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Additional analysis

Gabor Vali

This paper by Peckhaus et al. (2016; P16) presents a comprehensive set of results from freezing experiments with laboratory preparations of mineral suspensions. Most notably, it includes a variety of nucleation tests. The need for tests beyond those carried out with steady cooling has been argued in several recent papers (e.g. Vali, 2014; Herbert et al. 2014) in order to enable critical examinations of interpretations of heterogeneous nucleation. Results from experiments using only steady cooling (ramp, or constant cooling-rate experiments) can not provide evidence to distinguish between the time-independent (singular) and time-dependent interpretations. The data presented in this paper includes experiments with steady cooling at different rates (CR runs) some at steady temperatures (ISO experiments) and also freeze-thaw cycles (refreeze experiments). Samples with different concentrations of the suspended minerals extended the range of temperatures over which nucleation events were observed. Large numbers of sample drops provide for good statistical validity. Interpretation of data in the paper follows the soccer-ball model (SBM) of Niedermeier et al. (2011 and 2014).

My purpose in writing these comments is to explore whether the excellent data set presented in this paper could reveal additional detail when examined as differential temperature spectra, i.e. looking for preferred temperature regions of nucleating ability.

Dr. Kiselev kindly provided me with the raw data for the fractions of drops frozen in the experiments with FS02 and FS04 samples. These are the data plotted in Fig. 4A and 4D of the paper.

Nucleus spectra

In order to construct nucleus spectra of site densities in the manner described in Section 4.3 of Vali et al. (2015) the freezing frequencies in the raw data were binned into intervals of 0.25 °C. The differential nucleus spectra $k_{\mathrm{m}}(T)$ were calculated, using Eq. (11) from Vali(1971), as $k_{\mathrm{m}}(T) = 1/M \ln[1 - \Delta N/N_{\mathrm{L}}(T)]$, with N_L being the number of liquid drops (unfrozen) at temperature T and M as the mass of suspended mineral per drop[1]. In this way, $k_{\mathrm{m}}(T)$ is expressed as per gram of

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[1] For the 2 µL drops the values of M are $2 \cdot 10^{-11}$, $1 \cdot 10^{-10}$, $2 \cdot 10^{-10}$ and $1.6 \cdot 10^{-9}$ for the 0.01%, 0.05%, 0.1% and 0.8% suspensions, respectively

dry material and per degree temperature interval, with dimension of (g^{-1}°C^{-1}). Using the BET SSA reported in Table 1 of the paper the $k_\mathrm{s}(T) = k_\mathrm{m}(T) * SSA$ was also calculated; this is, essentially, the differential of n_s presented in section 5.6 of the paper. Results[2] are shown in Fig. C1.

Not surprisingly, the scatter of data points in Fig. C1 is greater than in the plots of fraction frozen in Figs. 4A and 4C or the plot of n_s in Figs. 9 and 11. This arises from looking at data per temperature interval and not in the cumulative form of activity above indicated temperatures. What is gained by this treatment is the potential for detecting local peaks or other features that might indicated preference for nucleation at some temperature or other. In fact, no local peaks are seen in the plots of Fig. C1, though there are indications for variations in the slope of the data points for individual samples and even for the overall data cluster. These variations in slope may also be seen in the cumulative curves but with less clarity. Limitations in identifying such patterns arise from the scatter of data points and are evident in the differences among samples of different mass loading. The large numbers of drops involved in the experiments (500-800, except for the most dilute sample of FS04) is helpful in limiting data scatter. Several other factors come into lay, most importantly perhaps unavoidable alterations of the samples due to settling, aging, coagulation, and so on.

In spite of the problems just discussed, it seems that FS02 exhibits some preferential nucleation frequency in the temperature range -20 to -25 °C and FS04 has an interesting plateau in the data between about -7 and -12 °C. The former might indicate the existence of some frequent site formation corresponding to nucleation near about -22 °C, while the latter might indicate that there is a paucity of sites that can cause nucleation between -7 and -12 °C. Neither of these patterns is strong, but they are perhaps indicative of some eventually identifiable surface characteristics of the minerals studied.

The overall trends depicted in Fig. C1 are, to a first order, exponential. For a quick characterization of the nucleating abilities of the samples and for comparisons with other data sets it is of some utility to consider these exponential fits through the slope ω defined in Eq. (7) of Vali (2014). These slope values are the same for differential and cumulative spectra. Values from visual fits to the data, and with vague attention to the different statistical significance attached to different points, $\omega = 0.46$ for FS02 and either 0.34 or 0.41 for FS04 depending on whether the highest dilution sample is included or not. These values are at the low end of the range in Table 1 of Vali (2014), as minerals generally are compared to other materials, but comparable to the values 0.34 and 0.52 shown there for ATD from Niedermeier et al. (2010) and from Wright and Petters (2013) and the range 0.25-0.4 for NX illite (Broadley et al. 2012). All these values of ω are given with units of $^{\circ}C^{-1}$.

Freeze-thaw cycles

The results presented in Section 5.2 of P16 are quite comparable to other data sets cited there, and fully justify the conclusion stated in the last three lines of this section. As a slightly stronger

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[2] No adjustment is made for one run having been made at a faster cooing rate since for FS04 no dependence on cooling rate is indicated in Fig. 8 of the paper, and even with adjustment factors based on other studies the change would be negligible compared to scatter of points in the data.

statement, I would say that (i) the average freezing temperatures of individual drops (over freeze-thaw cycles) are determined by the most active site found in that particular drop and (ii) random variations from that mean temperature in specific runs are limited to a narrow range of the order of a degree. It is important to state this limitation in order to avoid the mis-interpretation of randomness as extending over all temperatures observed for a set of drops. In terms of definitions included in Vali et al. (2015), one can say that the average freezing temperature of a drop is very nearly the same as the characteristic temperature T_c of the most active site and that the range of variability about that is defined by the steepness of the site nucleation rate coefficient J_site.

Another point I'd like to make is about the last sentence of the first paragraph of section 5.2. A lack of correlation of the ranking numbers may arise from the steep slope of the nucleus spectra ($K(T)$ or $n_\mathrm{s}(T)$), not from the steepness of the nucleation rate coefficient. A steep slope of the spectrum means that all drops in a sample freeze at nearly the same temperature. In that case, the drop-to-drop variations are similar in magnitude to the run-to-run variations for individual drops in subsequent cycles and that makes the rank order correlation disappear. This is not a failure of repeatability of freezing temperatures and can be readily resolved by diluting the sample until a larger range of freezing temperatures are observed for the set of drops.

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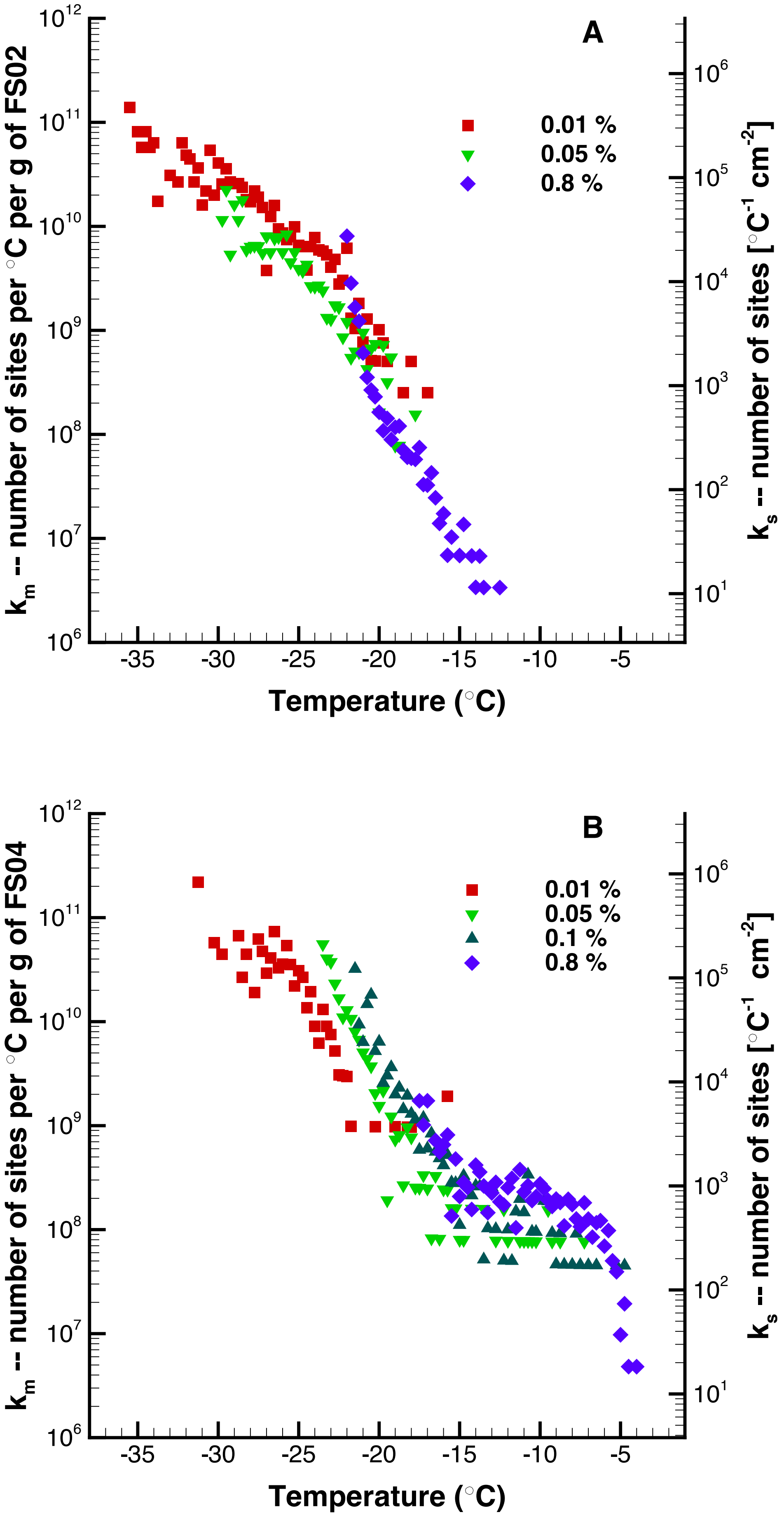

Figure C1: DIfferential nucleus spectra for (A) FS02 and (B) FS04.