Supplementary information: Solvent and cosolute dependence of Mg surface enrichment in submicron aerosol particles

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1 Details of "Method 2"

The number of Ca atoms per each Cl atom (X_{Ca}) at the surface of mixed $\mathrm{CaCl_2}$/$\mathrm{MgCl_2}$ particles from solution i is obtained by normalisation of the peak area ratio to that in pure $\mathrm{CaCl_2}$ reference p as

$$X_{\mathrm{Ca}} = \frac{A^i_{\mathrm{Ca3p}}/A^i_{\mathrm{Cl3s}}}{A^p_{\mathrm{Ca3p}}/A^p_{\mathrm{Cl3s}}} \cdot \frac{1}{2}. \tag{1}$$

Similarly, the number of Mg atoms per each Cl atom is

$$X_{\mathrm{Mg}} = \frac{A^i_{\mathrm{Mg2p}}/A^i_{\mathrm{Cl3s}}}{A^p_{\mathrm{Mg2p}}/A^p_{\mathrm{Cl3s}}} \cdot \frac{1}{2}. \tag{2}$$

The 1/2 multiplications account for the ion stoichiometry. The at%s are then

$$\mathrm{at\%(Ca)} = 100 \cdot \frac{X_{\mathrm{Ca}}}{X_{\mathrm{Ca}} + X_{\mathrm{Mg}} + X_{\mathrm{Cl}}}, \tag{3}$$

$$\mathrm{at\%(Mg)} = 100 \cdot \frac{X_{\mathrm{Mg}}}{X_{\mathrm{Ca}} + X_{\mathrm{Mg}} + X_{\mathrm{Cl}}}, \tag{4}$$

and

$$\mathrm{at\%(Cl)} = 100\% - \mathrm{at\%(Ca)} - \mathrm{at\%(Mg)}, \tag{5}$$

where $X_{Cl} = 1$. Similarly for NaBr/$\mathrm{MgBr_2}$ particles, one has

$$X_{\mathrm{Na}} = \frac{A^i_{\mathrm{Na2p}}/A^i_{\mathrm{Br3d}}}{A^p_{\mathrm{Na2p}}/A^p_{\mathrm{Br3d}}} \cdot \frac{1}{1} \tag{6}$$

and

$$X_{\mathrm{Mg}} = \frac{A^i_{\mathrm{Mg2p}}/A^i_{\mathrm{Br3d}}}{A^p_{\mathrm{Mg2p}}/A^p_{\mathrm{Br3d}}} \cdot \frac{1}{2}. \tag{7}$$

Then

$$\mathrm{at\%(Na)} = 100 \cdot \frac{X_{\mathrm{Na}}}{X_{\mathrm{Na}} + X_{\mathrm{Mg}} + X_{\mathrm{Br}}}, \tag{8}$$

$$\mathrm{at\%(Mg)} = 100 \cdot \frac{X_{\mathrm{Mg}}}{X_{\mathrm{Na}} + X_{\mathrm{Mg}} + X_{\mathrm{Br}}}, \tag{9}$$

$$\mathrm{at\%(Br)} = 100\% - \mathrm{at\%(Na)} - \mathrm{at\%(Mg)}. \tag{10}$$

2 Binding energies

The BEs are plotted in Fig. 1 as a function of the solute mixing ratio, obtained from single peak fits to the spectra, although it is apparent that the photoelectron peaks represent the full structural diversity at the particle surface and more than a single well-defined chemical state is expected. As noted in the main article, direct comparison of the BEs to other reference systems is not straightforward due to potential charging of the particles. We may however note that the observed BEs do not agree with those reported from aqueous solutions even if shifting of the energy scale is allowed for to account for a calibration offset. This indicates that the particle surface structure differs from that of aqueous solutions, which is in line with that the estimated water content is low.

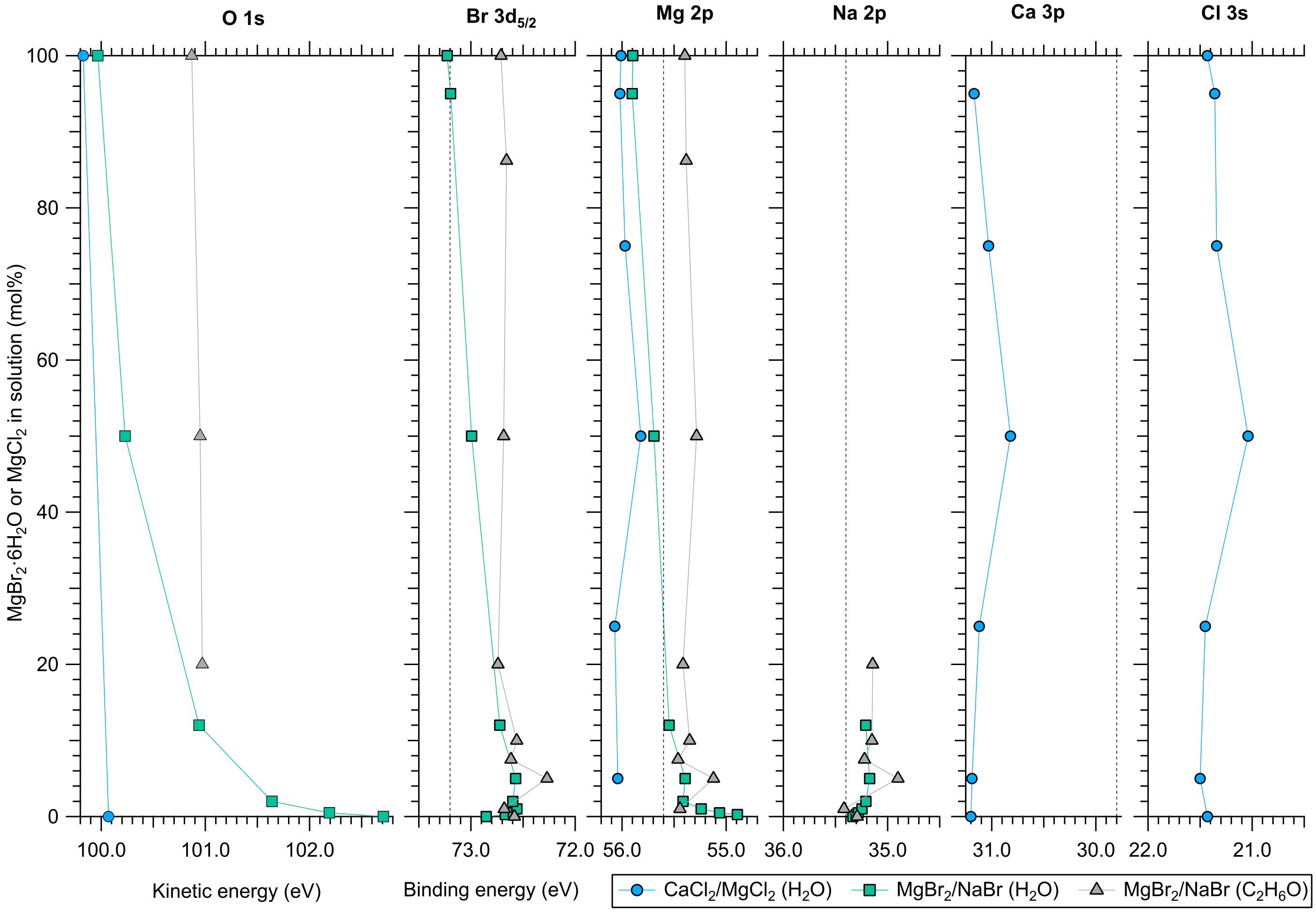

Figure 1 BEs as a function of the mixing ratio in bulk solution. For comparison, BEs of ions in aqueous solutions are indicated by the dotted lines for Ca^{2+} 3p[1], Mg^{2+} 2p[2], Na^{+} 2s[3], Na^{+} 2p[3] and Br^{-} 3d[3]. For Cl 3s a range of values has been given (see e.g. Ref. 4 and Refs. therein).

3 Details of the prepared solutions

Details of the prepared solutions are given in table 1.

Table 1 Details of the atomized solutions. Concentrations are calculated using the following molar masses: $M_{mol}(MgCl_2) = 95.211$ g/mol, $M_{mol}(CaCl_2 \cdot 2H_2O) = 146.98$ g/mol, $M_{mol}(MgBr_2 \cdot 6H_2O) = 292.204$ g/mol, $M_{mol}(NaBr) = 102.89$ g/mol. GM = Geometric Mean size and GSD = Geometric Standard Deviation of the number concentration measurement with the SMPS.

Spec.	Solvent	Solute 1			Solute 2			Total		GM	GSD
#			mmol/L	mol%		mmol/L	mol%	g/L	mmol/L	nm	
1, 29	H_2O	$MgCl_2$	20.96	**100**				2.0	20.96		
2	H_2O	$MgCl_2$	19.13	**95**	$CaCl_2 \cdot 2H_2O$	1.01	**5**	2.0	20.15		
3	H_2O	$MgCl_2$	13.85	**75**	$CaCl_2 \cdot 2H_2O$	4.63	**25**	2.0	18.48		
4	H_2O	$MgCl_2$	8.16	**50**	$CaCl_2 \cdot 2H_2O$	8.18	**50**	2.0	16.35	180	1.8
5	H_2O	$MgCl_2$	3.73	**25**	$CaCl_2 \cdot 2H_2O$	11.18	**75**	2.0	14.91		
6	H_2O	$MgCl_2$	0.70	**5**	$CaCl_2 \cdot 2H_2O$	13.29	**95**	2.0	13.99		
7, 30	H_2O				$CaCl_2 \cdot 2H_2O$	13.76	**100**	2.0	13.76	170	1.7
8	H_2O	Pure water									
9	H_2O	$MgBr_2 \cdot 6H_2O$	17.39	**100**				5.1	17.39	170	1.7
10	H_2O	$MgBr_2 \cdot 6H_2O$	17.40	**95**	NaBr	0.95	**5**	5.2	18.35	170	1.7
11, 32	H_2O	$MgBr_2 \cdot 6H_2O$	12.68	**50**	NaBr	12.80	**50**	5.0	25.48	190	1.7
12, 33	H_2O	$MgBr_2 \cdot 6H_2O$	4.78	**12**	NaBr	35.03	**88**	5.0	39.81		
13	H_2O	$MgBr_2 \cdot 6H_2O$	2.29	**5**	NaBr	42.46	**95**	5.0	44.76	180	1.6
14, 34	H_2O	$MgBr_2 \cdot 6H_2O$	0.94	**2**	NaBr	45.93	**98**	5.0	46.87	200	1.7
15	H_2O	$MgBr_2 \cdot 6H_2O$	0.47	**1**	NaBr	45.73	**99**	4.8	46.20	170	1.7
16, 35	H_2O	$MgBr_2 \cdot 6H_2O$	0.23	**0.5**	NaBr	45.33	**99.5**	4.7	45.56	140	1.6
17	H_2O	$MgBr_2 \cdot 6H_2O$	0.12	**0.25**	NaBr	48.25	**99.75**	5.0	48.37		
18	H_2O				NaBr	30.85	**100**	3.2	30.85		
19, 37, 38	C_2H_6O	$MgBr_2 \cdot 6H_2O$	5.72	**100**				1.7	5.72	300	1.7
20	C_2H_6O	$MgBr_2 \cdot 6H_2O$	0.51	**86**	NaBr	0.08	**14**	0.2	0.59	170	1.6
21, 39	C_2H_6O	$MgBr_2 \cdot 6H_2O$	1.01	**50**	NaBr	1.03	**50**	0.4	2.04	120	1.5
22, 40	C_2H_6O	$MgBr_2 \cdot 6H_2O$	2.38	**20**	NaBr	9.49	**80**	1.7	11.86	170	1.5
23	C_2H_6O	$MgBr_2 \cdot 6H_2O$	0.36	**10**	NaBr	3.19	**90**	0.4	3.55	120	1.5
24	C_2H_6O	$MgBr_2 \cdot 6H_2O$	0.98	**7.5**	NaBr	12.20	**92.5**	1.5	13.18	150	1.5
25	C_2H_6O	$MgBr_2 \cdot 6H_2O$	0.74	**5**	NaBr	14.22	**95**	1.7	14.96		
26, 41	C_2H_6O	$MgBr_2 \cdot 6H_2O$	0.18	**1**	NaBr	15.84	**99**	1.7	16.02		
27, 42	C_2H_6O				NaBr	16.20	**100**	1.7	16.20	190	1.6
28, 43	C_2H_6O	Pure ethanol									
31	H_2O	$MgBr_2 \cdot 6H_2O$	17.32	**100**				5.1	17.32		
36	H_2O				NaBr	48.61	**100**	5.0	48.61		

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