In Search of Frequency: Glass-induced Metal Corrosion in the Deutsches Bergbau-Museum Bochum

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Keywords

Deutsches Bergbau-Museum, formate, GIM, glass induced metal corrosion, miners' lamps, surveying instruments

Abstract

Together with humidity and oxygen from the air, electrolytes that form during glass decay can induce corrosion in neighbouring metals. The presence of sodium, potassium, and formate ions on glass leads to the formation of special metal corrosion compounds. The late discovery of this phenomenon in museum collections pointed to its rareness, but a survey in the cultural history collection of the Swiss National Museum discovered the proportion of affected objects was more than 20 %. The question arose whether this is a common phenomenon or if it only occurs in exceptional cases. For a new investigation and for an independent test on the frequency of this phenomenon, the collection of the Deutsches Bergbau-Museum Bochum (DBM) was selected. The museum has large collections of miners' lamps and surveying instruments, which exhibit glass-metal contact. In fact, severe cases of corrosion have rarely been detected, but light cases are in the order of 10 %. The compounds identified in the DBM technical heritage collection were the same as those found before in decorative arts collections.

Introduction

Metal corrosion occurs when susceptible metals come in contact with oxygen, water, and electrolytes. Museum displays and stores are full of sensitive metal objects, and the air around has plenty of oxygen and humidity. However, what about electrolytes? Electrolytes are compounds like acids or salts, which dissociate into cat- and anions in water providing the conductivity necessary for corrosion reactions rates to increase. Traces of acidic gases from the air, mainly CO_2 (now more than 400 ppm), but also pollutants like SO_2 and NO_x dissolve in pure water. Therefore, it becomes slightly acidic (pH ≈ 5) and traces of the anions CO_3^{2-}, SO_4^{2-}, and NO_3^- can be detected. Depending on the metal, corrosion is quite slow under such circumstances. The situation changes totally if additional sources of electrolytes are available: Metal corrosion involves the flow of charges, and on the liquid side, a high concentration of ions means a high electric conductivity accelerating the charge flow (i.e. the reaction rate).

Only 10 years ago (Eggert, 2010) it was fully realised that decomposing historic glasses may also provide electrolyte solutions inducing corrosion in neighbouring metals. This led to the design of the GIMME (= **G**lass **I**nduced **M**etal-corrosion on **M**useum **E**xhibits) explorative research projects 2012-2015 (Eggert and Fischer, 2012) at the Stuttgart State Academy of Art and Design (ABK) supported by Friede Springer Stiftung. It was followed by a project (2016-2019) on analysis and prevention of glass induced metal corrosion funded by the German Federal Environmental Foundation (DBU Az. 33255/01) which included the survey in the DBM reported here.

Glass Induced Metal Corrosion (GIM)

Manufactured glass forms an important part of our cultural heritage. Janssens' handbook (2013) provides details on 'Raw materials, Recipes and Procedures Used for Making Glass' (Janssen, 2013, Ch. 1.2, pp.23-36) and the development of 'Glass Composition over Several Millennia in the Western World' (Ch. 1.4, pp.67-78).

Due to its 3D network with strong Si-O-Si bonds (oxygen bridges), quartz (SiO_2), the main component of sand used for glass, has a melting point of 1.713 °C. Such extremely high temperatures could not be achieved in ancient melting furnaces. Therefore, to produce glass, fluxes like potassium (for potash glass) or sodium carbonate (for soda glass) were needed to sever some of these oxygen bridges. Scission of bridges can be achieved by O^{2-} ions occurring in oxides of sodium potassium, or clacium. These oxides are formed by heating the corresponding carbonates in the melt, e.g.:

$$Na^+{}_2CO_3{}^{2-} \rightarrow Na^+{}_2O^{2-} + CO_2\uparrow.$$

The oxide anion O^{2-} is a Lewis base (electron donor) which attacks the Lewis acid Si^{IV+} (electron acceptor) and transforms an oxygen bridge into two-charged non-bridging oxygens in the structure:

$$\equiv Si\text{-}O\text{-}Si\equiv + Na^+{}_2O^{2-} \rightarrow \equiv Si\text{-}O^-Na^+ + Na^+\,{}^-O\text{-}Si$$

Water molecules from aerial humidity can leach out these sodium cations forming silanol groups:

$$\equiv Si\text{-}O\text{-}Na^+ + H_2O \rightarrow \equiv Si\text{-}O\text{-}H + Na^+OH^-$$

Water is then absorbed forming alkaline liquid films of sodium hydroxide on the surface of historic glass. Bases readily absorb carbon dioxide from the air forming carbonate ($CO_3{}^{2-}$):

$$2Na^+OH^- + CO_2 \rightarrow Na^+{}_2CO_3{}^{2-} + H_2O$$

More details on ‘Historic glass and its interaction with the environment’ are given by Römich (1999).

Contrary to expectations, in the liquid surface films or the white haze on glass (when the relative humidity is below the deliquescence point of the salts), formate, not carbonate, dominates (Verhaar, 2018). A likely explanation is the base catalysed Cannizzaro reaction of the ubiquitous indoor pollutant formaldehyde[1] according to:

$$Na^+OH^- + 2H_2CO \rightarrow NaHCOO^- + CH_3OH\uparrow$$

Formaldehyde is indeed known to react on oxide surfaces (including SiO_2) producing formate at room temperature (Busca, et al., 1987). Like a dosimetre, the alkaline films absorb formaldehyde over decades and centuries and make formate ions directly available in solution such that no aerial adsorption on particles and oxidation are required. When glasses are stored in wood-based cupboards (e.g., made from oak), the films are also exposed to traces of acetic and, to a lesser degree, formic acid. Acetate can, therefore, also be detected in the films.

In many objects, glass is in direct contact to metal. Metallic parts are exposed to alkaline films on the glass, which, as aqueous electrolytes, are able to induce metal corrosion in the presence of air containing some humidity. The presence of Na^+, K^+ (from potash glass), OH-, $HCOO^-$, CH_3COO^-, and $CO_3{}^{2-}$ leads to the formation of special metal corrosion products indicative of the role of glass in their formation. Often, objects only show metal corrosion close to the glass and not elsewhere.

Fischer (2016) gives an overview of types of combined metal/glass heritage objects affected by GIM. Early Renaissance Limoges enamels, which are noted for their unstable glass composition (Smith, Carlson and Newman, 1987), are particularly at risk. Crystal growth can cause the spalling of enamel layers. By comparison, the risk to glass vessels, including the metal mountings, seems less substantial because the damage is not obviously associated with loss of material. However, Fischer (2016) also detected severe corrosion on gilt mountings, optical instruments or spectacles. Many folk jewellery objects decorated with glass gems also suffer from glass induced metal corrosion. In the case of daguerreotypes, miniatures with metal passe-partouts, and watches, the metal corrosion is triggered by the protective cover glass. Moisture trapped inside the sealed space promotes glass deterioration, which correspondingly affects metal corrosion. A major loss of material was observed on many objects where thin wire fixes glass components. This is the case with traditional bridal crowns, Christmas tree baubles, or reliquaries. Glass-induced metal corrosion consequently leads to wire breakage, resulting in glass beads and other decorative elements getting detached.

Green to blue Cu^{2+} corrosion products are found on copper and its alloys. This includes historic silver where only the minor amount of copper in the alloy reacts. The main compounds (Table 1) of these are copper formates. Sodium copper formate ① is detected in half of all GIM cases.

Mountable single crystals of this compound could not be detected under the binocular microscope. Nevertheless, its crystal structure could be derived from high precision X-ray Powder Diffraction (XRPD) (Dinnebier, et al., 2015) using state-of-the-art advanced methods of data evaluation. For the second most frequent compound (1/3 of all cases), copper formate trihydroxide ② (Eggert, et al., 2011), a single crystal was available for structure determination (Euler, et al., 2009). This compound often occurs together with sodium copper formate ①, indicating similar conditions of precipitation. On potash glasses, where nearly no sodium is available, copper formate trihydroxide is found on its own.

Zinc from the copper alloy brass also forms corrosion products. Zinc formate dihydrate ③ is detected most often in contact to glass (Fischer, et al., 2019) while reports on objects without glass (e.g. zinc coins in chipboard drawers) are rarer. The complicated structure of a new

Table 1. Detected GIM Compounds.

Name	Formula	References
Formates		
① Sodium copper formate hydroxide oxide hydrate	$Cu_4Na_4O(HCOO)_8(OH)_2\cdot 4H_2O$	Fischer, et al., 2018
② Copper formate trihydroxide	$Cu_2(OH)_3HCOO$	Eggert, et al., 2011; Fischer, 2016
③ Zinc formate dihydrate	$Zn(COOH)_2\cdot 2H_2O$	Fischer, et al., 2019
④ Zinc copper formate hydroxide hydrate	$Zn_4Cu_3(Zn_{1-x}Cu_x)_6(HCOO)_8(OH)_{18}\cdot 6(H_2O)$, $0 \le x \le 1$	Bette, et al., 2019
Carbonates		
⑤ Chalconatronite	$Na_2[Cu(CO_3)_2]\cdot 3H_2O$	Fischer, et al., 2020
⑥ Sodium copper acetate carbonate	$NaCu(CO_3)(CH_3CO_2)\cdot nH_2O$	Fischer, 2016
⑦ Sodium lead carbonate hydroxide	$NaPb_2(CO_3)_2(OH)$	Fischer, et al., 2013
⑧ Potassium lead carbonate hydroxide	$KPb_2(CO_3)_2(OH)$	Bette, et al., 2017
Unknown		
Compounds containing Na, K, Cu, and/or Zn, often carboxylates		Fischer, 2016

corrosion product, basic zinc copper formate (‘Zinc C’) ④, could also be derived from powder diffraction measurements (Bette, et al., 2019). The composition of the new corrosion product is somewhat variable, as either copper or zinc can occupy one type of sites in the lattice. A pure one-phase sample from GIM model experiments could be used: Brass coupons were dipped in alkaline carbonate solutions and then exposed to formaldehyde vapours in a desiccator for half a year. – A number of other hitherto unknown corrosion products, some containing zinc, still need further characterisation.

Copper carbonates are found much rarer than formates, although chalconatronite ⑤ seems to be the first definite GIM product to be reported (Magee, 1999). This corrosion product forms when copper alloys are exposed to sodium carbonate solutions. These derive here from glass deterioration (Fischer, Eggert and Stelzner, 2020). other sources reported earlier were Egyptian soil and conservation treatments. As chalconatronite ⑤ was also found in GIM simulation experiments with metals soaked in soda solution and then exposed to some formaldehyde, it is not clear why this compound is comparatively rarely found in GIM samples from objects. When objects containing chalconatronite are stored in wooden cupboards emitting acetic acid, sodium acetate and sodium copper acetate carbonate ⑥ (exact formula and structure unknown) are formed. Thickett and Odlyha (2000) first detected this compound on Egyptian bronzes in the British Museum. The same transformation can occur with chalconatronite from glass-induced metal corrosion (Fischer, 2016).

For lead, basic sodium (Fischer, et al., 2013, ⑦) or potassium (Bette, et al., 2017, ⑧) lead carbonates form, but no formates could be detected. Other metals used in history like silver, iron, and tin are also prone to corrosion but no special corrosion products occurring in the presence of glass have been reported (Eggert, 2010). Future research will have to identify further (modern) metals that may suffer from GIM.

Survey in the Deutsches Bergbau-Museum

Glass-induced metal-corrosion on museum exhibits, despite being so conspicuous, has only been identified in the last decade as a general phenomenon (Eggert, 2010). From 2004 to 2012, only 13 affected objects could be identified. This lead to the tentative assumption that this phenomenon is extremely rare. This view changed completely during the full-time GIMME research projects when Fischer (2016) collected 400 samples from 250 objects between 2012 and 2015. A survey in the Swiss National Museum of some 700 objects with glass-metal contact (Keller and Fischer, 2015) showed that the frequency varies between types of objects but the frequency was astonishingly high, on average more than 20 % were affected. This led to the new hypothesis that when more than a few per cent of combined glass-metal objects are

Figure 1. Safety lamp DBM Inv. no. 030140115000. Photo: A. Schorpp.

hit, every larger mixed collection will have GIM cases in its store. To test this hypothesis and to get an independent estimate for the frequency of the phenomenon, the collection of the DBM was selected, because:

- Given the longstanding research in Bochum on metal corrosion of heritage objects, the museum willingly agreed to cooperate and to make their collection accessible.
- The material science lab of the museum was able to use their portable X-ray Fluorescence Spectroscopy (p-XRF) instrument (Niton Xl3t GOLDD) for on-site analyses. For the first time in GIM research, the corroding materials could be investigated: the composition of the metal alloys and the type of glass (Soda? Potash? Lead?). The method is not ideal for glass because elements like Na or lighter cannot be detected at the atmosphere. Others like Mg or P can hardly be quantified. The measurement is also sensitive to corrosion effects in the surface zone. Nevertheless, p-XRF has found useful applications in glass analysis (Kaiser and Shugar, 2012) because it is quick and non-destructive. If no other fluxes, such as potash or lead, are detected, a soda glass can be assumed.
- The collection was *terra incognita*, no GIM cases were known to its staff so far. Therefore, any bias in selecting a collection with special very sensitive types of objects was avoided.
- From 2012 to 2015, the search for GIM cases was mainly focused on the decorative arts. Technical heritage objects provided a new challenge with more modern items.
- The movement of the collection from display to storage during renovation in summer 2016 gave a welcome opportunity of access (but with considerable time constraints for the survey).

As methodology for the survey of the collection it was decided to follow this sequence of steps:

1. To select suitable classes of objects with metal-glass contact to ensure that a large number of items could be examined.
2. Visual inspection of all these items (including magnifying glasses) for signs of corrosion.
3. Classification of the extent of corrosion into the grades GIM 1 (little, barely visible), GIM 2 (advanced, clearly visible) and GIM 3 (strong, big loss and danger for the whole object), as has proven successful in the Swiss National Museum.
4. Characterisation of the materials of affected objects with p-XRF and sample any corrosion product, whenever it was possible.
5. Analytical investigation of corrosion samples with µ-Raman spectroscopy. Additional analyses of the elemental composition with EDX-SEM for those compounds which could not be safely identified (for experimental details, see Fischer, et al., 2018).

The largest group of objects (570 examples) selected was the outstanding collection of miners' lamps, which documents the technical development in the 19th and 20th century. Lamps often contain glass cylinders in contact to metal, frequently brass. More modern ones contain electrical bulbs which were discovered as a new object type prone to GIM. In some cases, it was hard to distinguish between GIM and powder residues from earlier polishing treatment. Such residues can act as poultices for humidity and themselves can cause some corrosion, a phenomenon well known to all metal conservators. 25 miners' lamps showed signs of GIM. Only the safety lamp DBM Inv. no. 030140115000 (Figure 1) fuelled with oil made in 1872 was classified in the highest grade GIM 3. The broken protection glass had droplets of alkaline liquids from glass deterioration on the inside in-

Figure 2. View from top into the opened lamp (Figure 1): corrosion of the reflector at contact zones to glass. Photo: A. Schorpp.

Figure 3. Corrosion on the shiny reflector (Figure 2) at contact zones to glass. Photo: A. Schorpp.

dicating advanced glass corrosion. As the p-XRF could not detect any traces of potassium, it apparently consists of soda glass. The shiny white nickel silver reflector (p-XRF: ca. 60 % Cu, 24 % Zn, 13 % Ni) showed strong blue-turquoise corrosion in contact to glass (Figure 2). In both samples from the left and right hand side (Figure 3), particles of chalconatronite ⑤ and basic zinc copper formate ④ were identified by Raman spectroscopy. There was no evidence for nickel compounds.

The collection of instruments for mine surveying ('Markscheidewesen') encompassed 162 objects. They have been stored before 2010 in a basement room with periods of high humidity. A photograph of 2003 shows instruments in wooden cupboards (Figure 4).

These storage conditions might have caused the highest proportion (20 %) of GIM compared to the other groups. Glass-metal contact was not only found at optical lenses, but also at cover glasses of compasses and glass levelling gauges/vials. The repetition theodolite (Figure 5) DBM Inv. no. 030150289000 showed the most severe GIM case: A glass levelling gauge (Figure 6) with ca. 8 % K_2O (possibly a mixed soda-potash glass)[2] was mounted in brass (p-XRF: CuZn32Pb1): The corrosion product was identified by its Raman spectrum as sodium copper formate ①, the most frequently found in GIM research.[3]

Objects with cover glasses in contact to metal are prone to GIM as prior observations in other collections have shown, e.g. daguerreotypes, miniatures with metal frames and watches (Fischer, 2016). Therefore, pocket watches (62 pieces) were also selected. Only four showed visual signs of GIM. The different Raman spectra of the two samples which could be taken could not be attributed to any compound. Typical products for glass-induced metal corrosion (①-⑧) can be excluded.

Pewter of the lids of glass tankards may contain some lead. On a vessel from the Veste Coburg we could identify – a hitherto unique discovery – basic potassium lead carbonate ⑧ on the metal mounting of the potash glass (Bette, et al., 2017). Therefore, we added this small group

Figure 4. Storage of surveying instruments in wooden cupboards in 2003. Photo: Archive DBM.

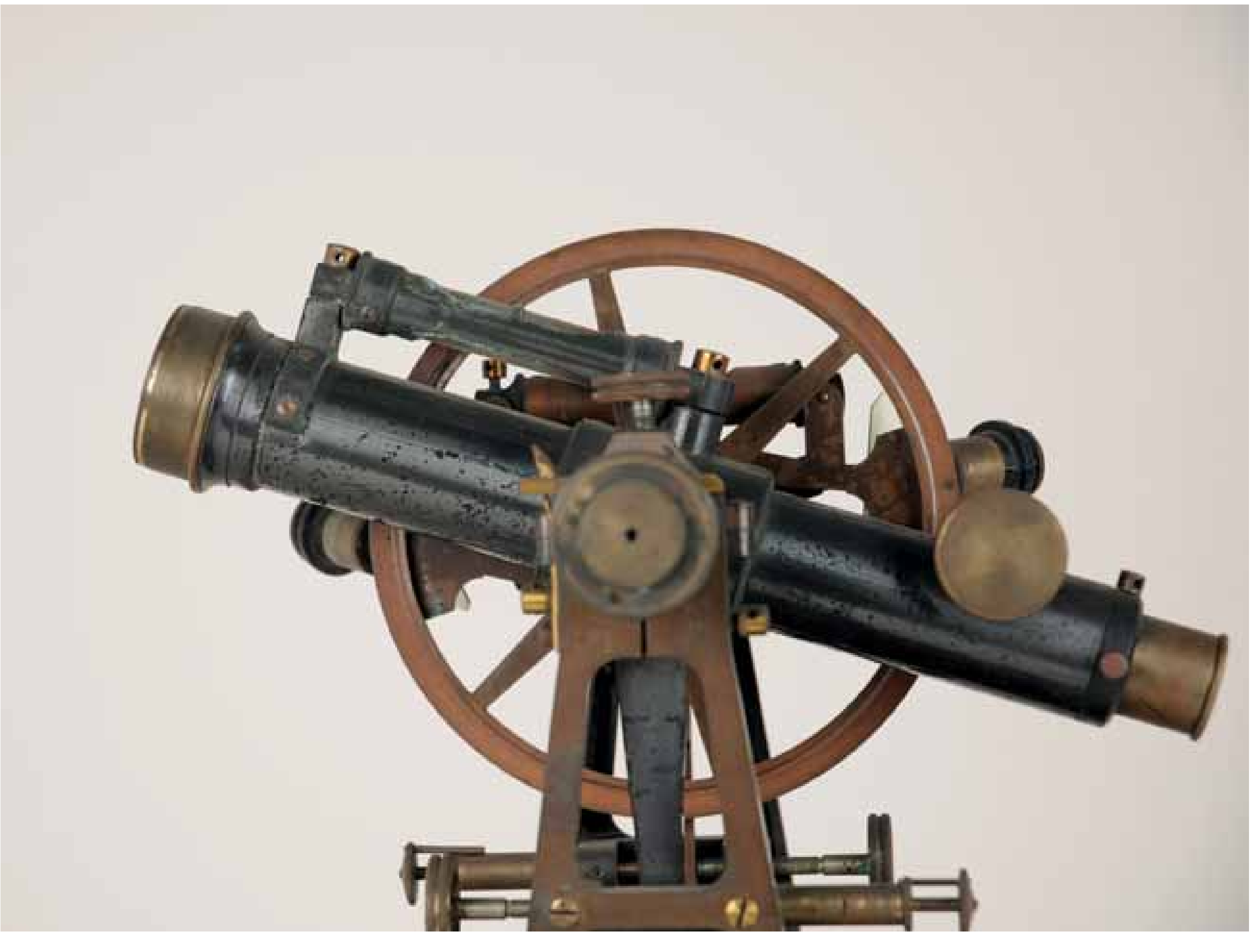

Figure 5. Repetition theodolite DBM Inv. no. 030150289000. Photo: M. Braun.

in the DBM (6 pieces) to the survey but could not identify any special corrosion product.

Raman analyses confirmed sodium copper formate ① and copper formate trihydroxide ② as most frequent GIM corrosion products, as was found previously in other collections. The presence of zinc in brass gave rise to the formation of zinc formate dihydrate ③ and the basic copper zinc formate ④. All these compounds are formates, but, interestingly, the carbonate chalconatronite ⑤ was also detected. As was found in a previous study (Fischer, 2016) a considerable number of compounds could still not be identified due to the lack of reference data in the literature.

All details of the survey can be found in the final report to DBU (Braun and Schorpp, 2017) which is archived in Bochum and Stuttgart.

In only about half (or less) of the sampled objects the GIM-phases were identified (Table 2). Other identified phases are only a few: calcium sulfate, sodium sulfate, atacamite, lead carbonate. We used visual observations for the calculation of frequency and assume that the corrosion samples are due to GIM. The somewhat surprising high number of unknown phases was also found before (Fischer, 2016). Even the formulas for the two most frequent products ① and ② were unknown before our research. Unfortunately, the DBM survey did not provide pure crystalline samples of ca. 1 mg suitable for XRPD and crystal structure determination of unknowns. According to Raman analyses, samples most often contained more than one compound.

Figure 6. Glass levelling gauge causing corrosion on the mounting brass. Photo: M. Braun.

Table 2. Results of the DBM survey.

Object group	Total no. invest.	Visual signs of GIM	Proportion	GIM grade	Sampled	Identification of compounds ①-⑧
Miners‘ lamps	570	25	4 %	GIM 1: 20 GIM 2: 4 GIM 3: 1	17	8
Surveying instruments	162	33	20 %	GIM 1: 23 GIM 2: 7 GIM 3: 3	23	13
Pocket watches	62	4	6 %	GIM 1: 4 GIM 2: 0 GIM 3: 0	2	0
Glass tankards	6	1	17 %	GIM 1: 1 GIM 2: 0 GIM 3: 0	1	0
Total	800	63	8 %	GIM 1: 48 GIM 2: 11 GIM 3: 4	43	21

Discussion

The statistical results of the survey are compiled in Table 2. The numbers will certainly have a margin of error as residues from polishing might have been mistaken for GIM and many objects could not be sampled in the interior to prove GIM. On the other hand, some GIM 1 cases with only local and slight corrosion might have been overlooked during the survey. But all in all, the numbers allow an estimate of the frequency. 0.5 % of all objects (4) with glass-metal contact surveyed (800) showed severe, eye catching corrosion of GIM grade 3; GIM 2 and 3 together involve just 15 objects, i.e. less than 2 %. Therefore, it is no wonder that GIM cases have not been reported before from the DBM. But if the objects of GIM 1 are included, which are only identified on closer inspection, then 8 % are affected. This again proves the common wisdom ‘You only see what you know’, which is our explanation that it took so long until the general GIM phenomenon was realised. As noticed before and is to be expected, frequency varies considerably with the classes of objects. This also explains why the frequency (overall, 22.5 %) was much higher in the Swiss National Museum. Here objects included thin wires and lamp-blown, easy-to-melt high-alkali glass. For instance, every third bridal crown (*Schäppeli*) with glass beads on wires showed GIM. The occurrence of GIM might be taken as indicator of glass instability, and then industrially produced glass for technical objects seems, on average, to be more stable than earlier historic glass.

Conclusion

The hypothesis that every large collection of glass-metal objects contains GIM cases could be confirmed for the DBM collection. Severe cases are indeed rare, but the order of magnitude for the overall frequency lies in the range of 10 %. Therefore, measures of preventive conservation need to be taken for such objects. The results from the DBU project and its model experiments advise to remove any source of formaldehyde. Therefore, wood-based materials should strictly be avoided in museum storage and display. If unavoidable, e.g. when sources of carbonyl pollutants like wood are part of the object itself or the ensemble which is displayed together, absorbents proved to be useful in model experiments. In objects without firm contact of glass and metal (e.g., glass beads on metal wire) separation layers (foils, lacquers) can be introduced for prevention of contact. The relative humidity should be lowered to those values recommended for ‘sick’ glasses, i.e. 35-42 % (Kunicki-Goldfinger, 2008). Lower values would even be better to decelerate corrosion, but the decomposition zone on the glass surface (‘gel layer’) is prone to cracks (‘crizzling’) when it dries out. The absolute lower values for storage of glass (and if there is just one value for all types of glass) are still a matter of discussion and need more experimental corroboration.

With now more than 500 samples from 350 objects in 40 collections analysed in Stuttgart, the existence of GIM as a frequent phenomenon has been established beyond reasonable doubt. The identification and characterisation of new corrosion products provided reference data useful for the whole conservation science community. Others will start their own investigations (see e.g. Holzleitner, et al., 2019) which will lead to the much-needed improvement of knowledge. The temporal behaviour, i.e. the dynamics/kinetics of GIM are nearly unexplored. The frequent use of p-XRF will give better ideas on the influence of the composition of glass and metals on GIM. Still too many corrosion products are simply unknown. With the software based crystal structure evaluation from high precision XRPD measurements[4], we now have an extremely useful tool at hand to overcome earlier limitations. Therefore, it is no risk to predict that GIM will stay in the conservation science news.

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Notes

1 for an overview of possible sources, see Salthammer, 2019)

2 Of 29 affected glasses, 11 contained more than 5% K.

3 The study focused on frequency. We do not have composition data for unaffected objects, therefore, we cannot say if potash glasses are more prone to this phenomenon.

4 As mentioned before, we owe the determination of formula and crystal structure of ①, ④, and ⑧ to data evaluation of XRPD. Hopefully, ⑥ is next.

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