Anonymous Referee #1

J. D. Yakobi-Hancock, L. A. Ladino, and J. P. D. Abbatt have undertaken a study of ice nucleation by feldspar minerals. Ice nucleation is a topic of contemporary interest given the importance of ice nucleation on cloud formation and therefore as an agent of indirect climate change. Feldspar minerals have recently gained attention in the work of Atkinson et al., published this June in Nature. Atkinson et al., similar to this work but using a different technique, showed a relatively high freezing temperature of ~-15 deg. C for feldspar minerals. Here, Yakobi-Hancock et al. perform experiments at somewhat lower temperature (-40 deg. C), thereby moving from Atkinson's more mixed-phase to a cirrus regime. The data are acquired with a different technique than Atkinson et al., a continuous flow diffusion chamber. The data are compared to a cloud seeding agent, lead iodide. A correlation of ice nucleation with feldspar is found and this complements the work of Atkinson et al.

The reviewer appropriately summarizes the paper. We note that study was not conducted with the intention of making a comparison with Atkinson et al. (2013). Indeed, we were unaware of the Atkinson et al. work until just prior to submission. The similar finding – that feldspars are IN active under two different freezing regimes – lends added support to this class of materials being potentially atmospherically significant.

The text is rather awkwardly written, there is a poorly supported use of wet-disperse aerosol, and the concluding paragraphs are not adequately supported or referenced. None the less, I think the authors can make the required changes and I recommend this work as both applicable for, and publishable by, ACPD.

We hope the changes outlined below address these points.

Comments:

1) A major weakness of this manuscript is the lack of clarity on washed versus unwashed samples. This is actually found in three places: (1) Experimental Procedure (Page 5, line 13), Page 6, line 3, and Section 3.3. Please move this important topic in its entirety to the Experimental section and not interspersed through the text.

The samples were washed for two reasons. The goals in the paper were, firstly, to create a relative ranking system of the IN properties of minerals, and secondly, to compare the results to the behavior exhibited by two multicomponent mixtures. In the first instance, soluble impurities were removed from the minerals through washings to avoid the effect of soluble material on IN properties, and therefore allow the IN properties of the minerals to be compared. ATD and MDD were also washed in order to allow the IN properties of these multicomponent mixtures to be directly compared to the minerals. We were afraid that such a solid comparison could not be made if soluble impurities had not been removed from multicomponent mixtures through washings. In sum, we wanted to be sure we were not studying nucleation on/via soluble material.

The reasons for washing the samples have been added to the section "2 Experimental Procedure", paragraph 1:

"Prior to experimentation, each compound was washed twice using Millipore water (18.2MΩ·cm). A selection of compounds (TiO_2, orthoclase, ATD, MDD) was not washed prior to experimentation in order to compare the IN properties of the washed and unwashed forms of these samples. The purpose of the washing was twofold. Firstly, it allowed a relative ranking system of the IN properties of minerals to be created without interferences from soluble contaminants that may be present at the particles' surfaces. If such materials are present, either through handling, laboratory contamination, or from the manufacturer, then they may affect the underlying abilities of the pure compounds to nucleate ice. Secondly, it allowed the behavior of these minerals to be compared to the multicomponent mixtures (ATD and MDD), which were washed as well, without interference from such material. We note that the washing procedure may also affect the surface composition of pure compounds; however, the research community is unclear about this. As well, the degree to which dust particles are "washed" in the environment is variable, depending on whether they undergo liquid water cloud processing or whether they experience rain when still on the ground."

2) Specific suggestion: The authors need to comprehensively show what washing does or does not do to the samples. Ideally, Table 1 should include onsets for both wet and dry dispersion.

This is an important point and we agree entirely that we would ideally compare the onset behavior for the same size of both wet and dry atomized samples. However, for reasons now described in the text (2 Experimental Procedure, paragraph 4) (i.e. that our dry dispersal system plus DMA size selection does not lead to efficient size discrimination with dry dispersed samples) we would not be confident whether such a comparison would indicate behavior related to the difference between wet and dry sources, or to the size of the particles instead.

Rather, the approach we took in the paper was to demonstrate the effects that arise with and without washing the samples, using wet atomization in each case. In particular, the conductivity measurements during these washing procedures have been included in Table 1 for TiO_2, orthoclase, ATD, and MDD in order to demonstrate that ions were being removed by washing. In all four cases the conductivity, and therefore ion concentration, decreased as the number of washings increased. This indicates that after the washings were conducted the IN experiments were conducted on samples that are more similar to the bare minerals.

Two final points: Given that most samples were obtained commercially, and may contain soluble impurities that have no relation to what may be present on these materials in the atmosphere, it seems well justified that washing should be performed. Indeed, "washing" of samples will occur in the environment as well as when, for examples, soil samples are rained upon prior to aerosolization, or when particles go through liquid water cloud processing. Thus, it is not an entirely foreign procedure from an environmental perspective. These points have been discussed in the section "2 Experimental Procedure", paragraph 1.

3) Currently, the authors state (page 15, line 3) "the washing procedure appears to alter their IN efficiencies to some degree. However, it does not alter the general conclusions about whether a particle is a good IN or not." – please explain, quantitatively, what "to some degree" means; leave it to the reader to judge if this does or does not alter the conclusions by presenting comparable data.

The text now states that, according to the Student's *t*-test, which is used to determine if two data sets significantly differ from one another, the RHi values of the washed and unwashed samples for each of the four materials considered were not significantly different from one another (section "3.3 Unwashed and Washed Samples", paragraph 1). We agree that the wording was unclear here, and we have removed this phrase "to some degree" from the paper.

4) If the authors are going to use wet dispersion, please prove from the onset that it doesn't alter the sample (as an aside, can the authors explain why wet generation was used at all? The authors here and in recent literature (Ladino and Abbatt, JGR, 2013) seem to indicate this changes surface character. I assume it is for ease of sample aerosolization but please specifically state.)

As described above (and in the text: section "1 Introduction", paragraph 6; "2 Experimental Procedure", paragraph 4), wet generation was indeed used to ensure preparation of the same size of particles, i.e. so that the same experimental conditions are used in each experiment and that large particles are not present. Ladino and Abbatt (2013) did find that 100nm atomized particles had higher critical supersaturations than particle sizes 240nm and larger, which was attributed to the presence of soluble material only in the smaller particles. To avoid the presence of soluble material, all the samples were washed repeatedly; we did not wash the samples in Ladino and Abbatt (2013). Also, while we don't believe that Ladino and Abbatt (2013) made any reference to changes in surface character, we now state in the paper (section "2

Experimental Procedure", paragraph 1) that this is a possibility with wet atomized samples.

5) 200nm particles of mineral dust are exceedingly uncommon and often correspond to solution droplets (suggested by the reference above) when using wet dispersion. Can the authors comment if this might be the case here?

Ladino and Abbatt (2013) suggested that 100nm particles were solution droplets, while 240nm particles were not. However Ladino and Abbatt (2013) did not wash their samples. By washing the samples repeatedly and finding that the results are not statistically different from the unwashed values, we are confident that solution droplets are not being studied.

6) Page 15, line 26 Two issues with this paragraph. First, the line "Although it is beyond the scope of this paper, it is well known that clay minerals undergo exchange between soluble cations and hydronium ions in solution, which may then affect their surface compositions, and hence IN activity.": This is NOT beyond the scope of the paper which should be apparent since the authors discuss it here as relevant. Please eliminate this qualifier.

The point we were making was that it was beyond the scope of this paper to experimentally address this point. We did not intend to imply that this issue is not relevant. And so, the qualifier "Although it is beyond the scope of this paper" has been removed. This is an important point, and it is an issue that we feel does need to be experimentally addressed in the future. To address it would require experiments in which the surface composition of soluble ions in minerals is altered in a known and reproducible manner. Ideally, a surface-sensitive analytical technique would be used to confirm the surface composition of the samples. Together, these experiments are a major undertaking, one that we have now initiated in our laboratory.

7) Second, the line ". . .most particles, especially those that participate in ice formation in the upper troposphere, are thought to pass through regions of water saturation before reaching altitudes at which cirrus clouds forms (Wiacek et al., 2010)." – this line is from a modeling study and appears unsupported by field data. For example, the recent paper from Cziczo et al. Science, 2013 indicates most IN don't appear to have significant surface modification / coating. This also seems to stand in direct opposition to this manuscript, which (per the title) is on deposition nucleation (that is to say, particles without surface water nucleating ice). It only appears to support the use of wet-dispersion which, as mentioned above, likely imparts surface changes. I don't think this justification is well supported and this paragraph should be removed.

This is a valuable point – thank you. The work of Wiacek et al. (2010) can be interpreted in multiple ways. One is that all particles must pass through water saturated conditions to reach the upper troposphere, thus justifying to some degree the wet atomization mode of particle preparation. Another way to interpret those results is that, as the Reviewer points out, the Wiacek et al. results are model results only, and it is possible that in the real atmosphere it is the few parcel trajectories that don't go through water saturation that deliver particles that are IN active to the upper troposphere. So, we have adjusted the text appropriately to indicate these possibilities in section "3.3 Unwashed and washed samples", paragraph 2:

"As well, most particles are thought to pass through regions of water saturation before reaching altitudes at which cirrus clouds forms (Wiacek et al., 2010). On the other hand, it is quite possible that the few trajectories that do not pass through water saturation are those that deliver the best IN to the upper troposphere. The work of Cziczo et al. (2013) indicates that the particles with the fewest soluble impurities appear to the best IN. Thus, while each aerosol preparation method has its merits, it is difficult to claim that either dry dispersal or wet atomization is universally the most atmospherically appropriate method."

Thank you for the suggestion of the reference of Cziczo et al. (2013) – now included in the paper – which appeared in print just at the point of submission of our paper.

8) In conclusion to this point regarding wet-dispersion: this would be a stronger paper if it used dry dispersion, not wet. That would seem the more consistent process for deposition nucleation. The authors at the bare minimum need to clearly describe the difference in dry and wet dispersion and eliminate unclear attempts to justify the latter.

We agree entirely that the relative merits of dry versus wet dispersal need to be clearly outlined in the paper. While we attempted to do this to some degree in the original manuscript, we thank the reviewer for this suggestion and have made changes at the following points of the manuscript to make this comparison more explicit: section "2 Experimental Procedure", paragraph 3; section "3.3 Unwashed and Washed Samples", paragraphs 3 and 4.

9) A second major comment regards Sections 3.1, 3.2 : This is titled "IN properties of pure compounds" but actually seems to include considerable information on mineral structure. Suggest separating mineral structure to the previous section (Experimental, perhaps a sub-section on samples) and restrict this section to a discussion of results (which is the stated subject of Section 3). As currently constituted this section incorporates elements of sample description, presentation of results and discussion. The content is good but confusing.

Thank you for this suggestion. A sub-section titled "Mineral Structures" has been added to the Experimental section.

10) Note also: The wording of this section is rather long (5 full pages of text on pure compounds). The manuscript appears rather lopsided with only 4 figures of data. The text could be shortened quite considerably.

This section is now shorter, with some of this material in the "Mineral Structures" subsection of the Experimental section. In addition, Section 3.1 has been renamed as "IN Properties of Pure Single Component Samples", and has been further divided into the subsections "3.1.1 IN Properties of Clay Minerals", "3.1.2 IN Properties of Feldspar Minerals", and "3.1.3 IN Properties of Other Pure Compounds".

11) A third major comment regards the awkward final paragraph which seems an attempt to indicate importance of this work: "Another conclusion from this work is that many species, such as metal oxides and carbonates, are poor deposition IN. Given that many metal oxides are formed by mining and smelting activities, it seems unlikely that there is an anthropogenic effect on ice nucleation through the release of such species to the atmosphere. On the other hand, if cloud seeding were to proceed under deposition mode conditions, for example in the seeding of cirrus clouds, it appears that feldspar minerals would be a good option; there would be no need to turn to an anthropogenic compound such as lead iodide." First, do smelting and mining only form metal oxides and carbonates? Can references be provided? How much is known about the abundance of metal aerosol in the atmosphere, specifically if the materials here are relevant compositions?

Ores are extracted through mining and then refined to obtain the metals of interest. They commonly include metal sulfides, oxides, and carbonates in addition to other species such as silicates and tellurides (Swaine, 2000). While the quantification of smelter emissions is difficult as they depend on several variables, including the ore's composition, studies considering the trace metal speciation of smelter-contaminated soils have reported that metal species included oxides, sulfides, and carbonates, among others (Swaine, 2000; Li and Thornton, 2001; Burt et al., 2003).

In addition, there has been evidence that industrial processes such as combustion produce metals in several forms, including oxides, carbonates, sulfates, and sulfides. For example, Aragón Piña et al. (2000) detected metal (Pb, Fe, Zn) sulphate, sulfide, and oxide – rich particles at air sampling stations near copper and zinc refineries using SEM-EDS. The most abundant heavy metal particles of relevance to our study were lead sulfates, iron oxides, and lead and zinc sulfides. While some of these were attributed to minerals having corresponding chemical compositions it was also mentioned that each composition also included impurities (other heavy metals) uncommon in the mineral. It is therefore likely that these particles were produced through industrial processes rather than being of crustal origins.

Similarly, Fernández et al. (2000) reported the emission of Fe, Al, and Cu carbonates and oxides from industrial sources by analyzing air samples collected from heights of 4-6m using flame atomic absorption spectrometry and sequential extraction. It was determined that resuspended land particles and industrial and traffic emissions were the dominant sources of heavy metals. 50-70% of Fe and Al, and 40-70% of Pb and Cu were reported to be present as carbonates or oxides, independent of particle size.

The references included here (Aragón Piña et al., 2000; Fernández et al., 2000; Swaine, 2000; Li and Thornton, 2001; Burt et al., 2003) have been added to section "4 Conclusions and Atmospheric Implications", paragraph 4.

12) Second, the authors should also reference Cziczo et al., 2013 here which discusses metal oxide particles found in cirrus clouds. It seems (as with Atkinson et al.) this work might have helped motivate this study; regardless it should be referenced either here or earlier.

Thank you for mentioning this; Cziczo et al. (2013) has been added to section "1 Introduction", paragraph 3. In addition, this reference was included in the introduction and discussion in the following locations:

Section "1 Introduction", paragraph 4: "Finally, Cziczo et al. (2013) identified metal oxides as another dominant component of the residual particles of cirrus ice crystals."

Section "3.1.3 IN Properties of Other Pure Compounds", paragraph 1: "These results are somewhat surprising, as Cziczo et al. (2013) found that in addition to mineral dust, metallic particles are a dominant component of ice crystal residuals in cirrus clouds."

Section "3.3 Unwashed and Washed Samples", paragraph 2: "The work of Cziczo et al. (2013) indicates that the particles with the fewest soluble impurities appear to the best IN."

Indeed, it was through informal conversations with Dan Cziczo (now included in the Acknowledgements) that we investigated metals. As noted above, we were entirely unaware of the work of Atkinson et al. (2013) when conducting our own study, and only heard of it just prior to submission of our paper.

13) Third, the statement regarding relative abundances and activities is unsupported. The authors reference Hoose and Moehler, 2012 in the introduction who describe that relative emission rates and atmospheric lifetimes (ability to act as a CCN or IN) is what sets abundances in the

atmosphere. Specifically, the authors should consider that feldspar might be so effective an IN that it is often removed before entering the free troposphere. The laboratory data here don't address this and the lines above should convey this uncertainty (instead of making unsupported statements).

It is true that feldspar may also be very active at warmer temperatures and lower altitudes. Therefore, it is possible that it would be removed before reaching the conditions that this study addressed. However, if feldspar particles were to enter the free troposphere they would be extremely efficient ice nuclei in comparison with the other minerals and dusts that were considered in this study.

In order to incorporate this uncertainty in section "4 Conclusions and Atmospheric Implications", paragraph 3 has been modified as follows:

"Although the presence of feldspars in dust particles is less than that of clay minerals, their effect may still be substantial as some may be significantly more active as IN in the deposition mode. For this reason it is important that these feldspar-containing particles be further investigated in order for their effects to be appropriately incorporated into global climate models. One issue to consider is the degree to which such good IN are removed by prior cloud processing prior to reaching the upper troposphere, where much cirrus cloud formation occurs."

14) Finally, why are there statements on cirrus cloud seeding? Is this a geoengineering proposal? If so please explicitly state this. Has someone proposed use of lead iodide to seed cirrus? If kept please reference suggestions of cirrus cloud seeding and the climate effect.

Lead iodide was a proposed cloud seeding compound by Schaefer (1966), Morgan and Allee (1968), and Parungo and Rhea (1970). It was found to be produced by the reaction of tetraethyl lead (in gasoline) and iodine vapors. We agree that this is not a widely discussed geoengineering proposal; however, we do feel it is important to note that some of the minerals investigated were as active as a compound that in the past was efficient enough to be considered as a cloud seeding compound. We have removed the word "geoengineering" from the manuscript.

15) Suggestion: Either remove this paragraph or comprehensively expand it. It appears an awkward collection of unsupported lines that try to increase the importance of this work. If the authors wish to keep any of these concluding statements (1: metal oxide abundance, 2: metal oxides as IN, 3: cirrus cloud seeding) then they need to break these into separate, fully referenced (and much more fully developed) paragraphs.

Thank you for this suggestion. To more fully introduce lead iodide section "1 Introduction", paragraph 5 has been modified as follows:

"Due to this similarity, early studies were conducted in the immersion/condensation and deposition regimes (Baklanov et al., 1991; Harris et al., 1963; Morgan, 1967; Reischel, 1975; Schaefer, 1954), and it was proposed as a cloud seeding compound by Schaefer (1966), Morgan and Allee (1968), and Parungo and Rhea (1970). However, no studies using modern experimental techniques have been conducted on this compound."

16) Editorial note: This manuscript would read more clearly if the authors could restrict (ideally eliminate) the repeated use of un-quantified qualitative terms. I note the repeated use of "very", "slightly", "significant", "large", "most efficient", etc. all used without a quantitation. Please either add quantitation or eliminate.

Thank you for this suggestion. In order to clarify the manuscript an effort has been made to limit the use of these qualitative terms.

Anonymous Referee #2

Review of "Feldspar minerals as efficient deposition ice nuclei" by Yakobi-Hancock et al. In this paper, the authors report a nice systematic study of ice nucleation on a range of minerals in the deposition mode. One of the main findings is that feldspar minerals are the best ice nuclei, a finding that is complementary to the recent paper by Atkinson et al., Nature, 2013. The topic and results are important and well suited for ACP. My major comments on this paper concern the method of producing particles (wet nebulization)
and the washing procedure used by the authors. The authors need to justify better the methods for nebulizing the particles and the washing procedure and also discuss fully the possible artifacts/modifications the nebulization and washing procedures may introduce. In addition, the authors should consider carry out experiments with a dry nebulization technique to support their findings. Listed below are major and minor comments. Once these comments are adequately addressed the paper should
be published in ACP.

Major comments:
1. I don't see the justification for doing washed samples. The authors indicate that this is done to remove soluble material. However, if the particles contain soluble material, experiments that include the soluble material seem most relevant for the atmosphere. Additional discussion on the atmospheric relevance of the washed samples should be given.

2. Page 17308, line 12-13. IF the outermost K+ ions of orthoclase are removed upon contact with deionized water, it is not clear how the washing experiments are applicable to deposition freezing in the atmosphere. Mineral dust will certainly be exposed to water during cloud activation, but after evaporation the water will be removed and K+ ions returned to the mineral, I assume? Again, please discuss the atmospheric significance of the washed experiments and conditions where mineral dust will be washed with water followed by deposition freezing.

The reviewer raises important questions, which are now addressed in considerably more detail in the paper (see section "2 Experimental Procedure", paragraph 1; section "3.3 Unwashed and Washed Samples" paragraphs 1 and 3). The issue of concern is whether there are soluble impurities present in the samples which are not necessarily atmospherically relevant. In particular, because a large majority of our samples are commercial, soluble material may arise through the manufacturing process, and so we wanted to be confident that our results were not affected by these impurities. In particular, the goals of the paper were to, firstly, to create a relative ranking system of the IN properties of these minerals, and secondly, to compare the results to the behavior exhibited by two multicomponent mixtures. For this reason we also washed the ATD and MDD in order to allow the IN properties of these multicomponent mixtures to be directly compared to those of the minerals.

We also point out in the paper (see "3.3 Unwashed and Washed Samples", paragraph 2) that particles in the atmosphere may also have been “washed” either when the ground is rained upon, prior to mineral dust aerosolization, or via liquid water cloud processing.

The reviewer brings up a good point about whether the soluble cations may simply return to the surfaces of the particles in cloud processing events, after droplet drying. However, the authors don’t know if it is established that the surface that was present prior to cloud processing is the same as that after, i.e. different cations may move to the negatively charged surface sites after drying.

That all being said, this is an important point, and we now emphasize in the paper in a number of locations (" section “2 Experimental Procedure”, paragraph 1; section "3.3 Unwashed and Washed Samples" paragraphs 1, 2, and 3; section "4 Conclusions and Atmospheric Implications", paragraph 1), that these results are for wet atomized and washed samples, and that it will be interesting to compare the results to those obtained with dry dispersed samples.

3. Page 17306, line 24-26. The authors suggest the difference between Welti et al., 2009 and the current studies may be because Welti et al didn’t wash their samples and non-washed samples may have IN-facilitating soluble material. First, some laboratory experiments suggest that soluble material will inhibit ice nucleation, not facilitate it (see (Cziczo et al., 2009) and references therein).

This is a good point. We cannot be sure of the reasons for the difference between our results and those of Welti et al. (2009), for a number of reasons. We have removed the specific sentence that prompted this comment.

Second, can the method of producing particles in the current study (generating particles by atomizing water suspensions) introduce insoluble material even if the water is clean? These points should be addressed in the manuscript.

It is hoped that insoluble material was not added to the particles through atomization. In particular, the atomizer was thoroughly cleaned between samples using Millipore water in order to remove any potential contaminants (insoluble material). Of course, we cannot be 100% confident that that is the case. However, if the IN results were dominated by this effect, we would not expect to see the strong differentiation between samples as was observed. For example, if atomization coated all particles with the same insoluble material, then we would have expected to see most samples display the same behavior. Instead, the species that we expected to be most active, such as lead iodide, were indeed the most active.

4. Abstract and Page 17311, paragraph 1-2. The authors are discussing the results for Mojave Desert Dust (MDD) and Arizona Test Dust (ATD). For this discussion they only refer to the washed results. Please make it clear though out the document which results are being discussed (i.e. washed vs. unwashed). Also, why only discuss the washed results at these locations? Are the washed results more atmospherically relevant?

Only the washed results were discussed as washing was necessary to make an inter-comparison between the ice nucleating properties of single component minerals and multicomponent mixtures. If the unwashed minerals were discussed this would not create a relative ranking system of the ice nucleating properties of the different minerals as these properties may be influenced by the presence of soluble material. Similarly, the unwashed mixtures were not discussed as the redistribution of soluble material due to atomization might affect their results, and so would prevent a proper comparison of the ice nucleating properties of these mixtures to the minerals therein.

As was stated in section "3.3 Unwashed and Washed Samples", paragraph 1, the effects of washing on the samples' IN properties were investigated by measuring the IN properties of a selection of washed and unwashed samples. In order to clarify the results of this investigation the following sentences have been added to this paragraph:

"According to the Student's *t*-test, the RH_i values of the washed and unwashed samples for each of the four materials considered were not significantly different from one another. Therefore, we conclude that washing does not alter the general conclusions about whether a particle is a good IN or not."

5. Page 17314, line 1-4. The authors argue that wet atomized particles is atmospherically relevant for deposition IN studies since particles in the atmosphere pass through regions of water saturation and cloud activation. I agree with this for single component minerals, but I am not convinced that wet atomized particles is atmospherically relevant for multicomponent mixtures such as MDD and ATD, since previous studies have shown that when multicomponent mixtures are wet atomized, soluble material can be redistributed on the particles in an unrepresentative way (Koehler et al., 2007). The authors should justify why the wet atomized experiments are relevant in light of the experiments by Koehler et al., 2007.

The reviewer is correct in that atomized multicomponent mixtures such as MDD and ATD may not be as atmospherically relevant due to the redistribution of soluble material, as was shown by Koehler et al. (2007). In order to clarify this, a third paragraph has been added to section "3.3 Unwashed and washed samples":

" An important additional point to make, as described by Koehler et al. (2007), is that atomized multicomponent mixtures such as MDD and ATD may lose some atmospheric relevancy due to the redistribution of soluble material, if there is a lot of soluble material present. However, for the goals of our paper, i.e. to compare the ice nucleating abilities of single component minerals to multicomponent mixtures, all of the samples were washed prior to atomization in order to remove as much soluble material as possible before making this comparison. As a result, their soluble material that may otherwise have been redistributed on the multicomponent mixtures was removed prior to atomization."

Minor comments:
1. The authors measure the electrical conductivity of the suspensions prior to nebulization. It would be beneficial to include this information in Table 1 or a supplemental table.

Thank you for this suggestion; this information has been included in parentheses after the corresponding sample names in Table 1.

2. Page 17303, line 19-21. "although particle size selection was accomplished with the DMA at 200 nm, roughly 25% of the total number of particles exiting the DMA were multiply charged particles larger than 200 nm." What fraction of the total surface area in the experiments can be attributed to 200 nm particles? If most of the surface area is from particles larger than 200 nm, then is it accurate to indicate that the experiments in the current manuscript focus on particles with diameters of 200 nm? Please discuss in the manuscript.

The wording in the manuscript was not accurate and reflected the upper limit of the total number of multiply charged particles observed. We now also include data representative of a species, Al_2O_3, which had a lower fraction, in section "2 Experimental Procedure", paragraph 4:

"Particle size selection was accomplished with the DMA at 200nm, with at most 25% of the total number of particles exiting the DMA being multiply charged particles larger than 200nm. For example, in the case of Al_2O_3, the fraction of particles that were multiply charged was only 7%, whereas it was 25% for ATD. The percentage of total surface area that cannot be attributed to 200nm particles was between 13% and 60% for Al_2O_3 and ATD, respectively."

In general, this is an excellent point that is rarely mentioned in our field and yet arises in all studies that use particle size selection, i.e. our size distributions are never truly monodispersed. For that reason, we now emphasize this point in the paper (section "2 Experimental Procedure", paragraph 4) where we point out that although size selection was chosen to be the same for all samples, it is probably that somewhat larger particles are indeed also participating in the ice nucleation process. As well, we point out (section "2 Experimental Procedure", paragraph 4) that another reason that wet atomization was used was that we could not be confident that we were not introducing much larger particles using our dry dispersal source.

3. Page 17302, 13-22. The point of this section is not clear. Are the authors making the point that only Zimmermann et al. and Atkinson et al. have studied extensively the minor components of minerals in a controlled manner? Please rewrite for clarity.

Yes, this was the point of this section. It has been re-written as follows:

"While the IN properties of the main components of mineral dusts have been examined before, the IN activities of the more minor mineralogical components have not been extensively studied in a controlled manner, with the most recent being studies by Atkinson et al. (2013) and Zimmermann et al. (2008). Firstly, Atkinson et al. (2013) focussed on the immersion IN properties of feldspar minerals, and secondly, Zimmermann et al. (2008) have used environmental scanning electron microscopy to observe ice growth on a number of mineralogical components."

4. Experimental procedure. The authors start by stating that each compound was washed twice prior to the freezing experiments. It would be more clear to state that for most experiments each compound was washed twice.

This has been clarified in section"2 Experimental Procedure", paragraph 1 as follows:

" Prior to experimentation, each compound was washed twice using Millipore water (18.2MΩ·cm). A selection of compounds (TiO_2, orthoclase, ATD, MDD) was not washed prior to experimentation in order to compare the IN properties of the washed and unwashed forms of these samples."

5. Page 17307, line 23-24. My understanding from the initial discussion is that kaolinite does not contain counterions. If this is the case, line 23-24 needs to be modified.

Thank you for pointing this out. The initial discussion of kaolinite has been moved to section “2.1.1 Clay Minerals”, paragraph 1, and has been modified as follows:

"The layers are held together by hydrogen bonds, and the surface consists of an alumina/hydroxyl sheet (Bear, 1964; Frost, 1998). As a result, the surface hydroxyl groups may be able to form hydrogen bonds with water molecules, thus causing kaolinite to be an efficient ice nucleus. Additionally, due to a low degree of isomorphic substitution of a fraction of the metal ions in the lattice by less charged metals, this clay carries a small net negative charge (1-10 mequiv/100g of clay) which is compensated by the presence of counter cations (Swartzen-Allen and Matijevic, 1974)."

As a result, the discussion of illite has been moved to section "2.1.1 Clay Minerals", paragraph 2, and has been modified as follows:

"Due to a high degree of isomorphic substitution this clay carries a large net negative charge (80-100 mequiv/100g of clay) which is compensated by the presence of counter cations (Swartzen-Allen and Matijevic, 1974)."

6. Page 17311, line 20-23. Here the authors indicate that the compounds were washed twice, implying all particles were washed twice. This statement leads to confusion since some of the particles were not washed. Also, my understanding is that soluble material inhibits ice nucleation, contrary to what the authors state here (see (Cziczo et al., 2009) and references therein).

Thank you for pointing this out. In order to avoid confusion in this section the following sentence has been added to section "Results and Discussion", paragraph 2:

" In the following discussion Sections 3.1 and 3.2 will focus on the relative IN properties of the washed samples, while Section 3.3 will compare the relative IN properties of a selection of washed and unwashed samples (TiO_2, orthoclase, ATD, MDD)."

7. Page 17313 line 7-24. The authors are making conclusions on the amount of soluble material based on the electrical conductivity measurements. To be exact, I think the authors should only make conclusions on the amount of soluble ions, not soluble material. Also on page 17304, line 10-12, the authors state that the amount of soluble material in each solution, was determined using a conductivity meter. The “amount of soluble material” should be changed to “amount of soluble ions”.

Thank you for mentioning this suggestion. This has been changed throughout the paragraph as follows:

"The other three washed samples contained a greater amount of soluble ions ($6x10^4$ - $2x10^5$ soluble ions per particle), which was less than a monolayer of ions ($5x10^5$ soluble ions per particle, assuming that a monolayer coverage is $5x10^{14}$ soluble ions/cm^2). The unwashed MDD, ATD, and orthoclase samples all contained a greater concentration of soluble ions than their washed counterparts."

8. Page 17314, lines 21-24. Can quartz also contain surface hydroxyl groups that can strongly hydrogen bond?

This is a very good point, and in order to include it the following sentences have been added to section "3.1.3 IN Properties of Other Pure Compounds", paragraph 2:

"Similarly, hydroxyl groups may be present at the surface of quartz, which would allow hydrogen bonding to occur between quartz and water molecules (Schlegel et al.,2002, and references therein). However, its poor IN activity may be attributed to its lack of structural charge. To compare, orthoclase has hydrogen bonding abilities due to the presence of surface Si-OH groups; however, this is due to the removal of potassium ions from its surface (Fenter et al., 2000). This also results in the exchange of potassium ions with protons or hydronium ions upon exposure to water (Fenter et al. 2000, and references therein). Therefore, the IN properties of orthoclase may be due to the presence of a surface charge and ions, as well as to its hydrogen bonding abilities."

9. Table 1. The uncertainties are high for a few compounds (e.g. k-feldspar and ATD). Is this due to an uncertainty in the measurements of RHi and temperature or a variability in the IN properties from day-to-day or sample-to-sample.

Because the CFDC is operated in the same manner for each experiment, we believe quite strongly that its operating conditions did not give rise to this variability. It is most likely that these uncertainties were due to a day-to-day variability in the IN properties, arising for unidentified reasons. Because each atomized solution was prepared from the same mineral or mineral dust sample this variability also demonstrates the high degree of variability in the samples themselves. For instance, it may be due to a difference in the degree of surface charge on each particle of one sample.

10. Table 1. I assume the authors want to organize the data by increasing critical RHi. However, some of the rows are out of order. For example MDD unwashed should be the second entry in the table.

We apologize for this error and have corrected Table 1.

11. I don't think Figure 1 is referred to in the main text.

Thank you for noticing this. Section "2 Experimental Procedure", paragraph 1 has been modified accordingly:

"Experiments were conducted on particles size selected at 200nm using the University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC) at a temperature of −40.0 ± 0.3°C, as illustrated in Fig. 1 (Kanji and Abbatt, 2009)."

12. Since feldspar is one of the focuses of this paper, I would like to see an activated fraction curve for feldspar included in Figure 2.

Thank you for this suggestion. An activated fraction curve for orthoclase has been added to Fig. 2.

Interactive Comment
H. Grothe et al.

Congratulations to the authors for this very nice paper. Their study investigates the ice nucleation activity of a broad set of atmospheric-relevant mineral samples in the deposition mode. The results support the hypothesis that the ice nucleation activity of natural dust is determined by the activity of single minerals such as minerals of the feldspar group. The results fit very well to results of the recent paper of Atkinson et al. (2013) who have investigated a similar set of minerals in the immersion freezing mode. Actually we have obtained almost the same result as Atkinson et al. (2013) by oil emulsion experiments partly presented at the ESF workshop "Atmospheric Ice Nucleation“ and the EGU General Assembly 2013. We think it is interesting to point out that higher activity of potassium feldspar is found for both phases (microcline and orthoclase). Actually, this indicates that the crystallographic structure is not the crucial factor determining the ice nucleation activity. Instead, the surface properties (ionicity) are the decisive factors as pointed by the authors. Our results even show that additional nucleation activity can be created by mechanical grinding. This supports the hypothesis that ice nucleation is initiated by ensembles of functional groups, which certainly need particular arrangements to be active. Another surface particularity is the difference between K- and Na-feldspar, which in principle should have a very similar surface structure as pointed out by the authors. However, all the experiments show very different ice nucleation activities e.g. in our study we find higher median freezing temperatures for microcline than for the other feldspars (andesine/Na-Ca feldspar = 240K; albite/Na-feldspar = 240K; microcline/K-feldspar = 249K). We believe that this difference can be only explained by different arrangements of water molecules in the vicinity of these cations. We think that the question, what triggers ice nucleation on a molecular level deserves more attention. Is it a particular site being responsible or is it the surface with a stochastic arrangement of functional groups structuring the first layers of water over a certain area, which is decisive?

Thank you for this comment. While the answer to this question remains unclear we hypothesize very generally that the IN properties of feldspars may be attributed to the interaction of water molecules with both the surface cations and the functional groups.

References:

Aragón Piña, A., Torres Villaseñor, G., Monroy Ferna, M., Luszczewski Kudra, A. and Leyva Ramos, R.: Scanning electron microscope and statistical analysis of suspended heavy metal particles in San Luis Potosi , Mexico, Atmospheric Environment, 34, 4103–4112, 2000.

Atkinson, J. D., Murray, B. J., Woodhouse, M. T., Whale, T. F., Baustian, K. J., Carslaw, K. S., Dobbie, S., O'Sullivan, D. and Malkin, T. L.: The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds., Nature, 498(7454), 355–358, doi:10.1038/nature12278, 2013.

Baklanov, A. M., Gorbunov, B. Z., Kakutkina, N. A., Sidorov, S. I., Silin, N. A. and Hvan, S. B.: The influence of lead iodide aerosol dispersity on its ice-forming activity, Journal of Aerosol Science, 22(1), 9–14, doi:10.1016/0021-8502(91)90089-Z, 1991.

Bear, R. E.: Chemistry of the soil, second., Reinhold Publishing Corporation, New York., 1964.

Burt, R., Wilson, M. A., Keck, T. J., Dougherty, B. D., Strom, D. E. and Lindahl, J. A.: Trace element speciation in selected smelter-contaminated soils in Anaconda and Deer Lodge Valley, Montana, USA, Advances in Environmental Research, 8, 51–67, doi:10.1016/S1093-0191(02)00140-5, 2003.

Cziczo, D. J., Froyd, K. D., Hoose, C., Jensen, E. J., Diao, M., Zondlo, M. A., Smith, J. B., Twohy, C. H. and Murphy, D. M.: Clarifying the dominant sources and mechanisms of cirrus cloud formation., Science, 340(6138), 1320–1324, doi:10.1126/science.1234145, 2013.

Fenter, P., Teng, H., Geissbuhler, P., Hanchar, J. M., Nagy, K. L. and Sturchio, N. C.: Atomic-scale structure of the orthoclase (001)- water interface measured with high-resolution X-ray reflectivity, Geochimica et Cosmochimica Acta, 64(21), 3663–3673, 2000.

Fernández, A. J., Ternero, M., Barragán, F. J. and Jiménez, J. C.: An approach to characterization of sources of urban airborne particles through heavy metal speciation, Chemosphere - Global Change Science, 2, 123–136, 2000.

Frost, R. L.: Hydroxyl deformation in kaolins, Clays and Clay Minerals, 46(3), 280–289, 1998.

Harris, F. S., Sparks, D. C. and Layton, R. G.: Nucleation of ice on lead iodide, Journal of the Atmospheric Sciences, 20, 149–152, 1963.

Kanji, Z. A. and Abbatt, J. P. D.: The University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC): A Simple Design for Ice Nucleation Studies, Aerosol Science and Technology, 43(7), 730–738, doi:10.1080/02786820902889861, 2009.

Koehler, K. A., Kreidenweis, S. M., DeMott, P. J., Prenni, A. J. and Petters, M. D.: Potential impact of Owens (dry) Lake dust on warm and cold cloud formation, Journal of Geophysical Research, 112(D12), D12210, doi:10.1029/2007JD008413, 2007.

Li, X. and Thornton, I.: Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities, Applied Geochemistry, 16(15), 1693–1706, doi:10.1016/S0883-2927(01)00065-8, 2001.

Morgan, G. M.: Technique for detecting lead particles in air, Nature, 213, 58–59, 1967.

Morgan, G. M. and Allee, P. A.: The production of potential ice nuclei by gasoline engines, Journal of Applied Meteorology, 7, 241–246, 1968.

Parungo, F. P. and Rhea, J. O.: Lead measurement in urban air as it relates to weather modification, Journal of Applied Meteorology, 9, 468–475, 1970.

Reischel, M. T.: Ice nuclei from reactions involving lead, ammonia, and iodine, Atmospheric Environment, 9, 955–958, 1975.

Schaefer, V. J.: Silver and lead iodide as ice-crystal nuclei, Journal of Meteorology, 11, 417–419, 1954.

Schaefer, V. J.: Ice nuclei from automobile exhaust and iodine vapor, Science, 154(3756), 1555–1557, doi:10.1126/science.154.3756.1555-a, 1966.

Schlegel, M. L., Nagy, K. L., Fenter, P. and Sturchio, N. C.: Structures of quatz (1010)- and (1011)-water interfaces determined by X-ray reflectivity and atomic force microscopy of natural growth surfaces, Geochimica et Cosmochimica Acta, 66(17), 3037–3054, 2002.

Swaine, D. J.: Why trace elements are important, Fuel Processing Technology, 65-66, 21–33, doi:10.1016/S0378-3820(99)00073-9, 2000.

Swartzen-Allen, S. L. and Matijevic, E.: Surface and colloid chemistry of clays, Chemical Reviews, 74(3), 385–400, doi:10.1021/cr60289a004, 1974.

Wiacek, A., Peter, T. and Lohmann, U.: The potential influence of Asian and African mineral dust on ice, mixed-phase and liquid water clouds, Atmospheric Chemistry and Physics, 10(18), 8649–8667, doi:10.5194/acp-10-8649-2010, 2010.

Zimmermann, F., Weinbruch, S., Schütz, L., Hofmann, H., Ebert, M., Kandler, K. and Worringen, A.: Ice nucleation properties of the most abundant mineral dust phases, Journal of Geophysical Research, 113, D23204, doi:10.1029/2008JD010655, 2008.