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Laminated altered layers in historical glass: Density variations of silica nanoparticle random packings as explanation for the observed lamellae

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ABSTRACT

One of the most striking but unexplained phenomena in the natural degradation of glass is the transformation of an almost colorless, transparent and homogeneous glass into a colored, opaque and heterogeneous degradation layer. In many cases, the degradation layer consists of numerous lamellae with a thickness between 0.1 and 10 μm. However, both internal structure and formation process of laminated degradation layers remain unclear. In this paper, a model is proposed where we assume that transformed (degraded) glass consists of a random packing of nano-sized silica particles while the lamellae are the result of different packing densities. The model is able to connect the texture of numerous lamellae observed by several types of microscopic techniques with the structure at molecular level determined by means of chemical analysis. In addition, the model is able to explain numerous properties such as the parameters responsible for the contrast between lamellae. This contrast can be caused by differences in color, density, elemental composition, or surface roughness.

1. Introduction

Healthy glass can usually be considered as a transparent, almost colorless and extremely homogeneous material. From a chemical point of view, historical glass contains at the μm-level only limited undissolved nuggets while at a cm-level only subtle concentration gradients are noticed [1]. Natural degradation processes are able to transform such glasses into colored, opaque materials that are characterized by complex microstructures and morphologies. Examples of heterogeneities are the presence of Mn-rich inclusions, cracks, precipitates or lamellae. Analyses of transformed historic glasses where lamellae have been observed, are reported in several publications [2–10]. Moreover, lamellae were spontaneously generated in accelerated ageing experiments, without periodically changing external conditions such as temperature or pH [11,12]. Roemich et al. [13] were able to generate lamellae by placing SiO_2-K_2O-CaO model glass samples vertically in plastic containers containing soil with pH = 8.0 to 9.0 [13]. Guillot [14] generated lamellae by filling a bottle made from low quality glass with a saturated $NaHCO_3$ solution (pH = 8.4). Similar degradation conditions were observed by Bacon [15] where glass bottles containing gin (i.e., gin is one of the alcoholic products of neutral or alkaline nature) show the formation of flakes. The flakes deposited at the bottom of the bottle are sometimes associated to formation of lamellae.

The basic mechanism of glass alteration is considered to be known for a long time and the resulting altered layer appears to be well described at the molecular level. However, the internal structure of transformed glass containing lamellae and the lamellae formation mechanism at the μm-level still needs to be explored in detail. The presence of lamellae is usually explained by cracks or gaps between the lamellae [3] or by lamellae with alternating composition [8,9]. However, these explanations are not able to describe all the observed properties (e.g., the rather strong attachment of lamellae to one another [4,5], phenomena (e.g., advanced diffusion fronts of Mn-rich compounds in low density lamellae [16]) and experiments performed on transformed glass (e.g., no voids remain inside transformed glass when Mn-rich inclusions are reduced and dissolved [17]).

A series of 14–17th century archaeological glass artefacts have been analyzed in detail by means of optical microscopy, confocal microscopy, electron microscopy and FTIR microscopy. The samples analyzed are exemplary for many historical artefacts. Some of them have specific features such as remarkable large lamellae, the presence of sublamellae or the presence of Mn-rich dendrites giving enhanced insights in the internal structure. The analytical results are extrapolated to a general model that connects the complex heterogeneous microscopic structure due to the presence of lamellae to the well-known molecular structure of altered glass. The model is able to explain numerous properties of altered glass that are found in literature, sustaining the extrapolation of our model. An example are the quantities responsible for the contrast between lamellae as observed with several microscopic techniques.

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2. Background

2.1. Basic definitions

The various and confusing terminology used to describe the degraded zone just beneath the surface of the solid illustrates that both internal structure and alteration mechanism are poorly understood. Examples are leached layer [18,19], gel layer [19], weathered glass [20,21], crust [22], multilayered crust [2,23], crust with gel lamination [24], deteriorated glass surface [20], corroded glass layer [25], film [3], decomposed glass [3], silica rich layer [6], silica-rich film [26], alkali deficient layer [6], hydrated surface layer [27], surface layer [28], altered glass [29], altered layer [17] or transformed layer [30]. In some cases the names/terms have a similar meaning, while in other cases authors use the names/terms with a particular meaning. For example, 'crust' is not only used to denote the transformed glass but also a layer of insoluble Mg and Ca salts formed on top of the glass surface [31]. The cacophony of terms hampers the understanding of the transformation process of glass. Attempts were made to clarify some of the terms by normalizing the definitions [32] but unfortunately only general terms such as 'ageing', 'deterioration' or 'weathering' were included in the norm. In addition, some authors do confuse a specific degradation state with the process leading to that state. To avoid confusion for the reader, throughout the remainder of the manuscript the more neutral term 'transformed glass' is used for the degraded zone. The degradation process leading to transformed glass is denoted by 'transformation process'.

2.2. Internal structure of transformed glass

At the molecular level, the internal structure of healthy glass is well described by the continuous random network model [33] or by the modified random network model [34]. At that level, several models exist that describe the internal structure of transformed glass. Some authors assume that it is similar to the three-dimensional silicate network originally present in the healthy glass but with a replacement of the mobile cations by protons [35]. Others assume that the original silicate network in healthy glass is partially destroyed and replaced by a three-dimensional silica network [36,37]. This drastic change in molecular structure goes along with the increase in the amount of bridging oxygens (BO, oxygens linking two neighboring Si atoms), while the amount of non-bridging oxygens (NBO, oxygen atoms bound to only one Si atom) decreases during the degradation process. For that reason, some authors state that transformed glass has a similar structure as vitreous silica [26]. Another hypothesis is that for durable glass the structure of the transformed glass is similar to that of the bulk, while for low durability glass a transformed layer is formed with a structure different from that of the bulk [38]. Bunker [39] claims that the transformation process goes along with an irreversible restructuring of the healthy glass into a material that resembles an aggregation of colloidal silica particles. Finally, some associate the structure of transformed glass with that of opal [29,40].

At the microscopic level, several models do exist that describe the internal structure of transformed glass containing lamellae. The 3 categories in which the models can be classified are described below. The first two models are regularly mentioned in heritage-related literature, while the model of Raman appears to be unknown in the heritage community. It is the intention of this article to develop the most accurate model to describe the internal structure of transformed glass containing lamellae. In order to realize this goal, several historical samples have been analyzed thoroughly using several analytical techniques.

1. Model proposed by Brewster [3]: Brewster was one of the first who saw a relation between the iridescent color of transformed glass and the presence of lamellae. Brewster came to that conclusion because the colors are the same as those generated by thin plates interposed with air (e.g. Newton's rings or Fabry-Pérot etalon). It was only in 1917 that Rayleigh gave a mathematical description of the 'color of old decomposed glass' due to reflection from a regular stratification [41]. Brewster also demonstrated that transformed glass containing lamellae is able to absorb water and other liquids, concluding that such material must be porous. He suggested that the porosity is located between the films, resulting in solid layers separated by thin layers of air. The films are not in optical contact but somehow they adhere to each other firmly. A similar model is still used by some authors, although the thin layers of air are sometimes described as cracks [7,17] or as interlaminar spacings [42]. Such gaps must have thickness of at least 100 nm to cause interference in the visible range. In case of numerous parallel cracks, their position must be quasi-periodic to allow interference. However, the firm adherence of subsequent lamellae on the one hand and the presence of air between the layers so that they are not in optical contact on the other hand is considered as contradictory [4].
2. Thin layers of transformed glass alternated with another solid material: if both transparent solid materials have a different chemical composition and thus a different refractive index, the layers are able to cause interference. Guillot [14] explained the formation of lamellae in his experiments by the formation of alternating layers of silica and calcium carbonate. Shaw [8] explained with such type of model the remarkable and repeatable periodicity of Ca and Si-rich layers. Also Sterpenich [9] noticed an anti-correlation between the oscillating signals of Al and Si on one hand and the signals of Ca and P on the other hand. Others identified the second solid as a smectite-like inter-lamellar material [43].
3. Model proposed by Raman [4,5]: the transformed glass is optically and mechanically a continuous structure, but there is a quasi-periodic distribution of cavities or pores in the structure. In this model, transformed glass consists of only one type of material. In this case, interference is governed by an effective volume-averaged refractive index, provided that the pore size is much smaller than the electromagnetic wavelengths of visible light [44]. This index changes with the porosity. An important argument in favor of this model compared to that of Brewster is that adjacent lamellae remain well attached to each other.

2.3. Transformation process

The best known theories describing the mechanism and kinetics of glass transformation processes are based on the leaching experiments performed by Douglas and Isard in 1949 [45]. From that publication onwards, glass transformation studies shifted gradually from the study of the internal structure of laminated transformed glass [3,4,5,14] to ion exchange and glass dissolution processes in accelerated ageing experiments without considering the formation of lamellae. However, a limited number of authors did make attempts to explain the formation of lamellae. An overview of the proposed mechanisms is given below.

1. Oscillating external conditions: some authors considered oscillating conditions outside the glass such a temperature cycles or seasonal wetting/drying events as the driving force for the formation of lamellae [22]. However, some authors remarked that lamellae were also formed at the bottom of the sea where external conditions are rather stable [43] and were produced in stable laboratory conditions [14];
2. Internal dynamics: others assume some internal dynamics of the transformation process itself as the cause of lamellae formation such as: (1) Liesegang-ring precipitations in a homogeneous matrix consisting of mainly silicic acid [10,14,46,47]. However, Raw [7] wonders if Liesegang ring intervals are ever so small. (2) A sequence of dissolution and precipitation reactions resulting in a layered structure with variation in chemical composition [48]. Or (3) a cyclic change of the pH of the attacking solution at the reaction front. This would control the formation of dissolved products by ion-exchange and silicate dissolution reactions, and by the solubility limits of the