

About the Formation of Basic Silver Carbonate on Silver Surfaces – An *In Situ* IRRAS Study

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Abstract: Air pollutants such as carbon dioxide play an important role in atmospheric corrosion processes and therefore in the degradation reactions occurring on metal surfaces exposed to an ambient atmosphere. It is known from macroscopic studies that ultraviolet (UV) light influences these surface reactions with respect to the reaction rate and the product formation itself even though the exact mechanisms have not been elucidated *in situ* at a sub- μm level so far. Therefore, the role of CO_2 in the humidified ambient atmosphere and the influence of UV light on the initial atmospheric corrosion behaviour of silver surfaces were investigated under *in situ* conditions using a combined InfraRed Reflection Absorption Spectroscopy (IRRAS) and Quartz Crystal Microbalance (QCM) set-up. To obtain 3-dimensional information about the depth distribution of the corrosion products formed, *ex situ* Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) measurements were performed additionally. The investigations revealed *in situ* the main and intermediate reaction products during the formation of basic silver carbonate on a polycrystalline silver surface. Furthermore, a strong dependency of the product formation rate with respect to the CO_2 concentration and the humidity content in the ambient atmosphere as well as the influence of UV light irradiation of the surface could be demonstrated.

Keywords: Silver, atmospheric corrosion, *in situ* IRRAS, QCM, TOF-SIMS.

1. INTRODUCTION

Silver is a very precious metal with favourable properties such as the highest electrical and thermal conductivity of all elements and for this reason used in electrical contacts and conductors. Furthermore, silver is used in dentistry, photography, solder and brazing, as catalyst and also for jewellery and decorative objects. Atmospheric corrosion is very complex because chemical, electrochemical and physical processes occur in the solid, liquid and gaseous phase and in the interfaces between them. This is the reason why the degradation behaviour of silver exposed to ambient atmospheres is worth investigating and in fact indispensable for developing strategies and methods to avoid or prevent such degradation reactions. Thus the atmospheric corrosion of silver has been recognized in literature but the knowledge about the occurring reactions on a sub μm level is still rudimentary [1-7].

Furthermore, the influence of UV light on the atmospheric corrosion process of silver was studied, as many important reactions are photolytic and the effect of UV light on corrosion rates of silver was only studied in long term experiments (3-5 months) where it could be proven that silver experiences photo-corrosion [8]. To obtain detailed information on the reactions occurring on the surface during such weathering experiments it is necessary to study those reactions *in situ* at ambient pressure [9-11]. For this reason a

self-constructed IRRAS/QCM set-up was applied which enables such *in situ* investigations gaining chemical, structural and gravimetric information from the surface in a sub- $\mu\text{m}/\mu\text{g}$ range [12].

In addition the influence of the relative humidity content of the ambient atmosphere with different levels of carbon dioxide as well as the photo-catalytic effect of UV light on the initial atmospheric corrosion behaviour of polycrystalline silver samples could be elucidated.

2. MATERIALS AND METHODOLOGY

2.1. Samples

The investigated samples are physical vapour deposited (PVD) silver-coated quartz crystals (99.99% purity) purchased from Maxtek[®] Inc. (USA, electrode material silver, diameter 2.54 cm, thickness 333 μm , AT-Cut). These polycrystalline silver samples are characterised by a homogenous distribution of round silver particles (around 70 nm in diameter), thus creating a well-defined surface to assure the generation of reproducible data sets during the weathering experiments without any necessary sample pre-treatment.

2.2. Weathering and Irradiation Experiments

The weathering experiments were carried out in an *in situ* IRRAS/QCM weathering cell. The moist air stream with or without the corrosive gas is generated by using a dry synthetic air flow which is provided by a compressor (Jun-Air, Germany, Model OF301-4B 5) in combination with a pure air generator (Sigma-Aldrich, Austria Nitrox Model 140). The quality of the pure air is achieved by using high efficiency pre- and post-desiccant filtration. One part of the dry

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air stream is humidified in a bottle containing distilled and deionised water and afterwards combined with the untreated airflow to the desired levels of relative humidity (RH). With this weathering system the humidified ambient atmosphere can be batched with 125 to 1000 ppm of CO₂ [13, 14]. All samples investigated were weathered for 12 h at a flow rate of 40 l h⁻¹ with 250 ppm and 500 ppm CO₂ with and without irradiation of UV light. The inner volume of the below described *in situ* IRRAS cell is approximately 25 cm³, leading to a mean residence time of the moist air in the cell of 2.25 sec. As a UV source a UV lamp 400 H/2 from Hönle UV Technology Germany was used. This lamp has a spectral range from 200-580 nm with the main intensities at 250-350 nm and an intensity of illumination of 100W.cm⁻¹ and was placed at a distance of 10 cm from the sample surface.

2.3. IRRAS – Measurements

Instrumentation

For the measurements a FTIR-Spectrometer VERTEX 80V of Bruker Optics® was used with an air cooled IR ceramic source and a KBr beamsplitter for a spectral range of 10,000 to 380 cm⁻¹. As an aperture 250 μm were chosen. The *in situ* cell with the below described external optical pathway was placed in the sample compartment of the FTIR-Spectrometer. IRRAS spectra were obtained by averaging 128 scans at a resolution of 4 cm⁻¹. The spectra were recorded as single channel spectra and afterwards converted to absorbance spectra (R/R_{dry}), where R_{dry} corresponds to the single channel spectra of the sample obtained after 15 min exposure to dry synthetic air before starting the weathering process (background), and R which is the single channel spectrum of the weathered sample.

In Situ IRRAS Measurements

The IRRAS cell (Fig. 1) for *in situ* investigations is made of acrylic glass with gas in- and outlets, two zinc-selenide windows, a polymethylmethacrylate window for the irradiation with UV light, a sample holder with the integrated QCM sensor head, and a rear panel to which a small cock with a spring

mechanism is attached [12]. For the measurements the silver quartz crystal is placed from the back of the cell and fixed into its position with a spring mechanism mounted on the rear panel. This assures that the investigated surface is always placed in the focal point of the IR beam. A stainless steel tube which is mounted 3 mm in forefront of the sample surface supplies the moist air stream. This distance leads to a turbulent flow and therefore the highest possible deposition rates in atmospheric weathering experiments can be achieved [2, 3]. The uncoated gold mirrors which are mounted on the base plate are rotate- and tilt- able and assure an angle of incidence of the IR beam of 78° off normal to the sample surface. This angle was chosen as for analysing molecules at surfaces the highest sensitivity is achieved with grazing angle measurements of >80° off normal with the incident light polarized in the plane of incidence [15]. The PMMA window is also located in front of the sample surface to permit optimum UV light exposure. Also shown in Fig. (1) is the optical pathway for the IR beam in the cell. The IR beam from the FTIR spectrometer is reflected by a plane uncoated gold mirror, passes through a perpendicular mounted ZnSe window, and hits the sample surface under a grazing angle of incidence. The reflected beam leaves the chamber through the second ZnSe window and is then reflected by another plane uncoated gold mirror onto the optical system of the spectrometer with a mercury cadmium telluride (MCT) mid band detector (cut-off frequency: 600 cm⁻¹) which allows sensitive detection of the IR radiation.

2.4. QCM – Measurements

The quartz crystal microbalance is a device able to detect mass changes < 0.4 ng.cm⁻². Due to possible degradation reactions occurring on the silver surface exposed to humidity and CO₂ with and without exposure to UV light these mass changes are recorded *in situ*. The used AT-cut silver quartz crystals have a resonance frequency of 5 MHz, which changes in proportion to a change in mass as described by the Sauerbrey equation [16]. The QCM sensor head is a modification of the Maxtek crystal holder and was integrated into the weathering cell. The QCM sensor head is placed

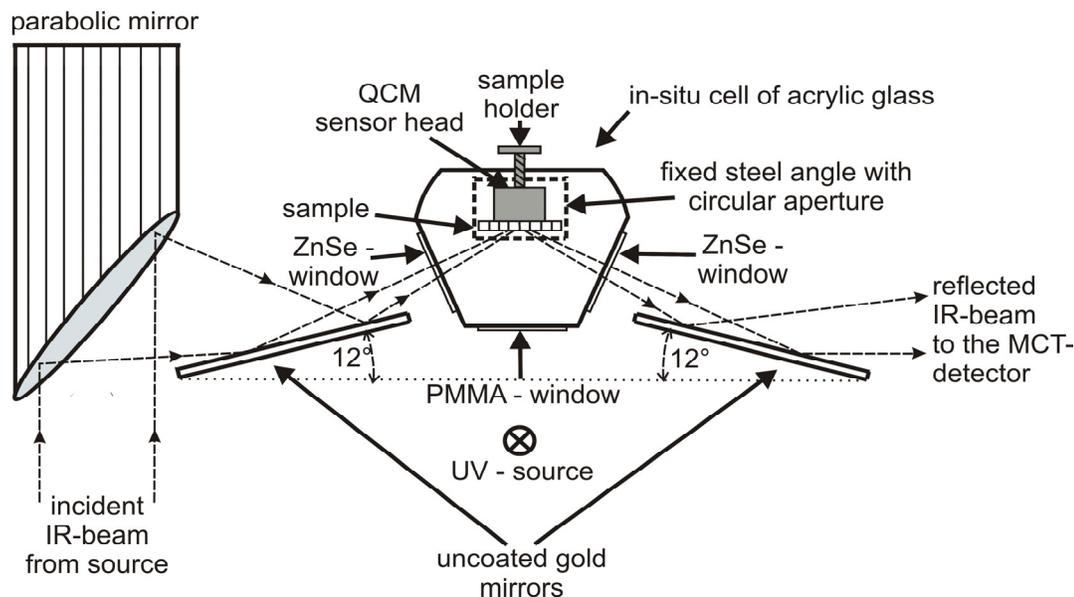


Fig. (1). *In situ* IRRAS/QCM weathering cell showing the optical pathway of the IR beam.

from the back into the cell, fixing the sample crystal in the sample holder [12].

2.5. TOF-SIMS – Measurements

Secondary ion mass spectrometry was performed with a *TOF-SIMS*⁵ (ION-TOF GmbH, Münster, Germany), equipped with a Bi⁺ LMIG (liquid metal ion gun) at 25 keV energy. For Depth Profiling two ion beams operate in the Dual Beam Mode. The first beam (Bi⁺) generates the secondary ions (from a 100 x 100 μm² area), which are analysed in a time of flight mass analyser. During the flight time, the second beam from a Cs⁺ thermal ionization source (for negative secondary ion detection) erodes a crater on the sample surface, in this case 300 x 300 μm². The Cs⁺ ions are of 0.25 keV energy for high depth resolution [17-18].

3. RESULTS AND DISCUSSION

The formation of basic silver carbonate like species on polycrystalline silver surfaces was studied *in situ* under different weathering conditions. Therefore, the relative humidity content and the CO₂ concentration in the ambient atmosphere were varied as well as the irradiation of the surface with UV light. The different contents of relative humidity chosen were 50 and 90% RH, respectively, resulting in approximately 2 to 8 surface water monolayers [1]. This formed surface water-layer is one of the crucial factors in atmospheric corrosion processes. The adsorbed water is the medium for the absorption of atmospheric gases for the subsequent chemical degradation reactions and furthermore acts as a solvent for the dissolution of the formed corrosion products. The CO₂ concentration in the ambient atmosphere was chosen to be 250 ppm and 500 ppm, as these concentrations are close to the real concentration in the atmosphere in urban

environments (around 360 ppm). In addition the influence of an increased CO₂ content in the ambient atmosphere with respect to the occurring degradation reactions could be proven therewith. To clarify the photo-catalytic influence of UV light on these surface reactions the samples were irradiated during weathering for a time period of about 30 minutes.

3.1. *In Situ* IRRAS Results

A typical unsmoothed *in situ* IRRAS spectrum obtained from a polycrystalline silver sample which was exposed for 12 hours to synthetic air with 90% RH and 250 ppm CO₂ and irradiated with UV light is shown in Fig. (2). The background spectrum (R_{dry}) was recorded in a dry ambient atmosphere. The occurring bands can be interpreted as follows: the band at 1600 cm⁻¹ corresponds to the scissors vibration mode from the gas phase water (δ), the band at 2347 cm⁻¹ to the asymmetric ν₃ vibration of the CO₂ gas phase and the broad band at 3000 cm⁻¹ to the physisorbed water signal. Furthermore, several bands occur due to the formation of basic silver carbonate (AgOHAg₂CO₃) like species on the sample surface [19]. As published in [12] the band at 1221 cm⁻¹ can be interpreted as signal caused by the asymmetric CO₃²⁻ stretching vibration and the band at 1160 cm⁻¹ might be due to Ag-OH surface vibrations. The band at 1109 cm⁻¹ corresponds to the -C-O asymmetric stretching vibration and the band at 922 cm⁻¹ seems to be the result of the [HO-CO₂]⁻ skeletal vibration. Therefore, the evolution of the bands at 1221 cm⁻¹, 1109 cm⁻¹, and 922 cm⁻¹ are of special interest within this work due to the fact that they can directly be correlated to the formation chemistry of AgOHAg₂CO₃ on the sample surfaces.

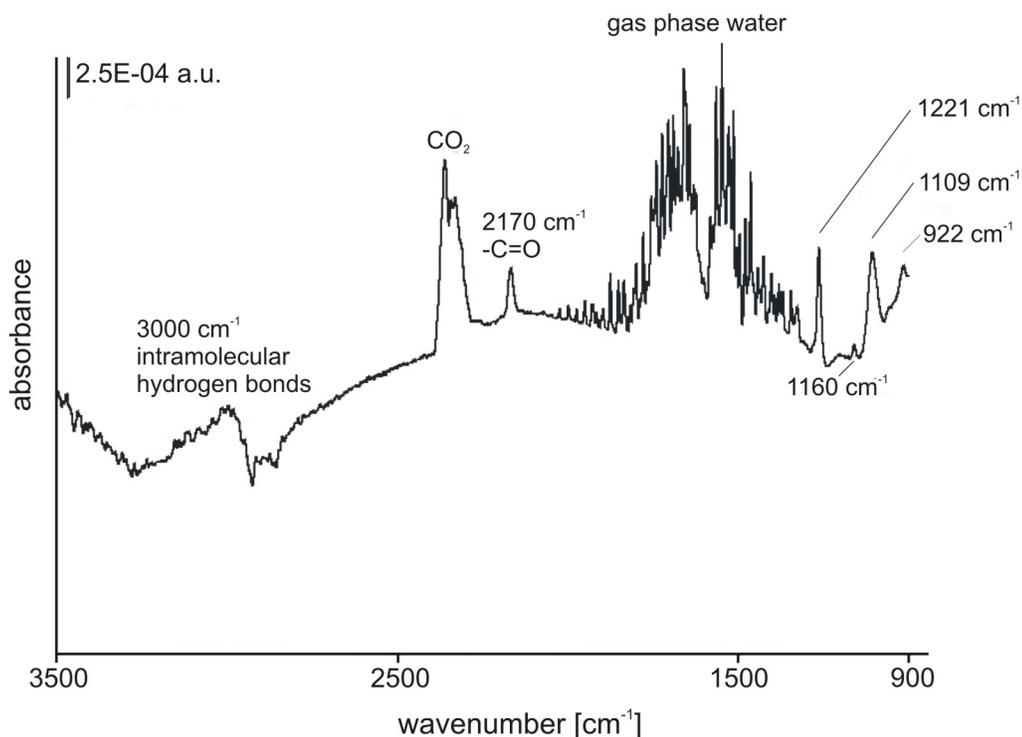


Fig. (2). Unsmoothed IRRAS spectrum of polycrystalline silver exposed to 90% RH with addition of 250 ppm CO₂ and irradiated by UV light showing the occurring absorbance bands.

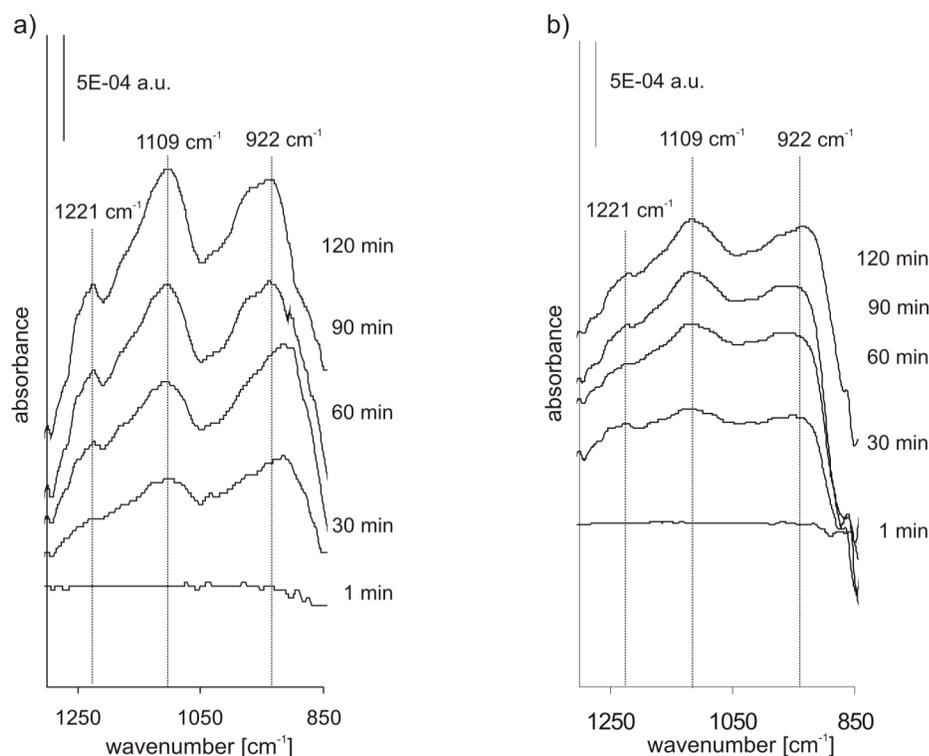


Fig. (3). Time-resolved *in situ* IRRAS spectra obtained from the polycrystalline silver samples exposed to (a) 90% RH with addition of 250 ppm CO₂ and (b) 50% RH with addition of 250 ppm CO₂. In both cases the evolution of the three bands associated to the formation of AgO-HAg₂CO₃ at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ is clearly visible.

a) Influence of the Humidity Content

Fig. (3) shows the unsmoothed time-resolved IRRAS (R/R_{dry}) spectra obtained from the polycrystalline silver samples exposed to 250 ppm CO₂ at relative humidity contents of (a) 90% and (b) 50% during the first 120 min of weathering without irradiation with UV light. As shown, the growth of the three above described absorbance bands, which can be correlated to the formation of a basic silver carbonate surface species, at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ can be observed in a time resolved way. The band at 1160 cm⁻¹ is seemingly not resolved due to the broad signal caused from the -C-O asymmetric stretching vibrations. The bands at 1109 cm⁻¹ and 922 cm⁻¹ are shifted during weathering to higher wavenumbers due to an increased surface disorder caused by the growth of surface features and according to the special surface selection rules in reflection experiments [20]. Integration of the bands and correlating the obtained results leads to following conclusion: For the sample exposed to 90% RH and 250 ppm CO₂ all three bands and therefore also the concentration of all three correlating surface species ([HO-CO₂]⁻, -C-O, CO₃²⁻) are increasing with time. The evolution of the bands caused from the -C-O and [HO-CO₂]⁻ signals is similar in the first 30 min of weathering. Afterwards the band at 1109 cm⁻¹ shows a higher increase with time compared to the results obtained from the integrated bands at 922 cm⁻¹ (Fig. 4a). This can be interpreted by the formation of a linked surface species at an expense of the dissolved hydrogen carbonate species from the surface waterfilm. Seemingly this linked surface species (correlated to the 1109 cm⁻¹ signal) acts somehow as a precursor for the formation of the carbonate surface species. This assumption is also affirmed by the constant growth of

the carbonate signal with time. The same absorption bands and band area correlations can be observed for the experiment at 50% RH with 250 ppm CO₂ (Figs. 3b, 4b), even though the relative intensities of these bands are much smaller compared to the results obtained from the sample weathered in 90% RH with 250 ppm CO₂. The progression with respect to the weathering time of the observed band areas (Fig. 4b) seems to be different compared to the band areas obtained from the sample weathered at 90% RH with 250 ppm CO₂ (Fig. 4a), as they only show an increase in the first 60 min of weathering and then remain nearly constant. This is a further hint for the importance of the surface waterfilm and its influence on the occurring degradation reactions with respect to the observed reaction rates.

Summing up the obtained results leads to following interpretation: The CO₂ in the atmosphere gets dissolved in the surface water film and forms hydrocarbon ions ([HO-CO₂]⁻) indicated by an absorbance signal at 922 cm⁻¹. These hydrocarbon ions subsequently react with the hydroxylated surface to form a basic silver carbonate like species (correlated to the signals at 1109 cm⁻¹ and 1221 cm⁻¹).

b) Influence of the CO₂ Content

To investigate the influence of the CO₂ concentration in the ambient atmosphere with respect to the occurring surface reactions the silver samples were all weathered for 60 min at 90% RH with either 250, 500 ppm or without CO₂ (Fig. 5). The sample weathered in 90% RH without addition of CO₂ does not show any significant absorbance bands between 1300 cm⁻¹ and 850 cm⁻¹. Only small signals in the region of 1160 cm⁻¹ are visible which may be correlated to the hydroxylated silver surface [13]. In agreement with the prior

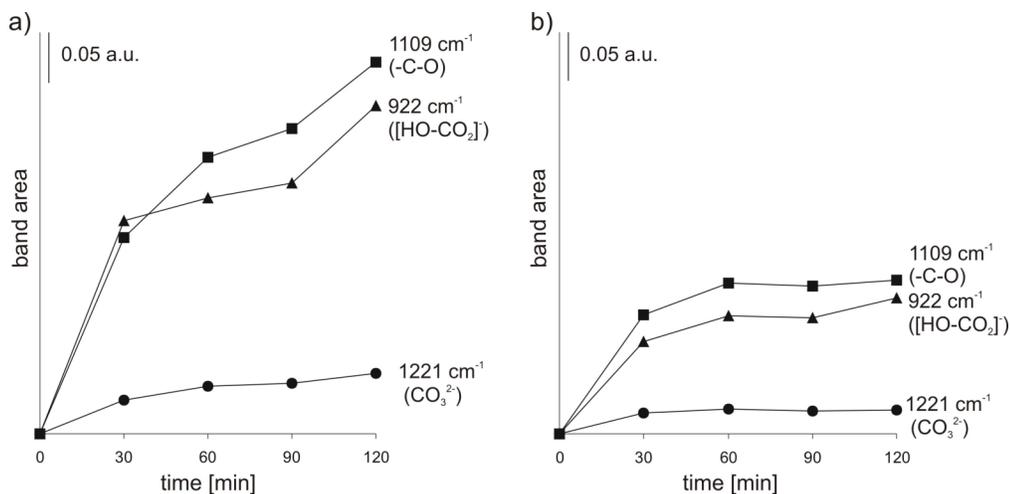


Fig. (4). Time-resolved relation between the integrated band areas from the polycrystalline silver samples weathered in (a) 90% RH with addition of 250 ppm CO₂ and (b) 50% RH with addition of 250 ppm CO₂.

experiments the three characteristic absorbance bands at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ can be observed for the sample weathered in 90% RH with addition of 250 ppm CO₂. The spectrum obtained from the sample weathered in 90% RH with 500 ppm CO₂ only shows two resolved absorbance bands at 1109 cm⁻¹ and 922 cm⁻¹. Seemingly the band at 1221 cm⁻¹ disappears in the signal of the 1109 cm⁻¹ band indicated by the asymmetric shape of this absorbance band. This also proves that the evolution of the basic silver carbonate species is clearly dependent on the CO₂ concentration in the ambient atmosphere and that the observed IRRAS signals are clearly caused from the basic silver carbonate formation reactions.

c) Influence of UV Light

To elucidate the influence of UV light on the occurring surface reactions during the weathering process the polycrystalline silver samples were exposed to 90% RH with 250 ppm CO₂ and 50% RH with 250 ppm CO₂ and additionally irradiated with UV light for the first 30 min of weathering. The obtained time resolved IRRAS spectra are shown in Fig. (6a, b). At both relative humidity contents the IRRAS spectra were taken after 1 min, 16 min and 30 min of UV light irradiation. The spectra obtained from the sample weathered in 90% RH clearly show the growth of the bands at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ with time. Comparing the obtained signals (Fig. 6a) with the signals obtained from the sample weathered without UV light (Fig. 3a) shows that the UV light clearly enhances the formation of the carbonate species on the surface. This is indicated by a higher relative intensity of the band at 1221 cm⁻¹ by a factor of approximately 4.2. Furthermore, the band at 1109 cm⁻¹ increases by 1.2 times and the band at 922 cm⁻¹ by a factor of 1.1. This increase of the 1221 cm⁻¹ signal is seemingly caused on the expense of the -C-O signal (1109 cm⁻¹) which is clearly decreased compared to the results obtained from the samples without UV irradiation. Also the intensity relation of the bands at 1109 cm⁻¹ and 922 cm⁻¹ is shifted for the benefit of the band at 922 cm⁻¹ in the experiments with UV irradiation. Therefore, it can be stated that UV light enhances the formation rate of the surface carbonate species. The sample

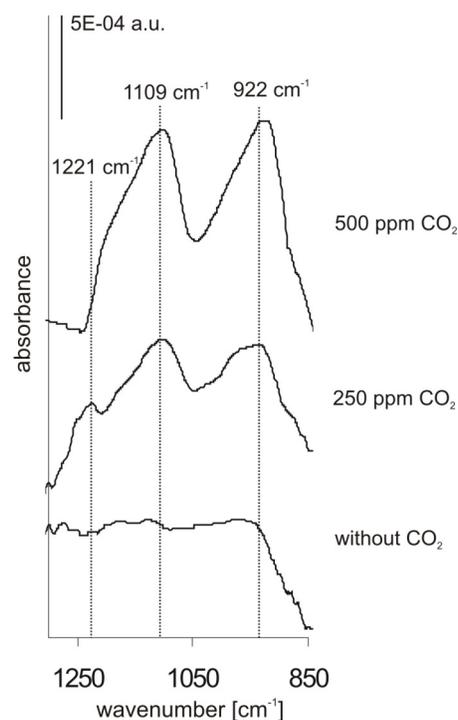


Fig. (5). *In situ* IRRAS spectra of the polycrystalline silver sample exposed for 60 min to 90% RH without addition of CO₂ and to 90% RH with addition of either 250 or 500 ppm CO₂.

weathered in 50% RH with 250 ppm CO₂ only shows bands at 1109 cm⁻¹ and 922 cm⁻¹ at very low intensities compared to the sample weathered in 90% RH with 250 ppm CO₂. This might be explained by the assumption that irradiating of the surface causes the adsorbed water and therefore the thinner water film at 50% RH to partly dry up resulting in a distorted surface chemistry. In accordance with Fig. (3), where the influence of the relative humidity content was shown to have a major impact on the silver carbonate species formation, also during UV light exposure the silver carbonate formation seems to be highly dependent on the relative humidity content. To get a deeper insight into the UV caused

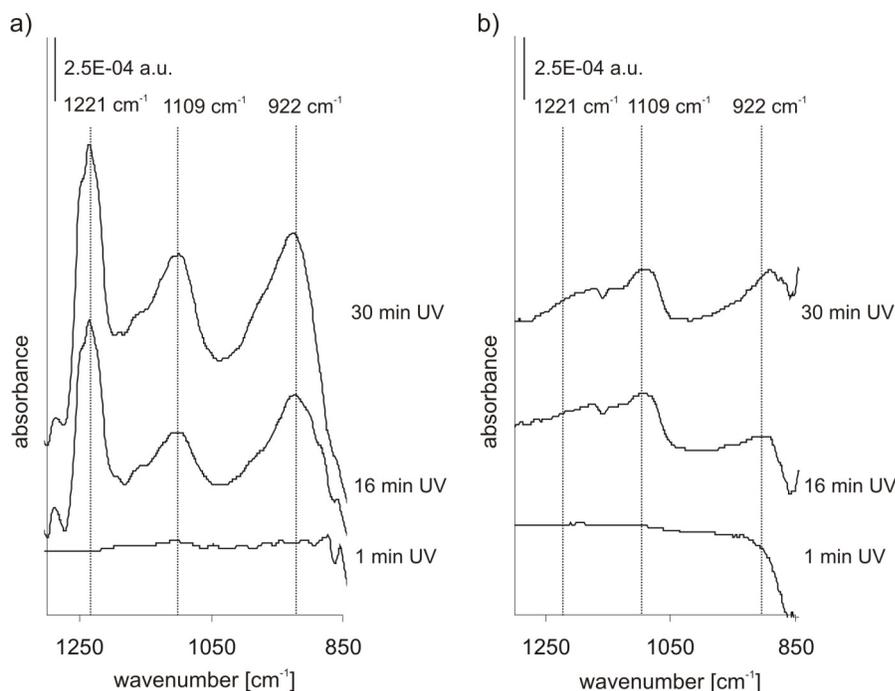


Fig. (6). Time-resolved *in situ* IRRAS spectra obtained from the polycrystalline silver samples irradiated with UV light and exposed to (a) 90% RH with addition of 250 ppm CO₂ and (b) 50% RH with addition of 250 ppm CO₂.

photochemistry on the silver surface the progression of the bands at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ was followed after the irradiation of the sample was stopped. Fig. (7) depicts the IRRAS spectra of the polycrystalline silver sample exposed to 90% RH with addition of 250 ppm CO₂ after 30 min of irradiation with UV light and after 30 and 90 min after turning-off the UV light. Corresponding to the results described above the three main absorbance bands at 1221 cm⁻¹, 1109 cm⁻¹ and 922 cm⁻¹ are clearly visible after 30 min of UV light exposure. 30 min after turning-off the UV light and continuing the weathering process with 90% RH and 250 ppm CO₂ the same three absorbance bands can be observed even though the intensity of the band at 1221 cm⁻¹ has shifted for the benefit of the 1109 cm⁻¹ signal. With increasing time this shift progresses until the 1221 cm⁻¹ signal is completely disappeared after 90 min of turning-off the irradiation source. As the band at 1221 cm⁻¹ was correlated to the Ag₂CO₃ formation, and the band at 1109 cm⁻¹ being a precursor of carbonate formation it can be concluded that the formed surface silver carbonate species is not stable after turning-off the UV light under these weathering conditions. This is a further strong hint for a change in the surface chemistry caused by the influence of UV light. Seemingly the - in the presence of UV light - formed carbonate species is detached to the surface and after turning-off of the UV light this carbonate species strips from the surface and is dissolved in the surface waterfilm indicated by an increased signal at 922 cm⁻¹ ([HO-CO₃]). This is also in agreement with [1] which states that silver carbonate is rather soluble in aqueous solution.

3.2. In Situ QCM Results

a) Influence of the Humidity Content

The correlating mass changes [$\mu\text{g}\cdot\text{cm}^{-2}$] on the sample surfaces during the weathering experiments were recorded

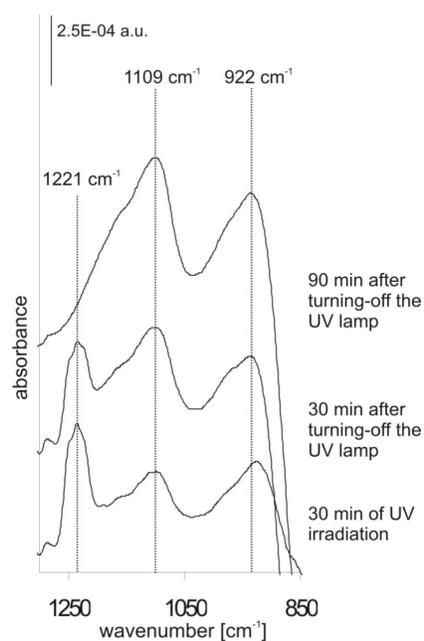


Fig. (7). *In situ* IRRAS spectra of the exposed silver sample (90% RH with addition of 250 ppm CO₂) while and after irradiation with UV light.

simultaneously to the IRRAS spectra by *in situ* QCM measurements (Fig. 8). The sample weathered in 90% RH with addition of 250 ppm CO₂ reaches a final mass of 0.3 $\mu\text{g}\cdot\text{cm}^{-2}$ after 120 min of weathering corresponding to a corrosion rate of 2.5E-03 $\mu\text{g}\cdot\text{min}^{-1}\cdot\text{cm}^{-1}$. Whereas the sample weathered in 50% RH with addition of 250 ppm only reaches a final mass of 0.2 $\mu\text{g}\cdot\text{cm}^{-2}$ (1.6E-03 $\mu\text{g}\cdot\text{min}^{-1}\cdot\text{cm}^{-1}$) after 120 min of exposure. This means that the mass increase of the

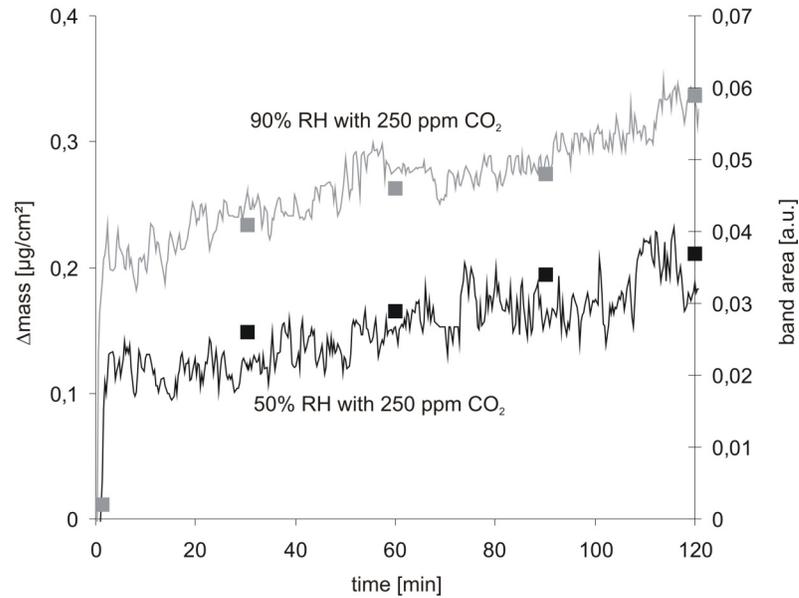


Fig. (8). Relation between the sums of the integrated band areas of the signals at 922 cm^{-1} , 1109 cm^{-1} and 1221 cm^{-1} measured by IRRAS (symbolized in the figure by the squares) and the equivalent time resolved mass changes measured simultaneously by QCM.

sample weathered in 90% RH with 250 ppm CO_2 is approximately 1.5 times higher compared to the sample weathered in 50% RH with 250 ppm CO_2 which is a further strong hint for the importance of the surface waterfilm for the degradation reactions occurring on the sample surfaces. Fig. (8) also shows the summed up integrated band areas from the signals at 922 cm^{-1} , 1109 cm^{-1} and 1221 cm^{-1} and the correlation of these signals to the overall mass progression during weathering. As proven by the progression of the signals shown in Fig. (8) there is a perfect correlation between the overall mass increases observed on the sample surfaces and the area of the integrated IRRAS bands causing this increase. Furthermore, these results show a clear dependence of the

formation rate of basic silver carbonate species on a silver surface on the relative humidity content of the ambient atmosphere.

b) Influence of UV Light

The QCM results of the silver samples weathered in 90% and 50% RH with addition of 250 ppm CO_2 under UV light exposure for 30 min are shown in Fig. (9). Both samples were weathered for 120 minutes and then the UV light was turned-on for 30 min (timescale 120-150 min in Fig. (9)). After 150 min the UV light was turned-off continuing with the same weathering conditions. After 120 min of weathering the sample exposed to 50% RH and 250 ppm CO_2 shows

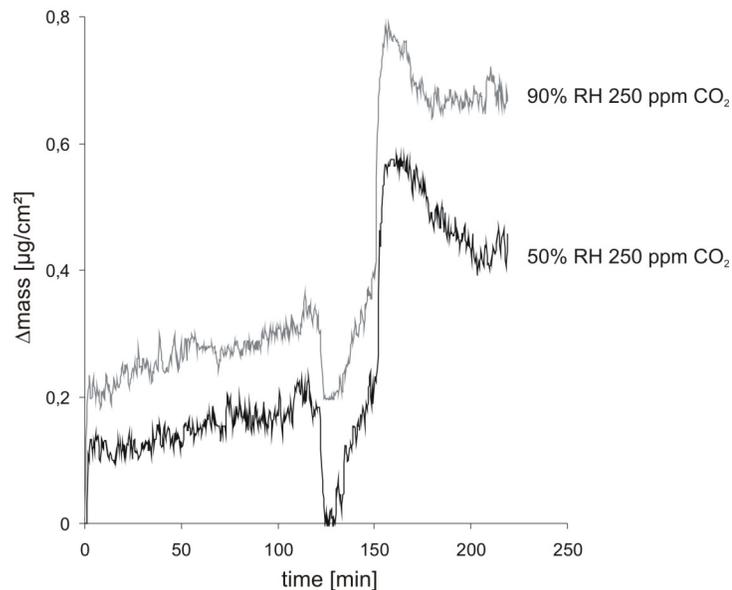


Fig. (9). QCM results obtained from the samples weathered in 90% and 50% RH and 250 ppm CO_2 . Both samples were irradiated for 30 min with UV light in the weathering period from 120 to 150 minutes.

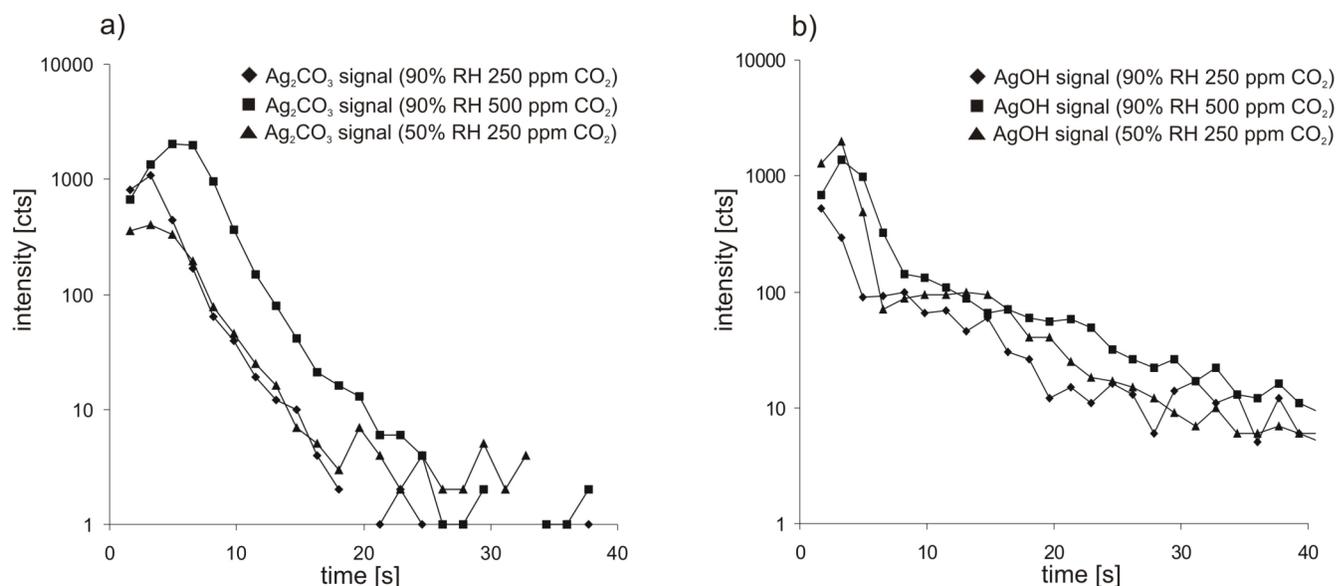


Fig. (10). TOF-SIMS signals obtained from the samples weathered in 90% RH with 250 ppm and 500 ppm CO_2 , and 50% RH with 250 ppm CO_2 , all irradiated with UV light for a period of 30 min.

a mass increase of $0.2 \mu\text{g}\cdot\text{cm}^{-2}$ and the sample exposed to 90% RH and 250 ppm CO_2 reaches a mass of $0.3 \mu\text{g}\cdot\text{cm}^{-2}$. Therefore, the mass increase of the sample weathered in 90% RH with 250 ppm CO_2 is enhanced by a factor of 1.5 compared to the sample weathered in 50% RH with 250 ppm CO_2 . When turning-on the UV light a sudden decrease of mass, followed by a fast mass increase can be observed for both samples. This decrease in the beginning might be due to the fact that the UV light irradiation causes a disturbance of the surface equilibrium. After 220 min a final mass of $0.69 \mu\text{g}\cdot\text{cm}^{-2}$ for the sample weathered in 50% RH with 250 ppm CO_2 and a final mass of $0.43 \mu\text{g}\cdot\text{cm}^{-2}$ for the sample weathered in 90% RH with 250 ppm CO_2 was obtained. This equals to a relative mass increase factor of 1.6 which is comparable to the results obtained without irradiation with UV light even though the absolute obtained masses are higher.

Being able to quantitatively relate the band areas obtained from the IRRAS measurements to the simultaneously obtained masses by the QCM measurements, the band areas from the IRRAS spectra were multiplied by the corresponding atomic masses for each of the three IRRAS bands for the samples with and without UV light and summed up. Dividing the obtained results from the calculations from the samples weathered with and without UV light irradiation leads to a relative ratio of approximately 2. Correlating this with the ratio of the QCM results, where a final mass of $0.32 \mu\text{g}\cdot\text{cm}^{-2}$ was reached by the sample without UV irradiation and $0.69 \mu\text{g}\cdot\text{cm}^{-2}$ for the sample exposed to UV light (both in atmospheres of 90% RH and 250 ppm CO_2) also leads to an approximated ratio of 2. This is a further strong hint for the presence of the three identified surface species.

3.3. Ex Situ TOF-SIMS

For a further prove of the assumed surface species *ex situ* TOF-SIMS investigations were accomplished on the weathered sample surfaces. Fig. (10) shows the Ag_2CO_3 and the AgOH TOF-SIMS signals obtained from the samples weathered in 90% RH with 250 ppm and 500 ppm CO_2 respec-

tively, and from the sample weathered in 50% RH with 250 ppm CO_2 . All three samples were exposed to UV light for 30 min during weathering. The depth profiles were obtained during sputtering with Cs^+ ions. To achieve better depth resolution an accelerating voltage of 0.25 keV was used. It is clearly visible that the Ag_2CO_3 and AgOH signal of the sample weathered in 90% RH with 250 ppm CO_2 decreases faster than the signal obtained from the sample weathered in 90% RH with 500 ppm CO_2 . This means that the sample weathered in 90% RH and 500 ppm CO_2 has formed a thicker Ag_2CO_3 surface layer compared to the sample weathered in 90% RH with 250 ppm CO_2 . The fact that even the sample in 50% RH and 250 ppm CO_2 seems to form Ag_2CO_3 species on the sample surface - although at much lower intensities - shows that even a thin water layer on the silver surface is able to hydroxylate and oxidize a silver surface. Furthermore, the AgOH signal shows the highest intensity for the sample weathered in 50% and 250 ppm CO_2 . This might be due to the thinner water layer formed on the silver surface which results in less formation of Ag_2CO_3 and therefore to a relatively higher hydroxylation of the surface. The *ex situ* TOF-SIMS results could prove the results of the IRRAS/QCM measurements by means of chemical species present on the surface.

4. CONCLUSION

The experimental work described herein could show for the very first time the *in situ* formation of a basic silver carbonate ($\text{AgOHAg}_2\text{CO}_3$) species under ambient atmospheres and pressure on silver surfaces applying a newly developed IRRAS/QCM setup. The reaction of a hydroxylated silver surface with CO_2 in the presence of humidity produces a $\text{AgOHAg}_2\text{CO}_3$ surface species which has three characteristic bands at 1221 cm^{-1} , 1109 cm^{-1} and 922 cm^{-1} . Furthermore, the results presented here prove that environmental influences such as CO_2 concentration, relative humidity content and irradiation with UV light have a major impact on the corrosion rate and the corrosion products formed on the sample surfaces.

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