

Experimental study of the surface chemical composition of sea salt crystallized during evaporation of seawater under natural conditions

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Under natural atmospheric conditions (at 45–55% RH and 25–30 °C) three sea-salt samples have been obtained by evaporation of sea waters from the Black Sea, Mediterranean Sea and Dead Sea, respectively, and then studied by XPS. The results show that the salt surfaces are enriched in Mg²⁺ ions as the Na⁺ ion amount is ~6 and ~20 times **lower** than that of the Mg²⁺ ions in the Black sea and Mediterranean Sea samples, respectively. Also enriched content of Br ions in all crystallized sea salts with respect to the chlorine concentration on the surface has been measured. Bromine ions are supposed to be localized in the top surface layer. Probably the first step of the crystallization sequence includes the formation of NaCl crystallites, followed by creation of a layer containing mainly MgCl₂ and MgSO₄ compounds. Additionally, this layer contains K⁺ ions, (HCO₃)¹⁻ and (CO₃)²⁻ groups and also Ca²⁺ ions in the case of Dead Sea salt. Relatively high surface concentrations of the (HCO₃)¹⁻ and (CO₃)²⁻ anions have been detected. Therefore, these ions together with the surface localized Br anions could play a significant role in the interaction dynamics on the surface of crystalized sea salts.

Key words: Sea salt, Ion concentration, Salt crystallization, XPS.

INTRODUCTION

The extents to which atmospheric particles affect the radiative balance of atmosphere depend on their chemical composition, physical state, and on their size as these properties depend on the relative humidity (RH). Sea salts aerosols are the largest species being highly hygroscopic and they initiate changes taking up water vapor from the atmosphere and forming aqueous droplets. Enhanced halide concentrations have been suggested at their liquid/vapor interface, which is important for the understanding of the atmospheric reactions [1]. Because the interactions occur on the surfaces of particles their surface chemical compositions have to be studied. This is the main motivation for the present study to investigate the chemical state and concentration of ions on the surface during the formation of sea-salt particles by evaporation of seawater.

The sequence of precipitation of the various ions, present in seawater during its evaporation, is crucial for the understanding the properties and reactivity of the formed sea salt particles. In that case the use of X-ray Photoelectron Spectroscopy (XPS) is particularly appropriate because it provides information about the chemical composition of the solid surfaces. There are a few studies on model laboratory samples using XPS, which contribute to the understanding of the surface segregation of different seawater ions. Zangmeister et al. [2] have studied the segregation of NaBr during the precipitation of mixed NaBr/NaCl crystals from aqueous solutions containing Br:Cl concentration ratio similar to that observed in seawater. The surface NaBr concentration has been found to be appr. 35 times higher than that in the crystal bulk but regardless of this NaBr segregation, most of the surface (~95%) remains occupied by NaCl [2]. The authors assume that a similar surface segregation of NaBr should be expected also in the case of the sea salt crystallization. However, based on the high Cl concentration found in seawater they have considered that also the sea-salt surface should be enriched mainly in NaCl.

Oppositely, Ghosal et al. [3] have used a significantly higher Br:Cl ratio, compared to that in sea-

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water, to a grown mixed NaBr/NaCl crystal. Their XPS measurements have shown higher Br:Cl ratio in the bulk of the crystals than the one measured by Zangmeister et al. [2]. An important result is that after water adsorption this ratio increases drastically leading to the conclusion that on the sea-salt surface the NaBr segregation should also be enhanced. Also segregation of Br⁻ ions has been observed on the surface of bromide-doped NaCl crystal at relative humidity above 40% due to water adsorption [4]. The Br-enrichment of the salt surfaces can play an important role in some global atmosphere processes like depletion of atmospheric ozone layer [3]. This makes the quantitative and qualitative researches on marine salt, from which salt aerosols are formed particularly important.

Harvie and Weare [5] have developed Na–K–Mg–Ca–Cl–SO₄–H₂O model in order to predict the mineral solubility and to understand the sequence of the mineral depositions at equilibrium evaporation of brine chemically similar to seawater. As an extension to the model Eugster et al. [6] have calculated phase relations within the same system Na–K–Mg–Ca–Cl–SO₄–H₂O at 25 °C and 1 atm pressure. The authors have noted that it is possible to estimate quantitatively the process of mineral precipitation for the natural carbonate-free waters based on the obtained results. Also, for this system a model called Spencer-Møller-Weare model has been parameterized not only at 25 °C but also at the subzero temperatures [7, 8].

The previous theoretical calculations of Christov [9, 10] and recent chemical kinetics experimental studies [11] show that assuming the sea salt as a simple halite (NaCl(cr)) salt, which is the main sea salt component, is a wrong approximation in the construction of a model for sea salt wetting behavior. It has been shown that the formation of surface solutions in equilibrium with magnesium chloride solids (bishofite (MgCl₂·6H₂O(s); DRH ≈ 34%), and carnallite (KCl·MgCl₂·6H₂O(s); MDRH = 34–52%) determined to a great extent the deliquescence behavior of sea salt under natural wet atmospheric conditions [9–11].

Now, using XPS we study experimentally the surface chemical composition of the sea-salt surface in order to shed more light and aid understanding of the bulk-surface disproportion of ions. XPS is a surface sensitive method, monitoring the chemical states of the elements and their concentrations within surface layers up to 2–3 nm depth [12]. Therefore, we expect to obtain results about the ion concentrations on the surface of crystallized sea salt leading to the understanding of the sequence of precipitation of various salts under natural evaporation conditions of sea water (45–55% RH and temperature of 25–30 °C).

EXPERIMENTAL

X-ray photoelectron measurements have been carried out on the ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10^{-10} mbar using twin anode MgK α /AlK α X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra are recorded at the total instrumental resolution (as it was measured with the FWHM of Ag3d_{5/2} photoelectron line) of 1.06 and 1.18 eV for MgK α and AlK α excitation sources, respectively. The energy scale has been calibrated by normalizing the C1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The processing of the measured spectra includes a subtraction of X-ray satellites and Shirley-type background. The peak positions and areas are evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different chemical species are determined based on normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [13].

The sea salt samples have been obtained by evaporation (at the natural conditions) of sea waters from Black Sea (BS), Mediterranean Sea (MS) and Dead Sea (DS). The ion concentrations on the salt surfaces measured by XPS are compared with the bulk data determined by the EUROTTEST – CONTROL EAD Company (Sofia, Bulgaria). The temperature is maintained at about 25–30 °C, whereas the relative humidity is controlled within 45–55% RH. The temperature is measured by a Pt100 thermometer. The relative humidity is being monitored by 808H5V6 Humidity transmitter during the whole evaporation period.

RESULTS AND DISCUSSION

Surface chemical composition of sea salts

As it was mentioned above, the three sea-salt samples obtained by evaporation of sea water from the Black Sea (BS), Mediterranean Sea (MS) and Dead Sea (DS), respectively, have been studied by XPS. One of the most intensive photoelectron peaks is located at about 200 eV and it originates from Cl2p core-level, characteristic of Cl⁻ ions giving respectively the largest concentration of these ions compared to all the other surface salt particles.

The presentation of our results begins with the C1s core-level region because the energy of the most intensive peak here is used for energy-scale calibration (Fig. 1). This peak at binding energy of 285.0 eV is characteristic of the C-H and/or C-C functional groups [14] most probably due to adsorbed hydrocarbons from residual gases in the vacuum chamber. Fig. 1 shows the different peak contributions, derived from

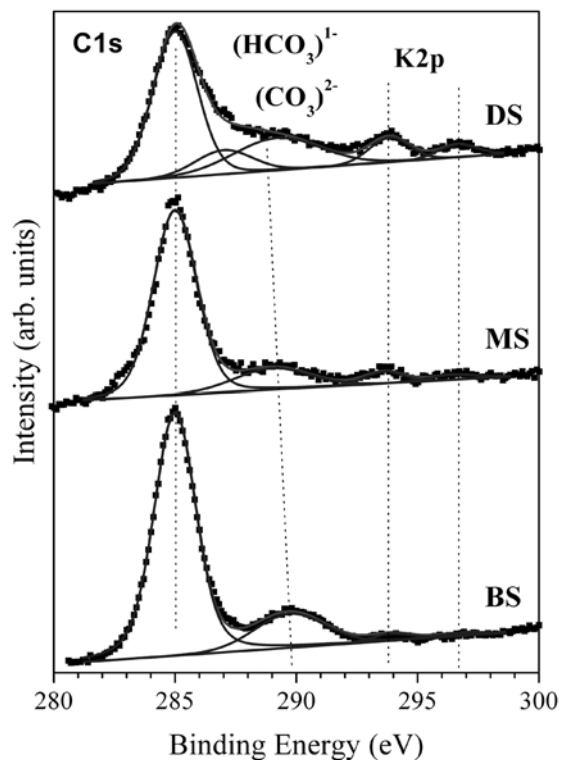


Fig. 1. C1s- and K2p-spectral regions of sea salts crystallized from different seawaters

the fitting procedure described in Sect. Experimental. The next two low-intensity broad peaks centered in a region of 287–290 eV can be attributed to negatively charged $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ functional groups as the higher negative charge of $(\text{CO}_3)^{2-}$ group determines its higher C1s binding energy [12]. The peak contribution of the $(\text{HCO}_3)^-$ group is more distinctly seen for the DS salt although the two functional groups are present in all the studied seawaters. Their bulk concentrations in seawaters are very small, between

70–300 times lower than the bulk-seawater concentration of Cl^- ions (Table 1) but in the surface layers of crystallized sea salts the corresponding ratio is significantly higher: the concentrations of $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ groups are only 6–8 times lower than that of chloride.

In the spectral region, shown in Fig. 1, the $\text{K}2p_{3/2}$ and $\text{K}2p_{1/2}$ peaks are measured at binding energies of 293.6 and 296.2 eV, characteristic of K^+ ions. No significant differences are detected for the K^+ ion concentrations with respect to those of the surface Cl^- species. The $\text{K}^+:\text{Cl}^-$ concentration ratio varies between ~70 for BS salt and ~43 for both MS and DS salts (Table 1). It should be noted that the concentration ratio of the same order is measured in the bulk seawaters. There is significant deviation only for DS seawater, which will be discussed at the end of this section. These $\text{K}^+:\text{Cl}^-$ ratio similarities between bulk and surface of liquid and crystallized phases, respectively, can be explained assuming that K^+ ions originate from the KCl compound. Surprisingly, the most intensive feature in XPS spectra cannot be connected with Na but rather with the presence of large amount of Mg on the surface. This is clearly shown in Fig. 2. The binding energies of the indicated peaks are characteristic of Mg^{2+} , Na^+ , Br and Ca^{2+} -ions [15]. The $\text{Na}2s$ peak intensity is almost invisible, while the $\text{Mg}2s$ peak dominates the whole spectral region, although their photoionization cross-sections are comparable, 0.422 and 0.575, respectively [13]. The ion concentrations in the surface layers of the crystalline salts are shown in Table 1. While in the bulk sea water from BS and MS the Na^+ ion concentration is 10 times higher than the Mg^{2+} concentration, on the surface of crystallized salt phase the Na^+ ion amount is ~6 and ~20 times lower compared to the Mg^{2+} amount, respectively. Again a deviation is observable in the Dead Sea sample results. In the bulk seawater the amounts of Mg^{2+} and Na^+ ions are almost equal, which can

Table 1. Surface ion concentrations (at. %) of salts evaporated from Black Sea (BS), Mediterranean Sea (MS) and Dead Sea (DS) water sample solution compared to the ion concentrations (at. %) in sea water from corresponding seas

Ions	BS water (at. %)	BS salt (at. %)	MS water (at. %)	MS salt (at. %)	DS water (at. %)	DS salt (at. %)
Na^+	43.82	6.6	42.12	1.8	17.85	0.8
Mg^{2+}	4.29	37.6	4.60	37.6	18.71	29.6
K^+	0.73	0.6	0.83	1.1	2.33	1.3
Ca^{2+}	0.90	-	0.99	-	3.10	3.7
Cl^-	47.40	41.2	48.93	46.2	57.12	56.7
$(\text{SO}_4)^{2-}$	2.09	5.8	2.29	6.8	0.04	0
$(\text{HCO}_3)^-$	0.40	7.2	0.08	6.0	0.28	6.9
$(\text{CO}_3)^{2-}$	0.26	-	0.08	-	0.06	-
Br^-	0.06	1.1	0.08	0.5	0.50	1.0

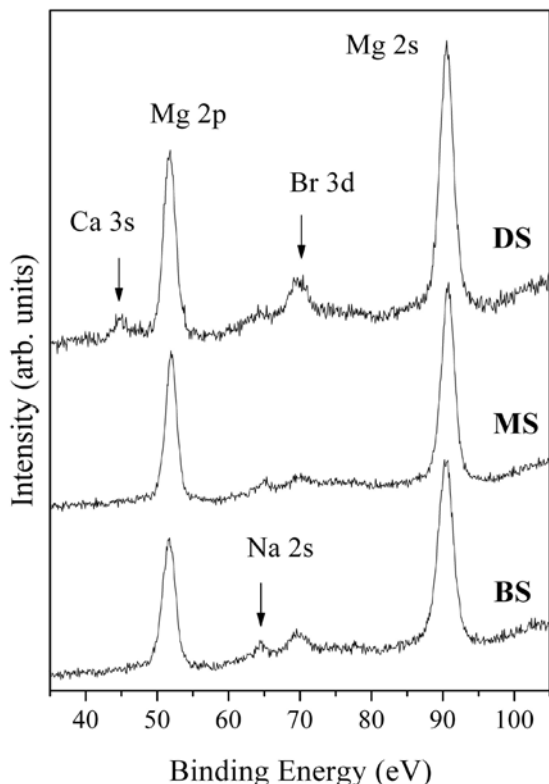


Fig. 2. Low binding-energy regions of crystallized sea salts from different seawater samples

be explained by the already started crystallization leading to the formation of small NaCl crystallites on the walls of the container with DS water. With

respect to BS and MS waters the smaller amount of Na⁺ ions in DS water leads to their smaller quantity in the surface layers of crystallized phase: 37 times lower than Mg²⁺ ion concentration (Table. 1). However, for all three crystallized samples one can conclude that the surfaces of sea salts are enriched in Mg²⁺ ions.

Another remarkable feature, which follows from our measurements, is the enriched content of Br⁻ ions with respect to the chlorine concentration on the surface of all crystallized samples. In the bulk of seawaters the Br⁻:Cl⁻ concentrations ratio is 0.001 for BS and MS, respectively, and 0.009 for the DS sample while on the sea-salt surfaces this ratio is measured to be 27, 10 and 2 times higher in the salts evaporated from BS, MS and DS, respectively (Table 1). Despite the very small bromide amounts they can be reliably measured by XPS due to the relatively high photoionization cross-sections of Br3d (5/2+3/2) electrons, calculated to be 1.68+1.16=2.84, respectively [13]. For comparison this value is about 5–7 times higher than the cross-sections of Mg2s and Na2s electrons, respectively, as it was mentioned above. In addition to the analysis of the results represented in Fig. 2 we should note here that only for the salt crystallized from DS water a small amount of Ca²⁺ ions is detected with corresponding weak peak of Ca3s electron core-level at 44.8 eV.

To complete the discussion of the surface chemical composition of sea salts the next intensive photoelectron lines of S2p, Cl2p and O1s should also be considered (Fig. 3). The sulfur amount is detected

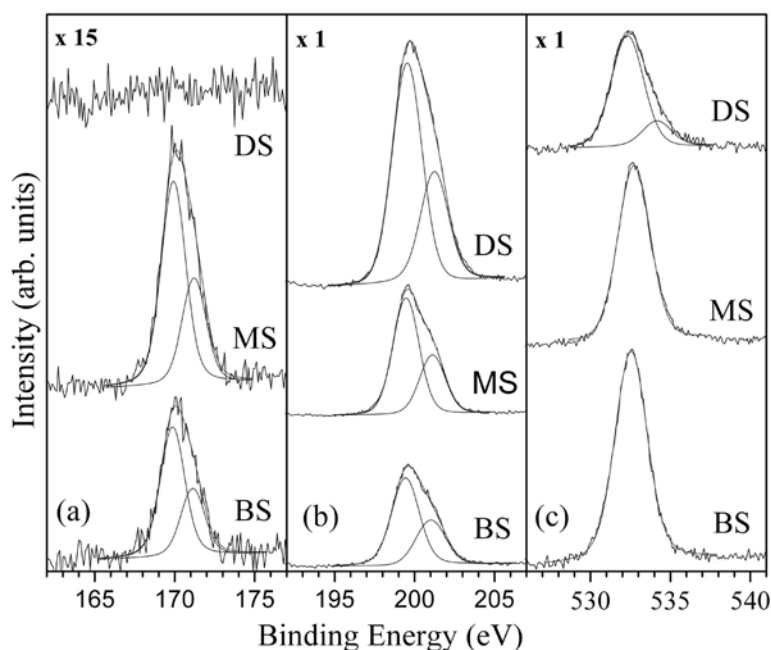


Fig. 3. Different spectral regions of crystallized sea salts: (a) S2p; (b) Cl2p; (c) O1s

only in the salts, crystallized from BS and MS waters. From the fitted S2p spectra a $S2p_{3/2}$ binding energy of 169.9 eV has been derived as well as 2p ($3/2-1/2$) spin-orbital splitting of 1.2 eV (Fig. 3a). This energy shows that the sulphur is in $(SO_4)^{2-}$ chemical state (Fig. 3a) [15]. The $(SO_4)^{2-}:Cl^-$ ions concentration ratio is almost equal (0.14) on the surfaces of both BS and MS crystallized salts, whereas in the bulk of seawaters this ratio is about 3 times lower (Table 1).

The spectral Cl2p region is characterized by one asymmetrical peak containing $2p_{3/2}$ and $2p_{1/2}$ components with separation energy difference of 0.7 eV (Fig. 3b). Although, the peak intensities for different crystallized salts increase in the order $BS < MS < DS$, the chloride concentration remains almost the same for BS and MS salts and it is higher by approximately 20% for the DS salt (Table 1). These results can be convincingly explained making a balance between the two possible $MgCl_2$ and $MgSO_4$ compounds, which may exist on the sea-salt surfaces using the concentrations of Mg^{2+} , Cl^- and $(SO_4)^{2-}$ ions from Table 1. On the DS salt surface no sulfur is detected and therefore almost all the Mg^{2+} and Cl^- ions are probably included in the $MgCl_2$ whereas on the BS and MS salt surfaces there are ~5–7% $(SO_4)^{2-}$ ions and therefore part of the Mg-ions is involved in the form of $MgSO_4$ compound. For this reason the amount of $MgCl_2$ compound and respectively Cl^- ions should be lower than those in DS salt. This concentration balance leads to the conclusion that $MgCl_2$ and $MgSO_4$ compounds may exist on the surfaces of BS and MS salts in $MgCl_2:MgSO_4$ amount ratio of ~3.

For the salts crystallized from BS and MS no differences are to be seen in their O1s peaks as evidenced by the spectra shown in Fig. 3c. Both O1s peaks are located at 532.5 eV which binding energy is characteristic of oxygen in organic molecules and/or $(HCO_3)^-$ groups [16], $(CO_3)^{2-}$ groups [17] as well as of $(SO_4)^{2-}$ groups [18]. Therefore the oxygen ions in chemically different environments in these three groups cannot be resolved based on their binding energies. For the sea salt evaporated from the DS water we detect an additional O1s peak at 534.1 eV, which can be attributed to OH^- groups [19]. As this peak does not exist in the BS and MS salt spectra and also having in mind that the only significant difference between the three sea-salt samples is the presence of Ca^{2+} ions in DS salt surface, one can suppose that the OH^- groups are connected with some compound also containing Ca^{2+} .

Sequence of mineral precipitation

As it was demonstrated in the previous sections, the chemical compositions of the surfaces of crystallized sea salts at 45–55% RH and 25–30 °C showed

a high concentration of Mg^{2+} ions, whereas the Na^+ ion amount was ~6 and ~20 times **lower** than the Mg^{2+} amount in the BS and MS salts, respectively. In addition, the $Br^-:Cl^-$ and $(SO_4)^{2-}:Cl^-$ ion concentrations ratios are established to be significantly higher than that in the bulk of seawaters. These surprising results can be explained by precisely determined sequence of deposition of the various minerals, contained in sea waters. Therefore, to examine this sequence it is necessary to analyze the amounts of different ions in the depth of the samples. For this purpose the sample surface has been “washed” with deionized water for a short time interval and the chemical composition of the treated newly formed surface has also been studied by XPS. Here, we present the results for the MS salt crystallized under natural conditions like the samples discussed in Sect. 3.2. The only difference is that the MS salt has been left for a few months under the conditions of its formation (at 45–55% RH and 25–30 °C), and as a result, the salt has been humidified. It should be noted that the original (before washing) and treated surfaces have been dried in vacuum before the analysis.

The most informative XPS spectra of the original and treated surfaces are shown in Fig. 4. Obviously,

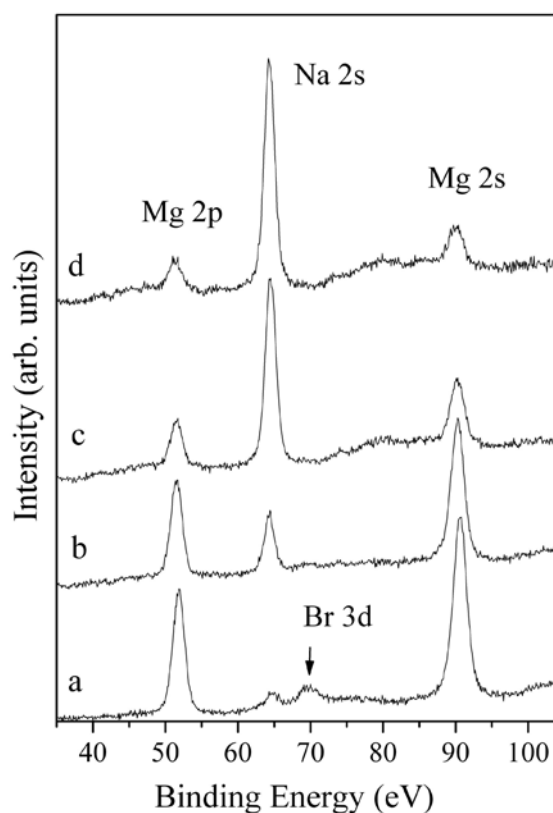


Fig. 4. Comparison of low binding-energy regions of treated sea salts: (a) before “washing” procedure and after (b) first, (c) second and (d) third lavement, respectively

Table 2. Surface ion concentrations (at. %) of wetted salt obtained by evaporation of Mediterranean Sea (MS) water and after three lavements of the salt surface with deionized water

Ions	Wetted MS salt (at.%)	1 st lavement (at.%)	2 nd lavement (at.%)	3 rd lavement (at.%)
Na ⁺	3.4	12.7	37.8	47.4
Mg ²⁺	36.2	31.5	11.4	7.1
K ⁺	0.9	2.6	1.4	0.8
Ca ²⁺	–	–	~0	~0
Cl ⁻	47.4	35.9	41.7	45.7
(SO ₄) ²⁻	5.6	12.9	4.7	3.3
(HCO ₃) ⁻	5.7	4.0	3.0	2.6
(CO ₃) ²⁻				
Br ⁻	0.8	0.2	0	0

the concentration of Mg-ions is significantly reduced after “the washing” treatment, while gradually the Na2s peak begins to dominate. The 3d peak of the bromide almost disappears after the first lavement of the salt surface. The concentrations of all ions are shown in Table 2. The results for the original salt surface are in good agreement with those for MS salt concentration, presented in Table 1, which shows the good reproducibility of our measurements. Several conclusions can be drawn on the basis of the results listed in Table 2.

After the first lavement the Mg²⁺ ions concentration is slightly reduced while that of (SO₄)²⁻ is increased 2 times. Also 25% reduction of Cl⁻ ions concentration is observed. The explanation can be found assuming the presence of a significant amount of MgSO₄ immediately below the top surface layers of the salt crystal. After the next steps of washing Mg²⁺ and (SO₄)²⁻ ion concentrations are decreased simultaneously but the Na⁺ and Cl⁻ amounts increase to a level characteristic of NaCl stoichiometry. Therefore, we believe that after the washing treatment of the salt surface relatively clean NaCl crystallites should appear indicating that their formation should be the first step in the crystallization sequence of the sea salt under natural conditions of seawater evaporation. Indeed, Table 2 shows that the concentrations of all ions are decreased except for those of Cl⁻ and Na⁺. Note, that in these considerations, the differences in the initial dissolution rates of the various salt components have been ignored.

Observed differences in DS salt features

Similar study to that, explained in previous section, has been performed with the salt evaporated from Dead Sea water. This salt has been stationed for five months under laboratory conditions. Because of the humidity in the room the salt becomes moistur-

ized and has been separated in two volume layers. The bottom layer in the container consists of wet precipitated crystallites, whereas above this layer an aqueous salt solution is observed. The top liquid layer has been dried first and then studied by XPS. Its corresponding XP spectrum is shown in Fig. 5 and it is compared with the spectrum of the original DS salt. The measured concentrations of the Na⁺, Mg⁺, K⁺, Ca²⁺, Cl⁻, and Br⁻ ions on the surface of the salt, obtained from the top aqueous layer, are 3.0%, 13.5%, 0.9%, 16.3%, 57.6% and 2.5%, respectively. In comparison to the original DS salt (see Table 1) the amounts of Ca²⁺ and Br⁻ ions are increased strongly

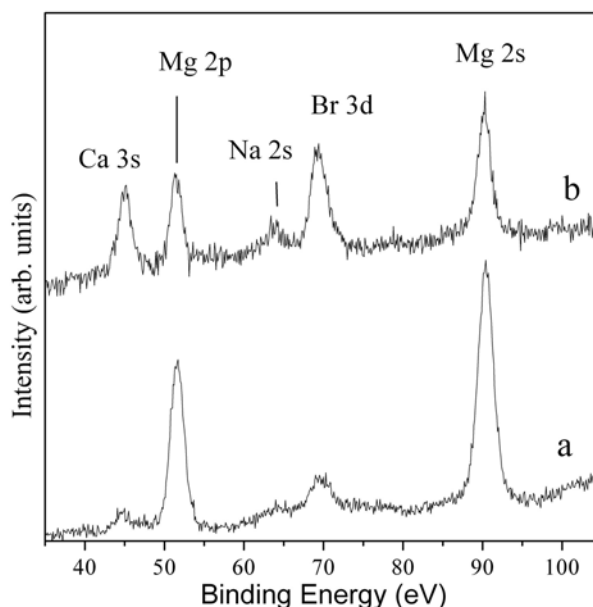


Fig. 5. Comparison of XP spectra of (a) original DS sea salt and (b) salt received from the top liquid layer as it is described in the text

more than 4 and 2.5 times, respectively. Therefore, we can suggest that these are the ions, dissolved in the formed liquid top layer, which were originally located on the salt crystal surface.

CONCLUSIONS

Three sea-salt samples obtained by evaporation of sea water from the Black Sea, Mediterranean Sea and Dead Sea, have been studied by XPS. The highest ion concentrations of about 41–46% are measured for the Cl^- ions in the BS and MS salts, and ~57% in the DS salt. In all the samples, the salt crystal surfaces are enriched in Mg^{2+} ions, while the bulk is dominated by the presence of Na^+ ions. While the Na^+ ion concentration in the bulk sea water from BS and MS is 10 times higher than the Mg^{2+} concentration, on the surface of crystallized salt phase the Na^+ ion amount is ~6 and ~20 times lower with respect to the Mg^{2+} amount, respectively. Another remarkable feature is the enriched content of Br^- ions with respect to the chloride ions concentration on the salt surface, which suggests that the bromide ions are supposed to be localized mainly in the top surface layer.

In an attempt to examine the sequence of salt crystallization we reached the conclusion that the first step should include the formation of NaCl crystallites followed by creation of a layer containing mainly MgCl_2 and MgSO_4 compounds. This second layer contains also small amounts of K^+ , $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ groups and also Ca^{2+} in the case of DS salt. The $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ concentrations in the bulk of seawaters are very low: 70–300 times lower than the bulk concentration of Cl^- ions. It is worth noting that in the surface layers the $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ ion concentrations are only 6–8 times lower than that of the chloride. These relative high surface concentrations of the $(\text{HCO}_3)^-$ and $(\text{CO}_3)^{2-}$ groups, together with the surface localized Br^- ions, might play a significant role in the interaction dynamics on the surface of crystallized sea salts.

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ЕКСПЕРИМЕНТАЛНО ИЗСЛЕДВАНЕ НА ХИМИЧЕСКИЯ СЪСТАВ НА ПОВЪРХНОСТТА НА МОРСКА СОЛ, ПОЛУЧЕНА ПРИ ИЗПАРИЕНИЕ НА МОРСКА ВОДА В ЕСТЕСТВЕНИ УСЛОВИЯ

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(Резюме)

При естествени атмосферни условия (45–55% RH и 25–30 °C) три проби от морска сол са получени чрез изпарение на морска вода от Черно море, Средиземно море и Мъртво море, съответно, след което са изследвани с РФС. Резултатите показват, че повърхността на солта е обогатена с Mg^{2+} йони, като концентрацията на Na^+ йоните е ~6 пъти по-ниска от тази на Mg^{2+} йоните в Черно море и съответно ~20 пъти по-ниска от тази на Mg^{2+} йоните в Средиземно море. Регистрирано е повишено съдържание на Br^- йони на повърхностите на всички кристализирани морски соли спрямо концентрацията на хлор. Бромните йони най-вероятно са локализиран в най-горния повърхностен слой. Вероятно първата стъпка на кристализационния процес включва образуването на кристали от $NaCl$, последвано от създаването на слой, съдържащ предимно $MgCl_2$ и $MgSO_4$ съединения. Освен това, този слой съдържа K^+ йони, $(HCO_3)^{1-}$ и $(CO_3)^{2-}$ групи, а също и Ca^{2+} йони в случая на сол от Мъртво море. На повърхността на образците концентрациите на $(HCO_3)^{1-}$ и $(CO_3)^{2-}$ йони са относително високи. Следователно, тези йони заедно с локализираните на повърхността Br^- аниони могат да играят важна роля в динамиката на взаимодействията върху повърхностите на кристализираните морски соли.