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# The Drying Kinetics of Salt Solution Droplets: Water Evaporation Rates and Crystallisation

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## Abstract

The drying and crystallisation of solution droplets is a problem of broad relevance, determining the micro-structures of particles formed in spray drying, the phase of particles delivered by, for example, aerosol formulations for inhalation therapies, and the impact of aerosols on radiative forcing and climate. The ephemeral nature of free-droplets, particularly when considering the drying kinetics of droplets with highly volatile constituents, has often precluded the accurate measurement of transient properties such as droplet size and composition, preventing the robust assessment of predictive models of droplet drying rates, nucleation and crystallisation. Here, we report novel measurements of the drying kinetics of individual aqueous sodium chloride solution droplets using an electrodynamic balance to isolate and trap single aerosol droplets (radius  $\sim 25\ \mu\text{m}$ ). The initial solution droplet size and composition is shown to be highly reproducible in terms of drying rate and crystallisation time when examined over hundreds of identical evaporating droplets. We introduce a numerical model that determines the concentration gradient across the radial profile of the droplet as it dries, considering both the surface recession due to evaporation and the diffusion of components within the droplet. Drying induced crystallisation is shown to be fully determined for this system, with nucleation and instantaneous crystallisation occurring once a critical supersaturation level of  $2.04 \pm 0.02$  is achieved at the surface of the evaporating droplet surface. This phenomenological model provides a consistent account of the timescale and surface concentration of free-droplet crystallisation on drying for the different drying conditions studied, a necessary step in progress towards achieving control over rates of crystallisation and the competitive formation of amorphous particles.

## Introduction

The drying of liquid droplets to form particles is an important process for a range of industries, from agriculture and inkjet printing to the production of pharmaceuticals, cosmetics and food.<sup>1–4</sup> In addition the propensity of an aerosol droplet to crystallise into solid particles has been shown to dramatically

influence the optical properties of atmospheric aerosols and, thus, their radiative forcing.<sup>5,6</sup> The evolving heterogeneities in particle microstructure as a droplet evaporates can be a highly complex process. Heat and mass transfer can be strongly coupled.<sup>7</sup> The competition between surface recession and internal flows such as convection, diffusion and Marangoni flows can result in an array of product morphologies, size and properties.<sup>8–10</sup> For some solutes, nucleation and crystallisation is sufficiently rapid that dry crystalline particles result, dependent on drying rate; for other systems, drying may lead to amorphous glassy particles.<sup>11,12</sup> The crystallisation of solutes present in a droplet is often the ultimate outcome of a droplet-drying processes. The time at which nucleation occurs within an evaporating droplet can be directly linked to the initial droplet size and solute concentration, allowing some control over the final crystalline particle size and morphology. Our objective here is to examine the drying kinetics and crystallisation of inorganic solution droplets. Through refined measurements of the drying rates of individual droplets, we will show that the crystallisation time and surface composition at crystallisation are highly reproducible over ranges of starting droplet composition and temperature, providing a phenomenological model for predicting the formation of crystalline particles.

Although there has been considerable work on the study of droplets drying on surfaces, i.e. sessile droplets,<sup>13–15</sup> far fewer studies have examined the drying kinetics and crystallisation of free droplets or aerosols. There are numerous unique experimental challenges associated with studying the drying dynamics of free droplets that are easily overcome when examining sessile droplets. Free droplets are ephemeral and difficult to follow in position unless a single particle is isolated and captured, such as with an optical trap,<sup>16</sup> electrodynamic balance<sup>17</sup> or acoustic trap.<sup>18</sup> Even then, the timescales of evaporation processes can be <1 s, presenting a significant challenge to infer characteristic properties (e.g. size, composition at point of crystallisation) on such short timescales. Ensuring reproducibility in droplet generation and drying events is also crucial if sufficient statistics are to be achieved to infer the key microphysical details of the drying process. Finally, sampling the particles for off-line structural analysis requires deposition, which may also lead to a phase change or change in particle composition.<sup>19</sup> However, studying free droplet evaporation remove the complexities of the substrate-droplet interactions and Marangoni flows that occur for sessile droplets. In addition, the absence of a surface simplifies the symmetry for modelling, reduces the possibility of heterogeneous nucleation and limits the treatment of heat-transfer to conduction into the vapour phase. Free droplets drying in air is also more representative of industrial processes such as crop-spraying and spray-drying. Thus, a greater understanding of how the particle-formation process can be predicted and controlled would be integral to improving the efficacy of many industrial drying processes.

Spray-drying is the process of rapidly drying a stream of aerosolised-solution droplets in a hot air flow, such that micron-sized particles are formed. Its application in many industries can be attributed to the speed and efficiency of the one-step process, and the short residence time of the droplets enables the use of heat-sensitive precursor compounds.<sup>20</sup> Although widely used, the process of particle formation

from aerosol droplets is an active area of research as it is highly condition-dependent.<sup>21</sup> A better understanding of the factors governing the evaporation kinetics and how compositional heterogeneity develops within an evaporating droplet is critical to allow ultimate fine-tuning of drying conditions and precursor components, and to deliver tailored final dry particles with desired characteristics.<sup>22</sup> Within a spray-drier, droplet evaporation is typically rapid, i.e. on timescales on the order of milliseconds to seconds. The rate of evaporation can outcompete the rate of diffusional solute mixing leading to the enrichment of solutes at the droplet surface; the rate at which solvent is replenished at the surface is much slower than the rate of surface recession. The Peclet number ( $P_e$ ) is used to provide a measure of the ratio between the diffusion rate within a particle and the evaporation rate:

$$P_e = \frac{\kappa}{8 D_i} \quad (1)$$

where  $\kappa$  is the evaporation rate and  $D_i$  is the molecular diffusion coefficient of species  $i$  within a particle.<sup>23</sup> A Peclet number lower than 1 indicates that an homogeneous composition is maintained throughout the drying process; the diffusional mixing is fast enough to replenish the surface with solvent from the droplet bulk. However, a  $P_e$  greater than 1 indicates that the surface is likely to become enriched as the droplet dries, with the surface receding at a greater rate than the time scale for diffusional mixing.<sup>24–26</sup>

In the bulk phase, crystallisation of solutes typically occurs upon reaching saturation. However, metastable supersaturated solute states are prevalent in the aerosol-phase, with crystallisation only occurring at high solute concentration and a water activity much lower than the solubility limit, often referred to as the efflorescence point. Classical nucleation theory (CNT) is built on an interplay between the interfacial free energy of the crystal-liquid phase boundary and the chemical potential difference between the liquid and crystalline phases.<sup>27</sup> The chemical potential difference rises with increasing level of saturation within the droplet, and the interfacial free energy acts as a barrier to formation of a crystal nucleus. Although surfaces and impurities, such as dust, can act as heterogeneous nucleation sites and reduce the free energy barrier to nucleation, the absence of a solid surface enables an aerosol droplet to reach very high levels of supersaturation before efflorescence occurs. Typically, inorganic solutions effloresce at a water activity reported in terms of the gas phase moisture content, or the efflorescence relative humidity (ERH). At atmospheric temperature and pressure, the aerosol is only able to hold the salt in aqueous-solution form under conditions of higher moisture-content than the ERH. Homogeneous nucleation is a rare event, and the stochastic nature means that efflorescence is typically reported over an RH range as there is inherent randomness in the occurrence of nucleation.<sup>28</sup> For sodium chloride, this range is narrow and whilst a size dependence of the droplet on the ERH has been reported<sup>29</sup> the ERH for droplets of the size range in this work is reported at 44-45% RH.<sup>30</sup> A water activity of 0.45 corresponds to a molality of 12.68 mol kg<sup>-1</sup>, a concentration of 648 g L<sup>-1</sup> and a supersaturation level of 2.04.<sup>31</sup>

A series of studies have investigated the drying of inorganic solution droplets evaporating both on surfaces and during levitation, inferring the nucleation rate as a function of supersaturation level reached.<sup>32,33</sup> We focus here on the crystallisation of evaporating sodium chloride droplets. Aqueous sodium chloride was chosen as the system for study as the thermodynamic equilibrium behaviour of aqueous sodium chloride aerosol is well characterised,<sup>31</sup> and the evaporation of water from aqueous NaCl sessile-droplets has been studied in detail.<sup>13,34</sup> Sodium chloride is also a common precursor compound used industrially. It is particularly prevalent in the preparation of food, and its particle formation process is relevant because of a drive to reduce salt intake in populations.<sup>35</sup> There have been reports stating that one can increase the intensity of salt flavour by adjusting particle size and morphology, allowing an overall lower mass of NaCl to be used.<sup>36,37</sup> In addition, NaCl is a large component of sea-spray, and thus it is important to understand its crystallisation and phase behaviour for climate models.<sup>38</sup>

In this work, we report measurements of the time-dependent radius of a rapidly evaporating sodium chloride droplet throughout the drying process, and the time of crystallisation. Trapping the droplet in free air whilst it dries eliminates any heterogeneous nucleation site such as a container wall, and only the homogeneous nucleation of NaCl crystals is probed. These measurements are performed on a large population of droplets, providing a comprehensive statistical analysis on the propensity to crystallise. Homogeneous nucleation of NaCl occurs above a certain critical supersaturation,  $S_c$ . The evaporation kinetics results are compared with simulations of the evolving internal concentration gradients within the evaporating droplets

## **Experimental Method and Assessment of the Particle Phase State**

The evaporation of water from sodium chloride solution droplets was studied using the electrodynamic balance (EDB) (see Fig. 1a). In all experiments, HPLC-grade water and BioXtra  $\geq 99.5\%$  NaCl (Sigma Aldrich) was used. The EDB instrument has been described in detail in previous work<sup>39</sup> and will only be briefly reviewed here. A droplet-on-demand generator is used to produce a single droplet of known composition which is charged ( $< 10$  fC, for example, from an imbalance in  $\text{Na}^+$  and  $\text{Cl}^-$ ) and injected in to the EDB trapping chamber. An AC voltage is applied to a pair of upper and lower concentric cylindrical electrodes, generating an electric field in which the droplet is trapped. The gravitational and drag forces acting on the droplet are offset by a DC voltage applied to the bottom electrode. A flow of dry nitrogen passes over the trapped particle at a rate of 0.03 m/s and the trap temperature (273 K to 323 K) is controlled by circulating ethylene glycol coolant through the electrodes.

The droplet is illuminated with a 532 nm CW laser and the resulting elastically scattered light pattern (phase function) is collected over an  $\sim 24^\circ$  angular range centred at  $45^\circ$  to the forward direction of the laser (see Fig. 1b). During the time-period that the trapped droplet is homogeneous and spherical, it produces regularly spaced interference fringes in the phase function which allow the size of the droplet

to be calculated. The angular separation between the light and dark fringes in the phase function is used to calculate the droplet radius,  $R$ , using the geometric optics approximation to Mie theory.

$$R = \frac{\lambda}{\Delta\vartheta} \left( \cos\left(\frac{\vartheta}{2}\right) + \frac{n \sin\left(\frac{\vartheta}{2}\right)}{\sqrt{1 + n^2 - 2n \cos\left(\frac{\vartheta}{2}\right)}} \right)^{-1} \quad (2)$$

where  $\lambda$  is the laser wavelength,  $\vartheta$  is the central viewing angle,  $\Delta\vartheta$  is the angular separation between the fringes and  $n$  is the droplet refractive index. This approximation can allow the determination of the droplet radius with an accuracy of  $\pm 100$  nm.

The concentration in  $\text{g L}^{-1}$  averaged across the droplet volume, is calculated as a function of time using the droplet volume, obtained from the radius measurement, and the dry mass of NaCl, which is known from the starting concentration. As the concentration of the aqueous-NaCl droplets increases and the water evaporates, radius data are corrected for the time-dependent change in droplet refractive index in a post-analysis step.<sup>39</sup> The refractive index of the droplet at all times can be calculated from the concentration using the molar refraction mixing rule.<sup>40</sup> This method assumes that the droplet composition is homogeneous, which is unlikely to be the case; rapid evaporation may lead to surface enrichment and an inhomogeneous droplet. Hence, there is an uncertainty in the radius resulting from the refractive index estimation, which increases as the droplet surface becomes more enriched. The error resulting from this is estimated in the supporting information. Even an appreciable surface enrichment does not significantly affect the refractive index, and only begins to affect the estimate of the radius in the last  $\sim 0.1$  s of the droplet lifetime where the error in the radius remains less than 5%. The experimentally determined crystallisation times are unaffected.

Crystal nucleation occurring within the droplet leads to a sudden lack of homogeneity in composition and shape, which is detectable from a dramatic change in the form of the phase function. The spacing of the interference fringes becomes highly erratic and the particle size can no longer be inferred (see Fig. 1b). The sensitivity of the EDB measurement for detecting the efflorescence time is therefore the minimum interval at which the phase function is recorded, which is typically 10 ms. This method can only identify the time frame at which particle crystallisation occurs, based on the dramatic changes in light scattering observed in the phase function; the method is unable to identify the time at which nucleation occurs. This method of identifying the point of efflorescence has previously been used to detect nucleation events in levitated aqueous NaCl droplets as they evaporate slowly in equilibrium experiments,<sup>41</sup> and also to observe ice nucleation events in homogeneous freezing experiments of sulfuric acid solution droplets.<sup>42</sup> The point of nucleation was determined to be the moment that the fringe diffraction pattern characteristic of a spherical droplet was lost from the elastic light scattering, leaving an incoherent speckle pattern. In this work, when slow step-wise changes in RH are made,

progressively drying the droplet to lower water activity, the loss of the regular scattering-pattern occurred at a water activity of 0.45, consistent with previous efflorescence studies that report an efflorescence RH of 45% for NaCl,<sup>43</sup> thus validating the method for efflorescence detection.

Further conclusive evidence that crystallisation occurs when an aqueous-NaCl droplet evaporates into dry nitrogen is provided in Fig. 2. In both measurements shown, the solution droplets crystallise after  $\sim 1.7$  s of evaporation. Then, for one of the particles, the RH was increased to  $\sim 85\%$  approximately 30 s into the experiment, increasing the gas-phase water content above the deliquescence RH of 75%.<sup>31</sup> As anticipated, the NaCl particle dissolved, water condensed and the particle became a homogeneous solution droplet allowing a precise measurement of size after  $t = 150$  s. Conversely, the RH surrounding a second crystallised particle was increased to 63%, i.e. below the deliquescence RH. In this case, the particle remained crystalline, precluding a precise determination of particle radius using the phase-function. The presence of a deliquescence transition at  $\text{RH} > 75\%$  confirms that the transition at  $\text{RH} < 45\%$  observed is indeed efflorescence.

## Results and discussion

The time taken for an evaporating aqueous NaCl droplet to effloresce was recorded for large populations of droplets at different gas-phase temperatures. Thus, only data acquired (and averaged) over many droplets are reported below unless otherwise stated. Firstly, we consider the reproducibility of the efflorescence behaviour of evaporating aqueous-NaCl droplets. Secondly, the impact of changing the gas-phase temperature and initial concentration on the efflorescence time is reported. The volume-averaged concentration of the evaporating droplets as a function of time is presented and discussed along with estimates of the respective Peclet numbers for each set of evaporation conditions. We then introduce a model that maps the evolving internal microstructure of the droplets, presenting the model-predictions of droplet surface concentrations which are in good agreement with the experimental observations of the crystallisation times of the droplets.

### *Reproducibility of efflorescence events across populations of droplets*

To demonstrate the reproducibility of the efflorescence events when measuring the kinetics of droplet evaporation, the drying profiles of 230 NaCl droplets evaporating into dry air at 293 K were recorded and the results are shown in Fig. 3a. The data demonstrates both the reproducibility in the droplet size generated by the droplet dispenser ( $24.0 \mu\text{m} \pm 0.1$ ), as well as the reproducibility in the timing of the efflorescence event, characterised by the point at which the radius can no longer be calculated using the optical fringes in the phase function. In Fig. 3a this occurred at  $0.95 \pm 0.02$  s following droplet generation. This equates to a solute concentration averaged over the droplet volume of  $636 \pm 7 \text{ g L}^{-1}$ . The micro-dispenser that produces the single-droplets is external to the EDB instrument and it requires approximately 0.2 s for the droplet to travel into the centre of the chamber where it becomes trapped.

Thus, the data points shown at  $t=0$  result from a back-extrapolation from the time-dependence of the square of the radius at the earliest times after the droplet is captured in the trap.

### ***Effect of evaporation rate on efflorescence time***

The evaporation rate of an aqueous sodium chloride droplet in dry nitrogen depends on two factors: the gas phase temperature and the solute concentration in the initial droplet. Increasing the gas phase temperature, or decreasing the solute concentration, leads to a higher droplet evaporation rate due to the resulting increase in the vapour pressure of solvating water present in the droplet. Conversely, an increase in solute concentration suppresses the vapour pressure of water and slows the evaporation rate. The consequences of changing the gas-phase temperature within the EDB chamber for the efflorescence time are shown in the histogram in Fig. 3b.

Firstly, it should be noted that the distribution in efflorescence time at each temperature is narrow, showing the reproducibility in the efflorescence behaviour of aqueous sodium chloride as a system. Previous reports have suggested that homogeneous nucleation is a stochastic process, with close fits of data of homogeneous nucleation at a specific level of supersaturation to Poisson distributions.<sup>44</sup> However, the distributions in efflorescence time in this work, as shown in Fig. 3b, cannot be presented as a probability of nucleation occurring as a function of induction time at a specific defined supersaturation level, as in the work of Durán-Olivencia *et al.*<sup>44</sup> Rather, in this work the droplets are exposed to rapidly increasing levels of supersaturation, and, thus, the ‘induction time’ cannot be readily defined.

Secondly, the timescale for particle efflorescence is observed to decrease as the gas phase temperature increases, falling from  $0.95 \pm 0.02$  s at 293 K to  $0.56 \pm 0.01$  s at 308 K and  $0.45 \pm 0.03$  s at 318 K. The higher gas phase temperature leads to more rapid evaporation due to the increase in water vapour-pressure and a rise in solute concentration and saturation to the point where nucleation and crystallisation occurs at an earlier time in the drying. In an analogous way, the impact of changing the starting concentration of NaCl in the aqueous droplet on the evaporation rate is also shown in Fig. 4a. The droplet with a higher starting concentration of NaCl ( $230 \text{ g L}^{-1}$ ) has a lower water vapour pressure and, thus, a slower evaporation rate than the  $24 \text{ g L}^{-1}$  NaCl droplet. Despite the slower evaporation rate for the more concentrated droplet, efflorescence still occurs earlier into the droplet lifetime for the higher initial concentration at both temperatures. The greater concentration in the initial droplet ensures that the critical supersaturation level for efflorescence to occur is reached earlier into the droplet lifetime.

### ***Volume-averaged concentration of evaporating droplets***

For the four drying conditions shown in Fig. 4a, the volume-averaged concentration of NaCl in each droplet was calculated, assuming a homogeneous composition and spherical shape, and the results are shown in Fig. 4b. The recorded efflorescence times and the volume-averaged concentration for the



different drying conditions are reported in Table 1. Three of the four datasets indicate that the droplets effloresced at average NaCl concentrations above the bulk solubility limit, but below the required supersaturation expected from previous measurements of the efflorescence RH. However, for the case of the initial NaCl feed concentration of  $24 \text{ g L}^{-1}$  and temperature of 318 K, the droplets effloresced at  $0.74 \pm 0.03 \text{ s}$  after the droplet was dispensed. This equates to a volume-averaged concentration at the point of efflorescence of  $200 \pm 20 \text{ g L}^{-1}$ , which is below even the bulk solubility limit of NaCl of  $318 \text{ g L}^{-1}$ . This indicates that crystallisation of the evaporating droplets cannot be triggered by processes in the droplet bulk as the solute supersaturation never achieves a sufficiently high value. We propose instead that the rapid evaporation of the droplets leads to a surface enrichment of solute, which exceeds the nucleation supersaturation. This leads to crystallisation at the droplet surface whilst the volume-averaged concentration remains low. Thus, we must not assume that complete crystallisation has taken place in the droplet immediately at the time that the light scattering phase function suggests the particle is no longer spherical. However, the fully dry gas phase will lead to the irreversible and complete loss of water from the droplet and a fully crystalline particle must form soon after crystallisation begins, even though this second stage of drying is not clearly resolvable in our measurements.

Increasing the gas phase, and thus droplet, temperature increases the evaporation rate, while also increasing the binary diffusion coefficient of water within the droplet according to the Stokes-Einstein relationship:

$$\frac{D_1}{D_2} = \frac{T_1}{T_2} \frac{\mu_2}{\mu_1} \quad (3)$$

where  $D_T$  is the binary diffusion coefficient at temperature  $T$ , and  $\mu_T$  is the dynamic viscosity of the solvent (assumed to remain constant between 293 K and 318 K for aqueous-NaCl solutions). Increasing the temperature also increases the bulk solubility of inorganic salts, although this is only a small increase, from  $317.5 \text{ g L}^{-1}$  at 293 K to  $321.7 \text{ g L}^{-1}$  at 318 K, for NaCl.<sup>45</sup> The observation that the droplets at higher temperatures effloresce earlier than those at lower temperatures, suggests that the increase in evaporation rate from 293 K to 318 K is sufficiently large that the supersaturation required for nucleation is achieved earlier in the evaporation process, despite the increase in the binary diffusion coefficient. Quantitatively, the average evaporation rate increases from  $2.52 \pm 0.01 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at 293 K to  $4.2 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at 318 K (a 66% increase); over this compositional range, the binary diffusion coefficient is increased by 8.5 % at the higher temperature (see Eq. 3). Thus, in this instance, observing efflorescence at earlier time when increasing the temperature is consistent with expectations from the Peclet model.

The Peclet number at  $t = 0 \text{ s}$  for the four datasets are shown in Table 1, as calculated using Equation 1. All four datasets show Peclet numbers that are well below 1, which would suggest that the initial binary diffusion coefficient within the droplets is sufficiently large when compared to the evaporation rate to keep the droplet well-mixed throughout the drying process, resulting in dense, homogeneous particles.

However, the experimental data in Fig. 4b suggest that crystallisation must occur at the surface, induced by surface enrichment during drying, as the average efflorescence concentration is below the critical supersaturation level. Aqueous NaCl solutions have been shown to increase in viscosity by as much as 5 times between dilution and the solubility limit in the aerosol phase<sup>46</sup> and, thus, the binary diffusion coefficient can be expected to decrease as the droplet evaporates. Taking this into account would imply that the binary diffusion coefficient near the surface would decrease leading to greater surface enrichment as the aqueous NaCl droplet evaporates than a simple evaluation of the Peclet number with a single value of the diffusion coefficient suggests. We now explore the evolving concentration profiles within the evaporating droplets more closely.

### ***Modelling the internal concentration profiles of evaporating droplets***

We present below an analysis of the internal concentration profile of the evaporating droplets, particularly examining the degree of supersaturation at the droplet surface throughout the evaporation process. We treat the droplet as a moving boundary problem which uses the experimentally-determined evaporation rates at each time step to provide the rate of surface recession. The solute profile evolution is obtained by numerically integrating the diffusion equation using finite-difference methods. The droplet is split into a series of radial shells with thickness  $\sim 20$  nm from which the solute concentration is calculated.

More specifically, we model the binary fluid droplet as a sphere of outer radius  $R(t)$ , where the initially uniform solute concentration evolves according to a diffusion equation neglecting temperature and convection effects. The solute concentration profile  $c(r, t)$  at distance  $r \in [0, R]$  from the centre-of-mass then evolves with spherical symmetry according to the non-linear diffusion equation

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) \quad (4)$$

Our previous measurements of the viscosity of aqueous aerosol droplets of NaCl solutions at 293 K reported that the viscosity depends on solute concentration (water activity), indicating that the binary diffusion coefficient  $D$  would also be affected by the changing NaCl concentration in an evaporating aqueous droplet.<sup>46</sup> To examine this effect, we have estimated the value of the binary diffusion coefficient  $D$  across the NaCl concentration range at 293 K using the Stokes-Einstein relation, as detailed in the SI and accounted for by equation (3). Assuming a general Einstein form for the relationship of the binary diffusion coefficient to temperature (i.e.  $D \propto k_B T$ ) we obtain values at arbitrary temperature using the scaling

$$D(T) = \frac{D(293 \text{ K})}{293} T \quad (5)$$

The model does not consider the change in droplet temperature due to evaporative cooling, which is likely to cause a reduction to the diffusion coefficient at the droplet surface.

Only the solvent evaporates at the surface leaving a constant total solute mass within the droplet, imposing zero flux through the outer boundary. Together with a compatibility condition at  $r = 0$  we obtain the complete set of boundary conditions for Equation 4 as

$$\left. \frac{\partial c}{\partial r} \right|_{r=0} = 0 \quad (6a)$$

$$\left. \frac{\partial c}{\partial r} \right|_{r=R} = -\frac{c(R)}{D} \frac{dR}{dt} \quad (6b)$$

The evolution of the outer radius depends on the mass flow through the outer boundary and the local density  $\rho(r)$ , itself a function of the concentration profile. Mass conservation gives the radial evolution in terms of the evolution of the total mass  $m(t)$  as:

$$\frac{dR}{dt} = \frac{1}{\rho(R)R^2} \left( \frac{1}{4\pi} \frac{dm}{dt} - \int_0^R \frac{\partial \rho}{\partial t} r^2 dr \right) \quad (7)$$

which requires a model for the solvent evaporation  $\frac{dm}{dt}$  for closure. Evaporation is modelled in similar experiments with the Kulmala model,<sup>47</sup> but in this work, where the dry air causes rapid evaporation rates, we find significant deviations from this semi-analytic model. The Kulmala model assumes that the temperature change at the boundary is small: an assumption that breaks down with rapid evaporation. Instead, given our primary aim is to track the internal concentration field throughout the measurement and to investigate the factors governing crystallisation, we fit the evolution of droplet sizes seen in the experiments with  $R(t)^2 = R(0)^2 - 2\kappa t$  obtaining

$$\frac{dR}{dt} = \frac{\kappa}{R} \quad (8)$$

with which Equations 4 and 6 can be solved. Constraining the modelled mass flux to the measurements through assuming a linear fit to the time dependence in the square of the radius is a reasonable assumption until very close to the time at which crystallisation is observed (within 0.1 s). This is shown in the supporting information in Figure S3.

To solve this moving boundary problem, it is convenient to transform into the coordinate system  $\tilde{r} = r/R$  in which the domain is fixed in time and Equation 4 acquires an effective flux term. In these coordinates, the system of Equations 4, 6 and 7 are readily solved using a second-order integration scheme<sup>48</sup> for an initial uniform concentration profile. Microcapillary experiments<sup>49</sup> suggest that homogeneous nucleation for NaCl is almost instantaneous at a fixed supersaturation, so we integrate until the concentration at the outer boundary reaches a solute supersaturation cut-off value. We confirm the numerical stability of the trajectories by varying the temporal and spatial resolutions over an order of magnitude, with no appreciable effect to the final result. As far as we are aware, there is no model that can accurately simulate the rapid evaporation and resulting microphysics, including crystallisation, in an inorganic solution droplet in dry air. As outlined previously, the microphysics of such a drying

droplet is highly complex due to the coupling between heat and mass transfer and the diffusional transport competing with evaporative flux. Hence, the model presented here is necessarily constrained to the experimentally-determined evaporation rate to set a boundary condition. Future developments of this model would include a simulation of the evaporation, independent of experiments, to provide a predictive determination of the crystallisation time in free-droplet drying.

The critical supersaturation value,  $S_c$ , at which efflorescence occurs has been measured experimentally by Desarnaud *et al.*<sup>49</sup> who reported homogeneous nucleation occurring in microcapillaries at  $S_c=1.6$ . Tang *et al.*<sup>50</sup> and Utoft *et al.*<sup>51</sup> reported  $S_c$  values of 1.87 and 1.9, respectively. Here, a  $S_c$  value of  $2.04 \pm 0.02$  was used, based on calculations from the E-AIM model<sup>31</sup> assuming a NaCl efflorescence RH of 45% equivalent to a solution with a water activity of 0.45. The value of efflorescence water activity of 0.45 and an associated error of  $\pm 0.01$  are consistent with literature values of the efflorescence RH under slow evaporation conditions in a large number of aerosol measurements and our own experimental data.<sup>30,31,52</sup> Using the E-AIM model, the NaCl solute concentration at a gas-phase RH of 45% at 293 K is  $648 \text{ g L}^{-1}$  i.e. a molality of  $12.68 \text{ mol kg}^{-1}$  and a supersaturation value of 2.04. The model terminates when the concentration in any region within the evaporating droplet achieves this value of  $S_c$ , identifying the point at which crystallisation is expected.

Validation for using the E-AIM predicted value of  $S_c = 2.04$  to terminate the model is provided in Fig. 5. The figure shows the deviation between the measured crystallisation time,  $t_{measured}$ , and the modelled crystallisation time,  $t_{model}$ , as a function of the value of  $S_c$  used to terminate the model. The two measurements shown are those performed at 293 K, consistent with the thermodynamic model predictions from E-AIM, which are based on aerosol measurements performed at room temperature. A value of  $S_c = 2.04 \pm 0.02$  yields consistency between the modelled and experimental crystallisation times for the two salt solution concentrations reported here. As we propose the critical efflorescence concentration to be the same for different conditions for NaCl,  $2.04 \pm 0.02$  is the only critical supersaturation for which the modelled  $t_{eff}$  matches the experimental  $t_{eff}$  within the experimental error. For measurements performed at 318 K, a value of  $S_c = 2.04$  is still used. However, the increase in the NaCl bulk solubility limit with temperature, from  $317.6 \text{ g L}^{-1}$  to  $321.7 \text{ g L}^{-1}$ , is explicitly included in the model when calculating the supersaturation.

In Fig. 6, we report the radial concentration profiles estimated as a function of time for droplets evaporating at different temperatures and starting solute concentrations, up until the point at which the nucleation supersaturation is exceeded in one of the radial shells. For all droplet compositions and gas phase temperatures, the model predicts the highest solute concentration to be at the droplet surface, supporting the case for nucleation occurring at the particle surface. Changing the temperature and the initial solute concentration strongly influences how the radial concentration profiles evolve with time. Consider the two droplets evaporating at 293 K (Fig. 6a and 6b): the droplet with the higher starting

concentration exhibits a clear radial concentration gradient from the very beginning of the evaporation process, which increases in magnitude steadily until the nucleation supersaturation is exceeded at the surface and efflorescence occurs. By contrast, the droplet with the lower starting concentration does not initially show a radial concentration gradient and undergoes substantial evaporation before a significant gradient becomes evident. Even though the rate of surface recession (the evaporation rate) of the lower concentration droplet is more rapid, its initial solute concentration is so low that there is insufficient NaCl at early times to significantly enrich the surface as it recedes. However, by the point at which efflorescence occurs in the lower starting concentration droplet, the magnitude of its concentration gradient is more severe than that observed for the higher initial concentration droplet.

Increasing the temperature from 293 K to 318 K causes a further increase in the magnitude of the radial concentration gradient, as shown in Fig. 6c and 6d. For both starting concentrations, evaporation at 318 K leads to a much greater degree of surface enrichment in an evaporating droplet than at 293 K, due to the increase in their evaporation rates. This can be seen more clearly in Fig. 4b. The corresponding lines show the calculated surface concentration of the droplets as a function of time, compared to the data-points that show the volume-averaged concentration of the droplets from the experimental measurements. The internal concentration profiles for all four evaporation conditions show a positive deviation in the surface concentration away from the volume-averaged concentration, indicating surface enrichment. As discussed above, the two droplets with the higher starting concentration show this deviation from the beginning of the evaporation process while the two droplets starting at  $24 \text{ g L}^{-1}$  have a surface concentration that is very similar to the average concentration, indicating a well-mixed droplet, until about 0.4 s into the droplet lifetime, at which time a sudden deviation from the averaged concentration line becomes apparent. The deviation is particularly large for the  $24 \text{ g L}^{-1}$  droplet evaporating at 318 K which shows the faster evaporation rate overall. At the time of efflorescence at  $\sim 0.8$  seconds, the difference between the surface concentration and the volume-averaged concentration is  $260 \text{ g L}^{-1}$ .

The radial concentrations at the point of crystallisation for each droplet, and thus the degree of surface enrichment, are reported in Fig. 7. The inset shows the time-dependent Peclet number, calculated with the experimentally determined evaporation rate and the composition-dependent binary diffusion coefficient value at the surface using Eq. 1. The binary diffusion coefficient as a function of concentration is provided in the SI, and ranges from values on the order of  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at the start of the evaporation process when the droplets are more dilute, down to values around  $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  when the concentration of NaCl reaches  $600 \text{ g L}^{-1}$ . This causes the Peclet number to rise by almost an order of magnitude throughout the drying process. Whilst the Peclet number for every droplet is initially very low, as shown in Table 1, the increasing viscosity as the droplet dries ultimately leads to compositional inhomogeneity across the radial profile. Crystallisation occurs at a concentration closest to the volume-averaged supersaturation value predicted by the E-AIM model for the dataset with the least degree of

surface enrichment at crystallisation (a starting solute concentration of  $230 \text{ g L}^{-1}$  at  $293 \text{ K}$ ). In addition, the dataset with droplets that exhibit the highest Peclet number at crystallisation (the  $24 \text{ g L}^{-1}$  at  $318 \text{ K}$  case) shows a volume-averaged concentration that is furthest from the predicted level of supersaturation.

The experimentally observed crystallisation times assuming a supersaturation of 2.04 at efflorescence, compared with those calculated using the model, are shown in Fig. 8 and there is very good quantitative agreement. The modelled crystallisation times for droplets evaporating into a gas phase at  $293 \text{ K}$  lie within the standard deviation of the measurements. For droplets evaporating into  $318 \text{ K}$ , crystallisation in the model occurs slightly later than observed. It is possible that the magnitude of the evaporation rates at the higher temperature causes significant evaporative cooling to occur within the droplets, which would reduce the binary diffusion coefficient at the surface beyond what is currently accounted for and, thus, the Peclet number, and extent of surface enrichment is likely to be higher than reported here.

Our interpretation of the abrupt crystallisation observed experimentally in terms of the developing radial concentration profile is critically dependent on choosing an appropriate value of the solute supersaturation at which crystallisation occurs. The  $S_c$  estimated from the E-AIM model was  $2.04 \pm 0.02$ ; this model has been developed over many decades based on parameterisations to a large database of experimental data including bulk phase measurements of osmotic coefficients up to the solubility limit of NaCl and, more crucially for this work, aerosol phase measurements of hygroscopic growth measurements, deliquescence and efflorescence.<sup>31,53</sup> However, we also must assume that the nucleation of crystals at both temperatures occurs instantaneously.

## Conclusions

We have explored the evaporation kinetics of aqueous sodium chloride solutions, providing an ideal model system to study the crystallisation of drying droplets and the dependence of the time required to achieve crystallisation on the evaporation rate, as governed by the initial solute concentration and gas phase temperature. Not only does NaCl show a remarkable degree of reproducibility regarding the time at which identical droplets effloresce, but there is a clear dependence of the crystallisation time on the temperature and evaporation rate. The internal concentration profiles at different radial points within the droplets are inferred using a Fickian integration model. Drying under all conditions investigated in this experiment led to droplets exhibiting an internal concentration gradient and an enriched solute concentration at the droplet surface. The basis for identifying solute crystallisation is that NaCl achieves a particular level of solute supersaturation at which the nucleation rate of forming a crystal increases by orders of magnitude, such that nucleation becomes instantaneous.<sup>49</sup> When assuming this, a remarkable level of consistency is observed in interpreting the crystallisation time across all drying environments investigated here if crystallisation is assumed to occur at a critical supersaturation of solute of  $2.04 \pm 0.02$ , a value that is always achieved first at the droplet surface.

On account of the consistency observed in the crystallisation time of NaCl, it should be recognised that this represents an ideal system for benchmark studies. Not only are equilibrium compositions of aqueous solutions of NaCl (i.e. solute molality, molarity) with variation in water activity well established to very high solute supersaturation, previous work has established accurate parameterisations for the solution density and refractive index to similarly high supersaturation, both essential for analysing measurements. In addition, slow drying measurements on aerosol have provided an accurate indication of the water activity at efflorescence. Necessarily, we neglect any period between crust formation (the time at which the supersaturation is achieved) and termination of the drying process. However, this is not likely to be true for a wider range of inorganic and organic compounds. If an aerosol droplet enters conditions drier than the ERH, it still may not necessarily precipitate, and certainly not immediately on reaching a threshold saturation. There must always be an interplay between the nucleation rate, and the drying rate. If a droplet evaporates very rapidly and the nucleation rate remains low, it is possible that the aerosol loses water more rapidly than crystal formation can occur, and an amorphous solid would be formed. Under these circumstances, crystal nuclei may have insufficient time to form within the narrow precipitation window. The precipitation window begins when the surface of a droplet passes the bulk solubility limit, thus passing into the supersaturation regime, and finishes when precipitation occurs within the droplet.<sup>54</sup> Efflorescence can occur at any point within this window.

Studies of the drying kinetics of aqueous spherical droplets avoid many of the complexities of studying the drying of droplets on a substrate. Droplets containing gradients in surface tension experience internal capillary flows from regions of low to high surface tension. This Marangoni effect is more prevalent in sessile droplets wherein the evaporation rate from different parts of the droplet are not constant, breaking the symmetry of the evaporating droplet and leading to concentration gradients along the surface profile. This in turn results in convection flows.<sup>55</sup> In aerosol droplets of aqueous NaCl, the spherically symmetric evaporation does not lead to such convections and, thus, Marangoni effects can be neglected. For a droplet of NaCl on a surface, the characteristic velocity of Marangoni flow has been reported to reach  $4 \text{ m s}^{-1}$ .<sup>56</sup> In such a system, the importance of this effect would have to be accounted for in a crystallisation model. In addition, the temperature suppression at the surface of evaporating droplets due to the required latent heat can induce thermophoretic flow, out from the droplet centre along the temperature gradient. Whilst this effect would be small, it acts against the diffusional flow induced by concentration gradients.<sup>57</sup> At the drying rates studied here, we have neglected this thermophoretic effect, and this could be a contributing factor to the marginal over-prediction of the crystallisation time.

This work reports a step towards a greater understanding in the concentration profiles developing in evaporating free droplets, and the first demonstration of the predictability in time and critical concentration of crystallising aerosol. The concepts in this study can be developed for progress towards

ultimately achieving product control in the crystallisation of complex formulations and rapid drying applications such as spray-drying.

### Supporting Information

The Supporting Information contains as follows: a discussion about the error in calculating the radius of the droplets caused by the surface enrichment; diffusion coefficients of aqueous NaCl as a function of concentration; applicability of using a linear fit to the time-dependent *radius*<sup>2</sup> for evaporation rate, method for determining the critical supersaturation for aqueous NaCl.

### Notes

The authors declare no conflicts of interest. The experimental data presented in each figure is provided through the University of Bristol data repository (DOI: 10.5523/bris.1r90ybi4mjn2h2gf2s5rcjsqip).

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## Figures

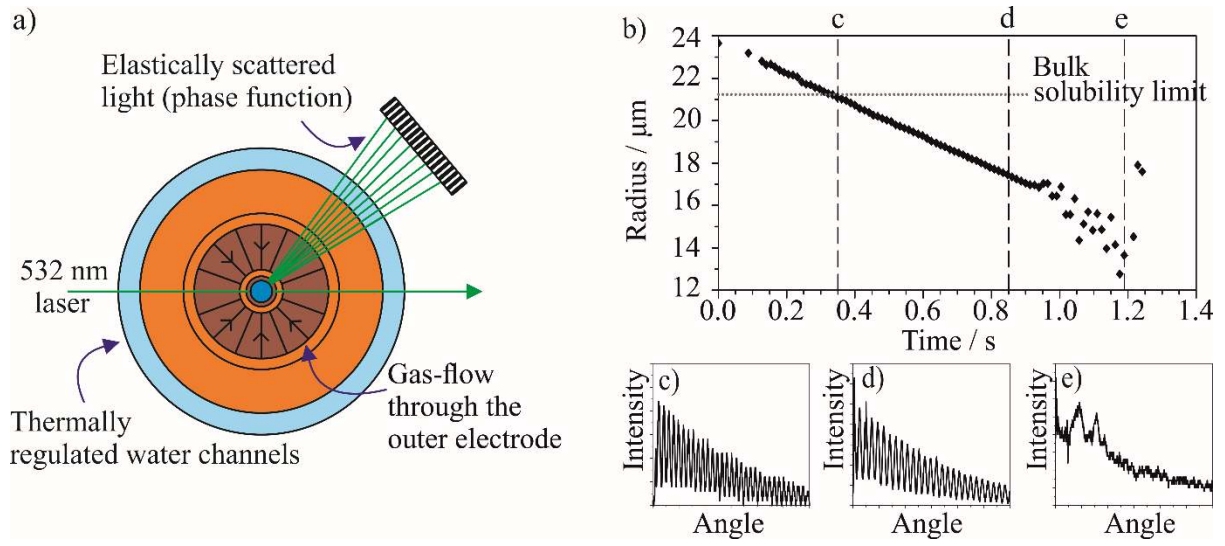


Figure 1: (a) Schematic of the electrodynamic balance double-ring electrode system, as viewed from above. The gas-flow passes through the electrode vertically and out of the page as shown. (b) The change in radius with time of a levitated aqueous-NaCl droplet (initial concentration 20% wt/wt) as it evaporates within the EDB. (c) The elastically-scattered light (phase function) collected at 0.3 s; (d) at 0.8 s; (e) at 1.0 s.

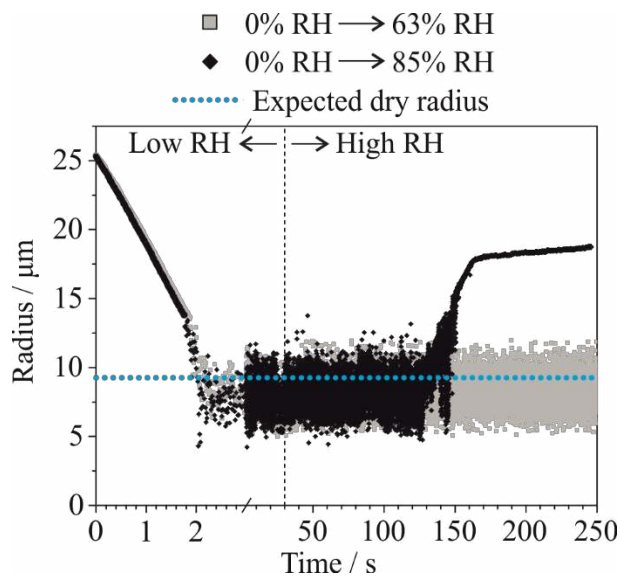


Figure 2: The evaporation of two aqueous NaCl droplets (initial concentration 10% wt/wt) into dry nitrogen, leading to efflorescence at  $t = 1.7$  s. The RH is increased to a higher RH after 30 s into the experiment. When the humidity is increased to 85% RH (black points), the crystalline particle absorbed water and subsequently deliquesced at approximately  $t = 150$  s. When the RH is increased only to 63% (grey points), deliquescence is not observed, and the particle remained in crystalline form. Also shown is the effective spherical radius of the solid NaCl particle estimated from the initial solution droplet wet-size and solute concentration.

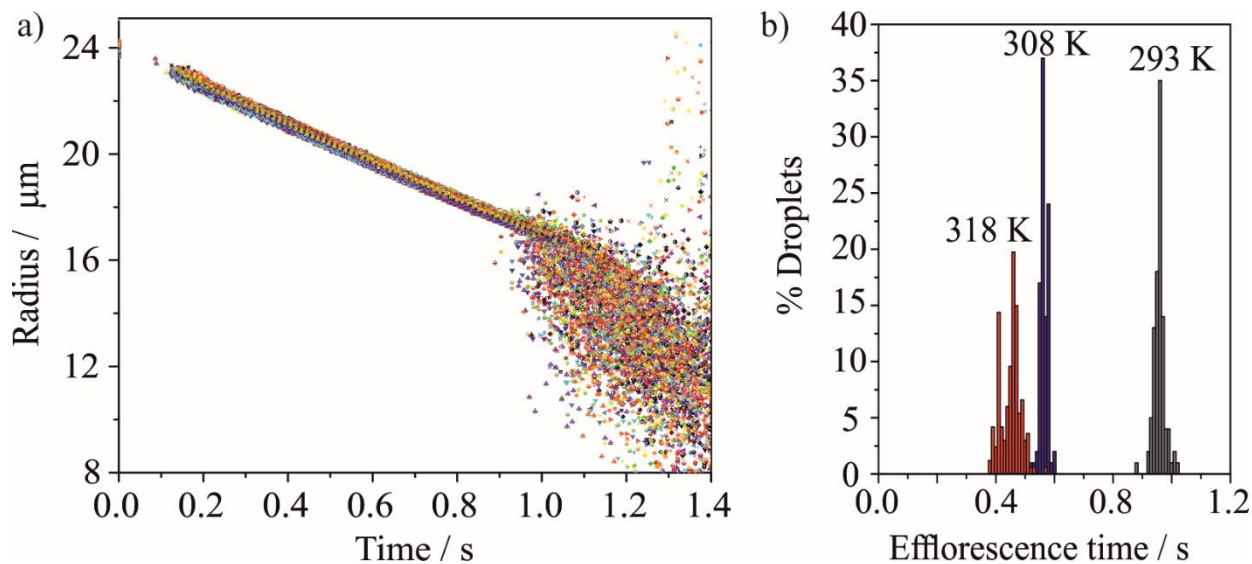


Figure 3: (a) The overlaid evaporation profiles of 230 aqueous NaCl droplets (20% w/w) evaporating in to dry air at 293 K. (b) The distribution in efflorescence times observed at different gas-phase temperatures for a large population of droplets (upwards of 200 in each case). Efflorescence time is defined as the time from the creation of the droplet until efflorescence is detected in the EDB.



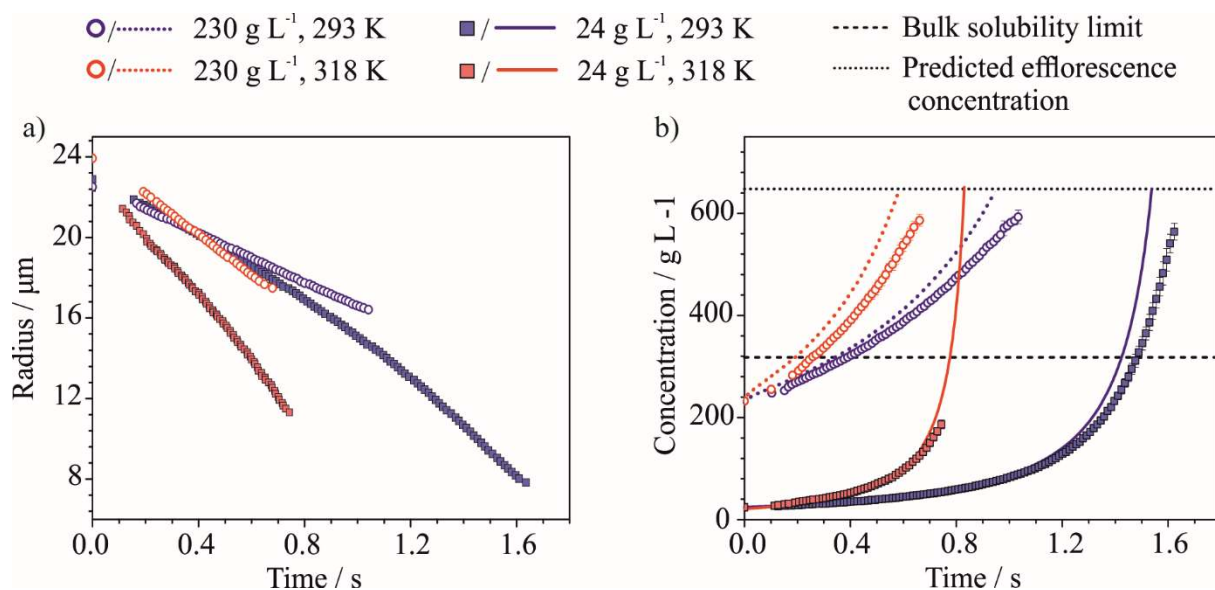


Figure 4: (a) The change in radius with time of aqueous NaCl droplets with different initial solute concentrations evaporating into dry nitrogen at different temperatures. Data-points show experimental data averaged over a minimum of 10 droplets. Error bars are smaller than the datapoints. (b) The change in the volume-averaged concentration of NaCl within the evaporating droplets as a function of time inferred from the experimental measurements of radius (points). The evolving surface composition calculated from the model is indicated by the lines. Data-points show experimental data averaged over a minimum of 10 droplets. Solid and dotted lines show the surface concentration as predicted by the model.

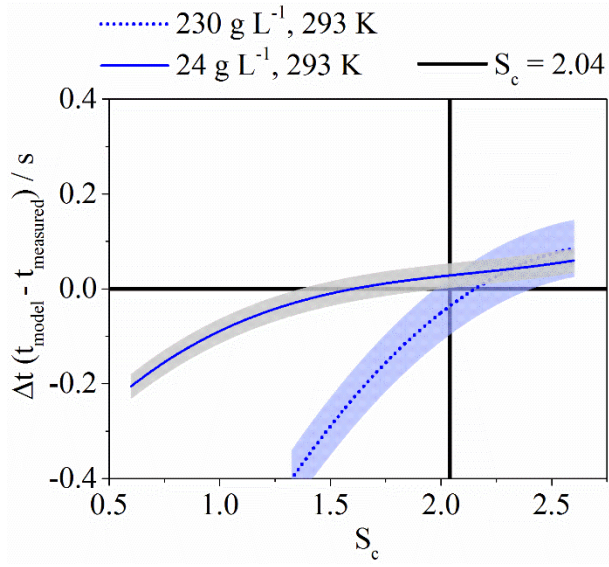


Figure 5: The deviation between the modelled crystallisation time and that measured experimentally, as a function of the chosen value of the critical supersaturation  $S_c$  at which crystallisation is assumed to occur. Previous aerosol phase measurements involving slow step-wise decreases in RH at 293 K are consistent with a value for  $S_c$  of 2.04. This value yields congruent modelled and measured crystallisation times for the droplet drying measurements reported here starting from different initial salt concentrations, within the experimental error.

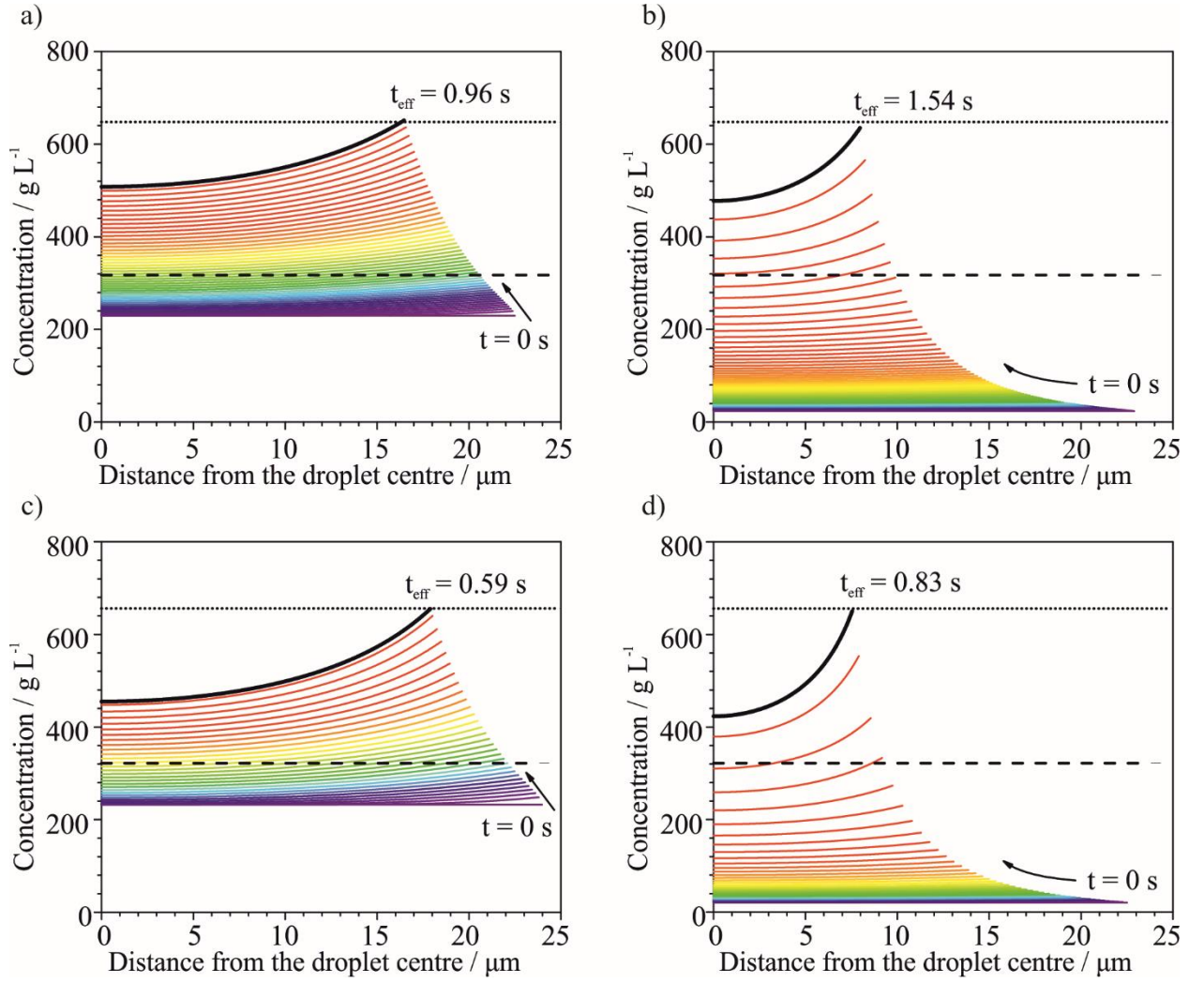


Figure 6: The radial concentration profiles within an evaporating NaCl droplet in dry air, at different initial concentrations and evaporating temperatures until the supersaturation level of 2.04 is reached. (a) Initial concentration of  $230 \text{ g L}^{-1}$  at  $293 \text{ K}$ ; (b)  $24 \text{ g L}^{-1}$  at  $293 \text{ K}$ ; (c)  $230 \text{ g L}^{-1}$  at  $318 \text{ K}$ ; (d)  $24 \text{ g L}^{-1}$  at  $318 \text{ K}$ . Lines are at time-steps of  $0.02 \text{ s}$ . The solid black line represents the radial concentration at the predicted efflorescence time ( $t_{\text{eff}}$ ). Dashed black lines and dotted black lines are the bulk solubility limit and efflorescence supersaturation, respectively.

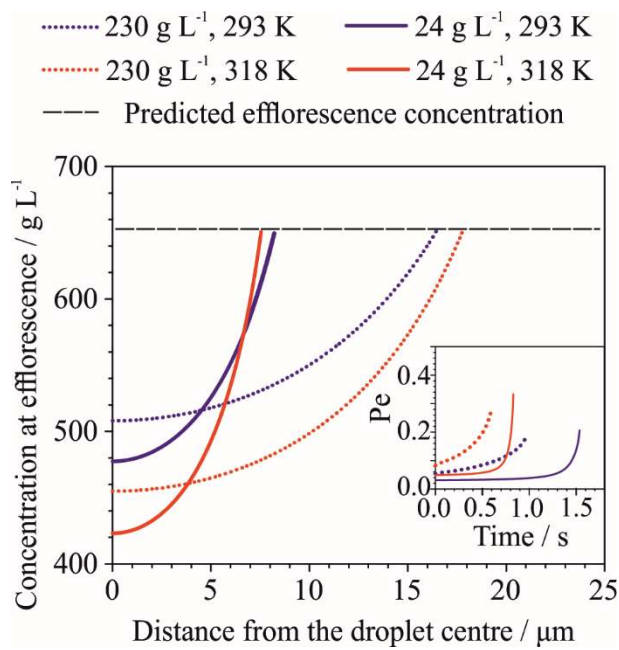


Figure 7: The radial concentration across the droplets at the predicted point of crystallisation, showing the degree of surface enrichment at crystallisation. Inset: The time-dependent Peclet number ( $Pe$ ) for each of the droplets, calculated using the experimentally determined evaporation rate and the binary diffusion coefficient at the surface of the droplet, up until the point of model-predicted crystallisation.

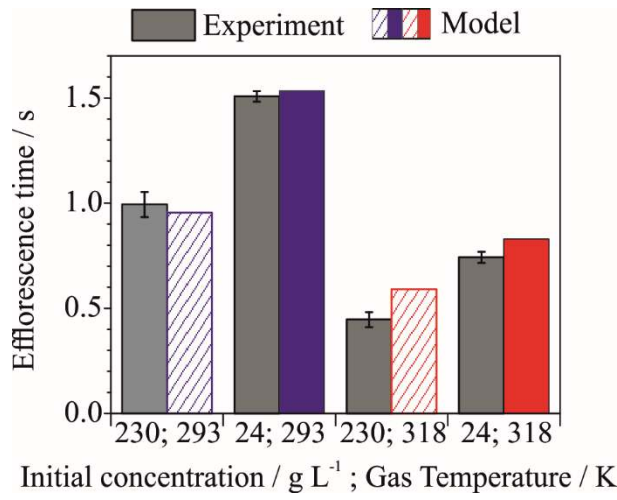


Figure 8: Comparison between experimentally-determined efflorescence time of the droplets in the EDB and the efflorescence time as predicted by the model, for the different gas-phase temperatures and initial starting concentrations. The error bars in the experimental data correspond to the standard deviation in efflorescence times averaged over more than 100 droplets.

## Tables

*Table 1: The recorded efflorescence times and final averaged concentrations (averaged over a minimum of 15 droplets) for different initial solute concentrations of aqueous NaCl droplets and different gas-phase temperatures*

Initial feed concentration of NaCl / g L <sup>-1</sup>	Gas phase temperature / K	Volume-averaged efflorescence concentration / g L <sup>-1</sup>	Efflorescence time / s	Initial Peclet number
24	293	630 ± 10	1.51 ± 0.02	0.023
24	318	200 ± 20	0.74 ± 0.03	0.037
230	293	636 ± 7	0.95 ± 0.02	0.054
230	318	640 ± 20	0.45 ± 0.03	0.082

*TOC graphic*

CK-EDB instrument

