Patina on Historic Glass:

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Cambridge Scholars Publishing

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This book first published 2020

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-5940-8
ISBN (13): 978-1-5275-5940-0

Front cover: Scanning Electron Microscope image of patina on glass from Cossack, Western Australia showing a range of internal structures. The prominent multilayered band oriented diagonally is the patina that is composed of laminated, colloform, micro-colloform, or micro-brecciated forms on a contact with glass (the white lower left area) that is planar to cuspate. The patina has a veneer of supra-patina crust that is composed of massive precipitate, embedded dust particles, and irregularly-shaped solution cavities. This image captures the important and recurring features of patina.

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CHAPTER 1

INTRODUCTION

This book is about patina (a very thin ‘crust’) developed by weathering of glass in soil, focussing specifically on bottle glass buried for 70-100 years in sand dunes in arid coastal Western Australia. It describes, for the first time, globally, patina to a detailed level that allows readers to delve into a microscopic world that holds a wealth of information about chronometry, hydrochemical and geochemical processes on buried glass, hydrochemical and geochemical processes in soils, on climate, and the complex products developed and expressed as laminations, layering, and other various structures. The patina can be used to help unravel recent climate history and, in this context, it has the potential to be a new and powerful tool in climatological studies. Similar to the study of tree rings (dendrochronology), it provides ultra-fine records of rainfall that is unparalleled in Nature, to determine the hydrochemical changes in rainfall, as well as providing insights into soil and soilwater processes. Patina also may prove to be a major chronometric tool in Archaeology.

Patination (weathering) of glass is complex, and this book is a World-first in the detail and holistic approach to its study. It describes and provides an interdisciplinary approach involving soil chemistry, granulometry, mineralogy, soil-water hydrochemistry, and glass chemistry, all necessary to study patina and fully appreciate its development and usefulness in sister sciences. Modern analytical techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) enabled mapping and analyses of patina and investigation of its contact with parent glass, and these, together with experimental leaching and pellicular water analyses of the enclosing sand and dust, have provided information and valuable insights into the development and paragenesis of patina on glass. This book highlights that to fully utilise patina for archaeological, hydro-chemical, geochemical, climatic, engineering, construction, and nuclear waste studies, a holistic multidisciplinary approach needs to be applied and this book, we believe, maps such a pathway.

This research into the patination of buried bottle glass began as an investigation into the feasibility of using its laminae as a dating tool for archaeologists, based on an holistic approach involving understanding the process of patination, including the influence and control of the composition of the parent glass on patina formation. Thereafter, however, as more information was obtained, the study expanded into investigating and understanding the micro-structures in the patina, the chemistry of the enclosing soil, the hydrochemistry of vadose and pellicular water, and the local climate as they all appeared to be interrelated. As the degree to which the glass was metastable became apparent, the study became holistic and multidisciplinary because the results and implications could be extended into other arenas, *e.g.*, for glass conservation, use of glass for storing toxic and radioactive wastes, and use of glass in construction and engineering.

The bottle glass used in this study, which was exposed to seasonal precipitation as the main agent of weathering, was retrieved from coastal carbonate-and-quartz sand dunes north of the historic township of Cossack in north-western Western Australia (Figure 1-1). With SEM, EDS, XRD, and ICP-MS, the patina on four (geochemically different) types of bottle glass was analysed to ascertain its structure and chemistry, and to determine the effects on primary glass material of short-term burial (70-100 years) in the sand, and the effects of exposure to seasonal precipitation in a tropical arid coastal environment.

The weathering of glass is a phenomenon which has attracted the attention of many researchers including industrial chemists, conservators, museum conservators, and archaeologists. There are many studies on the effects of different variables on glass weathering including humid atmospheres (Newton 1976; Schreiner *et al.* 1999; Garcia-Valles *et al.* 2003; Fearn *et al*. 2004), seawater and sea-bed sediments (Weier 1973; Cox and Ford 1989; Brzezinski *et al.* 2003), soil (Brewster 1863; Brill 1961; Brill and Hood 1961), and groundwater on the type and rate of glass weathering (Cox and Ford 1993). It is the potential for identifying the rate of glass weathering in different environmental circumstances that is of special interest to archaeologists because of its application to dating. In this study, we investigate this potential and its application for dating of glass from archaeological sites.

The process of weathering (patination) of glass is dependent, of course, upon the composition of the glass itself, the nature of the surface of the glass, the surface area exposed (Frank 1982), and aspects of the environment *e.g.,* the pH of the attacking solution and temperature, both of which act upon the glass (Newton 1971; Cox and Ford 1993). Weathering effects and products include: iridescence (Brewster 1863; Guillot 1934; Pollard and Heron 1996); crusts (Newton 1971); leached layers (Schreiner *et al*. 1999); pits and surface pitting (Maloney 1968; Garcia-Valles *et al*. 2003; Watkinson *et al*. 2005; Clifford 2008), plugs (Watkinson *et al*. 2005); crizells and dulling (Frank 1982; Fearn *et al.* 2004); and patinas (Garcia-Valles *et al*. 2003; Clifford 2008). Weathered glass may be found in a variety of archaeological locations and environments: *in situ* (*e.g.,* medieval window glass in monasteries and cathedrals in Europe); in the marine environment (*e.g.,* glass artefacts from shipwrecks); in historic refuse sites in humid climates (*e.g.,* glass from the cullet heap at Bagot's Park, Staffordshire, England [Newton 1976]); and in historic refuse sites in arid climates (*e.g.,* flat glass and bottle glass from Cossack, Western Australia, [Clifford 2008]).

As alluded to above, the study of the weathering of glass is important in many other disciplines. For instance, with the prolific use of glass in architecture in many polluted cities, its weathering is of concern as it affects the clarity and integrity of the glass.

Glass appears as artefacts in many archaeological sites, corroded and patinated to varying degrees, and the study of its patination for determining age of glass, time of weathering of the glass, and ancient environmental factors can be important and useful in the reconstruction and interpretation of archaeological sites. Further, glass decay affects the stained-glass windows of centuries-old monasteries and cathedrals, and unravelling the development of patina assists conservators whose aim it is to understand the processes of glass decay, and to restore and preserve such windows. In addition, glass has many applications in modern industries, one of the most important being the confining or storing of toxic waste products, including nuclear waste, in silicate glass matrices (Sterpenich and Libourel 2001) because how glass responds hydrochemically to fluids with which it is in contact is critical in this type of waste management. Glass also is finding use in the construction industry and in infrastructure (*e.g.*, glass-sand bricks, or glass-sand road material) and here the dynamics of glass weathering and decay has implications for its use and longevity in these engineering endeavours. It should be pointed out, however, at this stage, that while glass weathering and the formation of patina have implications for nuclear waste management, engineering, climate studies, and pedogenesis, all beyond the materials and scope in this book, the focus on patina and glass here is definitively on historic (archaeological) glass in the Cossack area, although the hydrochemical, micro-structural, and paragenetic results can be applied, in principle and as analogues, to management of these other endeavours.

Weathering occurs in many materials exposed to the weather and near-surface processes, and one of the products of weathering can be patina which occurs as a fine layer or encrustation, usually laminated, on the surface of rock or other material (Bates and Jackson 1987; Jackson 1997). The term 'patina' is also used with reference to the oxidation of metals such as bronze or copper, as well as for the layer on rock surfaces in arid regions (*e.g.*, 'desert varnish', *cf.* Bates and Jackson 1987; Jackson 1997). While various terms have been applied to the products of weathering or corrosion products on the surface of glass (*e.g.,* "crust" [Newton 1971; Cox and Ford 1993]; "weathered crust", or "weathering crust" [Brill 1961; Brill and Hood 1961; Newton 1976; Cox and Ford 1993; Schreiner *et al.* 1999]; "corrosion crust" [Brill and Hood 1961; Cox and Ford 1989]; encrustations, corrosion crusts), the term *patina* was first applied to the weathering crust on glass by Garcia-Valles *et al.* (2003). Brill (1961) and Brill and Hood (1961) believed that the number of layers often found in any patina on glass could be counted in much the same way that tree-rings are used to date wood.

Use of the term “weathering” or “weathered” for the altered surface of glass, or any crusts developed on glass, and for the development of the patina on glass is only justified if the encrustations can be shown to be an alteration product (at least in part) of the parent glass. It should not be used for micro-sedimentary features wholly accretionary on its surface such as for desert varnish as described by Garvie *et al.* (2008); or similar to diagenetic or pedogenic accretionary features such as the laminae of calcrete ooids, other soil ooids, or ironstone pisolites (see Figure 7 in Read [1974] and Plates 73 and 81 in Brewer and Sleeman [1988]). As will be shown in this study, while there has been accretion of laminae in the patina on the bottle glass from Cossack, this has been accompanied by corrosion and alteration of the parent glass, with remobilisation of silica and sodium from the parent glass which warrants the use of the terms “weathering” or “weathered”. However, patina is a complex product involving *in situ* alteration as well as accretion of laminae deriving from endogenic and exogenic sources. For this reason, for the bottle glass in this study, the term “weathering” alone does not describe the processes that produce exogenic accretionary laminae. The term “micro-sedimentation”, if it were to be applied, also does not describe the processes that involve corrosion and the invasive alteration of the parent glass. Both processes are occurring, and therefore the term *patina* is used to refer to both the weathering products and any micro-accretionary products developed on the bottle glass samples used in this study.

For the purpose of this study, a section has been included to provide definitions of the terms used, together with explanations of the technology used to provide information about the bottle glass under study. However, because *patina* is the focus of this study, it is expedient for a definition to be included at this point.

In *The Concise Oxford Dictionary of Archaeology* (2008) *patina* is defined as ‘the changes to the outer surface of an artifact … usually as a result of chemical, physical, or biological alteration through contact with the surrounding environment … [and] under normal circumstances takes time to form …’, however its use in the archaeological literature has almost exclusively been confined to naming the coating on metals, for example, bronze and copper. Again, the word, *patina*, is rarely used in the literature for the weathering of glass for which other terms have been used interchangeably, for example, *corrosion crusts* and *weathering crusts*. For the purpose of this study *patina* will be used throughout to describe any crust on the surface of weathered glass.

Other terms, which are frequently used interchangeably in the literature to describe the layers in the patina, are *laminae*, *lamellae*, *lamellar, laminoid,* and *layer(s)* and *layering.* Where the above terms are used by other researchers whose work is referenced in this study, those terms will be retained, however we will use the words *layer(s)* and *layering,* and *lamination*, *lamina* and *laminae* and *laminoid* (adj.) when describing such phenomena as part of this current study.

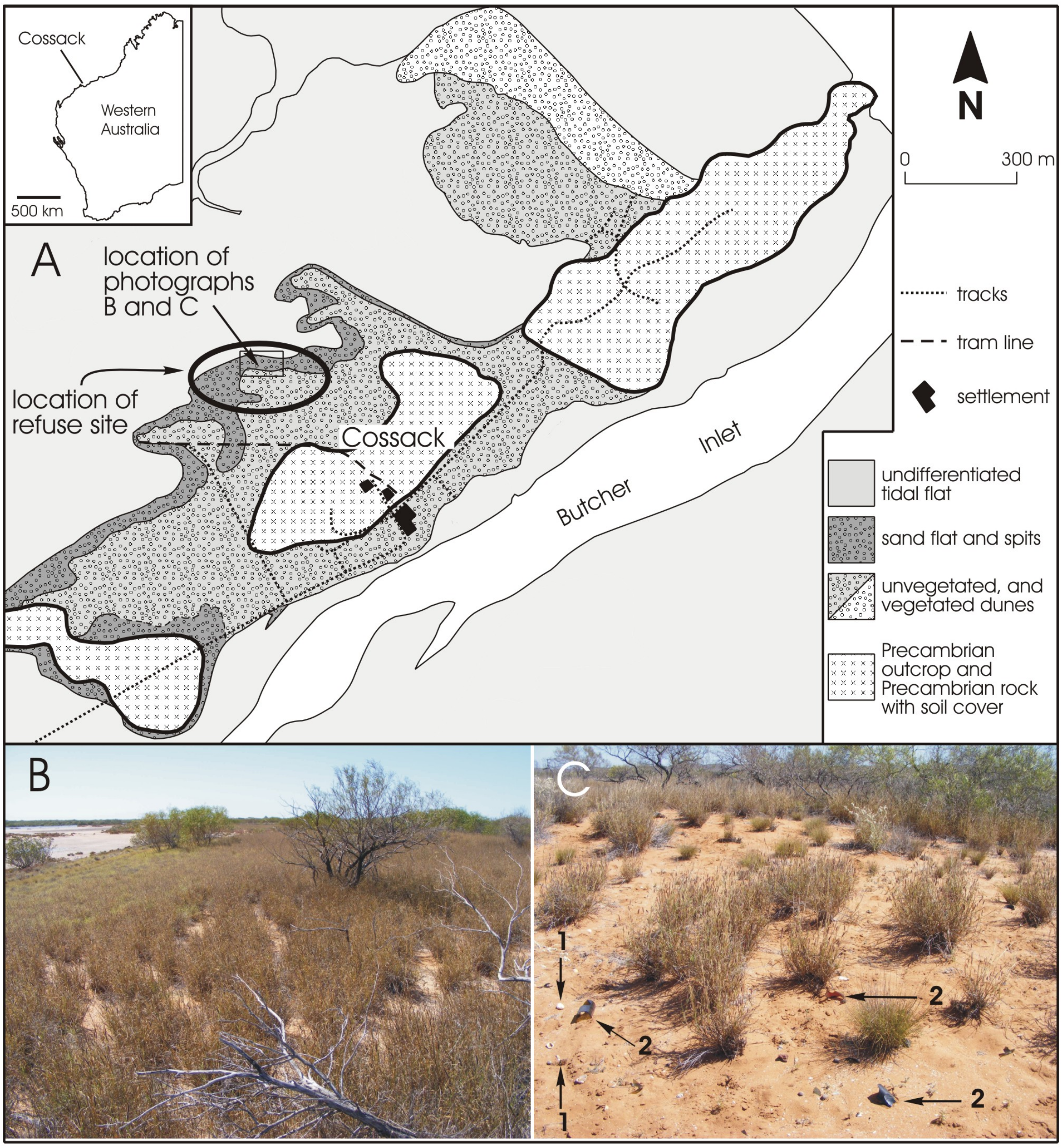

Figure 1-1: Location diagram of the field site. A. Location of Cossack in Western Australia, and map showing general nature of landforms north of Cossack where the study site is located. B. View of the sand dunes and sand spit, bordered by tidal flat. The study site is located on the sand spit and the sand dunes. C. Surface of the orange-coloured sand dune showing occurrence of (1) shell and (2) glass.

The glass being used in this study, as mentioned earlier, was recovered from the coastal dunes to the north of the township of Cossack which was declared as a town-site in 1863. It was the first port in the Pilbara region of Western Australia, and the hub of the pearling industry until the industry was relocated to Broome in 1886 following a Parliamentary enquiry which recommended the closure of the pearling banks in the Cossack area due to depletion of pearl stock (Shire of Roebourne 2007; Nayton 2011). The decline of the town continued into the early 1900s at which time use of the port was suitable only for smaller vessels, the larger vessels now using the new jetty at Point Samson. Cossack was abandoned in the late 1940s and while the town's buildings fell into disrepair before restoration in the early 2000s (Nayton 2011), at least one kilometre of scattered Indigenous sites remains in the immediate vicinity, extending to Settlers Beach. This once-thriving settlement, the population of which was of mixed ethnic origin, left behind a variety of artefacts (Nayton 2011), of which the weathered bottle glass used in this study is only a small portion.

In this study, emphasis is placed on the science underpinning patination of glass from the Cossack area because it is only through a thorough scientific understanding of the processes and products of patination that its archaeological and chronological implications and uses can be fully appreciated and robustly pursued. As such, in this study, glass structure and chemistry, patina structure and chemistry, and vadose hydrology and hydrochemistry were investigated to a scientific depth not normally developed in Archaeology.

An emphasis on science in archaeology reflects recent developments in the discipline which is evident in the literature, particularly at the microscale in patina (*e.g.*, Cox and Ford 1989, 1993; Schreiner *et al.* 1999; Garcia-Valles *et al.* 2003; Schreiner 2005; Silvestri *et al*. 2005; Barbera *et al*. 2012; Pinar *et al*. 2013; Lombardo *et al*. 2013). In fact, the last three decades have seen a steady growth of the application of scientific methods to Archaeology which is exemplified in part by the publication of the Springer journal, *Natural Science in Archaeology*, launched in the 1990s. This journal is dedicated to bridging the information gap at the interface between Archaeology and Science. The interdisciplinary approach using Science in archaeometry, for instance, is now considered indispensable and an integral part of archaeological studies. Interdisciplinary studies require a multidisciplinary background and, in this context, *Natural Science in Archaeology* covers a broad spectrum of physical, chemical, geological, and biological techniques applied to Archaeology.

It has been long noted that Archaeologists have been aware of the weathered surfaces on glass artefacts which, for instance, have been found in burial sites and in the remains of ancient cities, and have suggested its use for dating purposes. In a field where absolute dating of glass artefacts at present is not possible, some researchers believe that weathering of glass could prove to be a dating method for some ancient glass. We also are of this opinion, but temper our conclusion with the caveat that the chronometry using patina must be gauged against glass type, soil type, climate setting, and vadose hydrochemistry. With these matters addressed, patina holds potential to be a very useful tool in chronometric applications.

This study, in keeping with modern trends, places a strong emphasis on the Science underlying the development of patina on the bottle glass from Cossack and, in so doing, provides a robust and sound foundation for its interpretation from archaeological perspectives.

The manner in which the bottle glass is studied is described in the following chapters, commencing with a comprehensive review of previous research on patinated glass.

As such, this publication is a key to understanding patina on glass, how and why it forms, its use in Archaeology as a dating tool, and its use as a marker or tool for reconstructing pedogenic and vadose processes and reconstructing climate patterns, and its use in chronology. Further, as noted above, the results of this study have implications and important applicability to the fields of engineering, infrastructure, construction, and storing toxic and nuclear waste.

It should be emphasised here that the detailed analyses and descriptions of patina types and the processes operating to develop the patina presented in this book is provided (with intention) against a very detailed background of soil type (geochemically, mineralogically, and texturally), water type (arid climate, with specific hydrochemistry), and glass types. All this information serves as a detailed baseline with which to compare patina developed elsewhere in the World with their different glass types, soils, hydrochemistry, hydrology, and climate to be able to characterise patina types and micro-features to their various environmental settings.

CHAPTER 2

GLASS AND ITS WEATHERING PRODUCTS: A REVIEW

The purpose of this chapter, in the first instance, is to describe glass – what it is, followed by a short history of glass and glass-making, and how it weathers in the natural environment. Next follows a review of previous studies in the weathering of ancient glass, and studies of glass buried in the late 19^{th} to mid-20^{th} centuries. Case studies of weathered, buried glass are examined to identify processes, context, and gaps in the knowledge of the weathering of glass, followed by studies of the patina-forming processes. Finally, the application of weathered glass studies to Archaeology is examined.

What is glass?

The term *glass* originated in the Roman glassmaking centre at Trier, probably from the late-Latin term, *glesum*, derived from a Germanic word for a transparent, lustrous substance (Douglas 1972). In current dictionaries such as *The American Heritage Science Dictionary* (2005), glass is defined as 'usually a transparent or translucent material that has no crystalline structure yet behaves like a solid' adding further that 'common glass is generally composed of a silicate (such as silicon oxide, or quartz) combined with an alkali and sometimes other substances'.

A short history of glass and glass-making

Maloney's (1968) authoritative book on the subject of glass is the main source of information in this chapter.

The composition of glass has changed over the centuries with the availability of raw materials determining what type of glass was produced. However, modern glass for domestic use, as it was in the 19^{th} Century up to the present time, is a soda-lime-silica glass approximately in the ratio: (silica) SiO_2 (70%), (soda) Na_2O (15%), (lime) CaO (10%). The addition of soda (Na_2O) or potassium oxide (K_2O) to silica lowers the softening point of the silica being melted by several hundred degrees Centigrade. To improve chemical resistance, calcium oxide (CaO), and sometimes magnesium oxide (MgO) and aluminium oxide (Al_2O_3) are added (Maloney 1968).

The earliest examples of manufactured glass are believed to be glass beads and small glass vessels approximately 4,500 years old recovered from Ur in Mesopotamia. There is also evidence that glass was made by the Egyptians as early as 3,000 BCE. By the 6th Century CE, glass-making techniques had reached the eastern Mediterranean and later, during the Ptolemaic period, coloured glass rods were being produced through the addition of metallic oxides to the raw materials (Maloney 1968).

During the 1st to 3rd Century CE, the Romans perfected glass-making by improving the durability, clarity, and colour of glass. However, with the decline of the Roman Empire, the art of glass-making was lost until the Middle Ages when there was a resurgence, principally in the application of glass as window glass, and the skillful use made of stained glass for this purpose (Maloney 1968).

Commonly, early glass-making materials were sand, limestone, and soda ash producing glass known as “lime glass” which accounted for the bulk of glass production then as it does today (Maloney 1968). The formula for making glass varied from region to region, dependent upon the presence of vast tracts of forest which were the source of the raw materials for producing soda-ash. Soda ash is derived from the burning of wood - in northern Europe, oak and beech were the favoured sources for soda-ash production. On the other hand, the Venetian glass-makers burnt seaweed to produce potash which they used instead of soda-ash (Maloney 1968).

By the 19th Century, glass was utilized in a number of ways, principally to produce flat glass for windows, but also for tableware and storage containers. Wine, beer, gin, mineral water, sauces, preserves, and other commodities previously sold loose, were now available in glass containers (Maloney 1968).

Weathering of glass

Schreiner’s (2005) general observations about the relationship between the condition of artefacts, the nature of the material used, and the environment within which the artefacts were found, are particularly relevant to glass in an archaeological context. Many glass objects from archaeological sites are altered in some way, often physically damaged to such an extent that only fragments of the original object remain. In the sub-aerial, soil, or aqueous environment, glass weathers because it is, for the most part, an unstable material, especially the soda-lime-silica glasses, because of their chemical composition (Maloney 1968). When these glasses are exposed to water, the water dissolves the sodium ions out of the surface of the glass to form alkaline sodium hydroxide (Maloney 1968). Being exposed to such environments over time, glass may form weathering products such as pitted surfaces and crusts. An important weathering product is patina, a crust that coats the surface of the weathered glass (Figure 2-1), or one that "cannibalises" the parent glass by encroaching chemically downwards into the glass (Figure 2-2).

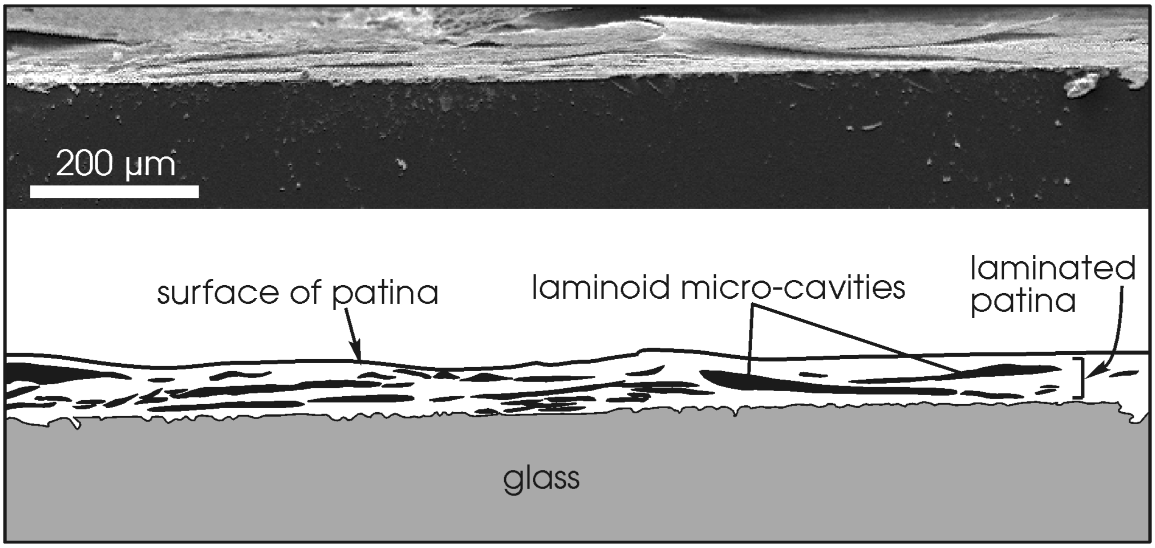

Figure 2-1: SEM image of patina, its micro-structures, and glass appear at the top of the figure, with a diagrammatic representation underneath (Clifford 2008).

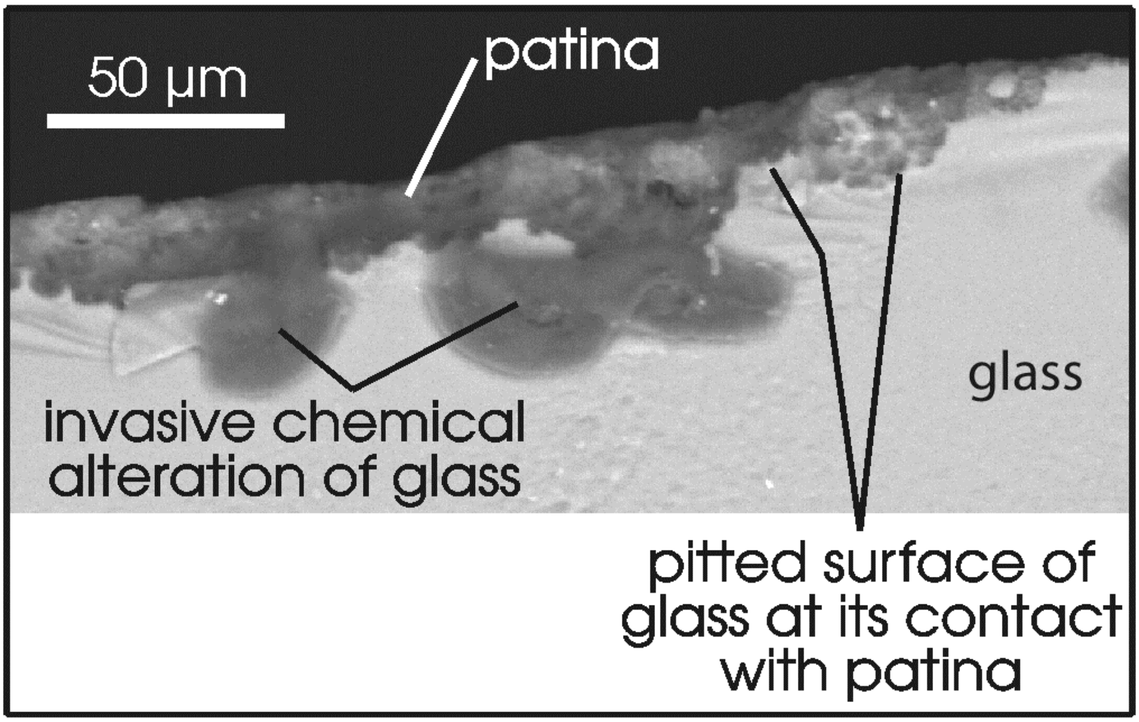

Figure 2-2: SEM image of patina and glass showing invasive chemical alteration of the glass, and pits on the surface of the glass at the point of contact between glass and patina (Clifford 2008).

In order to understand how and why glass forms a patina, it is necessary to know what glass is and how it behaves structurally, texturally, and chemically. The resistance of glass to weathering lies in its composition, with some glasses being more resistant to weathering than others.

Previous studies of the weathering of ancient glass

Research into the weathering of glass commenced approximately 150 years ago, and was undertaken for a number of reasons, for example: 1. because of an interest in the aesthetics of the optical phenomenon of iridescence which is occasionally displayed by weathered glass; 2. to find resolution to problems associated with the decay of stained-glass windows in centuries-old buildings; 3. because of the need to conserve ancient glass artefacts on display in museums; 4. to investigate the stability of glass, that is, its resistance to weathering and its potential for use as a safe storage medium; and 5. establishing whether it is possible to use the layers in patina as a tool for estimating the approximate period of burial of the glass.

The corrosion of glass has been documented since the 17th Century especially in Europe and the United States of America (Fearn *et al.* 2004). Some of the earliest research was carried out by Brewster (1863), who examined specimens discovered in archaeological excavations at Ninevah, located on the eastern bank of the Tigris River in modern-day Iraq (formerly Assyria). Newton (1971) cites Brewster's contemporary, Hausmann who, in 1856, conducted quantitative analyses of weathered crusts in the glass from Ninevah. Hausmann concluded that the crust was hydrated and that the metal alkalis, which had been essential ingredients in the glass, had been replaced by water, and that other metals such as iron, calcium, and magnesium had derived from the environment. Nearly a century later, Guillot (1934) investigated the iridescence of antique glass, as did Raman and Rajagopalan (1940) who, using modern analytical techniques, described its lamellae and colour effects.

Newton's (1976) study of hundreds of pieces of mediaeval stained glass from unspecified locations, failed to find any weathering crust on the surface of these pieces. While Newton concluded that the conditions of burial are far more damaging to glass than atmospheric weathering, he did provide an example of Austrian stained window glass that possessed a thick laminar crust but noted it differed from archaeological glasses which possessed laminae which were generally less than 20 µm thick (Newton 1976).

Newton (1976) also described the anomaly of the weathering crust on 300 kg of glass excavated from a cullet heap at the glassworks site at Bagot's Park in Staffordshire, England (dated to about 1535). Half of the glass displayed a heavy, opaque weathering crust while the other half was transparent without the weathering crust even though all the glass had been made at the same site, mixed together in the same soil, and subjected to the same weathering processes. Analysis of the glass showed that there were small differences in the SiO_2 and CaO content in the soda glasses, but none in the potash glasses. This anomaly was not understood until El-Shamy (1973) showed that the tendency for glass to form a crust increases rapidly as the silica content of the glass decreases below 66 mole percent (Newton 1976 Tables I and II). In the case of the Bagot's Park glass, the conversion of the analytical results from weight percentages to molecular (mole) percentages highlighted the effects of MgO and CaO on the durability of the glass, that is, its resistance to weathering (Newton 1976). In summary, Newton (1976) emphasized the importance of using the molecular weight of the constituents of glass rather than the weight percentages to obtain an understanding of the weathering process, and the role played by the minor constituents such as MgO and CaO. In the case of chemically-complex mediaeval glass which does not form a weathering crust, materials such as phosphorus pentoxide (P_2O_5), alumina (Al_2O_3), and titania (TiO_2) in the glass were found to play the same role as silica in its resistance to weathering (El-Shamy 1973).

More recently, Cox and Ford (1989), using SEM, electron-probe analysis, X-Ray and electron diffraction, described the nature of glass decay processes for alkali-lime-silicate glasses which had corroded while on the sea bed for approximately 240 years. The samples (fragments of glass containers) were retrieved from two in-shore shipwrecks: the *Drottengin af Sverige,* which was wrecked off Lerwick Harbour (Shetland Islands) in 1745; and the *Amsterdam*, which foundered off Hastings in 1749. The samples were extremely fragile and exhibited opaque corrosion crusts which were between 0.2 mm and 0.5 mm thick. Cox and Ford (1989) found that leaching and dissolution of the networks in the glass had occurred. Corrosion crusts comprising regular discrete layers (or laminae) were formed through re-precipitation, and were depleted of calcium (Ca) and magnesium (Mg), while aluminium (Al) was concentrated through the crusts and silicon (Si) was enriched at the glass-corrosion interface (Cox and Ford 1989).

Cox and Ford (1993) also examined the long-term corrosion of glass by groundwater. The samples of glass used in that study were excavated from several sites in the United Kingdom, (Eltham Palace, Kent; Rievaux Abbey, North Yorkshire; Stamford Castle, Lincolnshire; and Wroxeter, Shropshire). The samples were corroded soda glass and potash glass which had been exposed to groundwater for between 350 and 1,650 years. The corrosion crusts varied in thickness, colour, and uniformity of corrosion within and between samples. Cox and Ford's (1993) research showed that the surface layers on all samples had been depleted (to varying extents) of their principal constituents, with the exception of Si, Al and Fe to varying extents. They identified deposits of calcite, calcium phosphate and manganese-rich minerals occurring within the crusts which were largely of exogenic origin. As a result of their study, they proposed that the long-term behaviour of glass is not only a function of its composition, but one which is strongly influenced by environmental factors, especially the geochemistry of the local groundwater (Cox and Ford 1993).

Garcia-Valles *et al*. (2003) examined mediaeval stained glass from three restoration works to characterise glass decay. The mediaeval stained glass samples (from the 13th to 15th centuries) were from the Santa Maria del Mar Church, the Pedralbes Monastery church in Barcelona, and the Tarragon Cathedral in the northwestern Mediterranean area. The glasses were of two types: a Na-rich type and a K-Ca-rich type. Their research showed that Na-rich type glass did not weather (due to high SiO_2 content around 60% by weight), but the K-Ca-rich type of glass exhibited decay in the form of destructive (micro- and meso-pitting), and constructive (patina and micro-crust) glass surfaces (Garcia-Valles *et al.* 2003). The stained glass used in the study of Garcia-Valles *et al.* (2003) adds a level of chemical complication to the decay processes and the decay products that are not present in simple clear glass, therefore their results may not be directly comparable to this study. However, the results of Garcia-Valles *et al*. (2003) are useful in that they identify some of the chemical processes in the weathering of glass.

Silvestri *et al*. (2005) analysed green and blue-green glass fragments which were found in a wooden barrel in the wreck of the Roman ship, *Iulia Felix* (dated to about the 2nd Century CE), that foundered in the north Adriatic Sea and lay at a depth of about 15 m in carbonatic [sic] sand. Their study revealed that the processes of glass corrosion, hydration, ion exchange, and the precipitation of alteration crusts took place on the surface of the glass from the *Iulia Felix*, which was evidenced by the loss of Na_2O (sodium oxide) and SiO_2 (silica) at the glass/alteration interface (Silvestri *et al*. 2005), a process confirmed, in part, by the findings of this current research (refer to Chapter 5 – Description of sand, water, parent glass, and patina).

Table 2-1 summarises previous research into the weathering of glass, providing information on the types of glass, their weathering products, and the weathering environment of the glass.

Table 2-1: Summary of types of glass, setting, and weathering products

Type of glass	Setting	Weathering products
ancient glass (Brewster [1863]; Newton [1971] citing Hausmann [1856]); typically high soda glass (Newton 1976)	excavated from Ninevah (Iraq, formerly Assyria), located on the eastern bank of the Tigris River	thin layers of weathered crust; diffraction effects (iridescence) noted
ancient glass (Brill 1961; Brill and Hood 1961); composition not described	excavated from Sardis, Turkey; glass buried for about 1600 years	weathering crust comprising 1582 laminae
waste glass (Newton 1976); composition not described	excavated from a cullet heap at a glassworks site in Bagot's Park, Staffordshire, United Kingdom; exposed to groundwater for about 430 years	heavy, opaque weathering crust only on one half of the sample; the other half of the sample was transparent without weathering crust
mediaeval stained glass, typically high potash, high lime, and high magnesia (Newton 1976)	*in situ* stained glass in cathedrals and monasteries; exposed to humid atmosphere	no weathering crusts
alkali-lime-silicate glass (Cox and Ford 1989)	excavated from two shipwrecks (one located off Lerwick Harbour, Shetland Islands, the other off Hastings, United Kingdom); shipwrecks dated to 1745 and 1749 respectively	fragile opaque corrosion crusts between 0.2 mm and 0.5 mm thick arranged in regular, discrete layers
soda and potash glass (Cox and Ford 1993)	excavated from several sites in the United Kingdom; various samples exposed to ground water for 350 up to 1650 years	corrosion crusts varying in thickness, colour, and uniformity of corrosion within and between samples
Na-rich and K-Ca-rich glass (Garcia-Valles *et al*. 2003)	*in situ* stained glass (13^{th}-15^{th} centuries) at Santa Maria del Mar Church, Pedralbes Monastery church, Barcelona, and Tarragona Cathedral, north-western Mediterranean area.	glass decay in the form of destructive (micro- and meso-pitting) and constructive (patina and micro-crust) glass surfaces; in the case of the Mediterranean mediaeval stained glasses, development of generalised corrosion and associated thick crusts are absent
Roman soda-lime-silica glass (Silvestri *et al*. 2005)	recovered from the 1800 year-old shipwreck of the *Iulia Felix* foundered in 15 m of water in the northern Adriatic Sea.	multiple layers of iridescent lamellae on the coloured glass; an opaque white crust covered the surface of the colourless glass. Alteration products composed of a hydrated 'silica gel'

In the mid-20th Century, Brill (1961) embarked on a unique study of the laminae in weathering crusts on ancient glass buried between the late 3rd Century and the early 7th Century, and glass immersed in sea water, and water in wells. He postulated that the laminae reflected periodic or cyclic change (such as seasonal variations in temperature or alternating wet and dry seasons) that the glass was exposed to during its burial. Brill (1961) and Brill and Hood (1961) also proposed that dating of glass artefacts could therefore be achieved by counting the laminae of the weathering crusts on glass buried for many centuries.

Brill and Hood's study proved problematic for several researchers. Newton (1966) provided two explanations as to why this hypothesis of dating was flawed - one reason was that there can be variation in the number of layers from one part of a glass specimen to another due to fractures in the parent glass (see Newton 1966: Fig. 4); the other reason was a query as to how sea water could be affected by cyclic changes to produce laminae on glass immersed in it.

Demmy (1967), although enthusiastic about the use of patina as a dating tool, stated that Brill (1961) had acknowledged only successfully dating ten pieces of glass out of the hundreds he had studied to test his dating theory. Demmy's own research into patination using 19 samples from a *wide range of geographical areas* 'with a bias toward those which displayed well-developed crusts' resulted in his conclusion that 'the phenomenon of patination is simply too random a process upon which to base a dating technique' (Demmy 1967) and that further research was needed in the realm of glass chemistry before patina could be used for dating glass.

Pollard and Heron (1996) also were skeptical of Brill and Hood's (1961) explanation for the production of the laminae, stating their belief that the process depended strongly on local conditions, not on the annual cycles of alternating wet and dry seasons. This current study will show that local conditions *and* alternating wet and dry seasons are critical to the development of patina.

Previous studies of glass buried in the late 19th to mid-20th Century

Weathered glass that has been buried for approximately 100 years has received little or no mention in the literature. Clifford (2008) examined clear, flat glass using SEM, EDS, and XRD technology to identify and describe the undulating micro-laminae and other micro-structures of the patina, and to ascertain the elemental composition of the patina and that of the parent glass. The glass in that 2008 study had been partly buried for approximately 70 years in calcareous quartz sand at Cossack.

Case studies of weathered buried glass to identify processes, context, and gaps

Archaeologists have long been aware of the association of the weathering crust (patina) on glass with damp soil, groundwater, and sea water. While morphological studies on the patina have been conducted since the 1950s (*e.g.* Raw 1955; Geilmann 1956), and the majority of chemical analyses has revealed that corrosion products contained little of the alkali present in the original glass, the actual process of weathering (patination) of buried glass is not well understood.

Processes and context

Cox and Ford's (1993) study, which examined the long-term corrosion of soda and potash glasses by ground-water, highlighted the importance of ground-water in the alteration of glass. They found that the surface layers on all specimens were depleted of some of their principal chemical constituents and determined that other compounds occurring within the patina were of exogenic origin (Cox and Ford 1993).

In another study, Brill (1961) examined the layers in the patina and noted the role of water in the patina-forming process. He observed that decomposition of the glass was dependent principally on the action of water which leaches out the more soluble components from the glass, leaving behind a residue of silica (Brill 1961). He stated that the deterioration [of the glass] starts at the surface and proceeds into the glass, so that the outer surface of the weathering crust coincides with what was initially the outer surface of the glass itself (Brill 1961). Brill and Hood (1961) also postulated that the parallel laminae comprising the patina on the glass from Sardis, Turkey represented annual alternating cycles of wet and dry periods and temperature over a long period of time. On the other hand, Pollard and Heron (1996) were of the belief that the process of weathering depended strongly on local conditions because of the complexity of the soil environment, not on the annual cycles of alternating wet and dry seasons as proposed by Brill and Hood (1961).

Silvestri *et al*. (2005) conducted a study of the natural degradation of glass from Italian marine and terrestrial archaeological sites with the aim of understanding the role that the physical and chemical conditions of the environment played in the development of alteration products . They characterised the alteration products of buried glass only as iridescent lamellae mainly composed of a hydrated 'silica gel'. In describing the complex process of the alteration of glass, they identified the following factors:

1. The characteristics of the glass, for example: composition, heat treatment, and surface roughness; and
2. The external conditions such as micro-climate, temperature, time, pH, aqueous solution composition, exposure to sunlight, and micro-organisms (Silvestri *et al*. 2005).

Silvestri *et al*. (2005) also proposed that glass corrosion was a combination of three simultaneous partial processes, that is, hydration, hydrolysis, and ion exchange.

Gaps in the understanding of the patina-forming process

This review of the literature has revealed that a holistic study to fully understand the process of patination has not been undertaken by any researcher. Each study that has been presented in this literature review has focussed on different aspects of the phenomenon of weathered glass: for example, the chemical composition of the parent glass and the patina, the morphology of the patina, the number of layers within the patina and what they represent, the role of the various aspects of the environment, and the differences in appearance of the weathering products on glass which has been buried in sediment/soil, or submerged in seawater or groundwater, or exposed to the air.

The aspect of the weathering of glass by each researcher in his or her respective study is generally governed by the application of the knowledge deriving from these studies to solving specific problems: for example, conservation issues of glass in museums and stained glass windows of very old buildings; the storage of nuclear waste; or as a means of determining the length of time glass has been buried.

Current ideas of patina-forming processes on glass

To understand the process of the weathering of glass, (that is, the patination process), one needs to acknowledge that, first and foremost, it is dependent upon the understanding of the chemical composition of the parent glass which determines whether the glass will be durable and resist weathering, or otherwise. Maloney (1968) understood this when he commented that common glasses of soda-lime-silica composition ‘contain the seeds of their own chemical destruction’. An understanding of all aspects the environment of burial of the glass, and its contribution to the process is also essential.

Cox and Ford’s (1993) research found that the process of patination involved the depletion of principal chemical constituents in the glass, but at the same time the crust may contain compounds of exogenic origin. The conclusions of their study were that the long-term behaviour of glass is not just a function of its composition but one which is strongly influenced by environmental factors, especially the geochemistry of the local groundwater (Cox and Ford 1993).

Application of weathered glass studies to archaeology

Only Brill (1961) and Brill and Hood (1961) have sought to apply their research to the dating of the length of time of burial of glass by counting the layers in patina which they believed represented annual climatic cycles of wet and dry periods, and temperature fluctuations. Demmy (1967), in commenting on Brill's low success rate in dating glass (ten dated samples out of the many hundreds Brill had studied), said that such a random process as patination required further research before it could be used for dating glass. This current study will show that Brill's (1961) research into the layers in patina does have its place in archaeology, however Brill's approach needed to encompass a greater range of contributing factors, not just climatic cycles of wet and dry periods and temperature fluctuations to obtain a fuller understanding of the process as the key to greater success in the use of laminae in patina as a dating tool.

Conclusion

In conclusion, this literature review has highlighted the complexity of the patination process given that so many variables need to be taken into account.

In Chapter 4 (Methods), analysis of the composition of the parent glass, the patina, the sediment (sand) in which the glass was buried, and the chemical composition of the pellicular water will be described. This extensive analysis provides a comprehensive set of data to explain the weathering of glass buried at Cossack.

CHAPTER 3

DEFINITION OF TERMS

This chapter presents a glossary of terms which are drawn from Sinkankas (1964), Tebbutt *et al.* (1965), Davis and DeWiest (1966), Todd (1967), Bates and Jackson (1987), and Jackson (1997).

However, before the traditional terms for structure, texture, materials, methods, and instruments used in this study are defined and described, a brief definition of the term 'patina' (that is the main subject of this study) is provided, and a new term is coined that identifies and highlights the smaller-scale components of patina.

Definition of patina and a new term for patina components

As noted in the Introduction, *The Concise Oxford Dictionary of Archaeology* (2008) defines *patina* as 'the changes to the outer surface of an artifact … usually as a result of chemical, physical, or biological alteration through contact with the surrounding environment …'. Patina thus is a thin weathering crust on the surface of an artifact which in this study is glass. In this context, the entire crustose formation is axiomatically simply called 'patina'. In this study, the surficial changes effected on the glass to produce patina are compositional, structural, and microstructural. Patination is the process of the development of patina on glass.

However, patina has internal features and structures occurring in discrete intra-patina 'domains' (as patches, clots, sheets, micro-lenses that are internally laminated, colloform, massive [structureless], mottled, or breccioid) and while they may comprise a portion of the totality of patina, we consider that the term 'patina' referring to the whole of the crustose form should not be applied also to these smaller-scale subunit features. We coin the term '*patinelle*' to refer to the smaller-scale discrete structurally and/or compositionally distinct components of a patina. Thus, for example, a lamina of silica, or a lamina of calcite, or a micro-breccia patch within the patina (in cases where such subcomponents need to be referred to) will be termed a 'patinelle'. Clearly, a patina with internally complex features will be composed of an array of patinelles (Figure 3-1). Use of the term *patinelle* is analogous to the term *organelle* in biology; organelles are smaller structures within cells (as organs are parts of a body) - the suffix *-elle* signaling a diminutive, and noting that organelles are identified only by microscopy. In cell biology, while an organelle is a smaller-scale component of a cell, it has a specific intra-cellular function, but the term patinelle is used to convey the notion that a feature is merely a smaller component of the totality of the patina and has a scalar connotation only.

In summary, the entire thin crustose formation coating the glass is termed 'patina' and individual components such as silica laminae and clots of micro-breccia, for example, that are subunits of the patina, are termed 'patinelle'. Within the patina, patinelles can be sheet-like, lensoid, tubular, and structurally/compositionally (internally) they can be a silica lamina, a carbonate lamina, a breccioid patch, a mottled patch, a fenestral structure, or a structureless patch.

Definition of traditional terms

Amorphous or *X-Ray amorphous*: material that lacks definitive lattice structure such that it appears amorphous in X-Ray diffraction analysis; the atoms of the material are arranged in a random way similar to the disorder found in a liquid.

Botryoidal: having a shape resembling a cluster of grapes.

Colloform: structure or micro-structure (*i.e.*, colloform or micro- colloform) comprised of finely spaced, undulating to hemispheric layering simulating a cross-section of a cabbage-like structure.

Crystalline: material with atoms arranged in a regular or lattice pattern.

Cuspate: triangular, 'tooth-like' shape.

Dust: dry interstitial to grain-coating fine-grained sediment with particle sizes < 63 μm; also see '*sediment'* below.

EDS: Energy-dispersive Spectroscopy used to determine the elemental composition of glass while under a Scanning Electron Microscopy (SEM); used in conjunction with SEM, it is termed SEM/EDS; also see Appendix A.

Endoliths and micro-boring: endoliths are archaeons, bacteria, fungi, lichens, algae, and amoeba growing in the interior of rocks and other solid materials such as glass; endoliths produce micro-borings and micro-cavities.

Exogenic: derived from outside the environment; for patina, formed *in situ* in a vadose environment; this refers to constituents brought to the patina from external sources.

Endogenic: derived internally; for patina, formed *in situ* in a vadose environment, endogenic refers to constituents derived from the glass and earlier-formed patina.

*Fenestra (*pl: *fenestrae)*: small-scale cavity(ies) in patina; the term derives from Latin '*fenestra'*, meaning window or opening; first used in Geology by Tebbutt *et al*. (1965) to describe small-scale cavities in algal sediments; adjectives such as 'laminoid', 'platy', and 'irregular' provide a means to separate geometrically-different fenestrae; first identified in patina by Clifford (2008) to describe thin, laminar voids.

Gel: translucent to transparent, semisolid, apparently homogeneous substance in colloidal state, usually elastic and jelly-like, and containing a dispersion or network of fine particles which are coalesced to some degree (for silica gels, see Florke *et al*. 1991; Howard and Rabinovitch 2018).

ICP-MS: Inductively Coupled Plasma Mass Spectrometry is a mass spectrometric technique using inductively coupled plasma to ionize a sample, atomizing it and creating atomic and small polyatomic ions, which are then separated and detected on their mass-to-charge ratio; also see Appendix A.

Interstitial sediment: fine-grained sediment in the pore spaces or interstices of a coarser-grained sediment.

Invaginated: embayed interface with deeply penetrating embayments occurring as 'finger-like' intrusions.

Laminated, lamination: structure or micro-structure comprised of finely spaced, parallel layering; in Geology this lamination is spaced < 1 mm but in patina it can be < 0.1 mm.

Laminoid fenestra (fenestrae): fenestrae long and wide compared to their height (plate-like shape); they are the same dimension as laminae in which they are embedded.

Leachate: water that has percolated through materials and leached out some of the constituents.

Massive structure: structure that is homogeneous or structureless, *i.e.*, without any obvious lamination, mottling, or brecciation.

Meteoric water: water deriving directly from rainfall.

Micro-breccia and micro-breccioid: angular fragments in a matrix of finer-grained material; 'breccia' fragments are << 1 mm (hence the term 'micro-breccia'); fragments may be floating in a matrix, or in grain-support fabric, with interstitial finer-grained material; patina comprised of micro-breccia is also termed '*micro-brecciated*'; 'breccia-like' structures are termed 'micro-breccioid'.

Micro-stratigraphic relationships: the geometric inter-relationships of the various types of patina, patinelles, and the various layers of patina, and their relationship to the parent glass simulating stratigraphic relationships commonly found in Geology (Lahee 1961).

Micro-stratigraphy of patina: layers of patina, types of lamination/layering, occurrence of micro-discontinuities, and geometric inter-relationships of various types of patinelles.

Micro-unconformity: similar to an unconformity in Geology (Lahee 1961; Bates and Jackson 1987; Jackson 1997), a stratigraphic discordance where earlier laminae are discordantly truncated by a dissolution interface and where the younger laminae are concordant with the truncating interface.

Micro-vesicular: small-scale spherical to ovoid vesicles (cavities).

Mottled structure: irregular to equant patches of one material set in a matrix of another.

Paragenesis (*paragenetic*): the sequential order of crystallization and/or deposition in mineral deposits (Bates and Jackson 1987; Bowes 1989; Jackson 1997); for patina, it refers to its structural, textural, and compositional evolution enabling a reconstruction of its history.

Pedogenic: relating to soil processes involving physical, chemical and biological processes in the soil profile.

Pellicular water: thin film of water that coats or envelopes grains in the vadose zone.

Sand: sediment with particles between 63 μm and 2000 μm; also see '*sediment'* below.

Scalloped: small-scale curvilinear erosive interface that is broadly U-shaped; where there is a series of adjoining 'scallops' they are separated by cuspate protrusions.

SEM: Scanning Electron Microscopy using a microscope that produces high magnification images of samples by scanning their surface with a focused beam of electrons; the electrons interact with atoms in the sample, producing various signals that contain information about surface topography and composition; also see Appendix A.

Sediment: solid fragmental material originating from weathering/erosion of rocks and transported/deposited by air, water, or ice; sediment forms layers on the Earth's surface as loose, unconsolidated sand, gravel, silt, mud, *etc.*

Species (as in mineral species): 'A mineral distinguished from others by its unique chemical and physical properties; it may have varieties' (Bates and Jackson 1987; Jackson 1997).

Structure and micro-structure: the spatial array of interfaces in material; these may be laminar (laminated structure and micro-structure), irregularly arrayed (mottled structure and micro-structure), colloform, undulating laminar, brecciated; micro-structure is a very small-scale structure measured in scale of mm, μm, and nm.

Supra-patina crust: the thin cemented layer accreted onto the surface of the patina; this is a non-patina style of accretion outwards from the surface of the glass or, more commonly, from the surface of the uppermost layer of patina (the former glass surface); it is composed of various constituents (detrital mineral particles and precipitates).

Texture: the grain size of particles and their inter-arrangement in sediments and soils.

Vadose zone: the zone of aeration or under-saturation in a rock, sediment, or soil profile above the phreatic (saturated) groundwater zone.

X-Ray Diffraction (XRD) involves sample analysis with a focused beam of X-Rays which generates a diffraction pattern to determine crystal structure in terms of lattice orientations and lattice spacing (see Appendix A).

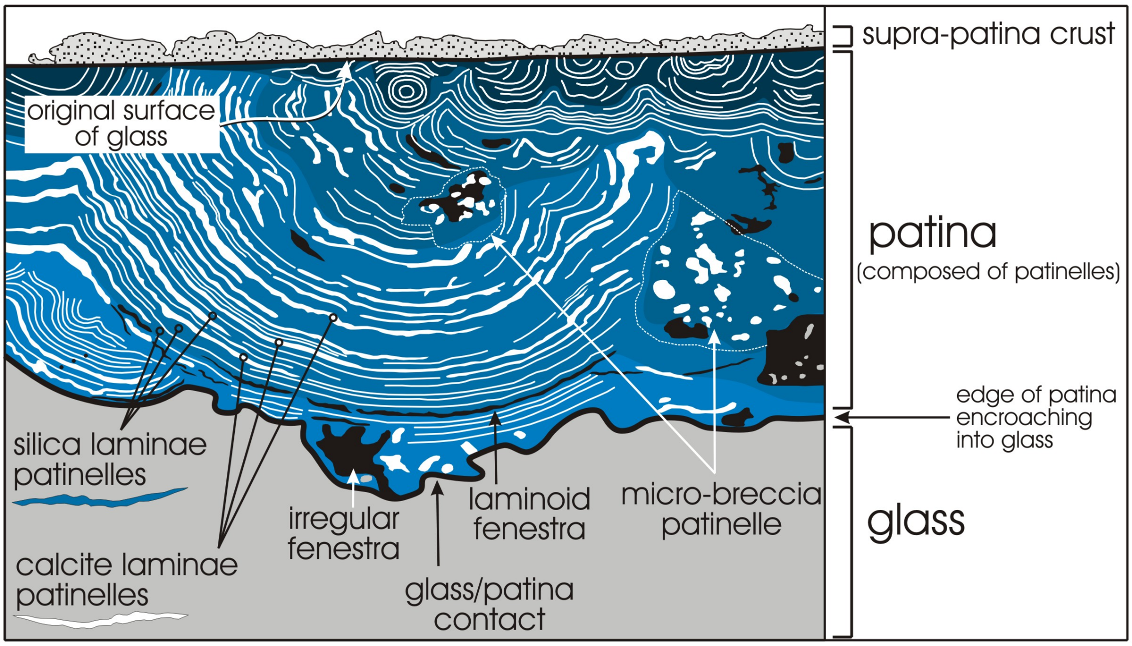

Figure 3-1: Annotated illustration showing a selection of features of patina and its relationship to parent glass: 1. silica laminae patinelles; 2. calcite laminae patinelles; 3. micro-breccia patinelles; 4. various fenestrae; 5. the former surface of the glass as a straight, sharp edge (arrowed); and 6. the thin sheet of supra-patina crust.

CHAPTER 4

METHODS

A review of the literature shows that patination of glass is complex with many variables to be taken into account to produce a comprehensive understanding of the process of weathering of which patina is a product. While previous research has revealed the reasons for the durability of glass, it has not provided answers for the different rates of weathering of glass in any given context, nor the role (if any) in the weathering process of the various elements in glass which give it its colour. To investigate these questions about the weathering of glass in the arid climatic and coastal-dune environment of Cossack, a range of methods were employed to explore the setting, processes and products of the patina-forming environment.

Structure of this Chapter

This chapter describing the methods used to undertake these investigations is organized into three steps as follows:

1. Description of the burial environment of the glass sample *i.e.*, the sand, dust and water, as a background to the environment and processes that will produce patina;
2. Identification of the chemical composition of the different types of bottle glass present in the Cossack sample and selected samples of each type;
3. Description and comparison of the patina on the different types of bottle glass identified in step 2.

The first of these steps involved:

1. A description of the grain size of sand and dust from the field site.
2. A description of sand and dust composition (using XRD, stereo-microcopy, and thin sections).
3. A determination of the calcium carbonate content of sand and dust using acid digestion.
4. A determination of the leachates derived from dust by pellicular water, experimentally in the laboratory.
5. An analysis of pellicular water on sand grains that will drive the chemical processes to form patina.