Supporting Information for Characterization of Nano-scale Mineral Dust Aerosols in Snow by Single Particle Inductively Coupled Plasma Mass Spectrometry

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Figure S1: Map showing sample locations. S1 and S2 were collected at downtown Denver (NADP site CO-06), S3 and S4 were collected in Rocky Mountain National Park (NADP Site CO-19), S5 and S6 were collected in Boulder Canyon (NADP site CO-94).



Figure S2: Effect of 1 month storage on PNC and median diameter for Al-bearing particles. Error bars represent one standard deviation of three measurements. Samples from the March 2021 precipitation events were not immediately available for analysis due to NADP sample processing times. Because the effect of storage on spICP-MS analysis is not yet clearly understood, we performed a study aimed at modeling this effect. A precipitation sample was collected in Denver by the same method (NADP sampler) and analyzed 1 day after collection (Initial). The sample was then stored in the dark at 4°C, and analyzed 2 weeks and 4 weeks after collection. Figure S2 shows a decrease in Al-bearing PNC of 29% 2 weeks after the initial analysis, and a further 8% at 4 weeks. Median particle diameter showed a similar trend, with a 21% decrease occurring after 2 weeks, and a further 2% at 4 weeks. The decrease in both particle number and median size was within the margin of error from 2 weeks to 4 weeks, indicating that most of the particle loss occurred in the first 2 weeks after sample collection. Despite storage, the majority of particles initially present in the samples were likely captured by spICP-MS analysis of samples.

Sample	spICP-TOFMS Critical Value (fg)	Fraction of particles detected on QMS with mass > TOF-MS Critical Value (%)	Ratio of PNCs from spICP- TOFMS and spICP-QMS (%)
S1	0.47	34	34
S2	0.45	19	18
S3	0.39	24	23
S4	0.45	17	17
S5	0.38	15	22
S6	0.41	15	21

Table S1: spICP-TOFMS and spICP-QMS PNC Comparison

Different sensitivities between spICP-QMS and spICP-TOFMS prohibited direct comparisons of particle numbers detected. Instead, particles detected by QMS larger than the TOFMS critical value were compared to the total particle number detected by TOFMS. For example in sample S1, 34% of the total number detected by QMS were larger than 0.47 fg. The total particle number detected by TOF (inherently above 0.47fg, the critical value) was also 34% of the total number detected by QMS. Close agreement between particle number in these fractions indicates that single particle measurements in this experiment are repeatable, even using different instrumentation.

	0.02 μm	0.02 μm	10 µm Dissolved		
	Dissolved	Dissolved (if	Concentration		
Sample	(µg/L)	Diluted) (µg/L)	(µg/L)		
S1	BDL⁺	4.4x10 ⁻⁴	0.4		
S2	0.9	0.02	0.1		
S3	0.3	1.32x10 ⁻³	0.2		
S4	0.7	0.01	BDL		
S5		8.4x10 ⁻⁴	BDL		
S6	4.4*	0.09	BDL		

*Likely an artifact of filtration such as a broken filter

⁺Below Detection Limit (0.1µg/L)

Table S2: Dissolved ²⁷Al signal from 0.02 μ m filtered samples, and hypothetical ²⁷Al concentration if 0.02 μ m filtrate had been diluted by the same factor as 10 μ m filtrate.

The effect of non-resolved particles raising the particle detection threshold is clear when examining the dissolved background measured from 0.02μ m filtered samples. This provides a more reasonable estimate of the dissolved contribution. Samples were undiluted, and 5/6 results were close to or below the instrument DL. Because the 10 μ m filtered samples were diluted 50x and 250x, applying these dilutions to the 0.02 μ m filtered samples would have produced a blank result (Column 3). This confirmed that small non-resolved particles were raising the threshold, rather than differing dissolved backgrounds between the samples.

Dilution factor	Peaks	Critical Value	Background	Mode Size	Slope (log
	Detected	(fg)	(µg/L)	(nm)	space)
10	13,400	1.11	20.0	286	-7.9
50	17,400	0.21	3.1	169	-4.9
100	15,800	0.10	1.3	137	-4.4
200	14,300	0.05	0.5	106	-3.7
500	13,600	0.02	0.1	77	-3.1
600	12,800	0.01	BDL	70	-3.0
800	12,900	0.01	BDL	64	-2.7
1000	8,800	0.01	0.1	72	-2.8

Table S3: Dilution experiment for Sample S1

To investigate the effect of dilution on both PNC and PSD, a large dilution series was performed for sample S1, ranging from 10x to 1000x. The phenomenon discussed in the paper clearly occurred, with large numbers of non-resolved particles being "uncovered" as a result of dilution. This occurred due to an artificially high threshold at low dilutions, with the lower threshold at high dilutions enabling more of the smallest particles to be analyzed. However, performing a dilution with the aim of obtaining the "true" particle number is complex for a natural, polydisperse sample. Instead of decreasing in proportion to dilution factor, particle numbers are low at the upper end of the PSD, making us less confident in PSD shape at larger sizes. The 200-600 dilution factors therefore represent the balance of managing coincidence at small sizes, and particle detection at large sizes.



Figure S3: The mode of each sample's PSD (replicates included) from QMS plotted against the particle detection threshold (replicates included).

The decision to consider particle sizes only above the mode of the was made based on the high correlation between sample mode and particle detection threshold. When filtered through a 0.2µm filter (to better approximate the dissolved Al background) the samples did not contain significant background levels (with the exception of S6, which was likely due to a sample preparation error). Without a difference in dissolved Al background, the particle detection thresholds should not have differed, as the purpose of the threshold is to differentiate dissolved signal from particle-generated signals. However, there were differences in threshold, likely due to small, non-resolved particles that generated a signal similar to a dissolved background. Therefore, we determined that the threshold was not a reliable parameter of the sample.

Furthermore, examining the shape of the PSDs between the threshold and the mode revealed similar patterns. Because there is noise associated with the signal generated from a particle of a given size, it is therefore impossible to measure all NPs at the size detection limit. The low numbers of particles near the threshold indicate that this is occurring, and the sharp increase that follows represents the increasing proportion of particles being recorded. Because the sample mode is correlated to the threshold, and because the shape of the distribution beyond the mode follows the Pareto distribution, we determined that data below the mode was influenced by analytical noise and should not be reported quantitatively.



Figure S4: PSD comparison between spICP-MS and SPOS

While spICP-MS was successful in characterizing nano-scale MDA, μ m sized particles cannot be accurately measured due to both low transport into the plasma, and incomplete ionization. Therefore, to gain insight into this larger fraction, Single Particle Optical Scanning (SPOS) was used to quantify this fraction of particles. Both PNC and PSD results were similar for particles analyzed by SPOS (1-10um). When the same data processing was applied, the slope in log space was similar (-2.87), suggesting that MDA follow the Pareto distribution at the μ m scale. A rolling 10-bin average was plotted for SPOS data, resulting in some values <1 on the y axis.



Figure S5: Dilution Experiment PSDs

PSDs for each dilution were plotted as dN/dD vs. Diameter above the mode in log space. Analysis of PSD slope in log space showed agreement with the Pareto distribution beyond a dilution factor of 200x (numbers given in Table S3). Therefore, we conclude that analysis of PSDs does not depend on obtaining the most accurate PNC measurement, and significant numbers of non-resolved particles still permit effective PSD analysis. However, excessive numbers of non-resolved particles eventually affect the PSD shape (PSDs are distorted below a dilution factor of 200x).

Table S4 spICP-TOFMS Operating Conditions

Sample Flow Rate	45 μL min ⁻¹
Nebulizer Gas (Ar)	1.0 L min ⁻¹
Auxillary Gas Flow (Ar)	1.2 L min ⁻¹
Cooling Gas Flow	14.5 L min ⁻¹
Plasma Power	1400 W
Sampling Depth	5.75 mm
Reaction Gas	H ₂
Masses Notched	18.4, 32.5, 38.65
TOF Extraction Frequency	83.3 kHz
Averaged Spectrum Acquisition Time	1.2 ms
Measurement Time	90 s
q _{Plasma} (mL/s)	0.132 μL s ⁻¹
Neb TE %	17.6%

Table S5. Isotopes used, Sensitivies, and $L_{C,\text{sp}}$ values for all samples

			Critical Values (<i>L_{C,sp}</i>) in mass (fg)					
Element Name	lsotopes Used	Sensitivity (counts fg ⁻¹)	S1	S2	S 3	S4	S 5	S6
Mg	²⁴ Mg	n/a						
Al	²⁷ AI	23.14	0.47	0.45	0.39	0.45	0.38	0.41
Ti	⁴⁸ Ti	47.03	0.18	0.18	0.16	0.19	0.16	0.20
Mn	⁵⁵ Mn	155.5	0.07	0.07	0.07	0.07	0.07	0.09
Fe	⁵⁶ Fe	134.7	0.19	0.15	0.16	0.17	0.15	0.17
Cu	⁶³ Cu, ⁶⁵ Cu	90.93	0.16	0.15	0.16	0.17	0.15	0.17
Zn	⁶⁶ Zn	22.76	0.47	0.54	0.44	0.49	0.46	0.53
Rb	⁸⁵ Rb	n/a						
Υ	⁸⁹ Y	243	0.031	0.030	0.028	0.032	0.031	0.032
Zr	⁹⁰ Zr	107	0.067	0.066	0.061	0.066	0.063	0.066
Nb	⁹³ Nb	161.6	0.055	0.055	0.059	0.059	0.055	0.058
Cs	¹³³ Cs	337	0.028	0.027	0.026	0.027	0.028	0.028
Ва	¹³⁸ Ba	n/a						
La	¹³⁹ La	564.3	0.014	0.013	0.013	0.013	0.014	0.014
Ce	¹⁴⁰ Ce	591.6	0.012	0.011	0.011	0.012	0.012	0.013
Nd	¹⁴⁴ Nd, ¹⁴⁶ Nd	159.1	0.045	0.045	0.045	0.045	0.049	0.048
Pb	²⁰⁷ Pb, ²⁰⁸ Pb	294.6	0.028	0.026	0.029	0.028	0.028	0.028
Th	²³² Th	223	0.026	0.027	0.028	0.027	0.026	0.027
U	²³⁸ U	237.5	0.026	0.025	0.026	0.025	0.026	0.026



Figure S6. Overall PNCs (particles mL⁻¹) of both smNPs and mmNPs found for each sample via spICP-TOFMS anlaysis. These PNCs include the 19 elements reported in Table S5. The relative differences in PNCs between the samples matches well with that found with Al-NP detection via spICP-QMS (see Figure 1).



Figure S7: Particle Number Concentration (PNC) normalized to that of Fe, the most abundant particle type in each sample.

spICP-TOFMS data was combined for each sample, as the major element composition was similar across samples. This is shown by normalizing element specific PNCs to iron. For the major elements examined in the study (Mg, Al, Ti, Fe), relative PNCs did not vary significantly between samples. Trace elements showed differences in PNC between samples, but this was likely an artifact of the low number of particles recorded for these elements.



Figure S8: Dendrogram resulting from the two-stage unsupervised hierarchical clustering analysis (HCA). In the text (Figure 4), we extract data from the two clusters with the highest number of particles: labeled here as the crustal-ratio cluster and the Ti-rich cluster. The heat map indicates the occurrence-normalized mean mass of each element in the found clusters and the PNCs (particles mL⁻¹) of each cluster are provided as bars on the righthand side. In the HCA heatmap of mean masses of elements in clusters, the mass of Mg is semi-quantitative because the sensitivity of ²⁴Mg+ was estimated based on the calibrated sensitivity of ²⁷Al+.



Figure S9: Grain viewer image from mineralogy analysis, filtered to show each of the particle classes detected by spICP-TOFMS.

Automated Mineralogy analysis detected the same multi-metal particle classes seen on spICP-TOFMS. The grain viewer image above shows that all three major particle classes were detected across a large range in particle size (5-100 μ m). This suggests that mineralogy was not size dependent, and thus validates AM as a complimentary technique to spICP-TOFMS.