

Table S1: Classification criteria for the single particle analysis. The classification is based on ratio criteria derived from the chemical quantification for each particle. Each elemental quantification value is noted as their chemical symbol. The ratios are given as atomic fraction values. Square brackets indicate a validity interval for a ratio. All criteria must be matched to qualify a particle for the according class/group. Processing stops at the first positive qualification. If a ratio value needs to be in an interval, the boundaries are given in square brackets. The symbol AE stands for the sum Na+Mg+Al+Si+P+S+Cl+K+Ca+Ti+Cr+Mn+Fe. If there is a size restriction applying, it is shown in the fourth column. The last column shows the pure compounds (including the elemental tracer in parentheses, if applicable) based on which the refractive index

was calculated by volume weighted averaging: sulf = ammonium sulfate (S) (mascagnite), soot = flame soot, calc = calcium carbonate (Ca), hem = hematite (Fe), sil = modified kaolinite (Si) (see text for details), nchl = sodium chloride (Cl), kchl = potassium chloride, rut = titanium dioxide (Ti) (rutile), qtz = quartz (Si). A "-" means that particles were neglected for refractive index calculation.

\*For the classification of these groups besides the chemical criteria in addition morphological criteria were used.

\*\*As the soot/ammonium sulfate mixture could not be quantified by chemical analysis, a fixed soot volume fraction  $V_S$  derived from TEM measurements was used: mineral dust situation in Praia  $V_S = 0.13$ , maritime situation in Praia  $V_S = 0.29$ , airborne measurements  $V_S = 0.2$

<i>class</i>	<i>group</i>	<i>criteria</i>	<i>size range (μm)</i>	<i>refractive index</i>
other	biological*	(K+Na+S+P+Ca)/AE=[0.4;1.1], P/AE=[0.05;0.8], Na/AE=[0.05;0.8], Ca/AE=[0.05;1.1], K/AE=[0.025;0.8], S/AE=[0.025;0.8], Mg/(Na+S+P+Ca)<0.1, Al/(Na+S+P+Ca)<0.05, Si/(Na+S+P+Ca)<0.1, Cl/(Na+S+P+Ca)<0.05, Ti/(Na+S+P+Ca)<0.05, Cr/(Na+S+P+Ca)<0.05, Mn/(Na+S+P+Ca)<0.05, Fe/(Na+S+P+Ca)<0.1	d>0.3	–
secondary	Na-rich*	Na/AE=[0.2;1.1], Cl/AE<0.02499, Mg/Na<1.1, Al/Na<0.75, Si/Na<0.25, P/Na<0.1, S/Na<0.1, C/Na<0.05, K/Na<0.5, Ca/Na<0.5, Ti/Na<0.05, Cr/Na<0.05, Mn/Na<0.1, Fe/Na<0.1		sulf
secondary	ammonium sulfate*	S/AE=[0.3;1.1], Na/S<0.1, Mg/S<0.1, Al/S<0.2, Si/S<0.25, P/S<0.1, Cl/S<0.1, K/S<0.1, Ca/S<0.1, Ti/S<0.05, Cr/S<0.05, Mn/S<0.05, Fe/S<0.1		sulf
soot mixtures	soot*	Mg/AE<0.05, K/AE<0.3, S/AE<0.05, Al/AE<0.05, Fe/AE<0.03, Cl/AE<0.05, Cl/Si<0.05	0.03<d<0.20	soot
soot mixtures	soot+ammonium sulfate*	Mg/AE<0.05, Si/AE<1.1, K/AE<0.3, S/AE=[0.05;1.1], Al/AE<0.05, Fe/AE<0.03, Cl/AE<0.05, Cl/Si<0.05	0.03<d<0.20	sulf+soot**
sulfates	Na sulfate	Na/S=[0.101;10], (Na+S)/AE=[0.1;1.1], Na/AE=[0.025;1.1], S/AE=[0.025;1.1], Mg/(S+Na)<0.5, Al/(S+Na)<0.1, Si/(S+Na)<0.15, P/(S+Na)<0.5, Cl/(S+Na)<0.1, K/(S+Na)<0.1, Ca/(S+Na)<0.05, Ti/(S+Na)<0.05, Cr/(S+Na)<0.05, Mn/(S+Na)<0.5, Fe/(S+Na)<0.1		sulf
sulfates	Ca Na sulfate	(Na+S+Ca)/AE=[0.15;1.1], Na/AE=[0.025;1.1], S/AE=[0.025;1.1], Ca/AE=[0.025;1.1], Na/Ca=[0.1;10], Mg/(S+Na+Ca)<0.5, Al/(S+Na+Ca)<0.05, Si/(S+Na+Ca)<0.05, P/(S+Na+Ca)<0.2, Cl/(S+Na+Ca)<0.1, K/(S+Na+Ca)<0.1, Ti/(S+Na+Ca)<0.05, Cr/(S+Na+Ca)<0.1, Mn/(S+Na+Ca)<0.5, Fe/(S+Na+Ca)<0.1, Ca/(S+Na)=[0.1001;10]		sulf
sulfates	Ca sulfate	Ca/S=[0.20;10], (Ca+S)/AE=[0.2;1.1], Na/(Ca+S)<0.1, Mg/(S+Ca)<0.35, Al/(S+Ca)<0.1, Si/(S+Ca)<0.1, P/(S+Ca)<0.1, Cl/(S+Ca)<0.1, K/(S+Ca)<0.1, Ti/(S+Ca)<0.05, Cr/(S+Ca)<0.05, Mn/(S+Ca)<0.5, Fe/(S+Ca)<0.1		calc
sulfates	other sulfate	S/AE=[0.2;1.1], Na/S<2, Mg/S<2, Al/S<2.5, Si/S<0.25, P/S<0.2, Cl/S<0.2, K/S<10, Ca/S<2, Ti/S<0.5, Cr/S<0.5, Mn/S<2, Fe/S<2		sulf
carbonates	Ca carbonate	Ca/AE=[0.2;1.1], Na/Ca<0.11, Mg/Ca<0.5, Al/Ca<0.151, Si/Ca<0.11, P/Ca<0.1, S/Ca<0.1, Cl/Ca<0.1, K/Ca<0.1, Ti/Ca<0.1, Cr/Ca<0.05, Mn/Ca<0.5, Fe/Ca<0.1		hem+sil+calc
carbonates	Ca Mg carbonate	(Ca+Mg)/AE=[0.4;1.1], Mg/Ca=[0.501;2], Na/(Ca+Mg)<0.5, Al/(Ca+Mg)<0.1, Si/(Ca+Mg)<0.2, P/(Ca+Mg)<0.1, S/(Ca+Mg)<0.1, Cl/(Ca+Mg)<0.1, Ti/(Ca+Mg)<0.1, Cr/(Ca+Mg)<0.05, Fe/(Ca+Mg)<0.1		hem+sil+calc
phosphates	phosphate	P/AE=[0.05;1.1], Al/(Ca+P)<0.2, Si/(Ca+P)<0.1		–
chlorides	Na chloride	(Na+Cl)/AE=[0.25;1.1], Na/AE=[0.01;1.1], Cl/AE=[0.01;1.1], Si/AE<0.0499, Al/AE<0.0299, Mg/(Na+Cl)<2, P/(Na+Cl)<0.2, S/(Na+Cl)<0.25, K/(Na+Cl)<0.15, Ti/(Na+Cl)<0.25, Cr/(Na+Cl)<0.25, Mn/(Na+Cl)<2, Fe/(Na+Cl)<0.25		nchl+sulf
chlorides	K chloride	(K+Cl)/AE=[0.3;1.1], Na/AE=[0.01;1.1], Cl/AE=[0.01;1.1], Na/(K+Cl)<0.15, Mg/(K+Cl)<0.1, Al/(K+Cl)<0.2, Si/(K+Cl)<0.25, P/(K+Cl)<0.2, S/(K+Cl)<0.25, Ca/(K+Cl)<0.5, Ti/(K+Cl)<0.25, Cr/(K+Cl)<0.25, Mn/(K+Cl)<2, Fe/(K+Cl)<0.25		kchl
chlorides	other chloride	Cl/AE=[0.25;1.1], Si/AE<0.0699, Al/AE<0.0099, Na/Cl<2, Mg/Cl<2, P/Cl<0.1, S/Cl<0.2, K/Cl<2, Ca/Cl<2, Ti/Cl<0.1, Cr/Cl<0.1, Mn/Cl<2, Fe/Cl<10		–
oxides	Fe oxide	Fe/AE=[0.25;1.1], Na/Fe<0.1, Mg/Fe<0.25, Al/Fe<0.2, Si/Fe<0.25, P/Fe<0.2, S/Fe<0.2, Cl/Fe<0.1, K/(Fe<0.1, Ca/Fe<0.1, Ti/Fe<0.25, Cr/Fe<0.05, Mn/Fe<1		hem+sil
oxides	Ti oxide	Ti/AE=[0.25;1.1], Na/Ti<0.18, Mg/Ti<0.1, Al/Ti<0.2, Si/Ti<0.25, P/Ti<0.2, S/Ti<0.2, Cl/Ti<0.1, K/Ti<0.1, Ca/Ti<0.1, Cr/Ti<0.05, Mn/Ti<0.25, Fe/Ti<0.25		rut+sil
oxides	Fe Ti oxide	Ti/Fe=[0.2501;4], (Fe+Ti)/AE=[0.25;1.1], Na/(Ti+Fe)<0.2, Mg/(Ti+Fe)<0.1, Al/(Ti+Fe)<0.2, Si/(Ti+Fe)<0.25, P/(Ti+Fe)<0.2, S/(Ti+Fe)<0.2, Cl/(Ti+Fe)<0.1, K/(Ti+Fe)<0.1, Ca/(Ti+Fe)<0.1, Cr/(Ti+Fe)<0.05, Mn/(Ti+Fe)<0.05		rut+sil
oxides	Al oxide	Al/AE=[0.2;1.1], Na/Al<0.2, Mg/Al<0.1, Si/Al<0.2499, P/Al<0.2, S/Al<0.2, Cl/Al<0.1, K/Al<0.1, Ca/Al<0.1, Ti/Al<0.1, Fe/Al<1		–
quartz	quartz	Si/AE=[0.4;1.1], Al/Si<0.2, Na/Si<0.1, Mg/Si<0.1, P/Si<0.2, S/Si<0.2, Cl/Si<0.05, K/Si<0.1, Ca/Si<0.05, Ti/Si<0.1, Cr/Si<0.05, Mn/Si<0.25, Fe/Si<0.1	d>0.2	hem+qtz
silicates	SiAl	Al/Si=[0.201;4], (Al+Si)/AE=[0.4;1.1], Al/AE=[0.05;1.1], Na/(Si+Al)<0.05, Mg/(Si+Al)<0.05, P/(Si+Al)<0.2, S/(Si+Al)<0.2, Cl/(Si+Al)<0.1, K/(Si+Al)<0.05, Ca/(Si+Al)<0.05, Ti/(Si+Al)<0.1, Cr/(Si+Al)<0.1, Mn/(Si+Al)<0.5, Fe/(Si+Al)<0.1		hem+sil
silicates	SiAlK	K/(Si+Al)=[0.101;3], Al/Si=[0.2;2], (K+Al+Si)/AE=[0.4;1.1], K/AE=[0.0025;1.1], Na/(Si+Al+K)<0.05, Mg/(Si+Al+K)<0.08, P/(Si+Al+K)<0.2, S/(Si+Al+K)<0.1, Cl/(Si+Al+K)<0.1, Ca/(Si+Al+K)<0.1, Ti/(Si+Al+K)<0.05, Cr/(Si+Al+K)<0.05, Mn/(Si+Al+K)<0.05, Fe/(Si+Al+K)<0.05		hem+sil
silicates	SiAlNa	Na/(Si+Al)=[0.101;3], Al/Si=[0.2;2], Ca/Na<0.25, (Na+Al+Si)/AE=[0.4;1.1], Mg/(Si+Al+Na)<0.15, P/(Si+Al+Na)<0.2, S/(Si+Al+Na)<0.1, Cl/(Si+Al+Na)<0.05, K/(Si+Al+Na)<0.05, Ca/(Si+Al+Na)<0.05, Ti/(Si+Al+Na)<0.05, Cr/(Si+Al+Na)<0.05, Mn/(Si+Al+Na)<0.05, Fe/(Si+Al+Na)<0.15		hem+sil
silicates	SiAlNaCa	(Ca+Na)/(Si+Al)=[0.101;3], Ca/(Si+Al)=[0.101;3], Al/Si=[0.2;2], Ca/Na=[0.2501;5.5], (Na+Ca+Al+Si)/AE=[0.4;1.1], Mg/(Si+Al+Na+Ca)<0.1, P/(Si+Al+Na+Ca)<0.2, S/(Si+Al+Na+Ca)<0.2, Cl/(Si+Al+Na+Ca)<0.05, K/(Si+Al+Na+Ca)<0.1, Ti/(Si+Al+Na+Ca)<0.05, Cr/(Si+Al+Na+Ca)<0.05, Mn/(Si+Al+Na+Ca)<0.05, Fe/(Si+Al+Na+Ca)<0.1		hem+sil+calc
silicates	SiAlNaK	(K+Na)/(Si+Al)=[0.101;3], Al/Si=[0.2;2], K/Na=[0.25;4], (K+Na+Al+Si)/AE=[0.4;1.1], Na/AE=[0.05;1.1], K/AE=[0.05;1.1], Mg/(Si+Al+Na+K)<0.05, P/(Si+Al+Na+K)<0.2, S/(Si+Al+Na+K)<0.2, Cl/(Si+Al+Na+K)<0.05, Ca/(Si+Al+Na+K)<0.1, Ti/(Si+Al+Na+K)<0.05, Cr/(Si+Al+Na+K)<0.05, Mn/(Si+Al+Na+K)<0.05, Fe/(Si+Al+Na+K)<0.05		hem+sil
silicates	SiAlCaFeMg	(Ca+Fe+Mg)/(Si+Al)=[0.101;3], Al/Si=[0.2;2], Ca/(Fe+Mg)=[0.25;10], (Ca+Fe+Mg+Al+Si)/AE=[0.4;1.1], Ca/AE=[0.05;1.1], Fe/AE=[0.025;1.1], Mg/AE=[0.025;1.1], Ca/(Si+Al)<0.5, Na/(Si+Al+Ca+Fe+Mg)<0.05, P/(Si+Al+Ca+Fe+Mg)<0.2, S/(Si+Al+Ca+Fe+Mg)<0.2, Cl/(Si+Al+Ca+Fe+Mg)<0.1, K/(Si+Al+Ca+Fe+Mg)<0.05, Ti/(Si+Al+Ca+Fe+Mg)<0.05, Cr/(Si+Al+Ca+Fe+Mg)<0.05, Mn/(Si+Al+Ca+Fe+Mg)<0.05		hem+sil+calc
silicates	SiAlKFeMg	(K+Fe+Mg)/(Si+Al)=[0.101;3], K/(Si+Al)=[0.101;3], (Fe+Mg)/(Si+Al)=[0.101;3], K/(Fe+Mg)=[0.25;4], (K+Mg+Fe+Al+Si)/AE=[0.4;1.1], Ca/AE<0.05, Na/(Si+Al+K+Fe+Mg)<0.1, P/(Si+Al+K+Fe+Mg)<0.2, S/(Si+Al+K+Fe+Mg)<0.2, Cl/(Si+Al+K+Fe+Mg)<0.1, Ca/(Si+Al+K+Fe+Mg)<0.05, Ti/(Si+Al+K+Fe+Mg)<0.05, Cr/(Si+Al+K+Fe+Mg)<0.05, Mn/(Si+Al+K+Fe+Mg)<0.05		hem+sil
silicates	SiAlFeMg	Al/AE=[0.1;0.8], Fe/AE=[0.05;0.8], Mg/AE=[0.05;0.8], Ca/AE<0.05, (Fe+Mg)/(Si+Al)=[0.101;3], Al/Si=[0.201;2], K/(Si+Al)<0.1, (Al+Si+Fe+Mg)/AE=[0.5;1.1], Na/(Si+Al+Fe+Mg)<0.05, P/(Si+Al+Fe+Mg)<0.2, S/(Si+Al+Fe+Mg)<0.2, Cl/(Si+Al+Fe+Mg)<0.05, K/(Si+Al+Fe+Mg)<0.1, Ca/(Si+Al+Fe+Mg)<0.1, Ti/(Si+Al+Fe+Mg)<0.05, Cr/(Si+Al+Fe+Mg)<0.05, Mn/(Si+Al+Fe+Mg)<0.05		hem+sil
silicates	SiMgFe	Fe/(Si+Mg)=[0.201;10], (Mg+Fe)/Si=[0.25;4], Al/Si<0.2, (Fe+Mg+Si)/AE=[0.4;1.1], Na/(Si+Fe+Mg)<0.1, Al/(Si+Fe+Mg)<0.05, P/(Si+Fe+Mg)<0.2, S/(Si+Fe+Mg)<0.2, Cl/(Si+Fe+Mg)<0.1, K/(Si+Fe+Mg)<0.1, Ca/(Si+Fe+Mg)<0.1, Ti/(Si+Fe+Mg)<0.05, Cr/(Si+Fe+Mg)<0.05, Mn/(Si+Fe+Mg)<0.05		hem+sil
silicates	SiMg	Mg/Si=[0.25;4], Al/Si<0.2, (Mg+Si)/AE=[0.4;1.1], Na/(Si+Mg)<0.1, Al/(Si+Mg)<0.1, P/(Si+Mg)<0.2, S/(Si+Mg)<0.2, Cl/(Si+Mg)<0.1, K/(Si+Mg)<0.1, Ca/(Si+Mg)<0.1, Ti/(Si+Mg)<0.05, Cr/(Si+Mg)<0.05, Mn/(Si+Mg)<0.05, Fe/(Si+Mg)<0.2		hem+sil
silicates	SiCaTi	Ca/Ti=[0.25;4], Al/Si<0.2, (Si+Ca+Ti)/AE=[0.4;1.1], Ca/Si=[0.101;10], Ti/Si=[0.101;10], Na/(Si+Ca+Ti)<0.1, Mg/(Si+Ca+Ti)<0.1, P/(Si+Ca+Ti)<0.2, S/(Si+Ca+Ti)<0.2, Cl/(Si+Ca+Ti)<0.1, K/(Si+Ca+Ti)<0.1, Cr/(Si+Ca+Ti)<0.05, Mn/(Si+Ca+Ti)<0.05, Fe/(Si+Ca+Ti)<0.2		rut+sil
mixtures	mixtures Si+S	Al/AE<0.05, S/AE=[0.05;0.9], S/Si=[0.5;4], Al/Si<0.2, (Si+S)/AE=[0.3;1.1], Na/(Si+S)<2, Mg/(Si+S)<2, Al/(Si+S)<0.2, P/(Si+S)<0.2, Cl/(Si+S)<0.05, K/(Si+S)<2, Ca/(Si+S)<2, Ti/(Si+S)<0.2, Cr/(Si+S)<0.1, Mn/(Si+S)<0.1, Fe/(Si+S)<5	d>0.2	hem+sil+sulf
mixtures	mixtures AlSi+S	Al/AE=[0.05;0.9], Si/AE=[0.1;0.9], S/AE=[0.1;0.9], S/Si=[0.5;10], Al/Si=[0.201;5], (Al+Si+S)/AE=[0.3;1.1], Na/(Al+Si+S)<5, Mg/(Al+Si+S)<5, P/(Al+Si+S)<0.2, Cl/(Al+Si+S)<0.05, K/(Al+Si+S)<5, Ca/(Al+Si+S)<5, Ti/(Al+Si+S)<0.2, Cr/(Al+Si+S)<0.2, Mn/(Al+Si+S)<0.2, Fe/(Al+Si+S)<5		hem+sil+sulf
mixtures	mixtures Cl+S	Cl/S=[0.201;10], (S+Cl)/AE=[0.2;1.1], Cl/AE=[0.025;1.1], S/AE=[0.025;1.1], S/(Na+Cl)=[0.1;20], Na/(S+Cl)<3, Mg/(S+Cl)<3, Al/(S+Cl)<0.2, Si/(S+Cl)<0.25, P/(S+Cl)<0.25, K/(S+Cl)<3, Fe/(S+Cl)<2		nchl+sulf
mixtures	mixtures NaCl+Si	Si/(Na+Cl)=[0.05;100], Al/Si<0.2, (Na+Na+Cl)/AE=[0.2;1.1], Cl/AE=[0.05;1.1], Na/AE=[0.05;1.1], Si/AE=[0.01;1.1]		hem+sil+nchl+sulf
mixtures	mixtures NaCl+AlSi	(Si+Al)/(Na+Cl)=[0.075;100], Al/Si=[0.201;100], (Si+Na+Cl)/AE=[0.2;1.1], Cl/AE=[0.05;1.1], Na/AE=[0.05;1.1], Si/AE=[0.025;1.1], Al/AE=[0.01;1.1]		hem+sil+nchl+sulf
mixtures	mixtures Ca+Si	Si/Ca=[0.2501;4], Al/Si<0.2, (Ca+Si)/AE=[0.2;1.1], Si/AE=[0.01;1.1], Ca/AE=[0.05;1.1], Si/Ca=[0.1001;100], Mg/(Si+Ca)<0.1, Al/(Si+Ca)<0.2, P/(Si+Ca)<0.2, S/(Si+Ca)<0.2		hem+sil+calc
mixtures	mixtures Ca+AlSi	Al/Si=[0.201;20], (Ca+Si+Al)/AE=[0.2;1.1], Al/AE=[0.01;1.1], Si/AE=[0.01;1.1], Ca/AE=[0.05;1.1], Si/Ca=[0.1001;100], Na/(Si+Ca)<0.2, Mg/(Si+Ca)<2, P/(Si+Ca)<0.2, S/(Si+Ca)<0.2, Cl/(Si+Ca)<0.05, K/(Si+Ca)<1		hem+sil+calc
silicates	other Si-dominated	Si/AE=[0.1;1.1]		hem+sil+sulf
other	steel	(Fe+Ti+Mn+Cr)/AE=[0.2;1.1], Fe/AE=[0.2;1.1]		–
other	other Mg-dominated	Mg/AE=[0.35;1.1]		–
other	other K-dominated	K/AE=[0.25;1.1]		–
other	other Ca-dominated	Ca/AE=[0.15;1.1]		–
other	other			–