on the drop size and the "cleaness" of the air. The smaller the drops and the cleaner the air, the greater is the observed supercooling, e.g., the freezing temperature of 1 mm droplets containing typical mid-latitude air impurities has been observed to be as low as $-24°C$ (Mason, 1975).

In polar regions, the air is very clean and undergoes proportionally larger seasonal changes in microparticle and soluable impurity concentrations, so one might well expect that the extent of supercooling and hence T_s could be considerably below $-10°C$. Furthermore, there could be a seasonal variation in T_s. One could go on to speculate that there could be secular changes in T_s due large changes in impurity loading in the atmosphere, say during the ice age. If there is a significant dependence of d on T_s and a weaker one between δ and T_s, it might help explain the (anti)correlations between δ, d and say microparticles found in ice cores in the Northern Hemisphere (Dansgaard et al., 1989; Fisher and Koerner, 1986, 1979).

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